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ORIGINAL ARTICLE

Futuristic isotope hydrology in the Gulf region

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Abstract

The Gulf region is one of the most water-stressed parts in the world. Water in the region is very scarce, shortage of supply and lacking of renewable water resources, while the demand for water is growing day by day. It is thus essential to implement modern approaches and technologies in addressing water-related issues. In this context, isotope hydrology will provide invaluable aid. Some of the most important areas of futuristic applications of isotope hydrology include evaluation of aquifer recharge, storage and their recovery system, understanding of dynamic changes due to long-term exploitation of the groundwater, development and management of shared groundwater aquifers, fresh groundwater discharge along the Arabian Gulf, identification and quantification of hydrocarbon contamination in groundwater; soil moisture and solute movement in unsaturated zone, paleoclimate reconstruction, etc. Literature survey suggests, in general, not many isotope studies on the above have been reported.

Keywords Environmental isotopes · Groundwater sustainability · Submarine groundwater discharge · Artificial recharge · Paleoclimate reconstruction

Introduction

Water is extremely essential for our livelihood (elixir of life) and has been rightly attracting worldwide attention due to the severe challenges in ensuring its reliable availability in adequate quality and quantity in a sustainable manner. It is even said that in future, conflicts among nations and regions would be over water (and not necessarily over oil or gold!), which is a distinct possibility!

It is thus imperative to continue to harness a variety of strategies, approaches and technologies in addressing water related issues in a holistic manner. In this context, the unique role of isotope techniques in providing certain invaluable contributions to hydrology has created a niche for itself. In addition, the isotope techniques provide information that cannot be obtained by other techniques.

Isotope hydrology was born just after the Second World War, mainly as a resultant of the knowledge collected in the monitoring of man-made radioactive nuclide fallout (specifically tritium) and the usage of radioactive isotopes as age estimation tools in geology with the theoretical understanding gained on the fractionation of isotopic species (Aggarwal, et al., 2005). Thus, a field called "Isotope hydrology—the use of isotopic tools in the study of water cycle" came into existence, and today isotope hydrology is considered as the most promising modern hydrological tools, apart from remote-sensing, for water resources managers and practitioners.

The significance of water is more noticeable in the Arabian Peninsula, home of the GCC countries. The GCC countries, namely, United Arab Emirates, Bahrain, Saudi Arabia, Oman, Qatar, and Kuwait (Fig. 1), are encountering severe shortages of water. Very minimal rainfall compounded with high evapotranspiration rates in this region causes limited availability of renewable water. Apart from limited availability of water, inadequate levels of management of natural water resources in this region during the last three decades causes threat to a healthy human life as well.

Quick population growth along with enhanced socio-economic growth in the Gulf countries during the last three decades caused substantial increase in water demands. In order to fulfill the rising demand for water (Fig. 2) (Economist Intelligence Unit Limited 2010), the authorities are

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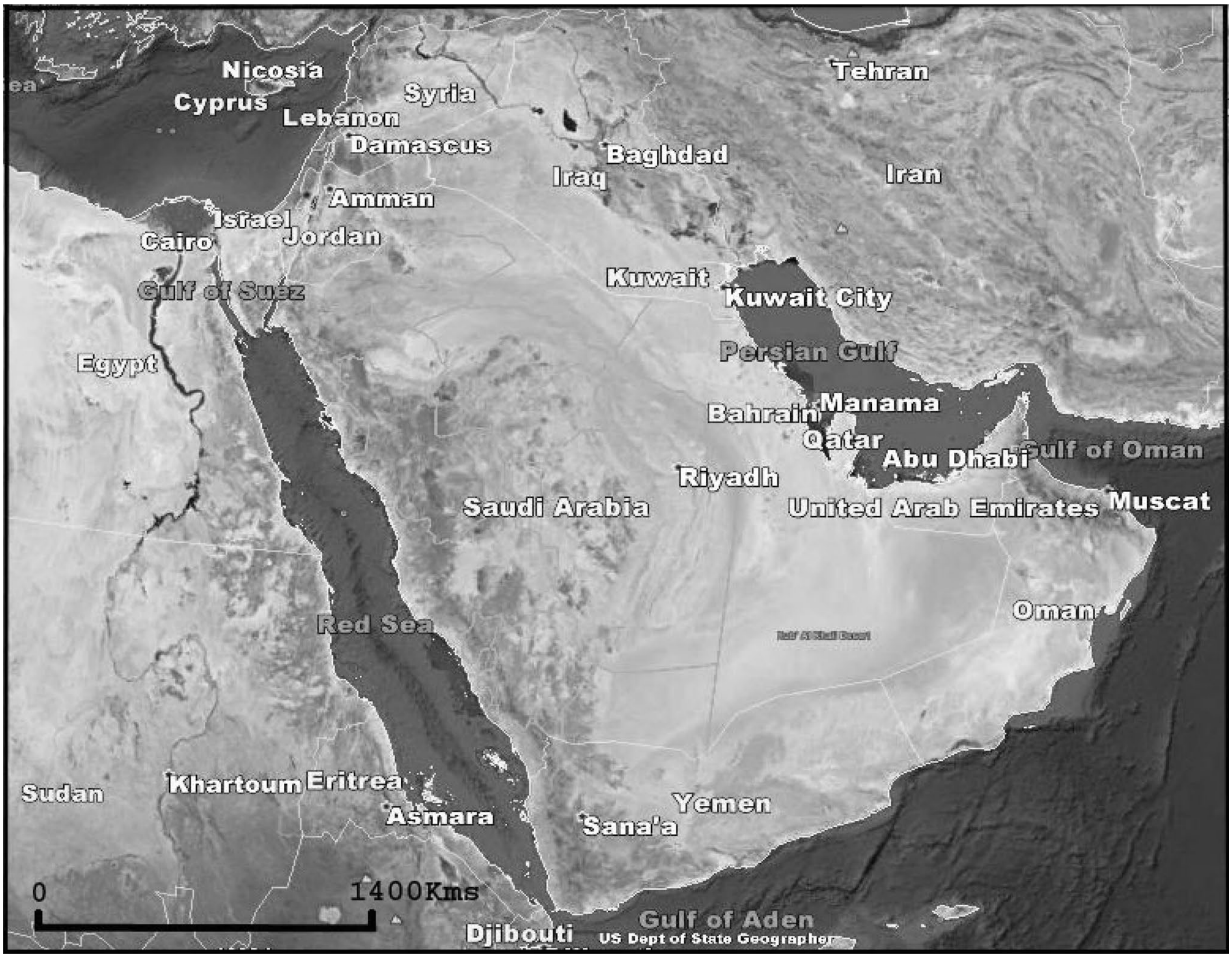

Fig. 1 Google earth map of Gulf countries

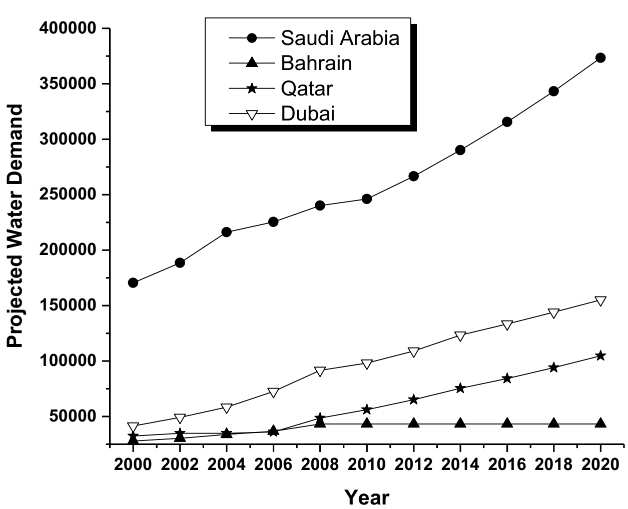

Fig. 2 Projected water demands in few GCC countries, millions of imperial gallons, 2000–2020. [Source: Economist Intelligence Unit Limited (2010)]

paying attention to the development and supply augmentation of the scarce natural water resources. The extensive demands are being fulfilled through the groundwater development, installation of desalination plants, increase in wastewater treatment and reuse, construction of dams to collect, store, and utilize runoff.

To deal with the massive challenges related to water resources management in the Gulf countries necessitates heroic reforms in the prevailing institutions and policies governing water resources, human resources development, improvement of governance, research and development in the hydrology and water resources field in the GCC region.

This manuscript highlights some of the important areas of futuristic applications of isotope hydrology techniques in groundwater management in the Gulf region based on the literature survey carried out. The manuscript is mainly targeted for the field hydrologists and practitioners, researchers and academia in the region for carrying out new or advanced research in the isotope hydrology field.

Isotopes applications to hydrological issues can be generally categorized on the basis of different sources of radioactive isotopes (Baskaran 2012), which are as follows:

- Atmospheric short-lived nuclides: ^{3}H, ^{10}Be, ^{14}C, ^{81}Kr, ^{129}I, ^{210}Pb.
- Decay series nuclides: ^{210}Pb, ^{222}Rn, ^{228,226,224,223}Ra, ^{234,235,238}U.
- Anthropogenic isotopes: ^{3}H, ^{14}C, ^{36}Cl, ^{129}I, ^{137}Cs.
- Radiogenic isotopes: ^{87}Rb, ^{238,235}U, ^{232}Th.
- Causes of variations in stable isotopes: $^{2/1}$H, $^{13/12}$C, $^{18/16}$O, ^{17}O, $^{87/86}$Sr, $^{11/10}$B, $^{34/32}$S, $^{15/14}$N, etc.

Generally, the natural (environmental) isotopes are used to obtain regional-scale information. For obtaining local-scale information, artificial radioactive isotopes such ^{3}H as tritiated water, ^{82}Br as aqueous ammonium bromide, ^{131}I as potassium iodide, ^{46}Sc as scandium oxide, etc., are used. The artificial isotopes are mostly used for the purpose of tracing water and sediment movement in both surface and groundwater bodies.

There are two fundamental approaches to measure the abundance of isotopes. Radioactive isotopes can be measured by quantifying the radiation due to decay, and then linking the decay rate to the abundance with the help of the well-known "radioactivity-decay" equation (Baskaran 2012). Several counting methods are used, mainly for short-lived radionuclides (alpha/beta/gamma spectrometry). The other approach is that atoms of any isotope can be measured directly by mass spectrometry (thermal ionization/inductively-coupled plasma source/gas-source-/accelerated mass-spectrometry techniques), that separates ions based on their mass and followed by direct counting. Such techniques require larger investment in instrumentation, but can often detect more delicate variations.

Isotope applications in hydrology are based on tracer concept (Mook 2001), in which naturally occurring (radioactive or stable) are used to understand hydrological processes on larger spatial and temporal merely through their natural distribution in a hydrological system. The isotopic variations in water occur mainly during the passage of water into and through the atmosphere and/or lithosphere. The explicit isotopic signatures produced by these processes are then imprinted on the terrestrial water bodies, forming the basis for the numerous applications of isotopes in hydrological studies.

Thus, environmental isotope techniques are unique in regional studies to know integrated characteristics of groundwater systems. The most frequently used ones, deuterium (^{2}H), tritium (^{3}H), oxygen-18 (^{18}O), carbon-13 (^{13}C) and carbon-14 (^{14}C), sulphur (^{34}S, as sulphate) and nitrogen (^{15}N, as nitrate) occurring in water either as an integral part of the water molecule or as a dissolved solute. ^{2}H, ^{13}C, ^{15}N, ^{18}O and ^{34}S are stable isotopes and ^{3}H and ^{14}C are radioactive isotopes.

The important isotopes' applications in groundwater studies include aquifer recharge and discharge processes; flow and interconnections between aquifers, and the sources, fate and transport of pollutants (Aggarwal and Bossaha 2005). Specifically, in arid and semiarid conditions, isotope techniques are the only feasible means for the characterization (identification and quantification) of recharge to any groundwater systems. Anthropogenic contamination of groundwater aquifers is one of the major challenging issues in the management of water resources. Environmental isotopes can be used to know the contaminant pathways and thereby assist in predicting the spatial distribution and temporal variations in contamination levels for planning suitable aquifer remediation measures.

Futuristic isotope hydrology applications in the Gulf region

A few isotopic case studies in groundwater management in the Gulf region have been reported in literature and they are, broadly, related to the delineation of hydraulic boundaries, identification and quantification of groundwater mixtures from different sources; understanding groundwater flow dynamics; paleoclimatic effects on the geohydraulic conditions; determination of groundwater ages; identification of fossil groundwater, groundwater pollution and salinization (anthropogenic, natural) processes, etc. (Robinson et al. 1991; Robinson and Gunatilaka 1991; Hadi and Al-Ruwaih 2008).

From the review of a number of studies in literature, the following have been identified as some of the important areas of futuristic isotope hydrology applications in groundwater management in the Gulf region:

Evaluation of groundwater aquifer recharge and aquifer storage and recovery system

Artificial recharge of a groundwater aquifer is the method of enhancing the natural recharge means through man-made structures, like infiltration basins, or injection wells. Aquifer storage and recovery is a specific type of aquifer recharge for supplementing groundwater resources and for recovering the same in the future for different purposes.

Artificial recharge of aquifers in the Gulf region can be used for storing usable water in order to reduce load on the desalination plants during peak seasons, when the demand is high, and in an emergency. A number of feasibility studies on AR and ASR have been carried out in Kuwait (Mukhopadhyay et al. 1994; Mukhopadhyay and Fadlelmawla 2012; Hamoda et al. 2012), and the investigators concluded that the method is technically feasible as well as economically viable.

Isotopic approaches for hydrogeological investigations related to AR and ASR would involve development of data on isotopic composition (^{2}H, ^{18}O,^{3}H and, at times, ^{14}C) of the groundwater and its water quality parameters (EC, pH, DO, T) in the vicinity of the AR locations prior to (baseline data) and during the implementation of AR measures. From the observed changes of these parameters subsequent to implementation of AR measures, if any, it is possible to evaluate the effectiveness of the AR measures and delineate its command area (area of influence). If required, at a few places, artificial tracers (rhodamine, fluorescein, ionic salts, isotopes, etc.) may also be used as a confirmatory tool to obtain localized information, such as groundwater flow and direction near the AR sites.

Submarine groundwater discharge (SGD) along the Arabian Gulf

The freshwater flow, either concentrated or diffused discharge, into the ocean from a coastal aquifer, or re-circulated seawater through the seabed sediments, or a combination of both (Mook 2001) is called an SGD. The driving mechanisms for the two components are quite different; the terrestrial component is governed by the groundwater hydraulic gradient, aquifer hydraulic conductivity, and many other factors, whereas the marine component depends on the oceanographic conditions (wave set-up, tidally driven oscillations, current-induced pressure gradients, etc.).

SGD, wherever groundwater is contaminated, can be a significant pathway for man-made and geogenic contaminants to reach the near-shore environment (IAEA 2008). Hence, identification and quantification of SGD is very important not only for quantifying the groundwater discharge but also for protection of the coastal zone from likely pollutants entering through SGD. The detection of SGD may be an additional source of water for various uses for the coastal community. SGD also helps in containing saltwater ingression into the coastal groundwater zones.

In the year 2000, as a 5-year plan, the International Atomic Energy Agency (IAEA), in collaboration with United Nations Educational, Scientific and Cultural Organization (UNESCO), made an initiative to assess methodologies for SGD, including isotopic approaches, and the salient findings on the applicability and limitations of them are summarized as a review article (IAEA 2008). The review article concludes that Rn and Ra isotope tracer-based method is the most promising method in comparison to other methods such as flow equation (analytical/numerical solutions), direct physical measurements using seepage meters, owing to heterogeneity, lumped model parameters, etc.). The advantage of Rn and Ra isotope tracer method over salinity as a tracer method is that Ra isotope tracers can distinguish off-shore groundwater discharge and re-circulated seawater and when used in conjunction with chemical and biological data (temperature, electrical conductivity, salinity, dissolved oxygen, nitrates, sulphates, biological oxygen demand, etc.) can provide information on sources, flow direction, exchange rates and chemical characteristics of the SGD. A number of successful case studies on SGD using Rn and Ra isotopes were carried out elsewhere in the world and published in various literatures (Fadlelmawla et al. 2008; Peterson et al. 2009; Li et al. 2009). However, very limited studies have been carried out in the Kuwait Bay and no studies in the Arabian Gulf have been reported.

For the Kuwait Bay or the Arabian Gulf, the SGD investigation would involve spatial and temporal sampling of groundwater along the coast and seawater for measurement of Rn and Ra isotopes. From the in situ measurement of ^{222}Rn, the locations of SGD can be identified. The laboratory measurement of $^{223,224,226,228}Ra$ would help in the quantification of SGD (off-shore gradient model). The $^{224}Ra/^{228}Ra$ ratio would enable the estimation of the average water residence time in the estuary. The $^{228}Ra/^{226}Ra$ ratio would help in distinguishing the likely SGD from the deeper carbonate Dammam Formation through the fracture from that occurring through the clastic surfacial Kuwait group aquifers.

Identification and quantification of hydrocarbon contamination of groundwater

As an aftermath of the Gulf War, a number of oil wells were destroyed due to which there are serious concerns about the possibility of groundwater contamination from the oil spills. A study has been carried out to know the nature and extent of hydrocarbon existence in groundwater in Kuwait employing several sensitive analytical methods that include gas chromatography/mass spectrometry (GC/MS) (Al-Awadi et al. 2009). The preliminary results of the study concluded groundwater contamination through anthropogenic and biogenic means, with the maximum contamination seen in the northern part of country, mainly in the Al-Raudhatain and Umm Al-Aish depressions. The authors also emphasized the need for further investigations for a more detailed characterization of the hydrocarbon contaminants in the Kuwait groundwater system.

Compound specific isotope analysis (CSIA), using a gas chromatograph (GC) combustion interfaced isotope ratio mass spectrometry (GC-C-IRMS), provides isotopic characterization of individual compounds and thereby enabling the assessment of the degradation processes in a quantitative way. The type and concentration of hydrocarbon compounds are important parameters for determining the quality of groundwater. A detailed investigation on the identification and quantification of various hydrocarbon groups in the groundwater bearing geological formation in Kuwait can now be carried out easily by CSIA technique. Subsequently, a development of a reactive transport model to assess different assisted natural attenuation processes and selection of an optimum one for the remediation of groundwater of the area are very essential.

Soil moisture and solute movement in unsaturated zone

The unsaturated zone (or vadose zone) is the part of the subsurface located above the groundwater table and containing water and air trapped in the pores (from: http://water.usgs.gov/ogw/unsaturated.html). The vadose zone contains clay and organic matter, and thus enabling sorption, biological degradation and transformation of contaminants in the subsurface medium. In agricultural and industrial areas, where hazardous wastes, pesticides or fertilizers contaminate the ground surface, the vadose zone may act as a buffer zone, i.e., protect the underlying aquifers (Zimmermann et al. 1967). The hydrogeological properties of unsaturated zone govern the deterioration of groundwater quality by man-made contamination.

Infiltration by rainwater is a complex process and can be expressed as piston flow (i.e., recent precipitation water pushes the older soil water to flow downward (Newman et al. 1997). Different precipitational infiltration profiles having unique isotopic content produce dissimilar vertical isotopic profiles. A sudden change in the isotopic profile within the soil can be noticed after a rainfall event having a distinct isotopic content. Thus, once the isotopic contents of rainwater, soil water, and groundwater are known, it would enable us to understand the rainwater infiltration processes and the depth of groundwater recharge by estimating the movement of isotopic peak along the soil profiles.

Zimmermann et al. (1967) first described the influence of evaporation on the stable isotopic compositions of soil water. Since then, several investigators (e.g., Gazis and Feng 2004; Newman et al. 1997; Gehrels et al. 1998; Brodersen et al. 2000) have determined the variation of deuterium and oxygen composition in soil water. The experiments on vegetated soil water were also seldom carried out and reported. Radioactive tritium (^3H) has been often employed especially in the unsaturated soil and arid environment to know the recharge to groundwater, variation of soil water movement and travel times (Lin and Wei 2006).

Management of shared groundwater aquifers

Generally, the main issues related to the management of shared groundwater aquifer are utilizing the shared aquifers on a sustainable basis so as to avoid potential source of dispute between riparian states, augmentation of groundwater recharge through artificial methods, lack of joint monitoring system and lack of sharing of information that eventually lead to practical difficulties for the development of a management model. The Gulf region is no exception to these issues or difficulties.

A joint research proposal on “Shared groundwater aquifers in GCC countries” is a key to the better development and management of groundwater resources in the region and can also be the starting step for alleviating sensitivity of the related issues. Broadly, the main components of the joint research proposal could be: (1) provenance of groundwater and estimation of groundwater recharge by multiple approaches including isotope hydrology, the other methods being hydrogeology, hydrochemistry, piezometric data, and hydrochemistry, and (2) flow, transport and geochemical modelling. Isotope hydrology techniques can also play a vital role in proving invaluable real-time data such as groundwater transit times (groundwater ages), source rock identification, etc., for the purpose of calibration and validation of some of the commercially or public domain available transport and geochemical models.

Paleoclimate reconstruction

A number of water resources on the earth are endangered by over-exploitation and contamination/pollution, hence sustainable management of the scarce water resources needs a profound knowledge of renewal rates and susceptibility to climatic changes. Any variation in the precipitation, along with variations in atmospheric temperature, not only affects input (recharge) and output (discharge) components of a groundwater system, but influence its’ water quality (Sukhija et al. 1998), modify the groundwater flow network, groundwater divides may move position (Dragoni and Sukhija 2008). In addition, it is also possible to relate the existence of certain chemical ionic species in groundwater to specific water–rock interactions that occurred during particular climatic conditions that existed in the past (e.g., wetter conditions with higher infiltration rates associated with low Mg/Ca, Sr/Ca).

In addition, an investigation on the impact of past sea level changes on the hydrology of the coastal aquifers (i.e., landward and seaward extent of seawater during the past transgression and regression episodes, delineation of buried paleochannels, if any, etc.) requires a good information on the past climates of a region. Paleoclimate records allow one to assess the full range of drought (or flood) variability by utilizing data that span longer periods of time. That is to know whether a historic and recorded flood or drought event is a representative (recurring) one or a rare extreme event, and if recurring, what its recurring time interval (i.e., hydrologic return period). A good paleoclimate record (data) helps in evaluating the regional sensitivity of global climate models (i.e., validation of global climate models) for predictive purposes and for its applications related to integrated water resources management. In other parts of the world, based on the groundwater isotopic composition, a number of studies on climatic change that occurred during the Late Quaternary have been obtained but not many reported in this region.

The temperature effect on the precipitation isotopic content is one of the basis for tracing waters in the hydrologic cycle and hence used to reconstruct paleoclimates and paleohydrology. Oxygen-18 and hydrogen-2 in meteoric waters (meteoric water line) have strong positive correlation with isotopically-depleted (more negative) waters associated with colder regimes while enriched (less negative) waters are found in warm regions. Hence, the meteoric water line provides baseline information on recharge conditions. The deuterium excess in precipitation ($d = \delta^2H - 8 \times \delta^{18}O$) is usually construed as an isotope signal dependent on climate conditions during evaporation. Stable oxygen-17 isotope and its excess parameter [$^{17}O = \ln(^{17}O + 1) - 0.528 \times \ln(^{18}O + 1)$] values of groundwater provides an estimate on the relative humidity at the time of recharge.

The noble gas temperature is a measure of the temperature at which groundwater equilibrated with the atmosphere during percolation, and it generally relates to the mean annual temperature of air (Stute and Talma 1998; Loosli et al. 2004). Groundwater ages obtained from its' ^{14}C values, ^{36}Cl and $^{4}He/^{222}Rn$ can be correlated with He, Ne, Ar, Kr and Xe noble gas thermometry to know the variation in temperature with age. Subsequently, stable isotopes and noble gases data are combined to establish the long-term relationship between oxygen isotope and temperature. The most commonly used models for interpreting noble gas results to obtain thermometry are closed-system equilibrium mode, iterative model and least-square model.

The groundwater noble gases data analysis needs "excess air" correction. In literature, three models have been widely used and they are; total dissolution of trapped bubbles, partial re-equilibration with the atmosphere after total dissolution, and closed-system equilibration of groundwater with partially dissolved entrapped air (Aeschbach-Hertig et al. 2000).

As a summary, the noble gases (He, Ne, Ar, Kr, Xe) will provide a measure of the temperature at the time of recharge (i.e., paleotemperature). Stable isotopes analyses of groundwater (^{18}O, ^{2}H) will help in obtaining the information on the sources of condensing moisture during Late Pleistocene and regional atmospheric circulation. Stable ^{17}O isotope of groundwater will provide an estimate on the relative humidity at the time of recharge. Radioactive ^{14}C (1 ka–60 ka B.P), ^{36}Cl (50 ka–1 Ma B.P) and stable ^{4}He (in combination with radioactive ^{222}Rn) isotopes (104–108 a B.P) will give an estimate on the residence time or ages of groundwater.

Apart from the above-mentioned areas of isotope hydrology applications, the other areas of interest could be; understanding dynamic changes due to long-term exploitation of the groundwater resources, assessment of freshwater lens at deeper sediments along the coastal parts, assessment of the source and origin of ^{222}Rn in groundwater, understanding the importance of flash flood events to recharge, etc.

Need for an isotope hydrology atlas of the Gulf region

An atlas showing the distribution of environmental stable isotopic species of water, namely ^{2}H and ^{18}O, in rainwater and groundwater in the Gulf region could provide much useful hydrogeological information for the future isotope hydrology projects. First, it facilitates the development of a local meteoric water line which is the main basis of application of isotope hydrology techniques for deciphering the source of condensing moisture (continental, coastal, evapotranspiration, recycled water, etc.) and that of groundwater recharge (rainwater, surface water). This when combined with a water age dating tool, such as environmental ^{3}H and ^{14}C, provides invaluable information on the identification of recharge area, regional groundwater flow direction; mechanism of recharge (direct infiltration, concentrated or diffused recharge, time of recharge, etc.); climatic conditions during recharge (humid, arid phase); and interrelationship between various water bodies (aquifer–aquifer, river–groundwater, etc.).

The aforementioned information in conjunction with geological, hydrogeological and hydrochemical data would provide a holistic picture on the various groundwater flow processes which is vital for the development, management and protection of scanty and precious groundwater sources in the region. Thus, there is a definite need for developing an isotopic hydrology atlas for the region. The isotope hydrology atlas should have location maps from where the various waters samples have been collected for isotopic analyses (^{2}H, ^{18}O, ^{3}H, ^{13}C, ^{14}C), relevant isotopic plots and summary statistics (iso-plots, median, mean), along with average annual precipitation, air temperature, etc. Thus, the generated isotope hydrology atlas will become a very handy tool not only for the water resource managers and policy makers but also for the researchers and academia for human resources development and for carrying out advanced research in the field of isotope hydrology.

Conclusions

The water environment in Gulf countries faces intimidating problems of unsustainable water demand, groundwater drawdown, degraded water quality and increasing vulnerability to extreme events. As the stress on water systems is increasing in Gulf countries, R&D is needed for better understanding of natural water system. In this respect, the development and practical implementation of isotope hydrology methodologies in water resources assessment and management is definitely need of the hour in the region. In addition, development through direct support to research and training, and verification of isotope hydrology methodologies through field projects are required by various researchers in the region, and constant efforts are essential to propagate the same to end-users.

Literature survey surmises that the important areas of isotope hydrology applications in groundwater management in the Gulf region are evaluation of aquifer recharge and aquifer storage and recovery system, groundwater discharge along the Arabian Gulf, identification and quantification of hydrocarbon contamination in groundwater, soil moisture and solute movement in unsaturated zone, management of shared groundwater aquifers in GCC countries, paleoclimate reconstruction, etc. Understanding dynamics changes due to long-term exploitation of the groundwater resources, assessment of freshwater lens at deeper sediments along the coastal parts, assessment of source and origin of ^{222}Rn in groundwater, etc., could also be the other areas of interest.

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