Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/ejrh

ejrh –

Identifying the seasonal variability in source of groundwater salinization using deuterium excess- a case study from Mewat, Haryana, India



G. Krishan^{a,*}, G. Prasad^a, Anjali^a, C.P. Kumar^a, N. Patidar^a, B.K. Yadav^b, M.L. Kansal^b, S. Singh^a, L.M. Sharma^c, A. Bradley^d, S.K. Verma^a

^a National Institute of Hydrology, Roorkee, Uttarakhand, India

^b Indian Institute of Technology Roorkee, Uttarakhand, India

^c Sehgal Foundation, Gurgaon, Haryana, India

^d The University of Iowa, Iowa City, Iowa, 52242, USA

ARTICLE INFO

Keywords: d-Excess Salinity mechanism Seasonal changes Mewat Haryana

ABSTRACT

Study region: Mewat (renamed as Nuh) district of Haryana, India having geographical area of 1507 km^2 , comes under semi arid climatic conditions and Aravali hill ranges separates it from Rajasthan state.

Study focus: Groundwater salinization is an emerging threat to water management. Understanding the sources of salinization, and their relative contributions by different sources and seasonal variability has become priority for planning best practices in water management and suggesting remedial measures. For identifying the sources of salinization, the direct application of the relationship between δ^{18} O and δ D is limited as it depends upon initial isotopic composition showing no isotopic variation in the mineral dissolution process. The present study advocates the use of deuterium excess which is independent of initial isotopic composition and extends this concept for identifying the relative contribution of different sources towards seasonal variability in salinization.

New hydrological insights for the region: The district showed an average salinity of 6.7 g/L in premonsoon; 7.3 g/L in monsoon and 7.4 g/L in post-monsoon season thus a variability of 0.7 g/Lobserved. The area affected by the salinization (> 2 g/L) also registers an increase from 86 % (pre-monsoon) to 99 % (post-monsoon) period. Mineral dissolution is found to be responsible for overall groundwater salinization with contribution of 97 %, declined to 86 % in post monsoon. In post monsoon season, contributions from initial salinity and evapoconcentration towards salinization increased by 8% and 3%, respectively.

1. Introduction

Groundwater is the largest freshwater reservoir in most parts of the world, and its consumption is only possible when it is free from any contaminants and pollutants including the salts. Excess salts in groundwater may lead to abandonment of supply wells. Groundwater salinization occurs at local and regional scales and may have diverse origins (Wen et al., 2005; Manivannan and Elango, 2019) as a result of geogenic sources initiated or facilitated by anthropogenic activities (Krishan, 2019b) has become a very serious

* Corresponding author.

https://doi.org/10.1016/j.ejrh.2020.100724

Received 16 June 2020; Received in revised form 21 July 2020; Accepted 22 July 2020

2214-5818/ © 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

E-mail addresses: drgopal.krishan@gmail.com, drgopal.krishan.nihr@gov.in (G. Krishan).

and widespread groundwater contamination issue throughout the world. Groundwater salinization is a very common along the coasts and in island systems, and was first identified more than a century ago (Drabbe and Ghijben, 1889; Herzberg, 1901). But increasing inland groundwater salinity in arid and semi-arid regions is also posing threats to populations living in those areas (Krishan et al., 2019a). Arid and semi arid regions already have fragile ecosystem that threaten the people living in these areas and increasing groundwater salinity further adds to the water resource issues of the area (Bennetts et al., 2006).

For healthier water resource management, it is important to identify the sources of salinity and understand mechanisms of groundwater salinization through its chemical evolution (Edmunds, 2009). In this context, various experiments have been carried out in many parts of the world which include effects of evaporation on groundwater salinity (Simpson et al., 1987); mobilization of salts due to change in hydrological regimes (Simpson and Herczeg, 1991); the effect of groundwater salinity on plant growth (He et al., 2006; Manchanda and Garg, 2008); and deterioration in water quality (Edmunds, 2003). For inland areas, studies have examined groundwater salinity arising as a result of mineral dissolution and evapo-transpiration taking place at local and regional scales (Hao et al., 2000; Phillips et al., 2003) controlled by factors such as source of groundwater recharge, aquifer characteristics and discharging areas.

Isotopes can be used as an effective tool in various hydrological evaluations including understanding salinity mechanisms (Krishan et al., 2020a, b). It has been reported by Barnes and Allison (1988) that precipitation water undergoes evaporative fractionation during the process of infiltration through the top layers of soil water infiltration, on the other hand few other researchers (Zimmermann et al., 1967; Foerstel, 1982) found no isotopic fractionation during salt drainage, plant transpiration or mineral dissolution. It has been found that stable isotopes of water (δ^{18} O and δ D) separately or in combination or their relations with salinity can not be used to examine the evaporation processes due to seasonal variations in source waters (Krishan et al., 2020a, b). To overcome this limitation, Huang and Pang (2012) proposed a method to explain salinity mechanisms using deuterium excess which is calculated from the stable isotopes (δ^{18} O and δ D). The proposed method works on the principle of mass loss ratio with a limitation of varying initial water due to different recharge sources and has been successfully tested in Tarim river basin, China. According to this method, δ D and δ^{18} O increases in a water body undergoing evaporation which results in decreased deuterium excess and increased salinity (Dansgaard, 1964).

Certain relationships between evaporation, salinity and mass loss ratio can be established. In the process of evaporation water gets lost to the atmosphere leaving the dissolved salts in the reserves of water resulting in increase in salinity. A similar phenomenon can be observed between water lost to atmosphere and enrichment of heavier isotopic ratio, for example, 1 % loss of water body in comparison to initial mass enriches δD value by 0.65‰ in Egypt (Simpson et al., 1987), 0.78‰ for northwestern Sahara (Fontes and Gonfiantini, 1967) and 0.62‰ for Australia (Simpson and Herczeg, 1991). A similar trend can be obtained between water body loss and enrichment of $\delta^{18}O$ (Gaye, 2001). However, both δD and $\delta^{18}O$ vary with season representing the unique signatures of their source (Clark and Fritz, 1997) but the ability to establish a relation between salinity and water body loss with availability of initial isotopic composition for each and every scenario is limited. Huang and Pang (2012) identified that although δD and $\delta^{18}O$ vary with season both for groundwater and surface water, the mass loss ratio remains the same. Thus, Dansgaard (1964) proposed the use of deuterium excess (d) represented by $d = \delta D - 8\delta^{18}O$ to determine the relation between evaporation and salinity.

In India, 70 % of food production and economy depend on the southwest monsoon which onsets during June to ends during late September exhibits large variability in space and time, and consequently leads to a considerable variation in groundwater recharge. Considering these facts, this purpose driven study was carried out for monsoon, pre-monsoon and post-monsoon seasons under National Hydrology Project (India) with the aims to (1) identify salinity mechanisms through the use of deuterium excess in the salinity-affected Mewat region of Haryana, (2) to understand the contribution of mineralization towards groundwater salinity, and (3) to determine groundwater residence time using Tritium (³H). With identification of source of salinity in semi-arid part of Mewat, an economical water management and salinity control plan can be created for the region. The outputs of the study will help controlling salinity and managing water in sustainable and economical manners in the semi-arid regions.

2. Study area

The Mewat district (renamed as Nuh) is a newly formed district of Haryana state, India (Fig. 1) with a geographical area of 1507 km² and population of 1,089,406 (Census, 2011). The district comes under semi arid climatic conditions with normal rainfall of 594 mm/year, out of which 80 % rainfall occurs in monsoon season; water level is 2-35 m below ground level (mbgl) in pre-monsoon season and 0.9-38.1 mbgl in post-monsoon season (Priyanka et al., 2016). Aravalli hill ranges occupy 199.65 km² in the district, separate Mewat from Rajasthan state and also check movement of sand from the Thar desert in Rajasthan. The Aravallis also help in recharging of groundwater, and aquifers in these ranges are interconnected. The digital elevation data shows depressions in the central part of the district with altitude decreasing from 450 m amsl (meters above mean sea level) to 150 m amsl (Fig. 2a). The district is comprised of five blocks, named Tauru, Nuh, Punhana, Nagina and Firozepur Jhirka. The Nagina and parts of Nuh and Firozepur Jhirka blocks are found with a very high groundwater salinity, which is increasing over time and is reported to be advancing on fresh water aquifers (Thomas et al., 2012; Krishan et al., 2017, 2019c). The major soil texture in the study area is loamy sand, sandy loam and silty loam (Krishan et al., 2018). Land use/land cover map (Fig. 2b and d) and the area statistics of land uses/ covers show that 64 % of the district and 48 % of the study area (Area = 393 km^2) is cultivated. Water bodies are 2 % of the study area. The geology of the district is dominated by middle-late Pleistocene and Holocene (Fig. 2c). Quaternary sediments alluvium deposits consists a sequence of inter layered clay/silt and sand with occasional kankar formations (Malik and Rajeshwari, 2011). The point lithologs of the borelogs along with different geological formations are shown in Fig. 3. The lithologs show intermittent good aquifer or multiple aquifer formations at particular depths, wherein the clay and silt layer formations have continuous areal extent at



Fig. 1. Study area showing sampling locations.

different layers.

3. Methodology

3.1. Sampling

In the year 2018, 18 random groundwater samples were collected from the salinity-influenced zone covering a 393 km² area in Nagina and Firozepur Jhirka blocks of the Mewat district during pre-monsoon (April-May); monsoon (July-August) and post-monsoon (October-November) seasons. The sampling locations shown in Fig. 1 include open wells, tubewells and handpumps with a depth range of 4–92 m. Six groundwater samples were collected from Nagina and Firozepur Jhirka blocks for tritium analysis.

3.2. Analysis

EC was measured on site using portable hand held Hach, HQ30d EC meter and then converted to salinity and expressed in g/L. The ratios of heavy stable isotopes (δ^{18} O and δ D) were measured using a Dual Inlet Isotope Ratio Mass Spectrometer DI IRMS (Isoprime GV instruments, U.K) with automatic sample preparation units at Nuclear Hydrology Laboratory of National Institute of Hydrology, Roorkee. Measurement errors (precision) in estimates were within the limits of \pm 0. 1‰ for δ^{18} O and \pm 1.0‰ for δ D. The isotope ratios for $^{18}O/^{16}O$ and D/H were expressed in per mil units using the δ notation relative to VSMOW (Clark and Fritz, 1997). Dexcess was calculated as: δ D-8* δ ^{18}O (Dansgaard, 1964) and globally it is 10‰, and it decreases with increases in evaporation and salinity. For the tritium analysis, 1000 ml of six groundwater samples were collected and distilled to reduce the conductivity; deuterium and hydrogen were removed by the process of physico-chemical fractionation in the tritium enrichment unit which is based on physico-chemical fractionation by difference in the strength of bonds formed by the light versus the heavier isotope of a given element. The values of tritium observed were low, so a total of 8–10 cycles (runs) were executed using Quintals process. Tritium concentration data files were created with the help of WinQ and Quick start software in Quintals process (Liquid Scintillation Spectrometer). The concentration of tritium in terms of tritium units (TU) of various samples was determined. Tritium error of the individual samples is given in Fig. 10. Water builds up in the aquifers in the years, so age was calculated using the radioactive decay equation and called "effective age" (Mazor, 2004) or "tracer age".



Fig. 2. Digital elevation model (b) Land use/land cover map (c) Geology and (d) percent land use/land cover of the study area, Mewat district, Haryana.

3.3. Salinity mechanism

Groundwater salinity is the result of the combined effects of evaporation, mineral dissolution and plant transpiration. When plants transpire, it excludes the salt present in the water, in arid and semi-arid climatic condition due to less rainfall in comparison to evapotranspiration the salt thus excluded gets deposited in the soil. When water seeps through salty soil layer it increases the salinity of groundwater (Fass et al., 2007; Barbeta and Peñuelas, 2017; Hasanuzzaman et al., 2017). But out of the three phenomena, it is only the effect of evaporation that is translated into a change in isotopic fractionation (Zimmermann et al., 1967; Foerstel, 1982).

'Craig's global meteoric line' (Craig, 1961) which defines the relationship between δ^{18} O and δ D in freshwater worldwide is described by:

$$\delta D = 8 \ \delta^{18} O + 10\%$$
(1)
where, $\delta = \{(R/R_{reference}) - 1\} \times 1000$
(2)

and 'R' is the relative abundance of an atom with respect to per thousand a most abundant atom and is termed as isotopic ratio.

This relationship undergoes a change with changes in prevailing climatic and geographic factors. When precipitation or source stream water undergoes evaporation, δD values declines more relative to $\delta^{18}O$ and the slope of regression line (equation-1) reduces to



Fig. 3. Lithologs of the borelogs and fence diagram.

less than 8 (Barnes and Allison, 1988). But the use of Eq. (1) becomes limited in estimating the effect of evaporation on water salinity as the isotopic composition of initial water varies with both season and between different precipitation amounts within the same season (Clark and Fritz, 1997). To overcome this limitation, Dansgaard (1964) proposed the use of deuterium excess (d) represented by:

$$d = \delta D - 8\delta^{18}O$$

(3)

Before the precipitation reaches the ground surface it undergoes evaporation and a relative abundance of δ^{18} O with respect to δ D can occur. The decline in deuterium excess represents the evaporation, on the degree of negative correlation in equation (3) represents the intensity of evaporation taking place in the area for a particular season.

During the process of evaporation, equilibrium is set between the surface layer of water reservoir where water molecules are removed and in the adjacent ambient air where water molecules are being exchanged, leads to isotopic fractionation and described by the Rayleigh Equation.

$$R = R_0 f^{(\alpha v-1-1)}(Clark and Fritz, 1997)$$

(4)

where, f is the remaining fraction of the water body; α_{v-l} -1 is the fractionation factor between product (vapour) and reactant (liquid water) including equilibrium and kinetic fractionation.

Combining equations (3) and (4) yields

$$\delta = (R_0 f^{(\alpha v - l - 1)} / R_{reference} - 1) \times 1000 = (\delta_0 + 1000) f^{(\alpha - 1)} - 1000(Huang and Pang, 2012)$$

(5)

(6)

Using Eqs. (5) and (2), deuterium excess can be obtained, as represented by Eq. (6)

$$d = (\delta_{OD} + 1000) f^{(\alpha D - 1)} - 8 (\delta_{O}^{18}O + 1000) f^{(\alpha 18}O^{-1)} + 7000(Huang and Pang, 2012)$$

where, $\delta_o D$ and $\delta_o^{18}O$ are initial δ values of water. Huang and Pang (2012) showed that at constant temperature and constant relative humidity, two water samples with different isotopic compositions the same salinity, when subjected to evaporation, have similar changes in d and f, independent of initial isotopic composition $\delta_o D$ and $\delta_o^{18}O$.

Seasonal variations in evaporation are related to changes in temperature and humidity over an area. When an equilibrium in water-vapour exchange (ε_{1-v}) is reached, humidity depends only on temperature (Majoube, 1971).

Clark and Fritz (1997) illustrated that the total isotopic fractionation (α_{l-v} - 1) and ($1/\alpha_{v-l}$ - 1) for open water and air respectively is the sum of fractionation factor for equilibrium water-vapour exchange (ε_{l-v}) and the kinetic factor ($\Delta \varepsilon_{bl-v}$) which is responsible for removal of water molecule from the surface of water is represented by the following equation.

$$\alpha_{l-v} = \varepsilon_{l-v} + \Delta \varepsilon_{bl-v} \tag{7}$$

The equilibrium water-vapour exchange (ɛl-v), dependent only on temperature, and can be obtained using (Majoube, 1971)

$$10^{3} \ln \varepsilon_{l-v} D = 24.844 (10^{6}/T^{2}) - 76.248 (10^{3}/T) + 52.612$$
(8)

$$10^{3} \ln \varepsilon_{\rm Lv}{}^{18}{\rm O} = 1.137 \ (10^{6}/{\rm T}^{2}) - 0.4156 \ (10^{3}/{\rm T}) - 2.0667$$
(9)

For determining the kinetic factor ($\Delta \varepsilon_{bl-v}$), Gonfiantini (1986) gave the following equations which are dependent on humidity (h) and in turn on temperature (T).

$$\Delta \varepsilon^2 H_{\rm hl-y} = 12.5(1-h)/1000 \tag{10}$$

$$\Delta \varepsilon^{18} O_{bl-v} = 14.2(1-h)/1000 \tag{11}$$

Once the seasonal salinity contribution of evaporation is identified, it can be separated from total salinity to determine the salinity contribution by mineral dissolution.

To analyse the seasonal variability in salinity and to find the source of such salinity the groundwater samples from Kotla is taken as the reference. Kotla, which is located at the foothills of Aravalli, possess groundwater which satisfies all groundwater standards and used for drinking purposes. For the δD and $\delta^{18}O$ in source water, firstly determined the average d value, then the approximate median value can be estimated because d is not related to specific δD and $\delta^{18}O$ value. For example, the d value of your source water for pre-monsoon is 8.24‰, calculated from $\delta^{18}O$ of -6.78‰ and δD of -46‰. For every value of d-excess, there is a specific value of fraction 'f', the initial salinity will be salinity of source water as 'S'. Contribution of evapo-concentration (E_c) and mineral dissolution (M_d) will be as below:

$$E_{c} = S/f_{i}-S$$
(12)

$$M_{d} = S_{o}S/f_{i}$$
⁽¹³⁾

Where S is Initial salinity (salinity of source water); f_i is fraction value of the sample; S_o is salinity value of sample

As shown in Fig. 4, the total salinity added to groundwater comes from both evaporation and mineral dissolution. If we consider that the initial volume of water is 'V', and the water volume after evaporation is reduced to 'f', then evaporation leaves behind the dissolved salt and the groundwater salinity increases S_o (V-f)/f. Thus, the salinity imparted by mineral dissolution (D) = Total salinity evapoconcentration-initial salinity = S- S_o (V-f)/f. S_o .



Fig. 4. (a) initial condition of water reservoir with a volume (V), salinity (S_o) before the start of evaporation process. (b) After the onset of evaporation, the volume of water in reservoir is changed to f and the new salinity accommodating the effect of evaporation and mineral dissolution becomes S.

Table 1

Isotope composition of groundwater in Mewat.

	Pre-monsoon		Monsoon		Post monsoon			
	δ ¹⁸ Ο (‰)	δD(‰)	δ ¹⁸ O(‰)	δD(‰)	δ ¹⁸ O(‰)	δD(‰)		
Ghagas village	-5.8	- 43.5	-4.4	-34.4	-3.7	-34.1		
kansali	-6.0	- 42.5	-4.1	-35.4	-3.9	-34.9		
Ghagas SF	-5.4	- 39.9	-2.3	-17.2	-2.4	-20.6		
Doha	-5.0	-38.2	-3.2	-28.7	-4.1	-34.5		
Kankar khedi	-4.6	-34.2	-5.3	-40.9	-5.3	- 39.6		
Nangli bhundi	-4.9	-37.9	-6.6	- 45.7	-6.7	-46.8		
Pat khori	-6.1	- 45.6	-5.3	-41.4	-5.2	-40.6		
Dhadoli	-6.4	-45.2	-5.4	-42.9	-5.4	-42.0		
Basai	-6.3	-47.2	-5.7	-44.0	-5.8	-44.8		
Naharika	-6.3	- 46.7	-5.1	-40.0	-5.1	-41.8		
Kaliketa	-5.9	-46.2	-6.8	- 48.6	-6.6	-47.5		
Mohmmad	-5.8	-44.9	-6.4	-44.9	-6.3	- 46.9		
Khedi khurd	-6.5	- 47.6	-6.5	-46.2	-6.5	- 47.9		
Raja ka pul	-7.8	-53.8	-6.0	-41.4	-5.7	- 45.9		
gouhana	-4.3	- 35.6	-5.8	-42.9	-5.9	-46.2		
Naglashahpur	-4.3	- 35.6	-6.6	- 47.5	-6.3	-49.1		
Saral	-5.1	-40.6	-5.3	-42.8	-5.3	-44.2		
Jaitako	-4.2	- 35.9	-6.4	-46.4	-5.6	-45.0		
Min	-7.8	-53.8	-6.8	- 48.6	-6.7	-49.1		
Max	-4.2	-34.2	-2.3	-17.2	-2.4	-20.6		
Mean	-5.6	-42.3	-5.4	-40.6	-5.3	-41.8		
Stdev	0.9 5.4		1.2	7.7	1.1			

3.4. Water level data

Groundwater levels were recorded for 40 monitoring wells during the time period 2011 - 15. The wells are developed by Sehgal foundation in the study area in Mewat district, Haryana. During this period, there is an average decrease of 29 % in water level in pre –monsoon and in general water levels decreased during pre-monsson period and increased during post monsoon period (Priyanka et al., 2016).

4. Results and discussion

To understand the source of seasonal variation in the groundwater salinity, 18 samples from different sites in the Mewat district, Haryana were collected and analyzed for δ^{18} O and δ D. The results are listed in Table 1. For the pre-monsoon season (April-May), the mean values of δ^{18} O and δ D for pre-monsoon season (April-may) with mean temperature 32.75 °C and humidity 26.25 % are -5.5‰ and -42.3 ‰ respectively. Whereas δ^{18} O is -5.5 ‰ and δ D is -42.3‰ with a mean temperature of 32.75 °C and mean humidity of 26.25 %. In contrast, for the post-monsoon season period (October), δ^{18} O is -5.3‰ and δ D is -41.8‰ with the temperature of 27.25 °C and humidity of 49.25 %. The variation in mean values of isotopic composition of pre-monsoon and postmonsoon is small. Rozanski et al. (1993) examined the relationship between isotopic composition and temperature (T) for precipitation over India, and showed that the seasonal Δ T is low and so there is little variation in isotopic composition δ^{18} O and δ D. There is also a strong influence of Dansgaard's amount effect in the region. Precipitation during low rainfall months experiences evaporation in low humid air column, and d-excess correlates with the seasonal variation in the precipitation. The seasonal variability in isotopic composition of precipitation gets captured by the groundwater samples.

To further examine the evaporation effect on groundwater of the study area, δ^{18} O is plotted against δ D as shown in Fig. 5. The slope of 5.5, 6 and 6 is observed for pre-monsoon, monsoon and post-monsoon seasons, respectively. Since the regression lines are subparallel to Global Meteoric Water Line (GMWL) given by Craig (1961) with slopes less than 8, it suggests occurrence of evaporation prior to the infiltration of water in the unsaturated zone (Krishan et al., 2020b; Huang et al., 2012; Kulkarni et al., 1989).

Seasonal variations in d-excess, remaining fraction and salinity during evaporation are shown in Fig. 6. It is found that salinity increases and d-excess decreases during evapoconcentation in all seasons. There is a linear relationship between d-excess and remaining fraction in all 3 seasons in all samples more scatter is found in salinity and remaining fraction values in 16 % of the samples indicating seasonal variations. Huang and Pang (2012) found that the salinity is doubled when half of the water is evaporated due to evapoconcentration, and a decrease in deuterium excess from 10% to -9.7 %.

The summary of water samples collected from Kotla is taken as reference and given in Table 2. As can be seen from Table 2, a relation between d-excess, f and salinity exists. In the monsoon period the salinity value is highest at 0.53 g/L; because these monsoon months have heavy rainfall, mineral dilution occurs, along with higher evaporation which is reflected in the lower values of fraction (f). In the post-monsoon period, with its lower temperatures, the evaporation decreases (f = 0.45) and the salinity comes down to 0.31 g/L. In the pre-monsoon period, the fraction (f) increases drastically and the salinity shows a decline to 0.05 g/L. This was



Fig. 5. Isotope characterization of groundwater in Mewat.



Fig. 6. Seasonal variations in d-excess (a) and salinity (b) versus remaining fraction in Mewat, Haryana.

Table 2

The salinity and isotopic parameters for the source water at Kotla.

Parameter	Pre-monsoon	Monsoon	Post-monsoon
δ ¹⁸ O	-6.78	-7.88	-7.59
δD	-46	- 53.97	-51.33
d-excess	8.24	9.07	9.39
Temperature(T) in Kelvin	305.75	304.88	300.25
Humidity (h)	0.265	0.768	0.493
Salinity(g/L)	0.05	0.53	0.31
Fraction (f)	0.756	0.36	0.45

possible because the groundwater level start to rise during pre-monsoon seasons. Dilution of the regional water source by rainfall recharge can be seen in the declining salinity. To understand the contribution of initial salinity, evaporation and mineral dissolution the value of d-excess, TDS and fraction after evaporation is calculated and tabulated in Table 3.

The value of d-excess depends upon the temperature and humidity values in the area. The seasonal variability in salinity and d-excess are shown in Figs. 7 and 8, respectively. It has been observed that the groundwater of the district showed an increase of 0.7 g/L salinity from pre-monsoon (6.7 g/L) to post-monsoon season (7.4 g/L). The d-excess shows a decline of 1.6 ‰ in post-monsoon when

Table 3

Season-wise salinity (TDS), deuterium excess (d), the remaining fraction (f), contribution percent of initial salinity, evapoconcentration and mineral dissolution (D) for groundwater in Mewat.

	Salinity (S-g/L); d-excess (d-ex ‰); fraction (f)								Salini MD-M	Salinity source contribution (%) IS-Initial salinity; EC-Evapoconcentration; MD-Mineral Dissolution								
	Pre monsoon			Monsoon			Post monsoon			Pre-monsoon			Monsoon			Post monsoon		
	S	d-ex	f	S	d-ex	f	S	d-ex	f	IS	EC	MD	IS	EC	MD	IS	EC	MD
Ghagas village	1.8	2.8	0.83	6.6	1.1	0.78	5.3	-4.5	0.63	2.97	0.61	96.42	7.95	2.19	89.87	5.90	3.44	90.66
Kansali	4.7	5.3	0.91	6.9	-2.6	0.68	7.1	-3.6	0.66	1.12	0.11	98.76	7.61	3.65	88.75	4.36	2.29	93.35
Ghagas SF	2.6	3.2	0.84	3.0	1.5	0.79	2.9	-1.5	0.71	2.06	0.39	97.55	17.44	4.58	77.98	10.56	4.36	85.08
Doha	4.8	1.8	0.80	4.1	-3.4	0.66	2.4	-1.7	0.70	1.11	0.28	98.61	12.98	6.63	80.39	12.82	5.39	81.79
Kankar khedi	24.1	2.7	0.83	24.9	1.6	0.79	24.9	3.1	0.84	0.22	0.05	99.73	2.12	0.56	97.32	1.24	0.24	98.52
Nangli bhundi	6.9	1.0	0.78	5.7	7.3	0.98	5.2	6.8	0.96	0.77	0.22	99.01	9.28	0.23	90.50	5.99	0.25	93.77
Pat khori	1.9	3.0	0.84	0.9	1.4	0.79	1.1	1.1	0.78	2.79	0.53	96.68	60.51	16.28	23.22	27.69	7.99	64.32
Dhadoli	2.3	5.7	0.92	2.4	0.0	0.75	2.4	1.1	0.78	2.29	0.20	97.51	22.41	7.55	70.04	13.18	3.81	83.01
Basai	0.7	2.8	0.83	3.2	1.4	0.79	3.0	1.4	0.79	8.10	1.66	90.23	16.70	4.49	78.81	10.40	2.80	86.81
Naharika	1.2	3.8	0.86	4.0	1.0	0.78	4.1	-1.3	0.71	4.59	0.75	94.66	13.04	3.77	83.19	7.55	3.02	89.43
Kaliketa	1.7	1.0	0.78	1.7	5.6	0.92	5.2	5.1	0.90	3.15	0.91	95.94	30.14	2.69	67.17	5.95	0.65	93.40
Mohmmad	2.3	1.2	0.78	2.2	6.6	0.95	2.3	3.1	0.84	2.33	0.64	97.03	23.48	1.18	75.34	13.61	2.55	83.84
Khedi	0.8	4.8	0.89	1.1	5.4	0.91	1.7	3.8	0.86	6.53	0.79	92.68	47.93	4.63	47.44	17.86	2.91	79.23
khurd																		
Raja ka pul	0.7	8.5	1.00	0.6	6.6	0.99	0.6	0.0	0.75	7.75	0.00	92.25	81.76	0.66	17.58	48.65	16.39	34.96
Gouhana	5.5	-0.9	0.72	5.4	3.2	0.84	5.9	0.8	0.77	0.96	0.37	98.67	9.75	1.86	88.40	5.28	1.56	93.17
Nagla	37.1	-0.8	0.73	34.2	5.4	0.91	35.1	1.2	0.78	0.14	0.05	99.80	1.54	0.15	98.31	0.88	0.24	98.87
shahpur																		
Saral	7.9	-0.1	0.74	7.2	-0.7	0.73	4.8	-1.5	0.71	0.67	0.23	99.10	7.32	2.71	89.97	6.50	2.68	90.82
Jaitako	13.4	-2.7	0.68	16.5	5.1	0.90	19.8	0.2	0.76	0.40	0.19	99.42	3.20	0.35	96.46	1.57	0.51	97.93
Min	07	2.7	0.60	0.6	2.4	0.66	0.6	4 5	0.62	0.14	0.00	00.00	1 5 4	0.15	17 50	0.00	0.24	24.06
Mor	0.7	- 2.7	1.00	24.2	- 3.4	0.00	25 1	-4.5	0.03	0.14	1.66	90.23	01 76	16 20	17.50	0.00 40.6E	16 20	00 07
Mean	57.1	0.0	0.82	34.Z	7.5	0.99	55.1 7 /	0.0	0.90	0.10	0.44	99.00	20.84	2 56	75 50	+0.03	3 30	90.07
Stdov	0.7	2.7 2.7	0.02	0.0	2.0	0.03	7.7	2.0	0.09	2.00	0.44	2 70	20.04	3.95	73.59	11.11	2.25	15 12
BILLEV	9.5	2.7	0.00	9.0	5.4	0.10	2.4	2.9	0.00	2.52	0.41	4.19	21.00	5.65	23.03	11.43	5.01	10.10



Fig. 7. Seasonal (a-pre-monsoon; b-monsoon; c- post- monsoon) variation in groundwater salinity in Mewat.

compared to pre-monsoon, it decreases from 2.4 % in pre-monsoon to 0.8 % in post-monsoon, which is as per the observations of Dansgaard (1964). Similar results showing control of seasons and climates were reported in precipitation and air moisture samples by Unnikrishnan Warrior et al. (2010); Purushothaman et al. (2012); Saranya et al. (2018) and Aneesh et al. (2019). The percent area under salinity values of > 2 g/L increased from 86 % in pre-monsoon to 99 % in post-monsoon while percent area with d-excess < 0 % increased from 4 % in pre-monsoon to 25 % in post-monsoon season which indicates the increase in saline affected area.



Fig. 8. Seasonal (a-pre monsoon; b-monsoon; c- post monsoon) variation in d-excess in Mewat.

The sources of salinity (initial salinity, evaporation, and mineral dissolution) in different seasons are shown in Fig. 9. The contribution of evaporation in total salinity is calculated using *p*-excess. It was found that in the pre-monsoon season salinity was due to mineral dissolution. However, in the monsoon and post-monsoon seasons, initial salinity also contributes to salinity. Percent area in groundwater salinity with s contribution of > 2 % from evapo-concentration increased from 0% in pre-monsoon to 94 %, with contributions of 2–8 % in groundwater salinity.

The contribution of mineral dissolution is found by separating the salinity value of evaporation from dissolution; the results were further tested by using Tritium (3 H) to distinguish between modern groundwater (recharge occurring last 60 years) and premodern groundwater (recharge occurring > 60 years). Fig. 10 shows the groundwater age map for the region along with the contribution of mineral dissolution in different seasons. Considering the 3 H input sequence of precipitation in the region with average values 8–10 TU but the TU is observed as high as 22. The decayed results show that groundwater 3 H with content below 2 TU likely recharged more than 60 years ago. This shows that groundwater has a long residence time in high saline affected areas. A majority of the samples show a contribution from mineral dissolution in the pre-monsoon season, with a slight decrease in monsoon and postmonsoon seasons. There is wide variation in tritium activities may be due to discontinue water flow or poor connectivity between aquifers. In some samples high tritium activities corresponds to percolation from nearby artificial tritium sources (Ramaroson et al., 2018).

The contributions from initial salinity, evapo-concentration and mineral dissolution in groundwater in the study area is given in Table 3. Mineral dissolution contributes most of the groundwater salinity (76–97 %). A decrease in the contribution of mineral dissolution occurs in the monsoon season as the initial salinity contribution increases to as high as 21 %. This is due to the increased groundwater recharge and mobilization of accumulated salts in soils either naturally or anthropogenic sources. This has also been explained through the Fig. 14, showing an increase in water level in salinity affected central part in post monsoon season. Allison et al. (1990) and Simpson and Herczeg (1991) have also reported mobilisation of salts in the Murray river basins, Australia due to hydrological regimes and land uses. In addition to landuse changes in arid and semiarid environments, irrigation and groundwater



Fig. 9. Season wise contribution of evapoconcentration and mineral dissolution to total salinity in Mewat.



Fig. 10. Groundwater age distribution using tritium in Mewat.

exploitation can also cause increase in salinity (Williams, 1999).

The percent area in groundwater salinity with contributions of < 5 % from initial salinity was 93 % in pre- monsoon season but changed to 97 % of area having contribution from initial salinity > 5 % in post-monsoon season (Fig. 11). This may be due to the spread of mobilized salt to more areas. The percent area in groundwater salinity with contributions of > 2 % from evapo-concentration increased from 0% in pre-monsoon to 94 % with contribution of 2–8 % in groundwater salinity (Fig. 12). The mineral dissolution contribution of > 95 % in groundwater salinity in the pre-monsoon season was in > 88 % of the area but it reduced to 80–90 % contribution in groundwater salinity in 79 % of area (Fig. 13). These results are very useful in understanding the salinity mechanisms in the area, and its relationship with the surrounding environmental phenomenon like the monsoon, can play an important role in making sensible water resource management decisions (Adams et al., 2001).

Fig. 14 depicts the water level map of the study area, it is evident from the Fig. 14 that water tables are deeper in the western region. The water is potable in these areas and resulting in higher water withdrawals. In the eastern and southern sides of the study area, water is saline and water tables are high. The contours of water level show a natural gradient from the Aravalli hills towards the central region but due to high groundwater extraction in the foothills regions of area, there is apprehension of movement of water from salinity affected areas to fresh water areas. Seasonal effects were found in the water levels, in post monsoon seasons the water

Journal of Hydrology: Regional Studies 31 (2020) 100724



Fig. 11. Seasonal (a-pre monsoon; b-monsoon; c- post monsoon) variation in percent contribution of initial salinity in groundwater salinity in Mewat.



Fig. 12. Seasonal (a-pre monsoon; b-monsoon; c- post monsoon) variation in percent contribution of evapo-concentration groundwater salinity in Mewat.

levels increased by 18 % in southern/south-western region of the study area as compared to pre-monsoon season. This rise was found in water level class of 210 - 230 m. There are possibilities of change in salinity mechanism due to the rise in groundwater levels due to precipitation.

5. Conclusions

The use of deuterium excess is an effective tool to determine season wise (pre-monsoon, monsoon and post-monsoon) contribution of evapo-concentration and mineral dissolution to groundwater salinity. The mineral dissolution contributes maximum average salinity (76–97 %). The decreases in mineral dissolution contribution in monsoon and post-monsoon seasons are compensated by increase in initial salinity to a large extent due to the mobilization of salts in groundwater. The increase in salinity affected groundwater area due to initial salinity was found in monsoon and post-monsoon seasons. This study is extremely useful for determining the salinisation mechanism, understanding salt movements to larger areas for their control and proper management.



Fig. 13. Seasonal (a-pre-monsoon; b-monsoon; c- post-monsoon) variation in percent contribution of mineral dissolution in groundwater salinity in Mewat.



Fig. 14. Water level map of study area.

Authors statement

The work described has not been published previously, that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgement

This work was carried out in a purpose driven study under National Hydrology Project (NHP) funded by World Bank. Funding received is duly acknowledged. GK would like to thank Dr. Tianming Huang, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ejrh.2020. 100724.

References

- Adams, S., Titus, R., Pietersen, K., Tredoux, G., Harris, C., 2001. Hydrochemical characteristics of aquifers near Sutherland in the western Karoo, South Africa. J. Hydrol. 241, 91–103.
- Allison, G.B., Cook, P.G., Barnett, S.R., Walker, G.R., Jolly, I.D., Hughes, M.W., 1990. Land clearance and river salinisation in the western Murray basin, Australia. J. Hydrol. 119, 1–20.
- Aneesh, T.D., Srinivas, R., Singh, A.T., et al., 2019. Stable water isotope signatures of dual monsoon precipitation: a case study of Greater Cochin region, south-west coast of India. J. Earth Syst. Sci. 128, 210. https://doi.org/10.1007/s12040-019-1234-2.
- Barbeta, A., Peñuelas, J., 2017. Relative contribution of groundwater to plant transpiration estimated with stable isotopes. Sci. Rep. 7 (1). https://doi.org/10.1038/ s41598-017-09643-x.
- Barnes, C.J., Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. J. Hydrol. 100, 143-176.
- Bennetts, D.A., Webb, J.A., Stone, D.J.M., Hill, D.M., 2006. Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. J. Hydrol. 323, 178–192.

CENSUS (2011). http://www.census2011.co.in/census/district/226-mewat.html.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis, Boca Raton.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436-468.

Drabbe, J., Ghijben, W.B., 1889. Nota in Verband met de voorgenomen putboring nabij Amsterdam. - Kon. Inst. Ing. Tijd-schr., 1888/89: 8-22, 11 Abb.; Amsterdam. - Edmunds, W.M., 2003. Renewable and non-renewable groundwater in semi-arid and arid regions. Dev. Water Sci. 50, 265–280.

Edmunds, W.M., 2009, Geochemistry's vital contribution to solving water resource problems, Appl. Geochem. 24, 1058–1073.

- Fass, T., Cook, P.G., Stieglitz, T., Herczeg, A.L., 2007. Development of saline ground water through transpiration of sea water. Ground Water 45 (6), 703–710. https://doi.org/10.1111/j.1745-6584.2007.00344.x.
- Foerstel, H., 1982. 180/160 ratio of water in plants and in their environment. In: Schmidt, H.L., Foerstel, H., Heinzinger, K. (Eds.), Stable Isotopes. Elsevier, Amsterdam, pp. 503–516.
- Fontes, J.Ch., Gonfiantini, R., 1967. Comportement isotopique au cours de l'evaporation de deux bassins sahariens. Earth Planet. Sci. Lett. 3, 258-266.
- Gaye, C.B., 2001. Isotope techniques for monitoring groundwater salinization. Hydrogeol. J. 9, 217-218.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.Ch. (Eds.), Handbook of Environmental Isotope Geochemistry. Elsevier, New York, pp. 113–168.

- Hao, A.B., Li, W.P., Liang, Z.Q., 2000. Using TDS and d18O to determine contribution of dissolution and evaporation to the salinization of inland arid area. Hydrogeol. Eng. Geol. 27, 4–6.
- Hasanuzzaman, M., Davies, N.W., Shabala, L., Zhou, M., Brodribb, T.J., Shabala, S., 2017. Residual transpiration as a component of salinity stress tolerance mechanism: a case study for barley. BMC BMC Plant Biol. 17 (June (1)), 107. https://doi.org/10.1186/s12870-017-1054-y. 2017.

He, X., Shao, D., Liu, W., Dai, T., 2006. Review of the researches on utilization of farmland drainage as resources. T. CSAE 22, 176-179.

Herzberg, A., 1901. Die Wasserversorgung einiger Nordseebäder. J. Gasbeleucht. Wasserversorg 44 (815–819), 842–844.

Huang, T.M., Pang, Z.H., 2012. The role of deuterium excess in determining the water salinization mechanism- a case study of the arid Tarim river basin, NW China. Appl. Geochem. 27, 2382–2388.

- Huang, T.M., Pang, Z.H., Edmunds, W.M., 2012. Soil profile evolution following landuse change: implications for groundwater quantity and quality. Hydrol. Process. https://doi.org/10.1002/hyp.9302.
- Krishan, Gopal, 2019b. Groundwater salinity. Curr. World Environ. 14 (2), 186-188.
- Krishan, Gopal, Ghosh, N.C., Yadav, Brijesh Kumar, Sharma, Lalit Mohan, Kumar, C.P., Singh, Surjeet, Das, A., 2017. Groundwater conditions in Mewat, Haryana. In: Proceedings of an International Conference "India Water Week 2017–Water and Energy for Inclusive Growth" (IWW-2017). 10–14 October, 2017 at New Delhi, India. pp. 157.

Krishan, G., Chandniha, S.K., Lohani, A.K., Yadav, B.K., Arora, N.K., Singh, S., Kumar, C.P., Sharma, L.M., Bhardwaj, A.K., 2018. Assessment of heavy metals in relation to soil pollution at Mewat, Haryana, India. Curr. World Environ. 13 (3), 299–306.

- Krishan, Gopal, Bisht, Mamta, Ghosh, N.C., Prasad, Gokul, 2019a. Groundwater salinity in north west of India: a critical appraisal. Environment Management. WSTL Book Series Chapter 19. Springer).
- Krishan, Gopal, Kumar, C.P., Yadav, Brijesh Kumar, Prasad, Gokul, Sharma, Lalit Mohan, Singh, Surjeet, Kansal, M.L., Bisht, Mamta, 2019c. Groundwater salinity causes and remediation- a case study from Mewat, Haryana. In: Proceedings of an International Conference "India Water Week 2019-Water Cooperation-Coping with 21st Century Challenges" (IWW-2019). 24–28 September, 2019 at New Delhi, India.
- Krishan, Gopal, Ghosh, N.C., Kumar, C.P., Sharma, Mohan Lalit, Yadav, Brijesh, Kansal, M.L., Singh, Surjeet, Verma, S.K., Prasad, Gokul, 2020a. Understanding stable isotope systematics of salinity affected groundwater in Mewat, Haryana, India. J. Earth Syst. Sci. 129, 109. https://doi.org/10.1007/s12040-020-1380-6. (2020).

Krishan, Gopal, Kumar, C.P., Prasad, Gokul, Kansal, M.L., Yadav, Brijesh, Verma, S.K., 2020b. Stable isotopes and inland salinity evidences for mixing and exchange. In: Proceedings of Roorkee Water Conclave (RWC-2020) During 26–28 February. 2020 at IIT Roorkee.

- Kulkarni, K.M., Rao, S.M., Singhal, B.B.S., Parkash, B., Navada, S.V., Nair, A.R., 1989. Origin of saline groundwaters of Haryana State, India, regional characterization of water quality. Proceedings of the Baltimore Symposium, May 1989, IAHS Publ. No. 182.
- Majoube, M., 1971. Fractionation of oxygen-18 and deuterium in water vapor. J. Chem. Phys. 68, 1423–1436.

Malik, S., Rsjeshwari, 2011. Delineation of groundwater potential zones in Mewat district. Int. J. Geomatics Geosci. 2 (1), 270-281.

Manchanda, G., Garg, N., 2008. Salinity and its effects on the functional biology of legumes. Acta Physiol. Plant. 30, 595-618.

Manivannan, V., Elango, L., 2019. Seawater intrusion and submarine groundwater discharge along the Indian coast. Environ. Sci. Pollut. Res. 26, 31592–31608.

Mazor, E., 2004. Chemical and Isotopic Groundwater Hydrology, 3rd edn. Marcel Dekker, Inc, New York ISBN 0-8247-4704-4706.

Phillips, F.M., Mills, S., Hendrickx, M.H., Hogan, J., 2003. Environmental tracers applied to quantifying causes of salinity in arid-region rivers: results from the Rio Grande basin, southwestern USA. Dev. Water Sci. 50, 327–334.

Priyanka, Krishan, G., Sharma, L.M., Yadav, B.K., Ghosh, N.C., 2016. Analysis of water level fluctuations and TDS variations in the groundwater at Mewat (Nuh) district, Haryana (India). Curr. World Environ. 11 (2), 388–398.

Purushothaman, P., Rao, M.S., Kumar, B., Rawat, Y.S., Krishan, G., Devi, P., 2012. Comparison of two methods for ground level vapor sampling and influence of meteorological parameters on its stable isotopic composition at Roorkee, India. Hydrol. Processes 28 (3), 882–894. https://doi.org/10.1002/hyp9623.

Ramaroson, V., Rakotomalala, C.U., Rajaobelison, J., et al., 2018. Tritium as tracer of groundwater pollution extension: case study of Andralanitra landfill site, Antananarivo–Madagascar. Appl. Water Sci. 8, 57. https://doi.org/10.1007/s13201-018-0695-9.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Relation between long term trends of oxygen-18 isotope composition of precipitation and climate. Science 258, 981–985.

Saranya, P., Krishan, G., Rao, M.S., Kumar, S., Kumar, B., 2018. Controls on water vapor isotopes over Roorkee, India: Impact of convective activities and depression systems. J. Hydrol. 557, 679–687.

Simpson, H.J., Herczeg, A.L., 1991. Stable isotopes as an indicator of evaporation in the river Murry, Australia. Water Resour. Res. 27, 1925–1935.

Simpson, H.J., Hamza, M.S., White, J.W.C., Nada, A., Awad, M.A., 1987. Evaporative enrichment of deuterium and O-18 in arid zone irrigation. In: Proc. Int. Symp., March-April 3, 1987. Vienna, IAEA, Vienna. pp. 241–256.

Thomas, N., Sheler, R., Reith, B., Plenner, S., Sharma, L.M., Saiphy, S., Basu, N., Muste, M.M., 2012. Rapid Assessment of the Fresh-Saline Groundwater Interaction in the Semi-Arid Mewat District (India). University of Iowa's Winterim Program Development of Resilient and Sustainable Agricultural Watersheds.

Unnikrishnan Warrier, C., Praveen Babu, M., Manjula, P., Velayudhan, K.T., Shahul Hameed, A., Vasu, K., 2010. Isotopic characterization of dual monsoon precipitation – evidence from Kerala, India. Curr. Sci. 98 (11), 1487–1495.

Wen, X., Wu, Y., Su, J., et al., 2005. Hydrochemical characteristics and salinity of groundwater in the Ejina Basin, Northwestern China. Environ. Geol. 48, 665–675. https://doi.org/10.1007/s00254-005-0001-7.

Williams, W.D., 1999. Salinisation: a major threat to water resources in the arid and semi-arid regions of the world. Lake Reserv. Res. Manage. 4, 85-91.

Zimmermann, U., Münnich, K.O., Roether, W., 1967. Downward movement of soil moisture traced by means of hydrogen isotopes. Geophys. Monogr. Ser. 11, 28–36.