# Chapter 12 Environmental Tracers in the Identification of the Groundwater Salinity—Case Studies from Northwest India



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# 12.1 Introduction

In the face of the burgeoning climate crisis and ever-increasing human consumption demands, the disparate distribution of the water cycle is greatly amplified, resulting in frequent extreme events like drought and flooding. Groundwater is the essential component of this water cycle which interacts with all other parameters. Several large aquifers worldwide face huge water scarcity due to excessive groundwater pumping for agricultural and industrial demand, reduced infiltration capacity due to land-use changes, and human-induced climate crises. The sub-surface component and the stream discharge of major rivers, supporting massive civilizations, are on the verge of drying up due to decreased base flow. Groundwater has been largely used as a major source of irrigation water. Its excessive use and a change in cropping pattern have led to its declination in quantity and deterioration in quality (MacDonald et al. 2016; Siebert et al. 2010; Wada et al. 2014). In addition to the anthropogenic contaminants in groundwater such as nitrates, pesticides, feeds (Burow et al. 2008; Harter et al. 2012), and geogenic pollutants such as arsenic, uranium, fluoride (Jurgens

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et al. 2010; Ravenscroft et al. 2013; Smith et al. 2018) groundwater is also contaminated by total dissolved solids (TDS) occurring naturally or anthropogenically cause groundwater salinity (Triki et al. 2014). One significant impact of low water quantity is on surface–subsurface water quality. In conditions of low aquifer recharge, the incomplete dilution of dissolved solids in groundwater leads to a spike in TDS levels inside the aquifer.

Moreover, the increased groundwater pumping from deep aquifers poses a threat to bringing up the ancient salinity in freshwater aquifers. Higher concentrations of salts have impacted agricultural productivity, and in some areas, it has caused a crisis in drinking water (Krishan et al. 2021a, b, c). World Health Organization (WHO) (WHO, 2012) and World Health Organisation Staff (2011) and BIS (2012) have set a standard value of 500 mg/l TDS in drinking water, as higher salts may show evidence of undesirable characteristics which are unsuitable for use in domestic and agriculture purposes. Several researchers have studied groundwater salinization due to seawater intrusions (Werner et al. 2013) and inland salinity. There are various causes and factors responsible for the inland salinity. Inland salinity may be a result of endorheic basins and playas (Krishan et al. 2021b, c); evaporation and soil salinization due to rising water levels (Chaudhuri and Ale 2014; Krishan et al. 2021b, c), and soil salinization due to irrigation (Hillel 2000; Krishan et al. 2021b, c); salinization due to excessive pumping and inability to discharge salts as a result of a closed groundwater system (Krishan 2019; Krishan et al. 2020a, b, c; Pauloo et al. 2020) to discharge salts.

There are three different types of salinity in underground water: 1) natural/primary saltiness, which is generated by solubilization from regolith (e.g. evaporites such halite, gypsum, carbonates, fluoride-salts, and sulphates) or salt accumulation over time (residence durations ranging from thousands to millions of years). Secondary salinity is generated by rising water levels that convey salt to the surface or the clearance of vegetation, that causes salt to collect in the soil layer and groundwater. In locations with considerable rainfall, the salts filter down, but they linger on the surface in arid and semi-arid areas. (iii) Tertiary/irrigated salinity is caused by the repeated soaking of water, which leads salts to concentrate.

Groundwater salinity has a widespread occurrence in India and is one of the major concerns. It has been reported in the arid and semi-arid states viz. Rajasthan, Haryana, Punjab, and Delhi of northwest India (Krishan et al. 2019). Approximately, 25% area in the Indo-Gangetic plains has salinity with TDS more than 1000 mg/L (as per World Health Organization (WHO) and World Health Organisation Staff 2004) or electrical conductivity greater than 1500  $\mu$ S/cm. Indiscriminate groundwater abstraction results in the expansion of salinization in freshwater aquifers due to evaporative sequences from deeper to shallower aquifers. Salinization problems are also due to the dense canal networks, less usage of groundwater, and high doses of fertilization. Groundwater salinity affects crop productivity, and hence food security. There is an immediate need to address the causes and factors of salinization and management of salinity to restore the ecosystem. Environmental tracers are nothing but natural or human-induced compounds widely distributed on earth.

In parts of Punjab and Haryana, groundwater salinity has been observed in pockets. In Punjab, salinity is mainly in the southwest part of the Malwa region of Punjab while in Haryana salinity is found randomly in the isolated pockets and higher salinity is located in the Mewat district. Salinity values and their causal mechanisms are different for both places. In this study, the authors have attempted to show the other salinity mechanisms under different conditions in Punjab and Haryana in the northwest part of India using environmental tracers. Environmental tracers ( $\delta^{18}O, \delta^{2}H/\delta D$ ) have been used successfully to find the salinization mechanisms and sources (Krishan et al. 2020a, b, c; 2021a, b, c).

In such conditions, it is essential to map the extent of salinity occurrence and use state of the art tools to understand the underlying processes that amplify the background concentration of salinity. Since any remediation method is site-dependent because of dominant control of hydrogeology and subsurface geochemistry, it is essential to understand the behaviors of elements. For example, the Aquifer Storage and Recovery method are proved as a valuable method in diluting the TDS and salinity concentrations however if not thoroughly investigated with hydrogeological conditions could lead to several adverse effects like pore-clogging, desorption of hazardous elements, and groundwater flooding.

Environmental tracers are now increasingly used to understand the hydrological process and proved as an effective hydrological tool in the last decades. By definition, the tracer is something that can be traced along a flow path to understand the path, processes and mechanisms a fluid is going through. Environmental tracers are the chemical substances that are widely abundant in the natural environment and understanding their mass balance aid in understanding hydrological processes. Environmental tracers characterize the pace at which water moves underground, similar to how footprints in the sand disclose the passage of animals. They have wide applications in tracking groundwater flow paths, understanding origin, evolution, surface water-groundwater interaction, inter-aquifer movement and interactions, geochemical processes between aquifer and groundwater, recharge and discharge zones, climatic interactions and many more. The application of environmental isotopes is immense in the water sector. Some environmental tracers (like 2H, 3H, 18O, 13C, 14C, and 36Cl) have been utilized in groundwater science for decades.

In the Hualien River basin in Taiwan's eastern section, (Yeh et al. 2014) employed stable isotopes of oxygen and hydrogen to determine the seasonal contributing ratios of rainfall to groundwater recharge. They discovered that river water had more depleted hydrogen and oxygen isotopes than precipitation, implying that it comes mostly from upstream watersheds. Furthermore, groundwater hydrogen and oxygen isotopes in Huanlian differed slightly from the oxygen and hydrogen isotopic meteoric water line. As a response, the freshwater in this basin may be a mix of river water and rainfall, with river water recharging having a more significant effect than infiltration. In the "Scansano-Magliano in Toscana" area, (Doveri & Mussi 2014) used environmental tracers to analyze and validate the idea of cracked groundwater carrying sandstone units. This method was used to create a groundwater framework, and the presence of a large and continuous groundwater body within the sandstone complex was proven. The gas tracing experiment was utilized by (Benson et al. 2014)

to measure reaeration rates in Alpine streams. The process of gas exchange at the air-water interface guarantees that the water column has enough dissolved oxygen (DO) to support life.

(Swarzenski et al. 2013) stable and nuclear tracers to define geochemical processes in a sophisticated coastal groundwater system and regulate rock/water interaction kinetics. Groundwater could be a complicated mix of native groundwater, oil-field brine water, intruded seawater, and non-native injected water in the research region. Coupling stable and radioisotopic analysis yields novel insights into aquifer features such as rock/water interplay, geochemical cycling, and underground transport and mixing. Environmental tracers, too, are essential for the SGD inquiry due to the longterm and large-scale nature of related hydrological processes. (Schubert et al. 2014) evaluates and compares the suitability of the preceding tracers for investigating SGD from a different undersea reservoir in a dolomite environment at Cabbé, France. In this site-specific context, radon appeared to be a good environmental tracer.

(Cowie et al. 2014) employed a combination of natural and industrial tracers, such as isotopes, cationic tracers, and fluorescent dyes to establish hydrologic relationships. In mine waters, tritium levels imply a fast-flowing system with typical residence durations of years rather than decades, but stable water isotopes (18O/D) indicate a well-mixed hydrological system. According to the addition of multiple independent tracers, water travels through mine workings with few barriers. A study that combined the use of salt and dye tracers demonstrated that both types of tracers might be utilized successfully in acidic mine water.

This study (Ivey et al. 2008) combined age-distribution modelling with geochemical data and environmental tracers (tritium/helium-3). A simulated test case was created to see if the technique could be used to identify specific recharge locations to a wellhead in the aquifers with modern water infiltration data. The model's results based on the artificial test case show that the technique given herein may detect localized locations of recharge contributing to a wellhead in a semiconfined aquifer layer situation with a mere quantity of data. Together with the technique's relative ease of use, these findings make it a helpful tool for gaining a better understanding of flow regimes at a wellhead, which gives accurate information for risk assessment.

## 12.2 Materials and Methods

#### 12.2.1 Study Area

#### 12.2.1.1 Punjab

Study was conducted in Bathinda, Fazilka, Faridkot, Firozepur, Mansa and Muktsar districts of the semi-arid region of southwest Punjab located in 29° 25′ and 31° 10′ N latitudes and 74° 05′ & 75° 30′ E longitudes. The study area is bound by Rajasthan and Haryana states in the west and south of the study area, respectively

(Fig. 12.1). Rainfall varies from < 300 mm (Fazilka and Muktsar) to ~ 600 mm in Firozepur district. In these areas, sand dunes are present in the form of thin-film over the alluvium deposited by the Indus river basin (Bonsor et al. 2017). Soils are arid brown, size and desert soils, calcareous with the problems of salinity and alkalinity. The thickness of alluvium is high in this part and the rocks of Pre-Cambrian age occur as buried ridges with rising basement topography. Water levels are shallow (<5 mbgl) with rising trends (Central Ground Water Board (CGWB) 2016; Krishan et al. 2021b, c). The water table elevation contours maps suggest the hydraulic gradient for the direction of groundwater flow towards the southwest direction and due to the gentle slope in these areas, the less groundwater movement results in increased waterlogged areas (Central Ground Water Board (CGWB) 2016; Krishan et al. 2021b, c). On the other hand, the water level is declining in central Punjab at the rate of 0–4 m (Central Ground Water Board (CGWB) 2016).

#### Geomorphology of Punjab

The geomorphic map (Fig. 12.2) shows that throughout much of Punjab, gradational landforms, particularly river landforms, have emerged due to sediment deposition and a low elevation flat topography. Dunes may be found in Punjab's southwestern districts, including Fazilka, Bathinda, Muktsar, and Mansa (Krishan et al. 2021c).



Fig. 12.1 Study area and sampling locations



Fig. 12.2 Punjab's geomorphological (left) and geological (right) map

The Siwalik Ranges, with structural hills and Piedmont landforms, is located in the state's northeastern region. Only a few portions of the Amritsar and Patiala districts have alluvial wetland landforms.

Landuse/Land Cover of Punjab

Landuse land cover map of Punjab was created (Figs. 12.3a, b) for the Rabi season and Kharif season using Landsat 8-OLI MSI Data of the 2018 year. Kharif season extends from June to October, and Rabi season from December to March. LULC map of Punjab showing agricultural land (Rabi season = 55%; Kharif season = 73%), Fallow land (Rabi season = 22%; Kharif season = 7%), Water bodies (Rabi season = 6%; Kharif season = 3%), Habitat settlement (Rabi season = 1%; Kharif season = 1%) and settlement (Rabi season = 17%; Kharif season = 16%). Paddy and Cotton are the main crops cultivated during the Kharif season and Wheat and Barley are mostly grown crops during the Rabi season (Krishan et al. 2021c).

#### 12.2.1.2 Mewat

District of Haryana state comes under semi-arid climatic conditions and as shown in Fig. 12.1. Mewat has been recently renamed Nuh and it occupies a 1507 km<sup>2</sup> geographical area with a population of 1,089,406 (Census 2011). The district has



Fig. 12.3 a land use/land cover map of Rabi and b Kharif seasons of Punjab

a normal rainfall of about 600 mm with major rainfall > 75% occurring from June to September. The depth of water level in the district varies in the range of < 5 m to > 20 mgbl (Central Ground Water Board (CGWB) 2012; Priyanka et al. 2016). The district is separated from Rajasthan state by Aravali hill ranges with an area of about 200 km<sup>2</sup>. The precipitation occurring in these Aravalis ranges with an altitude as high as 450 m contributes highly to groundwater recharge through interconnected aquifers that may extend up to the central low land area with an altitude of about 150 m AMSL (Krishan et al. 2020b). The district has five administrative blocks viz. Tauru, Nuh, Punhana, Nagina and Firozepur Jhirka. There is high salinity in the Nagina block, which extends to the freshwater aquifers (Thomas et al. 2012; Krishan et al. 2017, 2019). Soils in the district are loamy sand, sandy loam, and silty loam (Krishan et al. 2020b). The geological formations are dominated by the Delhi supergroup and Quaternary sediments (Malik and Rajeshwari 2011). There are intermittent good multiple aquifers (Krishan et al. 2020b).

#### Landuse/Land Cover Map of Mewat

Agriculture is the main occupation of the people in the study area as evident from land-use data that consists of 64% agricultural land, 12% of built-up area (human settlements including the residential sites), about 18% falls under hills, 1% underwater bodies, and 5% under fallow area without perennial rivers (Fig. 12.6) and a normal semi-arid and arid drainage. The principal crops are Rabi such as wheat,

gram, rice etc. The economy of this region depends on agriculture because there is no industrial setup in this region. Agriculture demands high irrigational water, but public water bodies do not meet the requirements. These stresses present water supplies in the study area (Krishan et al. 2020b).

#### Geomorphology of Mewat

The district has a rolling topography with an urn-shaped structure. The central part is largely flat, but the western part slopes NW-SE and the slope of the northeastern part NE-SW; altitude difference can be observed due to the presence of the Aravali Hills (Fig. 12.4). The majority of the study area is dominated by the alluvial plains, with the northwestern region camouflaged by moderately deserted hills and valleys extending to the southwest and some parts of the south-east, whereas some parts of the southeastern area are dominated by pediments and peneplain complexes with comparatively low water bodies (Krishan et al. 2021d).

#### Geology of Mewat

The Mewat district of Haryana is a part of Aravalli craton and settled over the gneissic banded complex. The district is surrounded by the Delhi-Aravalli fold belt of paleo-Meso Proterozoic time. The Delhi fold belt enclosed Mewat in East, West and South directions (Fig. 12.5). The major lithology is quartzite, schist and phyllites of the Alwar and Ajabgarh groups. The weathering of these Proterozoic mobile belts form the overlying younger quaternary deposits of the Pleistocene-Holocene period, deposited as aeolian deposits in form of lost oxidized sand and silt. The detailed geology of the region is given in Table 12.1.

# 12.2.2 Sampling and Analysis

#### 12.2.2.1 Sample Collection

Punjab sampling was carried out by dividing the total area into  $10 \times 10$  km<sup>2</sup>. The sample was collected from each grid in June 2019. Two hundred forty-two samples were collected from hand pumps and tubewells from the depth range of 15 m to 800 m in June 2019 (Fig. 12.1) as per the availability in the study area for analysis of stable isotopes and EC measurements. In Mewat, 41 random groundwater samples were collected from the Mewat district in April–May 2019. The detailed methodology for groundwater sample collection, transportation and preservation is followed as given by Krishan et al. (2021c).



Fig. 12.4 Geomorphological map of Mewat Haryana

#### 12.2.2.2 Sample Analysis

For salinity measurements, electrical conductivity (EC) was measured by using a hand-held meter (Hach, HQ30d portable meter) and from these, the total dissolved solids (TDS) values were determined using appropriate conversion factors. Stable isotopes ( $\delta^{18}$ O and  $\delta$ D) were measured using a Dual Inlet Isotope Ratio Mass Spectrometer-DI IRMS using the prescribed methodology (Krishan et al. 2021c).



Fig. 12.5 Geological map of Mewat Haryana

# 12.3 Results and Discussion

# 12.3.1 Total Dissolved Solids (TDS)

TDS in Punjab was found in the range of 234 mg/l to 9514 mg/l with an average value of 1619 mg/l, while in Mewat TDS was found in the range of 243 mg/l to 36,582 mg/l with an average value of 3984 mg/l (Table 12.2). Lower TDS values in Punjab as



Fig. 12.6 a Map of land use land cover of Mewat Haryana b LULC distribution percentage in different classes

Supergroup	Group	Formation	Lithology
Quaternary Alluvial Sediments	Newer alluvium	Loharu/Aeolian Deposits	Yellowish-brown loose sand
	Older Alluvium	Varanasi = Ambala = Ludhiyana	Oxidized silt clay and micaceous sand
Mesoproterozoic	Ajabgarh	Arauli	Carbonaceous phyllite
Delhi fold belt		Bharkol	Phylite, quartzite
		Asarwas	Feldspathic Quartzite and schist
		Undiffined	Phyllite, slate, limestone, quartzite, schist
	Alwar	Pratapgarh	Feldspathic Quartzite

Table 12.1 Detailed stratigraphy of Mewat, Haryana

compared to Mewat are due to the presence of an open basin while in Mewat it is more like a closed basin. In Punjab, there may be more surface water and groundwater interactions that maintain a balance between salinity that is naturally generated due to the formations within the basin while in Mewat there is no outflow by surface water or groundwater and evaporation is the dominant mechanism by which water exits the basin (Jones and Deocampo 2003). Since TDS concentrations in precipitation are low and most of the TDS originates from rock-water reactions may be on the surface or subsurface. Salts are accumulated at the evaporative boundaries or maybe in the surface depressions.

## 12.3.2 Environmental Tracers

Environmental tracers are now commonly being used to understand origins, groundwater flow processes, chemical reaction processes, recharge sources, water budget, and zones of deep aquifers etc. In the present study stable isotopes of water  $\delta^{18}$ ,O and  $\delta^2$ H/ $\delta$ D were used to understand the salinity mechanisms and recharge sources. Stable isotope values showed wide variations. In Punjab,  $\delta^{18}$ O values varied from – 10.86 to – 0.71‰ with an average value of – 7.14‰;  $\delta^2$ H/ $\delta$ D varied from – 76.42 ‰ to – 13.48‰ with an average value of – 49.96‰; d-excess varied from – 9.79 to 18.49‰ with an average value of 7.19‰. In Mewat,  $\delta^{18}$ O values varied from – 7.85 to 0.19‰ with an average value of – 5.57‰;  $\delta^2$ H/ $\delta$ D varied from – 56.44 to – 1.10‰ with an average value of – 41.47‰; d-excess varied from – 5.46 to 9.20‰ with an average value of 3.07‰ (Table 12.2).

Wide variations in isotope values at both places are due to the different recharge sources and processes. Fewer variations in isotope values in Mewat than the values at Punjab might be limited recharge sources. For finding the recharge sources, values of  $\delta^{18}$ O and d-excess were plotted (Fig. 12.7). It was found that major groundwater recharge sources in Punjab are canal, rain and groundwater while in Mewat are rain and groundwater.

In order to understand the salinity mechanism, TDS values were plotted against the  $\delta^{18}$ O values (Fig. 12.8). It was found that the mineral dissolution was responsible for primary salinity in Punjab which was further increased by the evaporative enrichment (Krishan et al. 2021b, c) while in Mewat, Haryana mineral dissolution was found the source of salinity (Krishan et al. 2020a, b, c).

Thus in Punjab less usage of groundwater in comparison to saline water has resulted in evaporative enrichment and building up of the salinity resulted. While Mewat is a closed basin there are no outlets, the area is irrigated and evapotranspiration is the dominant water outflow, leaving behind salts and these salts are leached down to the aquifers contaminating groundwater as a result of return flows and recharge from precipitation.

## 12.4 Conclusion

In Punjab average groundwater salinity is less as compared to Mewat Haryana and recharge sources were identified as canal, rain and groundwater; processes responsible for salinity are evaporative enrichment in addition to mineral dissolution while in Mewat salinity is higher and identified recharge sources are rain and groundwater with mineral dissolution is major salinity causing factor.

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Pun	jab (n = 242)				Mewat $(n = 41)$			
Ŭ	S (mg/l)	8 <sup>18</sup> O (%o)	8 <sup>2</sup> H (%o)	d-excess (%o)	TDS (mg/l)	8 <sup>18</sup> O (%o)	8 <sup>2</sup> H (%o)	d-excess (%o)
Min 23	5	-10.86	- 76.42	- 9.79	243	- 7.85	- 56.44	- 5.46
Max 951	4	-0.71	- 13.48	18.49	36,582	0.19	-1.10	9.20
Mean 161	6	- 7.14	- 49.96	7.19	3984	- 5.57	- 41.47	3.07
S dev 121	6	1.68	10.33	4.29	7308	1.23	8.36	3.62

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Fig. 12.7  $\delta^{18}$ O versus d-excess values in Punjab and Mewat



Fig. 12.8 **\delta18O** versus TDS values in Punjab and Mewat

It has been believed that over-development of groundwater may result in lowering of groundwater levels reducing the natural outflow. On the other hand, if there is a naturally closed basin there will be movement of salts to the upper parts due to the upward groundwater discharge. Again, these salts are mobilized to the groundwater with the return flow and precipitation recharge increasing groundwater salinity through recycling.

For proper management of salinity in southwest Punjab suggested techniques are encouraging the use of groundwater along with the use of surface water, controlling the depth of wells as there is high groundwater abstraction in central Punjab, and rationalizing water use in agriculture cropping patterns should be regulated. While in the Mewat district of Haryana the groundwater should be in a sustainable manner with an increasing recharge in a scientific manner. In the study area, this can be achieved by considering the aquifer types, geometry along with their typologies. In addition to these socio-economic considerations are also important.

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