Theme 14

ISOTOPIC TECHNIQUES IN GROUNDWATER INVESTIGATIONS AND MANAGEMENT

INTEGRATING HYDROGEOCHEMISTRY AND STABLE ISOTOPES TO UNDERSTAND THE GROUNDWATER SALINIZATION IN A COASTAL AQUIFERS OF ODISHA

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Coastal aquifers are important sources of freshwater for many communities, but they face increasing stress of seawater intrusion due to various factors like over-extraction of groundwater, influence of tidal activities, rising sea levels, etc. Seawater intrusion poses a significant effect on freshwater resources, leading to increased salinity and potential degradation of water quality, which can have considerable impacts on agriculture, human consumption, and the coastal ecosystem. The hydrological and geochemical processes that govern groundwater chemistry in coastal aquifers are very complex. Hence, there should be a proper understanding of how different mechanisms affect groundwater chemistry. This study utilizes a combined approach, integrating major ion chemistry, minor elements such as bromide (Br-) and lithium (Li+), and stable isotopes (^{18}O and ^{2}H) to delineate the extent of seawater intrusion and understand the hydrogeochemical processes along the coastal aquifer. Br- is conservative and often remains unchanged during various geochemical processes, making it an important indicator of seawater mixing. Li+, on the other hand, provides insights into water-rock interactions and the extent of seawater influence. Stable isotopes of hydrogen (δ^2H) and oxygen (δ^{18}O) are key tools in hydrological studies, as they provide insights into the recharge processes in aquifers. Seawater is typically enriched in heavy isotopes, making δ^{18}O and δ^2H useful indicators for identifying the presence of marine-origin water in a freshwater aquifer. This study aims to contribute valuable insights into these coastal salinization dynamics for better management and safeguarding of freshwater resources.

The study was carried out for the coastal regions of Puri district, in the Odisha state, in the eastern part of India. The study area is about 490 km^2 and covers coastal parts of the Astarang, Kakatpur, and Gop blocks of the Puri district. The area is densely populated and local people mainly depend on groundwater for drinking purposes and agricultural activities. For the present study, a total of 90 nos. of samples were collected during the post-monsoon period in December 2021 from the shallow tube well, surface water and seawater samples from within 10-12 km from the coast. pH, EC and TDS were analysed using a Hanna Portable meter. Groundwater samples were analyzed for major elements using Flame Photometer for Na+, K+, Spectrophotometer for SO_4^{2-}, NO_{3-} and by Titration method for Ca^{2+}, Mg^{2+}, Cl-, HCO_{3-} and minor elements, Bromine (Br-) and Lithium (Li+), using Ion Chromatography. Stable isotope ratios of δ^2H and δ^{18}O were measured using isotope ratio mass spectrometry (IRMS). Stable isotopes δ^{18}O and δ^2H were interpreted by comparing groundwater samples with the global meteoric water line (GMWL) and the local meteoric water line (LMWL).

Groundwater chemistry data revealed significant variations in major ion concentrations across the study area. pH varies from 5.9 to 8.5 and TDS varies from 45mg/l to 5278mg/l

with an average value of 820mg/l. The concentration of major cations Na^+, Ca^{2+}, Mg^{2+} varies from 6.5 mg/l to 1482 mg/l, 4 mg/l to 132 mg/l, 1 to 112 mg/l respectively and concentration of major anions such as Cl^-, HCO^{3-}, SO_4^{2-} varies from 14 to 2638 mg/l, 12mg/l to 503 mg/l, 3 mg/l to 297 mg/l respectively. Samples collected closer to the coastline in the Northeastern parts exhibited elevated levels of Na^+ and Cl^- as well as in the central part of the southeast part suggesting the influence of seawater mixing. However, the rest of the wells show relatively lower concentrations of these ions, indicating these zones are not affected or a lesser degree of seawater influence. The spatial distribution of major ions highlighted the region that is highly saline zone from lower saline zones. The concentration Br- varies from 0 µg/l (Below Detection limit) to 8.87 mg/l with a mean of 1.15 mg/l. Bromide concentrations were notably higher in the wells that showed higher chloride content, which is an important indicator of seawater mixing. The conservative nature of Br- allowed for a clear distinction between seawater-affected groundwater from the unaffected region. Lithium concentrations vary from 0 µg/l (Below Detection limit) to 2664 µg/l with a mean of 153 mg/l which also showed a similar pattern, with higher levels in wells with higher Br^- and Cl^-. The variability in Li+ concentrations provided insights into the rock-water interactions within the aquifer. When saline water stays for a prolonged period in the aquifer matrix then there will be an exchange between Na^+ in water and Li^+ in the aquifer which increases the Li+ in groundwater. The combined analysis of Br^- and Li^+ offered a detailed picture of the intrusion dynamics, revealing areas of mixing and interaction that might be difficult to understand through major ion analysis alone. Stable isotope analysis further supported the findings from major ion and minor element chemistry. The $\delta^{18}O$ and δD ranges from -2.21 to -7.03 ‰ with an average value of -4.95‰ and the Deuterium (δ^2H) varies from -14.41 to -48.82 ‰ with an average value of -32.20 ‰. It is found that the $\delta^{18}O$ and δ^2H values exhibited enrichment in the well having higher TDS and higher chloride, indicating mixing between freshwater and seawater and are plotted close to the seawater value. The Global Meteoric Water Line (GMWL) ($\delta D = 8*\delta^{18}O + 10$, Craig 1964) and Local Meteoric Water Line (LMWL) ($\delta D = 7.86 * \delta^{18}O + 8.81$) plotted almost parallel and overlapping on each other with similar slope. The scatter plot of $\delta^{18}O$ vs δD shows samples are distributed along the GMWL and LMWL lines indicating samples are derived from precipitation sources. However, most of the samples are shifted to the right of both lines which suggests that the samples have undergone some degree of evaporation which shifted them rightward. This study identifies seawater mixing, rock-water interactions, and evaporation processes as the key factors controlling groundwater salinization in the region. However, the groundwater particularly in the northeastern coastal and central-southeast regions showing elevated Na^+, Cl^-, Br^-, and Li^+ concentrations and covers around 20% of the study region has been affected by seawater mixing. It is suggested that further research using geophysical techniques to additional support to current understanding and develop better mitigation strategies.

Keywords: *Coastal aquifer, hydrogeo-chemistry, bromide, lithium, stable isotopes, seawater mixing*

STABLE WATER ISOTOPE IS AN INDICATOR OF SURFACE WATER AND GROUNDWATER INTERACTION IN SHALLOW AQUIFERS OF THE BRAHMAPUTRA RIVER SYSTEM, INDIA

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The interaction between surface water and groundwater is a fundamental aspect influencing the hydrogeological and ecological dynamics of shallow aquifers, particularly within widespread river systems. This work investigates the use of stable water isotopes ($\delta^{18}O$ and δD) as tracers to clarify the relationship between groundwater and surface water in the Brahmaputra River system. By examining the temporal isotopic compositions of precipitation ($n = 187$), river water ($n = 151$), and shallow aquifers ($n = 151$), the differences spotted emphasise the mixing and recharging processes. The study covered precipitation from October 2022 to 2024, while river water and shallow aquifer from Guwahati from April 2023 to October 2024. Meanwhile, spatial sampling of the shallow aquifer ($n = 48$) for the stretch of 800 km in the centre of Assam valley of the Brahmaputra River system. The results show a significant isotopic overlap between groundwater and surface water in some areas, suggesting a robust hydrological connection impacted by monsoonal inputs and seasonal flow patterns. The Isotopic ranges for precipitation is $\delta^{18}O$: –20.96 ‰ to 4.09 ‰ and δD: –154.92 ‰ to 40.91 ‰, for river water is $\delta^{18}O$: –11.87 ‰ to –6.54 ‰ and δD: –78.99 ‰ to –32.65 ‰, and for shallow aquifer temporally is $\delta^{18}O$: –6.32 ‰ to –4.31‰ and δD: –39.41‰ to –29.38 ‰. In regions that depend on interdependent water supplies, this study provides an overview for sustainable groundwater management and emphasises the importance of stable isotope studies in deepening our understanding of hydrological processes.

This study analyses the shallow aquifers spatially and temporally. For temporal observation, a daily dataset of stable isotopes from a shallow aquifer at Guwahati is observed. The spatial extent of groundwater samples was also gathered on the Sadiya - Dhubri stretch of 800 km in July 2022 along the Brahmaputra River's channel at the centre of Assam Valley. The stable isotope analysis was carried out using the liquid triple isotopic water analyser of LGR in accordance with the analytical protocol of laser-based, off-axis integrated cavity output spectroscopy (ICOS). A dual $\delta^{18}O$ and δD isotope space was used to analyse the isotope values, and empirical relationships were shown against the Global Meteoric Water Line (GMWL). In contrast to the GMWL, the Local Meteoric Water Line (LMWL: $\delta D = 8.137\ \delta^{18}O + 10.664$) had a different slope and intercept, indicating the isotopic makeup of the precipitation in the studied area. Since evaporation was shown to be the predominant process in this situation, the Local Evaporation Line (LEL: $\delta D = 6.05\ \delta^{18}O - 6.14$) was established. At our sampling locations, the relationship between the Local evaporation line (LEL) and the Local Meteoric Water Line (LMWL) is essential for determining the water sources and comprehending the evaporation and mixing processes. The isotopic composition of the water that is entering may be clearly defined at the point where the LEL and LMWL intersect, providing important information about its properties and source. The line-conditioned excess (lc-excess) has been computed for precipitation in order to efficiently normalise the evaporation signal in data because the precipitation station is situated in the centre of the basin. This calculation is represented by the following formula: lc-excess = $[\delta D - a \times \delta^{18}O - b]$

/ S, where the a and b correspond to the slope and intercept of the local meteoric water line and S shows the measurement uncertainty during the analysis of hydrogen and oxygen isotope.

The results of the isotope analysis indicate an amplified input of total annual precipitation during the monsoon, which signifies a notable nature of rock water interaction within the aquifer. The nature of rock-water interaction is shown by variation in oxygen isotope more than the variation in hydrogen isotope, which shows rocks carrying rock forming with oxides fractionate with recharged water. The geochemistry of stream water and groundwater in the basin area is largely influenced by the interaction between water and rock. According to the Gibbs diagram, the majority of samples are situated within the rock dominance area, indicating the significant impact of rock on the chemical composition of the water. Both stream water and groundwater exhibit similar hydrochemical evolution processes; however, groundwater, with its longer residence time in the subsurface, experiences more prolonged and intense water-rock interactions. This leads to considerably higher concentrations of solutes in groundwater compared to stream water. In contrast, stable isotopes are primarily affected by processes such as evaporation and the introduction of new water. Due to these influences, stable isotopes are regarded as more effective for tracing the interaction between surface water and groundwater. The influence of evaporation on isotope fractionation is profound, especially in the context of stream water. The process of isotopic fractionation, as water transitions from a closed system (groundwater) to an open system (stream water), leads to a notable enrichment of isotopic compositions. The isotopes of water in streams are affected by intensified evaporation, which causes them to differ from those in groundwater. This leads to underestimations of groundwater discharge ratios when using isotope tracers.

The importance of stable water isotopes ($\delta^{18}O$ and δD) as useful markers for analysing surface-groundwater interactions in the shallow aquifers of the Brahmaputra River system is emphasised by this study. A significant connection is shown by the isotopic analysis, which is impacted by fundamentals including river flow dynamics and seasonal monsoonal recharge. Different levels of interaction are revealed by spatial variations in isotopic fingerprints throughout the research region; certain zones exhibit a higher level of mixing because of particular hydrological and geomorphological conditions. These results demonstrate the significance of incorporating isotope-based research into water resource management and provide insightful information about the hydrological processes operating in the area. This study's main limitation is that the method for assessing indicator uncertainty primarily relied on the variation coefficients of groundwater discharge at each specific sampling site.

Keywords: *Lower Brahmaputra basin, stream water-groundwater interaction, stable water isotopes, seasonal variation, shallow aquifer*

UNRAVELLING GROUNDWATER FLOW PATHS AND CONTRIBUTIONS TO AQUIFERS EMPLOYING NATURAL TRACERS AND END MEMBER MIXING ANALYSIS IN THE SOUTH-WESTERN GHATS, INDIA

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Mountainous regions play a crucial role in global hydrological systems, functioning as “water towers” that supply freshwater to lowland areas. They support groundwater systems and rivulets, serving as vital sources of water for agricultural, industrial, and domestic purposes. This role is particularly significant in tropical regions, where seasonal variations heavily influence water availability. Understanding recharge processes in mountain Critical Zones (CZs) is therefore essential. The Southern Western Ghats of India exemplifies this dynamic, supplying water to the semi-arid lowlands on the eastern side of western Ghats through intricate groundwater flow paths. Despite their importance, research on hydrogeological processes in mountain ecosystems, particularly in tropical climates, remains limited. This study, conducted in the Munnar Critical Zone Observatory (CZO) in the Southern Western Ghats, investigates groundwater flow patterns and their seasonal variations. By utilizing natural tracers to analyse recharge dynamics, the study offers valuable insights for sustainable water resource management and landslide risk mitigation in the region.

To understand groundwater (GW) flow paths, 12 GW samples (7 borewells and 5 open wells) and 15 rivulet stream water samples were collected across different elevations of the mountain during pre-monsoon (PRM), southwest monsoon (SWM), and northeast monsoon (NEM) seasons, allowing for a seasonal analysis of recharge patterns. The samples were analysed for stable isotopes ($\delta^{18}O$, $\delta^{2}H$), tritium (^{3}H), chloride (Cl^{-} as a conservative tracer), and other major solute concentrations. These tracers provided critical insights into recharge sources and flow paths, as isotopic values serve as reliable indicators of water origin and dynamics. The isotopic values, along with elevation patterns, revealed the altitude effect, with groundwater samples displaying a clear depletion gradient indicative of recharge processes. Rainwater samples were also collected seasonally and spatially along varying elevations in the study area, enabling the construction of a Local Meteoric Water Line (LMWL). Based on the findings, $\delta^{18}O$ and $\delta^{2}H$ boxplots for groundwater and rivulets were generated, along with a ternary diagram plotting $\delta^{18}O$ (‰) against Cl^{-} concentrations (mg/L) on the Y-axis. These analyses revealed three distinct groups of groundwater sources characterized by unique tracer concentrations. Tritium (^{3}H) levels further differentiated the groups, confirming the presence of three major groundwater flow paths: Mountain Front Recharge (MFR), Mountain Block Recharge (MBR), and Front-Slope Recharge (FSR), each with distinct recharge mechanisms and dynamics. MFR, observed at lower elevations (<1500 m amsl), exhibited low $\delta^{18}O$ and Cl^{-} values and is influenced by rivulet flow losses and irrigation channels, indicating faster recharge processes. MBR, found at higher elevations (>2000 m amsl), displayed intermediate $\delta^{18}O$ values, elevated Cl^{-} concentrations, and low ^{3}H levels, suggesting longer residence times due to deeper infiltration within the mountain blocks. In contrast, FSR, located at mid-elevations (1500–2000 m amsl), showed high $\delta^{18}O$ and low Cl^{-} values, coupled with high ^{3}H levels, reflecting shorter residence times and recharge predominantly through direct precipitation on mountain slopes. These findings

highlight the distinct recharge mechanisms operating in mountainous regions. The spatial arrangement of recharge zones aligns with elevation gradients and local hydrological dynamics, while the combined use of isotopic and solute tracers effectively delineates groundwater flow paths.

The study employed End Member Mixing Analysis (EMMA) to quantify contributions from distinct groundwater flow paths-MFR, MBR, and FSR-using extreme values of natural tracers $\delta^{18}O$ and Cl^- as end members to determine the contributing fractions both spatially and temporally. Error propagation analysis was applied to account for uncertainties in the estimated percentage fractions, with variations in end-member concentrations considered to enhance result accuracy. The EMMA analysis revealed that FSR contributed an annual average of 47.2% to groundwater recharge, followed by MBR at 28.8% and MFR at 23.9%, emphasizing the critical role of FSR in maintaining regional water resources. Seasonal analysis indicated notable variability in recharge contributions. During the PRM season, elevated temperatures enhanced soil permeability, making FSR the dominant recharge process, particularly at higher elevations. In the SWM season, abundant rainfall and active surface water flow resulted in a more balanced contribution from MFR, MBR, and FSR. Conversely, the northeast monsoon (NEM) season, characterized by intermittent rainfall and reduced surface runoff, once again favoured FSR as direct infiltration became the primary recharge process, sustaining groundwater resources. These seasonal patterns underscore the complex interplay between climatic conditions and topographical features in shaping recharge mechanisms in the Munnar CZO. The study highlights that recharge mechanisms are closely tied to altitude and topography, which influence groundwater flow pathways. In mountainous terrains like the Munnar CZO, the interaction between groundwater and surface water is strongly influenced by steep slopes and ephemeral streams. These streams serve as natural conduits, particularly in lowland areas, where they significantly contribute to recharge through MFR processes. Additionally, the region's deep-cut streams and V-shaped valleys channel water into specific recharge zones, playing a pivotal role in shaping MBR and FSR dynamics.

These findings offer valuable insights into groundwater-surface water interactions and underscore the importance of understanding recharge mechanisms for sustainable water resource management in mountainous ecosystems. These results offer direct implications for sustainable groundwater management, providing insights that can guide groundwater extraction practices to ensure aquifer levels remain sufficient to support agriculture, local ecosystems, and community needs. Furthermore, the identification of FSR as the dominant recharge source in high-risk landslide zones holds significant potential for disaster management. However, the study acknowledges certain limitations, particularly the small number of sampled groundwater sources, which constrains the ability to assess broader spatial variability. To address this, future research could expand sampling networks, incorporate additional tracers, and employ continuous monitoring techniques to better capture temporal variations and enhance accuracy.

Keywords: *Mountain block recharge, groundwater, stable isotopes, end member mixing analysis, critical zone, western Ghats*

HYDROLOGICAL INVESTIGATIONS OF CHAMASARI SPRINGS USING STABLE ISOTOPES AS NATURAL TRACERS

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Environmental isotopes, oxygen and hydrogen, in particular, have been extensively used to study various environments of different climate extremities. Springs, the main source of fresh water for rural populations in the Himalayas, are drying up and eventually dying. The present study aims at using stable isotopes in Chamasari, Uttarakhand, India, to understand the nature of springs and if possible, find plausible ways to revive them. Samples from springs and precipitation were collected and analysed using the Isotope Ratio Mass Spectrometer (IRMS) instrument. The results thus obtained indicate that the Local Meteoric Water Line (LMWL) of the present study region deviates from the Global Meteoric Water Line (GMWL), with a slope lower than that of GMWL. Water samples show a variation in $\delta^{18}O$ values of about -0.28 per mil per 100 m elevation. Electrical conductivity (EC), spring discharge, temperature and other parameters measured on the field show a general decreasing trend of EC with an increasing discharge and altitude, with little deviations in some places. Based on the data and results, it can be concluded that spring water may have suffered evaporation or undergone mixing with some evaporated water and that $\delta^{18}O$ and δD isotopes of precipitation show an altitude effect. The deviation of EC from its general trend for the area may indicate an involvement of natural and possibly some anthropogenic factors, such as the interaction of water with the local geology of the area or the developmental activities of the rural population.

Keywords: *Stable isotopes, Springs, Chamasari, IRMS, Himalayas*

A δ^2H AND δ^{18}O ISOSCAPE OF GROUNDWATER IN THE EAST KHASI HILLS DISTRICT, MEGHALAYA, INDIA

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Groundwater is one of the preferred sources of water supply, sustaining drinking water supplies, irrigation for agriculture, and industrial processes. It serves as the primary source of freshwater, particularly in areas where surface water is scarce, and is used for drinking purposes by one-third of the global population. Consequently, in the present times, groundwater resources are under stress due to overexploitation, and pollution from different sources like agricultural runoffs, industrial effluents, and domestic waste, often rendering groundwater unfit for human use, and ecological health. The stress on groundwater resources necessitates long-term management approaches such as controlled extraction, pollution control, and efficient recharge systems. Stable isotopes of water (δ^2H and δ^{18}O) serve as important tracers and have been widely used to decipher the interactions among all compartments of the hydrological cycle. Integrating stable isotopes analyses will provide better insight into existing water sources and their recharge mechanisms and contamination pathways, thus enabling more precise modeling of management practices so as to ensure the long-term availability and retention of the quality of this essential resource.

The present study is the first attempt to assess the δ^2H and δ^{18}O distribution in the groundwater of the East Khasi Hills District, Meghalaya, India. The results from the study will help in understanding recharge mechanisms and help in defining better management practices ensuring long-term availability of this essential resource. The study was conducted in the East Khasi Hills District of Meghalaya, India. The study area's climate ranges from temperate humid in the northern region to subtropical humid in the southern region, with temperatures varying between 1.7°C and 24°C. This district is renowned as the wettest region on Earth, home to Mawsynram and Cherrapunjee, which receive an average annual rainfall of approximately 12,270 mm and 11,600 mm, respectively. The dominant rock types in the district comprise basement Precambrian granitic gneisses, overlain by Mesozoic quartzites, followed by the tertiary sequence. The major aquifer representing the water table occurs in the quartzites. This group of aquifer systems in the study area provides moderate groundwater potential. Water table occurs in the weathered quartzite under unconfined conditions and under the semi-confined conditions in the fractured and jointed rocks. The wells drilled at hydro-geologically suitable sites to depths of approximately 80–150 meters below ground level (bgl) yield moderately 5-15 m^3/hr, and are located in the weathered Pre-Cambrian rocks.

Seventeen (17) sampling locations across the district were selected for the collection of water samples. Freshly pumped groundwater samples from the borewells from different sampling locations were collected during April 2023. Electrical conductivity (EC) and total dissolved solids (TDS) measurements were taken using the Eutech CyberScan PCD 650 (pre-calibrated and set to automatic temperature compensation) on-site. For stable isotopes analysis, the samples were filtered through a 0.45µm syringe filter (Merck Millipore) in a dry, pre-washed and 10% nitric acid-rinsed 15 ml polypropylene bottle (Tarson) on-site. For chloride analysis, samples were collected in dry, pre-washed and 10% nitric acid-rinsed 125 ml polypropylene bottles (Tarson). All samples were stored at 4°C until analysis.

Hydrogen (^1H,^2H) and oxygen (^{16}O,^{18}O) stable isotope analyses were conducted using a continuous flow isotope ratio mass spectrometer (Isoprime, UK) at the Nuclear Hydrology Laboratory, National Institute of Hydrology (NIH), Roorkee (India). The results are expressed in delta notation (δ) as per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water), with a laboratory precision of $\leq$1.0 ‰ (1σ) for δ^2H and $\leq$0.05 ‰ (1σ) for $\delta^{18}O$. Deuterium excess (d-excess, ‰) was calculated following the standard equation. Chloride concentrations were determined using Ion Chromatography (Dionex ICS-5000, Thermo Fisher, USA) following standard procedures at the Nuclear Hydrology Laboratory, National Institute of Hydrology (NIH), Roorkee (India). The results are reported as mean (n=3). The δ^2H values in groundwater ranged between -51.60 ‰ and -29.60 ‰, with a mean of -42.28 ‰ (V- SMOW). The $\delta^{18}O$ values in groundwater ranged between -8.11 ‰ and -5.57 ‰, with a mean of -6.89 ‰ (V- SMOW). The d-excess values ranged between 10.10 ‰ and 14.93 ‰, with a mean of 12.86 ‰. The EC ranged between 28.02 and 464.30 µS/cm, with a mean of 149.56 µS/cm. The TDS ranged between 19.72 and 306.80 mg/L, with a mean of 102.61 mg/L. The chloride concentration ranged between 1 and 34.30 mg/L, with a mean of 8.98 mg/L.

The $\delta^{18}O$ and δ^2H values in groundwater showed a linear relationship ($\delta^2H = 8.8202 * \delta^{18}O + 18.517$) with $R^2 = 0.98$. The majority of the groundwater samples fall above the Global Meteoric Water Line (GMWL), with one sample close to it, indicating a minimal influence of evaporation. The $\delta^{18}O$ and d-excess showed irregular distribution, confirming negligeable evaporation. The higher d-excess values indicate that the rainfall in this region is from low clouds, which has undergone less sub-cloud evaporation and quick recharge in a humid environment. The relationship between $\delta^{18}O$ and TDS indicates mineral dissolution. The findings of the study will enhance the understanding of recharge processes and support the development of improved long-term strategies for safeguarding groundwater resources in the district.

Keywords: *Groundwater, isoscape, East Khasi Hills, Meghalaya, stable isotopes*

RADON LEVEL MEASUREMENTS IN GROUNDWATER SAMPLES OF DOON VALLEY OF UTTARAKHAND, INDIA

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Radon is formed as part of the Uranium-Thorium decay chain. It has an atomic number of 86 and a half-life of 3.82 days. According to the World Health Organization (WHO), breathing radon gas (^{222}Rn) ranks as the second cause of lung cancer after smoking cigarettes. More uranium in nearby rocks leads to higher radon levels in groundwater. Various factors like geological features, presence of shear zones, degree of metamorphism, soil porosity, and mineralization influence how much radon ends up in the water. This study utilized the Durridge RAD-7 to measure Radon (^{222}Rn) concentration in samples collected from 27 well locations from Haridwar and Dehradun districts of Uttarakhand state in India, during monsoon (July, 2021), pre-monsoon (May, 2022), and post-monsoon (November, 2022) seasons to track the radon variations effectively. Haridwar is a significant pilgrimage spot, drawing millions of devotees annually. Dehradun is a bustling tourist hub, welcoming diverse visitors seeking its natural beauty and cultural attractions. The wells were purged by pumping for 15 minutes to ensure sample quality. Specialized glass bottles with a 250 mL capacity were used to collect water samples to effectively measure radon in-water activity. A hand-held pH meter and EC meter recorded pH and EC values, respectively. Within 12 hours of sample collection, radon measurements were carried out using RAD-7. The detector was attached to a bubbling kit, which released radon from water into the air in a closed loop for measurement purposes. The Wat-250 procedure was utilized for both the 250 mL capacity vial on the RAD-7 and water sampling, ensuring an extraction efficiency of 94%. The RAD-7 provided a summary at the end of the measurement run. Pearson correlation was used to examine the relationship of radon with the EC and pH. A p-value test verified if the correlation observed was statistically significant or not. The background sample utilized in this study was millipore water from the National Institute of Hydrology, Roorkee with the mean value of radon as 1.897 Bq L^{-1}.

Results indicated that ^{222}Rn activity peaked during the monsoon season (July 2021) while it was lowest in post-monsoon season (November, 2022). During the monsoon season (July, 2021), samples revealed elevated radon concentrations. Out of 27 samples, 26 samples (i.e. about 96%) exceeded the Maximum Contaminant Limit (MCL) of 11.1 Bq L^{-1}set by the US EPA. The ^{222}Rn activity ranged from 10.15 ± 2.27 Bq L^{-1} to 42.42 ± 4.46 Bq L^{-1}, with an average value of 24.87 ± 3.33 Bq L^{-1}. The EC range at sampling sites varied from 40 to 1310 µS cm^{-1}, averaging 482.22 µS cm^{-1}. The pH range at sampling sites was between 7 and 8.7, with an average of 7.80. Radon values were scrutinized alongside EC and pH levels. Enhanced infiltration of rainwater through faults and fractures could mobilize radon-rich groundwater, slightly elevating EC levels due to the dissolution of minerals along the flow paths. Pearson correlation revealed a positive relation, although weak relation, between EC and radon levels. However, this correlation is statistically insignificant as per the p-value. This is likely to be due to the dilution from extensive rainwater influx, which reduces the overall ionic strength of the water. A moderate negative correlation was observed between

pH and radon levels, signifying statistical significance with a p-value of 0.0140. The observed significant negative correlation might be attributed to the acid-neutralizing interactions of rainwater (typically slightly acidic) with carbonate-rich lithologies. From samples during the pre-monsoon season (May, 2022), six sample sites surpassed the MCL. The ^{222}Rn activity ranged from 0.12 ± 0.5 Bq L^{-1} to 17.37 ± 2.89 Bq L^{-1}, averaging at 7.52 ± 1.83 Bq L^{-1}, being within the permissible limits according to EPA standards. The EC observed at sampling sites varied from 50 to 1140 µS cm^{-1}, averaging at 415.19 µS cm^{-1}, while pH levels ranged from 6.9 to 7.8 with an average of 7.40. The correlation between radon levels and EC remained weakly positive, and a p-value of 0.0093 was observed, signifying statistical significance. The weakly positive correlation may be due to the limited recharge which concentrates dissolved ions and radon in groundwater. Uranium-rich lithologies, such as granites in the Lesser Himalayas, contribute to elevated radon and ion levels, while faults and fractures facilitate deeper circulation, enhancing the co-occurrence of radon and dissolved solids. The correlation between radon levels and pH was weakly negative and statistically insignificant. This may be due to the buffering effect of carbonate-rich lithologies, which stabilize pH despite radon release. During post-monsoon season (November, 2022), 7 out of the 27 sampling sites surpassed the MCL. The activity of ^{222}Rn ranged from 0.10 ± 0.49 Bq L^{-1} to 18.13 ± 2.95 Bq L^{-1}, averaging at 6.20 ± 1.60 Bq L^{-1}. The EC ranged from 90 to 1110 µS cm^{-1} across the sampling sites, averaging 469.63 µS cm^{-1}. The pH levels ranged from 7.1 to 8.3, averaging 7.68. The radon values exhibited correlations with EC and pH. Both indicated a very weak negative correlation and were statistically insignificant. Post-monsoon groundwater systems often reflect a transitional state. Radon may still be mobilized from lithologies influenced by recharge, but dilution from the residual rainwater and aquifer mixing weakens the relationship between EC and pH.

The lithology of the Siwaliks and Lesser Himalayas, dominated by sedimentary and metamorphic rocks with uranium-bearing sandstone and granites, serves as a natural source for radon. It is observed that the Himalayan river systems in the N-W Himalayas, namely the Kulu, Kangra, Garhwal, and Dehradun areas, is conspicuous by its high dissolved uranium concentration. The Indian Department of Atomic Energy has reported uranium mineralization associated with the sandstone of the Middle Siwalik. Uranium has been reported from the fault and shear zones and Siwalik sandstone. The Siwaliks, rich in sandstones and clays, may exhibit limited radon emanation compared to the Lesser Himalayas. Faults and fractures act as conduits for groundwater flow. The decay of uranium isotopes within these rocks leads to radon enrichment in groundwater, especially in regions with significant aquifer-rock interactions. Higher radon concentrations are observed during the Monsoon season. So, precautions must be taken by the people to use the groundwater especially during the monsoon season. Radon concentrations in each site are determined by geology and groundwater dynamics. Allowing groundwater to stand before consumption, using aeration systems to release radon gas by bubbling water, and using GAC filters to trap radon are some radon mitigation strategies that can be followed.

Keywords: *Radon, RAD-7, groundwater, Haridwar, Dehradun*

ISOTOPIC CHARACTERIZATION OF SPRINGS OF LESSER HIMALAYA - A CASE STUDY OF KALSI REGION, UTTARAKHAND, INDIA

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Springs are the natural emergence of groundwater. Springs are created when a saturated aquifer zone intersects with the surface, causing the water to emerge as springs from rock pores, fractures, or depressions. These natural water sources serve as a primary source for drinking, domestic, and agricultural purposes for people in hilly regions. Additionally, springs play a crucial role in maintaining the base flow of rivers during the lean season. Despite its importance, a global decline in spring discharge has been observed due to climatic and anthropogenic reasons. The problem of drying springs and decline in discharge have also been reported from the Himalayan region. According to a study, nearly half the number of perennial springs in the Himalayan region have dried up or become seasonal. In addition to this, the seasonal springs in the Himalayan region are receding much more rapidly than perennial springs. The Kalsi region in the Lesser Himalayan region faces the same fate, with an increasing number of springs drying daily. So, the springs in the Himalayan region need a more comprehensive understanding of recharge source and processes, flow mechanisms, and their sustainability during the non-monsoonal season. The study has been carried out in the Kalsi region of the Lesser Himalayan region as a model pilot study to understand the hydrology of springs in the Himalayan region. The sustainability of springs depends on the recharging process, predominantly controlled by the rainfall patterns (monsoonal characteristics) and recharge time. Identifying the source and origin of springs is most important for systematically planning water conservation measures to sustain future development and needs. So, the artificial recharge process using rainwater harvesting is widely practiced for augmenting and managing the groundwater and spring resources. Many researchers have used different techniques to address the problem of drying springs. The environmental isotopic techniques have proven to be the most effective tools for solving critical hydrological issues. Environmental isotopes (stable and radioactive) have the distinct advantage of larger spatial and temporal resolutions for hydrological investigations. The use of the isotopic values in the present study will enhance the understanding of Himalayan springs.

The elevation range in the study area varies between 376 m to 2228 m whereas the elevation range of sampling sites lies between 949m to 2034 m. Springwater samples for stable isotopes were collected from 118 springs during the pre-monsoon and post-monsoon seasons. The samples were collected and sealed close to the discharge points to avoid further evaporation. All the physical parameters, such as electrical conductivity (EC), total dissolved salts (TDS), and temperature of springs and the environment, were collected in the field using portable instruments. In addition, 63 rain samples were also collected during this period from three stations using self-assembled rain gauges. To prevent evaporation of the rain samples, all the precipitation samples were collected early in the morning after the rainfall events. The stable isotopes (Deuterium and Oxygen) of spring and precipitation samples were measured in the GV-Isoprime Dual Inlet Isotope Ratio Mass Spectrometer (IRMS) lab of the National Institute of Hydrology (NIH), Roorkee. For hydrogen isotopic analysis, 1 ml of the water sample was equilibrated with H2 using a platinum catalyst at 50° C for 1 hour, and the resultant gas was introduced into the IRMS machine. The oxygen isotope of the sample was determined by equilibrating 1 ml of water with CO_2 gas at 50°C for 8 hours, after which the equilibrated gas was introduced into the mass spectrometer. All the measured values were represented in delta (δ) values. The measurement precision for the hydrogen isotope was ±1 ‰, and for the oxygen isotope was ± 0.1‰.

The isotopic values of springs for $\delta^{18}O$ isotopes during pre-monsoon season lie between -10.3 and -5.2 ‰ with an average of -8.9 ‰. The isotopic values of $\delta^{2}H$ show a wide variation with values ranging between -68.0 to -35.9 ‰ with a mean value of -58.1 ‰. The isotopic values of springs for $\delta^{18}O$ isotopes during post-monsoon season lie between -10.6 to -7.1 ‰ with an average of -8.9 ‰, whereas the isotopic values of $\delta^{2}H$ isotopes range between -63.9 and -46.2 ‰ with a mean value of -57.1 ‰. The isotopic values of precipitation for $\delta^{18}O$ isotopes range between -16.23 and 2.82 ‰, whereas the isotopic values of $\delta^{2}H$ isotopes vary between -125.08 and 20.51 ‰. The isotopic values of precipitation for oxygen and hydrogen isotopes show a wide spectrum of values due to source variation. Notably, the Local Meteoric Water Line (LMWL) line derived from the precipitation samples is positioned almost parallel to the Global Meteoric Water Line (GMWL) ($\delta^{2}H=8*\delta^{18}O+10‰$). The LMWL line has a slope (8.0) and intercept (11.7) derived from 66 samples collected from three rain gauges positioned at three different altitudes. The oxygen and hydrogen isotopic values of precipitation samples exhibited a good correlation ($r^2= 0.97$), while the individual rainfall events showed a more diverse range of isotopic values ($\delta^{18}O$ = -16.23 to 2.82 ‰, $\delta^{2}H$ = -125.0 to 20.5 ‰) for different rain events. The isotopic signature of springs from pre-monsoon (slope and intercept for pre-monsoon are 3.8 and -23.3) and post-monsoon (slope and intercept for post-monsoon are 5.6 and -7.2) seasons crossing the LMWL line showing the impact of evaporation in the spring's samples. The lapse rate of oxygen and hydrogen isotopes for precipitation are -0.4 ‰ and -4.1 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively, for a 100 m increase in elevation. The recharge elevation of all springs calculated from the isotopic lapse rate lies between the altitude range of 1386 to 2194 m in the study area.

This study used isotopic signatures of springs to understand the recharge source, recharge period, and recharge altitude in the lesser Himalayan region. The recharge altitude was calculated using the altitude lapse rate of the precipitation sample. The recharge altitude for each spring can be used to construct recharging structures like subsurface dykes, check dams, contouring, trenches, ponds, etc. These structures can help policymakers to mitigate the impact of climate change and anthropogenic stress. These isotopic results, along with on-field hydrogeological, hydrogeochemical, geospatial, and geophysical investigations, can enrich the comprehensive understanding of spring hydrology.

Keywords: *Spring, stable isotope, lesser Himalaya, LMWL, artificial recharge*

GROUNDWATER DATING IN TWO NORTHWEST INDIAN STATES

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This study investigates the groundwater age in the northwest Indian states of Punjab and Haryana using tritium (^3H) dating techniques. Tritium, a radioactive isotope of hydrogen with a half-life of 12.3 years, serves as a valuable tool for estimating the residence time, or age, of groundwater. This technique relies on the decay of tritium over time to determine how long water has been isolated from recharge sources, particularly effective for dating water with residence times of less than 60 years. The study aims to provide insights into the recharge potential and groundwater dynamics of the two states. The research focused on 16 locations across Punjab (including Ghanpur, Chamkaur Sahib, Guruhar Sahai, Sangrur, Dasuya, Garshankar, Sultanpur Lodhi, Kapurthala, Bhogpur, Saroya, Tanda, and Nakodar) and Haryana (including Firozpur Jhirka, Nagina, Kotla, and Karhera). These sites were chosen based on stable isotope values to assess recharge potential. To ensure data accuracy, a groundwater sampling protocol was implemented. The wellhead was secured, the surrounding area cleared, and well characteristics recorded. The static water level was measured to guide purging, which removed stagnant water until water quality stabilized. The sample volume required for tritium analysis was about 650 mL (millilitres). Groundwater was then collected from the pump discharge into designated containers, labelled, and transported to the Nuclear Hydrology laboratory of National Institute of Hydrology, Roorkee.

The tritium analysis involved a multi-step process. Pre-distillation removed impurities and enhanced conductivity, followed by electrolytic enrichment within a Tritium Enrichment Unit (TEU) over 25 days at low temperatures, typically between 0 and 5ºC. Post-distillation cleaning with lead chloride further purified the enriched water. Finally, the purified water was mixed with a scintillation cocktail (Ultima Gold) and analysed using a Liquid Scintillation Counter to detect beta emissions from tritium decay, enabling the determination of tritium activity (TU) in the original groundwater samples. Typical Minimum Detection Limits (MDLs) for modern Liquid Scintillation Counters with electrolytic enrichment range from 0.1 to 0.5 Tritium Units (TU). EasyView software was employed for data analysis and interpretation.

Determining groundwater age by analysing tritium concentrations using the radioactive decay equation: $t = (t_{1/2}) * \ln (A_0 / A) / \ln (2)$. Here, t represents the age of the groundwater, $t_{1/2}$ is tritium half-life (12.3 years), A_0 is initial tritium concentration in precipitation during infiltration, A is measured tritium concentration in the sample. The initial tritium concentration (A_0). To estimate initial TU values, rain samples were used. For Punjab, A_0 was determined to be 8 TU, while for Haryana, it was 15 TU. These values were used to calculate the age of groundwater at each sampling location. Standards with known high tritium activity were used to calibrate the analytical system and ensure reliable estimation of tritium concentrations in all samples, including those with very low or undetectable tritium levels. Groundwater is classified based on tritium concentration (TU) as: Modern Groundwater with >7 TU, indicating recent recharge; Mixture of Modern and Sub-modern Groundwater with 4-7 TU, showing a mix of recent and older water; Sub-modern

Groundwater with 2-4 TU, suggesting recharge from the pre-bomb era; and Old Groundwater with <1 TU, indicating recharge occurred well before the 1950s. The tritium analysis revealed a distinct contrast in groundwater age between the two states. Punjab is dominated by older groundwater, frequently with tritium concentrations below 1 TU, suggesting a slow rate of natural recharge. For example, Garshankar has a tritium level of 0.1463 TU. In contrast, Haryana shows a greater proportion of modern groundwater with higher tritium concentrations. Several locations displayed tritium levels exceeding 7 TU, indicating recent recharge. In some cases, the measured tritium concentration was higher than the initial concentration, suggesting very recent recharge. The contrasting groundwater age profiles observed in Punjab and Haryana reflect the influence of geological factors and proximity to the Himalayan rivers on recharge dynamics.

The prevalence of old groundwater in Punjab indicates a slow recharge rate attributable to fine-grained alluvial deposits of clay and silt that impede rainwater infiltration. The substantial thickness of alluvial deposits leads to deeper water tables, increasing travel time for infiltrating water. Conversely, the presence of modern groundwater in Haryana suggests more active recharge processes, influenced by the occurrence of sand and gravel lenses within the alluvial deposits, which facilitate greater infiltration. The thinner alluvial cover in Haryana potentially exhibits shallower water tables, promoting faster infiltration. Additionally, higher average rainfall in Haryana contributes to greater water availability for recharge. The report notes that while Haryana has more modern groundwater, Firozpur Jhirka (Mewat) shows older groundwater requiring further study of local hydrogeological conditions. The study provides a comprehensive analysis of groundwater age and recharge potential in Punjab and Haryana, emphasizing the influence of geological and climatic factors. This research also highlights the importance of employing advanced techniques like tritium dating to accurately assess groundwater age. Furthermore, the study emphasizes the need for careful monitoring of groundwater extraction and recharge rates to ensure the long-term sustainability of this vital resource in both Haryana and Punjab.

Keywords: *Groundwater recharge, tritium, Haryana, Punjab*

GROUNDWATER AGE DISTRIBUTION IN THE CAMBAY BASIN, INDIA: INSIGHTS FROM CARBON AND OXYGEN ISOTOPES

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The Cambay Basin is a graben structure defined by a prominent NNW–SSE-oriented fault system, with progressive down-faulting along parallel secondary faults that align with the main trend, along with intersecting orthogonal faults. The Deccan Basalt, dating back to the Late Cretaceous period, serves as the basement across most of the basin, except in the East Flank, where Proterozoic granitic rocks are also exposed at the surface. The basin's sedimentary cover, comprising Quaternary alluvial deposits overlying a sequence of Tertiary sedimentary formations, varies in thickness from a few meters near the eastern and western edges to approximately 3 km at the basin's center. The regional aquifer system within the Quaternary alluvium consists of alternating layers of sand and silty clay, with recharge occurring in the foothills of the Aravalli Mountains and discharge zones extending to areas such as the Little Rann of Kachchh, Nalsarovar, and the Gulf of Khambhat (LRK–NS–GK). Deccan Traps and Mesozoic sediments are exposed in parts of the West Flank, while the East Flank near the Aravalli foothills predominantly features granitic rocks.

This part of the Gujarat receives nearly 700 mm of rainfall and falls under the semi-arid region. In this area, groundwater plays a major role in providing water for irrigation and agriculture purposes. The high dependency on groundwater, lower rainfall, and unavailability of perennial rivers put this region into an overexploited zone in relation to groundwater abstraction due to the deeper groundwater mining going on. According to the Central Ground Water Board (CGWB) report on the quality of shallow aquifers, this area exhibits high levels of fluoride and nitrate in its shallow groundwater. The significant demand for water has led to using multi-aquifer bore wells, which sometimes function as artificial recharge structures for deeper groundwater. This allows pollutants from shallow aquifers to migrate to deeper ones. To investigate groundwater age distribution in the Cambay Basin, samples were collected from 58 locations, including hand pumps and tube wells, with depths ranging from 60 to 1100 feet. The samples were analyzed for stable isotopes of oxygen, hydrogen, carbon, and radiocarbon (^{14}C), following the standard protocols. Samples for stable isotope (δ^{18}O, δD) analysis were collected in a 30 ml airtight bottle after rinsing the bottle thoroughly with the groundwater to be sampled. Samples from the immediate vicinity of any surface water body (lake, stream, canal, etc.) were avoided. For ^{14}C measurement samples were collected in 500ml HDPE air tight bottles and poisoned by mercury chloride ($HgCl_2$). Samples for δ^{13}C measurement of dissolved inorganic carbon in groundwater were collected in a 60ml amber glass bottle after poisoning it with mercury chloride. The oxygen and hydrogen isotopic analyses (δ^{18}O and δD) of these samples were done using the standard equilibration method in isotope ratio mass spectrometer Delta V Plus in continuous flow mode using Gas bench II at Physical Research Laboratory (PRL), Ahmedabad. The reproducibility of measurement was found to be better than 0.1‰ for δ^{18}O and 1‰ for δD. 14C were measured in dissolve inorganic carbon (DIC) present in groundwater. For this, approximately 10 mL of 85%

orthophosphoric acid is placed in a ~1 L evacuated flask (~1×10^{-2} mbar) and then groundwater sample is injected in the flask using a syringe with the amount adjusted according to the DIC concentration. The released CO_2 gas flows through three U-tubes. The first U-tube, placed in an alcohol-liquid nitrogen slush (-80°C), captures moisture. The following two U-tubes, immersed in liquid nitrogen (-196°C), freeze CO_2. The CO_2 undergoes multiple freeze-thaw cycles between traps to eliminate any remaining water or impurities. The CO_2 is expanded into a calibrated chamber connected to a pressure gauge to measure its volume accurately. Purified CO_2 is then transferred to a pre-evacuated glass ampule, ready for use in the graphite preparation system. Purified CO_2 (50-100 µmol) is introduced into a graphite preparation line, with the vacuum system containing pre-treated iron (5 mg) and zinc (25 mg) powders. The CO_2 undergoes reduction to elemental carbon (graphite) as the iron and zinc powders are heated to suitable temperatures. The resulting graphite deposits onto the iron powder's surface. The graphite-coated iron is pressed into a pellet and loaded into a 1 MV accelerator mass spectrometer at the Physical Research Laboratory (PRL), Ahmedabad, for radiocarbon analysis. Alongside the samples, international standards (Oxalic Acid I, Oxalic Acid II) and background materials (such as anthracite) are analyzed. Age estimates are corrected for isotopic fractionation effects in both sample preparation and the AMS process. Conventionally, radiocarbon age (using Libby half-life of 5568 yrs.) of any sample is calculated using the basic decay equation.

In this study, groundwater samples from shallow as well as deep aquifers were collected in 2023 during pre-monsoon season (May June) and analysed for stable isotopes of oxygen and hydrogen as Stable isotopes of oxygen and hydrogen play an important role in understanding the movement and mixing of two different water masses. The shallow groundwater isotopic values range between -0.8‰ to -5.8‰ with an average value of -3.0‰ while deeper groundwater isotopic values range between -2.7% to -4.5‰ with an average of -3.7‰. The regression line for shallow groundwater has a slope (6.1 ± 0.3), while deeper groundwater has a slope (7.3 ± 0.5). The higher slope and more depleted $\delta^{18}O$ of deeper groundwater suggest they are recharged from different water sources. In some locations, the isotopic values of dipper and shallow groundwater have a similar isotopic composition, indicating the areas where shallow and deep groundwater might interact due to multi-aquifer penetrated borewells. Radiocarbon dating revealed groundwater ages ranging from 500 to 40,000 years BP (these age are corrected for carbonate dissolution and callibarated using oxcal), varying spatially across the basin. In the eastern boundary near the Aravalli foothills, groundwater exhibited modern ages (500 to 2000 years BP), while in the western parts, ages extended up to 40,000 years BP. The extraction of paleowater in the region is significantly impacting the groundwater balance, posing long-term sustainability concerns.

Keywords: *Cambay basin, groundwater, stable isotopes, radiocarbon, paleowater*

ISOTOPIC AND HYDROCHEMICAL INSIGHTS INTO GROUNDWATER SUSTAINABILITY IN THE MIDDLE GANGA BASIN, INDIA

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This study examines groundwater isotopic composition to understand its dynamics, recharge mechanisms, and sustainability. The main objectives are to identify recharge areas, evaluate recharge processes, and determine groundwater sources. Surveys under the Global Network of Isotopes in Precipitation (GNIP) and Rivers (GNIR) measured oxygen and hydrogen isotope contents, including $\delta^{18}O$, $\delta^{2}H$, and ^{3}H, in precipitation and rivers. Managed by the International Atomic Energy Agency (IAEA) with the World Meteorological Organization (WMO), GNIP includes around 900 monitoring stations across 100+ countries. For this study, data from 1998–2016 for rivers and rainfall in the Middle Ganga Basin were analyzed. Unlike traditional methods where isotopic data supplement hydro-chemical findings, this research prioritizes isotopic analysis to delineate recharge zones and assess sustainability.

The study integrates isotopic data (^{3}H, $\delta^{18}O$, $\delta^{2}H$), hydro-chemical parameters (bicarbonate and electrical conductivity), groundwater fluctuation trends (1998–2016), and rainfall records (1991–2020) to understand groundwater systems comprehensively. The first objective is to determine the isotopic composition of rainfall, river, and groundwater samples using $\delta^{18}O$ and $\delta^{2}H$ values and establish Isotopic Water Lines (IWLs) for each source. These include the Local Meteoric Water Line (LMWL), River Isotope Water Line (RIWL), and Groundwater Isotope Line (GWIL), providing insights into sources and pathways. The second objective explores correlations between isotopic values and chemical variables like chloride and nitrate concentrations. The study area covers 95,000 km² in the Upper-Middle Ganga Basin, bordered by the Sharda, Ghaghra, and Ganga rivers, with the Lower Shiwalik range forming the northern limit. Rivers such as the Ramganga, Sai, and Gomti, along with canals, support agriculture. Groundwater samples were collected once for isotopic and chemical analysis, covering 20 districts for isotopes and 27 districts for chemical data. Laboratory analyses using Isotope Ratio Mass Spectrometry (IRMS) focused on $\delta^{18}O$, $\delta^{2}H$, ^{3}H, nitrate (NO_3^-), and chloride (Cl^-). Data from groundwater trends (1998–2020) and rainfall records (1991–2020) were analyzed, and maps were created to visualize isotopic distributions, canal networks, and groundwater fluctuations using Inverse Distance Weighted (IDW) interpolation.

The results reveal that regions with high tritium content (4.0–8.0 TU) and elevated bicarbonate levels are active recharge zones, where rainfall ranges from 400 mm to 1300 mm. Correlations between stable isotopes and electrical conductivity further illuminate aquifer interactions, aiding groundwater sustainability assessments. The values of $\delta^{18}O$ vary from -7.93‰ to -5.32 ‰ for deep aquifers. The values of $\delta^{18}O$ vary from -8.4‰ to -4.2 ‰ for shallow aquifers. The $\delta^{18}O$ of Budaun and Bareilly varies from -8.2‰ to -7.56‰ while that of Bijnor, Moradabad, Sitapur, and Ambedkar Nagar varies from -7.55‰ to -6.81‰. The $\delta^{2}H$ of Prayagraj and Pratapgarh varies from -52.45‰ to -50.04‰ while that of Varanasi, Moradabad, and Rae Bareilly varies from -50.04‰ to -45.02‰. The class -62.3‰ to -55‰, -55‰ to -50‰, -50‰ to -47.5‰, -47.5‰ to -45‰ and -45‰ to -38.5‰ the area covered are 374.58 km², 7850.98 km², 17534.36 km², 23613.68 km² and 11811.9 km² respectively. for

class -9.8‰ to -7.8‰, -7.8‰ to -6.8‰ and -6.8‰ to -5.33‰ the area covered are 1323.682 km^2, 37425.02 km^2 and 22436.79 km^2 respectively. The value of d-excess follows the equation (d-excess = -87.6 + 1.7* Latitude + 0.57*Longitude -0.005* depth, and d-excess = 50.48 – 0.32*Latitude -0.42* Longitude -0.0005*depth) for d-excess ranges of 4‰ to 7‰, and 7‰ to 8‰, respectively.

The number of points or stations for Electrical Conductivity (EC), Chloride (Cl^-), and Nitrate (NO_3^-) are 190, 4, and 10 respectively. The groundwater quality in Uttar Pradesh (middle Ganga Basin) was investigated by collecting samples and analyzing key geochemical parameters, including EC and NO_3^- with values varying from 130 µS/m to 1620 µS/m, 0.32 ppm to 549 ppm, and 0 ppm to 174 ppm. There is a negligible linear relationship of the stable isotopes δ^2H or $\delta^{18}O$ or d-excess with latitude or longitude or depth (msl). In some aquifers, the contribution of water from rainfall is higher while in others the contribution of surface water is higher. The study concludes that the groundwater is recharged by water from different sources. The groundwater age of deeper aquifers (25 years and 45 years, TU = 1 TU to 8 TU) is more than shallow aquifers (0 years and 39 years, TU = 1 TU to 7 TU) in most of the areas. However, in some areas, the groundwater age in shallow aquifers is found to be higher (more than 60 years to 100 years). This may be due to longer travel time in shallow aquifers due to lower permeability and poor terrain features. There are many below 1 TU sites in the study area where dating with the help of Carbon. Uranium, Krypton, etc. must be carried out. These areas, characterized by stable groundwater levels, are largely supported by significant rainfall and dense canal networks. In contrast, regions with low ^3H content are marked by declining groundwater levels, indicating vulnerability to depletion.

This study has used an integrated approach and found a relationship between $\delta^{18}O$ and EC is EC = 104.56 $\delta^{18}O$ + 1405.8 with coefficient of determination equal to 0.0873. This relationship shows that the inter-aquifer interaction is limited to just 8.73% of all the samples taken. This study underscores the importance of isotopic analysis in assessing groundwater sustainability. The insights gained are invaluable for policymakers and water resource managers, providing actionable strategies to ensure the long-term viability of groundwater resources in the Middle Ganga Basin. This analysis will help assess the influence of human activities, such as agricultural runoff or urbanization, on the isotopic and chemical composition of the water. The results inform future monitoring and mitigation strategies aimed at improving water quality and ensuring sustainable water use in the region.

***Keywords**: Isotope hydrology, hydrogeology, environmental tracers, aquifers*

CONTROL OF AQUIFER MATERIAL ON GROUNDWATER MINERALIZATION REVEALED THROUGH ISOTOPIC AND HYDROCHEMICAL PROXIES IN CENTRAL GANGA PLAIN

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The Ganga alluvial plain (GAP) includes the Central Ganga plain, which is densely populated and comprises thick, highly permeable sand layers interbedded with less permeable silt, clay, and kankar carbonate deposits. The occurrence of an alternate sequence of sand, silt, and clay has resulted in a multitier aquifer system in the central Ganga plain. The shallow, unconfined aquifer, typically less than 100 m deep, is heavily exploited through hand pumps and private motorized wells for domestic and agricultural purposes. Unregulated groundwater extraction has led to rapid groundwater depletion and increased vulnerability to contamination. To address these pressing issues, a comprehensive study was undertaken in the Varanasi Urban area to investigate factors controlling groundwater chemistry's vertical and spatial fluctuation in this intensively populated region under prevailing aquifer heterogeneity.

In May 2021, 70 groundwater samples were collected for significant ion, trace metal, and isotope analysis during the pre-monsoon period. Samples were gathered from wells belonging to residents accessible for public use. A grid file covering the study area, measuring 1.5 × 1.5 km^2, was created using ArcGIS 10.5 to facilitate the collection of groundwater samples from various depths. Each central point within the grid was designated as a survey point. Groundwater samples were collected in 250 mL polyethylene bottles after flushing out stagnant water from the dug wells by pumping for several minutes. Samples were filtered using 0.45µm millipore membrane filters. The major ions and trace metals samples will be taken separately, in compliance with American Public Health Association (APHA, 2012) guidelines. To preserve the water sample's pH (<2) for trace metal analysis, they will be filtered and stored in a 15 ml conical tube. The temperature, pH, and EC were measured in situ using portable instruments. Major ions and trace metals were measured using IC and ICPMS, respectively, at the National Institute of Hydrology (NIH), Roorkee, India. The acid titration method determined the bicarbonate (HCO_3) concentration in the water. The ion balance indicates that errors in most samples are within ±10%.

The physical and chemical characteristics of 70 groundwater samples from the study area have been analysed. The chemometric, statistical, and isotopic analyses revealed a strong association between Na^+, Ca^{2+}, Mg^{2+}, K^+, F^-, and HCO_{3-}, indicating the dominant role of silicate weathering in controlling groundwater chemistry. The major facies observed are freshwater types of Ca-HCO_3 and Mg-HCO_3 and a few mixed facies of Ca-Na-HCO_3 water type. The widespread occurrence of calcite and dolomite nodules abundant in the older alluvium of the study area and their dissolution leads to the formation of Ca-HCO_3 and Mg-HCO3 water types. The formation of more evolved water type Ca-Na-HCO_3 results from increased groundwater residence time in the flow direction. The excess of Na^+ over Cl^- suggests additional sources of Na^+ from silicate minerals rich in Na^+ (orthoclase) brought and deposited by the rivers draining peninsular India. The study further revealed that F^-

enrichment is primarily confined to shallow groundwater and is linked to soil minerals like mica and amphibole. The higher NO^{3-} values were observed in areas adjacent to agricultural lands. These findings indicate that groundwater chemistry is primarily influenced by mineral dissolution processes within aquifer material. It is the main reason for aquifer hydrochemistry's spatial and vertical variability.

All trace metal groundwater samples in this study fall within the specified standard. As per BIS (2012) drinking water standards, concentrations of nearly all metals are below the permissible limits, except for Mn, Hg and U. In the analysed samples, Mn concentrations range from BDL to 615.28 µg/L, with a mean value of 13.39 µg/L. The threshold level for Mn was exceeded in 1.5% of groundwater samples. Numerous studies have indicated that Mn exposure can be attributed to anthropogenic activities like industrial waste, agricultural runoff, household sewage, and geogenic sources. The measured concentrations of Hg ranged from BDL to 1.5 µg/L, with a mean value of 0.086 µg/L. The threshold level for Hg was exceeded in 1.5% of groundwater samples. Elevated levels of Hg in samples may be attributed to both geogenic sources (Hg-bearing minerals) and anthropogenic activities like industrial waste, agricultural runoff, and household sewage. In the analyzed groundwater samples, U concentrations ranged from 0.72 µg/L to 44.74 µg/L, with a mean value of 8.40 µg/L. The threshold level for U was exceeded in 5.55% of groundwater samples.

The stable isotopic results ($\delta^{18}O$ and δ^2H) reveal that most groundwater samples exhibit a comparatively enriched isotopic composition. Urban Varanasi is characterized by a dense population and extensive built-up areas with a population density of 2400 persons per square kilometer. Further, hydro-geologically, the aquifer in this region is capped by a significantly thick clay layer, which limits infiltration and results in higher surface runoff into nearby depressions. Surface recharge occurs primarily through local water bodies such as ponds and lakes or in areas where the impervious clay capping is discontinuous, allowing for localized infiltration.

In this study chemometric, statistical and isotopic methods are applied to understand the hydrochemical characteristics and evolution of groundwater in the study area. The findings indicate that groundwater chemistry is predominantly influenced by mineral dissolution processes, with silicate weathering playing a dominant role in shaping the ionic composition. The major hydrochemical facies identified include $Ca\text{-}HCO_3$, $Mg\text{-}HCO_3$, and $Ca\text{-}Na\text{-}HCO_3$, influenced by the dissolution of calcite, dolomite, and silicate minerals transported by rivers. Elevated concentrations of F^- in shallow aquifers are linked to soil minerals, while localized NO_3^- enrichment is associated with agricultural practices. Trace metal analysis revealed that Mn, Hg, and U occasionally exceed permissible limits, attributed to geogenic and anthropogenic sources. Stable isotopic data ($\delta^{18}O$ and δ^2H) indicate limited recharge due to the impervious clay layer and urbanization impacts, with localized infiltration through water bodies and clay discontinuities. The insights gained from this study can contribute to developing sustainable groundwater management strategies in similar hydrogeological settings, mitigating the adverse impacts of excessive groundwater extraction for agricultural practices and promoting long-term aquifer health.

Keywords: *Hydrochemistry, shallow aquifer, mineral dissolution, Central Ganga Plain*

HYDROLOGICAL AND ISOTOPIC CHARACTERIZATION OF HIMALAYAN SPRINGS: INSIGHTS FROM STABLE ISOTOPES, TRITIUM ANALYSIS, AND SEASONAL PRECIPITATION IN THE TAKOLI GAD WATERSHED, INDIA

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Across the Himalayas, springs serve as a critical and reliable source of fresh water for rural and urban populations. However, these indispensable resources face increasing threats, as many springs exhibit drying trends. This decline leads to reduced water discharge and deteriorated water quality, significantly impacting local communities that depend on them for their livelihoods. Despite their importance, the role of springs in river water discharge studies remains underexplored, particularly in the glaciated and non-glaciated terrains of the Indian Himalayas. Considering the vital role of springs in the hydrological cycle, this study investigates the water isotopic composition and hydrochemistry of spring water and precipitation in the Takoli Gad watershed in the Lesser Himalayas.

Systematic water sampling was conducted across three key seasons: pre-monsoon, monsoon, and winter. A total of 434 spring water samples were collected, including 125 samples during the pre-monsoon season, 155 during the monsoon season, and 154 during the winter season. All the samples were analyzed for $\delta^{18}O$ and δD. Additionally, 29 representative spring water samples were collected and analyzed for Tritium dating. The lower number of spring water samples collected during the pre-monsoon season is attributed to the lean discharge period, during which some springs dry up. During each sampling session, in situ measurements of pH, electrical conductivity (EC), water temperature, and ambient temperature were recorded. The water samples were stored in high-density polyethylene bottles to prevent contamination. For stable isotope analysis, 125 mL bottles were used, while 1-liter bottles (29 samples) were utilized for tritium analysis. The bottles were tightly sealed and stored at 4°C until analysis. Stable isotope measurements ($\delta^{18}O$ and δD) were performed using an Isotope Ratio Mass Spectrometer MAT 253 PLUS coupled with Gas Bench II, adhering to stringent quality control protocols. The isotopic compositions were reported relative to Vienna Standard Mean Ocean Water, achieving a precision of ±0.1‰ for $\delta^{18}O$ and ±1.0‰ for δD. Tritium analysis involved electrolytic enrichment in a 20-cell unit, maintaining sample temperatures between 0°C and 5°C. Tritium activity was measured using an ultra-low-level liquid scintillation counter (Quantulus Wallac model 1220), with results reported in tritium units (TU) and a 2-sigma error margin.

The results revealed clear seasonal variations in isotopic composition and EC. $\delta^{18}O$ values ranged from -6.55‰ to -9.50‰ (pre-monsoon), -7.71‰ to -10.49‰ (monsoon), and -7.21‰ to -9.44‰ (winter), while δD values ranged from -43.78‰ to -65.94‰, -51.16‰ to -73.09‰, and -50.57‰ to -65.37‰, respectively. These seasonal shifts reflect monsoon precipitation's influence on spring recharge during the monsoon season, while evaporation processes drive isotopic enrichment during the pre-monsoon. This pattern is corroborated by d-excess values, which peaked during the monsoon and were lowest in the pre-monsoon.

Notably, winter rainwater exhibited the highest d-excess values due to the influence of westerly winds. Seasonal EC variations ranged from 70–1120 µS/cm (pre-monsoon), 50–730 µS/cm (monsoon), and 70–930 µS/cm (winter). High EC values during the pre-monsoon are attributed to limited rainfall, prolonged groundwater residence times, and reduced dilution, whereas the monsoon season’s lower values result from substantial precipitation-induced dilution. EC inversely correlated with elevation, as higher-altitude springs experienced shorter rock-water interaction times compared to their lower-altitude counterparts. Depression springs consistently displayed higher EC values, indicative of extended residence times and slower flow rates. Seasonal discharge fluctuations were also observed, with peak discharge during the monsoon and the lowest discharge during the pre-monsoon, directly influencing EC patterns.

Spring water pH ranged from slightly acidic to alkaline, with bicarbonate ions contributing to alkalinity via carbonic acid reactions. Tritium concentrations varied between 1.5 TU and 14.2 TU, indicating groundwater ages from recent to approximately 36 years. These findings underscore active recharge processes while highlighting the vulnerability of groundwater to environmental and anthropogenic changes. This comprehensive study enhances understanding of Himalayan springs' hydrological, isotopic, and ionic dynamics. The observed seasonal variations underscore the significant role of monsoon precipitation in recharging springs, complemented by winter precipitation influenced by westerlies. Fluctuations in EC and pH reflect the interplay of geological interactions, groundwater residence times, and seasonal dilution. These findings provide a scientific basis for sustainable spring rejuvenation practices and guide policymakers in conserving recharge zones, mitigating land-use changes, and adopting sustainable management strategies to ensure the longevity of Himalayan springs.

Keywords: *Himalayas, springwater, precipitation, stable isotopes, tritium, seasonality*

UNDERSTANDING SURFACE WATER GROUNDWATER INTERACTIONS IN THE UPPER NARMADA RIVER BASIN AND ITS HYDROLOGICAL IMPLICATIONS

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Groundwater and surface water are interconnected components of the hydrological system. In gaining streams, groundwater discharges into rivers and lakes, contributing to their base flow. Conversely, losing streams recharge underlying aquifers. This interaction is dynamic and depends on factors such as geology, land use, and climatic conditions. Understanding these interactions is critical for managing water resources holistically. The Narmada river is one such river which is perennial but non snow fed. This river originates from the Narmada Kund (a small reservoir) located at Amarkantak and travels nearly 1300 km before debouching into the Arabian Sea. This river is life line of Madhya Pradesh and Gujarat. Over half of the Narmada River basin is dedicated to agriculture, with groundwater serving as the primary source of irrigation and drinking water. Additionally, water from the Narmada River is transported via the Narmada Canal to water-scarce areas of Gujarat and parts of Rajasthan for agricultural and domestic purposes. Given the critical role of the river in sustaining water resources, understanding the interactions between groundwater and the river along its length, and how these interactions change spatially and temporally, is essential. Tools such as stable isotopes of oxygen, hydrogen, along with hydrogeological parameters, have been widely employed in hydrological studies to investigate various processes, including hydrograph separation, quantification of baseflow, and seasonal groundwater recharge dynamics. Our objectives for this study is to understand spatiotemporal variations in surface water groundwater interactions along the Narmada river for upper Narmada Basin (Amarkantak to Hosangabad, covers nearly 720 km length). To achieve this objective groundwater from shallow aquifers from 92 locations and river water (Narmada and its tributaries) from 23 locations were collected for pre-monsoon (June 2024) and post-monsoon (Nov 2024) seasons. These samples were collected from 30km interval along the river and across the river near the bank and 5km away up to 15km on both the sides.

Basic parameters such as pH, EC, and temperature were measured in field using Thermoscientific PC 450 Multi-parameter Meter Kit. The isotope samples were collected in 30ml HDPE airtight bottles after rinsing it thoroughly with the sampled water. The groundwater samples were collected from dug wells and hand pumps after purging it for 10 minutes to avoid the effect of evaporation from stagnant water while river water samples were collected from mid channels through rope and bucket to avoid any spurious signature from river water near bank due to some small channel contamination. These samples were analyzed for their stable isotope compositions of oxygen ($\delta^{18}O$) and hydrogen (δD) using Dual Inlet Isotope Ratio Mass Spectrometry (DI-IRMS) and Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS). Both instruments are housed in the Nuclear Hydrology Laboratory at the National Institute of Hydrology, Roorkee.

For the isotopic analyses, a gas equilibration method was employed, which is a widely recognized procedure for assessing water samples. A small volume of water (approximately 300 μL) was used for each analysis. For oxygen isotope analysis ($\delta^{18}O$), the water samples were equilibrated with carbon dioxide (CO_2) gas, while for hydrogen isotope analysis (δD), hydrogen (H_2) gas was used. During this equilibration process, the respective gases absorbed the isotopic characteristics of the water sample, allowing for a precise measurement of the isotopic ratios. The equilibrated gases, containing the isotopic signatures of the water, were then introduced into the mass spectrometer. The IRMS measured the ratios of the isotopes, specifically $^{18}O/^{16}O$ for oxygen and $^{2}H/^{1}H$ (D/H) for hydrogen. These ratios were further used to compute the delta values ($\delta^{18}O$ and δD) of the samples, which provide information about the relative abundance of the isotopes compared to a standard reference. The reproducibility of the measurements was ensured through repeated analyses of multiple aliquots of a secondary laboratory standard. The results demonstrated high precision, with reproducibility better than 0.1‰ for $\delta^{18}O$ and 1‰ for δD.

The isotopic compositions of oxygen and hydrogen are expressed using the delta (δ) notation, which represents the ratio of the less abundant isotope to the more abundant isotope (R = $^{2}H/^{1}H$ or $^{18}O/^{16}O$). This ratio is compared to a standard reference material (Vienna Standard Mean Ocean Water, or VSMOW) and is expressed in per mil (‰) units. The groundwater $\delta^{18}O$, δD, and d-excess for pre-monsoon season varies between -7.2‰ to -0.3‰, -46.4‰ to -11.6‰, and -12.1‰ to 16.0‰ with an average of -4.3‰, -29.4‰, and 4.8‰ while for the post-monsoon season the ranges are -7.4‰ to -0.4‰, -51.0‰ to -15.2‰, and -11.6‰ to 13.7‰ with an average of -4.5‰, -31.0‰, and 4.7‰. The river water $\delta^{18}O$, δD, and d-excess for pre-monsoon ranges between -4.4‰ to 4.0‰, -38.9‰ to 7.9‰, and -24.0‰ to 3.5‰ with an average of -1.7‰, -18.5‰ and -5.0‰ while the post-monsoon values varies between -6.7‰ to -4.0‰, -49.8‰ to -29.2‰, and 0.0‰ to 8.3‰ with an average of -5.3‰, -37.5‰, and 4.4‰. The average isotopic composition of groundwater indicates that there is no seasonal variation but when it plotted spatially some of the region shows depletion in post-monsoon season which indicates freshwater influx in groundwater during monsoon season. River water isotopic composition varies spatially as well as temporally during pre-monsoon season Narmada kund water isotopic composition was -2.7‰ as river flow towards Bargi dam (near Jabalpur) river water isotopic composition initially increases and went up to 4.0‰ and then started decreasing up to -1.7‰ after the dam river water isotopic composition was -4.9‰ and it went up to -4.1‰ similar kind of pattern was also observed during post-monsoon season but the values were much lower i.e. Narmada kund water isotopic composition was 5.9‰ it went up to -4.4‰ and it started decreasing up to -5.5‰ and after the dam river water isotopic composition was -6.7‰ and it went up to -5.6‰. Similar pattern was also observed in pH values of river water during both the season from Narmada kund to Hosangabad. Based on the isotopic data and pH some of the preliminary inferences drawn from this study are: (1) The initial increase in $\delta^{18}O$ value indicate higher extent of evaporation (2) The decrease $\delta^{18}O$ and pH before the dam indicated that this area receives base flow as groundwater in this part of lower isotopic composition and low pH values compared to river. (3) a decrease in isotopic composition after the dam is because of the stratification in isotopic composition of reservoir water (upper part of the reservoir water become enriched due to evaporation while bottom water preserves its initial and this water is further released in river).

Keywords: *Upper Narmada Basin, groundwater, stable isotopes, base flow, seasonal variation*

ISOTOPIC COMPOSITION AND VARIABILITY OF SNOWPACK IN THE HIMALAYA (2011–2022)

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The Himalayan region is known to be sensitive to changes in global climate and is considered a crucial component of the earth's climate system. The snow and ice cover in the Himalaya act as a natural archive of environmental and climatic changes, and the isotopic composition of the snow provides a valuable record of these changes. The stable isotopes of oxygen and hydrogen in snow and ice reflect the temperature and moisture conditions during snow formation and can provide information on the precipitation source, transport, and recycling processes. The stable isotopic composition of snow and ice in the Himalaya have significant spatial and temporal variations. Mountain hydrology research has increasingly focused on the role of isotopic analysis in understanding snowpack dynamics. Snowpack's are critical water reservoirs in mountainous regions contributing to downstream water security significantly. This study examines the snowpack's isotopic composition ($\delta^{18}O$, D, and d-excess) over a decade (2011–2022), highlighting spatial and temporal variability, relationships among isotopic parameters, and implications for hydrological modelling and climate studies. The work builds on foundational studies, including Dansgaard's framework on isotopic fractionation in precipitation and applications in snow hydrology. Snowpack samples were collected annually from a Himalayan site over the 11 years. The isotopic composition of the snowpack was analyzed using cavity ring-down spectroscopy (Piccarro), yielding high-resolution data on $\delta^{18}O$, D, and d-excess. Depth profiles were constructed to study vertical isotopic gradients, while temporal trends were assessed to identify inter-annual variability. Relationships between $\delta^{18}O$ and d-excess were explored, and the snowpack meteoric water line (SMWL) was derived.

The $\delta^{18}O$ profile exhibited significant variability with depth, reflecting processes such as fractionation during precipitation and post-depositional modifications. Enriched $\delta^{18}O$ values near the surface were associated with recent snowfall, while deeper layers showed depletion, indicating older snow and potential sublimation effects. These findings align with previous studies on Himalayan snowpack isotopes. The d-excess profile highlighted evaporative enrichment and moisture source variations. Elevated d-excess values in certain layers suggested contributions from non-local moisture sources, including westerlies, while lower values indicated local recycling. Such patterns are consistent with insights from studies on d-excess as a tracer for hydrological processes. Inter-annual variability revealed significant fluctuations linked to changes in atmospheric circulation patterns, such as the Indian Summer Monsoon and Western Disturbances. These findings underscore the sensitivity of snow isotopes to climatic drivers. The derived Snowpack Meteoric Water Line (SMWL) ($\delta^2H = 8*\delta^{18}O + 10\pm0.5$) closely aligned with the global meteoric water line (GMWL), suggesting minimal kinetic fractionation. Deviations in specific years indicated shifts in precipitation regimes. A negative correlation between $\delta^{18}O$ and d-excess was observed, reflecting the interplay between condensation temperature and moisture source dynamics. This relationship provides a robust indicator for tracing snowpack origin and evolution.

The isotopic signatures of snowpack provide critical insights into precipitation processes, snow dynamics, and climatic variability. Enriched $\delta^{18}O$ and variable d-excess values underscore the influence of both regional and local factors on snow isotopes. The SMWL's stability over the study period emphasizes the dominant role of synoptic-scale precipitation events in shaping isotopic patterns. The findings have significant implications for mountain hydrology. The isotopic characterization of snowpack enables improved parameterization of snowmelt models through isotope-derived insights into accumulation and ablation processes, enhanced understanding of snowpack contributions to streamflow, critical for water resource management and climate change impact assessments by linking isotopic trends to shifts in atmospheric moisture sources. This study highlights the value of isotopic analysis in advancing our understanding of snowpack dynamics in the Indian Himalaya. The observed variability in $\delta^{18}O$, D, and d-excess, alongside their relationships, provides a comprehensive picture of the interplay between climatic drivers and snow hydrology. Future work should focus on integrating isotopic data with high-resolution climate models to predict snowpack responses under changing climatic conditions.

Keywords: *Snowpack, stable isotopes, mountain hydrology, Himalaya, climate variability*

ASSESSING GROUNDWATER QUALITY IN JHAJJAR, HARYANA: HYDROCHEMICAL AND ISOTOPIC INSIGHTS FOR SUSTAINABLE MANAGEMENT

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The rapid urbanization and industrialization in alluvial plains, known for their high permeability, have led to an imbalance between water supply and demand, significantly impacting groundwater resources. Key factors influencing aquifer hydrochemistry include recharge water, rock-water interactions, land use, and human activities. Increased groundwater depletion and contamination are exacerbated by changing precipitation patterns, high-water-consuming crops, industrial operations, and population growth. The Indo-Gangetic Plain (IGP), particularly the Jhajjar district, illustrates these challenges, with excessive extraction since the Green Revolution resulting in depletion, salinization, and elevated levels of TDS and fluoride, posing serious health risks. The paper addresses the objectives (i) groundwater quality, contamination, and the pollution sources, (ii) hydrological processes involving groundwater recharge and evaporation dynamics, and (iii) management strategies to address salinization and contamination for sustainable resource use. This study focuses on the Jhajjar district in southwestern Haryana, part of the National Capital Region (NCR) of Delhi. Despite its potential as a freshwater recharge zone, the district faces groundwater deterioration due to fluoride, sulfate, chloride contamination, and salinity, raising health concerns like dental fluorosis. Groundwater serves as the primary source for drinking, industrial, and agricultural needs. The region, with alluvial topography consisting of clay, sand, and kankar sediments, faces challenges from over-irrigation, waterlogging, and salinity.

Groundwater samples were collected from 21 locations across a 10x10 km grid. Each well was purged for 5 minutes before sampling to prevent contamination. Sampling bottles were treated with hydrochloric acid (HCl), rinsed with water, and acidified with nitric acid (HNO_3) to preserve trace metals. On-site measurements included pH, EC, TDS, and water table depth. Anions and cations were analyzed using ion chromatography and atomic absorption spectrophotometry. Samples were stored at 4°C, and spatial analyses were conducted using ArcGIS 10.3. The saturation index (SI) was calculated using PHREEQC software. Stable isotopes $\delta^{18}O$ and $\delta^{2}H$ were analyzed by IRMS to study groundwater-surface water interactions, recharge, and geochemical processes. Cluster analysis categorized groundwater into distinct groups based on land use and climate influences. Hydrochemical analysis revealed that groundwater in Jhajjar district is predominantly alkaline, with pH values ranging from 7.52 to 10.31. Total Dissolved Solids (TDS) levels exceeded permissible limits in most samples, indicating significant salinization. Electrical conductivity (EC) values ranged from 700 to 18,430 µS/cm, and TDS from 351 to 9,215 mg/L. Elevated TDS and EC are mainly due to salt encrustation and irrigation return flows. Sulfate concentrations varied from 23.3 to 1,851.4 mg/L, influenced by agricultural chemicals, while bicarbonate levels ranged from 122 to 394 mg/L, caused by carbonate dissolution.

Nitrate contamination ranged from 10.2 to 54.3 mg/L, especially high in south-eastern and south-western regions, linked to excessive fertilizer use and agricultural runoff. Fluoride levels ranged from 0.6 to 6.8 mg/L, with 66% of samples exceeding the WHO limit of 1.5 mg/L, particularly in the north-eastern and central areas. Elevated fluoride concentrations are associated with alkaline pH, ion exchange, and local clay-silt formations. A correlation matrix indicated strong associations between pH, EC, TDS, Na^+, and Cl^-, showing that agricultural activities significantly contribute to pollution and salinity. The Mineral Saturation Index showed under-saturation concerning to anhydrite, gypsum, and fluorite, facilitating the dissolution of sulfate and fluoride ions. Hierarchical Cluster Analysis classified the groundwater into three groups, ranging from freshwater to highly saline, highlighting the variability in groundwater quality and the need for targeted management strategies.

The study found significant impacts of urbanization and irrigation on groundwater salinity and isotopic composition. Canal irrigation in peri-urban areas resulted in lower chloride concentrations and depleted $\delta^{18}O$ values, aiding aquifer recharge. In urban areas like Jhajjar, elevated chloride concentrations and enriched $\delta^{18}O$ values indicated evaporation and groundwater depletion, raising concerns about saline plumes. Fluoride concentrations were lower in canal-irrigated areas but higher in urban zones. Reverse ion exchange and carbonate weathering dominate the region's hydrological processes, with calcium being replaced by sodium in wastewater-infiltrated areas. Increasing EC and chloride concentrations from Water Group (WG) I to III indicates a transition to more saline conditions, with WG II and III resembling ocean-water ratios. The dissolution of gypsum and the region's flat, waterlogged terrain contribute to high sulfate concentrations, particularly in urban areas. Local precipitation is identified as the main groundwater source, with significant spatial variation in isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$). Canal irrigation and evapotranspiration play key roles in enhancing groundwater recharge, as indicated by elevated D-excess values.

The key findings of the study reveal significant concerns regarding groundwater quality, pollution sources, and hydrological processes in the district. Groundwater is primarily alkaline and highly saline, with TDS and EC levels exceeding WHO standards in 95% of the samples. Agricultural practices, particularly excessive fertilizer use, contribute to nitrate and fluoride contamination, with high fluoride levels in urban areas posing considerable health risks. Urbanization and irrigation practices also influence groundwater salinity and isotopic composition. Canal irrigation in peri-urban areas helps mitigate chloride and fluoride concentrations, while urban regions experience higher salinity due to evaporation and groundwater depletion. Hydrological processes such as reverse ion exchange and carbonate weathering play a crucial role in groundwater mineralization. Isotopic analyses indicate that local precipitation is the primary source of groundwater, with variations in $\delta^{18}O$ and $\delta^{2}H$ reflecting the impact of evaporation and recharge mechanisms. The study underscores the importance of targeted management strategies to address salinization and fluoride contamination. It emphasizes the need to protect recharge zones, promote sustainable agricultural practices, and raise awareness among stakeholders to safeguard water resources and public health.

Keywords: *Groundwater quality, salinization, isotopic composition, correlation matrix*

HYDROCHEMICAL AND ISOTOPIC DYNAMICS OF (SUB)-SURFACE WATER RESOURCES IN CHITTORGARH, RAJASTHAN

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The (sub)-surface water resources are highly susceptible to geological and anthropogenic processes. These resources are essential in meeting agricultural demands and providing potable water to the local communities. However, as water quality deteriorates and contamination levels increase, bridging the significant research gap in understanding the hydrochemical and isotopic processes that govern these resources becomes essential. This is particularly important for semi-arid regions like Chittorgarh in Rajasthan, where geological and anthropogenic factors interact significantly. Chittorgarh is located in the southern part of Rajasthan between 74° 26′ 54″ to 74° 51′ 43″ East and 24° 42′ 35″ to 25° 05′ 41″ North with a geographical area of 950 square kilometers and mean annual rainfall of approximately 850 mm. The groundwater in the region occurs mainly within the weathered, fractured, and jointed hard rocks like limestone, shale, granite, and gneiss, which exhibit very low permeability and poor storativity. In this context, surface water resources become the primary water sources; they are often insufficient or unreliable due to the region's erratic rainfall patterns.

This study focuses on analyzing the water chemistry, identifying the potential contaminants, and evaluating isotopic characteristics to better manage these (sub)-surface water resources in Chittorgarh, Rajasthan. It employs in-situ and laboratory-based methods to assess the hydrochemical characteristics of groundwater (n=44) and surface water (n=26) collected in the post-monsoon season of 2023 and the pre-monsoon season of 2024 using the grab sampling techniques. Additionally, for stable isotope (^{2}H and ^{18}O) analysis, six representative groundwater samples and four surface water samples collected in the post-monsoon season were analyzed. In-situ analysis of the samples was performed to measure pH, TDS, EC and DO using the multi-meter electrode. Ion chromatography (IC) was used to determine the concentration of major ions, including Calcium (Ca^{2+}), Potassium (K^{+}), Magnesium (Mg^{2+}), sodium (Na^{+}), Floride (F^{-}), sulphate (SO_4^{2-}), nitrate (NO_3^{-}) and Chloride (Cl^{-}). The titration technique was used to determine the alkalinity levels. The overall ion measurement accuracy was checked by charge balance error, and the values were within the acceptable limit (±10%).

The suitability of (sub)-surface water resources for irrigation was evaluated using parameters like percent sodium (%Na), sodium absorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), and magnesium hazard (MH). Meanwhile, the hydrochemical facies were identified based on the chemical composition of the water samples using the Piper plot and Gibbs diagram. The groundwater samples largely complied with IS 10500:2012 water quality standards. However, 46% of the groundwater samples exceeded the BIS acceptable limit (45 mg/l) for nitrate concentrations in the post-monsoon season, with this percentage increasing to approximately 87% during the pre-monsoon period. The elevated nitrate concentration, especially in the pre-monsoon period, could be attributed to several factors like excessive use of fertilizers, sewerage, animal waste, organic manure, the geology of sub-surface soil layers, etc. Additionally, the absence of significant water flow and limited recharge can cause accumulated nitrate concentrations to become more concentrated in the groundwater. In contrast, most surface water samples were within BIS-acceptable limits during pre- and post-monsoon season. This is likely due to the continuous flow and mixing in surface water, leading to the dilution of contaminants in the surface water samples.

The ratios of heavy stable isotopes were measured using Dual Inlet Isotope Ratio Mass Spectrometer-DI IRMS. The measured values were reported as delta (δ) values. The precision of measurement for δ^2H was ± 1‰, and that for $\delta^{18}O$ was ± 0.1‰ respectively. The mean value of $\delta^{18}O$ and δ^2H in groundwater was found to be -4.14 ‰ and -32.29 ‰, whereas the average value of $\delta^{18}O$ in surface water samples was found to be -1.56 ‰ and -22.81 ‰ respectively. The overall slope of the groundwater sample (3.64) was less steep than the LMWL (7.8), indicating the occurrence of very high evaporation in meteoric water before infiltration through the vadose zone. The variation in $\delta^{18}O$ and δ^2H reflected no significant interaction between groundwater and surface water resources, indicating these water bodies are primarily influenced by separate sources. The distinct variation in isotopic signatures of groundwater and surface water can be attributed to natural intermittent processes such as evaporation, infiltration, percolation, or anthropogenic-driven processes.

Contamination of (sub)-surface resources is a persistent challenge, particularly in semi-arid regions where (sub)-surface water resources are often limited and highly variable. This study emphasizes the importance of monitoring hydrochemical and isotopic parameters in understanding the behavior and quality of (sub)-surface water resources in semi-arid regions. Hence, properly managing these resources is imperative to avoid contaminating these water resources and make informed decisions for sustainable development. This research provides critical insights into developing effective management strategies for the region, contributing to the long-term sustainability of water resources in the Chittorgarh region.

Keywords: *Water quality, (sub)-surface water resources, semi-arid regions, ion chromatography nitrate concentrations, stable isotopes*