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Groundwater quality evaluation in relation to nitrate pollution in the Jam river basin at Nashik and Ahmednagar district, Maharashtra, India

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ABSTRACT

The hydro chemical investigation was undertaken at the Jam river basin to ascertain the state of groundwater and its evaluation related to nitrate pollution. During this study, sixty (60) representative samples of the ground water were taken from the Sinnar, Sangamner and Kopargaon tehsil, bore wells and dug wells which are used for irrigation and drinking reasons and samples were analyzed during pre and post monsoon 2021. The different physicochemical parameters like pH, EC, TDS, cations viz. Ca, Mg, Na, K and anions include HCO₃, CO₃, SO₄, PO₄, NO₃, F and Cl were determined. In the study, it was found that the samples from irrigated agricultural areas made up the majority have NO₃ levels that are higher than 45 mg/l. For groundwater from irrigated land usage, the Cl⁻/NO₃⁻ ratio is <2 indicates fertilizers are the main source of nitrate. The proposed research work is helpful in implementing groundwater quality management programs to avoid the hazards of contamination.

Key words : Groundwater hydrochemistry, Nitrate pollution, Jam river.

Introduction

Water is a valuable natural resource that is essential for maintaining life on earth. In general, soil moisture makes up 0.8%, shallow groundwater makes up 44.4%, and deep groundwater makes up 55.2%. (Shiklomanov, 1999). Groundwater quality typically declines over time as a result of industrialisation, urbanisation, and intensive farming techniques (Wagh *et al.*, 2020). Over 10 million people living in megacities depend on groundwater supplies in about 50% of cases. (Datta *et al.*, 2005). More than 90% of people living in rural areas use groundwater

for domestic purposes. The oversupply of fluoride, nitrate, and arsenic in some areas of the country's groundwater is causing major problems for the country (Sunitha *et al.*, 2012). Groundwater quality is threatened by natural geochemical, biochemical, and anthropogenic influences, which also endangers the sustainable management and development of groundwater resources (Tay and Kortatsi, 2008). In certain states of India, more than 90% of the population depend only on groundwater for drinking and other needs (Ramachandraiah, 2004). One of the planet's most important, renewable, and readily available resources is groundwater, which is also the

most vulnerable aspect of the environment (Das and Acharya, 2003).

Numerous elements, such as the interaction between soil and water, the types of minerals that dissolve, and anthropogenic activities, have an impact on rainwater's capacity to undergo chemical change (Faure, 1998; Subba Rao, 2002; Umar and Ahmed, 2007). Due to the dissolution of minerals from the underlying layers and worn zones by water percolation, the total dissolved solids rise in the post-monsoon season (Pandian and Sankar, 2007). Drinking groundwater in India that contains high levels of fluoride, nitrate, and arsenic puts the health of millions of people at risk (Wagh *et al.*, 2017a).

The exploitation of virgin land, improper irrigation management, overuse of nitrogenous fertilizers, and improper disposal of livestock manure all contribute to nitrate pollution (Sehmi *et al.*, 2000). The environmental system is at risk from groundwater resources with high nitrate concentrations (> 45 mg/l as NO₃ or 10 mg/l as NO₃-N) (Hill, 1982; Datta *et al.*, 1997 and Pawar and Shaikh, 1995). According to the literature that is currently available, there has not yet been any scientific monitoring of research re-

lating to groundwater quality in the Jam river basin. As a result, the proposed research project will start by looking into the groundwater quality as it relates to the level of nitrate contamination in the study area.

Study Area

A tributary of the Godavari river, the Jam river originates in the high Mhasha hill in Sinnar tehsil in Nashik district and joins the Godavari river at Kopargaon tehsil in Ahmednagar district. The basin has a total area of 636.67 square kilometre. It travels 52.2 kilometres from Sinnar tehsil's eastern portion to the southwest portion of Kopargaon tehsil in the Ahmednagar district of Maharashtra. The study region is situated between 19°04'27" to 19°05'18" N latitudes and 74°06'28" to 74°02'56" E longitudes in the Deccan Plateau, an eastern extension of the Kalsubai range (Fig.1). With average annual rainfall (Sinnar: 568.6 mm, Sangamner: 510.57 mm, and Kopargaon: 483.9 mm) from south-west monsoonal winds, blowing from June to September. Many villages from Sinnar, Kopargaon and Sangamner tehsil are advantageous from this river for irrigation and

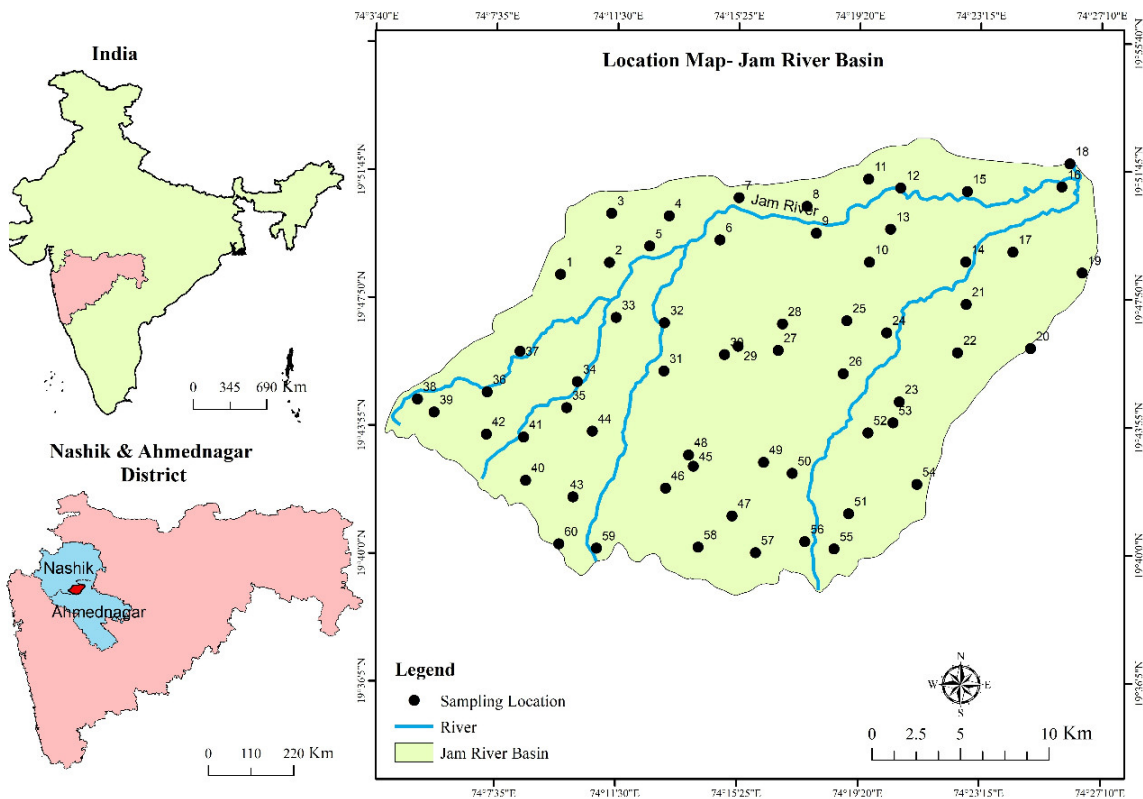


Fig. 1. Study area map with sample locations

drinking purposes. The present study investigates all the possible ways of contamination of river basin groundwater and its consequences regarding human health and agricultural pattern.

Materials and Methods

The pre- and post-monsoon analyses of the sixty (60) typical groundwater samples collected from both bore wells and dug wells that are utilized for irrigation and drinking reasons will help to track the chemical changes in the characteristics of groundwater. There are 11 bore well samples and 49 samples from dug wells. Arc GIS software used the GPS (Geographical Positioning System) to determine the locations of the water samples. Based on a preliminary geological and hydro-geological reconnaissance of the research region, the sample locations were chosen. samples taken in May, just before the monsoon, and November, just after it. APHA, AWWA, and WPCF protocols (2005) were used to conduct the analysis in a lab setting. Titrimetric analysis was used to determine the amounts of chloride (Cl⁻), total alkalinity (CaCO₃), calcium (Ca²⁺), magnesium (Mg²⁺), and total hardness. Alkali elements like sodium and potassium were tested using flame photometers, whereas nitrate, sulphate, phosphate, and fluoride were measured using spectrophotometric methods (Hitachi-2000) (Corning 400). Use the Stiff Computer Program to determine the

charge balance inaccuracy. CBE was computed to verify the analytical accuracy. Ion balance errors (IBE) of the examined parameters that were within $\pm 10\%$ were regarded as legitimate (Berner and Berner, 1987).

Results and Discussion

Assessment of domestic groundwater quality

The physico-chemical properties of groundwater samples (n = 60) are summarized in Table 1.

Temporal variations in pH, EC and TDS

According to the analytical results, the study's groundwater had pH levels ranging from 7.2 to 8.4 with an average of 7.9 during the pre-monsoon season and from 7.1 to 8.7 with an average of 7.6 during the post-monsoon season, which indicate that the water is generally alkaline. It decreases as the water table rises and symbolises the water's ability to buffer and resist a pH change. The high concentration of bicarbonates in groundwater and the stoppage of rain-fed recharge to the aquifer, on the other hand, can be blamed for the summer's small pH increase. Only sample number 34 (1.66%) goes beyond the allowed limit throughout the winter. Alkaline groundwater with an increased pH often has no negative effects on human health, however it could alter the taste of water and demonstrates a

Table 1. Physico-chemical characteristics of groundwater from Jam river basin of Nashik and Ahmednagar district, Maharashtra, India.

Parameter	Premonsoon (May 2021)				Post monsoon (November 2021)			
	Min	Max	Average	Standard Deviation	Min	Max	Average	Standard Deviation
pH	7.2	8.4	7.9	0.32	7.1	8.7	7.6	0.31
EC	337	7780	1942.14	1499.07	111	6390	1627.62	1392.17
TDS	217	4590	1158.51	949.90	79	4109	987.70	882.18
Na ⁺	23.21	1120.99	276.89	329.10	8.24	890.4	193.60	225.64
K ⁺	0.00	17.16	2.02	2.61	0.00	6.26	1.60	1.37
Ca ²⁺	63.12	537.07	223.17	93.49	40.48	352.70	132.92	59.43
Mg ²⁺	21.87	410.8	137.6	73.81	1.21	417.96	79.25	71.96
TH	400	3245	1227.16	629.73	268	1760	716.06	381.30
Cl ⁻	17.04	1710.2	389.57	387.89	65.32	1668.5	469.19	355.08
F ⁻	0.13	1.17	0.66	0.20	0.46	1.35	0.67	0.21
HCO ₃ ⁻	150	800	422.41	134.44	150	1225	450.32	205.13
SO ₄ ²⁻	13.77	1224.19	243.33	276.17	37.49	516.61	167.48	103.16
PO ₄ ²⁻	0.02	1.92	0.96	0.63	0.01	1.11	0.37	0.38
NO ₃ ⁻	0.82	66.71	25.86	15.84	3	75.67	29.18	19.91

Note: All major ions and TDS are expressed in mg/lit while pH on scale and EC in $\mu\text{S}/\text{cm}$.

close relationship with other ionic constituents of water (Wagh *et al.*, 2016a, b).

The relationship between electrical conductivity and the total amount of dissolved salts in water suggests that the amount of inorganic contamination in the water is higher (Morrison *et al.*, 2001). One finding shows that wintertime EC values (1627.62 $\mu\text{S}/\text{cm}$) are lower than summertime EC values (1942.14 $\mu\text{S}/\text{cm}$). The greater ground water levels brought on by rain-fed recharge during the monsoon season may have diluted the EC values in winter, which could be the reason of the decreased EC values. Increase in EC during the pre-monsoon season supports the conclusion that the pH is higher during this time. The EC value increases with temperature and varies with geological presence of soluble salts (Wagh *et al.*, 2019). The BIS has not prescribed any safe limit for the parameter EC.

Due to its ionic constituents, TDS is a crucial factor in the appropriateness of water for drinking and irrigation. Pre-monsoon TDS ranges from 217 to 4590 mg/l, while post-monsoon TDS ranges from 79 to 4109 mg/l. Increase in TDS throughout the summer supports the inference made regarding increased EC values during this time of year. The allowable limit for TDS has been set by the BIS as 2000 mg/l. It was found that 15% of the pre-monsoon samples (sample numbers 5, 6, 9, 15, 16, 18, 19, 34, 37) and 11.66% of the post-monsoon samples (sample numbers 5, 9, 11, 15, 16, 18, 19) exceeded the maximum permitted limit (Table 2) set by the drinking water standard (BIS, 2012). Since the winter standard deviation numbers are lower than those for the summer, the results are likely close to the mean. The dissolution of minerals from the basaltic

aquifer, salt percolation, and agricultural inputs are all thought to be the causes of the elevated TDS. In 2021, both the pre-monsoon and post-monsoon seasons will reveal high concentrations of TDS in the lower catchment area of the Jam River Basin, which is home to an intensive agricultural zone.

Temporal variations in cationic constituents

Groundwater has four significant cations: Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . During the summer and winter seasons, respectively, the groundwater's calcium concentration ranges from 63.12 to 537.07 mg/l and 40.48 to 352.70 mg/l. The allowable limit for calcium content in drinking water has been set at 200 mg/l by BIS (2012). When compared to both before and after the monsoon, calcium levels are higher. Table 2 shows that 10% samples (sample numbers 5, 11, 15, 20, 35, 39) and 50% samples (sample numbers 1 to 6, 11, 12, 15 to 24, 27, 33 to 37, 43, 46, 48, 52, 55, 57) in pre-monsoon had surpassed the acceptable level set by drinking water standard (BIS, 2012) and WHO. Therefore, the population may get kidney stones or joint pain if these well waters are consistently used for drinking. Pre-monsoon calcite precipitation in 2021 is suggested by variations in calcium content during the pre- and post-monsoon seasons (Pawar *et al.*, 2008).

During the pre-monsoon and post-monsoon seasons, the magnesium content fluctuates from 21.87 to 410.8 mg/l and 1.21 to 417.96 mg/l, respectively. Magnesium's acceptable limit has been set by the BIS at 100 mg/l. In the pre-monsoon and post-monsoon samples, the maximum permissible limit (Table 2) set by the drinking water standard has been exceeded in 61.66% (sample numbers 1, 5 to 13,

Table 2. Critical parameters exceeding the permissible limit in the study area.

Parameter	Indian Standards, drinkingwater – specification BIS: 10500:2012		Sample exceeding permissible limit in premonsoon %	Sample exceeding permissible limit in postmonsoon %
	Desirable Limit	Permissible Limit		
pH	6.5 to 8.5	Norelaxation	Nil	1(1.66)
TDS	500	2000	9(15)	7(11.66)
Ca^{2+}	75	200	30(50)	6(10)
Mg^{2+}	30	100	37(61.66)	13(21.66)
Cl^-	250	1000	5(8.33)	5(8.33)
F^-	1	1.5	Nil	Nil
SO_4^{2-}	200	400	6(10)	2(3.33)
NO_3^-	45	Norelaxation	8(13.33)	15(25)
TH, (as CaCO_3)	300	600	55(91.66)	29(48.33)

Note: All major ions and TDS are expressed in mg/l while pH on scale

15 to 22, 25, 28, 30 to 36, 38, 39, 41 to 43, 45, 49, 50, 51, 58) and 21.66% (sample numbers 5, 9 to 11, 15, 16, 18, 25, 27, 33, 34, 43, 45), respectively (BIS, 2012). When calcium and magnesium are present in excess, the water becomes too hard to drink. Although magnesium is one of the most vital electrolytes in the body, there may be a link between it and a reduced risk of osteoporosis. Magnesium has a high solubility, is prevalent in the earth's crust, and high concentrations can make people sick with diarrhoea (Hem, 1991). Rainwater recharge dilutes the basalt rocks' delivery of magnesium to groundwater (Pawar *et al.*, 2008).

In the pre-monsoon season, the sodium level of the groundwater ranges from 23.21 to 1120.99 mg/l, while in the post-monsoon season, it ranges from 8.24 to 890.4 mg/l. 200 mg/l of sodium is the recommended value according to WHO (1979). In pre- and post-monsoon samples, it has been shown that 31.66% of samples (sample numbers 1, 5, 8, 10 to 19, 30 to 34, 37) and 23.33% of samples (sample numbers 5, 8, 10 to 19, 33, 37) had surpassed the allowable limit. Numerous illnesses that are potentially fatal have been linked to the salt imbalance in tap water. As a result, it has been shown that consuming too much salt increases the chance of developing hypertension, high blood pressure, hyperosmolarity, vomiting, cerebral and pulmonary odema, arteriosclerosis, and stiffness and twitching of the muscles (Prasanth *et al.*, 2012; Varade *et al.*, 2014). Despite a minor increase during the pre-monsoon season, the potassium values are very low. The application of K-rich fertilizers has the biggest impact on the K content.

600 mg/l is the permissible limit of total hardness in drinking water (BIS, 2012). In the pre- and post-monsoon seasons, respectively, the total hardness values vary from 400 to 3245 mg/l and 268 to 1760 mg/l. Due to the leaching of calcium and magnesium bicarbonate during recharge, the difference in hardness is greater in winter samples than in summer samples. The summer months have high standard deviation values for practically all cations. The study reveals that the maximum permissible limit, which is set by the drinking water standard, was exceeded by 91.66% (sample numbers 1, 5 to 13, 15 to 29, 31 to 60), and 48.33% (sample numbers 1, 5, 7 to 9, 11, 15, 16, 18 to 21, 28, 33, 34, 36, 37, 39, 41, 43 to 46, 48, 49, 51 to 54) in the pre-monsoon and post-monsoon, respectively (Table 2). (BIS, 2012). As a result, it is discovered that the majority of the

samples in the irrigated area's downstream region have overall hardness levels that are higher than allowed.

Temporal variations in anionic constituents

The anions in the groundwater include HCO_3^- , Cl^- , SO_4^{2-} , F^- , PO_4^{2-} , and NO_3^- . Home appliances, other anthropogenic activities, septic tanks, fertilizers, garbage, and leachate from landfills are some examples of natural and synthetic sources of chloride (Loizidou and Kapetanio, 1993). During the pre-monsoon and post-monsoon seasons, the Cl^- value varies from 17.04 to 1710.2 mg/l and 65.32 to 1668.5 mg/l, respectively. Only a small number of samples have exceeded the maximum allowable amount (Table 2), which is set by the drinking water standard of 1000 mg/l. (BIS, 2012). The standard deviation values for the majority of anion species are low in the winter. The permitted limit for chloride is exceeded in 8.33% of samples (sample numbers 5, 6, 10, 15, 16) taken during the pre-monsoon and 8.33% of samples (sample numbers 5, 6, 12, 15, 16) taken during the post-monsoon.

Pre-monsoon groundwater contains 13.77 to 1224.19 mg/l of SO_4^{2-} , and post-monsoon groundwater contains 37.49 to 516.61 mg/l of SO_4^{2-} . The BIS has determined that 400 mg/l of sulphate is the permitted maximum. The pre-monsoon season's elevated sulphate concentration may be a result of human activity. In the pre- and post-monsoon seasons, only 10% (sample numbers 5, 15, 16, 18, 33, 34) and 3.33% (sample numbers 16, 17) of samples surpass the allowable limit. The quantity of sulphate released into groundwater by fertilizers that contain gypsum and are used to alter the physicochemical characteristics of soil (Todd, 1980). The alimentary canal may malfunction due to higher sulphate concentrations in water, which also have a cathartic effect on people's bodies (Deshmukh, 2011). There is no issue with too much sulphate not exist in study area.

Pre-monsoon groundwater has a PO_4^{2-} level of 0.02 to 1.92 mg/l, and post-monsoon groundwater has a PO_4^{2-} value of 0.01 to 1.11 mg/l. Phosphate fertilizers and inorganic phosphate found in soil are the sources of phosphorus. In the aquatic environment, eutrophication is a problem brought on by an overabundance of phosphorus.

In this study, pre- and post-monsoon bicarbonate (HCO_3^-) values range from 150 to 800 mg/l and 150 to 1225 mg/l, respectively. Since the origin of HCO_3^-

can be linked to the aquifer lithology, it is possible that the reason HCO_3^- was higher during the winter was due to the effect of CO_2 upon the fundamental components of soil and rock.

Fluorosis may result from fluoride exposure above 1.5 mg/l (BIS, 2012). The analytical results demonstrate a fluoride content below the permitted limit, confirming that all groundwater samples have acceptable fluoride levels for drinking. The source of the fluoride is anthropogenic, just like the phosphate fertilizer that is applied to crops.

Nitrate pollution and human health

Numerous health issues, including gastrointestinal cancer, methemoglobinemia, Alzheimer's disease, vascular dementia, and multiple sclerosis in people, are linked to nitrates in drinking water (Forman *et al.*, 1985; Deshmukh, 2012). According to the current study, post-monsoon nitrate concentrations are higher than pre-monsoon nitrate concentrations (Table 1). In pre- and post-monsoon samples, the NO_3^- value ranges from 0.82 to 66.71 mg/l and 3.0 to 75.67 mg/l, respectively (Fig. 2 & 3). Analytical results of nitrate from the 60 wells compared with drinking standards show that 8 samples, 13.33% (sample numbers 11, 12, 14, 15, 16, 19, 31, 47), and 15 samples, 25% (sample numbers 11 to 19, 24, 25, 30, 31, 34, 58), in the pre- and post-monsoon periods, respectively, exceeded the permissible limit of nitrate (>45mg/l) (BIS, 2012). In general, soil microorganisms convert nitrogen from nitrogen-containing fertilizers into ammonium nitrogen and nitrate nitrogen, which are utilized for plant growth. Excess nitrogen will leach through the soil and contaminate

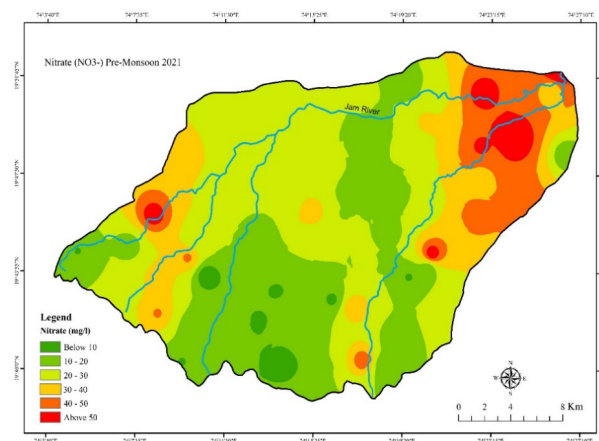


Fig. 2. Spatiotemporal distribution of NO_3^- in pre monsoon season 2021

groundwater (Deshmukh, 2013). As a result, the mobility, solubility, acidity/alkalinity, and breakdown characteristics of fertilizers determine how much nitrate leaches into groundwater (Houzim *et al.*, 1986).

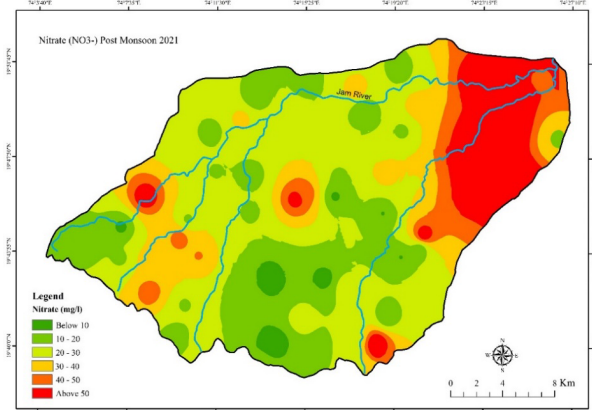


Fig. 3. Spatiotemporal distribution of NO_3^- in post monsoon season 2021

Contribution of land use in nitrate pollution

Compared to other land use types in the research area, sugarcane farming has greater nitrate concentrations (S. No. W11, W12, W14, W15, W16, W17, W18, W19 etc.). $\text{Cl}^-/\text{NO}_3^-$ computations took into account the substantial differences in ratio between irrigated and non-irrigated areas. This is caused by a number of variables, including fertiliser variation, nitrogen loss due to denitrification, the removal of more nitrogen than chloride by harvested crops, changes in the rate at which nitrogen fertiliser is applied, the use of agricultural fertilisers, and contamination from non-point sources (Pawar *et al.*, 1995; Deshmukh, 2013). However, it is noticed that the $\text{Cl}^-/\text{NO}_3^-$ ratio is slightly higher in the river's downstream section (S. No. W11, W12, W14, W15, W16, W17, W18, W19 etc.). This may be linked to water logging caused by saline groundwater. Lower $\text{Cl}^-/\text{NO}_3^-$ readings in the irrigated area upstream (S. Nos. W25, W31, W35, W58, etc.) indicate that fertiliser is the source of nitrate. However, it's interesting to notice that summertime $\text{Cl}^-/\text{NO}_3^-$ levels are lower than wintertime levels. Due to the diluting effect, there is a low concentration of chloride in the winter. For several of the samples (S. No. W2, W7, W8, W22, W38, W41, W42, W45, W49, W54, W55, and W59) at greater depth, the $\text{Cl}^-/\text{NO}_3^-$ ratio is low.

Nitrate has been shown to be in increasing order as depth increases. In the majority of the samples (S. No. W14, W25, and W58), higher nitrate concentrations (> 45 mg/l) match with lower $\text{Cl}^-/\text{NO}_3^-$ ratio values, indicating a build-up of nitrate in the groundwater.

Conclusion

The current study investigates that the conc. of TDS, total hardness Ca^{2+} , Mg^{2+} , Na^+ , and NO_3^- are exceeding the permissible limit of majority of the samples mostly from excess irrigated area which may limit domestic uses and drinking potential. TH or TDS were above permissible limit in 91.66 % of samples in pre-monsoon. Only 46.66% of the post-monsoon samples had TH or TDS levels that were over the allowable limit after dilution. Elevated NO_3^- , which exceeded the allowable limit in 13.33% of pre-monsoon and 25% of post-monsoon samples, has probably been caused by anthropogenic activity. The winter season has a higher sample count than the summer season does. This implies that the quality of groundwater resulting from the use of irrigated land is almost unacceptable for domestic purposes. The majority of the samples came from irrigated areas with NO_3^- concentrations more than 45 mg/l. It is assumed that excessive urea use may have increased the nitrate concentration of the groundwater samples. The groundwater of the irrigated land use has a $\text{Cl}^-/\text{NO}_3^-$ ratio is of < 2 , which indicates that fertilizers are a significant source of nitrate. High nitrate concentrations in wells with deeper water tables indicate that denitrification has reached its conclusion at greater depths. Denitrification processes have been blamed for lower nitrate levels in wells with shallow water tables. The present water availability condition in the study area is under great threat. Therefore, regular monitoring of water quality and best management activities for agriculture is recommended to improve understanding of pollution of nitrate in the groundwater at the Jam River basin of Nashik and Ahmednagar district.

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