Water Supply

Water Supply Vol 22 No 3, 2478 doi: 10.2166/ws.2021.458

A systematic study of uranium in groundwater and its correlation with other water quality parameters

Mansi Srivastava [a,*], P. K. Srivastava[a], Dharmendra Kumar[a] and Ajay Kumar[b]

[a] Department of Chemistry, Birla Institute of Technology, Mesra, Ranchi 835215, Jharkhand, India
[b] Health Physics Division, BARC, Mumbai 400085, India
*Corresponding author. E-mail: mansisrivastava795@gmail.com

MS, 0000-0003-2498-7068

ABSTRACT

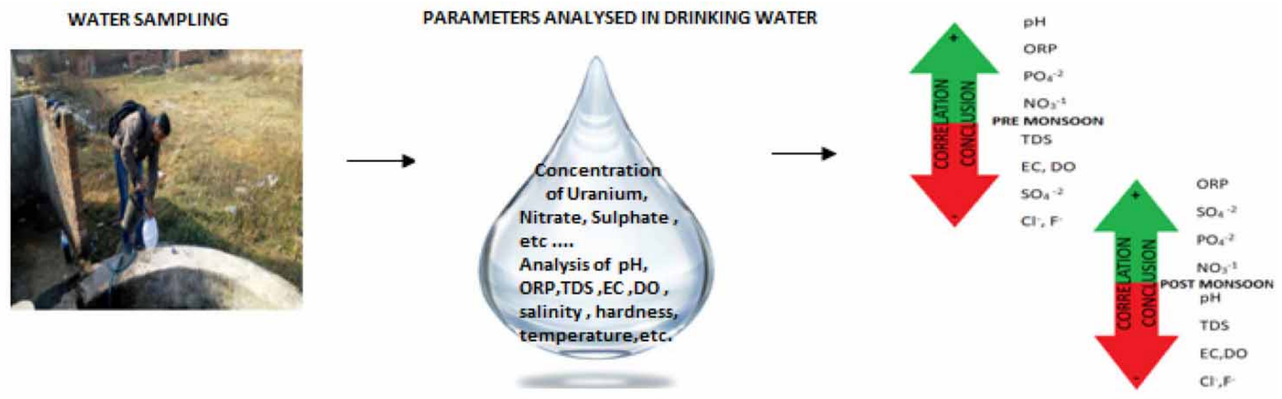
A parametric investigation was carried out to estimate the Uranium concentration and other associated water quality parameters for the groundwater in Deoghar district, Jharkhand. A total of 150 groundwater samples have been collected from dig wells, hand pumps, tube wells, etc. for the pre and post-monsoon seasons. A Quantalase Uranium analyzer was used to measure the uranium concentration. The distribution of pH, TDS, DO, nitrate, sulfate, uranium, along with the radiation, has been determined. It was found that the uranium concentration in groundwater varies from 0.10 to 11.30ppb in pre-monsoon and 0.15–6.50ppb in the post-monsoon, which is well below the normal tolerance limit (i.e.30 μg/l WHO). This low availability of Uranium has been attributed to the existence of a lesser number of rocks containing uranium as a source in that area. An attempt has been made to correlate the uranium concentration with the water quality parameters for both seasons. The correlation data reveals that ORP, nitrate, phosphate, calcium, and magnesium show a positive correlation with uranium concentration for both seasons; on the other hand TDS, EC, temperature, DO, fluoride, and chloride show negative correlation. The positive correlation implies that uranium may be present in groundwater as a dissolved salt of these parameters. Comparative studies for the parameters have been done for both the seasons and various factors have been discussed for the occurrence of the same. The annual effective dose associated with the ingestion of uranium by the population of the region has been estimated using USEPA equations.

Key words: correlation matrix, drinking water, groundwater, uranium concentration, water quality parameters

HIGHLIGHTS

- Cancer risk assessment.
- Ground water analysis.
- LED fluorimeter.
- Uranium correlation matrix.

GRAPHICAL ABSTRACT



INTRODUCTION

Human beings have always been exposed to radiation, either from natural or anthropogenic sources. Natural background contributes about 85% of the total radiation dose exposure to the population and the remainder includes medical exposure (14–20%); nuclear power plant production (0.1%); Chernobyl accident (0.1%); atmospheric weapon tests (0.18%) (UNSCEAR 2000). Uranium, one such naturally occurring element with heterogeneous distribution, is found in widely varying concentrations in rocks and soils depending on the specific site and geological material. Because of the ionizing radioactive nature of uranium it emits radiation, which carries enough energy to ionize matter with which it interacts. This increases the risk of cancer and kidney toxicity to the ones who are exposed to it. The exposure of natural radiation is mainly classified into four criteria; that is, cosmic, terrestrial, inhalation and ingestion through air, water and food materials (Benville & Lowder 1987). Water passing through and over geologic formations can dissolve the uranium. Hence, it exists in an aqueous solution having oxidation states +3, +4, +5, and +6. Amongst all of these, the +6 oxidation state is the most stable in an aqueous solution, present as uranyl cation (UO_2^{+2}). Though naturally occurring uranium has always been found in water supplies, man's idea of dominance over Mother Nature has resulted in depleting the natural resources. Uranium is found to be increasing in concentration in some parts of Punjab, Kerala, and Tamil Nadu (Singh *et al.* 2003; Bajwa *et al.* 2015; Selvi *et al.* 2016; Shalumon *et al.* 2021).

Jharkhand is one of the richest mineral zones in the world and boasts about 40 and 29% of India's minerals and coal reserves, respectively. Due to its large mineral reserves, mining and mineral extraction are the major industries in the state. It is the only state in India to produce coking coal, uranium, and pyrite. Water contamination by dint of heavy metal and radioactive elements is increasing day by day, which is of great concern. Similar results have been recorded for the Jaduguda district, Singhbum, and Bokaro (Giri *et al.* 2012; Patra *et al.* 2012; Tiwari *et al.* 2016). Uranium is easily transferred to humans through inhalation, drinking water, and terrestrial sources delivering the radiation dose to people. Chronic exposure to uranium radionuclide can lead to severe health risks (USEPA 1991; UNSCEAR 2000; ICRP 2007). The Environmental Protection Agency revised the Radionuclides Rule, which took in December 2003; uranium has become a regulated substance in public community drinking water supplies. According to the WHO standard, the concentration of uranium should be not more than 30 ppb (Radionuclides Rule 2003). As groundwater is the global source of freshwater which is utilized not only for drinking but other activities like domestic chores, irrigation purposes, industrial use, and many more (Soleimani *et al.* 2018), the quality of the water needs to be scrutinized.

The water quality parameters broadly include the physicochemical parameters like pH, TDS, EC, ORP, salinity, temperature, and so on along with many major and minor ions, trace elements, heavy elements, radionuclides, and organic matter (Guidelines for Drinking Water Quality 2008). The physicochemical parameters provide important first-hand in-situ information about the suitability of water for drinking purposes (Bajwa *et al.* 2015). Total dissolved solids (TDS) comprise inorganic salts and small amounts of organic matter that are dissolved in water. If the TDS range above 900 mg/L then it is considered poor for drinking as it can have pollutant solids from sewage, urban run-off, and industrial wastewater (Sheffer *et al.* 2016; Ostad-Ali-Askari & Shayannejad 2021). Electrical Conductivity (EC) is the ability of the solution to conduct electrical current. The pH is the scale of monitoring the acidity and basicity of the aqueous solution. ORP (Oxidation-Reduction

Potential) is the ability of a lake or river to cleanse itself or measure water's ability to oxidize contaminants. Higher ORP simply indicates a greater number of oxidizing agents, hence a lower ORP is preferred for consumption. These physicochemical parameters were further explored by calculating the Pearson Correlation Coefficient ® to assess the relationship between the water quality parameters and uranium. For this purpose, a correlation matrix was constructed by calculating the coefficient of different pairs of parameters. This research study provides a unique and systematic approach to account for uranium concentration and the changes related to the occurrence of the same by evaluating the co-relational data with other water quality parameters that reveal more information on the groundwater in the study area. The data obtained will help assimilate knowledge and develop information about the land area, as any alteration in the concentration of these ions and parameters can cause various repercussions to the environment. The objective is not only limited to proposing a graphical representation of the correlations; analyzing water quality parameters and their statistical correlation with uranium but practical implications of this have also been worked upon, which include the radiological risk assessment using the USEPA standard method, which is done to get the inference about the health status of the community living in the area. Due to a lack of systematic study of the groundwater quality that is used for drinking in the backward area of North Eastern villages, people are exposed to numerous diseases with the consumption of unhealthy water. Thus a systematic study has been undertaken into account to evaluate the groundwater and to check its utility. The data obtained were recorded and are further utilized for future researches.

MATERIALS AND METHOD

Study area

The present investigation is done in the Deoghar district of Jharkhand (Figure 1), which is surrounded by the districts Banka and Jamui in the north, Dumka in the east, Jamtara in the south, and Giridih in the west. It is located in the western portion of Santhal Parganas. The district extends from 24°28′ North to 24°48′ North latitude and from 86°42′ to 86°07′ east longitude. It has an area of 2,473.38 sq. km. and a population of 1,492,073 people according to the 2011 Census.

Surface lithology has exercised a profound impact on the development of soil types. The district is characterized by a wide variety of soils, which can be classified as clayey, loamy, sandy loam, and lateritic. Sandy loams to loamy sands are common in uplands, whereas loam to sandy loam is common in lowlands. Deoghar district is largely covered by Chotanagpur granites and gneissic complex associated with some metasediments and metabasic rocks. About 70% of the district area is underlain by hard and compact granitic rocks, known as Chotanagpur granite gneiss except for South Deoghar. Gondwana rocks are present in the South of the district. Rajmahal traps belonging to the lower cretaceous with interracial beds and Gneiss rocks are present in sporadic patches. The Rajmahal traps are composed of basaltic lava flows and form a multilayer system. The alluvium is composed of clay and sand. Weathering, fracturing, and jointing have introduced secondary porosities in these hard rocks and these govern the occurrence and movement of groundwater in these rocks. In these formations, groundwater occurs under unconfined conditions in the weathered mantle and is semi-confined to confined conditions in the fractures underneath (District census handbook 2011; Reddy 2013).

Sampling

The grid sampling technique has been adopted for water sample collection (Figure 2). The water sample was taken from the center of each grid or the nearest populated areas. Grids having very small land areas are not considered in the grid and no samples were collected from the same. The samplings were done for the pre-monsoon (Feb-Apr) and post-monsoon (Sept-Nov) periods. In total, 150 samples were collected. Some basic information like the type of rock around sampling location, and depth of water level of bore well, was collected. Sampling locations (longitude and latitude) were saved in GPS as well as radiation level of the area was measured by using a radiation meter (Polimaster, Belarus).

Methods

Pretreated polyethylene bottles firstly were soaked overnight in soap solution then in 10% nitric acid solution and finally washed with distilled water samples were filtered by 0.45-micron filter and a part of it was preserved by adding nitric acid to maintain $pH < 2$ for uranium analysis (to avoid wall adsorption and slow biological changes) and other parts were non acidified. Uranium content in the groundwater samples was measured by light-emitting diode (LED)-based ultraviolet (UV) fluorimeter (model LF2 M/S quantalase Private Limites Indore, Madhya Pradesh, India) which works on the principle of measurement of fluorescence of uranium complexes in the aqueous samples, in which a pulsed UV-light was used to excite

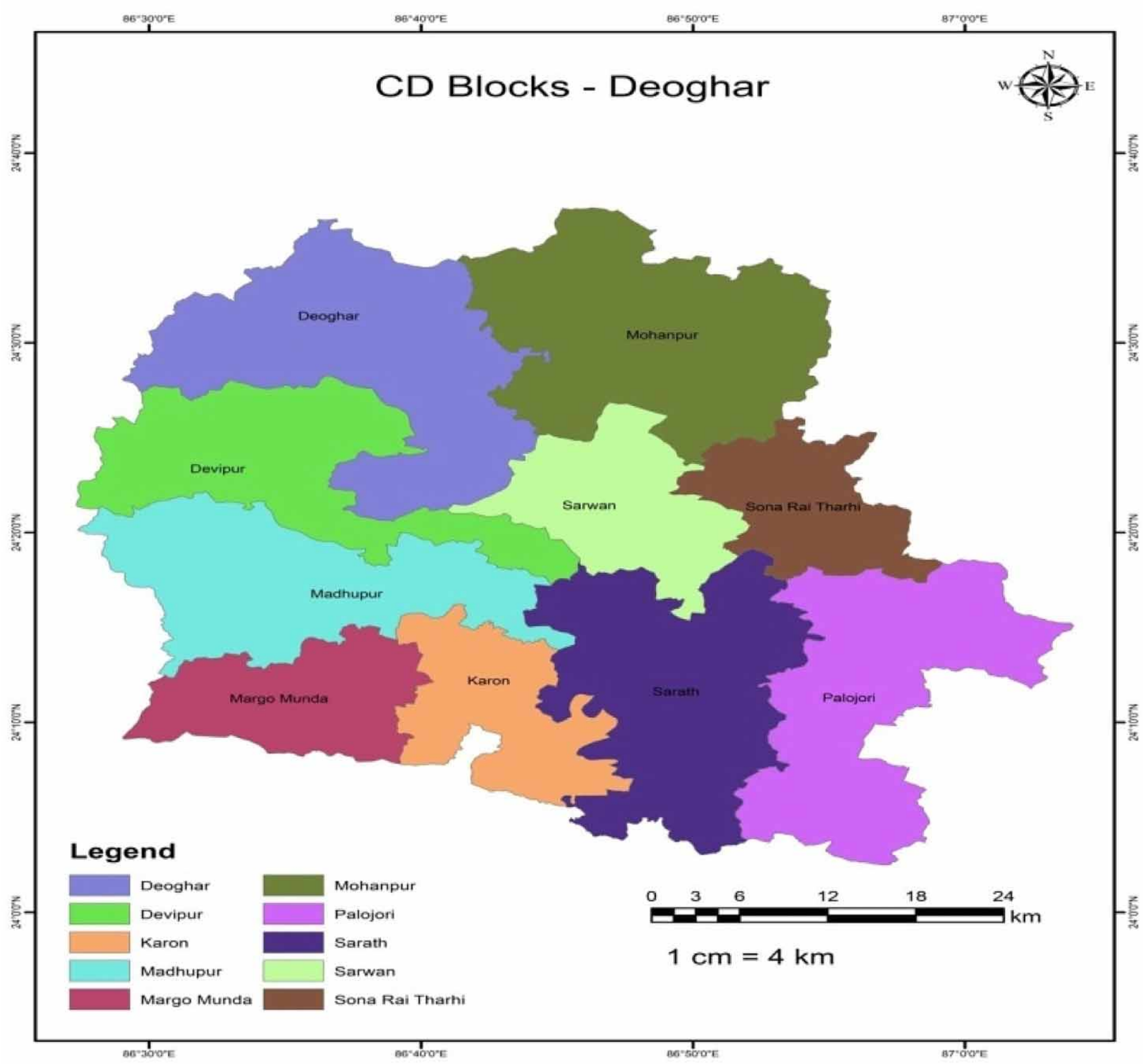


Figure 1 | Map showing the study area, Deoghar district.

uranyl species at 405 nm. Various parameters of water quality have been measured by different methods pH (pH meter), electrical conductivity (conductivity meter), total dissolved solids (TDS meter), salinity (salinity meter) ORP (ORP meter), and dissolved oxygen (Winkler's method), alkalinity (titrimetric method), Chloride (Mohr's method), sulfate (gravimetric method) Fluoride (Fluoride meter) Nitrate and phosphate (spectrophotometric methods).

Carcinogenic assessment

Uranium is a radioactive element, which means it is carcinogenic. The increase in the concentration of uranium in drinking water increases the probability of risk of cancer to humans. Therefore, a comprehensive study on the health effect due to ingestion of uranium through drinking water is required considering the risk-benefit approach. To keep a check on the carcinogenic risk some assessment should be done, USEPA approved equations were used to calculate the same:

$$\text{Cancer Risk} = A * \text{Risk factor} \tag{1}$$

$$\text{Risk Factor} = r * C * E \tag{2}$$

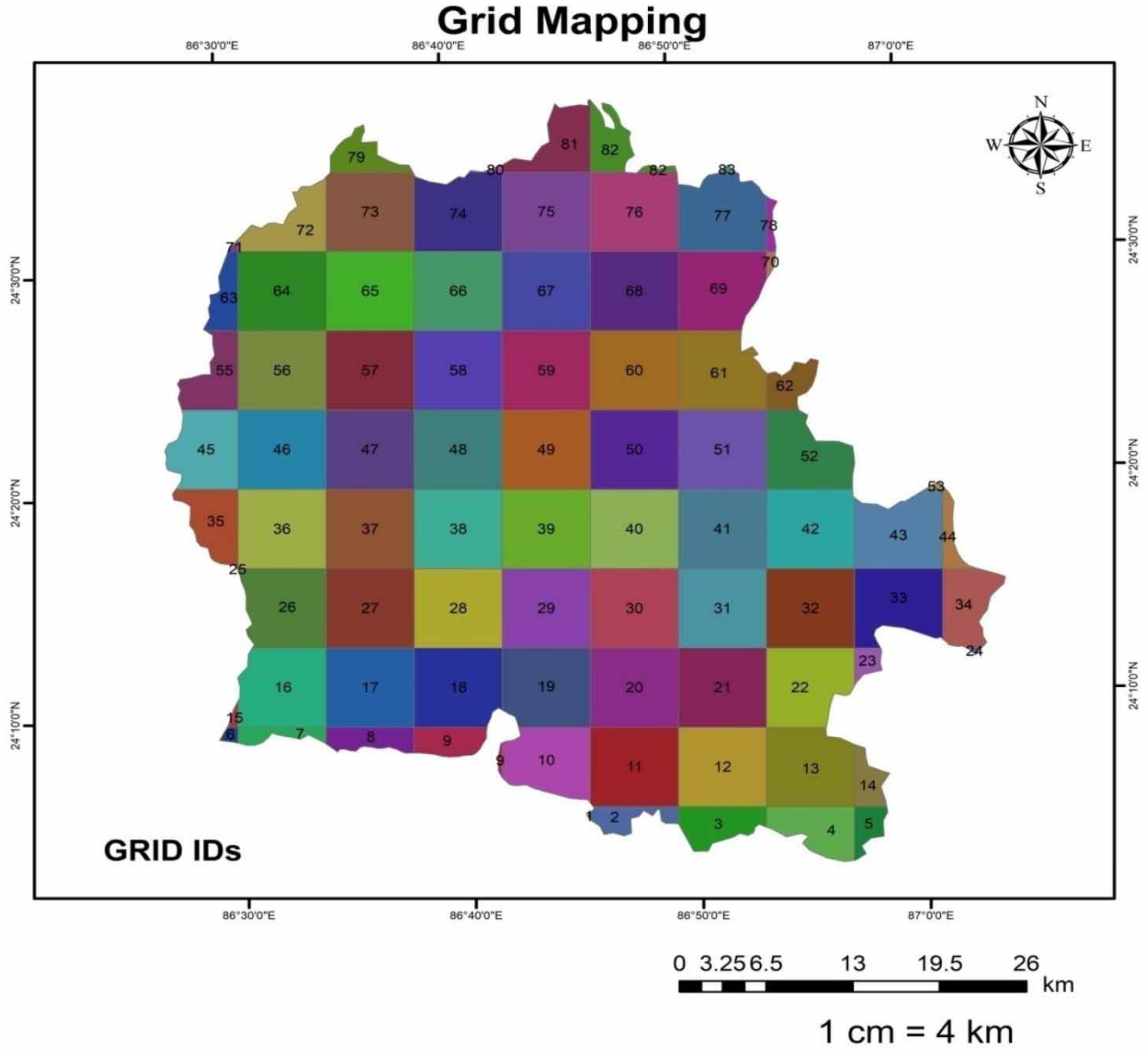


Figure 2 | Map showing grid mapping for sample collection.

where Risk factor is in (l/Bq), r is the coefficient for uranium mortality taken as 1.13×10^{-9} Bq^{-1}; C is consumption rate of water (l/day) and E is exposure time. For adults, the water consumption rate is 4.5 l/day with an exposure time of 24,820 days, for children the consumption rate of water comes to be 2 l/day with an exposure time of 3,650 days (Joshi 2020). A is the activity concentration of Uranium (Bq/l). Unit conversion factor $1\ \mu\text{g/l} = 2.528 \times 10^{-2}$ Bq/l (USEPA 1999).

RESULTS AND DISCUSSION

Water chemistry of uranium

Uranium is one of the most common elements found in the earth's crust, being more common than silver and gold. It can be found almost everywhere in rocks, soils rivers, oceans, and groundwaters. Naturally, uranium (^{nat}U) is composed of three radionuclides ^{234}U, ^{235}U, and ^{238}U), all of which decay by both alpha and gamma emissions. The composition of natural Uranium has ^{238}U isotopes, with the 0.72% of ^{235}U and 0.0054% ^{234}U isotopes in it. The most common primary uranium ores are Uraninite (UO_2), Branarite (U,Ca,Ce)(Ti,Fe)$_2$O$_6$, Uranophane (Ca[UO$_2$]$_2$ [VO$_4$]$_2$. 3H$_2$O. The primary uranium minerals weather and break down very easily as soon as it is exposed to water and oxygen to produce secondary oxidized minerals e.g. cartonite and autunite (AERB 2007). Some rocks that can soak up the water are called permeable like limestone, sandstone they act as aquifers and uranium enter in water by leaching from soils and rock. As uranium is soluble in water so when the groundwater which contains uranium flows through the sandstone aquifers it passes through it, and comes in contact with the beds rich in organic carbon. Uranium has a strong affinity for organic carbon and hence formed an amorphous organouranium complex near these high carbon beds. U(VI) forms different species in an aqueous system depending on the pH range as with the pH <5 it has uranyl ion UO_2^{+2} uranyl ion, it is highly soluble in water and dissolves readily in oxygen-rich water; for pH 5–9 the dominant species is $UO_2(OH)_2$ and for pH >9 it has $UO_2(OH)_3$. In more complex systems (natural waters) in anoxic conditions at pH 6, 7, 8, U(IV) exist as $U\,(CO_3)_4^{-4}$, U_4O_9, and UO_2, respectively. In oxic water at pH 9.2 $UO_2(CO_3)_3^{-4}$ becomes predominant species (Wanner *et al.* 1992; Kumar *et al.* 2011). Based on the study done on the evaluation solubilities of uranium taking TILA-99 as a reference, it was found that the pH and redox are the main parameters affecting the solubilities (Ollila and Ahonen 1998). They have also studied the thermodynamic parameter and determined the hydrolysis constant to predict the aqueous behavior of U(IV).

$$U^{+4} + 4H_2O \rightleftharpoons U(OH)_4 + 4H^+ \tag{3}$$

The solubility of Uranium U $(OH)_4$ (aq) has been studied which predicts lower stability for $U(OH)_4$ (aq). U(IV) primarily forms a hydroxide complex in the aqueous phase. The solubility of crystalline UO_2 is considered to limit the solubility in reducing conditions. The solubility is very low, in the absence of oxidants. The solubility of UO_2 increases even under mildly reducing conditions due to surface oxidation. The relative amounts of the U(VI) carbonate complexes and the U(IV) hydroxide complexes depend on the carbonate content, pH, etc. of the groundwater.

The water samples collected were analyzed for the various water quality parameters. The data have been recorded and compared with the standard values. Tables 1 and 2 show the minimum, maximum, mean, and median values for various parameters for the pre-monsoon and post-monsoon, which help us to interpret the quality of water and compare them on basis of the parameters determined for the two samples.

Table 1 | Pre-monsoon water quality parameters for Deoghar district

Parameter	Minimum	Maximum	Average	Median	BIS/ WHO limits (permissible limit)
Water depth (ft)	30	120	72.84	90	–
pH	7.4	8.7	7.9	7.9	6.5–8.5
TDS (ppm)	60	520	159.1	130.0	150–300
EC (μS/cm)	120	1,040	317.3	260.0	200–800
Salinity (ppm)	54	468	143.17	117	<600
ORP (mV)	130.0	334.0	206.7	206.0	200–600
Temp (^{0}C)	27	29.6	28.3	28.4	25–27
DO (ppm)	2.6	4.8	3.6	3.5	6.5–12
F^- (ppm)	0.02	1.2	0.638	0.62	1
Cl^- (ppm)	68	236	114.8	112	250
NO_3^-(mg/l)	1.7	34.34	16.15	17.3	45
SO_4^{2-} (mg/l)	0.98	109.18	37.2	33.78	200
PO_4^{3-} (mg/l)	0.14	0.89	0.50	0.47	–
U (ppb)	0.06	11.29	1.47	1.24	30
Total hardness (mg/l)	90	720	259.4	226	200
Ca^{+2} hardness (mg/l)	54	534	165.6	136	75
Mg^{+2}hardness (mg/l)	20	330	93.67	78	30
Total alkalinity (mg/l)	42.41	236.56	114.8	117.8	200

Table 2 | Post monsoon water quality parameters for Deoghar district

Parameter	Minimum	Maximum	Average	Median	BIS/ WHO limits (permissible limits)
Water depth (ft)	30.00	120.00	78.54	95	–
pH	7.3	8.2	7.8	7.8	6.5–8.5
TDS (ppm)	75	320	148.7	128	150–300
EC (μS/cm)	159	695	299	258.5	200–800
Salinity (ppm)	71	310	134.5	116	< 600
ORP (mV)	125	334.0	206.7	202.5	200–600
Temp (^{0}C)	27.2	29.6	28.4	28.4	25–27
DO (ppm)	2.5	4.5	3.38	3.2	6.5–12
F^- (ppm)	0.02	1.12	0.629	0.635	1
Cl^- (ppm)	74	231	112.91	110	250
NO_3^- (mg/l)	1.65	28.75	16.02	16.58	45
SO_4^{2-} (mg/l)	2.61	98.56	39.92	32.94	200
PO_4^{3-} (mg/l)	0.15	0.85	0.50	0.52	–
U (ppb)	0.15	6.56	1.37	1.23	30
Total hardness (mg/l)	85	695	242.64	210.5	200
Ca^{+2} hardness (mg/l)	52	532	151.87	131	75
Mg^{+2} hardness (mg/l)	26	274	88.62	73	30
Total alkalinity (mg/l)	42.4	178.9	111.75	116.5	200

On comparing Tables 1 and 2, the following inferences can be made: pH for both seasons comes within the desirable limit of the standard. The TDS value in the pre-monsoon shows a maximum value of 520 ppm, which when compared with the BIS the data obtained is good as the permissible limit is 500 ppm. For the post-monsoon season, the maximum value comes about 320 ppm, thus it can be concluded that the TDS is in agreement with the standards. The EC for the pre-monsoon lies between 120 and 1,040 μS/cm but for the post-monsoon, the value reduces to 159–695 μS/cm. Conductivity measures the water's ability to conduct electricity and a higher value of EC indicates the more ions are dissolved in water. But except for a few samples in the pre-monsoon season, the value for the EC is good for the water used for drinking. Thus, it can be stated that water samples taken for the present study are not considerably ionized and have a lower level of ionic concentration activity due to low dissolved solids. For the salinity value calculated in the pre-monsoon season, the value shows a maximum limit of 468 ppm but the post-monsoon season shows a maximum limit of about 310 ppm. Because the dissolved salts and other inorganic salts conduct electric current, the TDS, EC, and salinity can be said to be proportional to each other, and the values obtained prove the above statement (Rusydi 2018). This relation is further approved by the correlation matrix, where the coefficient value comes close to 1. The ORP value measures the oxidizing and reducing potential of the water body. It holds a good value for both seasons as it is directly dependent on pH. The value for the pH also came in a good range and so does the value of ORP.

Dissolved Oxygen comes less compared with the standard, as the optimum range is 6.5–8 ppm for drinking water. As the DO is dependent on the temperature with the fact that the warmer the water, the less is the dissolved oxygen. The concentration of Fluoride exceeds the desirable limit in a few cases for both seasons as the maximum value comes to be more than 1 ppm. The exceedance of the limit can be due to the aridity of the climate, dissolution of fluoride-bearing minerals and rocks such as fluorspar, fluorapatite, and so on, ion exchange concentration of calcium, and bicarbonate ions (Kumari & Pathak 2014; Yousefi *et al.* 2017). The concentration of Chloride shows no such pattern, the values come under the standard limit of 250 ppm (Yousefi *et al.* 2020). The concentration values for nitrate, sulfate, and phosphate comes in range with the standard. The hardness of the water is predominantly determined by the ions of calcium and to a lesser extent magnesium. The bicarbonates of calcium and magnesium are responsible for the temporary hardness of the water. The water samples exceedance of the concentration for magnesium and calcium may be due to the presence of feldspar ($CaAlSi_2O_8$) in the region. The hard water used can reduce the moisture and leave behind a scaly, thin film, and can also cause various diseases related to skin and abdomen (Cotruvo *et al.* 2011). The water samples collected show a high value for parameters in the pre-monsoon, which can be due to the high evaporation effect of water, which increases the number of ions in groundwater. The concentration of Uranium for the pre-monsoon season lies in the range of 0.06–11.29ppb and for post-monsoon, the value is less with the range of 0.15–6.56ppb. The low value of the Uranium concentration in samples for post-monsoon can be due to excessive dilution of water sources (Shalumon *et al.* 2021).

DETAILED DISCUSSION

Normally, rain is said to be generally acidic having a pH of about 5.4; as the CO_2 dissolves in it, it forms weak carbonic acid. But acidic rain is generally below this at between pH 4.2 and 4.4. The pie chart demonstrates the distribution of variation of hydrogen ion concentration in groundwater. Figure 3 (left) pre-monsoon shows that for the majority of the sample the pH lies in the range of 7.5–8.0 for both seasons. The data obtained lead to the inference that the concentration of SO_x and NO_x is low in the soil and thus in water. The pH is within the limit of standards but the post-monsoon data for the groundwater is better as more samples were in the range for the pH of distilled water.

The high value of TDS signifies that water is highly mineralized. The majority of samples in the pre-monsoon season were found to have the TDS concentration of 100–200 ppm but in the post-monsoon, the sample frequency decreases from 70% to 30% (Figure 4). Thus, it can be concluded that the TDS for the post-monsoon is less as the water level rises, due to dilution in the groundwater the concentration of solids dissolved gets reduced compared to the data for pre-monsoon. High values of TDS in groundwater are not generally harmful to humans but high concentrations of these may affect persons who are suffering from kidney and heart diseases. Water containing high solids can also cause laxative or constipation effects (Sheffer *et al.* 2016).

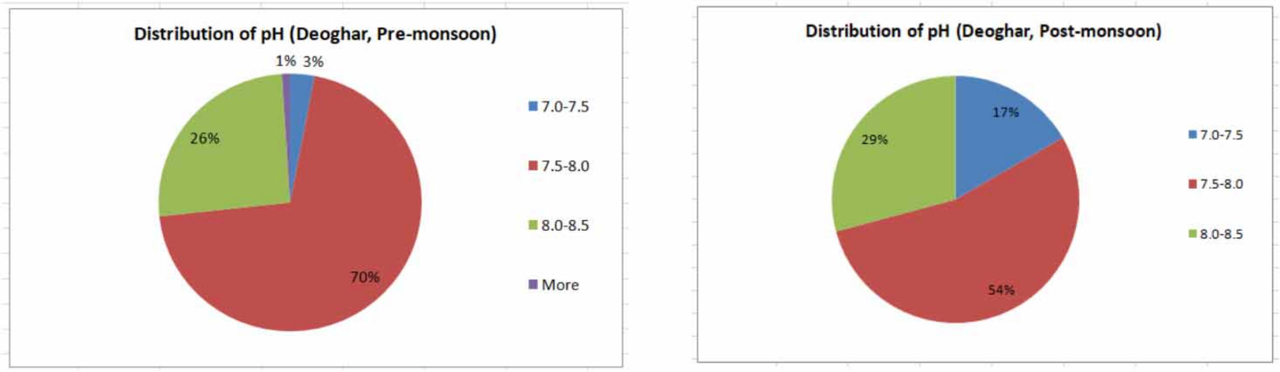


Figure 3 | Distribution of pH of groundwater for pre-monsoon and post-monsoon.

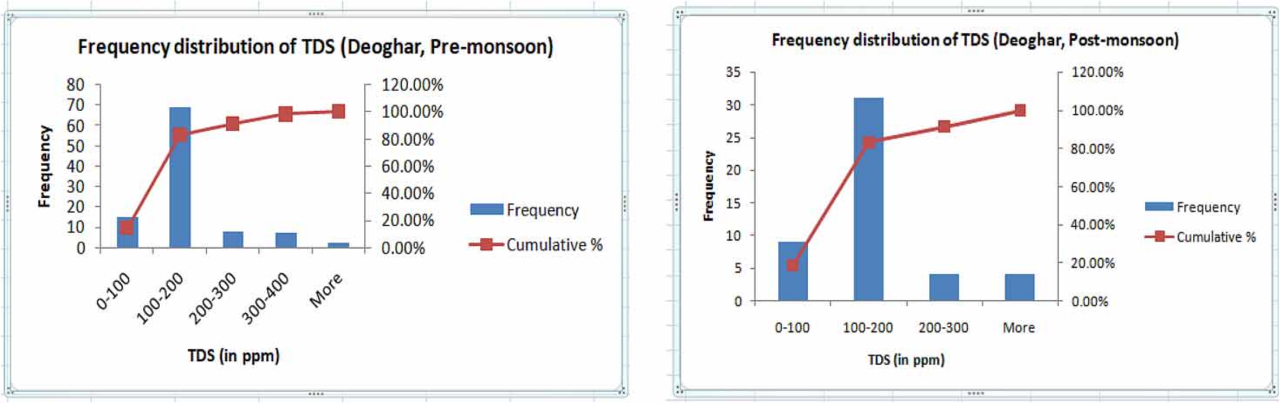


Figure 4 | Distribution of TDS in pre-monsoon and post monsoon.

The amount of dissolved oxygen gas is highly dependent on temperature and atmospheric pressure. The amount of oxygen (or any gas) that can dissolve in pure water (saturation point) is inversely proportional to the temperature of the water (Kulkarni 2016). The data obtained for the Dissolved Oxygen (DO) is given in Figure 5. The area chosen for the study is warm and humid so the temperature range for the groundwater comes in between the range of 27–28 °C for both seasons, which is a high-temperature value hence the value for the Dissolved Oxygen also be comes less. The pre-monsoon (left) data shows samples have the highest frequency for the DO of 0–3.0 ppm, which decreases as the DO concentration increases. Slight variation is seen around the ppm range 3.5–4.0. For the post-monsoon, though the frequency is low, the samples having a range of 4.0 ppm DO is more compared to the pre-monsoon.

The nitrate concentration is an important parameter to check diseases, particularly blue baby syndrome in infants (Meridae & Ayenew 2016). The primary source of nitrate is the nitrogen cycle, industrial waste, and in this case most importantly nitrogenous fertilizers. The data for the nitrate distribution in water in the pre-monsoon is more compared to the post-monsoon, as shown in Figure 6. The frequency of samples having 10–20 ppm nitrate comes at about 60%, which when compared to post-monsoon gets reduced to 32%. This reason for this can be a reduction in the use of nitrate fertilizers and low emission of waste from industries. As the overall concentration comes in range, it leads to the view that the nitrogenous fertilizers are used in adequate amounts.

Sulfate is mainly derived from the dissolution of salts of sulfuric acid and is found in all water bodies. The distribution of sulfate in pre-monsoon and post-monsoon is shown in Figure 7. The pre-monsoon frequency for the samples increases as the concentration of sulfate increases from 30 to 60 ppm and reaches up to an optimum limit. The post-monsoon data reveals that the sampling frequency gets reduced to 20% for the same ppm range (i.e. 30–60). A comparatively high concentration of sulfate in pre-monsoon may be due to more use of fertilizers containing sulfate during this period. It is concluded that the post-monsoon holds less concentration of sulfate compared to the pre-monsoon.

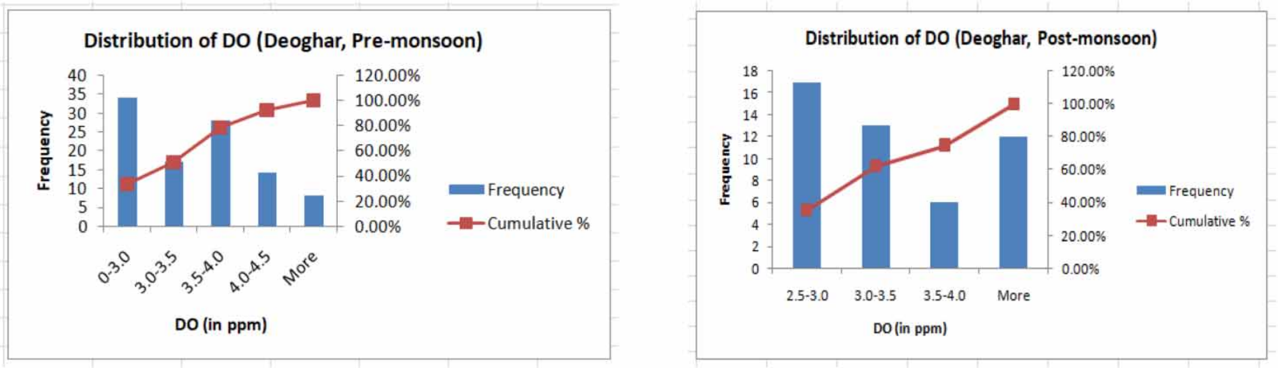


Figure 5 | Distribution of DO in pre-monsoon and post monsoon.

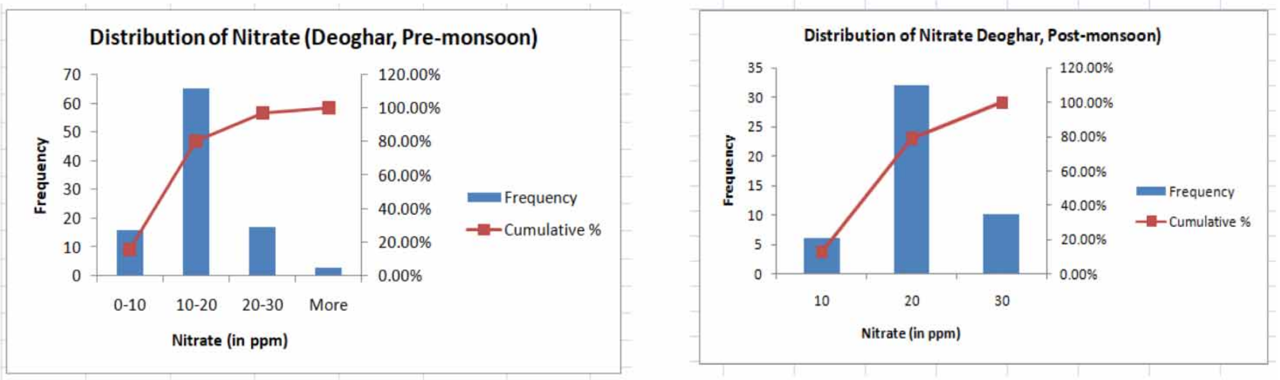


Figure 6 | Distribution of nitrate in pre monsoon and post monsoon season.

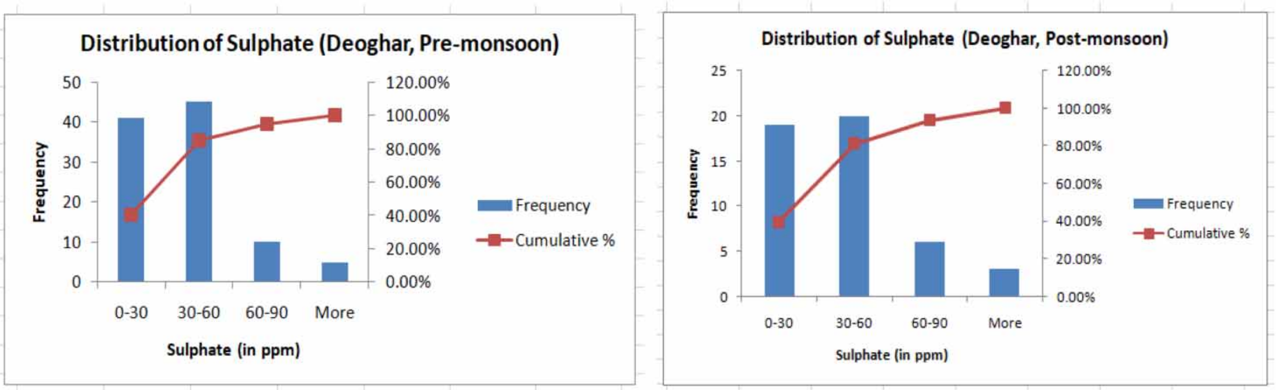


Figure 7 | Distribution of sulfate in pre-monsoon and post monsoon.

The distribution of uranium in the pre-monsoon period (Figure 8) ranges between 0 and 2 ppb with a sampling frequency of 80%. With further increase in the concentration, the sampling frequency decreases. The same order was observed with the post-monsoon graph, where the uranium concentration between 0 and 2 ppb has a frequency of about 40%. As the pH of the region ranges between 5 and 9 it is clear that hexavalent uranium species U (VI) is found in water, which must be $UO_2(OH)_2$ and the low concentration of Uranium can be due to the low availability of the uranium-containing rocks in the study region. On overall frequency comparison, it can easily be depicted that the amount of Uranium in drinking water is less during the post-monsoon period, which can be due to excessive dilution of water sources.

After studying the distribution of Uranium in water samples the histogram of radiation for pre-monsoon and post-monsoon is plotted in the histogram (Figure 9). The graph shows an increase in the frequency and cumulative frequency. For the pre-monsoon, the frequency of radiation is highest for the range between 150 and 200 nSv/hr which decreases for the further increase in range. The histogram of radiation (post-monsoon) has a frequency less than that of the pre-monsoon as it lies between 20 and 25% for the same range. The conclusion is that the radiation frequency is more in the pre-monsoon as compared to the post-monsoon, which is in agreement with the distribution of Uranium in water samples.

After attaining the data for water quality parameters and individually comparing them for both the seasons, it was found that the groundwater for the post-monsoon season is more adequate for the drinking purposes as its parameters were found to be in good agreement with the WHO/BIS standard. A better understanding of the water quality parameters and their dependency on the uranium concentration correlation matrix has been determined and is shown in Tables 3 and 4. The objective of the research was to propose a tool to help graphically evaluate the correlations between uranium and other water quality parameters in the study area.

Correlation is a statistical measure that expresses the extent to which two variables are linearly related, which describes simple relationships without making a statement about cause and effect. Correlation is defined numerically by a correlation coefficient and the sign of the correlation coefficient represents the direction of a relationship. The correlation matrix is used to summarize data, as input and into more advanced analysis, and as a diagnostic for advanced analysis (Chowdhary &

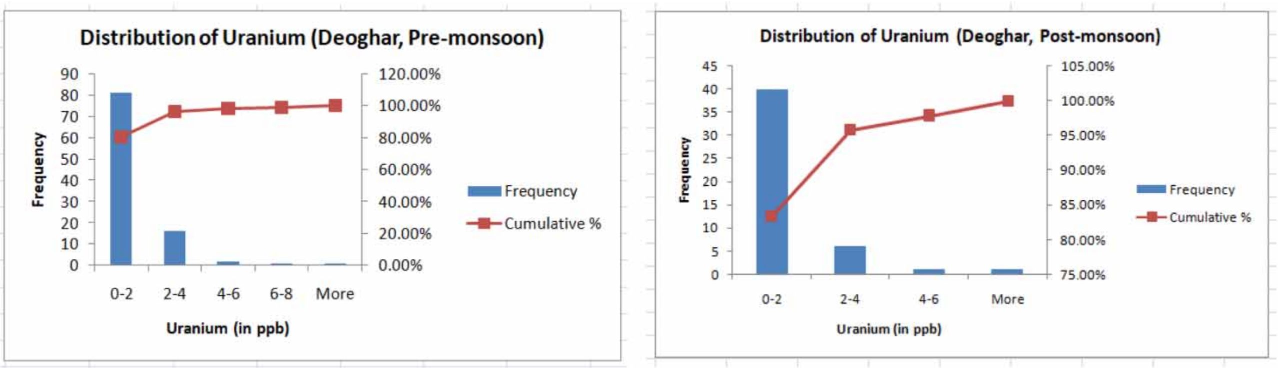


Figure 8 | Distribution of uranium in pre monsoon and post monsoon.

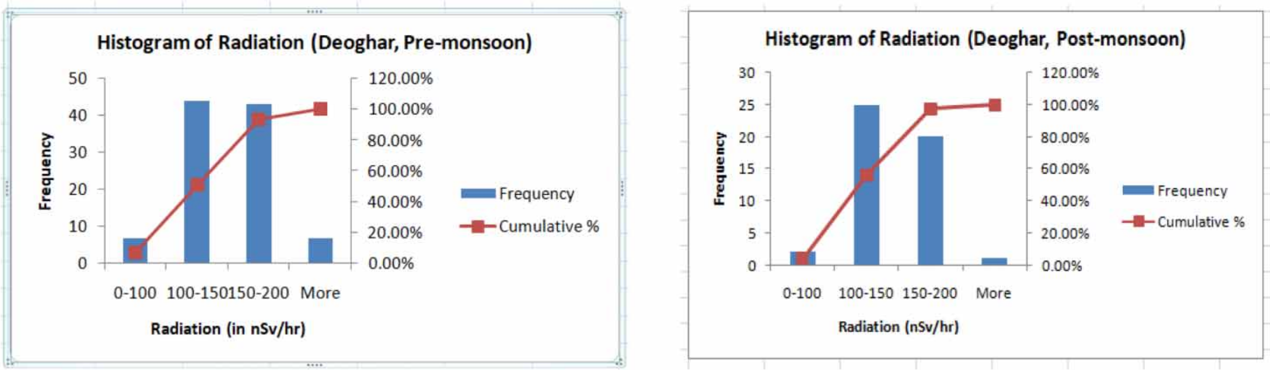


Figure 9 | Histogram of radiation of pre monsoon and post monsoon.

Tajmunnaher 2017). The most common correlation coefficient used in water quality is Pearson's Correlation Coefficient, which tells about the strength and direction of the linear relationship between the two variables. The positive coefficient indicates when the value of one variable increases the other variable (upward slope) and with the negative, vice versa (Khatoon *et al.* 2013). The correlation coefficient (r) has a value between $+1$ (strong positive relationship) and -1(strong negative relationship).

For each monitoring site, the Pearson Correlation Coefficient matrix was calculated among the parameters, as well as the *p*-value matrices (significance) with the software SPSS 15.0. The correlations were analyzed at two significance levels, with 0.05 and 0.01. This graphical analysis allows a new look at the relation of various physicochemical parameters and their relation with uranium. The correlation matrix for the pre-monsoon and post-monsoon is shown in Tables 3 and 4 respectively.

It is evident from the Correlation matrix 3 and 4 that the values obtained are less than 0.35 for maximum parameters, a similar observation was also reported in previous studies. Khare *et al.* (2015) reported that there was no strong correlation found between the Uranium and maximum parameters of water quality. This can be due to several reasons, as the concentration of uranium in groundwater is dependent on multiple factors that include the uranium content in the source rock and its leachability, the proximity of water to the source rock, and most importantly the concentration of the complex-forming species. All these factors are responsible for determining the leaching of Uranium from the source rock. One possible reason for the low concentration of uranium in water can be the low availability of rocks containing uranium in the study area (Sahoo *et al.* 2009). This directly shows that there is a low probability of finding uranium in water even when the complex forming factors are available.

Though from the correlation data some inferences can be made, as Uranium for both seasons show a very weak positive correlation with ORP, which signifies favorable conditions for Uranium transport and release in aquifers (Saikia *et al.* 2021). Dissolved Oxygen shows a negative correlation for the range of -0.13 and -0.168 for the pre and post-monsoons respectively, as for the fact that the increase in the concentration of Uranium in drinking water is hazardous and thus the negative correlation is justified (Guidelines for Drinking Water Quality 2008). For the concentration of Nitrate and Phosphate, the Uranium shows a weak positive correlation in both seasons. The positive correlation can be due to the agricultural practices in the area. It is reported that phosphate fertilizers contain natural radioactivity and are a credible uranium source in the environment. The use of chemical fertilizers enhances the leaching of phosphate through the soil, which precipitates as $UO_2(HPO_4)_2^{-2}$. Nitrate plays an important role in the dissolution of uranium from minerals like uranyl nitrate $[UO_2(NO_3)_2]$ (Saikia *et al.* 2021)]. The positive correlation coefficient for the hardness, calcium, and magnesium for the pre-monsoon season comes more in the range of 0.36, 0.30, and 0.32 respectively and decreases to a value of 0.20, 0.12, and 0.18 respectively in the post-monsoon as the concentration of the uranium decreases. This pattern for positive correlation of Ca^{+2}, Mg^{+2} with uranium implies that the uranium may be present in drinking water as a dissolved salt of these chemical parameters (Singh *et al.* 2003). The negative correlation of sulfate in the pre-monsoon may be due to lack of complex formation between the two, but for the post-monsoon, the uranium shows a slightly positive correlation, which indicates that the sulfate acts as an additional complexing agent for uranyl in the post-monsoon. The relation with hydrogen can be also understood by this. The change in the results can be due to some variations in the water samples. More researches are being undertaken to understand the occurrence of the same and is under investigation.

Table 3 | Correlation matrix of Uranium, Deoghar district [Pre monsoon]

	pH	TDS	EC	ORP	Temp.	Salinity	DO	F^-	Cl^-	NO_3^-	SO_4^{-2}	PO_4^{-3}	TH	Ca^{+2}	Mg^{+2}	TA	HCO_3^-	U
pH	1																	
TDS	−0.037	1																
EC	−0.029	.772**	1															
ORP	0.058	.218*	.213*	1														
Temp.	0.178	0.026	0.081	−0.113	1													
Salinity	−0.037	1.000**	.772**	.218*	0.026	1												
DO	0.176	0.028	0.089	−0.054	0.059	0.028	1											
F^-	0.001	−0.019	0.098	0.061	0.132	−0.019	0.17	1										
Cl^-	.214*	−0.031	−0.059	−0.028	0.109	−0.031	0.128	−0.002	1									
NO_3^-	−0.005	−.237*	−.229*	0.087	−0.096	−.237*	−0.184	−0.054	−.308**	1								
SO_4^{-2}	−0.053	0.117	.209*	0.078	−0.072	0.117	−0.052	−0.094	0.004	0.019	1							
PO_4^{-3}	−0.184	−.254*	−.311**	0.17	−0.108	−.254*	−.334**	−0.105	−0.072	.426**	0.032	1						
TH	−0.131	−0.043	−0.032	−0.1	−0.121	−0.043	−0.167	−0.172	0.047	0.085	0.09	.220*	1					
Ca^{+2}	−0.117	0.078	0.066	−0.052	−0.126	0.078	−0.05	−0.101	0.099	0.02	0.065	0.091	.914**	1				
Mg^{+2}	−0.101	−.228*	−0.182	−0.141	−0.061	−.228*	−.299**	−.219*	−0.06	0.157	0.098	.345**	.736**	.398**	1			
TA	−0.188	−0.074	−0.124	−0.026	−0.164	−0.074	−.268**	−0.079	−0.052	0.185	.200*	.327**	.362**	.332**	.266**	1		
HCO_3^-	−0.188	−0.074	−0.124	−0.026	−0.164	−0.074	−.268**	−0.079	−0.052	0.185	.200*	.327**	.362**	.332**	.266**	1.000**	1	
U	0.159	−0.036	−0.034	0.066	−0.083	−0.04	−0.11	−0.06	−0.097	0.19	−0.047	0.164	.363**	.299**	.320**	.241*	.241*	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

Table 4 | Correlation matrix of Uranium, Deoghar district [post monsoon]

	pH	TDS	EC	ORP	Temp.	Salinity	DO	F^-	Cl^-	NO_3^-	SO_4^{-2}	PO_4^{-3}	TH	Ca^{+2}	Mg^{+2}	TA	HCO_3^-	U
pH	1																	
TDS	−0.084	1																
EC	−0.091	.995**	1															
ORP	0.058	0.205	0.211	1														
Temp.	0.066	0.142	0.138	−0.218	1													
Salinity	−0.087	.997**	.998**	0.202	0.149	1												
DO	0.032	−0.092	−0.102	0.02	−0.004	−0.092	1											
F^-	−0.074	0.04	0.078	0.013	0.005	0.07	.292*	1										
Cl^-	0.004	0.123	0.106	−0.161	−0.025	0.11	0.012	−0.118	1									
NO_3^-	−0.084	−0.153	−0.161	0.111	−0.261	−0.159	−0.143	0.053	−.341*	1								
SO_4^{-2}	−0.028	.329*	.352*	−0.006	0.153	.336*	−.309*	−0.104	−0.025	−0.104	1							
PO_4^{-2}	−0.228	−.291*	−0.282	0.215	−0.232	−.293*	−0.243	−0.001	−0.162	.322*	0.016	1						
TH	−.313*	−0.068	−0.073	−0.03	−0.181	−0.065	−.297*	−.310*	0.08	0.164	0.115	0.268	1					
Ca^{+2}	−.311*	0.095	0.08	0	−0.171	0.096	−0.166	−0.251	0.183	0.157	0.012	0.157	.914**	1				
Mg^{+2}	−0.173	−.298*	−0.287	−0.035	−0.139	−.292*	−.384**	−.311*	−0.102	0.098	0.203	.377**	.781**	.468**	1			
TA	−0.228	−0.033	−0.037	−0.08	−0.134	−0.04	−.409**	−0.042	−0.218	0.251	0.248	.340*	0.252	0.151	.310*	1		
HCO_3^-	−0.228	−0.033	−0.037	−0.08	−0.134	−0.04	−.409**	−0.042	−0.218	0.251	0.248	.340*	0.252	0.151	.310*	1.000**	1	
U	−0.049	−0.177	−0.183	0.07	−0.272	−0.19	−0.177	−0.031	−0.102	.370*	0.001	0.152	0.206	0.123	0.185	0.176	0.176	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

Table 5 | Cancer risk assessment in population

		Cancer risk (Pre-monsoon)			Cancer risk (Post-monsoon)		
Category	**Years (up to)**	**Minimum**	**Maximum**	**Mean**	**Minimum**	**Maximum**	**Mean**
Children	10	0.125×10^{-7}	0.235×10^{-5}	0.3×10^{-6}	0.312×10^{-7}	0.136×10^{-5}	0.285×10^{-6}
Adults	68	0.191×10^{-5}	0.36×10^{-3}	0.468×10^{-4}	0.478×10^{-5}	0.2×10^{-3}	0.437×10^{-4}

The data in Table 5 reveal that the values obtained are in small numbers and hence it can be concluded that no such adverse harm is caused to the population as the concentration of uranium in drinking water is within the limit and thus the water is fit for consumption.

CONCLUSION

The uranium concentration in groundwater samples is below the permissible limit of WHO, AERB. The uranium concentration in groundwater varies from (min) 0.06 – (max)11.24 with a mean value of 1.47ppb in the pre-monsoon and the data for the post-monsoon ranges from (min) 0.15 to (max) 0.85, having a mean value of 1.37 ppb. On considering the pH of the study area, it was concluded that the predominant species of uranium is hexavalent, $UO_2(OH)_2$. The correlation matrix discussed shows that the parameters ORP, nitrate, phosphate, hardness, calcium, and magnesium show a positive correlation with uranium concentration, which may be due to the salts of such ions being found as complexing agents for uranium. The *p*-value significance of the water quality parameters tells the inter-dependency of TDS, EC, and salinity. For the pre-monsoon data value for correlation was significant for calcium, magnesium, total alkalinity and hardness whereas in the post-monsoon the data becomes significant for the nitrate only, but the values for other parameters were reduced. Carcinogenic assessment has been calculated for the population. The results obtained were in good agreement with the standard. Thus it can be concluded that the groundwater that is utilized for drinking purposes is under the permissible limit and safe for human consumption. It will be interesting to study the accumulation of uranium in the food chain through groundwater in plants, animals, and human beings and its carcinogenic assessment.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

AERB 2007 Radiological safety in uranium mining and milling, Guideline No. AERB/FE-FCF/SG, 2 Aug 2007. Atomic Energy Regulatory Board, Mumbai, India.

Bajwa, B. S., Kumar, S., Sahoo, S. K., Singh, S. & Tripathi, R. M. 2015 Uranium and other heavy toxic elements distribution in the drinking water samples of SW-Punjab, India. *Journal of Radiation Research and Applied Sciences* **10** (1), 13–19. http://dx.doi.org/10.1016/j.jrras.2015.01.002.

Benville, A. & Lowder, A. M. 1987 Human Population Exposures to Cosmic Radiation. In: *4th International Conference on the Natural Radiation Environment*, Lisbon, Portugal, Vol. 45, pp. 55–66.

Chowdhary, M. & Tajmunnaher, M. 2017 Correlation study for assessment of water quality and its parameters of Kushiyara Sylhet, Bangladesh. *International Journal of New Technology and Research (IJTNR)* **3** (12), 01–06.

Cotruvo, J., Fawell, J. K., Giddings, M., Jackson, P., Magra, Y., Festo, A. V. & Ohanian, E. 2011 *Background Document for Development of WHO Guidelines for Drinking Water Quality*. Report WHO/HSE/WSH/10.01/Rev1 Hardness in Drinking Water, Geneva, Switzerland.

District Census Handbook (District highlights) 2011 Deoghar village and town wise primary census abstract (pca), Jharkhand; Series -21, part XII B; Census of India.

Giri, S., Mahato, M., Singh, G. & Jha, V. N. 2012 Risk assessment due to intake of heavy metals though the ingestion of groundwater around two proposed uranium mining areas in Jharkhand, India. *Enviromental Monitoring and Assessment Springer* **184**, 1351–1358.

Guidelines for Drinking Water Quality 2008 3rd edn (incorporating 1st and 2nd addenda) Volume I Recommendations, WHO Library, World Health Organization, Geneva.

International Commission on Radiological Protection (ICRP) 2007 Recommendations of international commission on radiological protection, ICRP publication 103. *Ann. ICRP.* **37** (2–4), 1–332. doi:10.1016/j.icrp.2007.10.003.

Joshi, V. 2020 *SRS Based Abridged Life Table 2014–2018*. Office of the registrar general and census commissioner, India Ministry of Home affairs, Government of India, New Delhi, India.

Khare, A., Sharma, P., Mishra, K. & Prabodha, K. 2015 Measurement of uranium in different seasons in Ganges river water in Allahabad region. *Int. J. Eng. Res. Sci. Technol.* **4** (1), 179–185.

Khatoon, N., Altaf, H., Khan, S. & Rehman, M. 2013 Correlation study for the assessment of water quality and its parameters of Ganga river, Kanpur India. *IOSR Journal of Applied Chemistry* **579** (3), 2278–5736. doi:10.9790/5736-0538090.

Kulkarni, S. 2016 A review on research and studies on dissolved oxygen and its affecting parameters. *International Journal of Research and Review* **3** (8), 18–22.

Kumari, N. & Pathak, G. 2014 A review of groundwater quality issue in Jharkhand due to fluoride. *International Journal of Engineering Research and Applications* **4** (3), 65–77.

Kumar, A., Usha, N., Sawant, P. D., Tripathi, R. M., Raj, S., Mishra, M., Rout, S., Supreeta, P., Singh, J., Kumar, S. & Kushwaha, H. S. 2011 Risk assessment for natural uranium in subsurface water of Punjab State, India. *Human and Ecological Risk Assessment: An International Journal* **17** (2), 381–393. doi:10.1080/10807039.2011.552395.

Meridae, Y. & Ayenew, B. 2016 Drinking water quality assessment and its effects on residents health in Wondogenet, Ethiopia. *Environ Syst Res.* **5** (1). https://doi.org/10.1186/s40068-016-0053-6.

Ollila, K. & Ahonen, L. 1998 *Solubilities of Uranium for Tila -99*. Report code- POSIVIA 98–13, Posivia Oy, Helsinki, Finland.

Ostad-Ali-Askari, K. & Shayannejad, M. 2021 Quantity and quality modelling of groundwater to manage water resources in Isfahan-Borkhar Aquifer. *Environment, Development and Sustainability* **23** (3). https://doi.org/10.1007/s10668-021-01323-1, *Springer* Nature Switzerland AG.

Patra, A. C., Mahapatra, S., Sahoo, S. K., Tripathi, R. M., Jha, V. N., Purani, V. D., Dubey, J. S. & Lenka, P. 2012 An assessment of radiological scenario around uranium mines in Singhbhum East district Jharkhand, India. *Radiation Protection Dosimetry* **150** (4), 458–464. doi:10.1093/rpd/ncr431.

Radionuclides Rule 2003 (Information and Summary), National Primary Drinking Water Regulation. (EPA-2019), Environmental Protection Agency, USA.

Reddy, R. 2013 *Groundwater Information Booklet Deoghar District, Jharkhand*. Central Ground Water Board Ministry of Water Resources, Government of India State Unit Office, Ranchi, Patna, India.

Rusydi, A. 2018 Correlation Between Conductivity and TDS Solid in Various Type of Water: A Review. IOP Publishing, Global Colloquium on GeoScience and engineering 2017, Bandung, Indonesia. IOP Conference Series. *Earth and Environmental Science* **118** (1–6), 012019.

Sahoo, S. K., Mohapatra, S., Chakrabarty, A., Sumesh, C. G., Jha, V. N., Tripathi, R. M. & Puranik, V. D. 2009 Distribution of uranium in drinking water and associated age dependent radiation dose in India. *Radiation Protection Dosimetry* **136** (2), 108–113. doi:10.1093/rpd/ncp147.

Saikia, R., Bhattacharyya, K. & Chetia, D. 2021 Estimation of uranium in groundwater and assessment of age-dependent radiation dose in Nalbari district of Assam, India. *SN Applied Sciences* **3** (1). doi:10.1007/s42452-020-04071-5.

Selvi, B. S., Vijaykumar, B., Rana, B. K. & Ravi, P. M. 2016 Distribution of natural uranium in groundwater around Kudankulam. *Radiat Prot Environ.* **39**, 25–29.

Shalumon, C. S., Aravind, U., Aravindakumar, C. T., Jha, S. K., Radhakrishnan, S., Sahoo, S. K., Sanu, K. S. & Thomas, J. 2021 Analysis of uranium and other water quality parameters in drinking water sources of 5 districts of Kerala in southern India, and potability estimation of using water quality indexing method. *HydroResearch* **4**, 38–46. https://doi.org/10.1016/j.hydres.2021.04.003.

Sheffer, M., Fawell, J. K., Lund, U. & Mintz, B. 2016 *Background Document for the Development of WHO Guidelines for Drinking Water Quality*. Report: WHO/SDE/WSH/03.04/16, Total Dissolved Solids in Drinking Water, WHO, Geneva, Switzerland.

Singh, S., Mahajan, R., Rani, A. & Walia, T. 2003 Analysis of uranium and its correlation with some physico-chemical properties of drinking water samples from Amritsar, Punjab. *J. Environ. Mon.* **5** (6), 917–921. doi:10.1039/b309493f.

Soleimani, H., Abbasnia, A., Khorasgani, F., Mohammadi, A. & Mahmood, Y. 2018 Data on assessment of groundwater quality for drinking and irrigation in rural area Sarpol-e-Zahab city, Kermanshah province, Iran **17**, 148–156. doi:10.1016/j.dib.2017.12.061. Elsevier.

Tiwari, A., Mahato, M., Singh, A. & Singh, P. 2016 Risk assessment due to intake of metals in groundwater east Bokaro coalfield Jharkhand, India. *Spriinger* **8** (2), 265–275. doi:10.1007/s12403-016-0201-2.

UNSCEAR 2000 United Nations Scientific Committee on the Effect of Atomic Radiation, Vol. 1, Annex B, pp. 84–140, United Nations General Assembly, United Nations.

United States Environmental Protection Agency (USEPA) 1991 Review of RSC analysis. Report prepared by Wade Miller Associates (follow-up to USEPA 1990). U.S. Environmental Protection Agency, USEPA, New York.

United States Environmental Protection Agency (USEPA) 1999 Cancer risk coefficients for environmental exposure to radio-nuclides. Federal Guidance Report No. 13 EPA 402-R-99-001, Washington, DC. Guidelines for drinking water, (2004) Vol.1 Recommendations, pp. 145–196. WHO, Geneva, Switzerland.

Wanner, H., Forest, I. & Grenthe, I. & OECD Nuclear Energy Agency 1992 *Chemical Thermodynamics*, Vol. 1. Elsevier, Amsterdam, Netherlands.

Yousefi, M., Goochani, M. & Mahvi, A. 2017 Health risk assessment to fluoride in drinking water of rural residents living in the Poldasht city, Northwest of Iran. *Ecotoxicology and Environmental Safety, Elsevier* **148**, 426–430. doi:10.1016/j.ecoenv.2017.10.057.

Yousefi, M., Ahmadi, S., Ahmed, S., Changani, F., Hussain, A., Khan, A., Khan, N., Rahisuddin, M. A. & Vambol, V. 2020 Chlorination disinfection by products in municipal drinking water-a review. *Journal of Cleaner Production* **273**, 123–159. doi:10.1016/j.jclepro.2020.12315.

First received 18 July 2021; accepted in revised form 17 December 2021. Available online 30 December 2021