

A Comparative Study of Uranium Concentration Using Two Different Analytical Techniques and Assessment of Physicochemical Parameters in Groundwater

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Abstract: Uranium is present in most environmental matrices and can be transferred to living bodies by different pathways. In the current study, the effective concentration of uranium in collected groundwater samples used for domestic as well as agriculture purpose in Dehradun and Haridwar districts of Uttarakhand, India have been measured by LED Fluorimeter and ICP-MS techniques. The obtained results of uranium concentration in the studied samples varied from 0.03 to 19.19 μgL^{-1} with an average value of 2.83 μgL^{-1} using LED fluorimeter and from 0.41 to 27.53 μgL^{-1} with a mean value of 3.74 μgL^{-1} using ICP-MS, respectively. The comparison of results with both the techniques leads to the conclusion of a good agreement with both the techniques. The measured results with both the techniques are well below the reference range suggested by various health agencies. Radiological risk and chemical toxicity have also been estimated. The values of excess cancer risk (ECR) and hazard quotient (HQ) of all samples were found less than unity. The physicochemical parameters and their correlation with uranium content have also been studied.

Keywords: Inductively coupled plasma mass spectrometry (ICP-MS), LED fluorimetry, physicochemical parameters, Toxicity, Uranium.

1 Introduction

From past decades, it has been observed that many harmful radioactive elements are present in groundwater which adversely affects the exposed living beings [1, 2]. One of the most common dangerous radioactive elements which are present in all types of rocks, soil and fluids is uranium. Recent studies reveal that in various parts of the world, groundwater is contaminated with uranium from natural as well as industrial sources [3,4]. Besides other pollutants, above a certain level, the high concentration of uranium in drinking water and foodstuff is also hazardous. ^{238}U and ^{235}U are the most common isotopes of naturally occurring uranium. Particularly natural uranium consists of 99.27% atoms of ^{238}U , approximately 0.72% atoms of ^{235}U and a very small amount 0.0055% atoms of ^{234}U by weight. Uranium exists in four oxidation states; trivalent U^{3+} , tetravalent U^{4+} , pentavalent UO_2^{2+} and hexavalent UO_2^{2++} . The tetravalent compounds are almost insoluble in water. Therefore, the hexavalent state of uranium is specifically important [5]. The lithology, geomorphology and other geological conditions of the regions show the concentration

of uranium in groundwater varies from 0.1 to 500 ppb [6,7]. The interaction between rock and water are the main cause of the presence of uranium in groundwater. The distribution and concentration of trace elements in groundwater vary from one site to another depends upon the variables i.e. pH, Redox potential, Hydro-geometry and geological location etc. Uranium concentrations can additionally result from human exercises, for example; mining, burning from coal and other fuels, the utilization of phosphate composts and atomic power creation [8-12]. It has been demonstrated that the increasing levels of uranium from any source including drinking water may harm the kidney and lungs of the human body [13-15]. Being an alpha emitter, uranium has a variety of associated health risks and can damage the DNA. The harmful effect of uranium on human being health can be split into carcinogenic and non-carcinogenic impacts; these groupings depend on the radiological hazards by radiation of uranium isotopes and the chemical risk [16]. The inhaled uranium is not absorbed and leaves the body in excrement and the absorbed uranium release from the body through urine. The uranium which is inhaled if resides in the lungs for a long time, it can cause to damage lungs.

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Long-term exposure can increase cancer risk and lead to liver damage [17]. World health organization (WHO) has been determined uranium as a nephrotoxic which is the naturally occurred chemical and one of the causes of kidney damage. Additional documented health outcomes of concern include effects on the brain, diminished bone growth, DNA damage and developmental and reproductive effects [18-19]. The health risks from uranium in drinking water are greatest for infants and young children, who can suffer lasting damage from exposure at critical times in their growth [20]. The chemical toxicity of uranium has the more radiotoxic effect on the human body compared to its specific activity because it is low i.e. 25mBq L^{-1} . Chemical toxicity of uranium is a function of several environmental parameters. The prime is carbonate content; because of the formation of soluble carbonate complexes and divalent cation content (Ca^{2+} and Mg^{2+}); because of their competitive interactive ability with the uranyl ion (UO_2^{2+}) [21]. There are many reports on health issues related to U contamination [22-23]. Specifically, environmental monitoring of uranium in water frequently requires hydro geochemical prospection and assessment of the health risk due to the presence of uranium contents. A person will receive a dose of $100\ \mu\text{Svy}^{-1}$ by drinking 2Lday^{-1} water with uranium content of $100\mu\text{gL}^{-1}$ on a daily basis [24]. The various health organizations recommended the safe concentration of uranium in drinking water. The earlier reference level of uranium in drinking water was $15\mu\text{gL}^{-1}$ and $60\mu\text{gL}^{-1}$, fixed by WHO 2004 and AERB 2004 respectively whereas according to WHO 2011, the acceptable limit is $30\mu\text{gL}^{-1}$ [25-26]. As far as our knowledge the uranium concentration in the groundwater of the selected study area is not studied so far. The present study summarizes concentration of uranium via two different techniques in groundwater of the study area. The physicochemical parameters are also investigated. The obtained results are compared with given recommendations by various health agencies.

2 Study Areas

India is one of the most popular countries in the world. It comprises of 28 states and 7 union territories. Uttarakhand is one of state among them and it lies in the northern part of India covering 53483 km^2 areas. Dehradun and Haridwar is biggest and most popular district of Uttarakhand.

Dehradun is the capital city of the Uttarakhand state, lies between latitudes $29^\circ 55'$ and $30^\circ 30' \text{ N}$ and longitudes $77^\circ 35'$ and $78^\circ 24' \text{ E}$ with the geographical area of 3088km^2 , located in western part of the state. Dehradun is situated in the Doon valley on the foothills of the Himalayan surrounded by the lesser Himalayan ranges in the north and Sivalik hills in the south, the river Ganga in the east and the river Yamuna in the west. The Geological setting of the Doon valley includes the Sivalik group. The Doon valley and Sivalikrange are primarily composed of the rocks,

divided into the Lower, the Middle and the Upper Sivaliks. Structurally, it is an asymmetrical, longitudinal and synclinal valley. It extends 34km in length and 20km in average width. The climate of the Dehradun district is generally low temperature. It varies from tropical to severe cold depending upon the altitude of the area with an average annual rainfall of 2073.3 mm is in the area.

Haridwar district is located in the southwestern part of Uttarakh and State and lies from $29^\circ 35'$ to $30^\circ 40' \text{ N}$ latitude and $77^\circ 43'$ to $78^\circ 22' \text{ E}$ longitudes with the geographical area 2360 km^2 . It varies from moderate subtropical to a humid climate with average normal rainfall of 1174mm . Tube wells are major sources of drinking and irrigation and rainfall is the only source of water for groundwater recharge. Geologically, the area is classified into three zones viz. Sivalik, Bhabar and Gangetic alluvial plains from north to south. The outermost parts of Himalaya are constructed with Sivalik range and comprise the Tertiary group of rocks. The Upper Sivaliks constitutes boulders, pebbles of quartzites, sand, and clay. Middle Sivalikscomprises mainly grey micaceous sandstone and siltstone. The Bhabar are formed along the foothills of Sivaliks. Gangetic alluvial plains are in the south of the Piedmont plains and lithologically.

3 Experimental

3.1 Pre-Processing of the Sampling Bottles and Sampling

Before collecting the groundwater sample from the study area for Uranium analysis, pre-processing of the sampling bottles have been carried out in the Radiation Physics Laboratory of Dr. B. R. Ambedkar National Institute of Technology Jalandhar, Punjab, India. To collect the groundwater samples from two districts Dehradun and Haridwar of Uttarakh and, initially prepared a grid map based on latitude and longitude to cover whole study area. Before collecting the water samples, run the groundwater source for about 10 min and then collected the water samples in pre-processed 100 mL polypropylene bottles after rinsing twice with the sample water. At least five samples were taken from each location. Internal addition method was used to obtain a respective average of the particular location. Collected samples were brought to the laboratory and Filtration of all water samples was carried out using $0.45\mu\text{m}$, before the Uranium Analysis to remove the suspended impurities. Theuranium analysis of the samples has been completed within 48 hours. As our analysis is carried out at neutral pH ($\text{pH}\sim 7$), no extra acid was added.

3.2 Instrumentation

The technique for the determination of uranium in water should be highly sensitive, specific and precise. Various

analytical methods have been developed for the determination of uranium in water. In the present study assessment of Uranium concentration in groundwater was carried out using LED fluorimeter LF-2a (Quantalase Enterprises Private Limited, Indore, India). LED fluorimeter was used to detect and measure the trace quantities of uranium exist in water samples. It works on the principle of measurement of fluorescence of uranyl complex in the water sample. This instrument can measure uranium concentration as low as 0.5ppb and has an accuracy of +/- 10% in about 1sec. Calibration is done by ICP-MS-66N-0.01X-1 using concentration 100 $\mu\text{g mL}^{-1}$, which is manufactured by Accu-Standard (USA). The analytical procedure utilized is described in detail by K. Ajay et.al [27]. For the validation of uranium measurement, the analysis has been repeated by using another well established analytical technique ICP-MS (ELAN DRC-e, Perkin Elmer) at IIT Roorkee. ICP-MS is the simple, rapid and inexpensive technique for the analysis of multi-element trace element at very low detection limits (to sub parts per trillion levels) as well as minor and major elements (at parts per million levels) in the same analytical run on suitably diluted samples. It is mainly used for rapid, precise and accurate trace element determinations in liquid and solid samples and other applications including isotopic determinations and speciation studies. The plasma in ICP-MS is used to generate ions that are then introduced to the mass analyzer. These ions are then separated by a quadrupole and collected according to their mass to charge ratios. It is the full multi-elemental technique over a mass range of 3-238 and most suitable technique for in situ elemental analysis. It is a rapidly emerging technique, typically requires only 2 min for the analysis of each sample [28]. The important features of ICP-MS techniques are high samples throughput, small water quantity, and the lower detection limit.

"MAC" Digital pH/mV meter which employs C-MOS LSI technology is used for measuring pH value and redox potential of collected water samples. It has the temperature range of 0-100°C with an accuracy of $\pm 0.5\%$. "MAC" conductivity and TDS meters are micro-controller based instruments with a working range of 0-1000mmS and 0-1000ppm, an accuracy of $\pm 0.5\%$, respectively. The temperature scale provides temperature coefficient compensation manually.

4 Theoretical Formulations

4.1 Radiological Toxicity Risk Assessment

The radiological risks due to ingestion of uranium in water were evaluated by using the proposed method by the United State Environmental Protection Agency (USEPA 1999) (Equations 1,2) [29]:

$$\text{Cancer risk} = \text{Ac} \times \text{R} \quad (1)$$

In Equation (1), AC is the activity concentration of uranium in Bq L^{-1} . R is the Risk factor (Bq^{-1}L) which is a product of risk coefficient r and per capita activity intake I. Since radio toxicity of a radioelement depends on its specific activity, therefore the isotopic composition of uranium in water must be considered in addition to their physicochemical nature [30]. The cancer mortality risk coefficients (in Bq^{-1}) for the three isotopes of uranium namely ^{234}U , ^{235}U and ^{238}U were taken as 6.1×10^{-11} , 6.2×10^{-11} and 7.5×10^{-11} while cancer morbidity risk coefficients (in Bq^{-1}) were 9.5×10^{-11} , 9.8×10^{-11} and 7.5×10^{-10} respectively.

4.2 Chemical Toxicity Risk Assessment

The chemical/non-carcinogenic risk for uranium has been explained in terms of Lifetime Average Daily Dose (LADD) and Hazard Quotient (HQ), Equations (2) and (3):

$$\text{LADD} = \frac{\text{EPC} \times \text{IR} \times \text{IF} \times \text{D}}{\text{AT} \times \text{W}} \quad (2)$$

In the above expression; EPC is the exposure point concentration of uranium in water ($\mu\text{g L}^{-1}$), IR is ingestion rate (1.38 L day^{-1}), IF is ingestion frequency (365 days y^{-1}), D = Duration (69.89 y), AT = Average time and W is the ideal body weight (70 kg) [31].

$$\text{HQ} = \frac{\text{LADD}}{\text{RFD}} \quad (3)$$

Where RFD is the reference dose limit taken as $0.6 \mu\text{g/kg/day}$ [25].

5 Results and Discussion

5.1 Uranium Concentration in Ground Water

The uranium concentration and summary of the statistical distribution of groundwater samples with latitude and longitude of respective location are shown in table 1 and 2 respectively. The activity concentration of uranium in the studied samples were varied from $0.03 \mu\text{g L}^{-1}$ to $19.19 \mu\text{g L}^{-1}$ and from $0.41 \mu\text{g L}^{-1}$ to $27.53 \mu\text{g L}^{-1}$, with an average value of $2.83 \mu\text{g L}^{-1}$ and $3.74 \mu\text{g L}^{-1}$, using LED fluorimeter and ICP-MS respectively. The highest uranium concentration in water samples was found in Iqbalpur of district Haridwar and Pithuwala village of Dehradun. The results indicate that the average value of uranium concentration in district Haridwar was larger than the average value of district Dehradun. The results by ICP-MS were consistent with those obtained by the LED fluorimeter. Various health and environmental protection agencies have recommended the safe limit of uranium concentration in water that represent no significant health risk over a lifetime drinking of water under these set limits. The World Health Organization [23] and United States Environmental Protection Agency [32] have assigned a guideline value of $30 \mu\text{g L}^{-1}$ whereas International Commission on Radiological Protection [33] and United Nations Scientific Committee on Effects of

Atomic.

Table 1: Uranium concentration in groundwater samples with the physicochemical parameter.

Sr.No.	Sample Location	Latitude	Longitude	Uranium conc. ($\mu\text{g L}^{-1}$)			pH	RP (mV)	Temp ($^{\circ}\text{C}$)	TDS (ppm)	EC (μS)
				LED	ICP-MS	Ratio					
DISTRICT HARIDWAR											
1	Shyampur	29.865379	78.182093	9.97	12.47	1.25	6.55	64	26.7	559	708
2	Haridwar	29.945691	78.164248	4.29	2.73	0.64	7.73	31	26.7	311	400
3	Jwalapur	29.927059	78.107976	1.14	1.48	1.30	7.13	66	26.6	226	301
4	Sitapur	29.916327	78.106142	3.17	0.35	0.11	7.18	55	26.9	356	473
5	Bahadradabad	29.919514	78.040942	4.10	3.69	0.90	7	59	26.5	351	499
6	Roorkee	29.854263	77.888	1.48	1.81	1.22	7.58	29	26.8	147	184.3
7	Bhagwanpur(R)	29.941096	77.812426	12.33	16.14	1.31	7.66	25	26.6	613	771
8	Iqwalpur	29.871915	77.793275	19.19	27.53	1.43	7.75	35	26.6	442	525
9	Jhabrera	29.804342	77.796697	9.00	11.72	1.30	7.59	20	26.5	252	308
10	GurukulaNarsen	29.70236	77.849592	0.74	0.78	1.06	7	73	26.6	161	200
11	Jhabiran	29.784509	77.843875	2.39	3.09	1.29	7.46	46	26.6	231	302
12	Landhura	29.794741	77.908175	5.45	7.43	1.36	7.6	27	26.2	213	258
13	Dausni	29.773977	77.984572	2.88	3.62	1.25	7.52	62	26.7	626	756
DISTRICT DEHRADUN											
1	chakrata	30.702232	77.867854	0.41	1.67	4.11	7.61	18	26.7	373	458
2	Sahiya	30.611539	77.875315	0.36	0.49	1.34	7.62	24	26.6	99.8	125.6
3	Dumet	30.50109	77.83101	0.03	0.03	1.00	6.76	55	26.6	115.1	146.2
4	Dakpathar	30.497173	77.801978	0.10	0.17	1.72	7	67	26.7	130	187.5
5	Vikasnagar	30.475025	77.765235	0.05	0.09	1.80	6.67	110	26.4	102.5	137.2
6	Herbtpur	30.438286	77.736624	0.05	0.07	1.35	5.46	145	26.8	137.4	178.9
7	Selaqui	30.36713	77.857668	0.03	0.03	1.08	6.72	84	26.8	81.2	106.8
8	Bhagwanpur(D)	30.398632	78.070898	0.09	0.02	0.26	7.36	48	26.6	116.4	144
9	Dehradun	30.316495	78.032192	1.06	1.47	1.39	7.55	33	26.8	421	521
10	Pitthuwala	30.290034	77.986713	4.68	4.97	1.06	7.5	53	26.6	554	701
11	Rajpur	30.359227	78.067215	0.97	1.26	1.30	7.75	23	26.4	319	406
12	Raipur	30.309851	78.093717	0.26	0.41	1.58	7.62	37	26.7	306	381
13	Doiwala	30.173436	78.125085	0.07	2.77	37.39	7	72	26.7	109.6	140.9
14	Rishikesh	30.086928	78.267612	0.38	0.41	1.09	7.28	48	26.5	165	208.2
15	Thakurpur	30.054571	78.21842	1.01	1.32	1.56	7.27	51	26.6	225	284
16	Raiwala	30.025447	78.219132	1.13	0.41	1.17	7.32	47	26.6	342	430

Table 2: Summary of Statistical distribution for uranium concentration in groundwater sample of the selected study area-

District	Techniques used for the assessment of uranium concentration (µg/L) in water samples											
	LED Flourimeter						ICP-MS					
	Mean	Median	Max	Min	SD	SE	Mean	Median	Max	Min	SD	SE
Dehradun	0.42	0.31	1.13	0.03	0.41	0.10	0.97	0.41	4.97	0.02	1.32	0.33
Haridwar	5.86	4.10	19.19	0.74	5.38	1.49	7.14	3.62	27.53	0.35	7.92	2.20
Entire region	3.14	2.2	19.19	0.03	3.51	0.69	4.05	2.01	27.53	0.02	4.66	0.93

SD = Standard Deviation, SE = Standard Error.

Regulatory Board of India, Department of Atomic Energy, India [26] has recommended the threshold for uranium in water as 60µgL⁻¹. Evidently, the uranium concentration in all drinking water samples is safely below the advocated levels of WHO, USEPA, and AERB. However, 1 sample from Pitthuwalla of district Dehradun and 10 samples from district Haridwar exceed the prescribed limit 1.9µgL⁻¹ by ICRP, 1993 [33]. All samples from district Dehradun found well within the prescribed limit but 4 samples of Haridwar were exceeded the recommended limit 9 µgL⁻¹ by UNSCEAR, 2011 [34]. On considering 1.9µgL⁻¹ as a safe limit, most of the analyzed samples from Haridwar exceed this limit. The high value of uranium than permissible limit represent may be unsafe water for the human being and a health hazard of uranium. Previous studies on uranium in water carried out in different states of the country are summarized in Table 3.

Table 3: Uranium Concentration in Groundwater samples of the nearby area of selected study area.

Sr No	State/cities	Uranium Conc. (µg L ⁻¹)
1	Himachal Pradesh, Kullu	0.3-2.5
2	Punjab, Bathinda	11.7-113.7
3	Punjab, Malwa	5.4-43.4
4	Uttar Pradesh	1.4-19.2
5	Delhi	2.2-8.8
6	Ghaziabad	4.2-11.4
7	Western Haryana	6.3 – 43.3
8	Jammu and Kashmir	0.2 – 20.8
9	Rajasthan	0.4 - 123.9
10	Maharashtra	0.03-7.08
Present Study	Haridwar	0.35-27.53
	Dehradun	0.02-4.97

5.2 Health Risk Assessment

The statistical values of radiological and chemical risk due to ingestion of uranium for all collected groundwater samples of the study area have been reported in table 4. The value of average cancer mortality and morbidity risk for uranium isotopes ²³⁴U, ²³⁵U and ²³⁸U were found 1.85E-07, 1.11E-09, 8.35E-12 and 2.35E-07, 1.76E-09, 1.76E-09 respectively. In both categories, the risk from ²³⁸U is highest followed by ²³⁵U and ²³⁴U owing to its natural abundance.

In the proposed work, the lifetime average daily dose (LADD) was varied between 0.001 and 0.378µg kg⁻¹ d⁻¹ with mean value of 0.056µg kg⁻¹d⁻¹, which is much less than the reference dose (RFD) of 0.6µg kg⁻¹ d⁻¹ and 4.4 µg kg⁻¹ d⁻¹ prescribed by WHO 2004 [24] and AERB 2004 [25] respectively. The value of Hazard Quotient (HQ) fluctuated between 0.001 and 0.063 with an average value of 0.093 as given in table 5. The obtained result showed that HQ value is less than unity, which is indicating no considerable radiation risk to the population due to the consumption of water in the study area.

5.3 Physico-Chemical Properties of Ground Water

The summary of the statistical analysis of the physicochemical properties of tested water samples in both districts is presented in Table 5. The analyzed waters fall in a range of 5.46 to 7.75 with an average value of 7.25. It is clearly seen from the obtained data that 58% of the samples lie in 7-7.5 pH category. This suggests that the studied region has mostly alkaline environment. However, water sample of pH 5.46, belonging to Herbtipur fails to lie in the ideal range of 6.5-8.5 as recommended by BIS [35] and WHO [24]. Ph with a low value below 4 and higher value above 8.5 will produce a sour taste and alkaline taste of

water respectively. The low value of pH in water shows solubility of heavy metals. The studied samples have

concentration and different water quality parameters: pH, EC, TDS and RP. According to the A moderate positive correlation obtained between uranium concentration values

Table 4: Statistical analysis of associated toxicity of groundwater samples.

		Minimum	Maximum	Mean	Median	S.D	S.E.
Cancer mortality risk	U-238	1.70E-09	1.26E-11	1.85E-07	6.8E-08	2.95E-07	5.47E-08
	U-235	1.02E-11	7.54E-09	1.11E-09	3.81E-10	1.77E-09	3.28E-10
	U-234	7.68E-14	5.67E-11	8.35E-12	2.86E-12	1.33E-11	2.46E-12
Cancer morbidity risk	U-238	2.16E-09	1.59E-06	2.35E-07	8.04E-08	3.73E-07	6.93E-08
	U-235	1.61E-11	1.19E-08	1.76E-09	6.02E-10	2.79E-09	5.18E-10
	U-234	9.44E-12	6.97E-09	1.03E-09	3.52E-10	1.63E-09	3.03E-10
LADD ($\mu\text{g kg}^{-1} \text{d}^{-1}$)		0.001	0.378	0.056	0.019	0.089	0.016
HQ		0.001	0.630	0.093	0.032	0.148	0.027

electrical conductivity (EC) and redox potential (RP) in the range from 106.8 to 771 μS and 18 to 145 mV with the mean value of 353.16 μS and 51.97 mV respectively. The obtained TDS value varies between 81.2 and 626 mg L^{-1} with mean value 278.7 mg L^{-1} . Only 4 groundwater samples, 1 from Pitthuwala of district Dehradun and 3 from Shyampur, Bhagwanpur and Dausni of district Haridwar, exceed the secondary maximum contaminant level (SMCL) of 500 mg L^{-1} set by USEPA and BIS10500-1991 standard. However, except these 4 samples, all other samples have TD Slower than the permissible limit of 600 mg L^{-1} prescribed by WHO [23]. In our case, most of the samples with the low value of TDS following the simple rule: low TDS means low radioactivity. To confirm this fact a positive correlation is seen between uranium and TDS.

Table 5: Summary of statistical analysis of physico-chemical parameter for all groundwater samples of the study area

Parameter	pH	RP (mV)	TDS (ppm)	EC (μS)
Min	5.46	18	81.2	106.8
Max	7.75	145	626	771
Mean	7.25	51.97	278.79	353.16
Median	7.36	48	231	302
S.D.	0.49	27.48	163.02	202
S.E.	0.09	5.17	30.27	37.51

5.4 Correlation analysis

Table 6 showed the correlation analysis among the uranium

of uranium using ICP-MS and LED fluorimeter technique ($R^2=0.97$). The values of uranium concentration by LED and ICP-MS are obtained with the correlation coefficient of 0.97. The difference in the obtained values by both techniques might be due to the factors (sensitivity of the instrument, and detection limit) existing at the time of measurement. Both techniques lead to the same conclusions as far as the uranium is concerned in various location of the study area. For instance, on comparing uranium content in Iqbalpur location, it was found maximum with LED as well as ICP-MS. Although ICP-MS is a better instrument due to its lower detection limit, it is better suited to investigate those areas which have low levels of uranium concentration.

Table 6: Correlation coefficient matrix (r) for uranium and the physicochemical parameter of water.

	Uranium Conc.		pH	EC (μS)	TDS (ppm)	RP (mV)
	ICP-MS	LED				
ICP-MS	1					
LED	0.97	1				
pH	0.27	0.26	1			
EC	0.51	0.52	0.32	1		
TDS	0.53	0.53	0.34	1.00	1	
RP	-0.29	-0.31	-0.91	-0.29	-0.31	1

(using ICP-MS and LED) and EC ($R^2=0.51$) and ($R^2=0.52$), Uranium concentration values and TDS ($R^2=0.53$) and ($R^2=0.53$). A weak positive correlation was found among Uranium concentration values and pH (0.27) and (0.26),

conductivity and PH ($R^2=0.32$), TDS and pH ($R^2=0.34$). pH shows a very small but positive correlation with analyzed results of uranium concentration using ICP-MS and LED fluorimeter, conductivity, TDS but it is negatively correlated with redox potential (RP).

6 Conclusions

The level of uranium concentration was found higher in the groundwater of district Haridwar than the groundwater of district Dehradun. Cross method analysis has been done to verify the accuracy and reliability of the techniques. A strong positive correlation ($R^2 = 0.97$) has been found between the results of two techniques that assure the quality of water. As to the averages obtained by the two methods for the analysis of the uranium concentration, there was found a good agreement between them. Data analysis reveals that the average value of uranium concentration in the groundwater samples under study lower than the permissible limit prescribed by the various health agency. Therefore, we can conclude that depending on the level of uranium concentration, the groundwater of the studied region is radiologically safe. Some of the samples show higher uranium concentration than the prescribed limit might be due to leaching of uranium from the rocks. Nonetheless, the toxicity hazard analysis reassures that the estimated level of uranium exposure is low, suggesting negligible chemical health risk (hazard quotient <1) from drinking water pathway for local residents during their lifetime. The High value of TDS in water samples might be due to anthropogenic activities, urbanization, widespread use of pesticides and phosphate fertilizers. Also, uranium levels in groundwater are not much influenced by physicochemical properties like pH, EC, TDS but these parameters need to be regularly monitored to ensure the quality of drinking water.

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