J. Indian Water Resour. Soc.,
Vol. 42, No. 2, Apr., 2022

GEOCHEMICAL BEHAVIOUR OF URANIUM WITH OTHER CONTAMINANTS IN GROUNDWATER OF RAICHUR DISTRICT, KARNATAKA, INDIA

K. Ravichandran, Sailee A. Bhange, Lalitha B.H., D. Dhayamalar and Kunhambu V

ABSTRACT

Uranium occurs naturally in groundwater and surface water. Being a radioactive mineral, high uranium concentration can cause impact on water, soil and health. The health effects associated to consumption of uranium includes increased cancer risk and kidney toxicity. The maximum contaminant level for uranium, recommended by the World Health Organization is 30 µg/L. The purpose of this study is to understand the causes for the occurrence of uranium and its geochemical behaviour with other contaminants. A total of 27 groundwater samples were collected from different part of the study area includes shallow dug wells of mining area, domestic wells and irrigation wells and analysed for Uranium with other health affecting trace metals like Cu, Pb, Zn, Cr, Mn, Fe and As by using ICP-MS . Investigations were also carried out for Physico-chemical parameters like pH, electrical conductivity, total hardness, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulphate, nitrate and fluoride. Results of uranium were correlated with other Physico-chemical parameters and trace metals. The uranium concentration in groundwater was found to vary from 0.37 µg/l to maximum 54.63 µg/l with a mean of 9.05 µg/l. The Uranium concentration more than 30 µg/L was in positive correlation with Nitrate, Sulphate and Potassium of the groundwater samples from the irrigation wells. A few groundwater samples with higher value of Uranium were further subjected to radiation counts on Liquid Scintillation Counter, the graphical peaks and disintegration count values were found in affirmative compliance to uranium concentration observed.

Keywords: *Uranium; radioactive mineral; Liquid Scintillation Counter; Raichur*

INTRODUCTION

In recent years, many incidences of presence of uranium in ground water have been reported.[1-2] Uranium contamination in ground water is the major concern that uranium is naturally occurring radioactive element that is both radiological as well as chemically toxic. Uranium has both natural and anthropogenic source that could lead to the aquifer. These sources include leaching from natural deposits, release in mill tailings, and emissions from the nuclear industry, combustion of coal and other fuels, and the use of phosphate fertilizers that contains uranium and contribute to ground water pollution [1-4]. Uranium enters in to human tissues mainly through drinking water, food, air and other occupational and accidental exposures. Intake of uranium through air and water is normally low, but in circumstances in which uranium is present in a drinking water source, the majority of intake can be through drinking water. Water with uranium concentration above the recommended maximum acceptable concentration of 30 ppb [6-9] is not safe for drinking purposes as it can cause damage to internal organs, on continuous intake. Elevated uranium concentrations in drinking water have been associated with many epidemiological studies such as leukemia, stomach and urinary track cancer as well as kidney toxicity. A recent study,[5] found a strong correlation between uranium concentration in drinking water and uranium in bone, suggesting that bones are good indicators of uranium exposed via ingestion of drinking water. Therefore, such studies trigger further assessment of uranium's adverse health effects on humans and/or the environment for countries where elevated uranium concentration in drinking water has been observed. Hence, it becomes important to study the level of uranium in drinking water for health risk assessment. This study has been undertaken for the estimation of uranium concentration with other trace metals in groundwater collected from Raichur district, Karnataka, India, using inductively coupled plasma mass spectrometry (ICP-MS).

1. *Ministry of Jal Shakti, Central Ground Water Board, South Western Region, Bangalore*
Email: krchandran06@rediffmail.com

Manuscript No. 1575
Received : 16 July, 2022; Accepted : 21 July, 2022

MATERIAL AND METHODS

Description of the study area:

Raichur district is situated in north-eastern part of Karnataka state. It falls in the Northern Maidan region, between 15º 33'- 16º 34' North latitudes and 76º 14'- 77º 36' East longitudes. It lies between the two major rivers namely the Krishna and the Tungabhadra. The study areas with sampling location are shown in Fig.1

The net sown area comprises 69% of the total geographical area of the district. Paddy, Jowar, Maize, Cotton, Sugarcane, pulses and oil seed are the major crops grown in the district. Nearly 20% of the geographical area in the district is under irrigation. Canals, tanks, wells, bore wells, lift irrigation are the important sources for irrigation.

The normal annual rainfall of the district is 721 mm, nearly 67% of the rain is received during the southwest monsoon period (June - Sept) and the northeast monsoon contributes about 24%. Geomorphologically, Raichur district can be broadly classified into three major zones viz, (a). The Northern rugged plateau, (b) The Southern lower plains

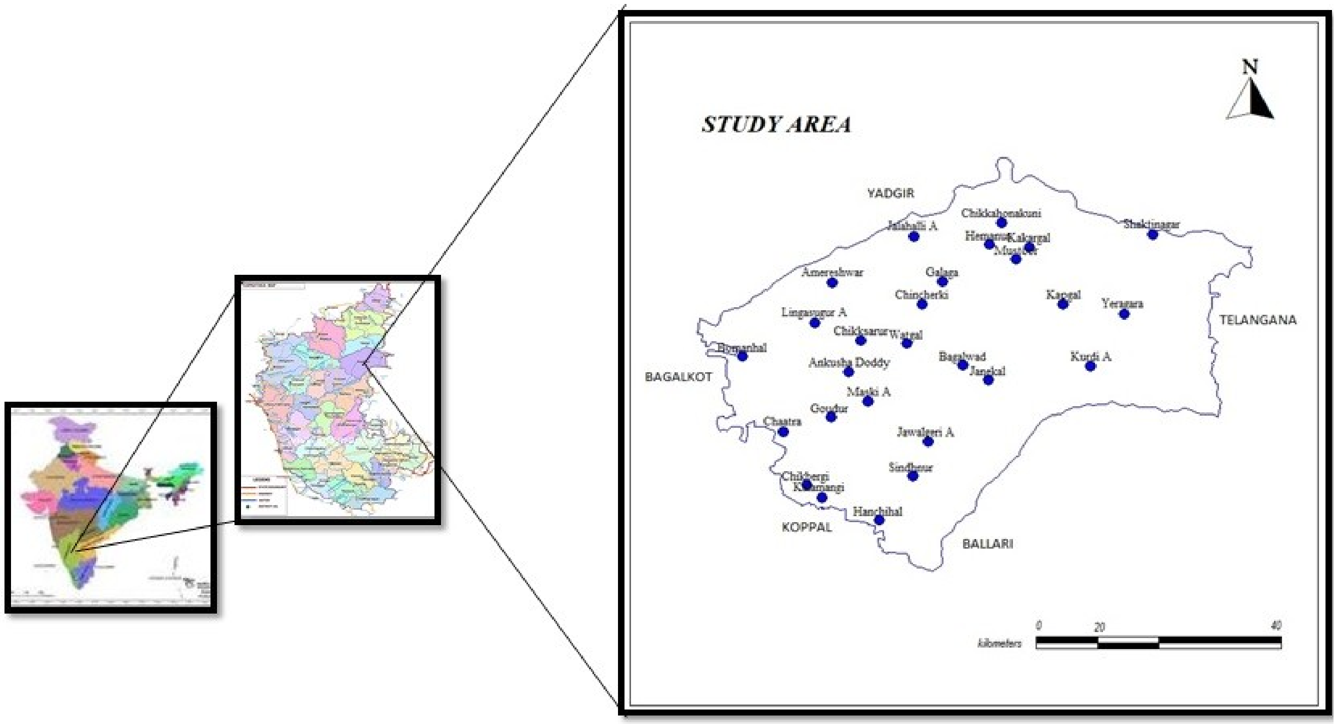

Fig. 1: Location map of the study area showing sampling sites.

with inselbergs and isolated hillocks and (c) Valley fills. The general slope of the terrain is towards the Krishna River in the northern part of the district and towards the Tungabhadra River in the southern part.

Hydrogeology

Granites, gneisses and Dharwar schists are the main rock formations in the district. These formations are grouped under 'hard rock', as they do not have any primary porosity. However, secondary porosity is developed due to faults, fractures, joints, and due to weathering, which improved permeability and water yielding capacity of these rocks. Ground water occurs under water table conditions in the weathered and jointed hard rock, and under confined to semi-confined conditions in the fractured rock. Since the district is covered predominantly by black cotton soils, which inhibit percolation and circulation of water, there are pockets of poor-quality ground water in the area

Sampling and Instrumentation

Groundwater samples were collected from 27 open wells from different part of the study area includes shallow dug wells of mining area, domestic wells and irrigation wells during May 2018 representing pre- monsoon seasons. The samples were collected for basic parameters in 1-litre HDPE bottles rinsed three to four times with the water sample before filling it to capacity and then labeled accordingly. Another set of samples were also collected in 120 ml HDPE bottles and acidified with aristar grade nitric acid for estimation of uranium and other trace metals. Prior to analysis in the laboratory, the samples were stored at a temperature below 4^0C. The methodology for the collection of sample, preservation and analysis, the standard methods (Hem 1985; APHA 2012) were followed. Using pH and EC meters, EC and pH of water samples were measured in the field immediately after the collection of the samples. Alkali metal ions (Na^+ and K^+) were measured using a flame photometer (Systronics Flame Photometer 128). Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. Chloride was estimated by $AgNO_3$ titration. Turbidimetric technique was used for the analysis of sulphate. Nitrate was analyzed using UV-Visible spectrophotometer. Fluoride content was determined by SPADNS method. Standard solutions for the above analysis were prepared from the respective salts of Analytical Reagent grade. All the basic parameters are expressed in milligrams per liter (mg/l), except pH (units). Uranium with other trace metals like Cu, Pb, Zn, Cr, Mn, Fe and As were analysed by using ICP-MS (Thermo make icap-Q model).

RESULT AND DISCUSSION

The statistical summary and analytical results of the uranium concentration and other trace metals obtained from the analysis of groundwater samples collected during May 2018 is given in Table 1 and table 2 respectively. The spatial distribution of electrical conductivity, fluoride, nitrate and uranium are shown in Fig 2 to 5, respectively. The electrical conductivity ranges between 687- 6720 µS/cm at 25° C with mean value of 2075 µS/cm. The concentration of nitrate ranges from 1 to 593 mg/l with a mean value of 74 mg/l. The concentration of uranium ranges from 0.38 to 54.63 µg/l with an average of 10.08µg/l.

The highest value of EC 6720 µS/cm, nitrate 593 mg/l and uranium 54.63 µg/l were recorded at location Hanchinal is in an area of intensive agriculture and the south western part of the study area. Elevated nitrate concentration was observed where drainage system is very poor and in areas under intensive agriculture. The spatial distribution contour of nitrate is parallel to electrical conductivity contour, which indicates that the source is same. It is also noticed that the concentration of uranium is more in irrigation wells than that of domestic wells. The uranium concentration in groundwater of irrigation and domestic wells is shown in Figure.6. It reveals that concentration of uranium is more in areas where irrigation is predominant. The total uranium source in phosphate rock is estimated at 9 x 10^6 metric tonnes of uranium. [(9).] Hence, phosphorous fertilizers manufactured from phosphate rock may also contribute uranium to groundwater in the agriculture region. Use of phosphatic fertilisers for agricultural activity in this area may also add up uranium in groundwater.

Correlation matrix of hydro chemical data of groundwater samples collected from study area is given in table 3. The correlation coefficient values exhibiting +1 or -1 between the variable reveals that there is strong correlation and the value at the zero indicates no relationship between them. In general, the geochemical parameter showing correlation coefficient >0.7 are considered to be strongly correlated whereas value between 0.5 and 0.7 shows moderate correlation. In this study, the relationship between various elements has been studied and the correlation matrix is given in Table 3. It can be observed that the highest correlation is found between EC and sulphate with correlation coefficient value of 0.94. Some strong correlation is also found between Mg^{2+} vs Cl^- and Na^+ vs SO_4^{2-} , which are 0.91, 0.89. The correlation coefficient for other constituents such as Ca^{2+}, K^+ and NO_3^- with EC reduces progressively. The correlation values are 0.83, 0.67, and 0.62 indicate proportionally reducing contribution of these constituents towards causing the pollution in groundwater. In the case of trace metals, uranium shows some correlation with nitrate with correlation coefficient values of 0.40 and no significant correlation with other trace metals, which also indicates that the source is from anthropogenic activity.

Table 1. Details of analytical methodology and basic statistics of groundwater samples.

Variable	Symbol	Method	Units	Min	Maximum	Mean	SD
pH	pH	Potentiometry		7.66	9.05	8.31	0.34
Electrical conductivity	EC	Electrolytic conductivity	µS/cm	687	6720	2075.26	1433.71
Total hardness	TH	EDTA titrimetric	mg/l	150	1510	484.44	328.72
Calcium	Ca	EDTA titrimetric	mg/l	16	168	62.22	34.98
Magnesium	Mg	by difference	mg/l	19	267	79.85	61.41
Sodium	Na	Flame photometry	mg/l	70	879	233.36	179.97
Potassium	K	Flame photometry	mg/l	3	413	63.74	107.91
Carbonate	CO_3	Titrimetric	mg/l	0	54	19.78	22.00
Bicarbonate	HCO_3	Titrimetric	mg/l	73	655	329.01	141.71
Chloride	Cl	Argentometry	mg/l	39	1264	279.27	257.17
Sulphate	SO_4	Nephlo–turbidimetry	mg/l	88	1600	339.26	350.41
Nitrate	NO_3	Spectrophotometry	mg/l	1	593	74.04	134.40
Fluoride	F	SPADNS	mg/l	0.18	6.10	2.30	1.65
Copper	Cu	ICP-MS	µg/l	0.01	33.13	13.96	7.60
Lead	Pb	ICP-MS	µg/l	0.12	2.61	0.79	0.56
Zinc	Zn	ICP-MS	µg/l	0.03	54.11	33.60	13.64
Chromium	Cr	ICP-MS	µg/l	37.64	609.35	144.81	136.23
Manganese	Mn	ICP-MS	µg/l	0.09	1985.30	208.59	447.86
Iron	Fe	ICP-MS	µg/l	0.79	2832.26	1085.35	597.70
Arsenic	As	ICP-MS	µg/l	0.19	10.55	2.86	2.45
Uranium	U	ICP-MS	µg/l	0.38	54.63	10.08	12.21

SD. Standard deviation,

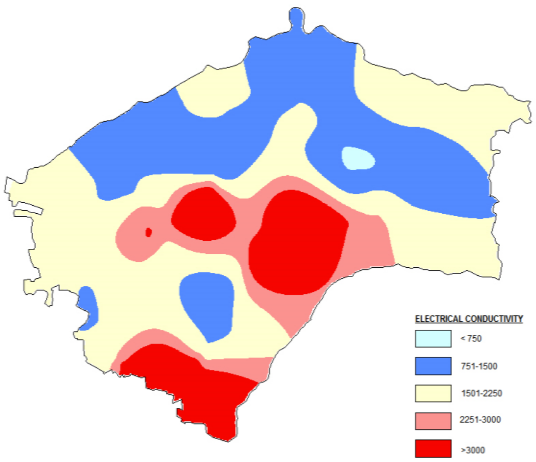

Fig. 2: Spatial distribution of electrical conductivity (µS/cm at 25° C) during May 2018.

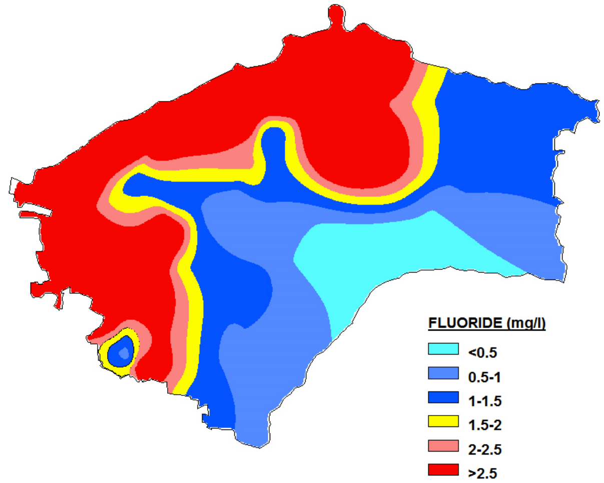

Fig. 3: Spatial distribution of fluoride during May 2018.

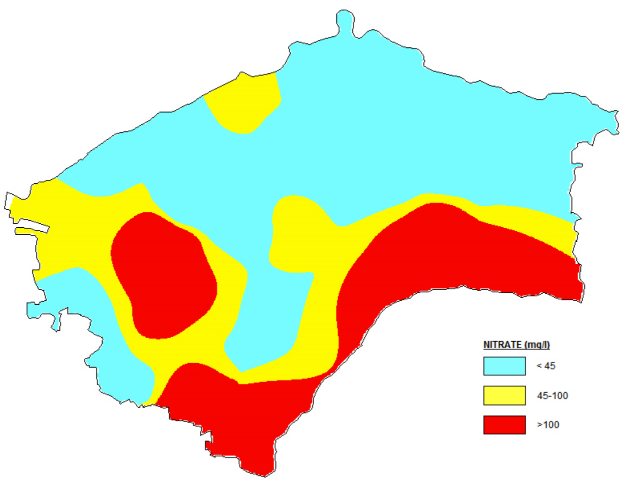

Fig. 4: Spatial distribution of nitrate in Raichur district during May 2018.

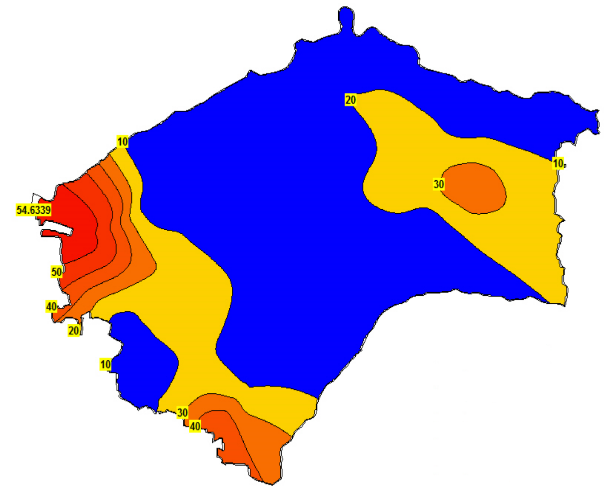

Fig.: 5. Spatial distribution of Uranium during in Raichur district May 2018.

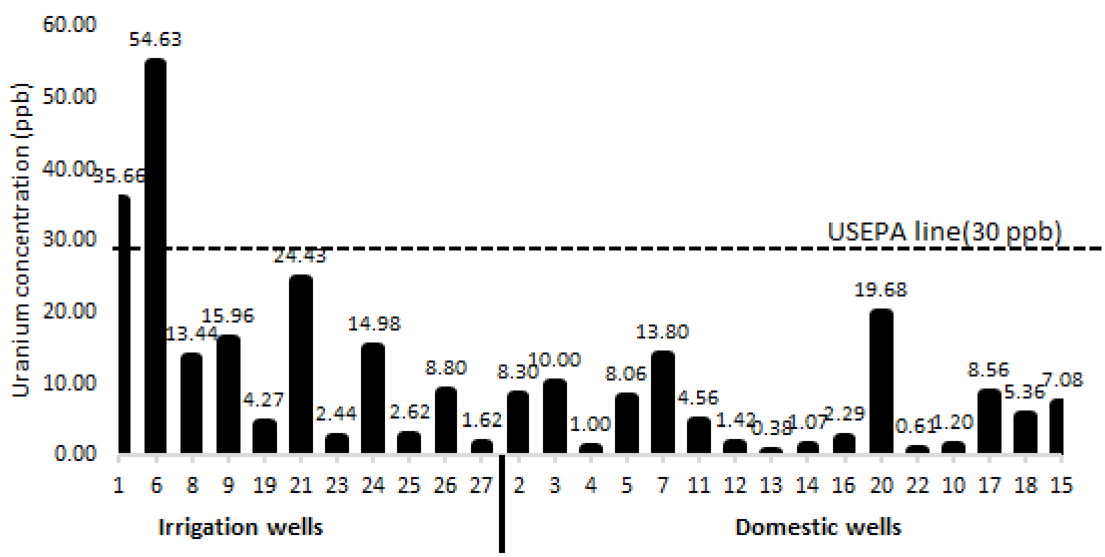

Fig. 6. Uranium concentration in groundwater (ppb) in irrigation and domestic wells.

Table 2: Analytical results of groundwater sample collected during May 2018 from Raichur district.

SL No	SITE_NAME	PH	EC	TH	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3	F	Cr	Fe	Mn	Cu	Zn	As	Pb	U
				<..........................mg/L...>											<..........................µg/L..>							
1	Hanchinal	8.03	6720	1280	168	209	879	228	0	384	536	1600	593	1.20	39.55	593.26	414.45	6.02	13.38	2.33	0.12	35.66
2	Sindhnur	7.79	1493	380	64	53	176	3	0	323	149	280	42	0.85	116.26	1434.25	37.28	18.54	43.32	1.13	1.14	8.30
3	Kalamangi	8.48	3070	390	48	66	614	6	54	655	192	890	20	2.90	52.66	728.82	26.68	9.28	33.41	10.55	0.72	10.00
4	Chikkbergi	7.66	1529	440	60	70	144	12	0	458	220	136	16	0.87	142.42	1906.09	1390.03	18.55	42.03	5.01	1.31	1.00
5	Chaatra	7.88	1473	420	80	53	152	9	0	403	192	180	21	4.80	55.69	683.16	16.74	7.75	21.49	0.30	0.35	8.06
6	Bomanhal	8.21	2220	440	60	70	281	98	0	478	376	284	55	3.40	97.47	1195.18	31.09	14.43	25.50	3.04	1.03	54.63
7	Maski	8.22	1615	360	56	53	130	156	0	397	178	208	126	1.50	82.39	1075.80	57.30	14.23	41.70	5.33	1.20	13.80
8	Goudur	8.25	1893	420	80	53	225	78	0	378	263	208	140	3.10	75.56	656.64	83.55	12.88	26.24	0.97	0.51	13.44
9	Ankusha Doddy	8.33	3030	960	92	177	341	89	36	360	525	310	372	3.20	63.82	660.21	13.48	9.22	19.76	1.67	0.41	15.96
10	Amareshwar	8.74	800	190	40	22	97	4	42	159	64	124	2	3.00	78.93	990.80	185.19	11.98	51.93	3.25	0.68	1.20
11	Lingasugur	8.86	1194	270	48	36	159	3	36	165	185	144	58	1.30	198.36	1124.29	35.98	17.33	46.09	1.38	0.76	4.56
12	Chikkesarur	8.15	2050	670	96	104	155	7	0	183	256	568	2	1.20	609.35	1648.56	26.70	28.56	51.69	2.50	1.07	1.42
13	Watgal	8.22	4320	840	60	168	508	3	0	214	781	850	1	0.57	166.95	1297.32	349.87	15.05	21.90	1.17	0.85	0.38
14	Chincherkki	8.17	883	330	60	44	93	3	0	476	39	88	24	2.10	155.86	1543.10	25.38	21.81	50.07	0.86	1.52	1.07
15	Jalahalli	8.42	1733	310	44	49	241	89	48	537	188	152	60	5.00	99.15	707.27	20.42	9.92	28.33	7.17	0.43	7.08
16	Galag	8.42	1206	430	44	78	72	26	18	299	163	136	21	1.20	567.81	1574.69	44.08	23.78	42.35	1.03	0.52	2.29
17	Hemanur	8.52	1299	310	32	56	175	3	48	397	142	140	2	4.60	132.11	957.03	122.08	12.54	54.11	3.81	0.73	8.56
18	Chikkahonakuni	8.52	1140	200	48	19	189	3	42	324	78	148	5	4.90	37.64	380.35	12.50	7.04	35.08	6.34	0.20	5.36
19	Mustoor	8.46	1655	280	40	44	260	4	42	390	185	204	4	6.10	203.96	2832.26	187.57	33.13	48.05	2.13	2.61	4.27
20	Kakargal	8.75	1267	250	32	41	189	3	54	328	142	112	23	2.80	151.73	2212.57	43.47	26.32	46.88	4.13	1.93	19.68
21	Yeragara	8.25	955	310	44	49	70	5	0	122	192	92	10	1.12	114.42	601.75	20.09	10.92	27.90	0.65	0.40	24.43
22	Shaktinagar	8.11	2010	620	60	114	162	6	0	153	256	564	1	1.10	52.38	744.89	322.51	6.25	16.72	0.19	0.30	0.61
23	Kurdi	7.80	2320	700	56	136	125	112	0	256	391	180	266	0.36	154.64	792.42	30.01	12.13	30.46	0.69	0.59	2.44
24	Kapagal	8.70	687	150	16	27	104	7	36	187	67	92	1	2.80	105.58	882.98	63.85	12.13	33.06	3.07	0.62	14.98
25	Janekal	8.03	5550	1510	164	267	345	413	0	287	1264	890	49	0.18	147.30	786.88	86.14	11.03	33.98	0.59	0.24	2.62
26	Bagalwad	8.39	2770	420	56	68	252	347	48	500	376	316	65	0.83	138.92	1293.24	1985.30	6.19	21.68	4.13	0.65	8.80
27	Jawalgeri A	9.05	1150	200	32	29	164	4	30	73	142	264	20	1.20	69.11	0.79	0.09	0.01	0.03	3.79	0.47	1.62

Table 3: Correlation matrix

	PH	EC	TH	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3	F	Cr	Fe	Mn	Cu	Zn	As	Pb	U
PH	1.00																				
EC	-0.34	1.00																			
TH	-0.49	0.90	1.00																		
Ca	-0.51	0.83	0.90	1.00																	
Mg	-0.46	0.88	**0.99**	**0.82**	1.00																
Na	-0.12	0.86	0.60	0.58	0.58	1.00															
K	-0.24	0.67	0.64	0.64	0.62	0.35	1.00														
CO3	0.74	-0.26	-0.44	-0.49	-0.40	0.02	-0.13	1.00													
HCO3	-0.27	0.18	0.00	0.09	-0.03	0.35	0.24	0.20	1.00												
Cl	-0.34	0.83	0.89	0.73	**0.91**	0.49	**0.70**	-0.33	-0.03	1.00											
SO4	-0.24	**0.94**	0.76	0.74	0.73	**0.89**	0.43	-0.24	0.10	**0.61**	1.00										
NO3	-0.26	0.62	0.59	0.61	0.55	0.60	0.41	-0.18	0.13	0.31	**0.52**	1.00									
F	0.29	-0.33	-0.42	-0.31	-0.44	-0.05	-0.33	0.52	0.38	-0.40	-0.33	-0.16	1.00								
Cr	-0.02	-0.12	0.04	0.00	0.05	-0.26	-0.11	-0.12	-0.20	-0.02	-0.07	-0.23	-0.23	1.00							
Fe	-0.11	-0.16	-0.15	-0.18	-0.14	-0.15	-0.16	0.06	0.19	-0.12	-0.19	-0.27	0.09	0.47	1.00						
Mn	-0.21	0.17	0.06	0.05	0.06	0.10	0.40	0.06	0.26	0.12	0.08	0.02	-0.28	-0.05	0.23	1.00					
Cu	-0.07	-0.24	-0.15	-0.15	-0.15	-0.25	-0.30	-0.03	0.05	-0.17	-0.24	-0.27	0.10	**0.65**	**0.90**	-0.12	1.00				
Zn	0.03	-0.40	-0.31	-0.24	-0.31	-0.39	-0.27	0.18	0.11	-0.31	-0.37	-0.38	0.18	0.44	0.63	-0.12	0.74	1.00			
As	0.31	-0.07	-0.33	-0.30	-0.33	0.24	-0.05	**0.60**	**0.54**	-0.29	0.03	-0.13	0.32	-0.21	-0.08	0.13	-0.16	0.08	1.00		
Pb	0.04	-0.30	-0.34	-0.33	-0.32	-0.18	-0.29	0.13	0.20	-0.27	-0.29	-0.30	0.22	0.22	0.89	0.05	**0.81**	**0.56**	0.06	1.00	
U	-0.04	0.23	0.10	0.19	0.07	0.35	0.19	-0.11	0.24	0.06	0.20	**0.40**	0.13	-0.27	-0.10	-0.09	-0.12	-0.25	0.05	-0.04	1.00

ACKNOWLEDGMENTS

Authors express their sincere thanks to Sh. K.C.Naik, Chairman, CGWB, Ministry of Jal Shakti, Govt of India, Faridabad for carrying out the present study and granting permission to publish this paper. Assistance provided by all the Chemist of chemical lab, CGWB, Lucknow during uranium analysis is acknowledged.

CONCLUSION

The concentration of uranium ranges from 0.38 to 54.63 µg/l with an average of 10.08 µg/l. The highest value of electrical conductivity 6720 µS/cm, nitrate 593 mg/l and uranium 54.63 µg/l were recorded at location Hanchinal is in an area of intensive agriculture and the south western part of the study area. Elevated nitrate concentration was observed where drainage system is very poor and in areas under intensive agriculture. The spatial distribution contour of nitrate is parallel to electrical conductivity contour, which indicates that the source is same. It is also noticed that the concentration of uranium is more in irrigation wells than that of domestic wells. Uranium shows some correlation with nitrate with correlation coefficient values of 0.40 and no significant correlation with other trace metals, which also indicates that the source is from anthropogenic activity. High Fluoride content in the ground water is a major problem in the district. Projects were implemented by the State Government, through Jalnirmal and Swajaldhara, schemes to provide safe drinking water to the affected villages. Further, surface water is drawn locally, from the rivers Krishna and Thungabhadra and extensively utilized for different drinking water supply schemes in the district, to meet the demands of the problematic areas. Artificial groundwater recharge techniques such as rain water harvesting can be adopted to improve the groundwater quality in the northern part the study area, where the elevated concentration of fluoride concentration was noticed. It is also important to continuously monitor the groundwater quality in this area to study the impact of uranium mineralisation.

REFERENCES

1. U.S. Environmental Protection Agency. National primary drinking water regulations: Radionuclides; final rules. Federal Register 2000; 65:76708-53.
2. Cothern CR, Lappenbusch WL. Occurrence of uranium in drinking water in the US. Health Phys 1983; 45:89-99.
3. Tadmor J. Atmospheric release of volatilized species of radioelements from coal-fired plants. Health Phys 1986; 50:270-73.
4. Spalding RF, Sackett WM. Uranium in runoff from the Gulf of Mexico distributive province: Anomalous concentrations. Science 1972; 175:629-31.
5. Lariviere D, Tomachev SY, Kochermin V, Johnson S. Uranium bone contents as an indicator of chronic environmental exposure from drinking water. J Environ Radioact 012; 121:98-103.
6. WHO, Guidelines for drinking-Water quality. Health criteria and other supporting information. Geneva. 2003
7. Bhangare RC, Tiwari M, Ajmal PY, Sahu SK, Pandit GG. Laser flourimetric analysis of uranium in water from Vishakhapatnam and estimation of health risk. Radiat Prot Environ 2013; 36:128-32.
8. Brindha.K, Elango L, Nair R.N. Spatial and temporal variation of uranium in shallow weathered rock aquifer in southern India. J. Earth. Syst. Sci. 2012; 5:911-920.
9. Bhangare RC, Tiwari M, Ajmal PY, Sahu SK, Pandit GG. Laser flourimetric analysis of uranium in water from Vishakhapatnam and estimation of health risk. Radiat Prot Environ 2013; 36:128-32.