CO-OCCURRENCE OF ARSENIC AND FLUORIDE IN GROUNDWATER IN CHANDRAPUR DISTRICT, CENTRAL INDIA

Rahul Krishna Kamble*

* Institution of Higher Learning, Research and Specialized Studies in Environmental Science
Sardar Patel College, Ganj Ward, Chandrapur, India

corresponding author: Rahul Krishna Kamble, e-mail: rahulkk41279@yahoo.com

Professional paper
Received: December 15th, 2023
Accepted: March 11th, 2024
HAE-23118
https://doi.org/10.33765/thate.15.1.4

ABSTRACT

The study was carried out to assess the co-occurrence of arsenic and fluoride in groundwater in Chandrapur district, Central India, and their possible future health risk to men, women, and children. A total of 36 groundwater sampling locations (n = 34 from hand pump and n = 2 from dug well) were identified using a systematic random sampling method. The sampling was carried out using the grab sampling method in the post-monsoon season. Various physicochemical parameters were analysed as described in APHA. The results showed that the average concentration of arsenic in the groundwater was 0.0316 mg/L (0.0158 - 0.0414 mg/L), while the average concentration of fluoride was 1.18 mg/L (0.5 - 2.32 mg/L). All groundwater samples had arsenic concentrations above the limit permissible by the Indian standard (0.01 mg/L), while they were within the desirable limit (0.05 mg/L). As for the fluoride in groundwater, 12 samples (33.33 %) were below the desirable limit by the Indian standard (< 1.0 mg/L) and five (13.88 %) were above the desirable limit (> 1.5 mg/L). The co-occurrence of arsenic and fluoride in groundwater from the study area was recorded at 47.22 % (n = 17) of the sampling locations. At 14 sampling locations (38.88 %), the concentrations of both arsenic and fluoride in groundwater were higher, while at 35 sampling locations (97.22 %) there was an elevated concentration of either arsenic or fluoride or both of these contaminants. The plausible reason for the presence of arsenic and fluoride in groundwater can be attributed to geogenic origin. The prolonged ingestion of the groundwater from the study area may pose a threat to the health of the inhabitants. The inhabitants should be aware of these contaminants, and local authorities should use these findings to identify hotspots where these contaminants have occurred. It is necessary to develop and apply low-cost, environment-friendly, and easy-to-adopt methods for the removal of arsenic in combination with fluoride.

Keywords: *arsenic, Chandrapur, fluoride, groundwater, health risk*

INTRODUCTION

Groundwater is the primary source of drinking water for more than 50 % of the world's population [1]. About 2.5 billion people depend on groundwater as the main source of daily drinking water [2]. Groundwater is sometimes the only source of drinking water for rural and small populations [3]. According to McDonald et al. [4], the only practical solution to address distributed rural water demand is groundwater mining. This is because it can be accessed from anywhere and requires less money to maintain and grow [5, 6].

According to Adimalla et al. [7], around 90 % of rural Indians are directly dependent on groundwater for drinking and irrigation. The 2011 Census of India [8] shows that hand pumps and tube wells account for 33.47 % of the total drinking water supply in India, while untreated sources account for 11.56 %, uncovered wells account for 9.44 %, and tube wells and bore wells together account for 8.47 %. Therefore, 62.5 % of the total source of drinking water in India comes from untreated sources. Rural India accounts for 76.6 % (43.63 % from hand pumps, 12.95 % from untreated sources, 11.76 % from uncovered wells, and 8.72 % from tubewells/borewells). These statistics show that untreated groundwater is the primary source of drinking water in rural India. Additionally, 20.5 % of people in rural areas are between the ages of 5 and 14, which is slightly more than the 17.3 % of people in urban areas. The population of rural children is vulnerable to exposure to toxins contained in groundwater.

Rapant and Krcmova [9] reported that contamination of drinking water with various chemicals and heavy metals released from various anthropogenic sources has become a worldwide issue. Pollution of water resource has significant effects on both the ecosystem and human health [10, 11]. According to the United Nations [12], 2.3 billion people worldwide have water-related diseases. The co-occurrence of arsenic and fluoride in groundwater at the global level is shown in Table 1. The table highlights the occurrence of these two elements in different regions of various countries around the world.

A literature review revealed that several studies were carried out on fluoride in groundwater in Chandrapur district, but no study was carried out on arsenic in groundwater and the co-occurrence of arsenic and fluoride. For this reason, this study was carried out with an aim to assess the co-occurrence of arsenic and fluoride in groundwater in Chandrapur district. The outcome of the study will add new understanding of the co-occurrence of arsenic and fluoride in groundwater in the study area. The findings will help to identify hotspots of co-occurrence of these two contaminants and their health risk for men, women, and children in the study area. In addition, it will help in the identification of suitable technologies for the removal of these contaminants.

Table 1. Co-occurrence of arsenic and fluoride in groundwater at the global level

Region, Country	Concentration of arsenic in groundwater	Concentration of fluoride in groundwater	Reference
Brahmaputra Flood Plain, India	25.1 μg/L	14 mg/L	[13]
Tripura, India	< 0.003 - 0.044 mg/L	< 0.005 - 4.8 mg/L	[14]
Bam, Iran	9.26 - 14.65 μg/L	0.91 - 1.12 mg/L	[15]
Zagros basin, Kurdistan region, Iraq	0.19 - 7.8 μg/L	0.01 - 2.1 mg/L	[16]
Latium, Central Italy	128.5 μg/L	6.1 mg/L	[17]
San Luis Potosi, Mexico	2.50 - 30.0 μg/L	0.20 - 3.5 mg/L	[18]
Inner Mongolia	0.31 - 47.0 μg/L	0.07 - 7.70 mg/L	[19]
Mexico	3.02 - 12.32 μg/L	361 - 1160 mg/L	[20]
Punjab, Pakistan	32 - 1900 μg/L	2.47 - 21.1 mg/L	[21]

Study area

Chandrapur district (19°25' to 20°45' N and 78°50' to 80°10' E) is located in the Vidarbha region of the Maharashtra state in central India, with an elevation range of 106 m to 589 m above mean sea level (amsl). The district has an area of 11364 km^2. There are 15 administrative blocks in the district. The area is rich in natural resources, including coal, limestone, iron, copper, and other minerals, as well as thick forests and fauna. The area has witnessed huge coal mines, cement factories, pulp and paper industry, and multiple thermal power plants due to the abundance of natural resources and minerals [22]. There is also the Tadoba Andhari Tiger Reserve with 93 tigers in the district [23].

The climate of the district is characterized by different climatic extremes, including hot summers (May, with temperatures up to 46 °C) and cold winters (December, with temperatures as low as 7 °C), as well as general drought throughout the year. The weather in the region can be categorised as tropical hot. During the monsoon season, the humidity is 70 %, and 20 % during the summer. The rainy season (June to September) is characterized by heavy rainfall from the southwest monsoon, with annual rainfall ranging from 1200 to 1450 mm and an average of 60 to 65 wet days. The district has an uneven distribution of rainfall. Rainfall is quite low in the Worora administrative block and increases progressively until it reaches a maximum near the Bramhapuri administrative block [22]. Geologically speaking, the Gondwana sedimentary basin includes the Chandrapur district. From Archean to more modern alluvium and laterites, the lithology of the Chandrapur area is diverse.

EXPERIMENTAL

Sampling and analysis of groundwater

For this study, groundwater sampling was done at 36 locations in the Chandrapur district (Figure 1). These locations included hand pumps (34, 94.44 %) and dug wells (2, 5.55 %). Stratified and purposeful random sampling was used. To collect groundwater samples, the grab sampling technique was used. The groundwater sampling was carried out in the post-monsoon season. Except for the field analysis parameter, the groundwater samples were immediately tested to determine physicochemical characteristics as listed in Table 2 and as described by the American Public Health Association (APHA) [24]. The glassware used in testing the physicochemical characteristics of groundwater samples was made of borosilicate, and all reagents were of Analytical Research (AR) grade (Merck). Reagent preparation was done using double-distilled water.

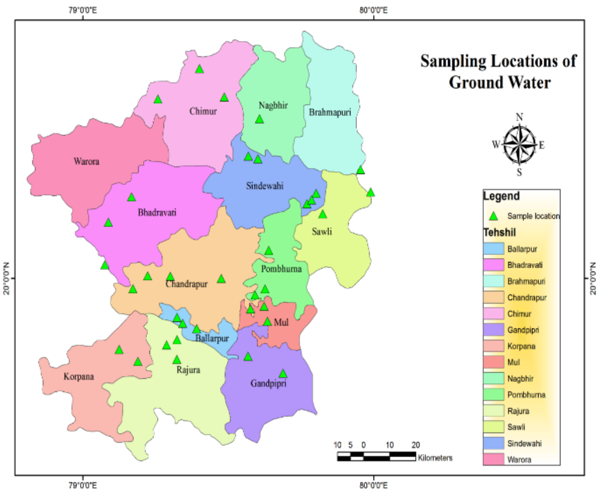

Figure 1. Groundwater sampling locations

Sample preparation

For the preservation of heavy metal samples (arsenic, in this study), concentrated HNO_3 (1 mL per 100 mL of groundwater sample, 16 N, Merck) was added on-site to another sampling container made of polyethylene (Poly lab, India). To prevent contaminants from entering the sampling container, the mouth was sealed with adhesive tape after closing with a screw cap. After acid digestion with concentrated nitric acid (HNO_3), the amounts of total heavy metal (arsenic) from the groundwater samples were determined. The samples were acid-digested in a pre-leached glass beaker on a hot plate at 95 °C and evaporated to 5 mL without boiling. Clean watch glass was used to cover glass beakers for the duration of the procedure. Metals from groundwater were completely extracted by this method. After cooling, a small quantity of 1:1 concentrated HNO_3 (16 N, Merck) was added to the digested sample, and it was then refluxed for an additional 15 minutes to dissolve any precipitate and evaporation-related residue. After cooling, the digested sample was put into a 25 mL volumetric flask and diluted with double-distilled water. Arsenic concentration in groundwater was determined using this acid-digested sample.

Sample analysis

The Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Dv 7000, Shelton, CT, USA) equipped with WinLab 32 for ICP version 4.0 software was used to analyse the presence of heavy metal [24, 25] under consideration (arsenic) at a wavelength of 193.61 nm with axial plasma view. The sample introduction unit consists of a cyclonic spray chamber and low-flow GenCone nebulizer. PerkinElmer NIST traceable quality control standard was used as the stock standard for preparing working standards.

Fluoride concentration in groundwater was determined using the 1,8-Dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6- disulfonic acid trisodium salt (SPADNS) method (a colorimetric method). The process is based on the principle that fluoride interacts with zirconium reagent SPADNS solution in an acidic environment, bleaching the "lake" (colour of SPADNS reagent) when ZrF_6 is produced. Bleaching is closely related to fluoride concentration because fluoride ions are a function of bleaching.

The anhydrous sodium fluoride (AR, Merck) was dissolved in distilled water to obtain 1.00 mL = 100.0 µg F^- of stock solution, which was further diluted to obtain a standard fluoride solution of 1.00 mL = 10.0 µg F^-. A series of standard fluoride solutions with concentrations of 0.5 mg/L, 1.0 mg//L, and 2.0 mg/L was prepared by dissolving an appropriate volume of standard fluoride solution in distilled water. The reference solution was used to set zero absorbance. At 570 nm, absorbance was determined using a Microprocessor Photo Colorimeter (Esico, Model 1312) with a light path of 10 mm at a yellow filter with transmittance at 570 nm. The standard fluoride calibration curve was used to calculate the fluoride concentrations in groundwater [25].

Table 2. Standard methods used for groundwater analysis

Parameter	Standard method	APHA (2017), Reference No.	Instrument
Temperature	Mercury thermometer	B of 2550	Gera, GTI, India
pH	Electrometric method	B of 4500-H^+	Digital pH meter, Electronics India, Model 101
Conductivity	Conductivity meter	B of 2510	Digital conductivity meter, Electronics India, Model 601
Total dissolved solids	Total dissolved solids dried at 180 ˚C	C of 2540	Hot air oven, Navyug, India
Total alkalinity	Titration method	B of 2320	NA
Hardness (Total, calcium, and magnesium)	Ethylene Diamine Tetra Acetic acid titration method	C of 2340	NA
Chloride	Argentometric method	B of 4500-Cl^-	NA
Sulphate	Turbidimetric method	E of 4500-SO_4^{2-}	Double beam UV/Visible spectrophotometer, Electronics India, Model 1372
Fluoride	SPANDS method	D of 4500-F^-	Microprocessor Photo Colorimeter, Esico, Model 1312, India
Arsenic (Total)	Inductively Coupled Plasma-OES	C of 3500-As	ICP-OES, Dv 7000, PerkinElmer, USA
Iron	Inductively Coupled Plasma-OES	C of 3500-Fe	ICP-OES, Dv 7000, PerkinElmer, USA
Manganese	Inductively Coupled Plasma-OES	C of 3500-Mn	ICP-OES, Dv 7000, PerkinElmer, USA

NA - not applicable

RESULTS AND DISCUSSION

Physicochemical parameters of groundwater from the study area are presented in Table 3. The following physical properties were determined, i.e. total alkalinity, hardness, conductivity, total dissolved solids, and temperature. Of the heavy metals, arsenic, iron, and manganese were analysed. Of the inorganic non-metallic constituents, chloride, fluoride, and sulphate were estimated. The obtained results were compared with the Indian standard for drinking water (IS 10500:2012).

Table 3. Groundwater quality

Sampling location (Water source)	Temp	pH	EC	TDS	Cl^-	T-Alkal	TH	CH	MH	F^-	As	Fe	Mn
Sonegaon (HP)	30.0	6.87	920	580	20	376	136	100	36	1.05	0.030	0.135	0.009
Telwasa (HP)	30.0	6.85	1210	770	45	348	276	272	4	1.10	0.026	0.498	0.005
Belora (HP)	30.0	7.23	960	600	34	376	132	124	8	2.00	0.026	0.155	0.031
Sagra (DW)	28.0	7.20	1690	1080	108	340	340	324	16	0.80	0.031	0.079	0.006
Pethbhansouli (HP)	28.5	6.96	1290	820	93	380	344	240	104	1.05	0.033	0.643	0.124
Bhisi (HP)	30.0	6.72	1720	1110	137	328	540	424	116	1.30	0.025	0.698	0.760
Pimpalgaon (HP)	30.0	7.18	2830	1820	272	388	644	416	228	0.90	0.029	1.464	0.007
Mowada (HP)	29.5	6.95	1500	960	105	340	364	264	100	1.10	0.023	0.163	0.003
Dongargaon (HP)	30.0	6.83	2420	1560	234	332	472	392	80	2.16	0.034	0.457	0.125
Lohara (HP)	29.0	5.74	330	200	15	108	100	84	16	0.50	0.033	0.265	0.005
Chichpalli (HP)	28.5	6.90	4710	3060	678	476	1448	548	900	1.50	0.031	0.166	0.086
Dabgaon (Tukum) (HP)	29.5	6.80	2270	1470	209	540	548	340	208	1.10	0.031	1.627	0.133
Naleshwar (HP)	31.5	6.45	1430	910	219	228	268	260	8	0.97	0.041	0.650	0.008
Karwan (HP)	30.0	7.23	960	610	51	332	212	96	116	1.76	0.030	0.184	0.033
Chikmara (HP)	30.5	7.02	1730	1110	129	392	552	304	248	1.30	0.033	0.084	0.016
Pathri (HP)	30.5	6.61	880	560	71	232	172	160	12	0.63	0.031	0.323	0.034
Gunjewahi (DW)	27.5	7.28	460	280	8	236	120	52	68	0.74	0.035	0.055	0.001
Mangali Chak (HP)	29.5	6.83	860	540	28	320	220	212	8	0.74	0.033	0.144	0.003
Govindpur (HP)	30.0	6.89	2390	1540	287	416	680	268	412	1.37	0.029	0.215	0.005
Ratnapur (HP)	31.0	6.86	1510	970	131	372	400	340	60	0.78	0.033	1.694	0.115
Antargaon (HP)	30.5	7.42	1040	670	15	440	60	32	28	2.32	0.029	0.098	0.003
Visapur (HP)	29.5	6.11	770	490	56	176	160	100	60	0.93	0.036	4.021	0.013
Ballarpur (HP)	29.5	6.02	900	570	57	160	152	120	32	0.63	0.033	3.713	0.025
Sasti (HP)	29.5	6.75	3930	2590	353	384	1360	852	508	1.10	0.029	0.202	0.005
Gowari (HP)	30.0	6.93	1700	1100	117	408	284	192	92	1.30	0.029	0.146	0.002
Arvi (HP)	30.5	6.78	1420	920	74	280	380	364	16	1.15	0.015	0.353	0.006
Awarpur (HP)	30.0	7.05	2330	1520	148	500	276	184	92	1.82	0.026	0.120	0.017
Lakhmapur (HP)	30.0	6.92	880	570	13	292	284	272	12	1.30	0.030	0.123	0.001
Kem (Tukum) (HP)	30.5	7.01	770	490	13	280	172	112	60	0.65	0.033	1.276	0.022
Ganpur (HP)	30.0	6.92	4550	3000	473	412	1104	684	456	1.10	0.033	0.157	0.002
Gondpipari (HP)	31.0	6.85	2300	1500	200	408	560	448	112	1.15	0.033	0.185	0.081
Pombhurna (HP)	30.5	7.04	1850	1200	149	432	556	300	256	1.10	0.035	0.160	0.003
Jam Tukum (HP)	30.0	6.89	2260	1480	215	436	344	268	76	1.30	0.036	0.114	0.016
Dongar Haldi (HP)	30.0	6.95	2700	1770	270	580	300	216	84	1.44	0.039	0.290	0.043
Durgapur (HP)	30.0	6.94	2923	1948	185	636	300	272	28	1.48	0.035	0.088	0.311
Morwa (HP)	29.0	7.03	2010	1310	134	332	360	240	120	0.93	0.036	0.214	0.003
IS 10500:2012	NS	6.5-8.5	NS	500	250	200	200	NS	NS	1.0	0.01	0.3	0.1

HP - Hand pump, DW - Dug well, Temp - Temperature in °C, EC - Electrical conductivity in µS/cm (10^3), TDS - Total dissolved solids, Cl^- - Chloride, T-Alkal - Total alkalinity, TH - Total hardness, CH - Calcium hardness, MH - Magnesium hardness, F - Fluoride, As - Arsenic, Fe - Iron, Mn - Manganese. All parameters are expressed in mg/L except temperature, pH, and EC. IS 10500:2012 is the drinking water standard of India

A summary of these groundwater quality parameters for various statistical tests is given in Table 4. These statistics include minimum, maximum, average, standard deviation, variance, skewness, and kurtosis. In addition, the cumulative percentiles for the respective groundwater quality parameters are also presented.

The co-occurrence of arsenic and fluoride in groundwater is shown in Table 5 (Figure 2). It can be seen from the table that the minimum concentration of arsenic in groundwater of 0.0158 mg/L was recorded in Arvi (HP). The average concentration of arsenic in the study area was 0.0316 mg/L with a standard deviation of ± 0.004. As for the fluoride in groundwater, the minimum concentration was recorded in Lohara (0.5 mg/L), and the maximum in Antargaon (2.32 mg/L). The average concentration was 1.18 mg/L with a standard deviation of ± 0.042. At the minimum concentration of arsenic in groundwater of 0.0158 mg/L (Arvi, HP), the concentration of fluoride was 1.15 mg/L, while at the maximum concentration of arsenic in groundwater of 0.0414 mg/L (Naleshwar, HP) the concentration of fluoride was 0.97 mg/L. In case of fluoride, the minimum concentration of 0.5 mg/L was recorded in Lohara (HP), where concentration of arsenic was 0.0339 mg/L. In Antargaon (HP), where the maximum fluoride concentration of 2.32 mg/L was recorded, the concentration of arsenic in the groundwater was 0.029 mg/L. Furthermore, it was observed that at 14 sampling locations (38.88 %), the concentrations of both arsenic and fluoride were higher. At 35 sampling locations (97.22 %), there was an elevated concentration of either arsenic or fluoride or both of these contaminants. Only in Pimpalgaon (HP), the concentrations of arsenic and fluoride in groundwater were lower. From these findings, it was observed that at the minimum concentration of one of the observed contaminants, the concentration of the other contaminant is higher. Thus, it can be concluded that contaminant concentrations in the groundwater are elevated, and one contaminant suppresses the concentration of the other. Thus, at any given point, inhabitants in the study area are under constant threat from them leading to health risks.

Table 4. Summary of groundwater quality

Parameter	n	Min.	Max.	Average	SD (±)	Variance	Skewness	Kurtosis	Cumulative percentiles				
									25^{th}	50^{th}	75^{th}	95^{th}	98^{th}
Temperature, °C	36	27.5	31.5	29.8	0.81	0.65	- 0.87	1.51	29	30	30	31	31
pH	36	5.74	7.42	6.86	0.33	0.11	- 1.64	3.64	6.82	6.91	7.02	7.24	7.32
EC, µS/cm (10^3)	36	330	4710	1788	1052	1107501	1.21	1.44	950	1600	2307	4085	4598
TDS, mg/L	36	200	3060	1157	695	484201	1.21	1.41	595	1025	1505	2692	3018
Chloride, mg/L	36	9.0	678	149	140	19857	1.91	4.93	49	123	210	383	534
Total alkalinity, mg/L as $CaCO_3$	36	108	636	361	110	12316	0.08	0.65	313	374	413	550	596
Total hardness, mg/L as $CaCO_3$	36	60	1448	406	320	102755	1.99	4.15	202	320	542	1168	1386
Calcium hardness, mg/L as $CaCO_3$	36	32	852	274	171	29467	1.40	2.95	151	266	340	582	734
Magnesium hardness, mg/L as $CaCO_3$	36	4.00	900	132	182	33278	2.70	8.56	25	78	117	469	625
Arsenic, mg/L	36	0.015	0.041	0.031	0.004	$2.29e^{-}5$	- 0.93	2.49	0.029	0.032	0.034	0.037	0.04
Fluoride, mg/L	36	0.500	2.32	1.18	0.42	0.18	0.90	0.74	0.92	1.1	1.31	2.04	2.20
Iron, mg/L	36	0.055	4.022	0.582	0.92	0.84	2.82	8.07	0.14	0.19	0.53	2.19	3.80
Manganese, mg/L	36	0.002	0.761	0.058	0.13	0.02	4.42	21.92	0.004	0.011	0.03	0.177	0.44

n - Number of sampling locations, Min. - minimum, Max. - maximum, SD - Standard deviation (±), EC - Electrical conductivity, TDS - Total dissolved solids

Table 5. Co-occurrence of arsenic and fluoride in groundwater

Sampling location (Water source)	As	F^-
Sonegaon (HP)	**0.0305**	**1.05**
Telwasa (HP)	0.0268	**1.10**
Belora (HP)	0.0263	**2.00**
Sagra (DW)	**0.0312**	0.80
Pethbhansouli (HP)	**0.0339**	**1.05**
Bhisi (HP)	0.0251	**1.30**
Pimpalgaon (HP)	0.0291	0.90
Mowada (HP)	0.0230	**1.10**
Dongargaon (HP)	**0.0345**	**2.16**
Lohara (HP)	**0.0339**	0.50
Chichpalli (HP)	**0.0312**	**1.50**
Dabgaon (Tukum) (HP)	**0.0314**	**1.10**
Naleshwar (HP)	**0.0414**	0.97
Karwan (HP)	**0.0302**	**1.76**
Chikmara (HP)	**0.0334**	**1.30**
Pathri (HP)	**0.0317**	0.63
Gunjewahi (DW)	**0.0352**	0.74
Mangali Chak (HP)	**0.0334**	0.74
Govindpur (HP)	0.0295	**1.37**
Ratnapur (HP)	**0.0337**	0.78
Antargaon (HP)	0.0290	**2.32**
Visapur (HP)	**0.0366**	0.93
Ballarpur (HP)	**0.0332**	0.63
Sasti (HP)	0.0295	**1.10**
Gowari (HP)	0.0290	**1.30**
Arvi (HP)	0.0158	**1.15**
Awarpur (HP)	0.0265	**1.82**
Lakhmapur (HP)	**0.0308**	**1.30**
Kem (Tukum) (HP)	**0.0335**	0.65
Ganpur (HP)	**0.0330**	**1.10**
Gondpipari (HP)	**0.0336**	**1.15**
Pombhurna (HP)	**0.0358**	**1.10**
Jam Tukum (HP)	**0.0365**	**1.30**
Dongar Haldi (HP)	**0.0396**	**1.44**
Durgapur (HP)	**0.0355**	**1.48**
Morwa (HP)	**0.0367**	0.93
Minimum	**0.0158**	**0.5**
Maximum	**0.0414**	**2.32**
Average	**0.0316**	**1.18**
Standard deviation (±)	**0.004**	**0.42**

Values are expressed in mg/L and bold indicates higher concentration

A thematic map showing the co-occurrence of arsenic and fluoride in groundwater is presented for three ranges of fluoride concentration in groundwater (Figure 2). The first range was from 0.50 to 1.00 mg/L with 12 (33.33 %) sampling locations. This range of fluoride concentration in groundwater can cause dental caries. The second range was from 1.001 to 1.50 mg/L with 19 (52.77 %) sampling locations. This range is considered safe according to the Indian drinking water standard (IS 10500:2012). Five (13.88 %) sampling locations that had fluoride concentrations in groundwater from 1.501 to 2.32 mg/L are shown as the third concentration range. Two concentration ranges were identified for arsenic in groundwater. A total of 11 (30.55 %) sampling locations had arsenic concentrations in groundwater in the range of 0.0158 - 0.030 mg/L. The remaining sampling locations (n = 25, 69.44 %) had arsenic concentrations in groundwater in the range of 0.0301 - 0.0414 mg/L. It can be seen from Figure 2 that the concentrations of arsenic and fluoride in groundwater are evenly distributed in the study area.

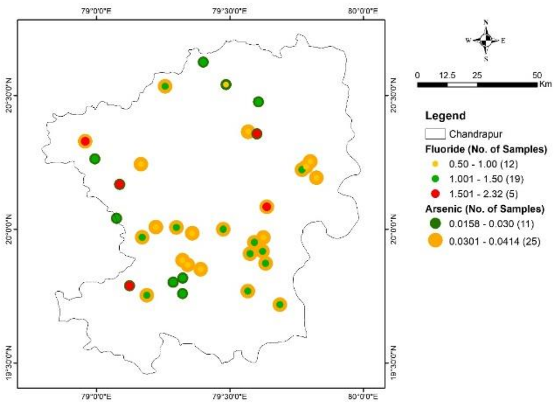

Figure 2. Co-occurrence of arsenic and fluoride in the study area

A statistical summary of the co-occurrence of arsenic and fluoride in groundwater in the study area is presented in Table 6.

It can be seen from the Table 6 that fluoride concentration in groundwater below (< 1.0 mg/L) and above (> 1.5 mg/L) the Indian drinking water standard for fluoride was recorded at 12 (33.33 %) and five (13.88 %) sampling locations, respectively. At these sampling locations, the concentration of arsenic in groundwater was above the desirable limit (0.01 mg/L) according to the standard. Thus, the co-occurrence of arsenic and fluoride in groundwater in the study area was in 47.22 % (n = 17). The concentration of arsenic in groundwater in the range of 0.01 - 0.030 mg/L was observed at 11 (30.55 %) sampling locations, while at 69.44 % (n = 25) the concentration was 0.031 - 0.0414 mg/L.

Table 6. Statical summary of co-occurrence of arsenic and fluoride in groundwater

	N (%)		N (%)
Fluoride concentration within the desirable limit by the Indian standard for drinking water (1.0 - 1.5 mg/L)	19 (52.77 %)	Arsenic concentration within the desirable limit by the Indian standard for drinking water (0.01 mg/L)	Absent
Fluoride concentration below the desirable limit by the Indian standard for drinking water (< 1.0 mg/L)	12 (33.33 %)	Arsenic concentration between 0.01 - 0.030 mg/L	11 (30.55 %)
Fluoride concentration above the desirable limit by the Indian standard for drinking water (> 1.5 mg/L)	5 (13.88 %)	Arsenic concentration between 0.031 - 0.0414 mg/L	25 (69.44 %)
Co-occurrence of arsenic and fluoride in groundwater 17 (47.22 %)			

The concentration of fluoride in groundwater within the desirable limit by the Indian drinking water standard (1.0 - 1.5 mg/L) was recorded at 19 (52.77 %) sampling locations, with an average value of 1.22 mg/L. At these sampling locations, arsenic in groundwater ranged from 0.0158 - 0.0396 mg/L, with an average value of 0.0307 mg/L. This concentration of arsenic in groundwater was above the desirable limit of the Indian standard. The concentration of fluoride below the desirable limit of Indian drinking water standards (< 1.0 mg/L) was recorded at 12 (33.33 %) sampling locations, with an average value of 0.766 mg/L. Within these fluoride ranges, the concentration of arsenic in groundwater ranged from 0.029 - 0.041 mg/L, with an average value of 0.0341 mg/L. The concentration of fluoride in groundwater above the desirable limit by the Indian drinking water standard was observed at 5 (13.88 %) sampling locations, with an average value of 2.01 mg/L. In such conditions, the concentration of arsenic in groundwater ranged from 0.0263 - 0.0345 mg/L, with an average value of 0.0293 mg/L. At all the sampling locations, the concentration of arsenic in groundwater was above the desirable limit (0.01 mg/L) according to the Indian standard, but was within the permissible limit (0.05 mg/L). Thus, co-occurrence of arsenic and fluoride in groundwater in the study area was found at 17 (47.22 %) sampling locations, which represents the risk of dental or skeletal fluorosis and health problems related to arsenic. The co-occurrence of arsenic and fluoride in groundwater in the study area was distributed throughout the district. The probable reason for their presence can be attributed to geogenic origin.

Chronic exposure to arsenic in drinking water, even at low to moderate levels, may be a risk factor for gallbladder cancer, according to two-year research conducted in major tertiary care hospital receiving patients from various parts of Assam and Bihar in India [26]. Inhabitants from the study area may be at risk of developing gallbladder cancer due to consumption of arsenic-contaminated groundwater.

Residents from Inner Mongolia who consume groundwater may be concerned about F^- and As. No relationship was observed between well depth or any geographical variation and groundwater quality [19]. The results obtained from the study area are partially in accordance with the results stated in the study.

Farooqi et al. [27] reported that fluoride and arsenic contamination occurred in the oxidizing and alkaline conditions of the groundwater. These findings agree with the findings reported from the study area. In the study area, 47.22 % (n = 17) of sampling locations had co-occurrence of arsenic and fluoride, while in the Dharmanagar region of Tripura, India, it was observed in 59 % of the analysed samples [14]. Therefore, from these findings, it can be stated that the co-occurrence of fluoride and arsenic is a common phenomenon and must be investigated in areas contaminated with either of them. A strong positive correlation (in scatterplot) was observed between arsenic and fluoride in aquifers with arid, oxidizing conditions, particularly in the Yuncheng Basin of northern China [28] and in Chihuahua, Mexico [29].

CONCLUSION

The obtained result in this study indicates the presence of arsenic and fluoride in groundwater in the study area. The findings showed that the average concentration of arsenic in groundwater was 0.0316 mg/L (0.0158 - 0.0414 mg/L), while the average concentration of fluoride was 1.18 mg/L (0.5 - 2.32 mg/L). All groundwater samples had arsenic concentrations above the limit permissible by the Indian drinking water standard (0.01 mg/L), but within the desirable limit (0.05 mg/L). As for the fluoride in groundwater, 12 samples (33.33 %) were below the desirable limit of the Indian standard (< 1.0 mg/L) and five (13.88 %) above the desirable limit (> 1.5 mg/L). The co-occurrence of both of these elements was observed at 47.22 % (n = 17) of the sampling locations. The probable reason for the presence of arsenic and fluoride in groundwater can be attributed to geogenic origin. Long-term consumption of groundwater from the study area can lead to diseases among the inhabitants. The local authorities should use the findings obtained in this study to identify vulnerable locations that may pose significant health risks. In case of unavailability of alternative sources of drinking water, local authorities should make available a source of drinking water through tankers. Furthermore, residents should be introduced to the cheap method of defluoridation (Tulsi, *Ocimum sanctum*) [30]. In addition, arsenic removal methods need to be developed that can be combined with fluoride removal options. Future studies about cases of cancer occurrence and long-term effects on the health of children and adults will help decision-making authorities to ensure sustainable health and sustainable living.

REFERENCES

[1] A. Fry, Water Facts and Trends, World Business Council for Sustainable Development, 2005.

[2] World Water Assessment Programme (WWAP), The United Nations World Water Development Report 2015, Water for a Sustainable World, Paris, UNESCO, 2015.

[3] H. Häni, The analysis of inorganic and organic pollutants in soil with special regard to their bioavailability, International Journal of Environmental Analytical Chemistry 39(1990) 2, 197-208. https://doi.org/10.1080/03067319008027697

[4] A. MacDonald, J. Davies, R. Calow, J. Chilton, Developing Groundwater: A Guide to Rural Water Supply, ITDG Publishing, United Kingdom, 2005.

[5] E. Bresline, Sustainable Water Supply in Developing Countries, Geological Society of America, Paper No. 194-1, USA, 2007.

[6] O. Habila, Groundwater and the Millennium Development Goals, Proceedings Groundwater and Poverty Reduction in Africa, International Association of Hydrogeologist, United Kingdom, 2005.

[7] N. Adimalla, R. Manne, Y. Zhang, P. Xu, H. Qian, Evaluation of groundwater quality and its suitability for drinking purposes in semi-arid region of Southern India: An application of GIS, Geocarto International 37(2022) 25, 10843-10854. https://doi.org/10.1080/10106049.2022.2040603

[8] Census of India 2011, Chandrapur district profile, Directorate of Census Operation, Maharashtra, Ministry of Home Affairs, Government of India, India, 2011.

[9] S. Rapant, K. Krčmová, Health risk assessment maps for arsenic groundwater content, application of national geochemical databases, Environmental Geochemistry and Health 29(2007) 2, 131-141. https://doi.org/10.1007/s10653-006-9072-y

[10] E. Emmanuel, M.G. Pierre, Y. Perrodin, Groundwater contamination by microbiological and chemical substances released from hospital wastewater and health risk assessment for drinking water

consumers, Environment International 35(2009) 4, 718-726. https://doi.org/10.1016/j.envint.2009.01.011

[11] S. Muhammad, M.T. Shah, S. Khan, Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan, Microchemical Journal 98(2011) 2, 334-343. https://doi.org/10.1016/j.microc.2011.03.003

[12] United Nations Commission for Sustainable Development, Comprehensive assessment of freshwater resources of the world, USA, 1997.

[13] N. Das, A. Das, K.P. Sarma, M. Kumar, Provenance, prevalence and health perspective of co-occurrences of arsenic, fluoride and uranium in the aquifers of the Brahmaputra River floodplain, Chemosphere 194(2018), 755-772. https://doi.org/10.1016/j.chemosphere.2017.12.021

[14] P. Bhattacharya, S. Adhikari, A.C. Samal, R. Das, D. Dey, A. Deb, S. Ahmed, J. Hussein, A. De, Antara Das, M. Jordar, A.K. Panigrahi, T. Roychowdhury, S.C. Santra, Health risk assessment of co-occurrence of toxic fluoride and arsenic in groundwater of Dharmanagar region, North Tripura (India), Groundwater for Sustainable Development 11(2020), Article ID: 100430. https://doi.org/10.1016/j.gsd.2020.100430

[15] A. Toolabi, Z. Bonyadi, M. Paydar, A.A. Najafpoor, B. Ramavandi, Spatial distribution, occurrence, and health risk assessment of nitrate, fluoride, and arsenic in Bam groundwater resource, Iran, Groundwater for Sustainable Development 12(2021), Article ID: 100543. https://doi.org/10.1016/j.gsd.2020.100543

[16] O. Mustafa, R. Mohmmud, O. Sracek, S. Seeyan, Geogenic sources of arsenic and fluoride in groundwater: Examples from the Zagros basin, the Kurdistan region of Iraq, Water 15(2023) 11, Article ID: 1981. https://doi.org/10.3390/w15111981

[17] D. Parrone, S. Ghergo, E. Frollini, D. Rossi, E. Preziosi, Arsenic-fluoride co-contamination in groundwater: Background and anomalies in a volcanic-sedimentary aquifer in central Italy, Journal of Geochemical Exploration 217(2020), Article ID: 106590. https://doi.org/10.1016/j.gexplo.2020.106590

[18] J.C. Fernández-Macias, A.C. Ochoa-Martínez, S.T. Orta-García, J.A. Varela-Silva, I.N. Pérez-Maldonado, Probabilistic human health risk assessment associated with fluoride and arsenic co-occurrence in drinking water from the metropolitan area of San Luis Potosí, Mexico, Environmental Monitoring and Assessment 192(2020), Article number: 712. https://doi.org/10.1007/s10661-020-08675-7

[19] K. Nakazawa, O. Nagafuchi, U. Otede, J.G. Chen, K. Kanefuji, K. Shinozuka, Risk assessment of fluoride and arsenic in groundwater and a scenario analysis for reducing exposure in Inner Mongolia, RSC Advance 10(2020) 31, 18296-18304. https://doi.org/10.1039/D0RA00435A

[20] M.T. Alarcón-Herrera, D.A. Martin-Alarcon, M. Gutiérrez, L. Reynoso-Cuevas, A. Martín-Domínguez, M.A. Olmos-Márquez, J. Bundschuh, Co-occurrence, possible origin, and health-risk assessment of arsenic and fluoride in drinking water sources in Mexico: Geographical data visualization, Science of the Total Environment 698(2020), Article ID: 134168. https://doi.org/10.1016/j.scitotenv.2019.134168

[21] A. Farooqi, H. Masuda, M. Kusakabe, M. Naseem, N. Firdous, Distribution of highly arsenic and fluoride contaminated groundwater from East Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle, Geochemical Journal 41(2007) 4,

213-234. https://doi.org/10.2343/geochemj.41.213

[22] Central Ground Water Board (CGWB), Ground Water Information, Chandrapur district, Maharashtra, Ministry of Water Resources, Government of India, Central Ground Water Board, Central Region, India, 2009.

[23] Times of India (TOI), Tadoba Tiger Count Rising, Experts Fear Reserve on Cusp of Saturation, November 10, 2023, India, 2023.

[24] Standard Methods for the Examination of Water and Wastewater, 23rd Edition, eds.: R.B. Baird, A.D. Eaton, E.W. Rice, American Public Health Association, American Water Works Association, Water Environment Federation, 2017.

[25] Manual on Water and Wastewater Analysis, National Environmental Engineering Research Institute, Nagpur, India. 1998.

[26] A. Kumar, M. Ali, V. Raj, A. Kumari, M. Rachamalla, S. Niyogi, D. Kumar, A. Sharma, A. Saxena, G. Panjawani, P. Jain, A. Vidyarthi, N. Kumar, M. Kumar, P. Kumar Niraj, Md. Samiur Rahman, A. Bishwapriya, R. Kumar, M. Sakamoto, S. Kumar, M. Singh, A. Kumar Ghosh, Arsenic causing gallbladder cancer diseases in Bihar, Scientific Reports 13(2023), Article number: 4259. https://doi.org/10.1038/s41598-023-30898-0

[27] A. Farooqi, H. Masuda, N. Firdous, Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources, Environmental Pollution 145(2007) 3, 839-849. https://doi.org/10.1016/j.envpol.2006.05.007

[28] A.M. Khair, C. Li, Q. Hu, X. Gao, Y. Wanga, Fluoride and arsenic hydrogeochemistry of groundwater at Yuncheng basin, Northern China, Geochemistry International 52(2014) 10, 868-881. https://doi.org/10.1134/S0016702914100024

[29] V.M. Reyes-Gómez, M.T. Alarcón-Herrera, M. Gutiérrez, D. Núñez López, Fluoride and arsenic in an alluvial aquifer system in Chihuahua, Mexico: Contaminant levels, potential sources, and co-occurrence, Water, Air, Soil & Pollution 224(2013) 2, Article number: 1433. https://doi.org/10.1007/s11270-013-1433-4

[30] R.D. Amgaokar, R.K. Kamble, Defluoridation of water using Basil (*Ocimum sanctum* Linn.) leaves and its stem, Indian Journal of Environmental Protection 32(2012) 1, 37-44.