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Assessment of Arsenic and Fluoride in Ground Waters of Sedam and Shahabad Regions of Gulbarga District

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Abstract. The present study has been carried out to assess arsenic and fluoride concentration in groundwater from June 2014 to May 2015. Every month water samples were collected and analyzed according to APHA. All the Physico-chemical parameters of the groundwater of study area are within the permissible limit. Heavy metal analysis was carried out through AAS. Data is subjected for statistical analysis.

KeyWords: Kalaburagi, physico-chemical, heavy metals, groundwater, India.

1 Introduction

Arsenic ranks 20th in abundance among the elements in the earth crust. Arsenic is introduced into environment from the natural sources (e.g. volcanic activity and weathering of minerals) and from anthropogenic activity (e.g. oar smelting, burning if coal, pesticide use) and the ratio between the two type of sources has been estimated at 60:40(1). Levels and speciation of arsenic in drinking water (including natural mineral and other bottled water) is a matter of concern in many countries as arsenic level exceeding 200 mg/l have been reported (6). Several reports in the literature of similar or even higher arsenic concentration level in well and in ground water reflects this problem.

The most toxic forms of arsenic food and water are inorganic (III) and (V) (9). And the International Agency for Research for Cancer (IARC) has classified in organic arsenic a human carcinogen. (10). The inorganic arsenic trioxide has a well known history as a poisonous compound often used in the cases of homicide.

The provisional tolerable daily intake of inorganic via food and water was established by WHO at 2 µg/kg body weight in 1983(14). And later changed to the equivalent provisional tolerable week intake (PTWI) at 15 µg/kg body weight in 1988 (15). The epidemiological data used for this risk assessment refer too inorganic arsenic in drinking water. However, a similar recommendation for organic arsenic species in food could not be established by WHO due to lack of appropriate toxicological data. This recommendation has been repeated and substantiated by the US agency for toxic substance and disease registry (16). The recommended WHO guidelines level for inorganic in drinking water is 10 µg/l (17) and according to these guidelines 20 % of the PTWI is allocated to drinking water.

In contrast to its toxicity, the possible essential role of arsenic (18) is a matter of controversy (19). The underlying animal experiments, however, do not allow for any conclusions regarding a possible essential function of arsenic to human.

Epidemiological studies have shown human health effects after long term oral exposure to inorganic arsenic species in drinking water from wells in areas where the soil is geochemically rich in arsenic. The long term daily intake of organic at 10-50 µg/kg body weight contributed to vascular problems which may ultimately lead to necrosis and gangrene of hands and feet. (Black foot disease) (16). The united states Environmental protection Agency (USEPA) has estimated the excess skin cancer risk from lifetime exposure to arsenic via water (21) containing 1 µg/l of inorganic arsenic at 7X10-5. Therefore drinking water concentration of arsenic exceeding this level is a matter of concern. At the 10 µg/l WHO guidelines level of arsenic in drinking water, the estimated lifetime risk for arsenic induced skin cancer has been estimated (17) at 6x10-4.

Arsenic is introduced into soil and groundwater during weathering of rocks and minerals followed by subsequent leading and runoff. It can also be introduced into soil and groundwater from anthropogenic sources. Many factors control arsenic concentration and transport in groundwater which include Redox

potential (Eh), adsorption/desorption, precipitation/dissolution, Arsenic speciation, pH presence and concentration of competing ions biological transformation etc.

Therefore, rigorous geochemical investigation for adequate understanding of arsenic geochemistry under different hydro-geological and geo-environmental conditions of aquifers is essentially required for evolving sustaining solution.

Fluoride is the 13th most abundant element on earth. It cannot exist outside a controlled environment without combining with outer substance to become fluoride. Three main anthropogenic sources were identified as fertilizers, combusted coal and industrial waste with phosphate fertilizer being the most significant source of fluoride. 13. There are ionizable, non-ionizable organic and inorganic fluoride. Fluoride is probably an essential element for animals and humans. Low concentration provides protection against dental caries, especially children. Minimum concentration of fluoride in drinking water required to produce protective effect is approximately 0.5 µg/l.

2 Methodology

Gulbarga district lies in the northern plains of Karnataka state, which covers an area of 16244 sq. km. and lies between 16^0-11' and 17^0-19' N latitude and 76-54' E longitude, with average rainfall of 35-56 mm and maximum and minimum temperature being 45 ^{0}C and 12 ^{0}C respectively. NEM, SWM and summer seasons of 12 months. These water samples collected were subjected to chemical analysis as per standard methods (APHA, 1989) and other physical-chemical parameters and statistical analysis of the data presented.

The samples one liter were filtered in the laboratory and preserved by adding 5 ml of concentration HNO3 by which pH was lowered to 1-2 preserved samples were determined by using AAS (iCE3XXXCO93300198Vl.30). The procedure followed to analyze the heavy metals concentrations were taken from standard methods (APHA).

3 Objectives and Study Area

1. To analyze the physic-chemical characteristic of water sample with special emphasis on fluoride and arsenic contents.
2. To assess the suitability of water for human consumption and irrigation.
3. To find out the sources of pollution.
4. To create awareness about health hazards from fluoride and arsenic content in drinking water.
5. Analysis of heavy metals in the groundwater and surface water.

The study areas are two regions of Gulbarga District. One Sedam is taluk head quarter which falls under 17. 1784^O N and 77.2873^O E which is 80 km away from Gulbarga city and Shahabad falls under 17.130318 N Latitude and 76.943504 E Longitude 30 km away for Gulbarga city.

4 Results

Table 1. Monthly average values of four bore wells physico-chemical parameters of sedam station 1

Month/ Parameters	At. Temp.	Water. Temp.	PH	DO	Total Hardness	Ca	Mg	Chloride	Alkalinity	NO3	PO4	Fluoride
June -2014	32	22	7.1	2.1	480	254	192	400	350	67	0.78	1.2
July	31	22	7.1	2.1	496	260	202	426	355	65	0.76	1.3
August	30	22	7.1	2.2	550	282	156	446	380	85	0.82	1.4
September	30	22	7.1	2.3	572	264	152	452	365	68	0.83	1.5
October	29	22	7.2	2.4	590	322	186	496	425	78	0.95	1.6
November	28	22	7.2	2.3	628	312	198	398	415	72	1.0	1.4
December	26	22	7.3	2.3	652	356	212	345	425	88	1.12	1.3
January-2015	27	22	7.1	2.1	644	352	202	386	420	70	1.15	1.4

February	33	23	7.1	2.0	610	304	188	389	335	66	0.62	1.1
March	37	22	7.1	1.8	482	298	183	402	310	54	0.60	1.1
April	38	23	7.1	1.9	480	286	192	363	325	52	0.63	1.1
May	39	23	7.1	1.8	496	244	182	365	285	50	0.62	1.2

Table 2. Seasonal average values of arsenic and other heavy metals parameters of sedam station 1.

Seasons/Heavy metals	Cu	Fe	Zn	Mn	Cd	Si	V	Ti	Cr	Mo	As
SWM	0.078	0.2	0.018	0.05	0.030	7.18	0.28	2.52	0.12	0.152	0.211
NEM	0.009	0.21	0.18	0.07	0.076	6.98	0.72	2.02	0.11	0.192	0.22
SUMMER	0.007	0.21	0.036	0.09	0.072	9.12	0.86	2.10	0.13	0.210	0.23

Table 3. Monthly average values of four bore wells physico-chemical parameters of sedam station 2.

Month/ Parameters	At. Temp.	Water Temp.	PH	DO	Total Hardness	Ca	Mg.	Chloride	Alkalinity	NO3	PO4	Fluoride
June -2014	32	22	7.1	2.4	510	192	110	380	295	78	0.82	0.12
July	31	22	7.2	2.4	546	186	132	376	310	62	0.78	0.98
August	30	22	7.2	2.3	562	232	136	356	305	58	0.82	0.96
September	30	22	7.3	2.5	568	244	138	350	355	62	0.86	1.6
October	29	22	7.3	2.6	620	258	150	450	375	78	0.96	1.42
November	28	22	7.3	2.5	610	286	148	456	365	72	0.98	1.58
December	26	22	7.3	2.5	598	268	132	396	350	86	0.92	1.66
January-2015	27	22	7.3	2.4	572	222	102	390	355	98	1.12	1.52
February	33	22	7.4	2.2	510	232	108	320	330	96	1.02	0.9
March	37	23	7.3	2.1	566	208	98	356	315	88	68	0.9
April	38	23	7.4	2.1	570	210	92	348	310	74	72	0.9
May	39	24	7.4	2.2	532	212	102	338	310	72	76	0.8

Table 4. Seasonal average values of arsenic and other heavy metals parameters of sedam station 2.

Seasons/Heavy metals	Cu	Fe	Zn	Mn	Cd	Si	V	Ti	Cr	Mo	As
SWM	0.088	0.21	0.020	0.09	0.042	8.12	0.32	3.32	0.18	0.16	0.32
NEM	0.092	0.232	0.019	0.08	0.092	7.92	0.56	3.15	0.19	0.18	0.29
SUMMER	0.008	0.23	0.036	0.09	0.12	8.12	0.88	2.90	0.21	0.20	0.31

Table 5. Monthly average values of physico-chemical parameters of shahabad station 1

Month/ Parameters	At. Temp.	Water Temp.	pH	DO	Total Hardness	Ca	Mg.	Chloride	Alkalinity	NO3	PO4	Fluoride
June -2014	32	22	7.9	2.5	660	302	169	335	310	78	0.7	1.5
July	32	23	7.4	2.6	680	272	157	310	325	58	0.9	1.6
August	33	22	7.3	2.5	696	296	180	320	355	56	0.92	1.5
September	26	22	7.4	2.6	710	318	200	365	435	85	0.92	1.7
October	30	22	7.4	2.8	738	350	212	385	425	96	1.4	1.7
November	29	21	7.4	2.8	750	366	210	360	465	88	1.62	1.8
December	31	21	7.3	2.8	815	354	212	355	495	78	1.58	1.9
January-2015	32	22	7.3	2.8	802	332	214	355	450	110	1.68	1.8
February	33	23	7.4	2.8	762	312	126	320	430	102	1.52	1.8
March	35	23	7.4	2.2	652	300	130	225	420	98	0.8	1.8

April	37	23	7.4	2.2	610	298	144	235	360	92	0.9	1.6
May	39	23	7.4	2.3	650	272	123	215	350	86	0.8	1.5

Table 6. Seasonal average values of arsenic and other heavy metals parameters of shahabad - station 1.

Seasons/Heavy metals	Cu	Fe	Zn	Mn	Cd	Si	V	Ti	Cr	Mo	As
SWM	0.0054	0.125	0.014	0.022	0.019	22.3	0.611	1.446	0.084	0.156	0.237
NEM	0.0062	0.152	0.021	0.028	0.022	25.5	0.696	1.565	0.089	0.168	0.288
SUMMER	0.0071	0.182	0.039	0.036	0.028	35.6	0.824	1.889	0.098	0.201	0.356

Table 7. Monthly average values of physico-chemical parameters of shahabad station 2

Month/ Parameters	At. Temp.	Water Temp.	pH	DO	Total Hardness	Ca	Mg.	Chloride	Alkalinity	NO3	PO4	Fluoride
June -2014	32	21	7.6	2.6	552	186	124	285	265	66	096	1.6
July	32	21	7.5	2.6	574	250	112	295	285	62	0.86	1.8
August	33	22	7.5	2.7	598	236	120	280	305	62	0.72	1.9
September	26	22	7.4	2.6	642	296	122	305	315	72	0.68	1.6
October	30	23	7.5	2.5	652	280	132	315	355	76	0.98	1.7
November	29	22	7.3	2.7	650	322	156	320	360	82	1.02	1.8
December	31	21	7.3	2.6	664	328	158	325	320	96	1.22	1.9
January-2015	32	21	7.3	2.6	658	282	162	285	305	84	1.28	1.9
February	33	23	7.4	2.6	540	296	158	270	295	72	1.66	1.8
March	35	23	7.5	2.5	528	232	132	265	250	78	1.26	1.6
April	37	23	7.5	2.3	534	220	132	255	255	68	0.66	1.5
May	39	23	7.5	2.3	520	196	120	250	235	64	0.68	1.6

Table 8. Seasonal average values of arsenic and other heavy metals parameters of shahabad - station 2.

Seasons/Heavy metals	Cu	Fe	Zn	Mn	Cd	Si	V	Ti	Cr	Mo	As
SWM	0.0054	0.1104	0.016	0.022	0.025	6.80	0.66	1.67	0.088	0.130	0.02
NEM	0.058	0.1189	0.018	0.065	0.056	7.01	0.72	1.68	0.089	0.156	0.02
SUMMER	0.0065	0.1212	0.026	0.097	0.068	8.62	0.86	1.98	0.097	0.187	0.03

All the physico –chemical parameters of the groundwater Sedam and Shahabad regions of Gulbarga district have been analyzed and presented in the table No. 1 to 8. The values of four borewells of Sedam region are consolidated (in Table No. 1 to 4) depicting physic-chemical and heavy metals values of the Sedam town. The atmospheric temperature and water temperature are recorded maximum 39^{o} C in May and 23^{o}C in Summer season. Similarly minimum atmospheric temperature recorded 26 ^{o}C in January and water temperature 22 ^{o}C in Northeast Monson and Southwest Monson Seasons respectively. The pH values were highest 7.3 and 7.4 during the month of December and April and May. Similarly lowest 7.1 and 7.2 in Southwest and Summer monsoon Season respectively. The total hardness, calcium hardness and magnesium hardness values were noticed maximum 652 mg/l., 352 mg/l. and 212mg/l in station I and 650 mg/l , 250 mg/l and 150 mg/l in October Station 2 respectively . The DO values ranged from maximum 2.4mg/l. in October and minimum 1.8 mg/l. in March and May in Station 1 and highest 2.6 mg/l in October and lowest 2.1 mg/l in March in Station II respectively. Likewise, total alkalinity values were highest 425 mg/l. during October and December and lowest 285 mg/l. in May. Phosphate values were much higher 1.15 mg/l. in January and lower 0.60 mg/l. in March in station I likewise in station 2 minimum and maximum values ranged between 68 mg/l in March and 1.12 mg/l in January respectively. Similarly, the fluoride values recorded highest 1.6 mg/l. in October and lowest 1.1 mg/l. in April in station 1 and lowest values 1.66 mg/l in December and 0.8 mg/l in May.

The heavy metals were analyzed and average values of seasonal results are depicted in Table No. 2.

The Cu values of the station-1 recorded highest 0.078 mg/l. during South West Monsoon (SWM) and Northeast Monsoon Season (NEM) and lowest values 0.007 mg/l. recorded during summer. The Fe, Zn and Cd higher concentrations are noticed maximum 0.21 mg/l, 0.018 mg/l and 0.076 in NEM season and lowest values noticed 0.2 mg/l, 0.018 mg/l and 0.030 mg/l SWM respectively. The Mn, Si, V, Cr, Mo and Arsenic concentrations were recorded highest 0.09 mg/l, 9.12 mg/l,0.86 mg/l, 0.13, 0.210 and 0.23 mg/l in Summer Season and lowest values recorded 0.05 mg/l, 6.98 mg/l 2.02 mg/l & 2.02 mg/l respectively. The values of V, Mo and As were maximum 0.28 mg/l, 0.152 mg/l and 0.211 mg/l in SWM season and Si, Ti Cr were maximum in 6.98 mg/l, 0.02 mg/l and 0.11 mg/l in NEM season respectively.

The seasonal average values of heavy metals of Sedam station 2 were shown in table 4. The highest values of Cu and Fe recorded highest 0.092 mg/l and 0.232 mg/l in NEM season and lowest values noticed 0.008 mg/l in summer 0.09 during SWM season respectively. The maximum concentrations of the Zn, Mn, Cd, Si, V Cr and Mo recorded 0.036 mg/l, 0.09 mg/l, 0.12 mg/l, 8.12 mg/l, 0.88 mg/l 0.21 mg/l and 0.20 mg/l in summer season and lowest concentrations noticed 0.019 mg/l, 0.08 mg/l,7.92 mg/l, in NEM season and 0.042 mg/l, 0.32 mg/l, 0.18 mg/l and 0.16 in SWM season respectively. The As and Ti values ranged highest 0.32 mg/l and 3.32 mg/l in SWM season and lowest 0.29 mg/l and 2.90 mg/l. summer season.

In the present study both the stations of Shahabad regions the seasonal average values of the Physico-chemical parameters are presented in Table No. 5 and Table No. 7 value of the atmospheric temperature and water temperature were highest 39 °C in may and Atmospheric temperature lowest recorded 26 °C in the month of September. Water temperature recorded is 21 °C highest in summer and lowest in winter season throughout the study period. The pH values maximum are 7.9 and 7.6 in June and minimum 7.3 in both station I and II in December and January respectively. Total hardness maximum and minimum concentrations ranged between 815 mg/l. to 610 mg/l. in December and April in station-I and highest 644 mg/l. in December and lowest 520 mg/l. in May respectively. Calcium hardness recorded maximum 366 mg/l. in November and minimum 272 mg/l. in the months of May and July, similarly in station II recorded 386 mg/l. in December and lowest 186 mg/l. in June respectively. Magnesium hardness noticed highest 214 mg/l. during the month of January and lowest values noticed 123 mg/l. in May in station II in January and 112 in July. Chloride highest and lowest concentrations ranged between 385 mg/l. and 215 mg/l. during the months of October and May respectively, similarly in station II highest value 325 mg.l. in December and lowest value 250 mg/l. in May. Total alkalinity and Fluoride concentrations were recorded maximum 495 mg/l. and 1.9 mg/l. in December and minimum 310 mg/l. and 1.5 mg/l. in June respectively, likewise TA recorded 360 mg/l in November and lowest 235 mg/l. in May, Fluoride 1.9 mg/l. in August and lowest 1.5 mg/l. in April respectively. Phosphate concentrations were recorded maximum 1.68 mg/l. in January and minimum 0.8 mg/l. in June. Similarly 1.66 in February and lowest 0.66 mg/l. April NO3 is highest 110 mg/l. January and lowest 56 mg/l. in August 96 mg/l. in the month of December and lowest 62 mg/l. in August.

5 Discussion

The temperature is one of the physical parameters which are directly related with chemical reaction in the water and biochemical reaction in the living organisms. It is very important in determination of solubility of dissolved oxygen CO_2 and determination of pH and conductivity. The higher air and water temperature observed during summer and SWM (South West Monsoon) Season. It must be due to the presence of cloudy weather according to Uyeno (1966). Similar observations are made by Baswaraj *et al.,*

Alkalinity of the water is its capacity to neutralize a strong and is characterized by the presence of hydroxyl ions capable of combining with hydrogen ion. Most of the alkalinity in heated water is formed due to dissolution of CO_2 in water. In the present study higher concentration of alkalinity observed in NEM season and lower values in Summer season. The similar observations are made by Gopal and Bhargav (1982), Tiwari (2001) and Majagi (2008).

Chloride occur naturally in all types of water on natural freshwater, however, most important source of chloride in the waters discharge of domestic waste. In the present investigation chlorides have shown higher concentration during NEM season and lower values recorded in Summer. Mamata Goyal (2006) observed similar findings in some part of Unnao district. It may be due to the increase in the mineral content.

NO_3 Nitrate represents the highest oxidized form of nitrogen. Many of groundwater has significant quantities of nitrates due to leaching of the nitrate with the percolating water. Groundwater can also be contaminated by sewage and other wastes rich in nitrates. Hence, nitrate concentration observed higher values during NEM and lower values during SWM seasons.

PO_4 Phosphorus being an important constituent of biological systems, may also be present in the organic form. Some major phosphorus is domestic sewage, detergents, agriculture, effluents and fertilizers (Pandey *et al.,* 1979, Sinha *et al.,* 2000). Higher concentration of PO_4 is higher in NEM and lower in summer. According to the water pollution Act, 1997 Regulation, 1998 (SINO.258), in order to prevent eutrophication of surface water, groundwater levels should not exceed 0.03 mg/L orthophosphate (Robert *et al*., 1983).

Fluoride is naturally present in water, and it becomes toxic to animal and human beings when present at more than 1 mg/l. concentration in drinking water (Mamata Goyal, 2006). According to WHO the limit of fluoride concentration is 1.5 mg/l., in our study higher values in NEM and lower in summer are due to sedimentary formation of bhima group which is constituted by conglometer, sand stone, shale and lime stone (Ramesh, 2002).

pH is the measure of the intensity of acidity and alkalinity and measure the concentration of hydrogen ions in water. The pH of water gets drastically changed with time due to the exposure to air, biological activity and temperature change. Determination of pH is one of the important objectives in treatment of wastes. In the present study pH values were higher during NEM season, and similar findings were observed by Aboo *et al.,* (1986), Singh and Shah (1981), Verma *et al.,* (2000), Majagi (2008).

Dissolved oxygen is one of the most important parameters in the water quality assessment and reflects the physical and biological process preventing in the water. The concentration of oxygen will also reflect whether the process undergoing is aerobic or anaerobic. Low oxygen concentrations are generally associated with heavy contamination by organic matter. DO of the study area recorded more during NEM season and less during Summer season. Lower oxygen is generally associated with contamination by organic matter. Similar observations noticed by Jain *et al.,* (2000 (a) & (b)), Adak and Purohit (2000).

5.1 Heavy Metal Analysis

Heavy metals are among one of the pollutants of freshwater which pose severe threats to the biodiversity with the development of aiming smelting and other industrial activities. Some of these metals act as micro nutrients, small concentration in living organisms for their normal physiological activities but accumulation in higher concentration becomes toxic to most life forms (Lasat 2002, cheng, 2003). Seasonal variation of the heavy metals (Cu, Fe, Zn, Mn, Cd, Si, V, Ti, Cr, Mo, Al, As) of Sedam and Shahabad is measured concentration of heavy metals shown drastic difference associated with seasons.

Table 9. Correlation significant at.

Parameters	Correlation
Atmospheric temperature	Water temperature P<0.01
Water temperature	PO 4, P<0.01, pH <0.05
pH	DO P<0.01, NO3 P<0.01
DO	Harness, Calcium hardness, NO3 P<0.01, Chloride and Fluoride P<0.05
Hardness	Dissolved oxygen, Alkalinity, P<0.01
Ca	Magnesium hardness, Alkalinity and fluorideP<0.01 and Chloride P<0.05.
Mg	Alkalinity, Chloride P<0.01Fluoride and PO4 P<0.05
Chloride	
Alkalinity	NO3 and Fluoride P<0.01 and NO3 P<0.05
NO3	PO4 Fluoride P<0.01
PO4	Fluoride P<0.01

6 Conclusion

1. All the water samples subjected for analysis are found moderate and parameters are within permissible limit found good for human consumption.
2. Sources of pollution are geological factors and percolation of pollution water in the catchment area.
3. Analysis of heavy metals through atomic absorption spectrophotometer was done and presented in table no. 2, 4, 6 and 8. All the values are found with in permissible limit.

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