Fluoride Toxicity in Ground Water of Banas River Basin Area of Jahazpur Tehsil, (Bhilwara, Rajasthan, India) and Its Impact, Causes and Prevention

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ABSTRACT

Fluoride is required by the human being for mineralization of bones and teeth. Hydro-Chemical condition is the main source of fluoride contamination in ground water but run off and atmospheric depositions are also responsible for additional fluoride concentration. This study is carried out to assess the fluoride concentration, causes and its toxicity level in ground water of Banas River Basin area of Jahazpur tehsil, (Bhilwara, Rajasthan, India) and its impact on human physiology on populace, possible sources and prevention, where ground water is the main source of drinking water, for this purpose ground water samples were collected from different locations of study area and analyzed. The analytical results indicated considerable variation of fluoride concentration among the analyzed samples. The maximum fluoride concentration was reported in Taswaria II village (5.2 mg/L) and minimum in Ronpa village (0.151 mg/L). In 34 areas (68% samples) F- concentration comply with BIS and WHO standard, but in 16 areas (32% samples) excess concentration reported than permissible limits. In some village’s dental and skeletal fluorosis and others fluoride related health hazards cases were reported. The socioeconomic impacts of fluoride contaminated water in study area revealed that impact is inequitably distributed in society and the impact was inversely related with the income and education level of people. The possible sources of fluoride in study area are geogenic activities, presence of fluoride bearing minerals, decrease in rainfall, slow rate of water flow etc. In society impacts of fluoride contaminated water in study area is inequitably distributed and the impact was inversely related with the income and education level of people.


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1. Introduction

Water is an essential natural resource, and it is life and blood of our environment, without water no living being can survive. It requires for continuity of life and sustainability of ecosystem, but over the last few decades the water quality and quantity is deteriorating due to it’s over exploitation. Fluoride is an ion of the chemical element fluorine which belongs
to the halogen group. It is the most electronegative and reactive of all elements. It occurs as F\(^{-}\) ion naturally in soils and water due to chemical weathering of some fluoride containing minerals. Fluorides are ubiquitous in air, water and the lithosphere, where they are seventh in order of frequency of occurrence (0.06-0.09% of the earth crust) WHO (1994). The higher fluoride concentration may cause fluorosis and extreme condition causes even skeletal fluorosis. The F\(^{-}\) content in the ground water is a function of many factors such as availability and solubility of F\(^{-}\) minerals, velocity of flowing water, Temperature, pH, concentration of Ca and HCO\(_3\)\(^{-}\) ions in water.

The natural sources of fluoride in ground water are various types of rocks and volcanic activities. The common F\(^{-}\) bearing minerals are Fluorspar CaF\(_2\), Cryolite (Na\(_3\)AlF\(_6\)), Fluoroapatite (Ca\(_3\)(PO\(_4\))\(_2\)Ca(FCl)\(_2\)), Fluorite is principle bearer mineral of fluoride and is found in granite, gneisses and pegmatite Deshmukh et al. (1995), Rao (2009). Igneous and volcanic rocks have a fluoride concentration from 100 ppm to 1000 ppm, sedimentary rocks have from 200 ppm to 1000 ppm and metamorphic rocks from 100 ppm to more than 5000 ppm Frencken (1992). In general F\(^{-}\) rich sediments exist with Ca-poor ground water, and these sediments are mostly acidic and intermediate volcanic origin in subducting areas of the earth crust. High F\(^{-}\) in ground waters are mainly associated with a NaHCO\(_3\) water type water and relative low Ca and Mg concentration such water types usually have high pH value. The arid regions are prone to high F\(^{-}\) concentration here, ground water flow is slow and the reaction time with rocks is therefore long, but in humid regions F\(^{-}\) increase is less pronounced because of high rainfall inputs and their diluting effect of ground chemical composition Frencken, (1992). Apart from natural sources of fluoride in ground water anthropogenic activities also contribute fluoride, burning of coal, manufacturing of steel, bricks, phosphate fertilizer industries, aluminium processing Deshmukh (1995), Arison et al. (1991), and Smith & Hodge (1979).

The strong electro negativity of fluorine is attracted by Ca-ions in teeth and bones, the excessive intake can causes teeth and bone fluorosis Brouwer et al. (1988). Though fluoride enters the body through food, water, industrial exposure, drugs and cosmetics etc, but drinking water is the major contributory (75-90%) of daily intake among them Sarala et al. (1993). According to whiteford (1997) the 75-90% of ingested fluoride is absorbed by body. In an acidic stomach fluoride converted into HF and once absorbed into blood, fluoride readily distributes throughout the body, with approximately 99% of body burden of fluoride is retained in Ca-rich areas such bones and teeth (Dentine and enamel) WHO (1996). In body fluoride associates with calcified tissue (bone and teeth), and has been to be useful in the control of caries development for more than hundred years Sampaio & Levy (2011). Fluoride is not essential for tooth development but fluoro-hydroxyapatite that obtained by replacing OH\(^{-}\) ion by F\(^{-}\) in hydroxyapatite of tooth enamel, is more resistant to acids than hydroxyapatite, at pH 5.5 dissolution of apatite begins for hydroxyapatite and 4.5 for fluoroapatite. The teeth which contain fluoroapatite are less likely to develop caries because of greater resistance to ingested acids or acids generated from ingested sugars by the oral bacteria Beltran & Burt (1988), Buzalaf et al. (2011).

In Indian context the fluoride is dissolved in ground water mainly from geological sources. 80% surface water of India is polluted Times of India (2015). Fluoride epidemic has been reported mostly in granite and gnisiss geological belts of different states of India Tripathy et al. (2005), Agrwal (1997), Raju et al. (2009). As per reports of UNICEF and WHO a total of 17 (out of 32) States are reported to have endemic fluorosis in India, 20% of the fluoride affected area in the world are in India and out of these 10% are in Rajasthan. This is indicating that fluorosis has emerged as one of the most alarming public health problem of the country. The most seriously affected areas are Andra Pradesh, Punjab, Haryana, Rajasthan, Tamilnadu, Utter Pradesh Teotia et al. (1984). In India F in ground water was first reported at Nellore district of Andra pradesh in 1937 Ayoob & Gupta (2006) since then considerable work has been done in different parts of india to explore the F water sources Meenakashi and Maheshwari (2006).

In Rajasthan all 33 district are endemic for fluorosis Yadav et al. (2008). Fluoride level in ground water is spread in all the 33 districts and become a health hazard in 25 districts. In Rajasthan study pertaining to fluoride concentration in ground water has been conducted by different researchers. In Nagaur district Arif et al. (2013), in Bassi tehsil (Jaipur) Saxena & Saxena (2013), in some area of Ajmer district Vikash et al. (2009), in Malpura tehsil (Tonk) Tailar & Chandel (2010), in dungarpur Choubisha (2013), in Deoli tehsil (Tonk) (Meena et al. (2011). All suggested that fluoride pollution in study area is due to natural processes.
Figure 1. The location map of study area

Figure 2. Fluoride concentration in ground water of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India).
2. Material and Method

2.1. Study Area

Rajasthan 60% land is part of Great Indian Desert, Thar Desert that suffering from acute water crisis, Rajasthan state being largest state of the country having 10.4% of total geographical area of the country with only 1% of water resources available to the state for 5.5% population. The Banas River originates in the Khamnur Hills of Arawali range, about 5 Km from Kumbhalgarh in Rajasthan district and meets the Chambal river near the village of Rameshwar in Swai Madhopur district. It lies entirely within Rajasthan and it flows in Rajsmand, Chittorgarh, Bhilwara, Tonk and Swai madhopur district in Rajasthan, and aligned NE-SW and the major tributaries of this are Berach, Menali, Kothari, Khari, Dai and Morel. The Banas drains a basin of 45833 km², and located in east-central Rajasthan, between latitudes 24° 15' and 27° 20'N and longitudes 73°25' and 77° 00' E. The basin extends over parts of Jaipur, Dausa, Bundi, Chittorgarh, Ajmer, Tonk, Bhilwara, Swai Madhopur, Udaipur, Rajsmand and Pali district. It is a seasonal river that dries up during the summer, total length of the river is about 512 km. Jahazpur tehsil (Fig. 1) is located in the Bhilwara district in Rajasthan (India) and it is surrounded by Ajmer, Bundi and Tonk districts and the tehsil head quarter is connected by NH-12 and NH-79 through State Highway-39. The Jahazpur tehsil is situated between 25°42'16"N to 25°46'23"N longitude and 75°2'50"E to 75°27'42"E latitude and has an average elevation of 334 meter (1095 feet) from mean sea level. The climate of the tehsil is generally dry except in the short south-west monsoon season. The average annual rainfall in the tehsil is 280-630 mm. Jahazpur belt rocks are considered as early proterozoic Sinha Roy et al. (1998) and these rocks are encompassed by quartz, soda feldspar, biotite, potash feldspar, hornblende, actinolite along with zircon and apatite.

2.1. Methodology

Ground water samples from fifty area located in Banas basin river of Jahazpur tehsil (Bhilwara, Rajasthan, India) were collected pre cleaned polythene bottles during June 2014 with necessary precautions. The samples were collected from open wells, bore wells, hand pumps and PHED supply. The fluoride concentration was determined by using fluoride ion selective electrode APHA (2012) that measures fluoride concentration of range 0.01 mg/l to 1000 mg/l. The standard fluoride solutions of 1 ppm and 10 ppm were prepared from a stock solution of 100ppm of sodium fluoride solution and TISAB was used as buffer solution. The ion meter was calibrated for of -59.2±2 (APHA, 2012). Colour, Odour and Taste were determined by conventional methods and EC, Temperature and pH were determined on site using portable instruments.

3. Results and Discussions

The results reported for fluoride concentration in ground water of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India) are illustrated graphically in Figure 2. The ground water of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India) is categorised upon the basis of fluoride concentration in ground water, these five categories of water represented in Table 1.

Category-I of water include 52% samples have lower fluoride concentration in ground water and category-V with 4 % samples have the highest fluoride concentration (Figure 3). In 34 area or 68% samples the fluoride concentration in ground water was comply with WHO and BIS standard, but in 32% samples (Table 2) fluoride concentration was found more than permissible and desirable limits of WHO (1996) and BIS (2012). The fluoride concentration in study area was range. The range of fluoride concentration in ground water of study area reported was from 0.151 mg/l to 5.2 mg/l and the maximum concentration was reported in Taswariya Village (5.2 mg/l) and minimum was in Ronpa village (0.151 mg/l) (Table 3). 52% samples (Figure 4) fall in category-I in which fluoride concentration in ground water determined was below 0.1 mg/l, use of this water for drinking purpose is safe for populace. In this area no possibility of any kind of dental and skeletal fluorosis and this concentration has anti caries effect to teeth enamel. 16% of samples were found in category-II in which fluoride concentration is between maximum desirable limit and the maximum permissible limit as recommended by BIS -10500 (2012). 22% of samples fall in category-III, in which fluoride concentration was 1.5 mg/l to 3.00 mg/l, and in 6 % samples the fluoride concentration was determined above 3.00 mg/l and below 5.00 mg/l and these fall in category-IV and 4% fall in category-V in which fluoride concentration was recorded above 5.00 mg/l. The most alarming condition of health hazards was observed in these areas. In 32 % samples and 16 areas of category III, IV and V the fluoride concentration was exceeded the permissible and desirable limits, ground water of these area was found unfit for drinking purpose, hence this water cannot be used for drinking...
Table 1. Categorisation of ground water of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India) based on fluoride concentration.

<table>
<thead>
<tr>
<th>Category of Samples</th>
<th>Range of Fluoride Concentration</th>
<th>No. of Area</th>
<th>Representing Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat I</td>
<td>&lt; 1.00</td>
<td>26</td>
<td>S1, S2, S3, S5, S6, S7, S8, S9, S10, S11, S12, S13, S14, S17, S18, S19, S20, S31, S36, S37, S38, S39, S43, S44, S45 &amp; S49</td>
</tr>
<tr>
<td>Cat II</td>
<td>1.00-1.5</td>
<td>8</td>
<td>S15, S16, S29, S30, S32, S33, S34 &amp; S46</td>
</tr>
<tr>
<td>Cat III</td>
<td>1.5-3.00</td>
<td>11</td>
<td>S4, S23, S24, S25, S35, S40, S41, S42, S47, S48 &amp; S50</td>
</tr>
<tr>
<td>Cat IV</td>
<td>3.00-5.00</td>
<td>3</td>
<td>S2, S26 &amp; S28</td>
</tr>
<tr>
<td>Cat V</td>
<td>&gt;5.00</td>
<td>2</td>
<td>S22 &amp; S27</td>
</tr>
</tbody>
</table>

The distribution of fluoride concentration in ground water of Banas river basin villages of Jahazpur tehsil (Bhilwara, Rajasthan, India)

Figure 3. % of each category of water sample of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India).

Table 2. Fluoride Concentration in Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India) comparison with WHO Standards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>WHO Standard</th>
<th>% of the Samples Exceeding Limits</th>
<th>No. Villages Exceeding Limits</th>
<th>% of the Samples within Limits</th>
<th>No. Villages within Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Highest Desirable Limit (mg/L)</td>
<td>32%</td>
<td>16</td>
<td>68%</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Maximum Permissible Limit (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Range of Fluoride Concentration in Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India).

<table>
<thead>
<tr>
<th>No of Samples</th>
<th>Fluoride Concentration in Samples in mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
</tr>
<tr>
<td>50</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>52</td>
</tr>
</tbody>
</table>

Categorisation of Fluoride Concentration in Banas River Basin Villages of Jahazpur Tehsil (Bhilwara, Rajasthan, India)

Figure 4. No. of area and their % each Category of ground water of Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India).

Figure 5. Dental fluorosis and skeletal fluorosis.
In the populace of 16 area (32% samples) of study area which belong to category III, IV and V cases of fluoride health hazards reported such as morphological and physiological changes in calcified tissues (teeth and bones), Dental fluorosis (Figure 5) which is characterized by discoloured, blackened, mottled or chalky white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth were developing. Chronic intake of excessive fluoride can lead to the severe and permanent bone and joint deformations termed as skeletal fluorosis (Figure 5).

Fluoride has been found to have adverse effects on the structure and functions of the animal nervous system Varmer et al. (1998), Shivarajashankara et al. (2002), Esvar et al. (2011). Over the last two decades more subtle injuries from human F exposure in the form of lower intelligence have been reported in several countries Chen et al. (2008), Susheela (2012), Poureslami et al. (2011). This effect of F may be due to its ability to cause CNS (central nervous system) cellular injury through several mechanisms including free radical generation and excitotoxicity Bhatnagar et al. (2011).

Excessive intake of fluoride causes problems of Thyroid gland and skin of animals Prerna Sharma (2007) and may cause adverse effect on fertility of human being, level of mental work capacity and intelligence quotient of children Lu et al. (2000), and the excess fluoride concentration also affect Ca functioning which is for bone formation, muscle movement and contraction, blood clotting and constant dysfunction leads to the knock knee system, excessive accumulation of calcium fluoride in the renal system, and leading to stones formation in the kidney and eventual renal failure Meena et al. (2012). Complaints of the male infertility with an abnormality in sperm morphology and also low testosterone levels are said to involve fluoride toxicity Tailar & Chandel (2010). Recent reports also indicate that early cataract development of cataract in human eyes due to excess consumption of fluoride The Guardian UK (1995).

A lack of fluoride intake during development will not alter tooth development but may result in increased susceptibility of enamel to acid attacks eruption. However, caries is not a fluoride deficiency disease. Acute ingestion of a large fluoride does can provoke gastric and kidney disturbances, and can be lethal Whitford (2011), Acute excess fluoride intake interferes with calcium metabolism and many enzyme activities, activating both proteolytic and glycolytic functions and cell respiration by inhibiting Na+/K+ - ATPase, and can be fatal with doses of 5-10g in adults and 500mg in small children Lech (2011).

Socioeconomic impact of fluorosis concentration studied in populace of study area, the percentage of fluoride debility cases found less with rising income and the impacts of poor quality water are distributed inequitably within the studied society. The social, health, and economic impacts of contaminated ground water depends on spatial distribution of fluoride, dependence of the populace on fluoride contaminated water, awareness of water quality, levels education and economic status of populace at risk. Good nourishment and medical care could be reason for this decline. Higher income group of society could escape the ill effects of fluoride contaminated water. Low rainfall increase reaction time of fluoride bearing rocks with water and slow down the movement of water that increase fluoride content in ground waters, whereas increased rainfall decrease fluoride content. Arid climate are prone to high fluoride content. Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India) is part of arid semi zone that is why higher fluoride content is present in ground water.

4. Conclusions
From this study it is conclude that fluoride is distributed nonuniformly in ground water of study area. Study revealed that 32 % village’s populace (16 area) of this area is at higher risk due to excessive intake of fluoride and 68% village’s populace 34 area) is safe from the fluoride related health hazards and the fluoride concentration range reported in ground water of Banas basin river area ranges was from 0.151 mg/l to 5.2 mg/l. The major contributory source of fluoride concentration in ground water in natural activities such as weathering of fluoride bearing rocks, rate of water flow, amount of rainfall, pH of water and climate conditions. The concentration of fluoride in ground water is inversely related to Ca- concentration in earth crust, higher concentration decrease solubility of F- because Ca binds with F- to form CaF$_2$. The correlation study (Figure 6) of fluoride concentration with pH for ground water revealed that alkaline pH favours higher concentration of fluoride since alkaline pH increases solubility of fluoride from minerals of fluoride Saxena & Ahmed (2003) and acidic pH favours adsorption of fluoride in clay.

In the populace of 16 area (32% samples) of study area which belong to category III, IV and V cases of fluoride health hazards reported such as morphological and physiological changes in calcified.
tissues (teeth and bones), Dental fluorosis (Figure 5) which is characterized by discoloured, blackened, mottled or chalky white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth were developing. Chronic intake of excessive fluoride can lead to the severe and permanent bone and joint deformations termed as skeletal fluorosis (Figure 5). No sign of fluoride deficiency have been identified, but excess concentration causes number of physiological and morphological changes in human body. Skeletal fluorosis occurs after many years of excessive fluoride intake (10-20mg/day). It increases risk of bone fracture (stiffness of joints deformities). F is not irreversibly bound to bones WHO (1994), Khandre (2004). The partial substitution of fluoride for the OH- groups alter the mineral structural of the bone, that make bones compact and increase density and hardness but not necessarily increase the mechanical strength Chahra et al. (1999). Gastric absorption, distribution in the body and renal excretion are pH dependent. At low pH it occurs as HF and less as ionic F-. Whiteford (1996). HF crosses preferentially the cell membrane than ionic F- F is not metabolised and not substrate for any enzyme. F is absorbed by passive diffusion in stomach and small intestine, in stomach as HF and intestine as F-. Ca, Mg, Al and phosphorus decrease absorption of F- since they get bind with F. Absorbed F- which not deposited in calcified tissues is mainly excreted via the kidney - 60 % Villa et al. (2010). Low pH of urine reduces renal excretion of F-. Renal clearance of F- is 30.50 ml/min) in adults and via faces 10-20% of the daily excreted. The effect of fluoride contaminated water in society is distributed inequitably, and lower income group people are at high risk since there approach for recourses and good quality water is limited. Excessive fluoride intake may be prevented by using alternate sources of drinking water using surface water and rain water, consuming adequate Ca rich foods items and vitamin C, Ca and P reduce fluoride retention capacity of body. This risk can be minimised by educating the people about the fluoride toxicity and disfunctions of excessive fluoride, avoiding consuming black salt and fluoridated toothpaste, educating people about good quality water, fluoride health hazards and providing village friendly, and cheap and reliable water treatment techniques.

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Figure 6. Correlation between pH and Fluoride concentration of ground water in Banas river basin area of Jahazpur tehsil (Bhilwara, Rajasthan, India).
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