



International Journal of ChemTech Research

CODEN (USA): IJCRGG ISSN: 0974-4290 Vol.9, No.02 pp 71-79, **2016**

Assessment of Fluoride, Arsenic and Other Heavy Metals in the Ground Water of Tea Gardens Belt of Sonitpur District, Assam, India

Joydev Dutta

Department of Chemistry, Chaiduar College, Gohpur, Sonitpur, Assam, India

Abstract: The Sonitpur district is one of the most important tea growing district of Assam. There are big tea estates (under multinational companies) as well as a large number of small tea gardens growing which is like a green revolution. In these gardens heavy amount of artificial agrochemicals are used which contaminates soil as well as drinking water sources. Ground water is an essential and vital component of our life support system. The groundwater resources are being utilized for drinking, irrigation and industrial purposes. There is growing concern on deterioration of groundwater quality due to geogenic and anthropogenic activities. Groundwater, being a fragile must be carefully managed to maintain its purity within standard limits. In tea gardens belt the agro-chemicals affect the quality of groundwater so this investigation has been carried out to assessment the quality of water in this area. Now the Fluoride and Arsenic are major problems in ground water in India and Bangladesh, the heavy metals also effect the chronic health hazards of the people in this area so it is very important to investigation of ground drinking water sources. The ground water of this area is of high iron, manganese, fluoride and arsenic concentration is observed. Finally, stress zones in the study area were delineated using Arc GIS spatial analysis.

Keywords: Groundwater quality, Heavy metals, Small tea gardens, Sonitpur, India.

1. Introduction:

The Sonitpur district is one of the most important tea growing district of Assam. In Assam tea production system is characterized by two sectors of opposite structure existing next to each other plantation management versus smallholder production. Both sectors can be distinguished by their typical production system. The big tea gardens are under multinational companies and the small tea gardens are running by local cultivators. The small tea gardens of Assam have a countable contribution to the total tea production. More than 70,000 small tea gardens are grown and 9, 00,000 people are involved in the small tea growing business of Assam. Almost 2, 50, 000 hectares of land is covered by such plantations. They contribute to 30 percent of the total tea production in Assam, which is 14 percent of the total tea production of India¹. In these tea gardens heavy amounts of artificial fertilizers are used which leaching to the drinking water sources and contaminated, so it is urgent need to monitoring the drinking water sources for better management.

We never know the worth of water till the well is dry². Water covers almost 71% of the earth's surface. On earth, it is found mostly in oceans, seas and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor, clouds (formed of solid and liquid water particles suspended in air), and precipitation³. Oceans covers 97.2 % of surface water, 1.8% is glaciers and polar ice caps, 0.02% is other land surface water such as rivers, lakes and ponds, 0.9% is groundwater and 0.001% is atmospheric water vapor at

any given time. A very small amount of the earth's water is contained within biological bodies and manufactured products.

Water for human consumption should be free from germs and toxic matters although should contain essential minerals. However a clear and colourless water sample without a taste or odour does not guarantee of purity and safety for drinking. Chemical contamination of drinking water, either naturally or by anthropogenic sources, is a matter of serious concern as the toxic chemicals do not show acute health effects unless they enter in to the body in appreciable amounts, but they behaves as cumulative poisons showing the adverse health effects after a long period of exposure⁴. High rates of mortality and morbidity due to water-borne diseases are well known in India. Access to safe drinking water remains an urgent necessity, as 30% of urban and 90% of rural households still depend completely on untreated surface or groundwater⁵.

Safe drinking water is a fundamental need of every human being, despite of any socio-economic status. The health and happiness of the human race are closely tied up with the quality of the water used for consumption where the per capita consumption of water is an index of quality of life of the people as well as their economic and social condition. There is a clear correlation between access to safe drinking water and GDP per capita⁶. Groundwater is the most significant source of drinking water throughout the world though surface water plays a vital role in the supply of water for drinking. It was estimated that, only 0.9% of the total water resources on earth is supplied from groundwater, though it is the major and the preferred source of drinking water in rural as well as urban areas. It covers 80% of the total drinking water requirement and 50% of the agricultural requirement in rural India.

Fluoride is the lightest member of the halogen group of elements. In number of respects its behavior is quite different from other halogens and it is reflected in natural water also. Fluoride is the common element in the earth's crust as component of the rocks and minerals. It is considered as one of the minor constituents of natural waters, but it is an important parameter in ascertaining the suitability of water for potable purposes. Intake of 1mg/l per day is very much essential for healthy growth of teeth, but level higher than the permissible limit of 1.5mg/l is dangerous to health? Fluoride contamination of ground water has now become a major geoenvironmental issue in many parts of the world due to its toxic effects even if consumed in trace quantities. Fluoride in ground water poses a great problem in most of the states of India⁸. Fluoride concentration in ground water of India varies widely ranging from 0.01ppm to 48ppm⁹. A high fluoride content in drinking water sources have been observed in 15 states of India¹⁰. Sever contamination of fluoride in ground water of Karbi Anglong and Nagaon districts of Assam, India and its manifestation in the form of fluorosis have been reported recently¹¹.

Fluorosis was first reported from India by¹². Fluoride also circulate in blood and effect foetus, nerves and heart. Fluoride reduces secretion of thyroid gland by affecting iodine in the body which may lead to monogolism. Apart from these, excess fluoride intake will also cause gastro intestinal problems like loss of appetite, nausea, vomiting, pain in abdomen, intermittent diarrohea, muscular weakness, excessive thirst etc.¹³. High fluoride intake over a period of time can cripple one for life¹⁴.

The groundwater sources are no longer been safe for drinking purposes as they are contaminated by As. Presence of As in groundwater of Assam was first reported in the year 2004¹⁵. During the period 2004-2005, a survey of PHED supported by UNICEF, collected 5729 water samples from 192 blocks of 22 district of Assam and analysed for As concentration. It was observed that, groundwater of 72 blocks of 18 districts had been contaminated by As where 6.3% samples of total collection contained As above 0.05ppm¹⁶. According to the report, the district Golaghat, situated in the Brahmaputra river basin is one of the most badly affected districts of Assam.

The heavy metals are important component of pollutants which not only causes phytotoxicity but also enters into the food chain causing hazardous impacts on human health and animals. The phytotoxic impacts of heavy metal pollution are very commonly observed on crops. Chemicals in drinking water which are toxic may cause either acute or chronic health effects. An acute effect usually follows a large dose of a chemical and occurs almost immediately. It is important to understand that primary standards for drinking water contaminants do not guarantee that water with a contaminant level below the standard is risk-free. Several research studies have been published on the concentration of heavy metals and their toxicity, from different corners of the globe¹⁷. In tea garden areas heavy amounts of fertilizers, pesticides, weedicides and other chemicals are used so

these chemicals contaminate the water sources studied the water quality in tea gardens of Lakhimpur district, Assam¹⁸. There is no earlier statistic of heavy metals contamination in water sources of small tea gardens in sonitpur districts are available..

In tea gardens area heavy amount of chemical fertilizers and pesticides, weedicides and other chemicals are used these chemicals have fluoride and other water contaminants substance e.g. fluoride is an impurities in normal and triple super phosphate. Which contaminate the drinking and other water sources. There is no earlier statistics of drinking water contamination in small tea gardens of Sonitpur district Assam, India. So it is very important to monitor the drinking water quality specially Fluoride, Arsenic and Heavy Metals concentration in the drinking water sources in the small tea gardens of Sonitpur district Assam, India.

2. Experimental

2.1 Study area

The district Sonitpur, (second largest district of Assam after Karbi Anglong in area.) which is taken as study area is located in the north east part of Assam. The total area of Sonitpur district is 5103 sq. kms. and lies 100 meter above the mean sea level (www.sonitpur.gov.in). It is surrounded by Arunachal Pradesh in north, the Brahmaputra river and Morigaon, Nagaon, Jorhat and Golaghat districts in south, Darrang district in the west, Lakhimpur district in the east and. Sonitpur district is located north bank of river the Brahmaputra within 26°2 and 26°6 N latitude and 92°2 and 93°5 E Longitude. Located between mighty Brahmaputra River and Himalayan foothills of Arunachal Pradesh, the district is largely plain with some hills. Land use in the district is divided primarily among tropical semi evergreen, moist deciduous, riverain forest, grassland agricultural land and tea garden. The temperature ranges from 7°C in January to as high as 38°C in May. Sonitpur District falls in the Sub-Tropical climatic region, and enjoys Monsoon type of climate. Summers are hot and humid, with an average temperature of 29° C. The annual rainfall in the district is 2393mm. The climatic conditions of this area are very suit for the tea cultivation. It is interesting to note that the Monabari tea estate, the biggest tea garden in Asia is situated in Sonitpur district. According to the estimate of 2004, in Sonitpur district itself, there are 62 large tea gardens and 207 registered tea gardens covering an area of 497.57 hectares¹⁹.

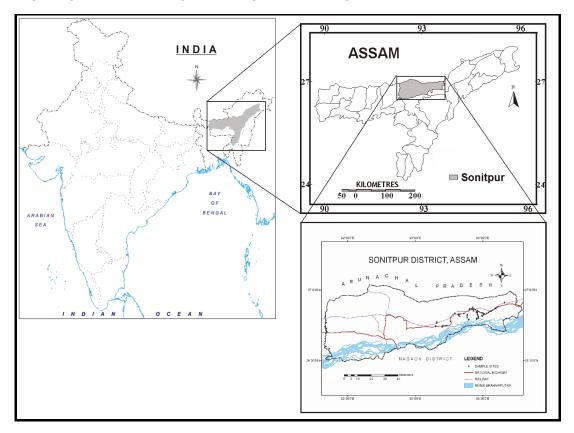


Fig. 1. Study area map of Sonitpur district, Assam, India

2.2 Sampling methodology

Total 90 numbers of water samples were collected from different drinking water sources of the fifteen small tea gardens of sonitpur district, Assam. The sources of the water samples were collected from shallow hand tube wells (HTW \sim 60ft deep, deep tube wells (DTW) like Tara pump (\sim 120ft deep) and mark tube well (\sim 180ft deep) and ring well. Tube wells were operated at least 10 minutes before collection to flash out the stagnant water inside the tube and to get fresh ground water. The water samples were collected in clean 1L Poly propylene bottles.

2.3 Sample analysis

pH of the samples was measured at the site of collection by using Pocket pH meter (Merck, India). After determination of pH, 1:1 HNO₃ solution was added to the each water samples collected (to pH less than 2) and sealed the bottles which were carried out to the laboratory for further analysis of water quality parameters. The analyses Ca and Mg were determined by EDTA titrametric methods. The concentration of the heavy metals namely Fe, Mn were determined using atomic absorption spectrometry (AAS; model Perkin Elmer 200, USA) at their respective wave length and slit width. Fluoride contents were determined by SPADNS method. Hydride Generation-Atomic Absorption Spectrometry (HG-AAS) was used for analysis of As in water samples. All the reagents and standards were prepared freshly at the time of analysis. For better sensitivity, As⁵⁺ was pre-reduced to As³⁺ before analysis. Pre-reduction was carried out following the standard method²⁰.

3. Result & Discussion

The chemical analysis of 90 ground water samples and present observance with WHO, 2008 standards and normal statistics are summarized in Table 1 & Table 2.

3.1 pH

pH is a term used universally to express the acidic and basic nature of a solution. The guideline value of pH in drinking water set by WHO is 6.5 to 8.5, in 2008. In this study, the range of pH was observed at 6.0 to 8.21 in inside tea gardens. Similarly in outside tea gardens the minimum and maximum values are 6.25 and 8.25. The most of the water samples in the study area were found to be acidic in nature in inside tea gardens but in case of outside tea gardens the sources are alkaline in nature. This may be due to use of fertilizers like ammonium sulphate and super phosphate in agriculture²¹. All of the samples in the inside and outside tea gardens are within WHO limit. So from the pH point of view the water in this area is good.

3.2 Fluoride (F)

Fluoride is the common element in the earth's crust as component of the rocks and minerals. It is considered as one of the minor constituents of natural waters, but it is an important parameter in ascertaining the suitability of water for potable purposes. Intake of 1mg/l per day is very much essential for healthy growth of teeth, but level higher than the permissible limit of 1.5mg/l is dangerous to health⁷. Fluoride in ground water poses a great problem in most of the states of India. Sever contamination of fluoride in ground water of Karbi Anglong and Nagaon districts of Assam, India and its manifestation in the form of fluorosis have been reported recently. Deficiency of fluoride leads to dental caries and higher concentration leads to dental and skeletal fluorosis. The concentration of fluoride with statistics in the water samples are given in the Table 1. In the present study the F⁻ contents varies inside tea gardens from 0.10 ppm to 5.60 ppm (ave.=1.28 ppm). In outside tea gardens the range are from 0.08 ppm to 4.93 ppm (ave. =1.31 ppm). From the study it was found that the presence of high amount of F in few water samples of the tea gardens area may due to use of synthetic agrochemicals or rocks presents in the aquifer. Modern agriculture practice, which involves the application of fertilizer coupled with pesticides, contributes F to ground water. In some small tea garden areas the concentration of F in the water sources were found below the desirable limit (1.0ppm) of WHO/BIS. This may be due to dilution of water by rain. Overall almost 19.44% of samples of the study area had F contents more than WHO guideline value for drinking water. The presence of high amount F in the ground water of Darrang district nearby to Sonitpur district (study area) and Nagaon and Karbianlong district were also been reported¹¹. From this point of view the variation of fluoride in the study area is not uniform so it is very important to monitoring the drinking water sources of whole region.

Table 1: Water parameters in the study area

| Statistics | I | Н | F(p | pm) | As (ppm) | | |
|---------------|--------|--------|--------|--------|----------------|-------------|--|
| | In | Out | In | Out | In | Out | |
| Min | 6.0 | 6.25 | .10 | .08 | BDL | BDL | |
| Max | 8.21 | 8.35 | 5.60 | 4.93 | 0.09 | 0.09 | |
| Median | 6.87 | 7.10 | .98 | 1.08 | 0.01 | 0.005 | |
| Mean | 6.80 | 7.12 | 1.28 | 1.31 | 0.017 | 0.014 | |
| ±S.D | ±0.40 | ±0.34 | ±1.27 | ±1.11 | ±0.022 | ± 0.020 | |
| Skewness | 0.544 | 0.658 | 2.227 | 1.60 | 1.871 | 2.103 | |
| Std. Error of | 0.354 | 0.354 | .354 | .354 | 0.354 | 0.354 | |
| Skewness | | | | | | | |
| Kurtosis | 2.321 | 2.943 | 4.828 | 2.805 | 3.614 | 4.265 | |
| Std. Error of | 0.695 | 0.695 | .695 | .695 | 0.695 | 0.695 | |
| Kurtosis | | | | | | | |
| Range | 2.21 | 2.10 | 5.50 | 4.85 | 0.09 | 0.09 | |
| 95% CL | 7.43 | 7.67 | 5.12 | 4.28 | 0.078 | 0.074 | |
| Below DL % | 22.22% | 2.22% | 51.11% | 48.88% | 46.66% | 51.11% | |
| Within WHO | 77.77% | 97.77% | 31.11% | 22.22% | 4.44% | 8.88% | |
| limit % | | | | | | | |
| Above PL % | 0 | 0 | 17.77% | 28.88% | 48.88% | 40% | |
| WHO limit | 6.5 | 5-8.5 | 1-1 | 1.5 | 0.01- No relax | | |

Table 2: Water parameters in the study area

| Statistics | Ca (ppm) | | Mg (ppm) | | Fe (ppm) | | Mn (ppm) | |
|---------------------|----------|--------|----------|--------|----------|------------|----------|------------|
| | In | Out | In | Out | In | Out | In | Out |
| Min | 15.20 | 20.79 | 4.28 | 7.82 | .31 | .60 | .01 | .02 |
| Max | 96.20 | 67.80 | 57.78 | 39.38 | 7.05 | 7.56 | 2.51 | 2.89 |
| Median | 52.22 | 37.50 | 26.00 | 18.48 | 3.62 | 3.40 | .69 | .94 |
| Mean | 50.28 | 40.20 | 26.46 | 18.73 | 3.65 | 3.45 | 0.95 | 0.99 |
| ±S.D | ±19.72 | ±10.59 | ±11.49 | ±7.74 | ±1.68 | ± 1.63 | ±0.82 | ± 0.71 |
| Skewness | 0.063 | 0.584 | .403 | .661 | 010 | .229 | .54 | .67 |
| Std. Error | 0.354 | 0.354 | .354 | .354 | .354 | .354 | .354 | .354 |
| of | | | | | | | | |
| Skewness | | | | | | | | |
| Kurtosis | -0.231 | -0.105 | .650 | .124 | 601 | 173 | -1.14 | 13 |
| Std. Error | 0.695 | 0.695 | .695 | .695 | .695 | .695 | .695 | .695 |
| of Kurtosis | | | | | | | | |
| Range | 81.00 | 47.01 | 53.50 | 31.56 | 6.74 | 6.96 | 2.50 | 2.87 |
| 95% CL | 88.83 | 58.64 | 51.12 | 35.63 | 6.52 | 6.61 | 2.34 | 2.25 |
| Below DL % | 91.11% | 100% | 62.22% | 100% | 0% | 0% | 15.55% | 8.88% |
| Within WHO limit | 8.88% | 0% | 37.77% | 0% | 6.66% | 11.11% | 15.55% | 8.88% |
| Above PL % | 0% | 0% | 0% | 0% | 93.33% | 88.88% | 68.88% | 82.22% |
| WHO limit | | 75-100 | _ | 30-100 | | 0.3-1.0 | | 0.1-0.3 |

3.2 Arsenic (As):

The presence of As in groundwater of Assam, Tripura, Manipur, Arunachal Pradesh (AP) and Nagaland had been reported²². Concentrations of As in groundwater samples of these regions exceeded .05ppm, quite

higher than the permissible level (.01ppm). It was reported that groundwater in 21 of 27 districts of Assam, 3 of 4 districts of Tripura, 6 of 13 districts of Arunachal Pradesh (A.P), 2 of 8 districts of Nagaland and 1 of 9 districts of Manipur had been contaminated by As (Singh, 2004). Although As contents beyond the guideline value of WHO have been found in a large number of samples, no arsenocosis patients have been reported until now²³. For the first time in the year 2004, As was detected in groundwater of the Upper Brahmaputra Plain. The range of concentration of As in inside tea gardens BDL to 0.09 ppm and in outside tea gardens BDL to 0.09 ppm. It is observed that groundwater samples of the study area fall under alert categories with respect to arsenic in some sources as some of the samples exceed and some are approaching the WHO guideline value of 0.01 ppm. Wide data range and high standard deviation in case of arsenic in inside and outside area likely to bias the normal distribution statistic.

3.3 Calcium & Magnesium:

Calcium (Ca) and Manganese (Mg) is one of the important trace elements essential for organisms. In drinking water a minimum amount of Ca & Mg is very important but excess amount causes toxic. In the present study it was noticed that the concentration of Mg was comparatively lower than the concentration of Ca. Mg usually occurs in lesser concentration than Ca due to the fact that the dissolution of Mg rich minerals is slow process and that Ca is more abundant in the earth's crust, so the concentration of Mg was comparatively lower than the concentration of Ca (Rai et. al., 2006). Mg tolerances by human body are lower than Ca. The Mg, like Ca, is a common element present in water environment has the property to produce hardness in water. The range of Ca inside tea gardens are 15.20 ppm to 96.20 ppm and in outside tea gardens the range are 20.79 ppm to 67.80 ppm. Similarly the range of Mg in the in inside tea gardens 4.28 ppm to 57.78 ppm and outside tea gardens the range are 7.82 ppm to 39.38 ppm. In this study ravels that all the drinking water sources the Ca and Mg concentration are within WHO limit.

3.4 Iron and Manganese:

Fe in water can cause staining of laundry and porcelain. A bitter sweet astringent taste is detectable at level above 1 ppm (WHO Permissible limit of Fe in drinking water). Fe is an essential element in human nutrition. But high Fe intake cause iron toxicity, higher Fe intake symptomized by fatigue, anorexia, dizziness, nausea, vomiting, headache, weight loss, shortness of breath and possibly a graying colour to the skin. In the present study iron contents shown in Table 1 and vary between 0.31 ppm to 7.05 ppm (ave.=3.65 ppm) in inside tea gardens. In outside tea gardens the ranges are 0.60 ppm to 7.56 ppm (ave. = 3.45 ppm). Out of the total samples, in inside tea gardens 93.3% are exceed the permissible limit (W.H.O./ BIS) and in outside tea gardens area 88.88% above tolerable limit (WHO). Manganese is one of the important trace elements essential for organisms. It has low acute oral toxicity, however, the chronic manganese poisoning leads to progressive deterioration of the central nervous system and symptoms resembling to those of perkinson's disease are observed. Mn often accompanies Fe in ground waters. At high concentrations in water it will cause an unpleasant taste, deposits on food during cooking²⁴ stains on sanitary ware, discolouration of laundry, deposits on plumbing fittings and cooking utensils, and will foster the growth of micro-organisms in water supply systems. In the present investigation Mn spreads between 0.01 ppm to 2.51ppm in inside tea gardens similarly 0.02 ppm to 2.89 ppm in outside tea gardens. Among the total samples in inside tea gardens 68.88% and in outside tea gardens 82.22% are above the permissible limit (WHO). From the study it was noticed that water quality of the study area was not good in terms of the Fe and Mn content.

4. Statistical analysis

The data were subjected to NDA (normal distribution analysis), and pearson correlation using SPSS (Ver. 14.0). NDA (involving mean, median, standard deviation, skewness and kurtosis) analysis is an important statistical tool for identifying the distribution patterns of the different water quality parameters in groundwater samples.

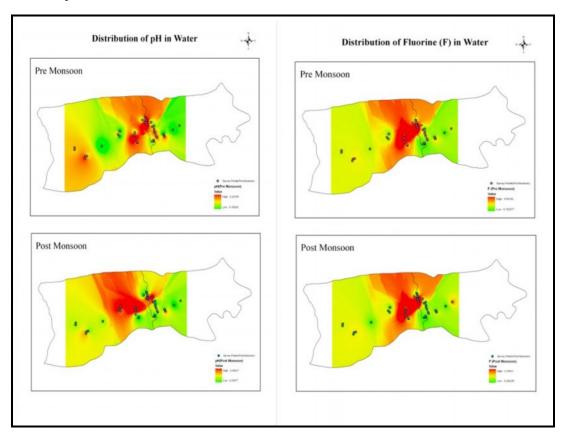
Kurtosis: Kurtosis is an indicator of the relative sharpness or flatness of the peak compared to normal distribution. Positive kurtosis indicates a sharp distribution while negative kurtosis indicates a flat one.

Skewness: A measure of the symmetry of the distribution. The normal distribution is symmetric, and has a skewness value of zero. A distribution with a significant positive skewness has a long right tail. A distribution

with a significant negative skewness has a long left tail. As a rough guide, a skewness value more than twice its standard error is taken to indicate a departure from symmetry.

5. GIS Modeling

The stress zones based on the selected hydro chemical data of ground water for Pre and Post Monsoon were delineated with Arc GIS (Fig. 1). The Arc GIS Spatial Analyst adds a comprehensive and wide range of cell-based GIS functions and among the three main types of GIS data (raster, vector and TIN), the raster data structure provides for spatial analysis. The sampling locations were mapped with the help of Survey of India Toposheet of the scale 1:50000 and Global Positioning System (GPS). The seasonal water chemistry data are related with its spatial dimension and further specially interpolated using Inverse Distance Weighted Method (IDW). This interpolation determines cell values using a linearly weighted combination of a set of sample points. The weight is a function of inverse distance. The surface being interpolated should be that of a locationally dependent variable. Based on the analysis the hotspot traced towards the different directions for different parameters.



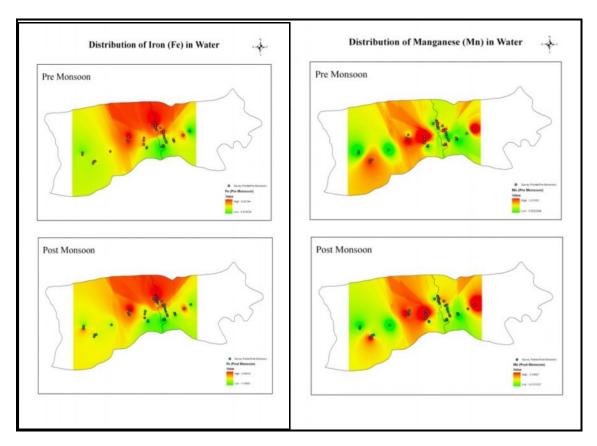


Fig. 2 Spatial analysis of water parameters

5. Conclusion:

The study has provided useful baseline information on the shallow ground water (ring well and tube well) quality of inside and outside small tea gardens area for better management. As found out from the experimental results, water in and outside the tea gardens of Sonitpur district, Assam, generally have properties that make their management somewhat difficult. A statistical analysis of water quality parameters has been carried out with special reference to pH, F, As, Ca, Mg, Fe, Mn, Different statistical estimations, viz. mean, skewness, and kurtosis, performed for each parameter indicate that their distribution in the study area is widely off normal with a long asymmetric tail either on the right or left side of the median. Wide data range in case of arsenic indicates the presence of extreme values in the form of outliers. In some small tea gardens area the fluoride in drinking water sources is alarmingly high and some gardens area is very low than the WHO limit. Measures of fluoride monitoring should be taken where alternative source for direct use is not feasible and diet of rich calcium and phosphate are suggested where high level fluoride is found and the gardens where low level fluoride is found a ground water management program is suggested. In most of the samples the concentration of iron is much higher than the guideline value of W.H.O (0.3 ppm) i.e. 95.55% in inside and 92.215% in outside tea gardens samples have iron content above the permissible limit in both seasons. It is, thus, required that the water sources be properly protected from potential contamination of these harmful elements and appropriate treatment be selected for future use of water in the region.

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