

**ASSESSMENT OF FLUORIDE IN GROUNDWATER  
AND ASSOCIATED HEALTH RISKS IN SOME  
VILLAGES OF HARYANA, INDIA**

*Dissertation submitted to  
Delhi Technological University, Delhi  
in partial fulfillment of the requirements for the award of  
the degree*

**Master of Technology**

**in**

**Environmental Engineering**

*by*

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under the guidance of

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**DEPARTMENT OF ENVIRONMENTAL ENGINEERING**

**DELHI TECHNOLOGICAL UNIVERSITY, DELHI**



## **DECLARATION**

I, Manjeet Rani, hereby declare that this dissertation titled “Assessment of Fluoride in Ground water and Associated Health Risks in some villages of Haryana, India” is carried out by me in the department of Environmental Engineering of Delhi Technological University, Delhi. The work is original and has not been submitted earlier whole or in part for the award of any degree / diploma at this or any other Institution / University.

Date:

Place

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**DEPARTMENT OF ENVIRONMENTAL ENGINEERING**

**DELHI TECHNOLOGICAL UNIVERSITY, DELHI**



**CERTIFICATE**

This is to certify that the dissertation titled “Assessment of Fluoride in Ground water and Associated Health Risks in some villages of Haryana, India” is submitted by **Ms. Manjeet Rani** in partial fulfillment of the requirements for the award of the degree of **Master of Technology in Environmental Engineering**, Delhi Technological University. The work is comprehensive, complete and fit for final evaluation.

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Manjeet Rani

## ABSTRACT

Ground water is the vital source of drinking in rural areas of India. Fluoride intake through drinking water is the major source of fluoride in human body. The intake of elevated fluoride concentration has critical adverse effect on human body. Fluoride concentration in groundwater of some villages in Hansi block of Hisar, Haryana varied from 0.5 to 5.5 mg/L and the mean concentration was 2.4 mg/L, which is above the national and international prescribed standards. As a biomarker of  $F^-$  exposure, the urinary  $F^-$  among school children varied from 0.6 to 8.9mg/L in girls and from 0.13 to 12 mg/L in boys. Dental fluorosis survey showed that 24% girls and 30% boys have moderate to severe dental fluorosis. Also the health risk assessment was calculated for the population and its range varied from 0.46 to 5.19, 0.33 to 3.67, and 0.26 to 2.94 for children; adolescent; and adults respectively. Assessment of non- carcinogenic risk in study area showed that 73% children; 63% adolescent; and 63% adults had surpassed the safe limit for health quotient *i.e.* 1.0 as prescribed by the USEPA. Also the observation indicates that younger population is more prone to non- carcinogenic health risk due to fluoride exposure. The hydro geochemistry of ground water revealed mixed  $Ca-Mg^{2+}-Cl^-$  type and  $Ca^{2+}-Cl^-$  type groundwater in the study area. Rock dominance and evaporation crystallization are the dominant water quality controlling phenomenon in the study area and majority of the samples exceed the standard limits for most of the parameters prescribed by BIS and WHO.

The significance of this study is to assess the fluoride concentration in ground water and correlating its concentration to human health by assessing dental fluorosis and fluoride in urine, also the associated health risk is calculated in the residents.

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## 1.1 Overview

Nearly one third of the world population relies on groundwater for drinking (International Association of Hydrologists, 2020). Ground water becomes essential resource due to lack of precipitation and bounded surface resources in subtropical and dry regions of the world(Li et al., 2017)and assumed safe also due to lower level of microbial contamination(Hybel et al., 2015; Mohebbi et al., 2013). In India around 85% rural population relies on ground water for drinking and other purposes (World Bank, 2012). Its contamination has become a major concern from past few decades which could be either by natural sources or by anthropogenic.(Ali et al., 2018; Saha et al., 2016; Sarkar et al., 2016; Shekhar and Sarkar, 2013).

Fluoride is a natural element and found in subsurface water, food, beverages (IPCS, 2002). Elevated concentration of fluoride in subsurface water has effected around 35 Nations worldwide containing Argentina, Mexico, Russia, China, India, Korea, Sri Lanka, Pakistan, some parts of Africa, Iran, etc. (K. K. Yadav et al., 2018).

Fluoride released in ground water by leaching and weathering of fluorine bearing minerals (Abiye et al., 2018). Fluorite is one of the major mineral of fluorine which generally found in granitic rocks (Turekian & Wedepohl, 1961). Apatite, amphiboles, hornblende, biotite, haematite, some specific clays are some other constituents bearing fluorine in nature (Bloss et al., 1959; Boyle, 1992; Foster, 1964). Industrial waste, excessive use of fertilizers, brick kiln, etc. are some anthropogenic activities which elevate fluoride concentration (Ali et al., 2016). F<sup>-</sup> enrichment in groundwater is mainly controlled by groundwater circulation, hydraulic conductivity of the aquifer, various geochemical processes (Li et al., 2014).

Fluoride has both beneficial and adverse effect on human health. The World Health Organization has prescribed a range between 0.5 to 1.5 mg/L for F<sup>-</sup> in drinking water (WHO, 2017). Intake of F<sup>-</sup> less than 0.5 mg/L can cause dental cavities and above 1.5 mg/l may lead to dental fluorosis further leading to skeletal fluorosis if exposed for a long term with a high dose (>8mg/l) (WHO, 2017). Fluoride enriched drinking water is the primary source of fluoride absorption in human and animals.

Fluoride intake through drinking water in body and then distributed throughout the body via blood. It's excreted via saliva, plasma, sweat, renal excretion (35 to 70% of ingestion) (Ekstrand et al., 1978; Oliveby et al., 1989). So, these can be used as biomarkers for fluoride disclosure in human body. Fluorosis is among the prominent health concerning issue in Haryana state in northern India. The present work was conducted to assess the fluoride in the ground water and in children urine. Prevalence of fluorosis among children and health risk assessment is also determined which is an essential tool to assess the health hazards due to various substances. This study can be helpful for future planning regarding health and water related issues in state and awareness in habitats regarding health problems due to elevated concentration of fluoride.

## **1.2 Objective**

To study the assessment of ground water and related health risks for fluoride in the related area so that it will helpful in planning regarding health and water related issues in state and awareness in habits associated with fluoride.

## 2.1 Ground Water

Ground water is an essential resource for drinking and other purposes worldwide specifically in arid and semi-arid regions where precipitation and surface water sources are limited (Li et al., 2017). Microbial contamination is comparatively lower level in ground water than surface water sources and assumed safe for drinking (Hybel et al., 2015; Mohebbi et al., 2013).

Natural activities such as natural deposition of minerals and anthropogenic activities such as urbanization, industrialization, fertilizers in agriculture are some activities which may responsible for ground water contamination (Ali et al., 2018; Saha et al., 2016; Sarkar et al., 2016; Shekhar and Sarkar, 2013).

## 2.2 Fluoride and its Availability

Fluoride becomes major concern from past few decades as one of the major contaminant in ground water. Elevated concentration of fluoride in subsurface water has effected around 35 Nations worldwide including Argentina, Mexico, Russia, China, India, Korea, Sri Lanka, Pakistan, some parts of Africa, Iran, etc. (K. K. Yadav et al., 2018). In India, the states such as Jammu and Kashmir, Telangana, New Delhi, UttarPradesh, Andhra Pradesh, Gujarat, Karnataka, Chhattisgarh, Haryana, Orissa, Jharkhand, Punjab, Tamil Nadu, Rajasthan, Kerala, Maharashtra, Madhya Pradesh, Bihar, Assam, and West Bengal contains elevated concentration of fluoride in groundwater (Adimalla Narsimha & Rajitha, 2018).

Fluorine is distinguished as most electronegative and reactive of all elements. It is the thirteenth common element in earth crust with concentration approx. 625mg/kg. (Ali et al., 2016; Brindha & Elango, 2011).

Weathering and leaching of the natural element in subsurface water is one of the important natural mechanisms controlling fluoride concentration in ground water. Fluorite is the major element of fluorine in nature and associated as an auxiliary mineral in granite rocks. Granite rocks contains 20-3600ppm of fluoride (Turekian & Wedepohl, 1961).

Apatite, amphiboles, hornblende, muscovite, biotite, micas, certain types of clays are some other constituents in nature which contains fluoride.(Bloss et al., 1959; Boyle, 1992; Foster, 1964).

Weathering and leaching of the natural element in subsurface water is the one of the important mechanism controlling fluoride concentration in ground water.

Salinity in irrigated areas of Haryana is the common problem in the state as used for irrigation from long time period with the intense use of fertilizers. Soil containing salinity may be the possible source of fluoride (Datta et al., 2000).

Industrial waste, excessive use of fertilizers, brick kiln, burning of coal, extraction of aluminum, and steel are some anthropogenic activities which elevate fluoride concentration in environment(Ali et al., 2016; Saxena et al., 2012).

### **2.3 Concern to Human Health**

Fluoride plays an important role in regulating various corporal activities of the body. Where intake of fluoride above or below some certain limits can cause dental cavities, dental fluorosis, skeletal fluorosis etc. The World Health Organization has set a range between 0.5 to 1.5 mg/L for drinking water (WHO, 2017).

Fluoride is beneficial for human and other animals for the formation of teeth and bone structure especially at early period of life. It helps in preventing dental caries and enhanced the remineralization of dental enamel. Fluoride concentration lower than 0.5 mg/L can cause dental cavities and above 1.5 mg/l may lead to dental fluorosis further leading to skeletal fluorosis if

exposed for a long term with a high dose (>8mg/l) (Ghaderpoori et al., 2019; Yousefi et al., 2018).

## **2.4 Fluoride in Human Body**

Enamel and dentin are the calcium rich constituents of teeth and have strong affinity with fluoride during formation. When fluoride accumulates in teeth, calcium fraction becomes lower level and thus gradually reduction in calcium left weaker teeth with pitted and discolored.

Skeletal fluorosis is the critical stage and happens when accumulated dose of fluoride in ingested for a long period of time. It affects the accumulation and resorption of bone tissues and further alters the bone mineral metabolism. This leads to increased bone mass and density, exostosis, development of cartilaginous wounds in the cancellous bones . Drinking water is the major source for ingestion of fluoride in human body. Other sources which contain some trace of fluoride are food and beverages i.e. wheat, spinach, cabbage, milk, tea, etc.(Cao et al., 1998; Susheela, 2003).

Tea, tobacco, toothpaste, pan masala also have traces of fluoride. Children some time swallow some part of toothpaste unknowingly which may lead to ingestion of fluoride.(A. K. Yadav et al., 2007).

Ingested fluoride is distributed in the body via blood and major portion get deposited in bones and teeth. Fluoride chronic exposure to kidney is relatively higher to plasma and soft tissues because its accumulation is higher in kidney (Kaminsky et al., 1990).

Ingested fluoride is excreted via saliva, urine, plasma; sweat etc. saliva excretes around 1% of ingested fluoride. Plasma and sweat excrete comparatively less to saliva. Renal excretion is around 35-70% of ingested fluoride. So, urine, plasma, saliva are used as biomarkers of exposure to fluoride in human body (Ekstrand et al., 1978; Oliveby et al., 1989).

Prevalence of dental fluorosis at younger age is reported in much research. Some studies reported that children at age 8-12 have more prone to fluorosis than above ages. Its further leads to permanent teeth decay as moderate, severe fluorosis (Del Carmen et al., 2016; Haritash et al., 2018).

## **2.5 Associated Health Risk Assessment**

Human health risk assessment is a method to assess the potential adverse health risk in humans that may be exposed or in future to chemicals through the environment. About 90% of endemic fluorosis in India is caused by the intake of fluoride contaminated water for a long period of time (A. Narsimha & Sudarshan, 2017).

The US Environmental Protection Agency (USEPA) prescribed a standard to calculate health risk for non-carcinogenic substances such as nitrate, fluoride, arsenic etc. this help in assessing the relative health risk to that substance in any particular area and making future policies or decision to tackle the health risk.

$$CDI = [C_w \times IR \times EF \times ED] / [B_w \times AET]$$

$$HQ_{\text{fluoride}} = CDI/RfD$$

USEPA mentioned some standards for the factors like standard weight, RfD (reference dose), exposure frequency etc. USEPA gives factor one as a safe limit or if health quotient value is above one then it indicates potential of human health risk (USEPA, 1993).

Many studies reported health risk due to fluoride worldwide. It's calculated for different age groups like infants, children, teenager, and adults. Children are more prone to health risk which may be due to their body weight. Studies in Iran, china, Europe has indicated high risk assessment due to higher fluoride concentration in drinking water (Ali et al., 2019; Ashrafi et al.,

2020; Yousefi et al., 2018). In India also many studies indicated high risk assessment due to intake of high fluoride contaminated drinking water (Ali et al., 2019; Adimalla Narsimha & Rajitha, 2018; K. K. Yadav et al., 2019).

## **2.6 Hydro geochemistry of ground water**

Hydro geochemistry of ground water is analyzed by many charts and method in context of fluoride. Piper diagram is a graphical representation for the geochemical interpretation of water analysis using multiple-trilinear diagram. Natural water contains few dissolved constituents, with cations (metals or bases) and anions (acid radicals) in chemical equilibrium. Cation constituents are basically two types; alkaline earths (Ca, Mg) and alkali (Na, K). Most common anions are weak acids ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) and strong acids ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ). In natural water cations are in chemical equilibrium with the anions. The trilinear plotting describes the chemical character of water relative to its constituents not according to the absolute concentration. The diamond shaped field describe the over- all chemical character of the water. The several dissolved constituents are measured in terms of percentage of reacting value i.e. their "equivalents per million" expressed as percentage of the sum of the equivalents for all the constituents (Piper, 1944).

## **2.7 Mechanism controlling ground water chemistry**

There are three major mechanisms which control the chemical composition of water on earth. Atmospheric precipitation, rock dominance and evaporation and crystallization are three major mechanisms controlling water chemistry.  $\text{Ca}^{2+}$  is considered as major cation for fresh water bodies and  $\text{Na}^+$  for high saline water bodies. The weight ratio of  $\text{Na}/(\text{Na} + \text{Ca})$  with the variation in total salinity i.e. for cations and  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$  with the variation in salinity for anions are plotted to understand the mechanism of water chemistry. The chemical compositions of low-salinity waters are controlled by the amount of dissolved salts furnished by precipitation in the



first mechanism i.e. atmospheric precipitation. The second mechanism i.e. rock dominance is dominated by the dissolved salts of rocks and soil and the evaporation crystallization which comprised the third mechanism is dominated by Na rich, high salinity, and precipitation of  $\text{CaCO}_3$  due to evaporation at the end point. Evaporation increased the dissolved salt and precipitation of  $\text{CaCO}_3$  increase the relative portion of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  in the basin, majorly in tropical regions. Also evapotranspiration and irrigation contributes towards increased mineralization in water (Feth & Gibbs, 1971; Gibbs, 1970).

## **2.8 State study related to fluoride**

Haryana is an agricultural dominant state of India. Many studies have witnessed high fluoride in ground water of the state. In last two decades urbanization and industrialization has risen up due to ease of business and its vicinity to the NCR-Delhi. Elevated concentration in ground water has been reported in many districts like Jhajjar, Sonapat, Panipat, Sirsa, Hisar, Gurugram, Bhiwani etc. (Ali et al., 2018; Haritash et al., 2008; Meenakshi et al., 2004; Singh et al., 2007; A. K. Yadav et al., 2007; K. K. Yadav et al., 2018).

The weight ratio of  $(\text{NO}_3^- + \text{Cl}) / \text{HCO}_3^-$  with the variation of total salinity (TDS), indicates the influence of human activities which may control or influence the chemical composition of ground water. Agricultural products such as use of fertilizers, sewage wastes are examples of human activities controlling the chemical composition of the ground water (Li et al., 2019; Marghade et al., 2012).

### 3.1 Study Area

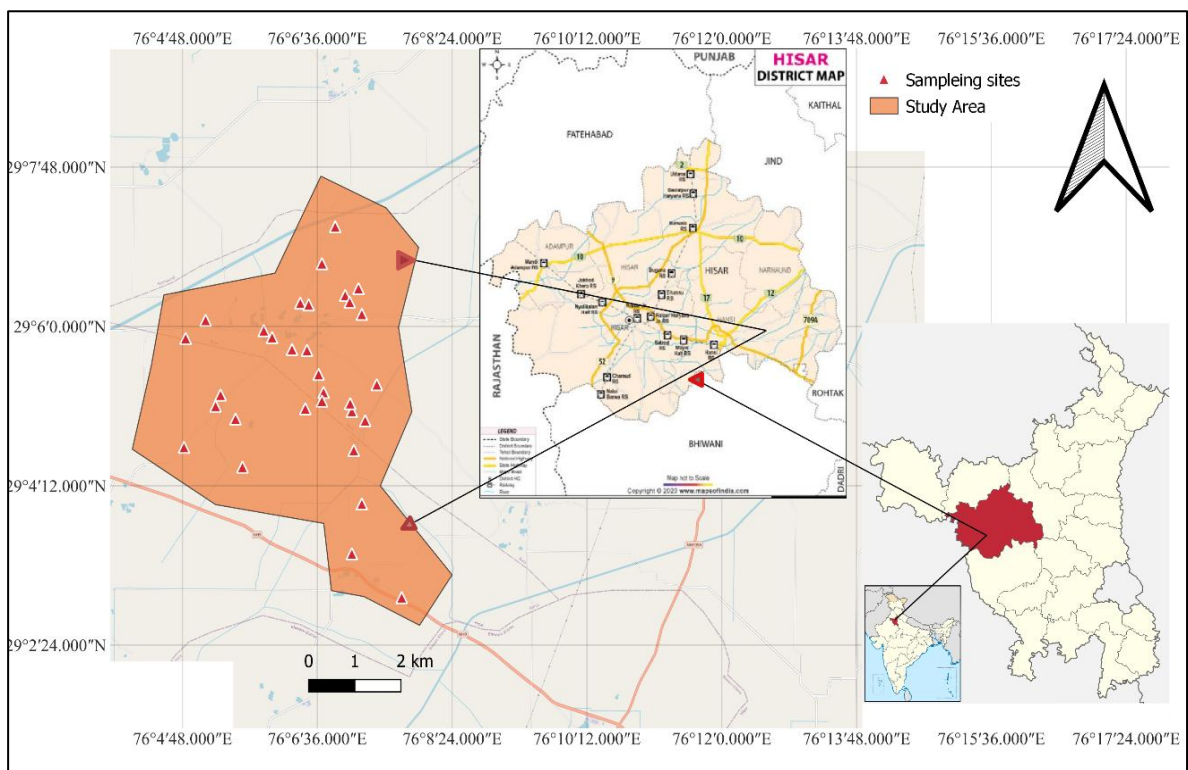
Haryana is one of the major agricultural states of India and located in northwest of the country. The state have a total area of 44,212 sq.km. The area of the present study is located in Hansi, block-II of Hisar district. The climate of area is semi-arid and alluvium deposits of quaternary age and average rainfall in the state is around 350mm.

The climate of district depends on southwest monsoon. The temperature of Hisar varied 40 to 46 de1.4 gree calcius in summer and 1.2 to 4.1 degree calcius in winter season. . Four villages were selected for the study in Hansi block having rural area.

All the villages have the major agricultural dominated region. Bhatol –Jattan village having population of 40000, Kharkara having population of 3800, Jeetpura having population of 2800, and Sorkhi having population of around 6700 . These villages are located in the region of water scarcity area as declared by the department of science and technology(Haritash et al., 2008, 2018). Groundwater is the major source of drinking in the study area. All the groundwater samples were collected from agriculture and domestic areas.

Dental fluorosis and urinary fluoride test were carried out in govt. secondary school (Bhatol-Kharkara) since this is the only secondary school in the nearby villages. Urine samples of children were collected and analyzed for fluoride in school. Many of the previous research in context of fluoride highlights many regions of elevated fluoride concentration in the state (Haritash et al., 2008, 2018) and the study area falls under the region where scarcity of water is the concerned issue.

All the groundwater sampling sites were showed in figure1, with the map of the district and highlighting the study area.



**Figure 1.** Location of the study area with sampling sites

### 3.2 Sample collection of ground water

A total of 30 ground water samples were collected from the domestic and agricultural land. The water samples collected in pre-washed 1000ml polyethylene bottles as per the guidelines of (APHA, 1999). The tube wells and hand pumps were pumped for 5 to 10 minutes until the physical and chemical parameters such as pH, electric conductivity has become stable. All the bottles are washed and rinsed many a times using water has to be sampled.

### 3.3 Sample collection of urine for fluoride assessment

Govt. Sec. School (village Bhatol - Kharkara) was selected to examine fluoride concentration among children as urine is biomarker of fluoride assessment in human. The school children of

the age 14 to 17 were selected to assess the fluoride through urinary test. The urine samples (total 40) were collected in 250ml cleaned plastic contains. The urine samples were collected with the prior consent of school authority and parents. The urine were collected from the first urination i.e. at home and then at school and the timing is between 6:00AM to 5:00 PM and examined in the school premise as per the guidelines of (WHO, 2014).

To examine the prevalence of dental fluorosis a cross survey of these children and some other children with a total of 145 children, having 70 girls and 75 boys has been done. Children were selected as such the major drinking water sources of these villages were covered and fluoride in source and prevalence of dental fluorosis were correlated. This survey is being carried as per the Dean's Index (Dean, 1942).

### **3.4 Analysis of water samples**

All the samples were analyzed in the laboratory, department of environmental engineering, DTU University Delhi as per the guidelines (APHA, 1999).

#### **Various Physical and chemical parameters**

##### **3.4.1 pH**

pH is expressed as the negative log of hydrogen ion in the solution or the measures of the acidity or alkalinity. pH can be measured by colorimetric method using indicator solutions or by using hydrogen ion-sensitive electrode.

##### *Reagents*

- pH buffer 4.0, 7.0, 9.2

### *Procedure*

- In the study pH of the samples was measured using pH meter. pH meter was standardized by using buffer solution of pH 4.0, 7.0, and 9.2. samples were measured and pH meter was calibrated in between and samples were repeated to check the accuracy.

### **3.4.2 Electric Conductivity**

Electric conductivity is the ability of an aqueous solution to flow an electric current. This capability depends on the presence of ions; their concentration, mobility, valence; and temperature of at the time of measurement.

### *Reagent*

- Potassium Chloride (KCL)

### *Procedure*

In the study EC was measured using Bench top Multiparameter Water Quality meter. The EC meter was calibrated with standard KCL solution (0.10N) and the solution was made by liquefying 0.7474g of KCL in 100ml of water. The EC of the stock solution was set at 12.88 mhos/cm and 25°C. All the samples were measured in the units of  $\mu\text{s}/\text{cm}$ .

### **3.4.3 Hardness**

Total hardness generally, expressed as the sum of the calcium and magnesium concentrations in the water. Other polyvalent cations also may cause hardness but they are often in complex and their role in water may be minimal so it expressed in terms of calcium and magnesium ions as calcium carbonates in water. Hardness in water is expressed as carbonate harness and

bicarbonate hardness. Carbonate hardness is equivalent to total alkalinity of water when hardness is greater than the sum of carbonate and bicarbonate alkalinity and the amount which in excess is called bicarbonate hardness. Hardness in water affects the soap bubble making and mainly in industries like where boilers are used.

#### Reagents

- 3.72 gm disodium salt of ethylenediaminetetraacetic acid dissolved in distilled water to form a total volume of 1000ml in a volumetric cylinder.
- Ammonium acetate buffer solution
- Eriochrome Black T

#### Procedure

- 10ml of sample taken in conical flask.
- Add 1ml of ammonium acetate solution in the sample and mixed well and then one pinch of EBT indicator added.
- After that it is titrated with and titrated with EDTA (0.01 M) until the color changed from reddish pink to blue color and the readings were noted down as initial volume consumed and final volume consumed.

#### Calculations

TH as  $\text{CaCO}_3 = (A \times B \times 1000) / \text{ml of sample used}$

Where,

A= ml of EDTA solution used and B= mg

$\text{CaCO}_3$  equivalent to 1.00 mL EDTA titrant

### 3.4.4 Alkalinity

Alkalinity is defined as its capacity to neutralize acids. Alkalinity of waters is majorly a function of carbonate, bicarbonate and hydroxide content which can be caused by the inorganic mineral or by the decomposition of organic matter in water.

#### *Reagents*

- Sulfuric acid (0.02N)
- phenolphthalein
- methyl orange

#### *Procedure*

- 10ml of groundwater sample was taken in a conical flask
- 2-3 drops of phenolphthalein were added in the sample. If the color of the sample changed from colorless to pink after adding phenolphthalein, then it was titrated with  $H_2SO_4(0.02N)$  until it became colorless and the readings were noticed.
- After the adding of phenolphthalein if color not changed then 2-3 drops of methyl orange were added and titrated until the reddish orange color appeared and reading were noted down.

#### *Calculations*

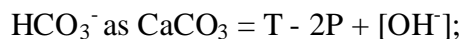
- Alkalinity as  $CaCO_3 = (A \times N \times 50000)/ml$  of sample;

Where,

A= ml of  $H_2SO_4$  used; and N= normality of  $H_2SO_4$  (0.02)

#### *$HCO_3^-$ as $CaCO_3$*

$HCO_3^-$  is present if phenolphthalein type alkalinity is less than the half of the total alkalinity.

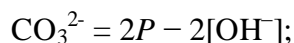


Where,

T= total alkalinity; and P= phenolphthalein type alkalinity



Carbonate alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity



Where,

P= phenolphthalein type alkalinity;

OH= alkalinity when phenolphthalein alkalinity is greater than half the total alkalinity

### **3.4.5 Major Anions ( Cl<sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup> )**

#### ***Chloride***

Chlorides have mild effects on living organisms, their excessive intake may cause toxicity to the living body. chlorides naturally present in water and also induced from leaching or direct discharge from industries, sewage waste, agriculture etc.

#### ***Reagents***

- Silver nitrate
- potassium chromate

#### ***Procedure***

- 25Mml of sample was taken in conical flask
- 2-3 drops of potassium chromate (K<sub>2</sub>CrO<sub>4</sub>) indicator were added to the sample and color changed to yellow
- The solution was titrated with AgNO<sub>3</sub> and readings were noted before and after titration.



### *Calculations*

CF (mg/l) = (A x N x 35.5×1000)/ml of sample;

Where;

N=normality of AgNO<sub>3</sub> (0.028N) and A= volume of AgNO<sub>3</sub> consumed

### ***Phosphate (PO<sub>4</sub><sup>2-</sup>)***

PO<sub>4</sub><sup>3-</sup> is a critical nutrient in the growth of algae. PO<sub>4</sub><sup>3-</sup> in water may be due to the discharge or leaching of sewage, detergents, and agricultural waste to the water source.

The digestion of nitric acid (HNO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) was used as a technique to determined total PO<sub>4</sub><sup>3-</sup>. The concentrated HNO<sub>3</sub> converts bounded PO<sub>4</sub><sup>3-</sup> to the boundless form. By using ammonium molybdate and stannous chloride (SnCl<sub>2</sub> ·2H<sub>2</sub>O) method, the total PO<sub>4</sub><sup>3-</sup> in the sample digested with concentrated acid, precipitated, detected, and read directly by spectrophotometer.

### *Procedure*

- 11 standards (0.1-1.0ppm) were prepared from stock solution of phosphate (100ppm) by serial dilution to obtained calibration graph .
- 10 ml sample was taken, 0. 4ml of concentrated H<sub>2</sub>SO<sub>4</sub> and 2 ml of concentrated HNO<sub>3</sub> were added.
- Set for 5-10 minutes at 200Kw, the sample were kept in the digestion unit, and the oven was turned on.
- After digestion, the solution was neutralized with NaOH. The solution turned pink – a color that appeared after the addition of 2-3 drops of phenolphthalein.
- Then, NaOH were added to the digested samples.

- 10ml of the sample was taken, and then 0.4ml of ammonium molybdate was added and mixed well.
- 4-5 drops of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were added to the solution and the solution was thoroughly mixed.
- After 5 minutes, the solution appeared blue.
- Then, the concentration was measured at a wavelength of 690 nm using the spectrophotometer and results were noted.

### *Sulphate ( $\text{SO}_4^{2-}$ )*

Sulfate is measured using the technique, which depend on the concept that Ba and  $\text{SO}_4^{2-}$  will form solids with nanometer size and this precipitated form by Ba and  $\text{SO}_4^{2-}$  is heightened in HCl acid, NaCl.

The concentration of sulfate was determined using a microprocessor UV-VIS single-beam spectrophotometer, Labtronics model-LT-290 at 420nm wavelength.

### *Reagents*

- Gelatin
- $\text{BaCl}_2$
- HCl
- $\text{Na}_2\text{SO}_4$

### *Preparation of reagents*

#### *1. Conditioning reagent*

- 0.3 gm of gelatin was dissolved in 100ml distilled water, then warmed and mixed until dissolved properly. then, cool and keep in the refrigerator for 12 hours.
- Allowed it to come to room temperature and add 3gm of  $\text{BaCl}_2$  and dissolved

## 2. Stock solution

- 0.14gm of anhydrous sodium sulfate dissolved in 1L of distilled water.
- 1L of concentration HCl was taken and added to 9L of distilled water.

### *Procedure*

- To make standard solutions, serial dilution from the stock solution were taken and standards were prepared varying to 5 to 100ml
- 20ml sample was taken and 1 ml of HCl was added
- 1ml of conditioning reagent was added and mix for 30 seconds.
- Wait for 30 minutes and absorbance noted.
- By plotting a graph, data obtained (concentration vs. percentage absorbance).
- Trace the points for the sample against measured absorbance.

### *Nitrate ( $\text{NO}_3^-$ )*

Nitrate is an essential nutrient for eutrophication. domestic sewage, natural runoff, agricultural wastes, industrial waste are some sources of  $\text{NO}_3^-$  in water. in small amount it is not harmful as it serves as an indicator of the decomposition of organic matter. But if nitrate is present in higher concentration it can cause methemoglobinemia or blue baby to the infant and children.

### *Reagents*

- Potassium nitrate ( $\text{KNO}_3$ )
- Hydrochloric acid

### *Procedure*

- Standard stock for nitrate was prepared from potassium nitrate then serial dilution to obtained standards solutions (1 to 5 ppm) for calibration graph with a blank .
- 10 ml of sample was taken

- 0.2ml HCL (1M) added and analyzed on spectrophotometer at a wavelength of 220nm

### *Fluoride (F<sup>-</sup>)*

Fluorine is distinguished as the most electronegative and reactive of all elements. Fluoride released in ground water by leaching and weathering of fluorine bearing minerals and also by anthropogenic activities. In the study fluoride concentration was determined by using an ion specific electrode (Orion 96-09 BNWP) fitted with an Orion Star A329 ISE Meter.

### *Reagents*

- NaF
- CDTA
- TISAB II

### *Procedure*

- Stock solution of fluoride was prepared from NaF i.e. 57gm of NaF taken and dissolved in distilled water to make up to 250ml in measuring cylinder.
- Standard solutions (10,5, 1.0ppm) from standard stock of fluoride (100ppm) were prepared for calibration of multi meter in sequence of lower to higher.
- Electrode is checked and filled with the specific solution and then rinsed with distilled water and dried by tissue.
- Slope was taken between (-59 to -62) on ISE mode.
- Then, 10ml of sample taken
- 1ml of CDTA was added to the sample
- Readings were noted and the meter was calibrated with standards after 5-7 samples.
- Samples were analyzed 2-3 times to check the accuracy.

- Samples were analyzed with 10 ml of sample and adding 1 ml of CDTA using ion electrode, ISE mode and having slope

### *Silica (SiO<sub>2</sub>)*

Silicon is the 2<sup>nd</sup> most abundant naturally occurring element on the earth crust. natural weathering of silicate from minerals containing silica, rocks are some source of silica in groundwater. Volcanic and polymeric states or waters heated with the earth are often rich in silica. The SiO<sub>2</sub> concentration in natural water bodies generally lies between 1 to 30mg/L. However, high concentration of SiO<sub>2</sub> are typically seen in brackish water(>1000mg/l). SiO<sub>2</sub> is objectionable in many industries because it forms silica and silicate scales. Silica concentration in samples was determined using spectrophotometer.

The concentration of SiO<sub>2</sub> was determined using Molybdosilicate Method.

### *Reagents*

- Sodium bicarbonate – NaHCO<sub>3</sub>
- H<sub>2</sub>SO<sub>4</sub>
- HCl

### *Procedure*

#### *1. Developing the color*

- 10 mL of sample was taken
- 0.2 mL of HCl and 0.4mL of ammonium molybdate reagent were added to the sample and mixed and for 5-10 minutes
- Then. 0.4ml of oxalic acid were added and mixed thoroughly
- Observe the color between 2 to 15 minutes to ensure that the solution shows yellow color.

## 2. *Preparation of standards*

- About 45 mL, of which  $\text{NaHCO}_3$  is 200 gm, and 1.0 N  $\text{H}_2\text{SO}_4$  is 2.4 ml added to the standard solutions
- Diluted to 50.0 mL

## 3. *Calibration curve and sample analysis*

- Standard solution (5 to 25 mg/l) from the stock solution (100mg/l) was prepared and calibration graph was obtained with these standards and one blank of distilled water.
- Samples were analyzed and a blank solution and at least one standard of samples was taken to confirm that the curve had not shifted as plotted with standard solutions.

### **3.4.6 Cations ( $\text{Ca}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Li}^+$ )**

#### *Calcium*

Calcium is an alkaline earth element present in the earth crust. The most common forms of calcium are calcium carbonate and calcium-magnesium carbonate. Calcium is the major ion impart total hardness in water. Calcium carbonates solubility depends on dissolved  $\text{CO}_2$  and pH. It is an important nutrition for animals and plants.

Calcium, in the present study samples was calculated by EDTA method and flame photometer method.

#### *EDTA titrimetric method*

#### *Reagents*

- EDTA
- sodium hydroxide
- murexide

### *procedure*

- 10ml of sample taken in conical flask
- 0.25ml of NaOH(6N) was added in the sample
- Then one pinch of murexide added in the solution
- Initial reading of the burette were noted for the titrant
- The solution was titrated with EDTA (0.01M) until the purple color appeared and the final reading

### *Calculations*

$\text{Ca}^{2+}$  as  $\text{Ca}^{2+} = (A \times B \times 400.8) / \text{ml of sample}$

$\text{Ca}^{2+}$  as  $\text{CaCO}_3 = (A \times B \times 1000) / \text{ml of sample}$

Where

A= ml of EDTA used , B= mg of  $\text{CaCO}_3$  equivalent to 1.00 ml EDTA titrant

- $\text{Ca}^{2+}$  concentration was also determined by using the Systronics make Flame Photometer 128 $\mu\text{C}$  model.

### ***Flame photometer Method***

Cations concentration is measured by using Flame photometry. Flame photometry is a division of atomic absorption spectroscopy. atomic, which focuses on electromagnetic radiation and the concentration of various cations are determined by illumination and wavelength .

### *Procedure*

- Open the lid, insert a suitable filter, and close the lid
- Enclosure the PVC free end and remove the duct in distilled or ultrapure water.
- Adjust the instrument and make sure that the device has 00 after adjusting it
- Adjust each channel until it reads 100 on the display screen

- Repeat the 3rd and 6<sup>th</sup> steps until 0 and 100 were shown only when blank solution and the standard solution, were draw out into the flame.
- Remove the PVC and the duct in distilled or ultrapure water for 2 – 3 minutes to wash the chamber carefully.
- Put PVC again into it, and capillary actions absorbed some sample; the concentration of the parameter being checked was recorded from the displayed on the screen.
- Intermittently insert the standard solutions whose concentrations are known from the calibration of the instrument and crosscheck the 00 with the blank solutions.
- Ca, K, Li, Na concentration were determined by Flame photometer in the study.

### ***Magnesium***

Magnesium commonly found in the minerals magnetite and dolomite and the common aqueous species is  $Mg^{2+}$  ions in water. Magnesium is an important element in plants and in red blood cells but few salt of magnesium is toxic by ingestion or inhalation.

Calculation

$$Mg^{2+} \text{ hardness as } CaCO_3 = [\text{Total hardness (as } CaCO_3/l) - \text{calcium hardness (as } CaCO_3/l)] \times 0.243$$

### ***Potassium***

$K^+$  is also found naturally. The concentration of  $K^+$  is generally lesser than  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ . In the study, the  $K^+$  concentration was determined by using the Systronics make Flame Photometer128H model. Higher potassium concentration in water is majorally by agriculture products and industrial wastes.



## ***Sodium***

Sodium is one of the essential cations that occur naturally with silicates and salt deposits. It may occur may occur in water by anthropogenic activities also like sewage, industrial waste excites ratio is important in human body and agriculture. Soil permeability can be affected by a high sodium ratio. In high concentrations it may affect persons with cardiac difficulties.  $\text{Na}^+$  concentration was determined by using the Systronics make Flame Photometer128H model.

### **3.5 Fluoride determination in Urinary**

Ingested fluoride is excreted via saliva, urine, plasma, sweat etc. Urinary excretion is around 35 to 70% of ingested fluoride . Fluoride among children urinary was determined using orean ion specific electrode (Orion 96-09 BNWP) fitted with an Orion Star A329 ISE Meter in the school.

#### ***Requirements***

- ISE specific electrode for fluoride analysis
- TISAB II
- Children Urine
- Standards solutions (0.1,1.0, 10.0ml) of  $\text{F}^-$  for the calibration of instrument
- Distilled Water
- Plastic measuring cylinder of different volume (10ml to 250ml)

#### ***Procedure***

- Bench top meter is connected to ISE specific electrode
- Calibrated with standards solution of  $\text{F}^-$  (0.1,1.0, 10.0ml) in lower to higher order and the standards were prepared in laboratory from stock solution of  $\text{F}^-$
- Electrode was washed with distilled water and dried with tissue after every reading

- 10ml Samples of urinary were taken in measuring cylinder after washing the cylinder with the sample
- Samples were measured and readings were noted down
- Instrument was calibrated with standards after every 10-15 samples analysis

### 3.6 Human Health Risk Assessment

Human health risk assessment is a method to assess the potential adverse health risk in humans that may be exposed or in future to chemicals through the environment. About 90% of endemic fluorosis in India is caused by the intake of fluoride contaminated water for a long period of time (A. Narsimha & Sudarshan, 2017). USEPA had given the formula to calculate health risk due to various non- carcinogenic substances. Many studies reported health risk due to fluoride worldwide. It's calculated for different age groups like infants, children, teenager, and adults.

So the health risk assessment due to daily ingestion of the fluoride via drinking water is estimated. The US Environmental Protection Agency (USEPA) prescribed a standard to calculate health risk for non-carcinogenic substances such as nitrate, fluoride, arsenic etc. This help in assessing the relative health risk to that substance in any particular area and making future policies or decision to tackle the health risk. Chronic daily intake (CDI) of fluoride is calculated as per the guide lines (USEPA, 1993).

$$CDI = [C_w \times IR \times EF \times ED] / [B_w \times AET]$$

Where CDI is expressed in mg/kg/day,  $C_w$  denoted the concentration of fluoride in ground water, IR indicated the ingestion of water in l/day, EF indicates exposure frequency in days/year, ED denotes exposure duration in years,  $B_w$  indicates the average body weight, and AET denotes the average exposure time which is the product of exposure frequency and exposure duration.

CDI is calculated for children , Adolescent (7-18), and for adults (above 18). In the present work, daily intake of water is taken as 0.85, 2, 2.5L/day by children, adolescent, and adults respectively. Exposure duration are taken as 12 years for children and 64 for adults and adolescence (Narsimha and Rajitha, 2018) and exposure frequency 365 days (Karunanidhi et al., 2019). Average body weight is taken as 15, 50, and 78 kg for children, adolescence and adults respectively. For calculating CDI age of children were considered between 2 to 6, for adolescent as 7 to 18 years, and for adults above 18 in the study.

Health risk for fluoride comes under non-carcinogenic risk and calculated as  $HQ_{\text{fluoride}}$  (Hazard Quotient of fluoride) as per equation:

$$HQ_{\text{fluoride}} = \text{CDI}/\text{RfD}$$

Where RfD is taken as a reference dose for the chronic oral exposure of fluoride i.e., taken as 0.06mg/kg/day according to (USEPA, 1993).  $HQ_{\text{fluoride}}$  value > 1 indicates severe effect on human health and < 1 is acceptable as per (USEPA, 1993)

### **3.7 Statistical analysis**

All the descriptive statistics such as average, standard deviation, minimum and maximum for the subjected parameters were estimated by using the Excel 2013 software and statistical analysis such as one-way ANOVA test analysis was done by using SPSS (IBM Corp.SPSS Statistics for Windows, Version 28.0). Piper chart was plotted using GW Chart and study area map using QGIS (3.18) software. Gibbs diagram was plotted using AQqa (Rock ware incorp.) and other graphs and correlating matrix using SPSS software with one-way ANOVA test .



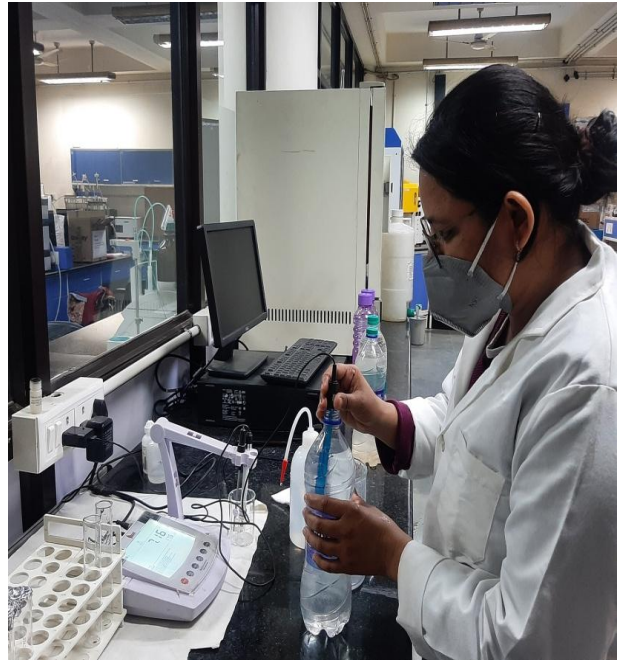
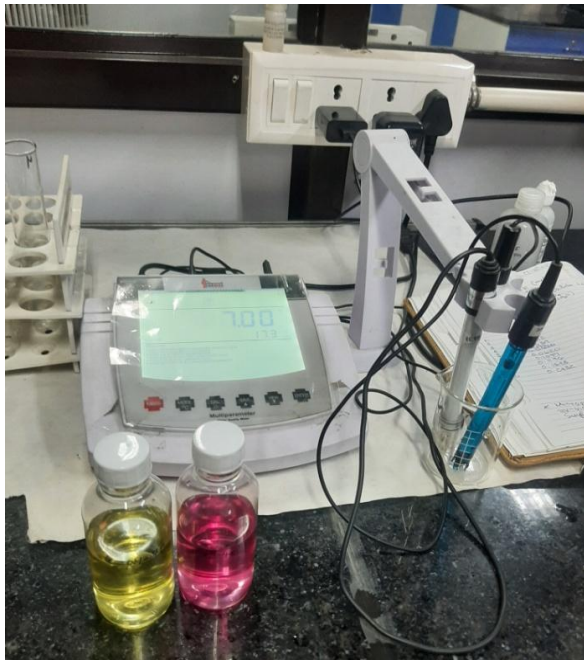
**Figure 2** Ion specific F meter (Orion make star 320 model) used for analysis



**Figure 3** , Spectrophotometer analysis (, Labtronics model-LT-290 ) for determination of chemical characteristics of water



**Figure 4** titration method for determination of alkalinity



**Figure 5** Benchtop multiparameter to analyze general parameters of water samples

### 4.1 Physical and chemical parameters

The various physical and chemical parameters of water are analyzed to determine the quality of water and its suitability for various purposes. The physical and chemical parameters of the ground water were statistically analyzed and compared with Indian standards (BIS, 2012) and International standards (WHO, 2017). All the results are shown in table 1 and table 2 having their mean, max, min, and standard deviation.

#### 4.1.1 pH

The ground water in this study was slightly alkaline as the range of hydrogen ions was between 6.5 to 7.3 and the mean was 7.0 with standard deviation of  $\pm 0.2$ . The desirable limit for pH is prescribed between 6.5 to 8.5 by both Indian standards (BIS, 2012) and international standards (WHO, 2017) and all the samples have pH values within the limits.

#### 4.1.2 EC

Electrical conductivity generally varied due to the ion concentration and their mobility in water. Conductance in water is concerned when present in higher concentration and not suitable for drinking, agricultural and other purposes. EC concentration in the present study was very high. The values of conductance ranged from 617 to 11260  $\mu\text{s}/\text{cm}$ . The max value of EC is observed 11260  $\mu\text{s}/\text{cm}$  and the average concentration observed was 3324  $\mu\text{s}/\text{cm}$  which is higher than standard value. The desirable limit for EC is prescribed  $\leq 1500$   $\mu\text{s}/\text{cm}$  (WHO, 2017) and around 70% sampled have values above than the limits. It may be high due to agricultural use of land from a long period.

### 4.1.3 TDS

Normally ground water has higher total dissolved solid compared to surface water. TDS concentration of the ground water samples were ranged from 308 to 5530mg/ and the mean concentration observed 1667 mg/l. the desirable limits for TDS in water as per Indian (BIS, 2012) and International standard (WHO, 2017) is <500 mg/l. Around 93% of the samples have exceed the desirable limits and not safe for drinking.

### 4.1.4 Total Hardness

Total hardness in the water is basically by the presence of cations, majorly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the water. The total hardness of the ground water samples ranged from 300 to 3160mg/l with an average of 1257mg/l. The desirable limit for hardness in drinking water as per Indian standard is <200mg/l and <500mg/l by International standards. All the groundwater samples have exceeded the limit for total hardness as compared to Indian standards and not suitable for drinking purpose.

### 4.1.5 Alkalinity

Total alkalinity in water is due to hydroxyl ions and hydrolysis of salts which formed by carbonates and bicarbonates. Total alkalinity in water samples is governed by  $\text{HCO}_3^-$ . Alkalinity is expressed as mg of  $\text{CaCO}_3$ /l in water. Total alkalinity in the groundwater samples ranged from 390 to 1160 mg/l as  $\text{CaCO}_3$ . The average concentration of  $\text{HCO}_3^-$  was 607mg/l as  $\text{CaCO}_3$ . According to Indian standards (BIS,2012) the maximum permissible limit for alkalinity is 600mg/l with desirable limit of 200mg/l. Around 73% of the samples in the present study exceed maximum permissible limit of the Indian standards. Lower concentration of alkalinity in not concerned but higher value is concerned in some industries.

#### 4.1.6 Sodium

Sodium value ranged from 36 to 1061 mg/l in the groundwater samples. The average value was 666mg/l with standard deviation of  $\pm 299$  mg/l. The acceptable limit for alkalinity in drinking water as per International standard is up to 200 mg/l. Around 57% of the samples have exceeds this limit.

#### 4.1.7 Potassium

Potassium value ranged from 3 to 384 mg/l in the groundwater samples. The average concentration was 29 mg/l with standard deviation of  $\pm 71$  mg/l. The acceptable limits for potassium in drinking water as per International standard is  $<10$ mg/l. Around 66% of the water samples have exceeds this limit.

#### 4.1.8 Calcium

Calcium is the major ion present in water which imparts hardness to water. Calcium value ranged from 4 to 318 mg/l as  $\text{CaCO}_3$  in the groundwater samples with an average of 138 mg/l. The acceptable limits for calcium in the drinking water as per Indian standards and International standards is  $<75$ mg/l. Calcium is essential element to human, animals and plants but when intake higher concentration than it may harmful.

#### 4.1.9 Magnesium

Magnesium is determined as the difference of total hardness and calcium. Calcium and magnesium both imparts hardness in water. Generally,  $\text{Mg}^{2+}$  hardness is lower than calcium in the water but in the present study magnesium hardness was observed higher than calcium. Magnesium hardness ranged from 190 to 1710 mg/l with an average of 705 mg/l. The acceptable limit for  $\text{Mg}^{2+}$  in the drinking water as per Indian standard is  $<30$  mg/l and  $<50$ mg/l by International standards. All the groundwater samples have exceeds the permissible limits.



#### 4.1.10 Carbonates and bicarbonates

Carbonates and bicarbonates both impart alkalinity to water.  $\text{CO}_3^{2-}$  concentration were ranged from 0 to 108 mg/l as  $\text{CaCO}_3$  in the groundwater samples.  $\text{HCO}_3^-$  value ranged from 350 to 980 mg/l in the water samples. The acceptable limit for  $\text{HCO}_3^-$  is <300mg/l as per International standards. all the groundwater samples have exceeded this limits.

#### 4.1.11 Chloride

The higher concentration of  $\text{Cl}^-$  in water is due to sewage or agricultural products. Chloride concentration is higher in almost all samples than the permissible limits i.e. 250mg/l (BIS, 2012) and the maximum value observed was 4400 and average 872mg/l. It may be higher due to fertilizer used in agriculture.

#### 4.1.12 Sulphate

The acceptable limit for  $\text{SO}_4^{2-}$  in the drinking water as per Indian standard is <200 mg/l and <400mg/l by International standards.  $\text{SO}_4^{2-}$  value ranged from 157 to 373 mg/l in the groundwater samples with an average of 305 mg/l. Almost 933% samples exceeds the permissible limits of Indian standards but all the samples have concentration below the International standards. the higher value of  $\text{SO}_4^{2-}$  in water may contributed by anthropogenic activities.

#### 4.1.13 Nitrate

Sewage, industrial effluents, agricultural wastes are the major source of  $\text{NO}_3^-$  concentration in water. The concentration of nitrate in the groundwater varied from 0 to 23mg/l with an average of 3mg/l. The Indian and International standards both prescribed the desirable limit <45 mg/l. The samples have concentration below the prescribed limits. Higher value of  $\text{NO}_3^-$  in

water leads to eutrophication in water bodies and also causes blue baby syndrome (Methaemoglobinaemia) in children.

#### **4.1.14 Phosphate**

$\text{PO}_4^{3-}$  value ranged from 0 to 0.2 mg/l in the samples. The acceptable limit for  $\text{PO}_4^{3-}$  is <0.3mg/l as per International standards. All the water samples have concentration within the prescribed limit. Higher concentration of phosphates leads to growth of algae in water bodies and harmful for aquatic lives as well as to human.

#### **4.1.15 Fluoride**

Fluoride has both beneficial and adverse effect on human body. The acceptable limit for  $\text{F}^-$  in drinking water as per Indian standard is <1mg/l and <1.5mg/l by International standards .  $\text{F}^-$  value ranged from 0.5 to 5.5 mg/l in groundwater samples. The average value observed 2.4 mg/l, standard deviation of  $\pm 1.4$  mg/l. Fluoride is beneficial formation of teeth at early ages. Fluoride concentration lower than 1 can cause dental cavities and higher concentration can cause dental fluorosis and further skeletal fluorosis when exposed for a long period. Around 73% of groundwater samples exceed the permissible limits as prescribed by Indian standards.

#### **4.1.16 Silica**

Silicon is the 2<sup>nd</sup> most abundant naturally occurring element on the earth crust. Volcanic and polymeric states or waters heated with the earth are often rich in silica. The  $\text{SiO}_2$  concentration in natural water bodies generally lies between 1 to 30mg/L. However, high concentration of  $\text{SiO}_2$  are typically seen in brackish water (>1000mg/l).  $\text{SiO}_2$  value in samples ranged from 34 to 62 mg/l.

**Table 1.** *Physic-chemical parameters of ground water samples*

S. No.	pH	EC ( $\mu\text{s}/\text{cm}$ )	TDS (mg/l)	TH (mg/l)	Alkalinity (mg/l)	Salinity (mg/l)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)
1	6.9	1706	853	1120	690	820	51	73	42	740
2	6.5	1194	601	580	390	520	95	5	35	350
3	6.8	1074	542	610	450	480	76	6	30	380
4	6.8	11260	5530	3160	730	6150	862	4	318	1540
5	7.0	3780	1904	1550	1160	1960	555	12	158	1220
6	6.8	6060	3050	1900	850	3260	788	13	236	1320
7	7.1	8220	4140	2390	670	4510	1020	14	264	1710
8	7.1	9690	4870	2480	780	5370	1061	11	304	1450
9	7.0	4940	2480	2680	470	2610	150	384	233	1050
10	6.9	5330	2680	2230	610	2840	459	12	260	940
11	7.1	5010	2540	1460	850	2670	837	16	240	860
12	6.9	2240	1124	800	790	1110	417	11	138	500
13	6.9	1473	741	590	650	690	226	16	83	430
14	7.1	1883	941	710	680	910	200	101	105	350
15	7.1	1567	784	480	870	740	302	12	86	330
16	6.9	1269	635	550	770	580	141	41	67	390
17	6.9	2960	1480	1310	600	1500	384	4	175	570
18	6.7	3540	1776	2790	680	1820	124	23	211	1250
19	7.1	1936	968	840	530	940	256	13	133	420
20	7.3	709	356	300	500	290	140	3	50	740
21	7.1	617	308	370	430	230	36	5	4	190
22	6.9	2880	1444	920	680	1460	562	6	171	440
23	6.9	1598	802	960	680	760	146	10	116	460
24	6.9	2810	1414	960	730	1420	571	16	169	520
25	6.9	1294	645	600	430	590	109	11	70	320
26	7.1	5260	2670	2030	590	2820	606	12	23	1100
27	7.1	1485	742	680	620	700	175	5	89	220
28	7.1	2010	1015	900	650	980	207	3	13	410
29	7.2	3010	1513	910	610	1520	550	7	177	340
30	6.8	2920	1476	860	850	1480	435	8	127	620

*Contd.*

S. No.	Li (mg/l)	CO <sub>3</sub> <sup>2-</sup> (mg/l)	HCO <sub>3</sub> <sup>-</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	SiO <sub>2</sub> <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	PO <sub>4</sub> <sup>3-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	F <sup>-</sup> (mg/l)
1	0.8	180	510	100	50	319	0.1	1	5.5
2	0.2	40	350	160	37	275	0.1	1	3.1
3	0.2	40	410	108	43	277	0.1	3	0.7
4	0.3	100	630	4400	61	367	0.1	5	0.8
5	0.4	180	980	840	62	330	0.1	9	3.0
6	1.3	80	770	1800	60	347	0.1	3	2.6
7	1.5	60	610	3000	52	348	0.1	5	2.4
8	1.0	60	720	3000	50	368	0.1	9	5.2
9	1.3	40	430	600	40	373	0.1	3	0.9
10	1.4	40	570	1800	59	345	0.1	3	3.0
11	1.0	60	790	1200	51	349	0.1	5	4.1
12	1.0	80	710	600	46	322	0.1	1	2.8
13	0.2	60	590	400	48	272	0.1	2	2.4
14	0.3	40	640	600	39	298	0.1	23	1.2
15	0.3	100	770	480	59	233	0.1	0	4.9
16	0.4	80	690	400	51	239	0.1	0	3.4
17	0.4	40	560	800	37	338	0.1	4	1.0
18	0.9	60	620	520	55	370	0.1	3	2.3
19	0.3	60	470	680	49	295	0.1	1	2.8
20	0.0	40	460	320	44	157	0.2	1	2.3
21	0.1	40	390	200	36	172	0.1	0	3.8
22	0.2	40	640	920	55	334	0.1	2	0.7
23	0.1	40	640	280	66	326	0.1	4	0.6
24	0.7	60	670	680	47	345	0.1	5	1.2
25	0.1	40	390	520	34	237	0.1	1	1.0
26	0.8	0	590	680	47	370	0.1	2	3.0
27	0.1	0	620	240	55	265	0.1	0	1.2
28	0.1	40	610	140	39	291	0.1	1	0.5
29	0.4	40	570	200	40	316	0.2	0	2.1
30	0.4	40	810	480	54	279	0.1	3	4.0

**Table 2.** *Statistical analysis of various physicochemical parameters of water samples*

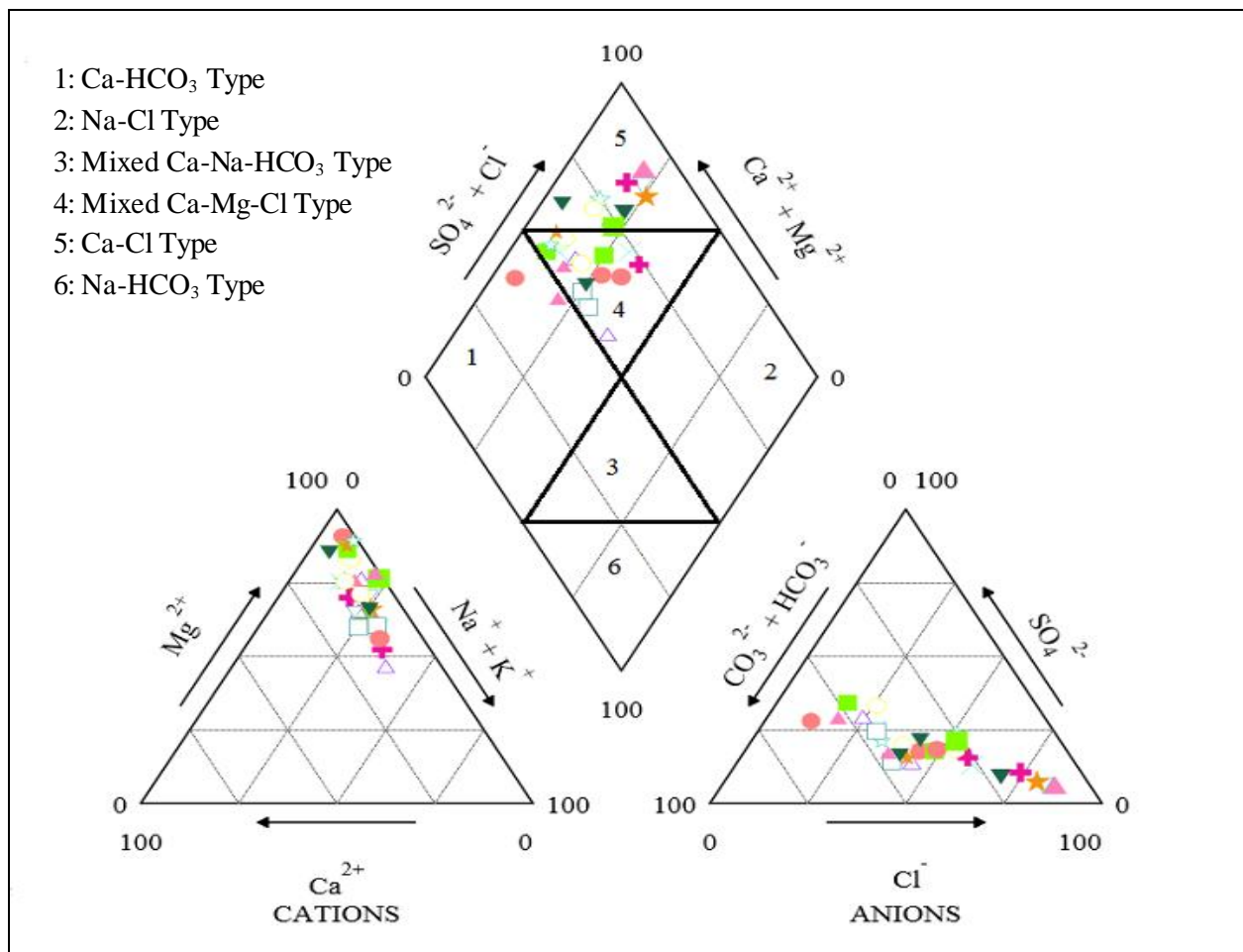
Chemical Parameter	Concentration				Desirable Limits	
	Minimum (n=30)	Maximum (n=30)	Mean (n=30)	Standard Deviation ( $\pm$ )	BIS (2012)	WHO (2017)
pH	6.5	7.3	7.0	$\pm 0.2$	6.5-8.5	6.5-8.5
EC ( $\mu\text{s}/\text{cm}$ )	617	11260	3324	$\pm 2651$	-	< 1500
TDS (mg/l)	308	5530	1667	$\pm 1322$	< 500	< 500
TH (mg/l)	300	3160	1257	$\pm 813$	< 200	< 500
Ca <sup>2+</sup> (mg/l)	4	318	138	$\pm 90$	< 75	< 75
Mg <sup>2+</sup> (mg/l)	190	1710	705	$\pm 432$	< 30	< 50
Na <sup>+</sup> (mg/l)	36	1061	385	$\pm 298$	-	< 200
K <sup>+</sup> (mg/l)	3	384	29	$\pm 70$	-	< 10
HCO <sub>3</sub> <sup>-</sup> (mg/l)	350	980	607	$\pm 142$	-	< 300
Cl <sup>-</sup> (mg/l)	100	4400	872	$\pm 998$	< 250	< 200
NO <sub>3</sub> <sup>-</sup> (mg/l)	0	23	3	$\pm 4$	< 45	< 45
SO <sub>4</sub> <sup>2-</sup> (mg/l)	157	373	305	$\pm 57$	< 200	< 400
PO <sub>4</sub> <sup>3-</sup> (mg/l)	0.1	0.2	0.1	$\pm 0.0$	-	< 0.3
F <sup>-</sup> (mg/l)	0.5	5.5	2.4	$\pm 1.4$	< 1.0	< 1.5

## 4.2 Hydro geochemistry of Ground Water

### 4.2.1 Piper Diagram analysis

Piper diagram is a graphical representation for the geochemical interpretation of water analysis using multiple-trilinear diagram. Natural water contains few dissolved constituents, with cations

(metals or bases) and anions (acid radicals) in chemical equilibrium. Cation constituents are basically two types; alkaline earths (Ca, Mg) and alkali (Na, K). Most common anions are weak acids ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) and strong acids (Cl,  $\text{SO}_4^{2-}$ ). The piper diagram demonstrate that the alkaline earth ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are dominant over alkalis ( $\text{Na}^+$ ,  $\text{K}^+$ ) and strong acids (Cl,  $\text{SO}_4^{2-}$ ) dominant over weak acids ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ). The hydro geochemistry of ground water can be categorized of two types: as shown in figure 6, i.e. is mixed type and around 50 % samples fall in this category (no cation- anion exceeds 50 %) and category 5 i.e.  $\text{Ca}^{2+}$ - Cl type and almost 50 % fall in this category.  $\text{Mg}^{2+}$  is the dominating cation and Cl is dominating anion.



**Figure 6.** Hydro geochemical classification of the ground water based on Piper Diagram

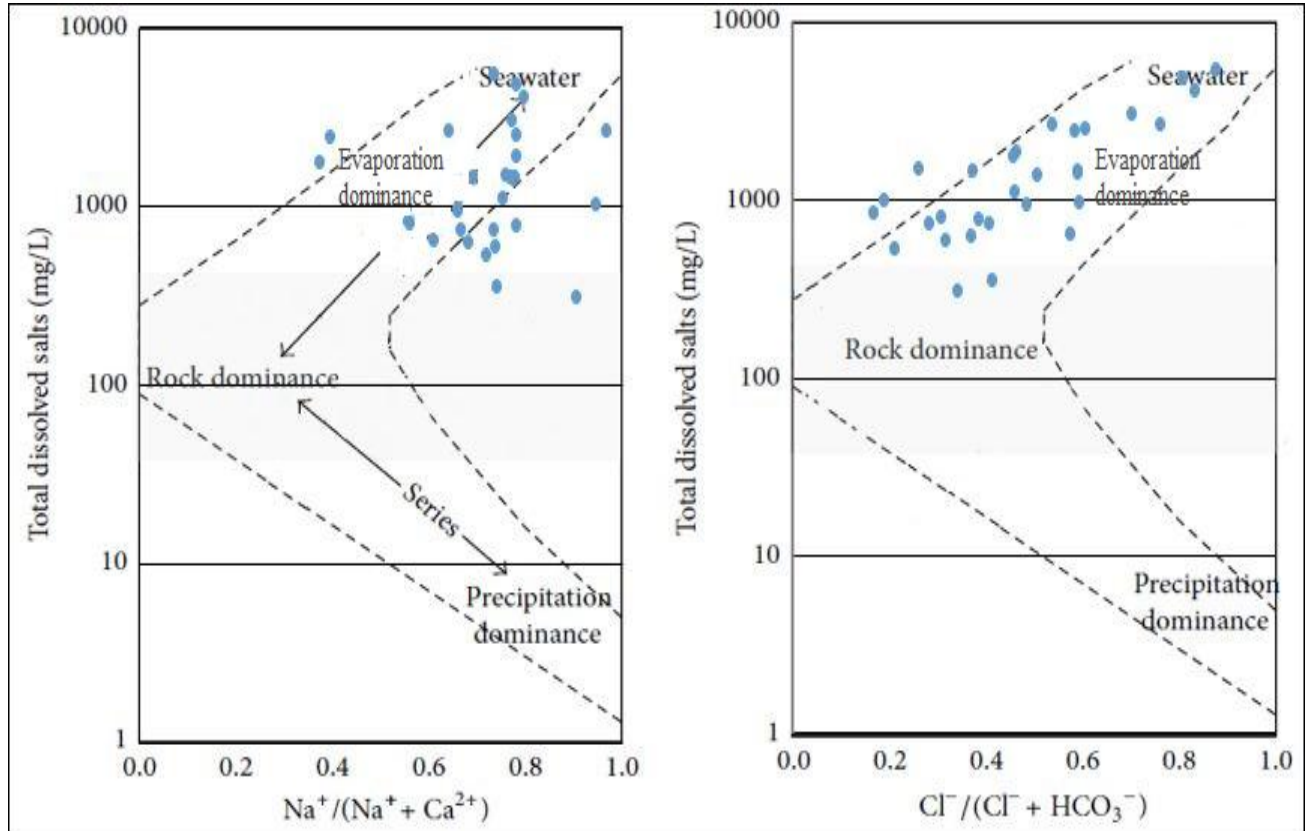
## 4.2.2 Mechanism controlling groundwater chemistry

### 4.2.3 Gibbs Classification

There are three major mechanisms which control the chemical composition of water on earth. Atmospheric precipitation, rock dominance and evaporation and crystallization are three major mechanisms controlling water chemistry.  $\text{Ca}^{2+}$  is considered as major cation for fresh water bodies and  $\text{Na}^+$  for high saline water bodies. The weight ratio of  $\text{Na}/(\text{Na} + \text{Ca})$  with the variation in total salinity i.e. for cations and  $\text{Cl}/(\text{Cl} + \text{HCO}_3^-)$  with the variation in salinity for anions are plotted to understand the mechanism of water chemistry. The chemical compositions of low-salinity waters are controlled by the amount of dissolved salts furnished by precipitation in the first mechanism i.e. atmospheric precipitation. The second mechanism i.e. rock dominance is dominated by the dissolved salts of rocks and soil and the evaporation crystallization which comprised the third mechanism is dominated by Na rich, high salinity, and precipitation of  $\text{CaCO}_3$  due to evaporation at the end point. Evaporation increased the dissolved salt and precipitation of  $\text{CaCO}_3$  increase the relative portion of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  in the basin, majorly in tropical regions. Also evapotranspiration and irrigation contributes towards increased mineralization in water (Feth & Gibbs, 1971; Gibbs, 1970). The third mechanism is dominated by sodium rich, salinity and precipitation of  $\text{CaCO}_3$  due to evaporation at the end point the chemical compositions of low-salinity waters are controlled by the amount of dissolved salts furnished by precipitation in the first mechanism i.e. atmospheric precipitation.

Gibbs diagram (figure 7) revealed that the quality of ground water is predominately governed by evaporation crystallization and rock dominance phenomenon i.e. second and third mechanism of Gibbs classification. Water depth in the study area is around 3-4 m and evaporation dominance as the regulating mechanism shows that anthropogenic activities may also responsible for the

hydro geochemistry (Li et al., 2019). Evaporation mechanism and rock dominance may be responsible for the accumulation of fluoride in the study area.

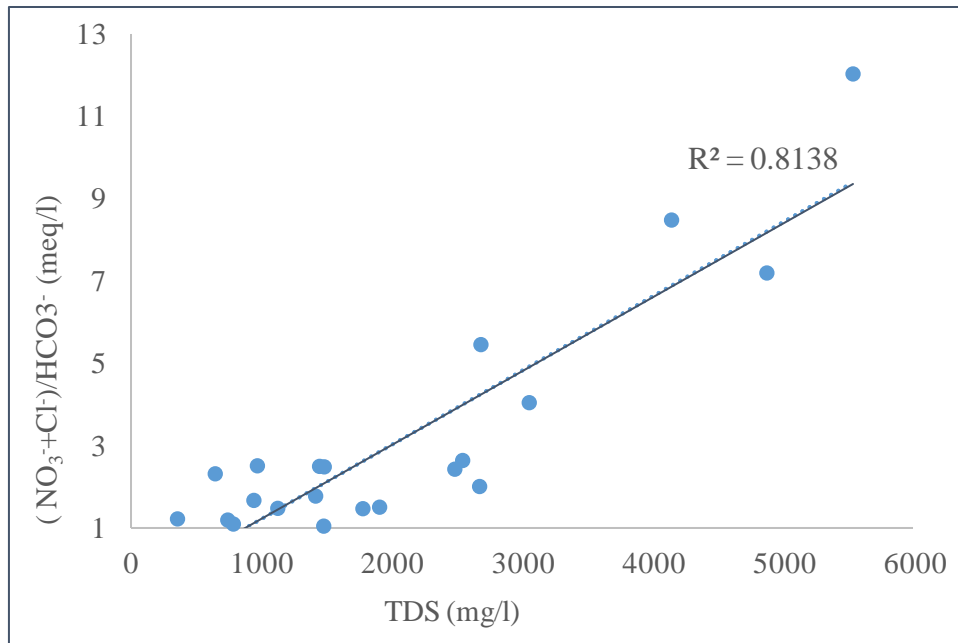


**Figure 7.** Gibbs diagram indicating the mechanism of regulating ground water chemistry

#### 4.2.4 Bivariate plot of $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$ and TDS

Bivariate plot of  $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$  and TDS were plotted. This plot (fig. 8), shows positive trend between  $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$  and TDS which shows anthropogenic interaction and it's basically an agricultural from a long period, fertilizers may contribute as the primary source of activities (Li et al., 2019; Marghade et al., 2012). Nitrate and chloride both have higher concentration due to anthropogenic activities and bicarbonate presents basically naturally in water and the plot showed there ration above the one.





**Figure 8.** Bivariate plot of TDS and  $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$

#### 4.2.5 Correlation Matrix (Pearson coefficient)

The correlation matrix (table 3) indicates fluoride has positive correlation with pH, bicarbonate, sodium, potassium, and negative with Calcium, sulfate, phosphate and nitrate.

Observations indicates strong correlation of  $\text{F}^-$  with carbonate ( $r=0.436$ ) and bicarbonate ( $r=0.266$ ) and weak correlation with  $\text{Ca}^{2+}$  ( $r=-0.008$ ) and  $\text{Mg}^{2+}$  ( $r=0.162$ ). This matrix shows that the value of fluoride in the groundwater increases as the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  content in water increases and decreases when the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  increases (Dey et al., 2012). Also  $\text{F}^-$  has positive correlation with  $\text{Na}^+$  and many studies suggested that  $\text{F}^-$  concentration is associated with increasing the  $\text{Na}^+$  concentration (Moghaddam & Fijani, 2008; A. Narsimha & Sudarshan2017).

**Table 3.** Correlation matrix for various physical and chemical parameters of water samples

Variables	Ph	EC	TDS	F <sup>-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	K <sup>+</sup>
pH	1													
EC	-0.003	1												
TDS	0.001	<b>1.000**</b>	1											
F <sup>-</sup>	0.097	0.082	0.088	1										
Cl <sup>-</sup>	-0.027	<b>.933**</b>	<b>.930**</b>	0.042	1									
Ca <sup>2+</sup>	-0.056	<b>.826**</b>	<b>.826**</b>	-0.008	<b>.787**</b>	1								
Mg <sup>2+</sup>	-0.040	<b>.872**</b>	<b>.874**</b>	0.162	<b>.774**</b>	<b>.713**</b>	1							
CO <sub>3</sub> <sup>2-</sup>	-0.130	0.123	0.120	<b>.436*</b>	0.159	0.131	0.292	1						
HCO <sub>3</sub> <sup>-</sup>	0.086	0.313	0.316	0.266	0.255	<b>.382*</b>	0.330	<b>.415*</b>	1					
NO <sub>3</sub> <sup>-</sup>	0.097	0.249	0.250	-0.106	0.252	0.264	0.218	0.092	0.309	1				
SO <sub>4</sub> <sup>2-</sup>	-0.242	<b>.685**</b>	<b>.688**</b>	-0.108	<b>.489**</b>	<b>.696**</b>	<b>.633**</b>	0.119	0.338	0.297	1			
PO <sub>4</sub> <sup>3-</sup>	<b>.373*</b>	-0.249	-0.247	-0.127	-0.342	-0.175	-0.282	-0.268	-0.069	<b>-.361*</b>	-0.227	1		
Na <sup>+</sup>	0.155	<b>.847**</b>	<b>.851**</b>	0.170	<b>.796**</b>	<b>.749**</b>	<b>.698**</b>	0.105	<b>.539**</b>	0.237	<b>.590**</b>	-0.124	1	
K <sup>+</sup>	0.051	0.068	0.069	-0.134	-0.088	0.155	0.124	0.006	-0.207	0.169	0.232	-0.057	-0.205	1

\*\* p < 0.01 (2-tailed) ; \* p < 0.05; N=30

### 4.3 Fluoride in Urine

Ingested fluoride is excreted via saliva, urine, plasma; sweat etc. saliva excretes around 1% of ingested fluoride. Plasma and sweat excrete comparatively less to saliva. Renal excretion is around 35-70% of ingested fluoride. So, urine is the major biomarkers of exposure to fluoride in human body (Ekstrand et al., 1978; Oliveby et al., 1989). Urinary fluoride among children were examined by prior studying the source where most population depend on ground water and 3 stations were selected where no. of population using ground water for drinking and cooking is high. All the data are shown in table 4 and 5; for boys and girls.

Fluoride urinary concentration was examined between 6:00 am to 5:00 pm in children having boys and girls each 20. Fluoride was examined at spot and concentration of  $F^-$  in boys is shown in table 6, with the time period of urinary void. The urinary fluoride ranges between 0.1 to 12mg/l in boys. The mean concentration of  $F^-$  in boys is higher than girls, having 4.2 in boys and 2.9 in girls (table, 6).

Also, the children are assigned as per their source of drinking water and their mean concentration of fluoride is analyzed (table, 7) with respect to the  $F^-$  level in source.

In table 6, this demonstrates that average fluoride in urine is higher than the source which may be due to additional ingestion of fluoride via intake of tea, milk, vegetables, etc. Similar observations of higher  $F^-$  in urine have been made in other studies too (DeI Carmen et al., 2016; Haritash et al., 2018; Szymaczek and Lewicka, 2005; Paez & Dapas, 1982) ascribing the reason to additional intake of bioavailable fluoride through food.

It's also noticed that  $F^-$  concentration is high among children in the morning urinary extraction which is shown in figure 9.

**Table 4.** *Urinary Fluoride concentration (Boys) at different time periods*

S. NO.	Age (Years)	Concentration (mg/l)			
		Time <sub>1</sub> (6:00 AM - 8:00 AM )	Time <sub>2</sub> (12:00PM- 1:00 PM )	Time <sub>3</sub> (2:00PM- 3:00 PM )	Time <sub>4</sub> (3:00PM- 4:30 PM)
1	15	2.3	-	2.3	-
2	15	1.5	5.8	2.5	0.5
3	14	1.0	0.7	-	0.1
4	13	3.1	3.3	-	-
5	14	2.2	-	5.7	-
6	15	1.2	1.4		-
7	13	4.1	-	8.7	-
8	15	4.9	-	5.6	-
9	15	3.0	-	1.9	-
10	14	4.0	-	7.7	-
11	13	2.9	3.2	5.6	-
12	14	1.6	-	1.9	-
13	15	9.8	6.0	8.7	-
14	14	5.3	-	6.1	5.9
15	15	6.0	-	1.2	2.2
16	16	12	6.1	-	-
17	14	10	-	1.9	-
18	15	4.2	6.1	-	-
19	13	6.1	6.0	-	-
20	15	3.1	1.6	-	-

**Table 5.** *Urinary fluoride concentration (Girls) at different time periods*

S. NO.	Age (Years)	Concentration (mg/l)			
		Time <sub>1</sub> (6:00 AM - 8:00 AM )	Time <sub>2</sub> (12:00PM- 1:00 PM )	Time <sub>3</sub> (2:00PM- 3:00 PM )	Time <sub>4</sub> (3:00PM- 4:30 PM)
1	14	3.1	1.0	1.0	-
2	13	1.8	3.1	-	1.6
3	14	4.0	4.2	3.2	-
4	14	4.3	1.0	1.1	-
5	16	4.2	4.6	3.8	-
6	13	3.3	4.5	1.9	-
7	13	3.3	0.7	1.4	-
8	14	8.9	0.7	1.4	-
9	15	6.6	4.2	-	4.9
10	15	1.2	1.0	-	1.4
11	14	3.3	1.1	-	4.1
12	13	3.5	1.8	3.1	-
13	13	3.5	1.0	1.2	-
14	14	4.1	2.1	-	2.9
15	13	5.1	3.1	-	3.6
16	15	4.1	3.1	-	4.2
17	14	2.5	-	2.1	-
18	13	3.3	-	1.9	-
19	13	4.4	2.6	-	-
20	15	2.4	-	1.4	-

#### 4.4 Dental Fluorosis among children

Dean classification is a very older method to determine or identify fluorosis by examining the teeth. The classification divided in six categories from normal teeth to severe dental fluorosis. These are defined by examining the surface of teeth and the patched of color like yellow to turning brown. Normal teeth have all the teeth clearly visible white and as the severity increased the color on teeth changed covering 10-20% color changed with mild and further the percentage increased from 30-50, and in severe condition all teeth turned yellow to brown and also teeth decay started.

Fluorosis as per the Dean chart, examined in 145 children as shown in table 7. A total of 70 girls and 75 boys' teeth were examined for fluorosis and correlated with their source of drinking and classified as per Dean Chart from normal to severe. Dental fluorosis survey was done in school and also door to door and there source of drinking was asked and values classification is assigned to their source of drinking to analyze the correlation of dental fluorosis and fluoride concentration in the source.

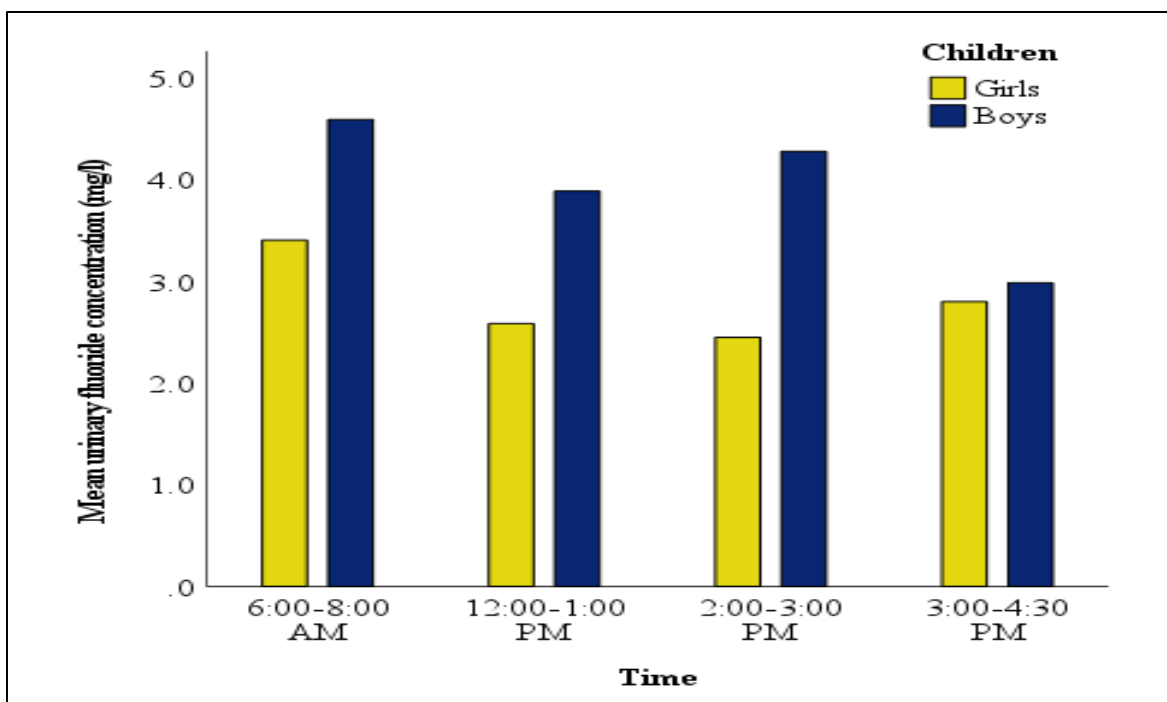
Figure 10, shows that ; 17% girls and 16% boys have very mild; 47% girls and 45% boys have mild; 21% girls and 22% boys have moderate and around 2.5% girls and 6.5% boys comes in severe category. Fluorosis in children is also compared (shown in figure 7,) with the source and its observed no. of mild fluorosis at all stations were almost same. No. of severe cases are higher at station with higher  $F^-$  concentration in ground water. It's also observed that  $F^-$  concentration and no. of prevalence of fluorosis is high in boys as the drinking and food ingestion is more.

**Table 6.** *F<sup>-</sup> Mean concentration in urine of children at different time periods*

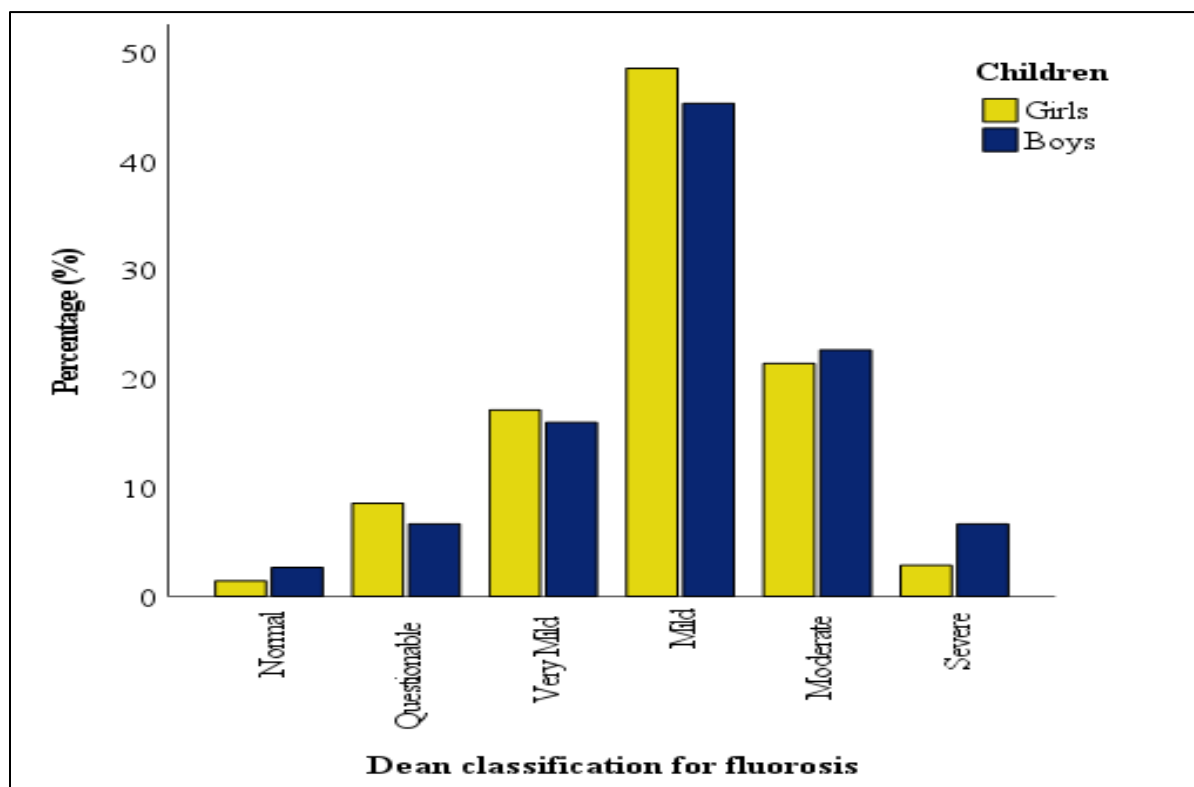
Children (n=40)	F <sup>-</sup> Mean concentration of urinary F <sup>-</sup> with time				Min	Max.	Mean	Standard Deviation (±)
	T <sub>1</sub> (6:00-8:00 pm)	T <sub>2</sub> (12:00-1:00 pm)	T <sub>3</sub> (2:00-3:00 pm)	T <sub>4</sub> (3:00-4:30 pm)				
Girls (n=20)	3.9	2.3	2.0	3.2	0.6	8.9	2.9	±1.0
Boys (n=20)	4.4	4.5	4.6	2.2	0.1	12	4.3	±2.3

**Table 7.** *Correlating the F<sup>-</sup> in source with F<sup>-</sup> in urinary and dental fluorosis*

F <sup>-</sup> in source	Fluorosis in children as per Dean classification							F <sup>-</sup> in urinary	
	Normal	Questionable	Very Mild	Mild	Moderate	Severe	Total (n=145)	No. of children	Average F <sup>-</sup> in urinary
3.1	1	4	8	19	9	2	43	14	4.0
2.4	1	3	5	12	11	2	34	12	2.7
4.9	0	2	5	19	9	3	38	14	4.0
1.2	1	2	6	18	3	0	30	-	-

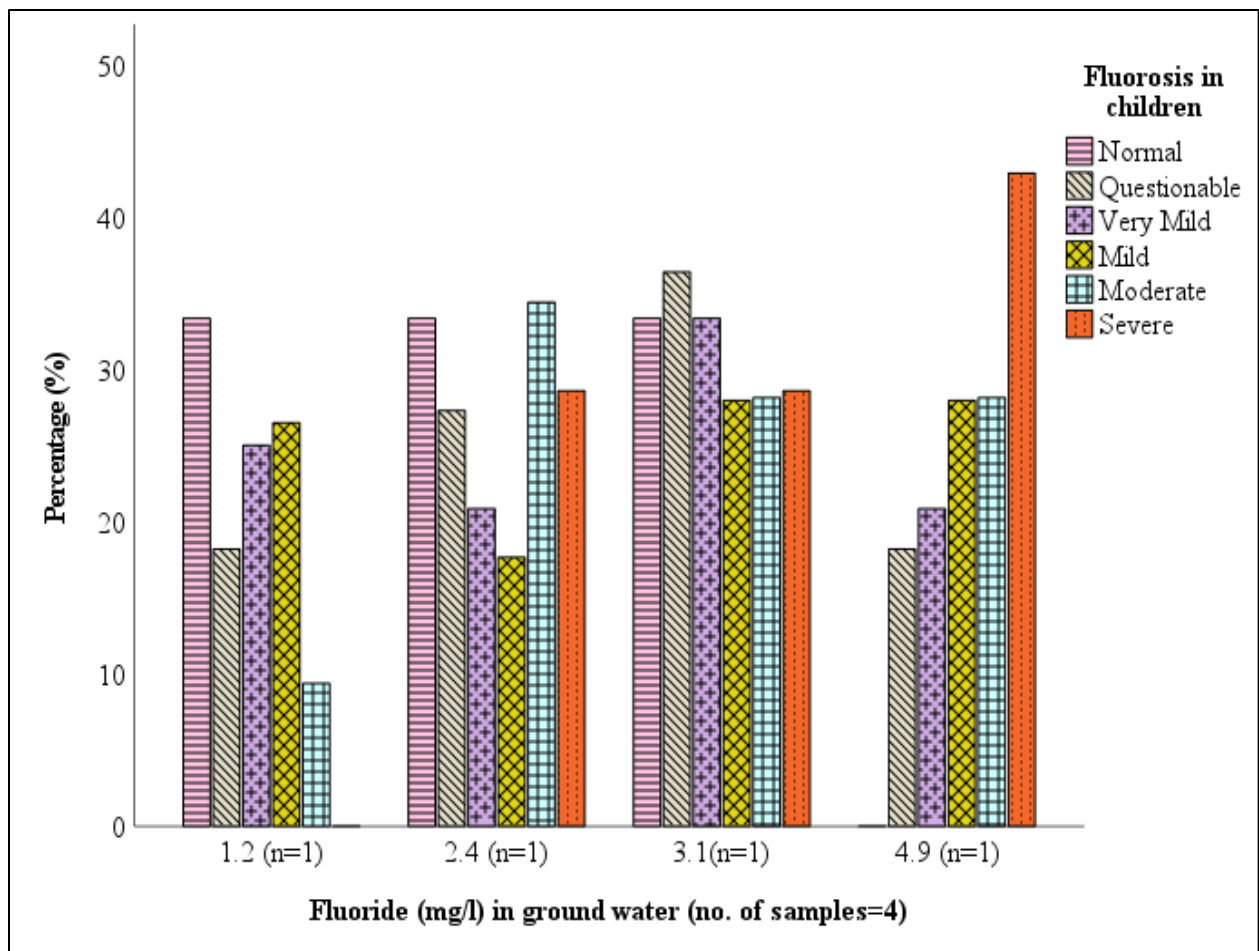


*Figure 9.* Mean Urinary F<sup>-</sup> concentration in children



*Figure 10.* Percentage of children suffering from different stages of dental fluorosis





**Figure 11.** The expression of dental fluorosis in relation of concentration of  $F^-$  in groundwater

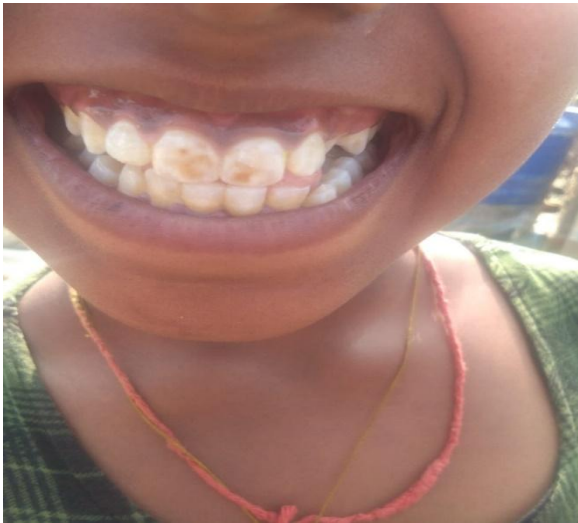
Figure 11; correlate the dental fluorosis and fluoride in source. Total four stations were selected as these are the major source of drinking in each village. The percentage of normal teeth was higher at station with lower value of  $F^-$  having around 34% as normal and around 10% of severe of the total of at that station. Severe dental fluorosis cases were found where  $F^-$  concentration was higher, around 45% of the total cases at that station falls under this category. Also aggregating the total cases, 17% girls and 16% boys have very mild; 47% girls and 45% boys have mild; 21% girls and 22% boys have moderate and around 2.5% girls and 6.5% boys comes in severe category.



Figure 12 Dean Classification for dental fluorosis having very mild dental fluorosis



Figure 13 Dean classification for dental fluorosis having mild dental fluorosis



**Figure 14.** Dean classification for dental fluorosis having moderate dental fluorosis



**Figure 15.** Dean classification for dental fluorosis having very mild dental fluorosis

## 4.5 Health Risk Assessment

Human health risk assessment is a method to assess the potential adverse health risk in humans that may be exposed or in future to chemicals through the environment. About 90% of endemic fluorosis in India is caused by the intake of fluoride contaminated water for a long period of time (A. Narsimha & Sudarshan, 2017).

The US Environmental Protection Agency (USEPA) prescribed a standard to calculate health risk for non-carcinogenic substances such as nitrate, fluoride, arsenic etc. this help in assessing the relative health risk to that substance in any particular area and making future policies or decision to tackle the health risk. Health risk is calculated as per the guidelines prescribed by USEPA .Based on the calculation the HQ in children ranges from 0.46 to 5.19, in adolescent ranges from 0.33 to 3.67 and in adults in the ranges 0.26 to 2.94. The mean of HQ as in table8, 2.28; 1.61; 1.29 in children, adolescence and adults respectively. HQ is high in children may be due to their weight factor as used in calculation. Assessment of non- carcinogenic risk in study area showed that 73% children; 63 adolescent; and 63% adults had surpassed the safe limit for health quotient 1.0 as prescribed by the United States Environmental Protection Agency.

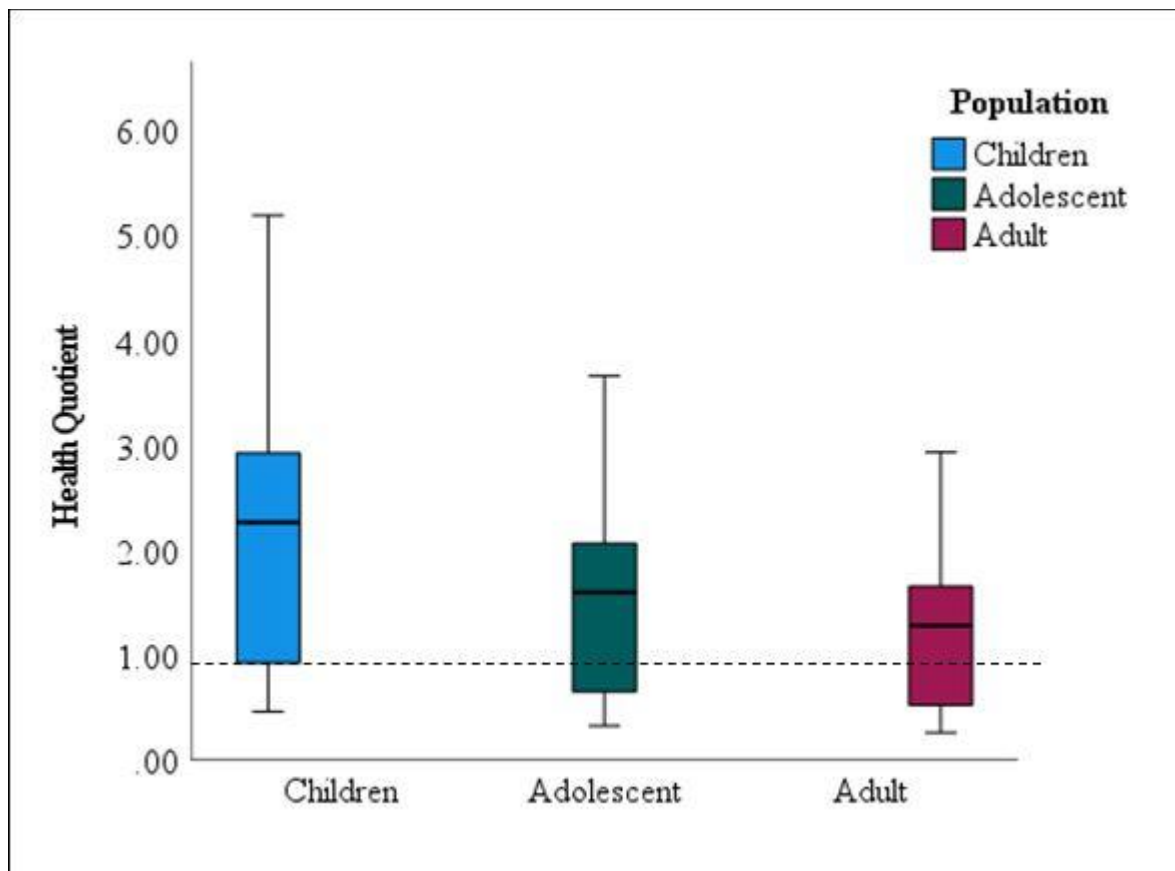
**Table 8.** *Chronic daily intake and health quotient in the different age groups of the study area*

Statistical	CDI			HQ		
	Children	Adolescent	Adults	Children	Adolescence	Adults
Min	0.03	0.02	0.02	0.46	0.33	0.26
Max	0.31	0.22	0.18	5.19	3.67	2.94
Mean	0.14	0.10	0.08	2.2	1.61	1.30

Figure 16, (box plot) illustrates the different age groups with HQ range which is median, min, max i.e. 25<sup>th</sup> percentile and 75<sup>th</sup> percentile.

25<sup>th</sup> percentile of dataset of children falls below 1. Median of all the age group is above 1.0. Population of children has under high risk as all the samples had higher value than 1. For adolescent around 75<sup>th</sup> percentile of population had value higher than 1. The highest value for health risk is around 5, for children. The mean of health quotient for all the age group was above 1 and highest for children having value around 2 as showed in figure 16.

Children are at higher risk and it may be due to their weight factor also as used in calculation.



**Figure 16.** Health risk assessment for the different age groups

## Outreach of the present research

Govt. Secondary School (Kharkara-Bhatol) was the govt. school in nearby villages. A program having presentation and a discussion with teachers and students was held in the school. Around 200 students and 15 teachers were there and an awareness program was conducted covered the topics like fluoride concentration in drinking water, health issues related to fluoride, treatment of water and preventive measures. Other water quality parameters and environment related topics were also covered to better understand and correlation of various fundamentals. Then detailed about collection of urine samples, testing, concentration of fluoride in the urine and dental fluorosis classification to identify the severity of dental fluorosis among them. Students and teachers had also shown their interest with cross questions. Students had also tried to classify the dental fluorosis. Teachers had also interacted with the problems of dental fluorosis, water sources, water quality in nearby areas, related alternatives, treatment and preventive measures.



*Figure 17.* A program outlined to aware the students about concerned health issues

**5.1 Based on the results obtained in the present study, the following conclusions were made**

- Ground water is the major source of drinking in the study area. The range of F in ground water varies from 0.49 to 5.5; with an average of 2.41. Gibbs diagram reveals that's evaporation crystallization is the major hydro geochemical process in the study, also bivariate plot of  $(\text{NO}_3^- + \text{Cl}^-) / \text{HCO}_3^-$  with total dissolved solids revealed that agriculture use of land from a long time has significant effect in controlling the ground water chemistry.
- Fluoride in urine ranges from 0.61 to 8.9 for girls and .13 to 12 for boys in the present study area and the value of F in urine is high in the morning time as the children comparatively consume less water and other items (food, beverages). Correlation of dental fluoride with fluoride concentration of that source shows that shows that numbers of severe cases are at the source with higher concentration of fluoride. Also the fluoride concentration was higher in boys as the food diet and water consumption rate is comparatively high in boys.
- Prevalence of fluorosis in children shows that almost 55% of children (both girls and boys) have come under mild to severe category.
- HQ can be used as a tool to calculate non-carcinogenic health risk to decrease health problems. HQ values shows that residents are at higher health risk to fluorosis due to the fluoride concentration in ground water.

- For future studies, it is suggested to that research should involve other source of fluoride such as food, soil, beverages etc. in the state.
- Also a surveillance program should be outlined to aware local people and will help future water resource planning in the area exposed to elevated fluoride or treating the existing water resources with economical and efficient methods in rural areas.



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