DISTRIBUTION, EXPOSURE, AND RISK-ASSESSMENT OF FLUORIDE IN IN RURAL AREAS OF NORTH-WEST DELHI, INDIA

A PROJECT REPORT
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CANDIDATE'S DECLARATION

I, Mamta Ghunasham, Roll No. 2K18/ENE/15 student of M.Tech Environmental Engineering, hereby declare that the Project Dissertation titled "Distribution, exposure, and risk assessment of fluoride in rural areas of North-West Delhi, India" which is submitted by me to the Department of Environmental Engineering, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

23/06/2020

(MAMTA GHUNASHAM)

Place: DTU, Delhi, India

Date: 23rd JUNE 2020

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CERTIFICATE

I hereby certify that the Project Dissertation titled “Distribution, exposure, and risk assessment of fluoride in rural areas of North-West Delhi, India” which is submitted by Mamta Ghunasham, Roll No. 2K18/ENE/15, Department of Environmental Engineering, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the students under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

23.6.2020

PLACE: DELHI

DATE: 23rd JUNE 2020

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ABSTRACT

Fluoride is regarded as a pollutant in the different environmental matrices. The presence of F^- ions in water, predominantly the one that serves both drinking and irrigation is the main concern across the globe. The present study was undertaken during the month of March 2020, whereby samples (water, soil and vegetables) depending upon the availability were collected from areas of endemic fluorosis. A total of 6 villages namely Bajitpur, Mungeshpur, Pooth Khurd, Daryapur, Auchandi and Qutubgarh, lying in North-West part of Delhi, were targeted for sample collection. The objectives behind the study were to gauge the quality of water and soil in the study area. A particular interest was directed towards determining the level, if any, of fluoride. Besides, since food items contribute to the fluoride content, assessment of bioavailable fluoride in vegetables and crops was also carried out. The quality assessment was made through the estimation of various physico-chemical parameters like pH, EC, TDS, F^-, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+} for drinking water while some irrigation parameters like % Na, SAR, RSC and PI were calculated for all 19 water samples. The fitness of the samples for the different purposes was evaluated by matching the acquired values against the approved standards and indices. Fluoride concentration as high as 7.3 mg/l was recorded in the water sample from location 15 (Mungeshpur). A maximum of 1.60 µg of F g^{-1} of soil was registered at Mungeshpur (Location 12). An equally high transfer factor coupled with maximum bioavailable F^- concentration of 0.3 mg/g of fresh weight was registered in Spinach, at the same place. Base-exchange and the meteoric percolation combined with rock-water interaction aided in increasing the richness of F^- in the groundwater. The risk assessment was accomplished by calculating the Estimated Daily Intake (EDI) based upon the USEPA guidelines, and 14 water samples were found to have a hazard quotient exceeding unity, therefore classified into the high-risk zones. Classification of the EDI as per the age group confirmed that the children are the most at risk, hence retarded growth, stiffness of joints, lower IQ in children, along with dental and skeletal fluorosis are some of the possible outcomes. Monitoring, defluoridation, diet editing and treatment of symptoms are some of the measures suggested.

Keywords: Fluoride, water, soil, vegetables, risk- assessment, remediation.

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ACRONYMS AND ABBREVIATIONS

AA	Activated Alumina
ANOVA	Analysis Of Variance
APHA	American Public Health Association
ASTDR	Agency for Toxic Substances and Disease Registry
BCF	Bio-Concentration Factor
BIS	Bureau of Indian Standards
CAI	Chloroalkaline Index
CCMEWQI	Canadian Council Minister of Environmental Water Quality Index
CDTA	1,2-Cyclohexylenedinitrilo Tetraacetic Acid
CEC	Cation Exchange Capacity
CGWB	Central Ground Water Board
DO	Dissolved Oxygen
EC	Electrical Conductivity
EDI	Estimated Daily Intake
EWQI	Entropy Water Quality Index
FAO	Food and Agriculture Organization
FTIR	Fourier-Transform Infrared Spectroscopy
GIS	Geographic Information System
HIACMO	Hydrated Iron(III)–Aluminum(III)–Chromium(III) Ternary Mixed Oxide
HQ	Hazard Quotient
IOM	Institute Of Medicine
IRIS	Integrated Risk Information System
KR	Kelly's Ratio
MEDLINE	Medical Literature Analysis and Retrieval System Online
MOHFW	Ministry of Health and Family Welfare, Government of India
NOAEL	No Observed Adverse Effect level
NPPCF	National Program For Prevention And Control Of Fluorosis

PAC	Poly-Aluminium Chloride
PCA	Principal Component Analysis
PI	Permeability Index
PS	Potential Salinity
RSC	Residual Sodium Carbonate
SAR	Sodium Absorption Ratio
SD	Standard Deviation
SEM	Scanning Electron Microscope
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
SPSS	Statistical Package for Social Sciences
SSP	Soluble Sodium Percentage
TA	Total Alkalinity
TH	Total Hardness
TDS	Total Dissolved Solids
TF	Transfer Factor
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNICEF	United Nations International Children's Emergency Fund
USEPA	United States Environmental Protection Agency
USSL	United States Salinity Laboratory
WAWQI	Weighted Arithmetic Water Quality Index
WHO	World Health Organization
WQI	Water Quality Index
XRD	X- Ray Diffraction

CHAPTER 1 INTRODUCTION

Water is the elixir of life. Availability of safe water is essential for the co-existence of different spheres of life (Naditkala *et al.,* 2020). Numerous studies have portrayed groundwater as being an essential element for drinking, agricultural, and industrial uses in our daily life routine (El Baba *et al.,* 2020; Khatri *et al.,* 2020; Rao *et al.,* 2020). Currently, 12 million people rely on unsafe sources for water (UNICEF, WHO,2015). Regrettably, many studies have revealed groundwater contamination (Wu and Sun, 2016; Jia *et al.*,2019; Schwartz, 2020), whether naturally (Preziosi *et al.,* 2019) or induced as an aftermath of various activities related to mankind. As it happens, fluoride contamination appears to be among the contaminants affecting the quality of water, much to one's dismay, to a national level (Adhikary *et al.*,2014; Manikandan *et al.*,2014; Mondal *et al.*,2014) or even at an international scale: Asia (Kitano and Funikawa,1972; Naseem *et al.*,2010; Jayawardhana *et al.*,2012; Chen *et al.*,2012), Africa (Rango *et al.,* 2012; Sracek *et al.,* 2015; Shakir *et al.,* 2016) and other continents (Indermitte *et al.*,2009; Nicolli *et al.*,2012; Reyes – Goméz *et al.*,2015). Globally, estimates show that more than 200 million people (UNESCO, Internet source) still depend on drinking water having a level higher than prescribed by WHO guidelines *i.e.* exceeding 1.5 mg/l.

Fluoride, a highly electronegative element occurring as complexes in nature, is believed to be released via the weathering processes, volcanic emissions and by marine aerosols as well (Symonds *et al.*,1988). Besides, the rock-water interaction, *e.g.* the presence of aquifer rocks or various minerals such as biotite, fluorite, and their associated hosts *e.g.* granite, syenite *etc*. contain fluoride that is liberated in the water bodies, mostly groundwater (Veeraswamy *et al.,* 2019). Chemicals and industrial processes, on the other hand, are regarded as anthropogenic sources of fluoride, for instance, the industries dealing with aluminium smelting, cement, glass *etc*. (Chuah *et al.,* 2016), the irrational and impulsive use of phosphate-based fertilisers (Kundu and Mandal, 2009; Gray, 2018), the use of superphosphate (Rao,1997) which in most of the cases leading to an exceedance of the chemicals and without forgetting, the industrial wastes (Ali *et al.*,2016).

Considered as the 13th most abundant element, fluoride ion has been associated with health in myriad ways *i.e.* both beneficial and detrimental. Findings carried out have revealed the beneficial aspect of fluoride with the prevention of dental caries, which usually takes place when the F^- ion concentration is less than 0.5 mg/l. Conversely, the continued intake of elevated fluoride content in drinking water can certainly lead to fluorosis (Adimalla and Qian 2019a) and more associated complications *e.g.* debilities, paralysis, anaemia to name few.

Given that the presence of F^- pertains significantly to numerous health issues, research works have been undertaken to determine the underlying causes, the associated factors and the mechanism of fluoride has been an integral part of the whole scenario. The groundwater chemistry, soil conditions (*e.g.* pH, type of soil), hydrology related properties (*e.g.* time of residence) and climate associated parameters (*e.g.* precipitation, amount and rate of evapotranspiration), have been evidenced to influence the release of fluoride content (Valenzuela-Vasquez, 2006) or be it due to anthropogenic causes as aforementioned.

In terms of the number of victims and prevalence, fluoride is one of the two contaminants as far as the Indian context is concerned (Sahu, 2019). Since India is exposed to almost 12 millions out of 85 million tons of F^- fluoride content lying in the Crust of Earth, the residents have to face many difficulties in various ways – health, environment and others. As a result of which, nearly 25 million people are already affected by fluoride, while at least 66 million cases across the country are expected, out of which 7 million of victims are children (UNICEF State of Art Report,1999). A total of 205 out of 569 districts of India, are the prey to contamination, mostly owing to the presence of industries (phosphate, fertilisers) and brick kilns. As per the records of Government of India, all the districts in the Rajasthan State have fluoride contamination while, 27 districts of Gujrat as well as Orissa, 18 districts of Uttar Pradesh, 15 districts of Andhra Pradesh, 13 districts of Punjab, 12 districts of Haryana and Karnataka, respectively, and 10 districts of Maharasthra and Madhya Pradhesh each have fluoride levels exceeding the prescribed limits.

As far as 85% of inhabitants of India mostly residing in rural areas are concerned, owing to the limited supply of water, rely on groundwater as the source for multi-purposes. In fact, in North Indian villages, groundwater is still being widely opted as the main source for drinking water, use in agricultural setup, and also in the industrial milieu (Haritash *et al.,* 2016). Moreover, without forgetting that, the agrarian economy of India gulps down 50-80% of the groundwater in the form of irrigation (Raju, 1998). Furthermore, reports demonstrate that about 52 % of Delhi residents rely on groundwater for the daily routine (Gupta *et al.,* 2016) and as per the findings of another report (Government of India, 2019), around 54 % of the groundwater is undergoing rapid descent as far as the water level is concerned, since often the low water level gives room to dissociation of fluoride as per studies conducted till date. Undeniably, fluorine being the smallest halogen that does not exist in its elemental state (Fawell *et al.,*2006), undergoes reactions with other elements to form fluoride compounds. Usually, this strong electronegative ion undergoes combination with Calcium, Sodium and others cations existing in water and soil. The various processes that take place in nature, for instance, infiltration helps in the movement of fluoride ions across the different medium in the ecosystem. All these factors clubbed together can prove to be harmful to mankind in many ways, for example, it is projected that a minimum of 6 million people will be having issues such as limited access to clean water by 2050 (United Nations World Water Development Report, 2018). Needless to say that, health concerns arising due to increased level of fluoride and other contaminants, *etc* are enlisted as well.

As mentioned before, the various processes taking place are directly or indirectly allied with the existence or translocation of substances in the environment. Movement of water molecules across soil matrix, quality of water, the associated land use and type of cultivation in a particular area are related to the soil (Schoonover *et al.,* 2015). The soil profile is greatly dependent on the parent material and its inherent physico-chemical qualities and in the long run, the soil development, in turn, gets influenced by the climatic conditions (*e.g.* rainfall patterns and intensity). Above and beyond, the soil in itself is a product of decay and physical breakdown of bedrocks, specifically rich in fluoride, hence, inevitably contains a certain percentage or fraction of F^- (Muhammad *et al.,* 2013). Moreover, even the soil type and quality play a role in the movement of F across it, for instance, acidic soils favour the solubility of F, hence the diffusion via the routes (Kanduti *et al.,* 2016) and the same is believed to be limited by the addition of Calcium Oxide (Bear, 1954).

Similarly, as per reports, the type of soil and the amount of fluoride present vary. Relatively less accumulation of F is observed in clay loamy soil, unlike the sand.

Fluoride, though considered as an vital element for plants, animals, as well as humans, may, however, over time, an excess or deficit of the same are known to have equally injurious effects (Kabata-Pendias, 2001). Till date, standards have been generated for water only *i.e.* a maximum of 1.5 mg/l or even 1.0 mg/l depending upon regions, however, since there are no stringent guidelines as such for plants and soil, possible health complications can be expected on the behalf of humans. Studies have proved that in regions where endemic fluorosis is prevalent in water, the soil, plants, vegetables, and fruits have been tested positive for the presence of fluoride (Singh *et al.*,1993).

Fluoride, regarded as highly toxic for plants, figures among those air pollutants which eventually find its way to the plants' tissues (Weinsteinand Alscher-Herman, 1982). Fluoride accumulation in plants takes place via two routes - gaseous and particulate form (Baunthiyal and Raughar, 2013). Cultivation in the proximity of factories or industries have been seen to release fluoride which remains suspended in the air, before ultimately settling on the leaves shoots, and other parts of the plants (Delschlager,1974), while the gaseous emissions of fluoride lead to phytotoxicity (Banerjee et al., 2019; Choudhary *et al.*, 2019). Besides, irrigation using F-rich water (Pettenati *et al.*, 2013), also finds its way to the plants and of course, in the food chain over time. Uptake of fluoride via a passive diffusion process by the plants has also been revealed in studies (Arnesen,1997; Sharma and Kaur, 2018). The manifestation of the properties of fluoride on vegetation may be in the form of physiological changes, biochemical alterations together with damages at the structural level, and findings have revealed the importance of the concentration accumulated within the sap of cell as the major control factor (Miller, 1993). Previous studies have shown accumulation of F in various parts of the plants up to a certain extent. In addition, studies have proved that higher concentration does not necessarily mean higher toxicity, likewise for the inverse.

Narrowing down to the Indian scenario, few field-based studies have been undertaken so far (Mukherjee and Singh, 2018; Singh *et al.*, 2018). Indian states registering elevated level of fluoride levels such as Rajasthan, Uttar Pradesh, and Andhra Pradesh, groundwater is used for cultivation (Gupta and Banerjee, 2009) and presence of fluoride have been noted in the harvest be it at the national level (Yadav *et al.*, 2012; Naik *et al.*, 2017) or a global scale – dates (Messaïtfa, 2008); tea grown in brick kiln areas (Cao *et al.*,1996); fruits (Bergmann,1995); vegetables (Mumtaz *et al.*, 2015).

There are various modes *via* which Fluoride reaches the human body namely – consumption of food and water along with inhalation of air (Keramati *et al.*, 2019). In India, excess of fluoride in groundwater is a prevalent issue ever since it has been first reported in 1937 in the state of Andhra Pradesh (Short *et al.*,1937). Given that drinking water is of affordable price, it remains the most effective pathway for fluoride to reach the human body. Though fluoride makes its entry in the body during the ingestion of food, exposure to drugs and cosmetics and many more, drinking water is said to be contributing almost 75- 90 per cent of the daily intake (Sarala *et al.*,1993). The impact of fluorine varies in a multitude of way. Healthwise, the chemical aspect of fluorine is vital, to determine the manifestation of fluorine related impacts~~.~~ Fluorosis, referred to as a crippling disease, occurs as an aftermath of the build-up of fluorides in both the soft and hard body tissues. Severe health issues related with chronic fluorosis has been reported in various parts across the globe (Yang *et al.*, 2000; Srikanth *et al.*, 2002; Chen *et al.*, 1997; Binbin *et al.*, 2004; Kamoza *et al.*, 2006), while fluorosis, considered as being endemic, has been identified in 230 districts of 20 states in India (Teotia and Teotia,1984; Choubisa, 2001).

Access to safe water is regarded as an elementary human right and plays a vital role in determining the health and quality of life a person lives. Keeping all these in mind, a study was undertaken in the rural areas of the North-West Delhi, during the month of March 2020 aiming at:

i. Determination of fluoride content in both groundwater and soil samples;
ii. Determination of the amount of bioavailable F^- present , if any, in fruits and vegetables within the study area.

iii. Assessment of the exposure and health risks entrained upon ingestion of the food items and *via* drinking water.

CHAPTER 2 REVIEW OF LITERATURE

Fluoride contamination across the Indian territory has been extensively covered, particularly by various reviewers Sharma (2002), Mukherjee and Singh, (2018) and Karunanithi *et al.,* (2019) to name a few of them. Attempts have been made to gauge the extent of fluoride present in various types of water bodies. Unfortunately, in many places, relatively much quantity of F^- was reported, *i.e.* almost 20 times that of the ones prescribed by the WHO guidelines. The outcomes of the studies seem to be corresponding to other studies carried out in different states namely Andhra Pradesh, a concentration as elevated as 5.2 mg/l was found (Srikanth *et al.,* 1994), followed by 15 mg/l in Nawabganj block, Uttar Pradesh (Mukherjee *et al.,* 1995) and 18 mg/l in Jaipur, Rajasthan (Agrawal *et al.,*1997).

The concentration of F was found to vary depending upon the places. As mentioned by Lalumandier and Ayers (2000), water with a F content varying between 0.7 to 1.2 mg/l is supplied to more that one- third of the residents of Canada (Health Canada, 2017). Similarly, more than 75% of the Americans rely on municipal water supply, having a certain fluoride concentration (CDC, 2016). As per Näsman *et al.,* (2016) in Sweden, the concentration of naturally fluoridated water was seen vary between 0.1 to 2.7 mg/l. Endemic fluorosis is prevalent in Asia. Groundwater contamination due to fluoride was recorded between 5 to 10 mg/l in different studies carried out across the globe namely in Northern Chinese territory (Li *et al.,* 2012), Saudi Arabia (Alabduaaly *et al.,* 2013) and Mongolia (Nakaza *et al.,* 2016). Similarly, concentration ranging between 10 to 20 mg/l, was observed partly in Anatolia and Turkey (Oruc, 2008), in the Sri Lankan context (Chandrajith *et al.,* 2012) and the Indian scenario, precisely in West Bengal (Batabyal and Gupta, 2017). In Gaza, Jabal *et al.,* (2014), reported F concentration of between 0.3 to 6.5 mg/l. Furthermore, even higher concentrations were registered. The concentration varies from 20 mg/l to as elevated as 79.2 mg/ l, as per investigations carried out in the different places namely: in the Pakistani territory (Farooqi *et al.,* 2007), Vietnamese Republic (Le Tu, 2008), in the Malaysian (Shamsuddin *et al.,* 2015) and Afghan context as well (Hayat and Baba, 2017). As far as China is concerned, Li *et al.,* (2015), stated F concentration of 14.1 mg/l in the Yuncheng basin.

Different works of literature in countries such as Tanzania, Kenya, Ethiopia, Sudan, Uganda and a few more have proved that indeed fluoride pollution is equally widespread in Africa. The record-breaking F^- of 2800 mg/l was registered in Kenya, precisely at the Nakuru lake by Williamson (1953). Cradled in the Rift Valley, the concentration of F that was registered by Tekle-Haimanot *et al.* (2006), in Lake Shala was reported as 264 mg/l, while at Abijata, the concentration was reported as 202 mg/l. Unlike other African countries, in Tunisia, the F concentration in water which was conveyed by Guissouma *et al.* (2017), was more or less equal to 2.4 mg/l.

The sources of F^- differ in nature. As mentioned earlier and in accordance with the literature survey carried out, usually, there are two sources from where fluoride tends to originate namely: from natural sources or anthropogenic ones. To begin with the natural sources, findings related to Fluoride studies have concluded the key sources of fluoride in groundwater to be the fluoride-rich rocks namely apatite, rock-phosphate, topaz, fluorite, fluorspar, fluorapatite, cryolite and hydroxylapatite (Teotia *et al.*,1981; Agarwal *et al.,* 1997), and biotite-granite (Chuah *et al.*,2016). In a study undertaken by Shaji *et al.,* (2007), in an intensive endemic fluorosis area of Phalghat (Kerala), the excess of F^- present in the groundwater has been credited to the presence of crystalline rocks exposed to weathering intensity, hard rock aquifers and phreatic zones comprising of cracked mineralised rocks. In addition, conditions such as excess Na^+, lowered Ca^{2+} ions, increased period of residence of water in the underground bed, and over-irrigation has also been recognised to be contributing to percolation of F^- rich substances.

Furthermore, studies have even enlisted hot-springs as a source of F^-. An investigation was undertaken by Kundu *et al.,* (2001), to study any possible association between the relatively higher concentration of fluoride and the hot spring water. Groundwater samples were gathered from the sources in the village of Singhpur and Sagargaon (Nayagarh, Odisha). A relationship was observed between the Tarabalo hot spring having a F^- concentration > 10 mg/l and groundwater located in the study area. The mixing that usually takes place was held responsible for the fluoride distribution. In around 65% of the samples, the rock-forming mineral $CaCO_3$ was found to be dominant. Similarly, a linear relationship was witnessed between F^- and Na^+ and F^- and HCO_3^-, while an inverse relationship between F^- and Mg^{2+}, and likewise for F^- and Ca^{2+}. As reported, the mixing of the hot spring water with other water bodies, could not help, but propagate the fluoride contamination in the locality. The investigators further state that the geography of the area plays a vital role. On the other hand, in Japan, hotels resorting to the usage of water from hot-spring is a well- known practice. In fact, as per a study by Qian *et al.*, (1999), UNICEF has even declared Japan as a country whereby endemic fluorosis is prevalent and that drinking water in Japan is spiked by the presence of F^-. The wastewater that is generated has F concentration as high as 8mg/l and the same is believed to help in the spread of fluoride. Concurrently in Africa, hot springs accompanied by high pH, gases emanating from the crust of the Earth, and activities linked to volcanoes have been linked to a high concentration of F. Till date, despite several studies have been undertaken, the absence of study regarding the prolonged monitoring of F in water has been deplored by Malago *et al.,* (2017).

A study dealing with the distribution of Fluoride and Arsenic in Eastern Punjab, Pakistan (Farooqi *et al.,* 2007), reported the anthropogenic activity as another contributor to the fluoride contamination across the different localities. The Fluoride concentration in 75% of the samples was exceeding the maximum threshold established *i.e.* > 1.5 mg/l. A positive correlation was observed between F^- / Na^+ and F^- / HCO_3^- and a negative correlation of F^- with respect to Ca^{2+} and Mg^{2+} was confirmed. In addition, alkaline pH, sulphate and alkalinity seem to be contributing to the release/presence of F^- in groundwater. Conversely, aluminium plants operating in industrial zones was found to be emitting F^- in the atmosphere, which ultimately made its way to the soil and the same could be detected. Samples were collected by digging at various depths (0-5;10-15; and 15-30 cm). Analysis carried out proved that the water solubility of F^- was a major contributor leading to F^- pollution. Also, the depth at which the samples were collected, was seen to vary inversely with the F^- concentration, hence proving that industrial activity was indeed providing a helping hand in increasing the F^- content. Similarly, the city Panipat (Haryana), finds itself enlisted among the industrial hubs growing at a very fast pace. Comprising of almost 500,000 inhabitants that still rely on groundwater for drinking and other household-related activities, unscientific disposal of wastewater leading to pollution of the groundwater sources, unplanned solid waste management together with minerals materials have led to unsafe drinking water. In a study by Bishnoi and Malik (2008), all the solutes were classified into hard to very hard category, while the F^- level fluctuated between 0.3 mg/l to 9.3 mg/l across the 41 locations in Panipat.

Likewise, a study was undertaken by Reza and Singh (2013), in an enterprise zone of Angul (Odisha), before and after monsoon periods. Samples of water were brought up from both open and tube wells. The hydro-geochemical activities were finally found to be the reason behind the high level of F^-. Besides, as per the matrix correlation and study of the various factors, run-off and atmospheric deposition were found to be contributing to the presence of the additional fluoride ions post-monsoon. Similarly, the hydrochemistry of groundwater in Chithar Basin, situated at Tamil Nadu (India) was considered by Subramani *et al.* (2005), to evaluate the quality of groundwater which serves for dual purposes: drinking and its use in the agronomy sector. The physicochemical parameters of groundwater such as pH, TDS, electrical conductivity, anions and cations content were established. Strong acids twinned with alkali earths (Ca^{2+}, Mg^{2+}) were found to be moderately dominant over acids of weak strength HCO_3^- and CO_3^{2-} as well as over alkalis Na^+ and K^+. Groundwater in the study area contains hardness ions, with high salinity, and slightly alkaline characteristics. The localised elevated TH and TDS resulted in the unacceptability of the water for both the aforementioned purposes. Measures such as sufficient draining and alternate cropping of plants with sufficient salt tolerating ability are suggested. As far as F^- and Boron is concerned, the values were corresponding to the permissible range for irrigation as well as consumption by humans. Further, a study by Chitrakshi and Haritash (2018), comprised of a collection of groundwater samples from Mahendragarh, Haryana to evaluate the influence of stone quarrying over the water quality. The water parameters were evaluated to determine its fitness for drinking and irrigation. Base exchange and silicate weathering were found to be in control of the groundwater chemistry. The use of Piper trilinear diagram helped to further determine the dissolved components of the water, mostly the anions and cations. FTIR analysis helped to determine the parent materials, Kaolinite and calcite were responsible for the elevated parameters in water, and since the parent rock didn’t support fluoride, its concentration was reported within the limits in groundwater.

Further, according to Gupta and Sarma, (2013), groundwater characteristics demonstrate temporal and spatial variations with respect to numerous parameters, out of which one of them is fluoride. In West Bengal (India), Gupta *et al.*, (2012), carried out samples collection from 26 water table sedimentary aquifer. Around 54 % of the samples were seen exceeding the maximum allowable range prescribed by WHO. With the aim of assessing the spatial and seasonal variation of fluoride in Telangana, Narsimha and Rajitha (2018), collected 158 samples for 2 seasons and the mean concentration was found to be 1.5 times and 2.8 times higher than the stipulated values. Fluorosis is common in Haryana. In fact, upon assessment by Gupta and Misra (2018), poor water quality, with raised F content in 60 -70 % of the samples, was observed to be mostly related to sources of geogenic origin coupled with weathering processes. In the same manner, the spatio-temporal distribution of F^- was studied in Nairobi with the help of GIS software. Though all the samples of groundwater were found to be abiding by the guidelines of WHO, as far as F^- is concerned, however, uniformity in terms of the distribution of the ions was not found. Just like other studies, water found at depth was rich in F^- unlike that of the shallow water table. As add-ons, Wamwang (2013), divulged that the precipitation patterns, the changing course of water and use of pumps were seen to be influencing the quality, including the F^- concentration across the study area.

In order to determine the aptness of H_2O for a contemplated use, the Physico-chemical and the biological aspects of the water sample are gauged. Over the years, the water quality index has started figuring among such assessment, particularly when data interpretation is required. To simplify numerous water-related parameters into a single value or simple expression, water quality indices have been employed (Katyal, 2011). Evaluation of water pollution in villages are often given as much importance as in urban places. In villages, water is used for drinking, taking bath, cleaning *etc* hence monitoring of the water quality regularly is important. WAWQI and CCMEWQI were determined for fifty groundwater specimen sampled across nine villages, throughout half-year. WAWQI revealed that 46%

of the samples were good, while 54% of the samples, as per CCMEWQI, were of minimal quality. Hence, it could be concluded that the water present in these rural areas were free of contamination (Khatri *et al.*, 2020). In the same manner, an investigation by Ramakrishnaiah *et al.*, (2009), the groundwater specimens in Tumkur were evaluated for 12 parameters in a comprehensive manner. The WQI was found to be varying from 89 to 661 – a relatively high value attributed to elevated concentrations of fluorides, TDS, nitrates, bicarbonates and 4 more parameters. Treatment of the water is required prior to consumption.

Statistical methods have often been employed for a better understanding of the parameters and to establish correlation, if possible, amidst the different parameters. Lack of safe water for drinking is still a reality across the globe and Rao *et al.*, (2020) has deplored a similar fate for some of the villages of Wanaparthy, Telangana, India. Groundwater in the region is influenced by granite metamorphic rocks. Ionic Spatial Distribution (ISD), Principal Component Analysis (PCA) and Entropy Water Quality Index (EWQI) were adopted to assess the water quality. As per EWQI, the water was 3 - 47 % suitable for drinking. Carbonate hardness (63%) and non-carbonate alkali (17%), rock-water interactions, exchange of ions, mankind related activities influencing were some of the findings of this study. Alkaline nature of the groundwater samples leading to fluorosis and excess of K^+ arising from fertilisers usage and run off of irrigation water were reported as well. Aquifer re-injection and appropriate measures to treat the water before consumption is suggested. Furthermore, Gradilla—Hernández *et al.*, (2020), examined the variations across the distance and time to determine the quality of water. Besides, to be able to evaluate the influence of various mankind related activities, together with the one arising as an outcome of naturally occurring activities were also taken into consideration. Statistical methods such as discriminant, Cluster Analysis, one-way ANOVA analysis were undertaken for a comprehensive interpretation of the deviation of factors such as TDS, DO, TH, pH, temperature and many other such parameters. The results obtained when PCA was carried out proved to help assess the influence of the aforementioned genre of undertakings and their influence on the overall water quality. Spatial variations were observed for parameters such as pH, nitrate and nitrite, while, temporal variations proved pH, conductivity, hardness to be significantly dominant.

According to Singh *et al.*,(2020), Soil pollution related to fluoride is considered as an ancient problem, that is often not given due consideration. It is believed that ever since the first case recorded in 1937 in India, a surge has been observed in the number of such reports across the country. The contamination is believed to be triggered by either toxic spills, use of chemicals, the deposition of particles arising from volcanic eruption among others. As far as the mean F concentration is concerned, the value has been seen to vary depending upon zones. Moreover, pH, Salinity, type of soil, minerals present, the parent materials, the distribution of F across the medium, are some of the prime factors influencing the F content in soil. Coming up to the analysis, methods such as titrimetry, potentiometry, chromatography *etc* are adopted.

Previously, it was assumed that foodstuff is not an abundant source of F for its end-users, however, now it is well known that certain food type is not only good accumulators but contribute F largely in the food chains. The study of the movement of fluoride from one trophic level to another has been undertaken by numerous investigators (Gautam *et al.*, 2010; Paul *et al.*, 2011; Bhat *et al.*, 2015; Kazi *et al.*, 2019). Also, in other studies, the anthropogenic activities have been seen to be associated with the F^- in foliage. Though, not all plants depicted changes in terms of damages undergone, for instance, the death of plants, lack of chlorophyll content, *etc.* toxicity owing to fluoride was visible in some of the foliages. As per Haidouti *et al.*, (1993), the manifestation of the symptoms vary depending on features such as the nature of plants, level of pollution and the duration of exposure as well. An almost similar study conducted by Arnesen (1997), in Norway, detected the presence of F^- in the soil as far as 30 km away from the industrial site. Fluoride sensitive species, for instance, *Spondias dulcis* was evaluated as a biomarker by Sant'Anna-Santos *et al.*, (2019). The aim was to be able to detect and monitor the changes brought about by F^-, particularly those at the infancy stage. Damages caused to guard-cells results in reduced photosynthesis, and impaired conductivity across the stomata. Perturbations of the physiological functions followed by microscopic disruption are common in fluoride-exposed plants. Gas-analyzer and Scanning electron microscope are used to ascertain the presence and concentration of ambient F^- in *Spondias dulcis.*

Fluoride accumulation has been seen to take place in plants growing up in regions of endemic fluorosis (Weinstein, 1977; Saini *et al.,* 2013). As per a case study undertaken by Malde *et al.* (1997) in East Africa has highlighted the presence of fluoride in fish and other foodstuffs that are consumed in large quantities on a regular basis. Maize, regarded as a staple food in Africa had a concentration of 0.3 mg kg^{-1} of F^-, while in Spinach up to 7.7 mg kg^{-1} of F^-, both measured on a dry weight basis, was noted. Since starch is the most important element of an African meal, the investigators suggest that the relationships between F^- and the minerals to be studied deeply and to find ways to curb fluorosis associated with the oral health which is extensively prevalent in the study region. Reducing the intake of the mentioned items is being rejected owing to the other complications that can take place, as an outcome of deficit of some nutrients. Concurrently, in an investigation by Jha *et al.,* (2013), the accumulation of fluoride is seen to be following the trend: $F_{root} > F_{leaf} > F_{fruit} > F_{shoot}$. The same could be seen in the results obtained, *i.e.* 16 -106 mg kg^{-1} of F in the root, while 39 to 49 mg kg^{-1} of F was detected in the 'fruit' of lady finger growing in soil containing NaF. The Bio-concentration factor (BCF), on the other hand, was found to be increasing in the soil when NaF was being added, unlike the trend followed by the fruit. Saini *et al.,* (2013), have deplored the limited number of fieldwork with respect to F accumulation in vegetables and crops.

Moreover, studies taken up across the globe have led to believe that there are various factors that straightaway or in an indirect way help in supporting the presence of fluoride ions which in turn vary according to environmental setup. Findings of a study carried out in Karnataka by Latha *et al.,* (1999), highlighted the presence of F^- in groundwater. The toxicity entrained due to F^- was seen to be dependent on factors such as temperature, alkalinity and the prevalence of hardness ions. Upon microscopic analysis, 5-10% apatite, and 20-25% biotite, were held responsible for the presence of F^-, therefore suggestions such as F^- free drinking water and educating people about the complications entrained owing to the presence of fluoride ions were recommended. Additionally, Valenzuela-Vasquez, (2006) revealed that the nature of the soil, hydrology related properties and climate associated parameters are known to influence the release of fluoride as far as soil is concerned. Concurrently, Senkondo,(2017), has proved that the bioavailability of fluoride is dependent upon numerous factors such as pH, precipitation, complex-forming ability, absorption and many more. Singh *et al.,* (1995), even make reference to the medium being used for growing the plants as an important factor.

Over and above, a study was undertaken by Raju *et al.,* (2009), in Sonbhadra Uttar Pradesh reported that the elevated level of F^-, trigger health complications. A review twinned with meta-analysis and the non-carcinogenic risk evaluation with respect to fluoride was carried out by Keramati *et al.,* (2019) in 31 countryside areas of Iran. Data stored in the global databanks such as PubMed, Science Direct, and local databases such as Irandoc and SID were consulted and put to use to access data, particularly those from the year 2011 to 2017. Around 1706 samples from 40 studies are concerned. The minimum F^- concentration recorded was 0.19 mg L^{-1} (Kermanshah) and a maximum of 1.13 mg L^{-1} (Kerman), while the pooled concentration registered is 0.51 mg L^{-1}. For both grown-ups and kids, the HQ value was less than unity, hence implying no significant risk is prevailing. However, since F^- can enter through other pathways, the residents still run the risk, not necessarily only fluorosis but other health concerns. A similar task was undertaken in India by Ali et al., (2019). Around 63 studies consisting of 57 381 specimens were considered for the risk assessment and meta-analysis. The pooled concentration was found to 2.37 mg L^{-1}, a value which is higher than the established guidelines of WHO and BIS. Moreover, fluoride concentration in the rural areas was found to be 1.85 times greater than that of the urban locations. Rainfall was found to be inversely proportional to F concentration. The Total Hazard Quotient exceeded unity, particularly in the case of children. The study was also helpful in identifying the hotspots of F^- in India, hence customised solutions can be considered to resolve the problem. On the other hand, the same exercise was executed by Demelash *et al.,* (2019), in Ethiopia. Deep wells supply drinking water across the Great Rift Valley of Ethiopia. There have been several epidemiological investigations of F^- and its impacts in the region. It was concluded that elevated F^- concentration is prevalent. With the help of databases such as Cochrane Library, Google Scholar and MEDLINE, and based on 9 primary case study the pooled average F^- concentration was reported as 6.03 mg L^{-1}. Mild dental fluorosis among Ethiopians was 32%, moderate fluorosis was 29% and severe fluorosis as 24% with $p <$

0.001 in all the cases. More studies are required to be able to increase the accuracy and to determine the effect of duration of exposure, temperature and other pathways on F^-. Until then, interventions are needed to bring down [F^-] since the concentrations recorded were far ahead of the 1.5 mg L^{-1}, as approved by the World Health Organisation and other authorities.

Fluoride is closely associated with health. Low fluoride concentration is regarded as helpful for human health. However, the same compound at higher concentration induces a malady termed as fluorosis. A comprehensive review of the health status in the Asian countries was performed by Yadav *et al.,* (2019). Damages of systems namely reproductive, cardiovascular, urinary, endocrine and gastrointestinal related were highlighted. In the early days when fluoridation was being practised, toxicity due to F^- was common, unlike nowadays where other forms of health concerns are dominant, particularly dental fluorosis. The disturbance caused when the enamel is developing and erupting is called dental fluorosis (Kanduti *et al.,*2016). Studies have identified the sources as intake of water with a relatively high level of F^-, ingestion of fluoridated food items, *e.g.* fish, whereby the amount of fluoride present is proportional to the endemic F^- in the concerned habitat (Ganta *et al.,* 2015). The saliva is believed to be the mode, through which F^- reaches the teeth. Since fluoride absorption in teeth and bone reduces with age (Peckham and Awofeso, 2014), younger persons, for instance, children are the most exposed ones, since tooth development takes place during that phase. McDonagh *et al.,* (2000), have portrayed the link between the prevalence of mottled teeth and high [F^-] in water. On the other hand, Kanduti *et al.,*(2016), have concluded the stomach as being the organ to come under the wrath of fluoride upon acute toxicity. An affected stomach in turn trigger health issues at the level of the intestines. Next, according to Chlubek and Sikora (2020), the pineal gland which is responsible for converting signals between the nervous and the endocrine systems is mineralising in nature. F^- can easily pile up, resulting in calcified tissue, which in turn trigger insomnia or gain of weight. Once fluoride gains entry in the human body, around 90% accumulates in the gastrointestinal tract, with the breakdown for the same being as follows: a maximum of 25% in the stomach and almost 75% in the duodenum *i.e.* the proximal compartment of the small intestine. Furthermore, Sellami *et al.,* (2019), highlighted the fact that prolonged exposure to an excess of fluoride leads to skeletal fluorosis. The weakening of the bones, loss of elasticity, hardening of the tissues, are some of the 'symptoms' that eventually lead to easy fracture of the bones. Hyperparathyroidism, a state whereby parathyroid gland secretes hormones mostly in an uncontrollable manner, takes place due to excess of fluoride. This is further accompanied by secretion of Ca^{2+} in bloodstreams which trigger abdominal pains and painful muscles. Meanwhile, Sethi and Nitin (2012), have reported deformities of bone, osteosclerosis and calcified tendons usually arising as an outcome of exposure to elevated fluoride together with a poor diet. Bashir *et al.,* (2013), furthermore suggest that elevated F content leads to impaired neurological growth in infants and kids, while fractures of hips are frequent among adults. Sellami *et al.,* (2020), revealed that radiographic images depict an increase in the density and that ossification of the ligaments also takes place in the long run.

Health issues associated with poor water quality namely high fluoride content, presence of salts beyond the stipulated guidelines, high TDS among others are prevalent in Jhajjar, Haryana. Gupta and Misra (2018), propose both *ex-situ* and *in-situ* remedial measures: Nalgonda technique, absorption technology, dilution of contaminated water, and management in the form of training were suggested. To bring down the presence of F-, some of the measures *e.g.* fluoride removal, dilution of the 'contaminated' water, and increasing the calcium content have been suggested. Numerous studies have been undertaken to help in the elimination of F content present in drinking water. As far as remediation is concerned, rainwater harvesting has been proposed by Shaji *et al.,* (2007). According to Zhao *et al.,* (2010), experiments based on hybridization with the help of cellulose- hydroxyapatite nanocomposite using SEM, XRD, having been seen to be effective. Also, efficient F- exclusion aided by aq. Iron (III)- aluminium (III)-Chromium (III) ternary mixed oxide (HIACMO) revealed that adhesion of F^- occurs at the spur-of-the-moment along with the absorption of energy. pH was observed to influence the removal as attested by Biswas *et al.,* (2010). The findings of Na and Park, (2010), were seconded by a defluoridation using lanthanum hydroxide, whereby optimum results were disclosed for $pH < 7.5$. As far as competition between anions is concerned, no influence on fluoride removal was noted. Furthermore, as stated by Sujana and Anand (2011), the use of geomaterials (*e.g.* low/high-grade ores), have been seen to abide by the kinetics and the use of the multistage process, have brought down the F^- significantly starting at 10.25 mg L^{-1} and ending at < 1.0 mg L^{-1}. Besides, the use of inexpensive adsorbent for scavenging pollutants from air and water, for instance, fly ash is regarded as efficient (Wang and Wu, 2006; Klamrassamee *et al.,* 2010). Meanwhile, Yadav *et al.,* (2019), recommend various techniques such as nanofiltration, reverse osmosis, exchange of ions, and precipitation. Coagulation also figures among the extensively adopted practice of defluoridation. It encompasses the use of aluminium salts, lime, bleaching powder accompanied by quick mixing, followed by the formation of colloids or flocs, which eventually undergo settling. The mixture is then subjected to filtration to obtain treated water. Dubey *et al.,* (2018), suggest the substitution of alum with PAC (Poly-Aluminium Chloride) coupled with filtration (sand or a set of micro-filtration) as part of some of the recent developments when it comes to using coagulation techniques for fluoride removal. Furthermore, the use of nanomaterial in water purification is considered as a breakthrough. Unlike, the conventional materials, nano-adsorbents depict a better decontamination performance and equally efficient in paving the way to sustainable methods related to purification and supply of safe water. Zirconium, Silica, Magnesia and few more oxide nanomaterials promote the absorption of F^-, which makes it easy to scavenge fluoride. Parameters influencing the process are pH, temperature, size of the particle, surface area, contact time *etc.* As claimed by Khandare *et al.,* (2019), the non-toxic nature, high absorption ability and its relatively insoluble nature for water make nanoparticles a potential option that can be considered to bring down the F content.

In the opinion of Weerasooriyagedara *et al.,* (2020), contamination of fluoride is a major environmental issue owing to its long term prevalence, even if it is of relatively low levels in air, soil and water. Long term exposure, regardless of concentration may result in adverse effects. Hence, urgent actions to control, or even mitigate the adverse environmental impacts are required as far as possible. Mainly due to its high prevalence and effects, numerous traditional and modern methods have been developed, with the aim of scavenging F from groundwater. The expensive cost involved, need for regeneration, low ability, and its labour-intensive nature not only question its feasibility but also, explains for the need to look for other methods to by-pass the current ones. Removal of fluoride through an effective and eco-friendly manner consists of the use of potential plants to extract fluoride from environmental matrices. The mechanisms that help in the translocation of fluoride in plants are: firstly, exclusion of enzyme inhibition sites, sequestration reaction at the level of vacuoles, cation reaction, absorption of fluoride through metabolic pathways and the transfer of F^- up to the leaf. The plants studied are *Eucalyptus rostrata*, *Populus hybridus*, and *Pinus radiata*. Comprehensive information about hyper-accumulator plants is required for the same.

Collection of samples

The sampling exercise comprising of collection of water samples from Tubewells (T) and Handpumps (H); soil samples and wherever possible that of vegetables and crops grown in the rural areas of North - West Delhi was carried out. The sample collection was initiated during the month of March 2020 in 6 villages (Fig.1) namely: Bajitpur, Mungeshpur, Daryapur, Auchandi, Pooth Khurd and Qutubgarh. Overall, 19 water samples, 6 soil samples and vegetables' samples each were collected. The sites were identified and GPS marked to obtain the exact coordinates of the sampling location (Table 1).

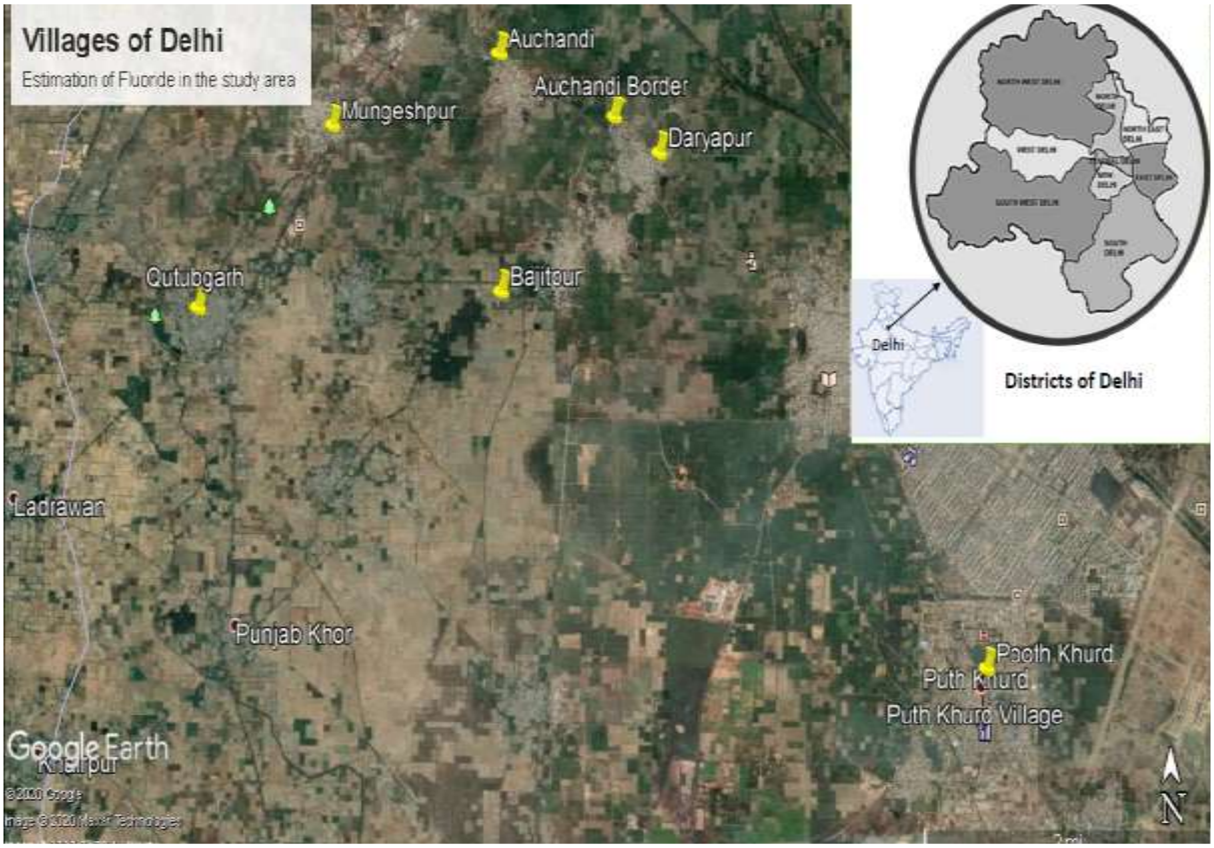


Fig. 1 Sampling locations in villages of North-West Delhi.

Table 1: Sampling locations with exact coordinates.

S.No.	**Coordinates**		**Village**	**Water sample(s)**		**Soil sample(s)**	**Vegetables' Sample(s)**
	Latitude (N)	**Longitude (E)**		**Source (T/H)**	**Depth (m)**		
1.	28°48'14.06"	76°59'40.66"	Bajitpur	T	9	-NA-	-NA-
2.	28°46'9.01"N	77° 3'4.26"E	Pooth Khurd	T	30	-NA-	Spinach, Wheat, Radish
3.	28°48'22.64"N	76°57'39.46"E	Qutubgarh	T	23	$N_s = 1$	-NA-
4.	28°48'40.02"N	77° 0'35.25"E	Daryapur	T	12	$N_s = 1$	-NA-
5.	28°48'40.42"N	77° 0'44.42"E	Daryapur	T	18	-NA-	-NA-
6.	28°49'6.38"N	77° 0'3.40"E	Auchandi	T	12	-NA-	-NA-
7.	28°49'34.34"N	76°59'28.03"E	Auchandi	T	9	-NA-	-NA-
8.	28°49'47.87"N	76°59'19.59"E	Auchandi	H	9	-NA-	-NA-
9.	28°48'37.75"N	76°58'54.27"E	Mungeshpur	T	9	-NA-	-NA-
10.	28°48'36.78"N	76°59'3.77"E	Mungeshpur	H	9	-NA-	-NA-
11.	28°49'33.34"N	76°59'9.62"E	Mungeshpur	T	12	-NA-	-NA-
12.	28°49'8.12"N	76°58'52.71"E	Mungeshpur	T	9	-NA-	Spinach, Cauliflower
13.	28°49'5.33"N	76°58'53.91"E	Mungeshpur	H	9	-NA-	-NA-
14.	28°49'5.39"N	76°58'59.46"E	Mungeshpur	T	9	-NA-	-NA-
15.	28°49'7.17"N	76°58'59.81"E	Mungeshpur	T	9	-NA-	Wheat
16.	28°49'3.64"N	76°58'59.38"E	Mungeshpur	T	9	-NA-	-NA-
17.	28°49'33.32"N	76°59'7.56"E	Mungeshpur	T	9	-NA-	-NA-
18.	28°49'33.10"N	76°59'6.04"E	Mungeshpur	T	9	-NA-	-NA-
19.	28°48'34.53"	76°58'9.08"	Mungeshpur	T	23	$N_s = 1$	-NA-

Where : H – Handpump ; T- Tubewell ; N_s = No. of Soil Sample (S) ; NA- Not Available.

Collection of water samples

Water samples were collected from the aforementioned 19 different sites during March 2020. The samples were collected in sterile plastic (polyvinyl propylene) bottles. The bottles were labelled numerically from 1 to 19 as per the sampling locations. Bottles were initially rinsed with the water at the sampling site before being filled up to the rim. Bottles were screwed tightly and immediately transferred to the laboratory. The analysis started soon after collection. All the parameters for each water sample were measured in triplicate and the average values were considered. The results represent the average/mean data for each site.

Fig. 2 (i) Collection of a water sample.

Collection of soil samples

Soil samples, wherever feasible were collected from 6 different sites namely: 1 at Bajitpur, Auchandi and Pooth Khurd each and 3 soil samples from Mungeshpur during March 2020. The samples were collected in plastic bags. The plastic covers were labelled numerically from 1 to 6 as per the sampling locations and immediately transferred to the laboratory. The analysis started soon after collection. All the parameters for each soil sample were measured in triplicate and the mean values were considered. The samples were also subjected to FTIR spectroscopy. The results represent the average/mean data for each site.

Fig. 2 (ii) Collection of soil sample.

Collection of vegetables/crop samples

Vegetables/crop samples, wherever available at the sampling locations were collected. Overall, 6 samples were collected from two locations *i.e.* from Pooth Khurd and Mungeshpur. The samples comprising of spinach, wheat, radish, and cauliflower were collected in plastic bags. The plastic covers were labelled numerically from 1 to 6 as per the sampling locations and immediately transferred to the laboratory. The analysis started soon after collection.

Fig. 2 (iii) Collection of vegetable sample under cultivation in the study area.

Analysis

Laboratory analysis included analysis of water for hardness, alkalinity, and chloride ions by volumetric analysis. Sulphate ions were recorded using the spectrophotometer method. Sodium, Potassium, and Calcium were measured using the flame photometer method while the fluoride content was determined using an ion-selective electrode.

The analysis also included the use of a multimeter kit to measure pH, TDS, electrical conductivity and salinity.

I) ANALYSIS OF WATER

i) pH:

pH measures the hydrogen ions concentration in water. It is measured on a log scale and equal to negative log 10 of hydrogen ion concentration. The pH can be measured by using either a colourimetric method employing various indicators or by using a hydrogen ion-sensitive electrode. pH was measured on the site using a Labmann LMMP 30 Model Multimeter kit.

ii) Total dissolved solids (TDS):

TDS denotes the various kinds of minerals in the water. TDS does not contain any gas or colloids. These can be determined as the residue left after the evaporation of the filtered sample. This was also measured by using Labmann LMMP 30 Model Multimeter kit.

iii) Conductivity:

Conductivity denotes the capacity of the substance or solution to conduct electric current. Conductivity is a measure of cations and anions in the sample. This was also measured using the Labmann LMMP 30 Model Multimeter kit.

iv) Salinity:

Salinity is the measure of all salts dissolved in water. It is usually measured in part per thousand. Salinity is an important factor in determining the many aspects of the chemistry of natural waters and biological processes within it and is a thermodynamic state variable that, along with temp. and pressure governs physical characteristics like density and heat capacity of water. This was also measured using the Labmann LMMP 30 Model Multimeter kit.

v) Alkalinity:

The alkalinity of water is its capacity to neutralize the acid. The amount of a strong acid needed to neutralize the alkalinity is called the total alkalinity, *T*, and is reported in mg/l as CaCO3. The alkalinity of some waters is due only to the bicarbonates of calcium and magnesium. The pH of such water does not exceed 8.3 and its total alkalinity is practically identical with its bicarbonate alkalinity. The stoichiometric relationships between hydroxide, carbonate, and bicarbonate are valid only in the absence of significant concentrations of other weak anions. This applies especially to the alkalinity (and acidity) of polluted waters and wastewaters.

Procedure:

1. Mix 50 ml of the sample with two or three drops of phenolphthalein indicator in the porcelain basin (or in a conical flask over a white surface). If no colour is produced, the phenolphthalein alkalinity is zero. If the sample turns pink or red, determine the alkalinity by titrating with standard acid until the pink colour just disappears. In either case, continue the determination using the sample to which phenolphthalein has been added.
2. Add a few drops of methyl orange indicator. If the sample is orange without the addition of acid, the total alkalinity is zero. If the sample turns yellow, titrate with standard acid until the first perceptible colour change towards orange is observed.

Calculations:

Phenolphthalein alkalinity as $CaCO_3$

$$P = (V_1 * N_1 * 50 * 1000) / V$$

Total alkalinity (T) as $CaCO_3$ (mg/l)

$$T = (V_2 * N_1 * 50 * 1000) / V$$

V_1 = Volume of standard acid solution (mL) to reach the phenolphthalein endpoint of pH 8.3.

V_2 = Volume of standard acid solution (mL) to reach the endpoint of methyl orange.

N = Normality of acid used

V = Total Volume of sample (ml)

Using 100 ml of sample and 0.01 mol L^{-1} standard acid solutions, the numerical value of alkalinity as mg L^{-1} $CaCO_3$ is 10 times the number of millilitres of titrant consumed.

vi) Total Hardness

Originally water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in milligrams per litre.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called “carbonate hardness”; the amount of hardness above this is called “non-carbonate hardness”. When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness and non-carbonate hardness is absent. The hardness may range from zero to hundreds of milligrams per litre, depending on the source and treatment to which water has been subjected.

Procedure

1) Take 50 ml of the sample in a conical flask.

2) Add 1 ml buffer solution, then add a pinch of Erichrome Black T.

3) Titrate with standard EDTA titrant till the colour changes to distinct blue.

Calculations

$$\text{Hardness (EDTA)as CaCO3} \left(\frac{mg}{l}\right) = \text{A*B*1000 (ml sample)}$$

Where,

A = mL titration for sample and

B = mg CaCO3 equivalent to 1.00 ml EDTA titrant (=1)

CATIONS

Flame Photometry:

Flame photometry (more accurately called flame atomic emission spectrometry) is a branch of atomic spectroscopy in which the species examined in the spectrometer are in the form of atoms. The other two branches of atomic spectroscopy are atomic absorption spectrophotometry and inductively coupled plasma-atomic emission spectrometry (ICP-AES, a relatively new and very expensive technique not used in Standard base experiments). In all cases, the atoms under investigation are excited by light. Absorption techniques measure the absorbance of light due to the electrons going to a higher energy level. Emission techniques measure the intensity of light that is emitted as electrons return to the lower energy levels. Flame photometry is suitable for the qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature (mainly Na, K, Rb, Cs, Ca, Ba, Cu). This technique uses a flame that evaporates the solvent and also sublimates and atomizes the metal and then excites a valence electron to an upper energy state. Light is emitted at characteristic wavelengths for each metal as the electron returns to the ground state that makes qualitative determination possible. Flame photometers use optical filters to monitor for the selected emission wavelength produced by the analyte species. Comparison of emission intensities of unknowns to either that of standard solutions (plotting calibration curve) or to those of an internal standard (standard addition method), allows quantitative analysis of the analyst metal in the sample solution. Flame photometry is based on the measurement of the intensity of light emitted when metal is introduced into a flame. A photoelectric flame photometer is a device used in inorganic chemical analysis to determine the concentration of certain metal ions, among them sodium, potassium, lithium, and calcium. The wavelengths of the colour tell us what the element is and the colour intensity tells us how much element is present. Flame photometry is also named flame emission spectroscopy because of the use of flame to provide the energy of excitation to atoms introduced into the flame. In principle, it is a controlled flame test with the intensity of the flame colour quantified by photoelectric circuitry. The sample is introduced to the flame at a constant rate. Filters select which colour the photometer detects and exclude the influence of other ions. Before use, the device requires calibration with a series of standard solutions of the ion to be tested. The spectrophotometer technique has proven to be one of the most reliable and used techniques for the determination of the concentration of Sodium, Potassium, Calcium and Magnesium.

Procedure:

Operating instruction:

1. Open the lid of the filter chamber. Insert an appropriate filter for the test opening and close the lids.
2. Insert the free end of the PVC takes up capillary in distilled water or the reagent. Adjust set zero controls to obtain 00 display on the readout.
3. Adjust the control of each channel to obtain a display exactly 100 on the readout of the channel.
4. Repeat operation of steps 3 and 6 to ensure 00 and 100 are displayed respectively when the blank and the working standard solution of highest concentration are aspirated into the flame.
5. Insert the free end of the PVC takes up capillary in distilled water for a minute or two to wash the mixing chamber thoroughly before the actual test.
6. Insert the free end of the PVC takes up capillary in the sample read the value of the concentration as displayed in the readout.
7. Feed the working standard solution of known concentration from time to time in a series of test to check the calibration. Check the 00 with the blank solutions. Beakers, Glass rod.

Calculations:

Concentration of Na^+, K^+, Ca^{2+}, mg/l = (mg/l samples in diluted liquid)*dilution factor.

i. **Sodium**

It is one of the important cations occurring naturally. Domestic sewage is one of the important sources of sodium to freshwater. Salts of sodium are highly soluble in water. The water with high sodium content is also not suitable for agriculture as it tends to deteriorate the soil for crops. Sodium associated with chlorides and sulphides makes the water unpalatable.

The concentration of sodium is determined using flame photometry method.

ii. Potassium

Potassium is also a naturally occurring element. However, the concentration remains quite lower than sodium, calcium, and magnesium. It has got more or less chemistry like sodium and remains mostly in solution without undergoing any precipitation. The concentration of potassium is determined using flame photometry method similarly as of sodium.

iii. Calcium

Calcium is an important element coming from crystal origin. It is an integral component of most of the rock minerals and ores. The weathering profile of the mineral rock determines its rate of solubilisation in water. Excessive dissolution of calcium salt results in an increase of total hardness in water. The presence of calcium ions in the water/soil interface regulates the Cation Exchange Capacity (CEC) of soil and uptake of nutrients from the soil. It also affects the cationic concentration in water and an effect on the quality of irrigation water. At high pH, much of its quantities may get precipitated as $CaCO_3$.

Procedure:

1. Take the volume of sample in a conical flask
2. To maintain the pH add 1 ml of a strong base i.e. 1N NaOH.
3. Add a pinch of murexide indicator. the solution turns pink in colour
4. Titrate the solution against 0.01M EDTA. The end pint is pink to blue.

Calculation:

$$\boldsymbol{Ca\ \left(\frac{mg}{l}\right) = \frac{Vol\ of\ EDTA\ used * Molarity\ of\ EDTA * 40 * 1000}{Vol\ of\ sample}}$$

iv. Magnesium

It occurs in all kinds of natural waters but its concentration remains generally lower than calcium. Like calcium, it is also one of the important ions imparting hardness to the water.

The concentration of magnesium is determined as the difference between (Ca+Mg) titration and the titration alone for Ca.

Calculation:

$$Magnesium\left(\frac{mg}{l}\right) = \left((y - x) * 400.8\right) * 1.645))/(ml\ of\ sample)$$

Where, x = EDTA used for Ca determination

y = EDTA used for hardness (Ca + Mg).

ANIONS

A) Chloride

Chlorides occur in all-natural waters in widely varying concentrations. They are not harmful to humans if the concentration is less than 250 mg/litre.

Chlorides can be readily measured employing the Argentometric method. This method recommends the use of 0.0141N solution of silver nitrate for titration.1 ml of this silver nitrate solution is equivalent to 0.5 mg of chloride ion. In the titration, the chloride ion is precipitated as white silver chloride.

$$Ag^{+} + Cl^{-} \leftrightarrow AgCl$$

The endpoint cannot be detected by the eye. So, an indicator is used to detect the presence of excess Ag^{+} present. The indicator normally used is potassium chromate; which supplies the chromate ions. As the concentration of Chloride ions approaches extinction; the silver ion concentration increases to a level at which the solubility product of silver chromate is exceeded and it begins to form a reddish-brown precipitate.

$$2Ag^{+} + CrO_4^{2-} \leftrightarrow Ag_2CrO_4$$

This is taken as evidence that all the chloride has been precipitated.

Procedure:

1. Take a 100 ml sample in a beaker.

2. Adjust sample pH to 7 to 10 with H_2SO_4 or NaOH if it is not in this range.

3. Add 1 ml potassium chromate indicator solution.

4. Titrate with standard $AgNO_3$ titrant to a pinkish-yellow endpoint.

5. Standardise the $AgNO_3$ titrant and establish a reagent blank value by the above titration method.

Calculation:

$$Cl^{-}\left(\frac{mg}{l}\right) = \frac{(A - B) * N * 35450}{ml\ of\ sample}$$

Where,

A = ml of titration for the sample.

B = ml of titration for blank.

N = Normality of $AgNO_3$

B) Sulphate

Sulphate is widely distributed in nature and may be present in natural waters in a concentration ranging from a few hundred to several thousand mg/l.

The turbidity metric method of measuring sulphates is based upon the fact that barium sulphate tends to precipitate in a colloidal form of uniform size and that this tendency is enhanced in presence of sodium chloride, hydrochloric acid and glycerol,

$$SO_4^{2-} + Bacl_2 \rightarrow BaSO_4$$

The absorbance of the barium sulphate formed is measured by a spectrophotometer at 420 nm and the sulphate ion concentration is determined by comparison of the reading with the standard curve.

Procedure:

1. Transfer blank to the sample tubes and place it in the chamber. Now the value of absorbance for the blank is displayed as 0.0185.
2. Then take standard 1 in the sample tube and place it in the chamber and take the reading.
3. Similarly, take readings for the rest of the samples

Calculation:

$$\boldsymbol{Concentration\ of\ Sulphate}\ \left(\frac{\boldsymbol{mg}}{\boldsymbol{l}}\right) = \frac{\boldsymbol{X * 1000}}{\boldsymbol{vol\ of\ sample}\ (\boldsymbol{ml})}$$

Where X = Sulphate in mg.

d) Fluoride

Procedure:

i) Stock Solution Preparation (1000 mg/l F^-)

Weigh 0.221 g of NaF, which was priorly dried for 120 mins at 110°C and stored in a desiccator. Dissolve the weighed NaF using distilled water and dilution was carried up to the 100 ml mark.

ii) Standard Solution Preparation (100 mg/l F^-)

Using a pipette, 10 ml of the stock solution was diluted using 100 ml of distilled water in a volumetric flask. Similarly, two more standard solutions i.e. 1.0 mg/l F^- and 0.1 mg/l F^- was prepared.

iii) Calibration of Ion-Selective Electrode (ISE)

Fluoride ISE is calibrated using standards that cover the expected sample concentration range.

1. Rinse electrodes and immerse in a standard of known concentration. Allow values to stabilise.

2. Once steady, the value is stored and step 1 is repeated for the other two standards.
3. A 3-point calibration curve is prepared by plotting the measured potential (mV) against the Fluoride concentration (mg/l).
4. If the slope is in the acceptable range (54-60 mV per decade of F), correction is not required. Calibration is completed.

iv) Fluoride concentration determination

1. Rinse the electrode thoroughly with distilled water and wiped using tissue paper to get rid of the excess of water.
2. The electrode is immersed in the sample and allow to steady. Value is noted.
3. Step 1 and 2 are repeated for determining the concentration of F in other samples.

Suitability for Irrigation

The development in the maintenance of successful irrigation projects involved not only supplying the irrigation water to the land but also to control the alkali and salt content reaching the soil. The characteristics of water for irrigation which are important for determining its quality are :

1. Percent Sodium (% Na)
2. Soluble Sodium Percent (SSP)
3. Residual Sodium Carbonate (RSC)
4. Sodium Absorption Ratio (SAR)
5. Magnesium Hazard
6. Kelly's Ratio

Percentage Sodium (%Na)

Sodium percentage is one of the most important factors to study sodium hazard. It is calculated as percentage of sodium and potassium against all cationic concentrations. It is also used for judging the water quality for agricultural uses. The use of high percentage of sodium water stunts the plant growth. The sodium reacts with the soil to reduce its permeability. Sodium percentage in water is the parameter computed to evaluate the suitability for irrigation. Usually little or only minor problems occur when %Na is less than 15%. However, when the percentage exceeds 15, reduced permeability results. The finer the soil texture and greater the organic matter content, greater will be the impact of sodium on water infiltration and aeration. Gypsum can be added to the soil to reduce the effect of high percent of sodium in irrigation water.

$$\% \text{ Na} = [(Na^{+}+K^{+}) * 100] / (Ca^{2+} + Mg^{2+} + K^{+})$$

Soluble Sodium Percent (SSP)

According to Eaton (1950), the percent is less than 60 percent, the water sample is said to be good quality and suitable for irrigation. On the other hand, percentage greater than 60 is said to be of poor quality and unsuitable for irrigation.

$$SSP = [Na^{+} / (Ca^{2+} + Mg^{2+} + Na^{+})] \times 100$$

Residual Sodium Carbonate (RSC)

The excess of carbonate and bicarbonate values over those of Calcium and Magnesium affect the suitability of water for irrigation. This is expressed as RSC, which is widely used to indicate the suitability of water for agricultural purposes. It is calculated as follows :

$$RSC = (HCO_3^{-} + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$$

Sodium Absorption Ratio (SAR)

The SAR is the most useful parameter for determining the suitability of surface water for irrigation purposes because it measures the alkalinity/sodium hazard. Sodium adsorption ratio is a measure of the amount of sodium (Na) relative to Calcium (Ca) and Magnesium (Mg) in the water extract from saturated soil paste. It is the ratio of the Na concentration divided by the square root of one-half of the Ca + Mg concentration. Soils that have SAR values of 13 or more may be characterized by an increased dispersion of organic matter and clay particles, reduced saturated hydraulic conductivity (K_{sat}) and aeration, and a general degradation of soil structure. Due to its effects on soil and plants, Na is considered one of the major factors governing the irrigation water. It can be determined using the formula :

$$SAR = Na^{+} / [(Ca^{2+} + Mg^{2+})/2]^{0.5}$$

Magnesium Hazard

Excess of magnesium in the soil affects the crop yield. Magnesium ratio greater than 50 is considered to be harmful and unsuitable. It may be due to the passage of surface water and sub-surface water through limestone, granite rock formation and many more taking place in the study area. The hazard is calculated as follows:

$$\text{Mg Hazard} = (Mg^{2+} * 100) / (Ca^{2+} + Mg^{2+})$$

Kelly's Ratio

Kelly in 1951 has suggested that the sodium problem in irrigation water could be very conveniently worked on the basis of the values of Kelly's ratio. In general, with KR > 1, it is considered to be unfit for irrigation. It is calculated as follows:

$$KR = Na^{+} / (Ca^{2+} + Mg^{2+})$$

Permeability index (PI)

The soil permeability is affected by long-term irrigation influenced by Na^{+}, Ca^{2+}, $Mg^{2+}$and HCO_3^{-}contents of the soil. The PI values indicate the suitability of groundwater for irrigation. The values are expressed in meq/l. The permeability index of less than 60 is considered suitable for irrigation. And more than 60 indicates the groundwater is unsuitable for irrigation.

$$PI = (Na^{+} + HCO_3^{-}) *100 / (Ca^{2+} + Mg^{2+} + Na^{+})$$

II) SOIL ANALYSIS

As mentioned earlier, 6 soil samples were collected across the study area for the determination of fluoride content. Prior to conducting the analysis of soil samples, the soil sample is brought into solution and the extract obtained at saturation point is used for testing. The procedure is as follows:

1. Measure 10 g of soil sample. Transfer to labelled conical flask and add 100 ml of distilled water.
2. Mix and transfer flasks to the orbital shaker at 120 rpm overnight.
3. Next day, remove the sample from the shaker and allow to contents to settle.
4. Transfer the supernatant (liquid part) equally in centrifuge tubes. Discard the settled

soil layer.

5. The centrifuge tubes are then placed into a centrifuge and the process is carried out at 10,000 rpm for 15 minutes.
6. After 15 minutes, allow the centrifuge to stop before procuring the tubes.
7. Transfer the supernatant to a labelled conical flask and cover with Aluminium foil.
8. The supernatant obtained post centrifugation is used henceforth used for determining the pH, EC, hardness, cations and anions etc. for the soil samples, in the similar fashion as for water samples.

i) Determination of F in soil

The F concentration was evaluated with the help of the ion-selective electrode. The method prescribed by Frankenberger *et al,* (1996), was followed for the same. The fluoride concentration obtained before the addition of any buffer solution such as TISAB (4g of CDTA + 58 g NaCl + 57 ml glacial acetic acid in 1000 ml of distilled water followed by adjustment of pH 5.0 - 5.5 with the help of NaOH), helps in determining the concentration of free F^- in the water sample. The addition of buffer (1:1) helps to dissociate the F complex (if any) and aids in obtaining a stable pH.

ii) Organic content of soil

The Walkley-Black (WB) titration method is one of the classical methods for rapid analysis of organic carbon (OC) in soils and sediments. The method is based on the oxidation of organic matter by potassium dichromate ($K_2Cr_2O_7$)-sulfuric acid mixture followed by back titration of the excessive dichromate by ferrous ammonium sulfate (Fe(NH4)2(SO4)2*6H2O). The average oxidation number for organic carbon is considered as zero and the reactions involved into the WB titration method are as following:

$C^0 + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$

$Cr_2O7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

Procedure:

1. Take known amount of sample (0.5 g).

2. Add 2 ml of distilled water.
3. Add 10 ml of 0.1 N $K_2Cr_2O_7$ solution.
4. Add 20 ml Conc. H_2SO_4 acid.
5. Allow the sample mixture to rest for 30 minutes.
6. Add 50 -100 ml distilled water.
7. Add 2ml orthophosphoric acid. Swirl to mix contents.
8. Add 1 ml Diphenylamine indicator.
9. Titrate against 0.1 N FAS until a green colour is observed at endpoint.

$$\% \text{ of Easily Oxidable Organic Content} = \frac{(\text{A} - \text{B}) * \text{Normality of FAS} * 0.003 * 100}{\text{weight of sample}}$$

Where A = Volume of FAS used for Blank ;
B = Volume of FAS used for sample .

$$\% \text{ TOC} = \frac{\% \text{ Easily Oxidisable Content}}{0.77}$$

$$\% \text{ Organic matter} = \frac{(\% \text{ TOC})}{0.57}$$

iii) Transfer Factor Determination

It is an important factor for determining the translocation of F between the soil and plants. A ratio > 1 indicates the possibility of a higher extent of accumulation in parts of the plants present in soil and the subsequent human exposure *via* ingestion of the plants as food. The Transfer Factor (TF) is calculated as follows:

$$\text{TF} = \frac{\text{Conc of water} - \text{extractable F in plant body growing in contaminated soil}}{\text{Conc of water} - \text{extractable F in contaminated soil}}$$

III) VEGETABLE AND CROP ANALYSIS

i) Preparation of samples

A portion of the vegetables was kept aside to determine the moisture content while the rest was processed as follows in the text. The collected vegetable samples comprising of spinach (location 2 and 12 each), radish (location 2) and cauliflower (location 12) were thoroughly washed firstly with tap water followed by distilled water before being pat dried using a cloth. Each sample was weighed, dried in a hot air oven at 70°C for several days, followed by grinding using an electrical blender and sieving. The sieved samples were kept aside for further processing for the F content determination.

ii) Fluoride determination in vegetables and crops

The total F content was determined by extracting the dried, ground and sieved samples with 0.1N perchloric acid (Villa,1979). Estimation of fluoride concentration was carried out with the help of Ion-Selective electrode (Thermo Scientific ORION SA G01104).

Fig.3. Sample preparation for determination of F content

iii) Moisture determination in vegetables and crops by gravimetric method

The edible part of the vegetables and crops were chopped into small pieces. Initial weight was noted for each sample and drying was carried out using the moisture balance (Precisa XM60) till a constant weight was achieved.

$$\boldsymbol{Moisture\ content = \left(\frac{W1 - W2}{W1}\right) * 100}$$

Where, W1 = Initial weight of vegetables, mg.

W2 = Final weight of vegetables, mg.

The values of the moisture content are required on a dry weight basis for calculating the exposure doses of F in humans.

Fig.4. Moisture Analysis of vegetable samples.

IV) RISK ASSESSMENT

a) Exposure dose determination

The first step in assessing the risk involved in terms of health is done by determining the exposure doses of fluoride. The exposure can be either by consumption of drinking water or by vegetables and crops. The exposure dose is calculated in terms of Estimated Daily Intake (EDI), with the help of a generic equation stipulated by USEPA (2014). The equation is as follows:

$$EDI = \frac{Cw * I * Ef * Ed * Af}{Wb * Ta}$$

Where: C_w - concentration of F^- in water, mg/l; I - Ingestion rate, l/day; E_f - Exposure frequency, days/year; E_d - Exposure duration, year; A_f - Absorption factor, unitless ;

W_b - weight of the body, kg; T_a – average time, days.

The same equation was used to determine the EDI for the vegetables/crops collected in the study area, whereby the concentration of fluoride was determined in terms of mg/g of fresh weight of the sample, and the ingestion rate was considered in terms of mg/day.

The Estimated Daily Intake, is a commonly used concept for determining the amount of exposure a person can sustain daily, normally throughout the span of life without being subjected to deleterious effects of the chemical/component in context.

b) Reference dose, R_fD

The reference dose refers to the estimation of the daily intake of fluoride by both children and adults, whereby no observed adverse effect level (NOAEL) is reported, particularly among the sensitive group despite exposure throughout the lifetime. The manifestation can be in terms of any statistically or biologically toxic effect of concern.

c) Risk Assessment

The risk assessment is carried out by compiling the Hazard Quotient (HQ). HQ is the overall F intake related risks. Referred to as the ratio of the Estimated Daily Intake and the reference dose, the equation is as follows :

$$HQ = \frac{EDI}{RfD}$$

Where: EDI: Estimated Daily Intake, mg/Kg-day; RfD = reference dose, mg.

Upon computation, if the Hazard Quotient is less than 1, non-carcinogenic effects are not expected to take place from any chemical. In contrast, if the Hazard Quotient is greater than 1, potential non-carcinogenic effects are expected.

CHAPTER 4 RESULTS AND DISCUSSION

The water, soil, and vegetable samples collected at across the various rural areas of North-West district of Delhi, India were analysed for their physicochemical constituents to evaluate its aptness for drinking and irrigation purposes as well. The characterization of the specimens was performed in a set of three as per the standard approved procedures (APHA 2005) using analytical grade (AR) chemicals and ultrapure (Type 1) water. The values obtained were then compared against the indices and norms. Based upon the type and nature of the dissolved chemical species in groundwater, its suitability for use in the agricultural setup, chiefly for watering can be commented upon; nevertheless, the presence of fluoride ions in the matrices remains the main concern.

Suitability for drinking

The pH of the groundwater specimens was determined using the help of a multiparameter kit (Labmann LMMP30) as mentioned. The pH was observed to be ranging from 7.2, specifically at Pooth Khurd (Location 2) to a maximum of 8.7 recorded at Mungeshpur (Location 15). The pH of the water was found to be typically neutral to somewhat basic just like other studies have confirmed (Frengstad and Banks, 2000), likewise for the case studies undertaken in Delhi (Alam *et al.,* 2012; Rawat *et al.,* 2018). The pH registered at all the 19 locations, were conforming to the BIS (2012) and the WHO guidelines (2017). From table 2, it is evident that as the depth at which sample was available /collected seems to be varying inversely with the pH. This particular deduction is seconded by the findings of a study, whereby the pH of both the soil and groundwater seemed to be increasing, as the depth increased from the surface (Indraratna *et al.,* 1995) and the same observation was associated with oxidation of pyrite, leading to the formation of acids. Pyrite dissolution, triggered by electrical means, is associated with calcium fluoride and acid mine drainage is promoted (Wang *et al.,* 2016) in mining areas and is even regarded as a pollutant of the surface water bodies. Additionally, the acidic medium is well – known to promote the absorption of fluoride ions while the reverse is equally true, whereby pH > 7.0 favours the release of F^- (Sreedevi *et al.,* 2006; Fantong *et al.,*2010).

Table 2: Physico-chemical parameters for evaluation of water quality for consumption purposes.

S.No.	Village	Source (T/H)	Depth (m)	pH	EC (µS/cm)	TDS (mg/l)	TA (mg/l)	TH (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K+ (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	CO_3^{2-} (mg/l)	HCO_3^{-} (mg/l)	F^{-} (mg/l)
1.	Bajitpur	T	9	7.6	4520	2270	160	850	190	58.3	341	9	550	347	14	332	2.5
2.	Pooth Khurd	T	30	7.2	3210	1611	192	1800	124	75.8	175	7	70	369	10	166	0.75
3.	Qutubgarh	T	23	7.4	6090	306	76	160	44	137.7	9	5	50	313	0	234	0.25
4.	Daryapur	T	12	7.3	5690	2860	240	1190	235	107.1	217	19	660	151	0	293	0.58
5.	Daryapur	T	18	7.9	406	203	60	155	217	8.0	373	12	750	63	0	73	0.11
6.	Auchandi	T	12	7.4	4540	2270	308	625	32	12.4	13	3	30	323	14	278	1.7
7.	Auchandi	T	9	7.4	6090	3040	260	405	185	78.7	307	7	580	338	19	537	0.6
8.	Auchandi	H	9	7.7	10660	5340	128	300	208	56.1	411	273	620	389	19	273	1.0
9.	Mungeshpur	T	9	7.7	2520	1260	264	345	273	35.0	1138	19	1720	342	34	215	1.6
10.	Mungeshpur	H	9	7.5	684	344	488	745	145	16.0	202	7	400	63	0	156	0.2
11.	Mungeshpur	T	12	7.4	3120	1561	272	470	102	40.8	156	9	90	270	14	220	1.8
12.	Mungeshpur	T	9	7.8	1678	848	216	530	52	14.6	21	4	40	183	19	264	4.7
13.	Mungeshpur	H	9	7.4	775	388	264	175	39	26.2	39	7	50	82	0	171	0.3
14.	Mungeshpur	T	9	8.1	744	371	140	305	70	16.8	113	4	40	135	43	5	2.6
15.	Mungeshpur	T	9	8.7	1169	585	112	195	43	8.0	33	12	60	184	77	15	7.3
16.	Mungeshpur	T	9	8.3	768	384	204	75	78	21.9	94	7	50	141	24	54	2.7
17.	Mungeshpur	T	9	8.0	1440	724	104	240	76	25.5	82	7	40	126	0	268	2.0
18.	Mungeshpur	T	9	7.9	1384	692	220	330	233	31.3	190	8	1250	183	14	229	2.1
19.	Mungeshpur	T	23	7.9	2210	1111	224	360	120	10.9	175	6	250	244	19	142	2.3

$CaF_2 + 2\ NaHCO_3 \rightarrow CaCO_3 + 2\ Na^+ + 2F^- + H_2O + CO_2$ -------- (1)

The alkaline pH, promotes the exchange of hydroxyl ions with F^- (Edmunds and Smedley, 2001) present in the parent materials, therefore, leading to a surge in the F content in groundwater :

$R\text{-} F + H\text{-} OH \rightarrow R\text{-} OH + H\text{-}F$ -------- (2)

This result is supported by similar observations across the globe (Das *et al.*,2003; Jeong, 2005; Vasquez *et al.*,2006). Therewithal, the association of increased depth of the well and higher F^- have been concluded at some instances (Apambire *et al.*, 1997), however, same was not supported by other studies (Muhammad *et al.*,2013), just like in this particular case though a recent report (Government of India, 2019) highlights the rapid descent of the level of groundwater in about 54% locations in India and as proved by studies earlier, lower levels of groundwater favour deep percolation which in turns results in solubilisation of rocks and minerals (Kumar *et al.*, 2018).

The Electrical conductivity varied between 406 µS cm^{-1}, being the minimum registered at Daryapur (location 5) and a maximum of 10660 µS cm^{-1} at Auchandi (location 8). Similarly, Dash *et al.*, (2010), in a study undertaken in Delhi, highlighted that the EC values registered in the North-West region are higher and the same was attributed to the presence of shallow aquifers. The average electrical conductivity recorded for the H_2O samples across each village of the current study area, varied between 1428 to 7097 µS/cm, which goes well with the trend, *i.e.*, the F^- dissociation is enhanced as the EC is increased (Garg and Malik, 2004; Brindha *et al.*, 2011). The localised surge in the fluoride level could be associated with the high EC values (Dash *et al.*, 2010). Elevated TDS in the area under study was equally reported in the study. Only 6 samples (32 %) were found to be conforming the lower limit stipulated for water meant for human consumption. The samples were collected from Qutubagarh (location 3), Daryapur (location 5) and Mungeshpur (location 10, 13,14 and 16). If the maximum allowable boundaries of 2000 mg L^{-1}, as suggested by the Bureau of Indian Standards (2012) is considered, then 68% of the samples are found to be suitable. High TDS values in Delhi has also been communicated by Kumar *et al.,* (2006) and Alam *et al.,* (2012). High TDS is often associated with the leaching of salts from the soil medium into the water bodies and another reason could be the mankind related activities (Prasanth *et al.*,2012). Jia *et al.,* (2017), go even further by stating that groundwater samples found at a depth of 0- 50 are more prone to report high TDS and Salinity. Moreover, high TDS has been found to be positively related to high F^- content in water (Subba, 2003). Typically, an increase in TDS is linked with enhanced ionic strength, which on the whole, facilitates the ability of F^- to dissolve (Plant, 1998). The correlation coefficient of TDS and F^- is -0.192 (Table 8), which confirms the existence of a weak link between these two parameters. Besides, it can also be concluded that high TDS not only affect the consumers in terms of direct health impacts but *via* indirect means as well, *i.e.* complications associated with the presence of relatively elevated presence of F^- ions. Upon calculation of the mineral saturation index, a positive index was obtained at all the locations, which hints at the supersaturated nature of water with respect to Calcite and Aragonite. Since the value exceeds unity, precipitation is favoured (El-Said *et al.,* 2016), which in other words boosts up the chances of fluoride distribution. Fluoride solubility being dependent on HCO_3^- is seen to be corresponding to the increased concentration of F^- (Okazaki *et al.*,1982), for instances as at location 12, Mungeshpur. It is considered as a common feature particularly, during the evolution of basins, interactions between rock-water take place. Usually, in strata found relatively deeper, the groundwater has a rich Carbonate and bicarbonate content, which enhances /encourages the release of F^- (Tirumalesh *et al.,* 2007; Kantharaja *et al.*,2012; Singh and Mukherjee, 2014), possibly arising as part of the previously mentioned rock-water reactions *i.e.* Fluorite and Water (Saxena and Ahmad, 2001) :

$CaF_2 + 2\ Na_2CO_3 \rightarrow CaCO_3 + 2F + 2\ Na$ -------- (3)
$CaF_2 + 2\ NaHCO_3 \rightarrow CaCO_3 + 2\ Na + 2\ F + H_2O + CO_2$ -------- (4)

These reactions help in the dissolution of CaF_2, hence, with time, the fluoride concentration is seen to be escalating. Similarly, Calcite ($CaCO_3$) also helps in liberating fluoride from mineral-rich materials:

$CaCO_3 + 2F + 2\ Na \rightarrow CaF_2 + HCO_3$ -------- (5)

$CaF_2 \rightarrow Ca + 2F$ --------- (6)

The attributes of water as a universal solvent can be linked with relatively high TDS, particularly at the locations where the water level in near the ground level, as compared to other sites. The organic and inorganic components of soil could be one of the underlying reason for the high TDS level. High TDS in groundwater samples have also been previously revealed in a groundwork by Kumar et al., (2006) and Alam *et al.*, (2009) in Delhi. The fluoride level ranged between 0.2 mg L^{-1} to 7.3 mg L^{-1}; with the smallest value being recorded at Mungeshpur (location 10), while the highest equally recorded at Mungeshpur, precisely at location 15. Previously, a concentration of 7.14 mg L^{-1} was reported by other investigation undertaken in Delhi (Shekhar and Sarkar, 2013), therefore showing that the current study is almost in line in terms of fluoride concentration. On an average, the fluoride value as per the villages was as follows: 2.5 mg/l at Bajitpur and Mungeshpur each, followed by 1.1 mg L^{-1} at Auchandi; 0.8 mg L^{-1} at Pooth Khurd; and 0.3 mg L^{-1} at Daryapur and Qutubgarh. The associations of elevated fluoride concentration with elevated Sodium content and Sodium-bicarbonate, resulting in lowered calcium concentration has been registered by a series of similar investigations undertaken over a while (Handa,1975; Chae *et al.*, 2007).

As far as cations are concerned, an elevated level of Sodium ions shadowed by Calcium, Magnesium, and Potassium ions was observed. The Na^+ level vacillated between 9 mg L^{-1} recorded as the minimum at Qutubgarh (location 3) and 1138 mg L^{-1} as the maximum at Mungeshpur (location 9). Calcium ions were found to possess a minimum concentration of 32 mg L^{-1} at Auchandi (location 6) while the highest value peaked 273 mg L^{-1} at Mungeshpur (location 9); while a minimum of 8 mg L^{-1} of Mg^{2+} ions at Daryapur (location 5) as well Mungeshpur (location 15) and a maximum of 138 mg L^{-1} at Qutubgarh (location 3). In the current study, 26% of the samples were seen to be complying to the lower prescribed limit of 75 mg L^{-1} as stipulated (for Ca) by BIS (2012), hence lowering down the percentage of suitability for drinking. Magnesium, in contrast, was reported as < 30 mg/l (BIS, 2012) at Daryapur (location 5), Auchandi (location 6) and Mungeshpur (location 10, 12-17 and 19), hence showing that around 53 % of the samples were in accordance to the standards. An increase in the Na^+ content could be seen to be negatively correlated with divalent cations namely that of Ca and Mg similarly to a previous study (Raj and Shaji, 2017), while positively correlated to F^- with r = 0.767 (Singh *et al.*, 2011; Jabal *et al.*, 2014). The ion-exchange process could be responsible and the same can be used to account for the elevated fluoride concentration. Generally, Ca^{2+} is inversely proportional with respect to F^-, therefore supporting the findings of these studies (Li *et al.*, 2015; Wang *et al.*, 2019). Water devoid of or having less Ca^{2+} concentration, liberate F^- owing to fluorite saturation milieu (Frengstad *et al.*, 2001). Excess of Na^+ and low Ca^{2+} provide a helping hand in enhancing the residence of water (Adimalla *et al.*, 2018a). The divalent cation, Mg^{2+}, just like Ca^{2+} enters the groundwater as an outcome of the aftermath if reactions with other elements, originating chiefly from magmatic rock or volcanic/plutonic activities. Just like all other parameters of water, low Mg^{2+} and Ca^{2+} concentration can be linked with elevated fluoride content (Maina and Gaciri, 1984; Xu *et al.*, 2013). The Potassium ions were found to be negatively correlated to fluoride with the minimum of 3 mg/l registered at Auchandi (location 6) and a maximum of 273 mg L^{-1} at Auchandi (location 8). The chloride ions were reported in the array of 30 to 1720 mg L^{-1}, with the minimum being recorded at Auchandi (location 6), while the maximum was registered at Mungeshpur (location 9). In terms of chloride, around 58% of the samples, mostly from the Mungeshpur village (8 locations), Pooth Khurd (location 2), Qutubgarh (location 3) and Auchandi (location 6) were found to be complying to the criteria established by the World Health Organisation (WHO) and Bureau of Indian Standards (BIS) for drinking, *i.e*. within 250 mg L^{-1}. A minimum of 30 mg L^{-1} and a maximum of 1250 mg L^{-1} of Chloride ions were conveyed in an investigation dealing with groundwater samples in non-urban areas of Delhi by Alam *et al.*, (2012), hence showing that the results of the current study are almost in-line with the previous one. An inverse association was established between F^- and Cl^-, similar to the conclusion drawn in this study (Rao, 2009). Sulphate, on the other hand, varied between 63 to 389 mg L^{-1} across the study area. As per the BIS (2012) standards, around 53% of the specimens were within the acceptable limits of 200 mg L^{-1}, compared to 100% samples complying to the stipulated guidelines of 500 mg/l by WHO (2017). In another study, an average of 442 mg/l and 112 mg/l of sulphate was registered during pre-monsoon and post-monsoon respectively in Delhi by Kumar *et al.,* (2006).

Hardness of the water is dependent on various ions. The hardness is dominantly triggered by the dissolution of Ca^{2+} to a greater extent compared to that of Mg^{2+}. Usually reported in terms of equivalent $CaCO_3$ (WHO, 2004), the hardness of the samples provides a background image of its geochemical features and the associated formations (Sawyer and Mc Cartly, 1978). BIS recommends 100 mg L^{-1} as the desired value while the maximum permissible limits tend to 500 mg L^{-1}. A minimum value of 75 mg L^{-1} was recorded, in other words, the presence of soft water was registered at Mungeshpur (location 16) and a maximum of 1800 mg/l at Pooth Khurd (location 2) of the study area. The values obtained in this study help in concluding that the hardness values are on the whole above the acceptable limits, hence corroborating with the conclusion of Adhikary *et al.,* (2012), a study dealing with the assessment of the quality of groundwater in Delhi. Given that the values noted are slightly on the higher end than the one reported by the previously mentioned study support the findings which depict that indeed in the North and West of Delhi, the hardness value was relatively on the lower side, which once again validates the outcomes of the current study. Similarly, an investigation of the groundwater samples across 50 locations spread throughout the rural area of Delhi by Alam *et al.,* (2012), reported the Total Hardness between 228 to 1673 mg/l.

The alkalinity, as $CaCO_3$, on the other hand, varied between 76 mg/l at Qutubgarh (location 3) to 488 mg/l at Mungeshpur (location 10). The average value was 219 mg/l $CaCO_3$, which exceeds the threshold of 200 mg/l prescribed by BIS (2012). The findings of the current study, though exceed the prescribed limits at 11 locations, the values are slightly on the lower end when compared to the TA values of 118 (min) to 751 (max) reported by Alam *et al.,* (2012).

The average value was determined for the studied parameters for each village and wherever possible the same was compared against the BIS (2012) and WHO (2017) norms for drinking water. At Bajitpur, the sample was found to be 100 % fit with respect to the minimum permissible limits of pH, TH and TA. Upon considering the upper permissible limits, the sample was found to be within the range with respect to $Mg^{2+}$and SO_4^{2-} . Fluoride and calcium ions were outside the range for the same location. Next, at Pooth Khurd, after considering the upper limits for Mg^{2+} the sample was declared fit for use. The maximum permissible limits were considered for Mg^{2+}, F^-, and SO_4^{2-} at both Qutubgarh and Daryapur. However, a high level of chloride was prevalent in the samples from Daryapur. Considering the upper acceptable limits, the samples were found to be almost 90% and 80% suitable at Qutubgarh and Daryapur respectively. At Auchandi, TDS > 2000 mg L^{-1} has been observed for all the samples, while F^- > 1.5 mg/l was reported at location 6. Lastly, at Mungeshpur, high fluoride has been reported at 9 locations out of 11, hence proving that fluorosis is endemic in the village. Overall, it can be established that the water samples are mostly fit for drinking. Appropriate measure needs to be taken in view of increasing the fitness of the water before consumed by individuals.

Suitability for Irrigation

As per FAO (2003), the groundwater accounts for 53 % of the irrigation in India. Almost half of the cultivated area rely on groundwater for irrigation as per CWC (2006), while Shah *et al.*, (2000) claims that groundwater serves 60 % of the irrigated agricultural produce. The groundwater samples were collected from an intensive agricultural belt of Delhi and subsequently subjected to Physico-chemical analysis to ascertain its fitness for the intended purpose, as per Table 3. In order to gauge the suitability of the water samples for irrigation purposes, various indices were calculated (Nagaraju *et al.*, 2014). The obtained values are as summarised in Table 4.

Table 3: Benchmarks for the categorisation of water employed for irrigation

Quality / Parameters	Very good	Good	Marginal	Poor	Harmful
EC (µS/cm)	< 1000 [a]	1000 - 2000	2000 - 4000	4000 – 6000	> 6000
%Na	20 [b]	20 - 40	40 - 60	60 – 80	80
RSC (meq/l)	< 0 [c]	0 – 2.5	2.5 – 5.0	5.0 – 7.5	> 7.5
KR	< 1 [d]		1 – 2	> 2	
SAR	0 – 10 [e]	10 – 18	18 – 26		> 26
Mg hazard	< 50 [f]			> 50	

a : Bhumbla and Abrol (1972) ; **b**: Wilcox (1955); **c** :Bishnoi et al., (1984); **d**: Kelly (1963) ; **e:** Richards (1954); **f**: Paliwal (1972)

Since Electrical Conductivity has an indirect link with TDS in water, the water quality can be a cause of concern. Almost 26 % of the samples, namely at the Daryapur (location 5) and

Mungeshpur (location 10, 13, 14 and 16) were classified into the very good category, as suggested by Bhumbla and Abrol (1972). Similarly, 21% of the samples classified as good were equally from Mungeshpur (location 12, 15, 17, and 18). Another 21% of the samples were in turn, declared as being of marginal quality were from Pooth Khurd (location 2) and Mungeshpur (location 9, 11 and 19). One sample from Bajitpur (location 1), Daryapur (location 4) and Auchandi (location 6) proved that almost 16% of the samples were of poor quality. Lastly, as far as EC is concerned, one sample from Qutubgarh (location 3) and 2 samples from Auchandi, had an EC > 6000 µS/cm, were declared as being harmful. High EC values were equally observed in a study of groundwater samples collected across the villages of Delhi by Alam *et al.,* (2012). However, when compared against the current study, the EC value observed is on the higher side and the same could be attributed to the elevated presence of ions and possible mineral pollution. The Sodium Absorption Ratio (SAR) ratio, was determined for all the locations. A minimum of 0 (Table 4), was recorded at Qutubgarh (location 3) and Auchandi (location 6), while a maximum of 17 was recorded at Mungeshpur (location 9). All the 19 water samples (100%) were declared to be good in terms of Sodium Absorption Ratio. The findings of Alam *et al.,* (2012), reported SAR value between 0.3 to 22.8, hence supporting the conclusions drawn from the current study. Elevated salt content in water results in saline soils, while high Na favours alkaline soil (Adhikary *et al.,* 2012). Usually, the prolonged use of water having high SAR ends up causing physical damage to the soil. Hardened and compact soil together with reduced permeability takes place, which in turn reduces productivity. Needless to say, a surge in Na facilitates Alkali hazard. Besides, the SAR value indicates the extent up to which water influences the exchange of positively charged ions in the soil. Another deduction that can be made from the high values of SAR is that presence of Na^+ ions is significantly higher as compared to the low levels of Ca^{2+} ions, which in turn favours a surge in the accumulation of F^- found in the samples (Simon *et al.,* 2016; Verma *et al.,* 2019). The presence of a high concentration of Na ions could be attributed to the exchange of ions that takes place between Na^+ and Ca^{2+} and can also be accredited to the weathering of parent rocks having an abundance of Na^+ (Guo and Wang, 2005; Guo *et al.,* 2007). Similarly, the values of % Na varied between 4 to 51%, with almost 11% of the samples lying in the very good to good category and the rest of them lying in the marginal to poor category. The Soluble Sodium Percentage (SSP) rose from 3 , recorded at Qutubgarh (location 3) to a maxima of 51 being registered at Bajitpur.

The Residual Sodium Carbonate (RSC), is an estimation of the exceedance of $NaCO_3$ after the divalent cations Mg^{2+} and Ca^{2+} have undergone precipitation. A negative RSC is regarded as ideal (Bishnoi *et al.*,1984), since the CO_3^{2-} and the HCO_3^- are lower than the divalent cations, and the same was found to be prevalent at 15 locations except for Auchandi (location 6) and Mungeshpur (location 12,15 and 17), which in other words, can be correlated with promising conditions for the dissolution of fluoride ions in the groundwater. According to Tiwari and Manzoor (1988), a negative value of residual sodium carbonate indicates that Ca^{2+} and Mg^{2+} are not precipitated completely. Another important parameter is Mg^{2+}, which assumes an equally significant role in deciding the suitability of water for watering purposes. The designated parameter, Mg Hazard, when exceeds 50, is considered as harmful and in this particular case, 84 % of the samples were found to be complying to the approved thresholds, hence declared as fit for irrigation. The Kelly's ratio was calculated and 63% of the samples were found to be less than 1, therefore indicating its suitability for use in the agricultural setup. A value greater than unity, indicates the presence of Na in excess and the same was visible in 26% of the samples.

Determination of the salinity hazard is vital for the assessment of water for irrigation. High salinity is associated with saline soil, limited salt uptake capacity by plants (Shanti and Safari-Sinegani, 2012) and health issues such as cardiovascular diseases (Cogswell *et al.*,2011) and others. Based upon the USSL diagram (1954), 84% of the specimens lies in the high to very salinity hazard. Management practices such as the addition of lime, are required before using the water. The Potential Salinity (Doreen,1964), proves that the appropriateness of water for irrigation may not necessarily depend on soluble salts solely, the low solubility salts are to be taken into consideration, for the proper water quality assessment. Defined as the 'ratio' dealing with chloride and sulphate concentration, the potential salinity value was found to be in the array of 2 to 61 meq/l. The potential salinity in the groundwater was found too high, hence proving that the water is unfit for irrigation.

Table 4: Physico-chemical parameters for assessment of water quality for irrigation purposes.

S.No.	Village	Base Exchange	Implications	Meteoric genesis	Type of percolation	SAR	RSC	SSP	%Na	Mg Hazard	Kelly Ratio	PS	PI	CAI
1.	Bajitpur	-0.1	Na_2SO_4	-0.1	Deep	6	-8	51	51	34	1.0	19	59	0
2.	PoothKhurd	0.8	$NaHCO_3$	0.8	Shallow	3	-9	38	38	51	0.6	6	46	-3
3.	Qutubgarh	-0.8	Na_2SO_4	-0.7	Deep	0	-10	3	4	84	0.0	2	17	1
4.	Daryapur	-1.2	Na_2SO_4	-1.1	Deep	3	-16	31	32	43	0.5	22	39	0
5.	Daryapur	-1.6	Na_2SO_4	-1.5	Deep	7	-10	58	59	6	1.4	23	62	0
6.	Auchandi	-0.2	Na_2SO_4	-0.2	Deep	0	2	17	19	39	0.2	2	84	0
7.	Auchandi	-0.4	Na_2SO_4	-0.4	Deep	5	-6	46	46	41	0.8	20	56	0
8.	Auchandi	0.1	$NaHCO_3$	1.0	Shallow	7	-10	54	62	31	1.2	21	61	0
9.	Mungeshpur	0.1	$NaHCO_3$	0.2	Shallow	17	-12	75	75	18	3.0	53	78	0
10.	Mungeshpur	-0.4	Na_2SO_4	-0.4	Deep	4	-6	51	51	16	1.0	14	60	0
11.	Mungeshpur	1.1	$NaHCO_3$	1.2	Shallow	3	-4	44	45	40	0.8	4	57	-2
12.	Mungeshpur	-0.1	Na_2SO_4	-0.1	Deep	1	1	19	21	32	0.2	2	63	0
13.	Mungeshpur	0.1	$NaHCO_3$	0.2	Shallow	1	-1	29	32	53	0.4	3	58	0
14.	Mungeshpur	0.4	$NaHCO_3$	0.4	Shallow	4	-2	57	58	19	1.3	6	62	-2
15.	Mungeshpur	-0.2	Na_2SO_4	-0.1	Deep	1	2	39	47	16	0.6	6	61	0
16.	Mungeshpur	0.3	$NaHCO_3$	0.4	Shallow	3	-1	48	50	22	0.9	5	66	-1
17.	Mungeshpur	0.2	$NaHCO_3$	0.3	Shallow	2	7	45	47	25	0.8	6	87	-1
18.	Mungeshpur	-3.4	Na_2SO_4	-3.4	Deep	3	-1	42	43	12	0.7	61	58	1
19.	Mungeshpur	-0.3	Na_2SO_4	-0.3	Deep	5	-2	57	58	8	1.3	16	72	0

The Permeability Index (PI), was determined as per the equation suggested by Raghunath (1987). Calculated with the ions expressed in meq/l, this index assumes a fundamental role in gauging the water being used in the agricultural milieu. Since the water being used has a close association with soil, the permeability of the soil remains at stake, particularly when the water is unfit for irrigation. The sample collected at Auchandi (location 6) and Mungeshpur (location 17) have a PI > 75%, hence regarded as excellent quality for irrigation. Conversely, water samples collected from Qutubgarh (location 3) falls in the class III category hence found unsuitable for use in the agricultural milieu. As far as the rest 16 samples are concerned, the water was found to be of good quality, *i.e.* belong to Class II segment. The findings, with respect to PI, of the current investigation are in-line with those reported by a study conducted in Delhi by Alam *et al.,* (2012).

The Chloroalkaline index proposed by Schoeller (1977), plays a significant part in the interpretation of groundwater chemistry. The exchange of ions between the parent material and the environment can be understood with the same. A negative CAI value, indicates the exchange of the base of the water, *i.e.* Sodium and Potassium with the Calcium and Magnesium present in the parent material. In case the ratio turns out to be positive, it is understood that no such base exchange is taking place. In this study, a positive value was obtained at all the locations, hence indicating the ion-exchange is not occurring.

As far as, fluoride is concerned, it has both beneficial and harmful effects on plants. Fluoride from water tends to either accumulate in the soil or taken up by the plants, thereby leading to biochemical, physiological as well as changes at the molecular levels in plants. The high concentration of F^- can directly or indirectly influence activities such as respiration, photosynthesis, and other activities involving the enzymes and many a time, the changes are asymptomatic in nature. Fluoride entry in plants takes place in the soluble form, where the movement is accomplished *via* the xylem and phloem to eventually reach the tips of the leaves (Threshow,1970). The manifestation of the same takes place initially in the form of necrosis at a smaller scale, starting from the upper part of the leaf until it ends at the base of the leaf. In the long run, chlorosis across the veins can be seen, particularly in the case of low concentration of F^- ions. Depending upon the concentration of the fluoride ions, the possible

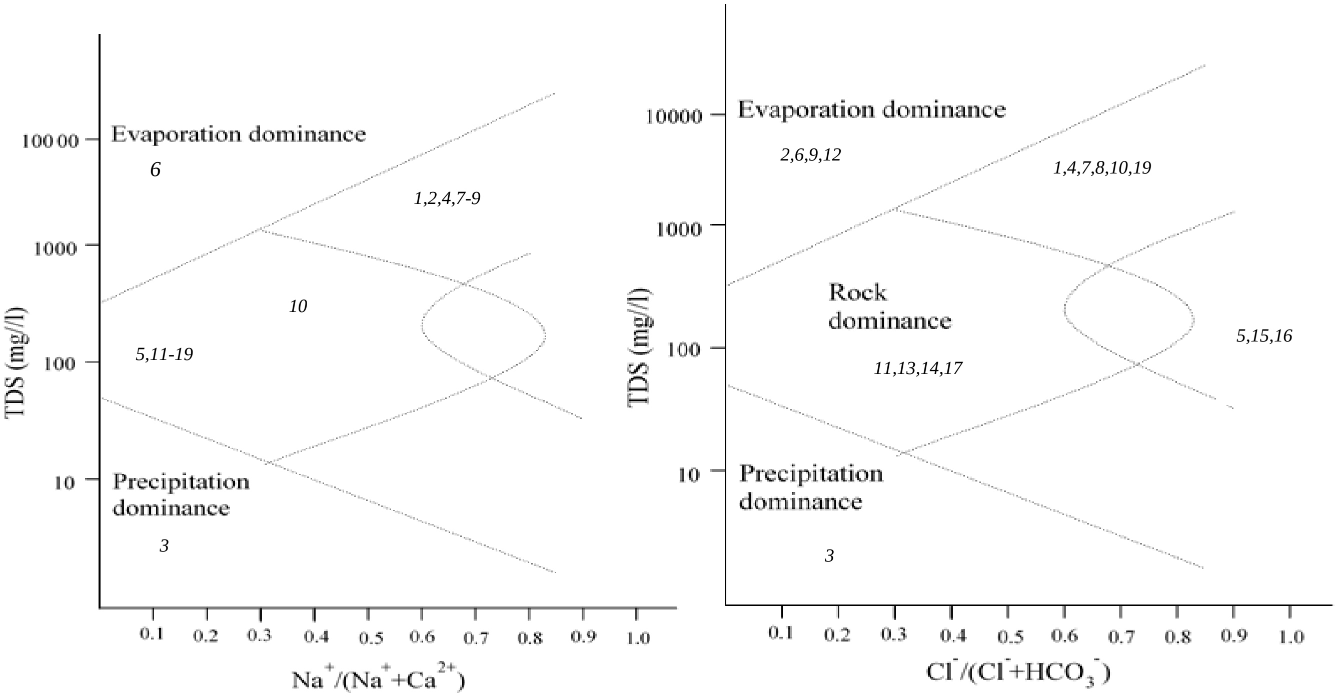
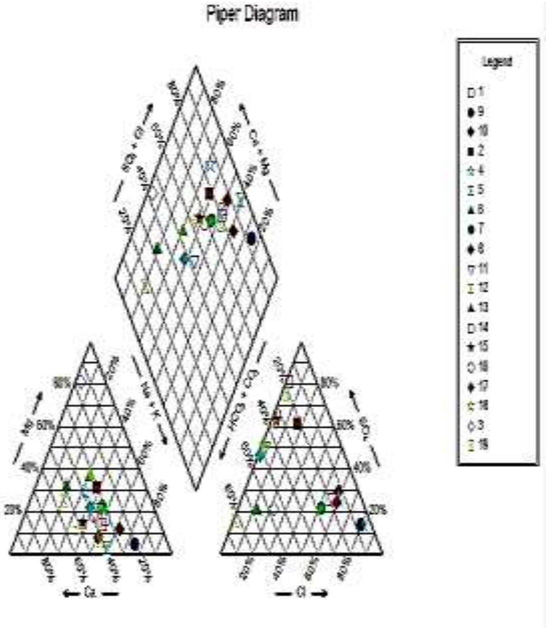


Fig. 5: Gibbs' Boomerang plot for the water samples



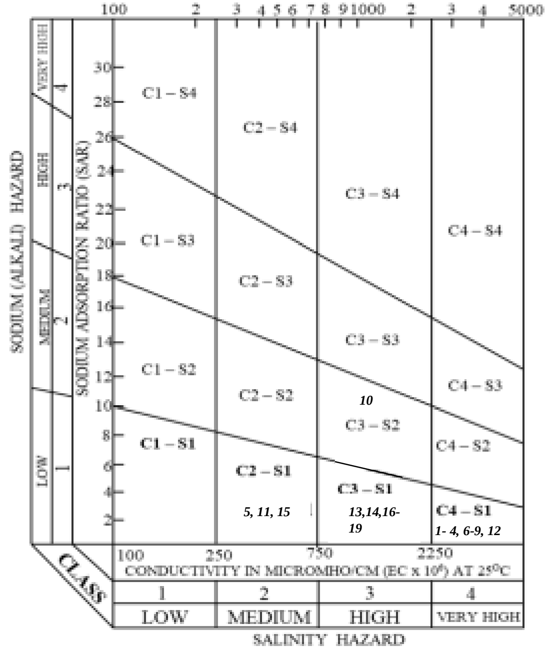


Fig. 6: Piper Trilinear plot for the water samples

Fig. 7: USSL diagram for the samples

death of cell sap can occur (Millner,1993). Degradation of the chloroplast (Kumar *et al.*,2013); localised death of living cells and abnormal yellowing of leaves (Landis *et al.*,2011); alteration of metabolic pathways (Elloumi *et al.*, 2005); inhibition of enzymes requiring co-factors such as divalent cations Mg^{2+} and Ca^{2+} (Panda,2015); reduced yield (Ando,1998); prolonged cropping period (Wollaeger,2015); decreased shoot length (Mondal and George,2015) and decreased level of proteins owing to stress in plants (Singh *et al.*,1985) have been reported. An average value was calculated, wherever possible, for the following indices: SAR, RSC, SSP, % Na, Mg Hazard, Kelly Ratio and Permeability Index to study the spatial variation across the study area and to determine the percentage suitability with respect to each of the 6 villages for the current case study. The water sample from Bajitpur had a very high EC, a % Na which is sightly above the acceptabe range and an equally borderline Kelly's ratio, therefore, the water was found to be almost 75% fit for use in the agricultural setup. Next, at Pooth Khurd, the EC was of marginal quality, while the remaining 7 parameters hinted at an almost very good to good classification, hence deemed appropriate for irrigation. Coming up to Qutubgarh, harmful EC and poor classification in terms of Mg Hazard was observed. The sample from Qutubgarh was therefore declared to be 63% fit for irrigation. At Daryapur, the samples were categorised as very good to good in terms of the indices considered for the study. The parameters were found to be mostly within the acceptable range except for %Na, therefore, the samples were declared to be almost 88% fit for the aforesaid purpose. Samples from Auchandi, on the other hand, had marginal EC, high % Na, was finally found to be only 75% fit. Lastly, the water samples from Mungeshpur, was almost 88% fit, except for the marginal quality owing to the high %Na.

Weathering profile and Geological characterisation

The major source accounting for the existence of anions and cations in water are namely from the atmosphere, the outcomes of anthropogenic activities and lastly as an aftermath of rock-water interactions (Subramanian,1987). The presence of F^- ions is dependent upon the Physico-chemical features of the groundwater (Saxena and Ahmed, 2003). As per the Gibbs' boomerang diagram (Fig. 5), majority of the samples were found to be mainly influenced by the rock-water interaction followed by a rising trend towards evaporation dominance

(Gibbs,1970). The average Ca/Na, Mg/Na, and HCO_3^-/ Na^+ ratio was found to be 1.3,2.7 and 1.8 respectively. Normally, the ratio indicates the potential silicate weathering that takes place (Gaillardet *et al.*,1999). Moreover, the ratio (Ca+Mg)/(Na+K) is 7.9, relatively far from unity which indicates that carbonate weathering is occurring as well. Reports by CGWB (2016), the physical disintegration of geogenic rocks containing minerals such as apatite, and fluorite, is contributing to the elevated level of fluoride across many regions of Delhi, with the major part being NorthWest and SouthWest districts. The Piper Trilinear diagram (Fig.6) was plotted with the help of AqQA software, to determine the hydrochemical characterisation of the groundwater samples (Piper,1953). The water samples were found to belong to Na-Cl (32%), Na-SO_4 (26%), Ca-SO_4 (11%), Ca- HCO_3 (11 %) and lastly of Mg-SO_4 and Mg-HCO_3 and Ca- Cl 5% for each type respectively. The outcomes are backed by the findings of a study undertaken by Haritash *et al.*,(2018) whereby Ca-Na-HCO_3 was seen to influence the geochemical character of the water samples in a fluoride dominant community in Haryana. Sodium bicarbonate facies tend to release F from the parent material (Handa, 1975). In addition, the strong acids *i.e.* Cl^- and SO_4^{2-} were found to be exceeding the weak acids (HCO_3^- and CO_3^{2-}). As far as classification as per the meteoric genesis is concerned, the two possible outcomes are deep meteoric water percolation when the Met. gen is less than unity and shallow meteoric water percolation takes place when Met. gen exceeds unity. In this study, 58% of the samples were found to belong to the deep meteoric water percolation type with the base-exchange being Na_2SO_4, while 42% of the samples belonged to the $NaHCO_3$ type and have a shallow meteoric water percolation.

Soil Analysis

Once fluoride is loaded into groundwater and the use of the contaminated water in agricultural fields is done, the chances of contamination of the soil increases. Moreover, the repeated use of fluoride-containing water further enhances the F content in soil over a span of time. In fact, contamination of soil by fluoride goes way back in the history of India, however the same was given less importance (Singh *et al.*, 2020). In an attempt to determine the soil quality with respect to fluoride, soil samples were collected across 6 locations of the study area and evaluated (Table 5). The mean F concentration was found to be 0.97 µg of F per g of soil, while a minimum of 0.33 was recorded for the soil sample collected at Auchandi (Location 6) and a maximum of 1.60 was noted at Mungeshpur (Location12). According to Kumar *et al.,* (2016), some of the prime parameters influencing the fluoride concentration in the soil are the pH,

Table 5: Fluoride content in soil samples and the associated implications

S.No.	Village	F^- in soil (ug /g of soil)	Transfer Factor (TF) and its implications	
1.	Bajitpur (Location 1)	0.77	-NA-	-NA-
2.	Pooth Khurd (Location 2)	1.20	0	Low risk of accumulation in plants
3.	Auchandi (Location 6)	0.33	-NA-	-NA-
4.	Mungeshpur (Location 9)	0.94	-NA-	-NA-
5.	Mungeshpur (Location 12)	1.60	> 1	High risk of accumulation in plant (Spinach)
			0	Low risk of accumulation in plant (Cauliflower)
6.	Mungeshpur (Location 15)	0.95	0	Low risk of accumulation in plants

Where, *NA: Not Available.*

the type of soil and Total Organic Content. Fluoride in soil has a close association with soil colloid and usually, the movement of F across the medium is dependent on pH, the salinity of the soil, the absorption ability *etc*. Besides, it is well-known that clayey have been seen to have a relatively higher F content compared to sandy and sandy-loam soil. The pH of the soil samples were found to be vary between 5.9 to 6.0 with minimal variance across the studies. The results obtained during the current case study is found to be in-line with the conclusions drawn by a study undertaken by Fauzie *et al.*, (2015) in Delhi, whereby a decrease in the pH of the soil and EC were observed to prevail over time while the SOM and the phosphate content were depicting a surge. As per a study by Abraham *et al.,* (2019), the pH of sandy soil sample collected at Rithala was 6.75, hence portraying a slightly acidic to almost neutral nature of the soil in the surroundings. The presence of F in the soil continuum is principally linked with the soil colloids, that acts as the natural electrostatic chemical reactor. Also, the fraction of clay content and that of the organic carbon coupled with the soil pH are regarded as major factors that have a close association with the F content being retained in the soil medium (Omeuti and Jones,1977). A surge in the adsorption capacity of fluoride was seen to manifest the highest at a pH of 5.5 (Barrow and Ellis, 1986). At pH less than 6, the F is essentially allied with Al or Fe (Elrashidi and Lindsay,1986), while a pH of ≥ 6.5, F is found as CaF_2 in case adequate $CaCO_3$ is available (Brewer, 1966). Likewise, as per Chatterjee *et al.,* (2018), sandy loam soil is common in Delhi, hence seconding the facts mentioned by Lal *et al.,* (1994). The same facts can be correlated to the study, whereby the presence of fluoride was confirmed and the sandy loam nature of the soil accounts for the 'low concentration' of F, unlike other studies undertaken in the past (Arnesen,1997; Kumar *et al.,* 2016). Moreover, the SOM was having a minimum value of 1, registered at Pooth Khurd (Location 2), while a maximum of 3 at Mungeshpur (Location 9 and 14). Three samples namely collected from Bajitpur (Location 1), Auchandi (Location 6) and Mungeshpur (Location 11), have been found to have a SOC was also determined for all the 6 locations. The values were found to be varying between 2 to 5 %, with the minimum being registered at Pooth Khurd (Location 2) and the maximum being recorded at two locations of Mungeshpur *i.e.* at both location 9 and 14. A low pH twinned with the presence of organic matter can lead to a surge in the F present in the soil, which in turn can boost up for the F uptake through the roots of the foliages (Kumar *et al.,* 2016). The high concentration of fluoride in the soil can also be linked to the use of phosphate fertilizers in the study area, which is also regarded as an intensive agricultural belt (Loganathan *et al.,* 2001). The PO_4^{3-} content was found to vary between 0 to 0.097 mg g^{-1} of soil, with the highest value being recorded at Mungeshpur (Location 12), hence agreeing to the conclusion drawn by the aforementioned study. Fluoride is omnipresent in phosphate-based fertilizers, and the magnitude of the same varies as follows: $F_{Fertiliser} > F_{Soil} > F_{Plants}$ (Larsen and Widdowson,1971).

The Transfer Factor (TF), wherever possible and the associated implications were evaluated. The TF plays an important role in gauging the translocation that takes place between the soil and plants, as well as is equally helpful in selecting the crops that can be cultivated in the F contaminated soil. In the present study, a TF having a value of 0 was obtained with respect to Spinach, Radish and Wheat at Pooth Khurd (Location 2), hence implying a low possibility of F accumulation, and same was observed at Mungeshpur for Cauliflower (Location 12) and Wheat (Location 15). On the other hand, a transfer of > 1 was recorded at Mungeshpur (Location 12), with respect to Spinach, a good accumulator, hence indicating a high risk of translocation of F taking place between the soil and the plant.

Bioavailable F in vegetables and crops

The journey of F initiating from the parent material, ends up reaching the water bodies, soil medium, plants before eventually making the way up to the human body *via* the diets. Unlike earlier, studies have proved foodstuffs as being equally contributing to the increased fluoride in humans (Radha *et al.*,2010). Accumulation up to 400 µg/g of fluoride without any sign of toxic effects *e.g.* necrosis, chlorosis (Sheldrake *et al.*,1978); low levels of F^- with the manifestation of toxic effects (Brewer,1966) and even sensitivity at levels < 20 µg/g of fluoride (Istas and Alaerts,1974). The fluoride content was determined in the vegetables and crops collected during sampling as represented in Table 7. The maximum concentration of fluoride of 0.3 mg/g F_w recorded in spinach grown at location 12, in Mungeshpur. In the other vegetables, analysed namely radish and cauliflower, no fluoride content was detected, be it in the edible parts of the leaf. A similar result was obtained when the cereals *i.e.* wheat were analysed.

Furthermore, studies have proved that the bioavailability of fluoride is dependent upon numerous factors such as pH, precipitation, complex-forming ability, absorption and many more (Senkondo, 2017; Li *et al.*,2019). Cereals normally have a F concentration of less than 1 ppm and the accumulation usually take place in the embryo and the outer part of the seed (Kumpulainen & Kovistoinen,1997). The fluoride content normally does not exceed 30 mg/kg dry mass in tissues of plants growing in uncontaminated sites (Kabata-Pendias, 2001). Apart from spinach, renowned for its accumulating ability, the fluoride content of leafy and root and vegetables do not vary much from that of cereals (Madhavan and Subramanian, 2006). The uptake of fluoride by plants is a process that begins at the root level because fluoride in the soluble form undergoes (Brewer,1965), hence highlighting that bioavailable F is of biological importance to foliage and animals (Davidson,1983). Studies have even proved that elevated concentration of F in soil coupled with alkaline pH makes the milieu favourable to promote the potential uptake of bioavailable fluoride by the plants (Wenzel and Blum,1992). All these mechanisms can be put forward to account for the presence of F^- in plant tissues. The high F^- concentration in spinach is considered as a potential accumulator of fluoride ions (Sheldrake *et al.*,1978), which once again have been seconded by this study undertaken in Delhi. Another possible explanation for the F^- content in spinach could be that leafy vegetables are exceptionally more prone to air pollutants' depositions over the large surface area of the leaves (Jassir *et al.*,2005) and these criteria, in particular, can account for the absence of F^- in spinach at the location, where probably fewer sources of fluoride are present. In addition, fluoride accumulation takes place in the following order: $F_{root} > F_{leaf} > F_{fruit} > F_{shoot}$, hence, it can further explain the presence of F in the leafy vegetables, particularly in areas of endemic fluorosis. This plausible route can be considered for phytoremediation of fluoride (Weerasooriyagedara *et al.*,2020).

Risk assessment for humans

Till date, few studies including clinical studies as well as research work have been undertaken to determine the effect of fluoride at various concentrations on human health. Since drinking water is considered as one of the major pathways through which fluoride reaches the human body, an assessment regarding the potential risks that humans run upon ingestion of fluoride was determined. However, since some of the studies carried out previously show that ingestion of food also contributes F the human body (Linhares *et al.,* 2018; Kabir *et al.,* 2020), the F^- intake via food (vegetables/cereals) were determined simultaneously. Since there are no stringent guidelines at the national level regarding the dose-effect relationship, the values adopted by the Integrated Risk Information System (IRIS) of USEPA, whereby the reference fluoride dose through oral ingestion is 0.01 for food and 0.06 mg/kg/day for drinking water.

Table 6: Estimated Daily Intake (EDI) and Hazard Quotient (HQ) for each location.

S.No.	Villages	Conc. of F^- (mg/l) in water samples	Estimated Daily Intake (EDI), mg kg $^{-1}$ day $^{-1}$	Hazard Quotient (HQ)	Category of Risk	Possible Implications	Conc. of F- (mg/g) of Fwt in vegetables		Estimated Daily Intake (EDI), mg kg -1 day -1	Hazard Quotient (HQ)	Category of Risk
1.	Bajitpur	2.5	0.225	5	High	Severe fluorosis; decreasing birth rate.	-NA-		-NA-	-NA-	Low
2.	Pooth Khurd	0.75	0.0675	1	High	Fit for consumption.	Spinach	0.0	0	0	Low
							Wheat	0.0	0	0	Low
							Radish	0.0	0	0	Low
3.	Qutubgarh	0.25	0.0225	0	Low	Conducive to dental fluorosis.	-NA-		-NA-	-NA-	Low
4.	Daryapur	0.58	0.0522	1	Low	Fit for consumption.	-NA-		-NA-	-NA-	Low
5.	Daryapur	0.11	0.0099	0	Low	Conducive to dental caries	-NA-		-NA-	-NA-	Low
6.	Auchandi	1.7	0.153	3	High	Mild to Moderate fluorosis.	-NA-		-NA-	-NA-	Low
7.	Auchandi	0.6	0.054	1	High	Fit for consumption.	-NA-		-NA-	-NA-	Low
8.	Auchandi	1.0	0.09	2	High	Fit for consumption.	-NA-		-NA-	-NA-	Low
9.	Mungeshpur	1.6	0.144	3	High	Severe fluorosis; effects on hormones**.**	-NA-		-NA-	-NA-	Low
10.	Mungeshpur	0.2	0.018	0	Low	Conducive to dental caries.	-NA-		-NA-	-NA-	Low
11.	Mungeshpur	1.8	0.162	3	High	Mild to Moderate fluorosis.	-NA-		-NA-	-NA-	Low
12.	Mungeshpur	4.7	0.423	8	High	Moderate fluorosis.	Spinach	0.3	0.00281	0.003	Low
							Cauliflower	0.0	0	0	Low
13.	Mungeshpur	0.3	0.027	1	Low	Conducive to dental caries.	-NA-		-NA-	-NA-	Low
14.	Mungeshpur	2.6	0.234	5	High	Mild to Moderate fluorosis.	-NA-		-NA-	-NA-	Low
15.	Mungeshpur	7.3	0.657	13	High	Skeletal fluorosis	Wheat	0.0	0	0	Low

16.	Mungeshpur	2.7	0.243	5	High	Mild to Moderate fluorosis.	-NA-	-NA-	-NA-	Low
17.	Mungeshpur	2.0	0.18	4	High	Mild to Moderate fluorosis.	-NA-	-NA-	-NA-	Low
18.	Mungeshpur	2.1	0.189	4	High	Mild to Moderate fluorosis.	-NA-	-NA-	-NA-	Low
19.	Mungeshpur	2.3	0.207	4	High	Mild to Moderate fluorosis.	-NA-	-NA-	-NA-	Low

Firstly, the Estimated daily intake (EDI mg/kg/day) was calculated as per the USEPA equation (2014), followed by the Hazard Quotient, which is in turn based on EDI and the Reference dose. The health risk assessment is regarded as an effective method to determine the probability and the extent of the impacts linked with the fluoride concentration on human health (Means, 1989; USEPA,1993; Uras *et al.*, 2014). The risk assessment of a particular chemical on the human health consists of 4 stages: identification of hazard, the setpoint values for toxic effects, the evaluation of exposure and lastly the classification of the risks (Selinus *et al.*,2018). The EDI and the Hazard Quotient were calculated for each location (Table 6), considering that 90% of ingested F through drinking water is absorbed, particularly on empty stomach (WHO, 2004; ASTDR, 2001). It is evident that as the concentration of fluoride present in the water resources, the associated risk increases. The minimum EDI was found to be 0.0099 mg/kg/day and was recorded at Daryapur (location 5), while the highest EDI was found to be 0.657 mg/kg/day recorded at Mungeshpur (location 15), where the highest concentration of F^- was equally recorded. As far as the Hazard quotient and categorisation of risk are concerned, the minimum risk (HQ = 0) was noted at Mungeshpur (location 10) and Daryapur (location 5), and the highest risk was found to be in the village of Mungeshpur (location 15) with a risk hazard quotient as high as 13. The value obtained for EDI and HQ, for spinach which as mentioned earlier was tested positive. For the presence of fluoride were 0.00281 mg/kg/day and 0 respectively. Upon comparison against the limits set by Hargreaves (1990), for adults, almost 58% of the samples were found to be exceeding the prescribed limits of 0.0214 – 0.0571 mg/kg/day, which in other words imply that villages are exposed to relatively high risk of developing symptoms or having fluorosis especially since the combined intake of water and food containing F^-, certainly endangering the residents in terms of fluorosis. The usage of water with elevated F, have been seen to escalate the level in Hungary (Schamschula *et al.*, 1988). Some of the possible complications associated with the different intake are tabulated.

The total intake dietary intake is prescribed by IOM (1999) for people belonging to different age groups. Following the same, the EDI and HQ were calculated for three age groups namely 3-15 years; 15-18 years and 19-70 years for different locations. As per the HQ values, it can be concluded that both Bajitpur and Mungeshpur were exposed to the highest risk of fluorosis, for all the three age groups; while Daryapur and Qutubgarh were running the lowest risk, among the other villages. Since both low and high risks have effects on human health, along with measures to bring down the level of fluoride, surveillance and monitoring is essential at all the villages concerned in this study. Experimental and clinical studies have proved that the influence of the concentration of F^- has different impacts on health (Grigoryera *et al.*,1993; Rozier,1999). Previous studies undertaken suggest that young children are more susceptible to the effects of fluoride since the risks associated, under the normal circumstances is inversely proportional to the body weight, hence proving that the children are the 'easy targets' (Prathoshni *et al.*, 2017; Suresh *et al.*, 2019).

Despite all the risks that an individual is exposed to, fluoride has been associated with beneficial aspects as well. Previously, the undertaken studies have demonstrated the benefits of using fluoridated water and lowered dental cavities, minimized acid attacks owing to the anti-bacterial characteristics of fluoride (Brown & Konig, 1977; Petrovich *et al.*, 1995) as well as overall improved dental health in different places of US and European countries in the 1940s (Dean *et al.*, 1942). Keeping this particular aspect, artificial fluoridation has been promoted on many occasions and places as required on a global scale for example in Australia, New Zeland and Canada. In fact, as per a report of WHO, as of 2004, more than 355 million people are dependent on artificially fluoridated water. The protective effect of fluoride on the enamel, particularly in children have been investigated at the onset of the 20th century itself (Iheozor-Ejiofor *et al.*, 2015), following which the use of fluoridated dental products for their cariostatic effects was encouraged (Wong *et al.*,2011; Cagetti *et al.*,2013). Besides, investigations have also allied low concentration of fluoride as a means of killing bacteria in water (Rwenyonyi *et al.*,2000). However, unlike the developed countries which already have better decontamination options for water can afford to skip the fluoridation process in their purification, sometimes this practice becomes difficult to manage, hence triggering adverse effects on the health.

It is well-known to everyone that F^- having a concentration < 0.5 mg/l is conducive to dental caries while the F^- concentration ≥ 1.5 mg/l lead to dental fluorosis unlike F^- concentration $\geq$ 6.0 mg/l lead to skeletal fluorosis. In terms of dietary composition, in regions of endemic fluorosis, deficiencies of Ca, Mg and other vitamins are prevalent (Biro *et al.*,1996; Zaichchick *et al.*,1996). Also, the elevated EDI, in terms of fluoride is manifested in the form of change in the number of irreplaceable amino acids, variation in the levels of proteins, carbohydrate disbalance (Fordyce *et al.,* 2007). The aforementioned effects are often characterised as inadequate mineralisation, particularly that of the bones. Acute toxicity mostly arising post accidental intake of F overdoses or accidental ingestion of pesticides or inadvertent use of dental products having fluoride content include hemoptysis, cramps, cardiac arrest and sometimes death (Whitford,1992; Basch and Kernan, 2016; Crauciuc *et al.,* 2018).

On a similar note, dental fluorosis begins with the appearance of white bands on the surface of the tooth, chalky white patches of discolouration to more yellowish/brownish/blackish stains. Pits and structural damages such as chipping teeth are also observed (WHO, 1999; Rao, 2003). The worst involves the loss of the proteins' matrix as the enamel starts developing as an aftermath of mineralisation. Further, depending upon the exposure dose, abnormal large gaps in the crystalline anatomy followed by a surge in the number of pores, which in turn makes space for fluoride accumulation causing cracks have also seen as part of results of studies undertaken (Aoba and Fejerskov,2002; Vierra *et al.,* 2004). International pieces of literature have even revealed that upon consumption of water having > 2mg/l F^-, at least 60% of the end-users have been subjected to fluorosis compared to 100% of the population which have experienced fluorosis after the concentration > 6 mg/l (Fordyce *et al.,* 2007; Apambire *et al.,*1997).

Skeletal fluorosis is another impact triggered as a result of an excess of fluoride. Though the associated mechanisms are not clear, sufficient details about the different stages involved are provided in numerous publications (WHO,1999; Rao, 2003; Edmunds and Smedley, 2005). At the infancy stage, stiffness at the joint levels, osteosclerosis which eventually give rise to stiffness across the spines, paralysis attacks and most advancing towards deformities, damages of the neurones and even compression of muscles, joints and spine. Possible complications at the renal level have been observed in people consuming water with F^- level in the range of 2 – 8 mg/l (Kaminsky *et al.,*1990) either over a span of time of 7 years (Felsenfelf and Roberts,1991) or ten years (Whyte *et al.,* 2005). Studies have also been undertaken to determine any possible link between fluoridation of water and secondary bone cancer in people of 18 years and above (Crnosija *et al.,* 2019).

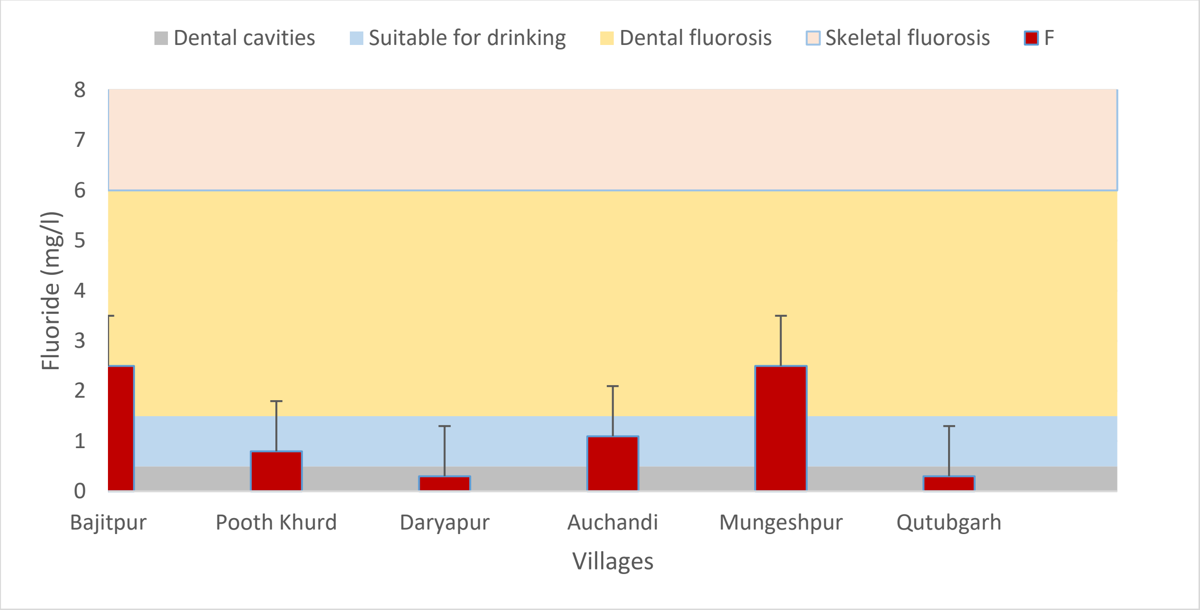


Fig. 8: Average spatial fluoride distribution and its associated risks in the area under study.

Influences triggered by an excess of fluoride have been witnessed in terms of reproductive effects. Drinking water having greater than 3 mg/l has been associated with a decline in the birth weight of the newborn in areas where fluorosis is prevalent (Diouf *et al.*, 2012), and changes at the level of hormones (Ortiz-Perez *et al.*, 2003). Furthermore, complications during the development of organs owing to the ingestion of food/water contaminated by the presence of high F^- concentration has also been experienced. Transfer of fluoride *via* the placenta (Gupta *et al.*, 1993), Down's syndrome (Whiting *et al.*,2001) especially observed in children born to mothers' in the 30's age group (Takahashi,1998), low IQ levels particularly in cases where children are exposed to F > 2 mg/l (Trivedi *et al.*, 2007), neurotoxicity arising when fluoride concentration varies between 2 – 4 mg/l (Spittle *et al.*, 1998), development of kidney stones upon drinking water with a fluoride content of 3.5 – 4.9 mg/l (Singh *et al.*, 2001) have also been reported. Primary effects of fluorosis related to the endocrine system are impaired thyroid function, Type 2 diabetes, a higher rate of Calcitronin function as a result of which bone-breaking is common (Doull *et al.*, 2006) and Goître (Jooste *et al.*, 1999). As per Doull *et al.*,

Table 7: Spatial variation of fluoride risk assessment with respect to age group

S.No.	**VILLAGE**	**3-15 years**			**15 - 18 years**			**19 – 70 years**		
		EDI mg/kg-day	**HQ**	**INFERENCE**	**EDI mg/kg-day**	**HQ**	**INFERENCE**	**EDI mg/kg-day**	**HQ**	**INFERENCE**
1.	Bajitpur	0.158	3.2	High Risk; retarded growth; low IQ levels.	0.115	2.3	High Risk; dental fluorosis; possible onset of skeletal fluorosis.	0.103	2.1	High Risk; dental fluorosis ; skeletal fluorosis.
2.	Pooth Khurd	0.050	1.0	Border line	0.037	0.7	Low Risk	0.033	0.7	Low Risk
3.	Qutubgarh	0.019	0.4	Low Risk.	0.014	0.3	Low Risk	0.012	0.2	Low Risk
4.	Daryapur	0.019	0.4	Low Risk	0.014	0.3	Low Risk	0.012	0.2	Low Risk
5.	Auchandi	0.069	1.4	High Risk ; retarded growth; low IQ levels.	0.050	1.0	High Risk; dental fluorosis; possible onset of skeletal fluorosis.	0.045	0.9	Low Risk
6.	Mungeshpur	0.158	3.2	High Risk ; possible retarded growth; low IQ levels.	0.115	2.3	High Risk; dental fluorosis; possible onset of skeletal fluorosis.	0.103	2.1	High Risk; dental fluorosis ; skeletal fluorosis.

(2006), gastrointestinal complications is another set of issues that cannot be ignored. Besides, the lack of evidence has resulted in an unsuccessful correlation of fluoride in drinking water and its carcinogenic effects (Steiner, 2002; Harrison, 2005). Unlike the studies dealing with the oncological effects of fluorosis concerning oral and skeletal cancer, limited studies are available regarding fluoride in drinking water and its contribution towards blood and colon cancer (Takahashi *et al.,* 2001), uterine cancer (Yang *et al.,* 2001), that of the oesophagus (Menya *et al.,* 2019) and lastly proteoglycans and its association with cancer (Spittle, 2019).

Fluorosis is allied with anaemia (Shruthi and Anil, 2018; Sukumar *et al.,* 2018). The use of iron and folic acid supplements is the approach adopted in India to improve the dietary intake to combat anaemia. However, investigations have highlighted the contribution of fluoride in the destruction of intestinal linings and the prevention of absorption of nutrient in question. Removal of fluoride by modifying the diet to exclude fluoride while increasing the other important nutrients among some 2420 teenagers across 6 schools in Delhi have successfully corrected anaemia and the intestinal linings. Diet counselling and modification of the components of the diet have proved to be beneficial to curb the progression of diseases associated with F, if not, to overcome the harmful effects of fluoride (Rustagi *et al.,* 2017; Mondal, 2018; Susheela *et al.,* 2018; Liu *et al.,* 2019).

Remediation

Finally, it can be concluded that excess of fluoride is harmful to the health, hence there is the urgent need for coming up with appropriate measures to combat the same. Investigations suggest adsorption to be among the elite defluoridation techniques that can be adopted. The reasons for choosing this particular method are namely the ease with which the process can be carried out, its inexpensive cost and the absence of complex processes involved made it even a far better option (Yadav *et al.,*2018). Activated alumina (AA), has been widely considered for the elimination of F^- from water (Mondal and George, 2005). This process has proved to be highly efficient at pH 4.4 with an absorption capacity of 8.4 mg/l. The models that serve best for this purpose are Langmuir isotherm and quasi- second order kinetics. However, health issues related to the percolation of Aluminium, cannot be overlooked. Different classes of graphites have been taken into consideration for the eradication of fluoride. Carbon has been seen to depict characteristics that are negatively correlated to fluoride, hence making it suitable to bring down or even remove fluoride from aqueous medium (Karthikeyan and Elango, 2008). Furthermore, calcium-based removal of F^- has also been explored (Gandhi *et al.,* 2013). The factors influencing the process are enlisted as the concentration of F^-, the amount of adsorbent being used and the duration of contact of ion and adsorbent. In addition, the ion-exchange process for the same purpose was tried and tested (Alkan *et al.*, 2018; Samadi *et al.*, 2014). Despite marvellous results were obtained (up to 95% removal), the exorbitant cost of resins, the large quantity of fluoridated waste generated, and the difficulty encountered in disposing of such waste makes it less likely to be adopted (Jadhav *et al.*, 2015). Lately, the development of nanotechnology has led to massive exploration opportunities and remedies. Cupric oxide nanoparticles (Bazrafshan *et al.*,2016), gamma-alumina with sol-gel (Singh *et al.*, 2016) and single-walled carbon nanotubes (Balarak *et al.*, 2016) are some of the methods/materials adopted to scavenge fluoride efficiently with the highest efficiency recorded being 96% from water. Natural materials can be considered as well. Zeolite, clay, chitosan, brick powder and even soil have been successfully used. The chemical stability, high surface area, and the structural characteristics help in exploring the aforementioned materials as potential options (Srinivasan, 2011; Vinati *et al.*, 2015). Current desorption systems are ecologically not manageable. Financially speaking, suitable absorption procedures are currently required. Other possibilities involve Nalgonda technique, reverse osmosis and electrodialysis. Last but not the least, the use of limestones from various geological formations have been effective in eliminating fluoride up to 65% from water (Labastida *et al.*, 2017).

As far as F contaminated soil is concerned, suggestions such as lesser usage of fluoride contaminated water, cultivation of plants/crops having a poor absorption capacity of F, determination of F content before the addition of fertilizers to the soil and determining the amount of fluoride to be added needs to be taken into consideration to break the chain of transfer as well as bringing down the fluoride content in soil.

In the absence of customised and stipulated guidelines to cure fluorosis, certain measures can be considered to at least curb the debilities and crippling effects entrained due to the exceedance of F ions and to enhance the quality of life. Control of fluorosis can be done solely by tackling the symptoms (Sellami *et al.*, 2020), therefore the proposed suggestions arising as an aftermath of chronic manifestations of symptoms related to fluorosis are: firstly, to augment the intake of Ca, Vitamin C and D, and antioxidants in the diet either through food items or *via* the commercially available supplements. Secondly, the treatment of the disfigured anatomy of the malformation can be carried out. In addition, decompression of the compressed body parts *e.g.* compressed spine and other body parts, myelopathy *etc.* Another treatment that can be considered is the cosmetic surgery for the discoloured teeth and the pitted ones. Coming up to the 'cure' of the acute toxic effects of fluoride involves: firstly, the surveillance and follow up; management techniques such as gastric irrigation (also referred to as lavage), treatment of the irregular heartbeats, use of antacids coupled with supplements (Ca, Mg, Al), increase the intake of milk, monitoring and therapy for dyselectrolytemia and lastly, carrying out dialysis is of utmost importance (Gupta, 2015; Goenka and Marwah, 2014). Improvement of the nutrition especially for young children and lactating mothers twinned with avoiding products rich in F^- for instance rock salts, mouth rinse solutions, tobacco *etc* in endemic areas are suggested (MOHFW, 2012; National Health Portal, India). Sensitisation campaigns to spread awareness through IEC *i.e.* Information, education and communication activities in fluorosis hotspots is primordial. The National Program for Prevention and Control of Fluorosis (NPCCF) which involves regular dental checkup and full-body screening of school children across 195 districts of 29 states should be extended to a larger scale (MOHFW, 2014).

Statistical analysis

Statistical methods were employed for a better understanding and data interpretation. The Physico-chemical analysis of the parameters was determined and the percentage of the samples abiding by the prescribed recommendations for drinking water (Table 2) and irrigation (Table 4) were determined. Further, basic statistical analysis of the groundwater samples was carried (Table 8).

Table 8 : Basic Statistical analysis of water samples

Parameters	**Min**	**Max**	**Mean**	**SD**	**Median**
pH	7.2	8.7	7.7	0.4	7.7
EC (µS/cm)	406	10660	3037	2665	2210
TDS (mg/l)	3	5340	1361	1324	848
F^- (mg/l)	0.1	7.3	1.8	1.8	1.7
Ca^{2+}(mg/l)	32	273	130	18	120
Mg^{2+}(mg/l)	8	138	41	36	26
Na^+(mg/l)	9	1138	215	57	175
K^+ (mg/l)	3	273	22	14	7
Cl^- (mg/l)	30	1720	384	108	90
SO_4^{2-} (mg/l)	63	389	224	110	184
CO_3^{2-} (mg/l)	0	77	16	19	14
HCO_3^- (mg/l)	5	537	204	126	220

Where: Min – Minimum, Max – Maximum, SD – Standard Deviation

Given that spatial variation was observed as far as the fluoride concentration is concerned, the average value was determined for each of the 6 villages. Upon analysis, it was found that 21.1% of the samples had a F^- concentration of less than 0.5 mg/l, which implies that those samples are contributing to dental caries. Similarly, 21.1 % of the samples were found suitable in terms of the Fluoride content, compared to 52.6 % of the samples which favoured dental fluorosis and 5.3% of the samples were exposing the individuals to skeletal fluorosis. On an average basis, it could be concluded that dental fluorosis is more dominant in the study.

A box and whisker plot (Fig. 9) was generated for the groundwater samples collected. Upon analysis, it can be concluded that the minimum (Q_1) recorded at Mungeshpur (N = 11), was 0.3 mg/l, while the median of the upper half (Q3) was 2.7 mg/l of Fluoride. The median was 2.1 mg/l for the same location, while 3 outliers namely at location 2,13 and 16 where a

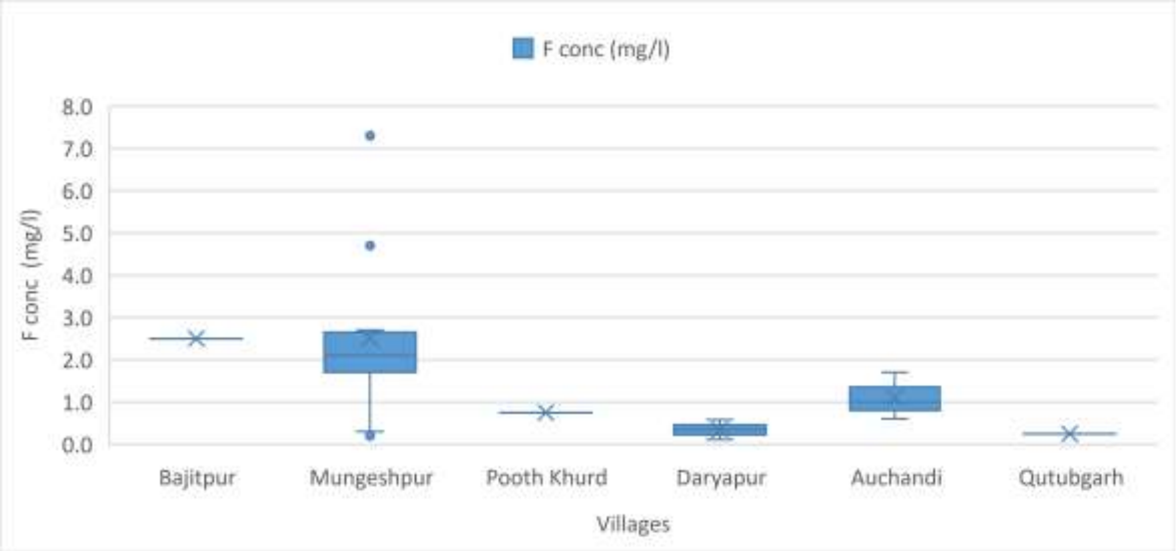


Fig. 9: Box and Whisker Plot for groundwater samples

concentration of 0.2, 4.7 and 7.3 mg/l were registered respectively. On the other hand, for Daryapur (N = 2), the Q_1, Q_2 and Q_3 were found to be 0.1, 0.3 and 0.6 mg/l respectively. Concurrently, at Auchandi (N = 3), the Q_1, Q_2 and Q_3 were as follows: 0.6, 1.1 and 1.7 mg/l of F^-. As far as, the villages are concerned, the Physico-chemical analysis has confirmed the manifestation of fluoride in groundwater samples, hence the skewness of the distribution was determined. The skewness value for Mungeshpur was 1.48, with the distribution being skewed to the left, unlike at Auchandi, where the skewness was 0.78, with the distribution more on the positive side. Conversely, owing to the limited number of samples at Bajitpur, Pooth Khurd and Qutubgarh, lesser interpretation could be made. Nevertheless, as mentioned earlier, on an overall basis, the presence of fluoride was confirmed at each location, though the concentration has depicted a spatial variation (Fig. 7). Therefore, a quick analysis of the samples, as a whole, hints at mostly a positive skewness with the value being 1.9. In short, it can be deduced that the distribution depicts a biasedness towards elevated F^- concentration, as seen in Table 2. In terms of fluoride variation, the largest range was that of Mungeshpur (7.1), followed by Auchandi (1.1) and lastly for Daryapur (0.47).

Table 9: Pearson correlation matrix for the physicochemical parameters of groundwater samples (N = 19)

Variables	**pH**	**EC**	**TDS**	**F^-**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**TA**	**TH**	**Cl^-**	**SO_4^{2-}**	**CO_3^{2-}**	**HCO_3^-**
pH	1													
EC	-.448	1												
TDS	-.361	.887**	1											
F^-	.748**	-.292	-.192	1										
Ca^{2+}	-.190	.274	.407	-.364	1									
Mg^{2+}	-.575**	.652**	.355	-.441	.200	1								
Na^+	-.092	.160	.257	.767**	-.220	.029	1							
K^+	-.008	.695**	.743**	-.118	.288	.112	.232	1						
TA	-.407	-.136	.015	-.231	-.083	-.182	-.114	.126	1					
TH	-.567*	.188	.284	-.206	.382	.352	.142	-.020	.281	1				
Cl^-	-.067	.118	.202	-.228	.895**	.062	.848**	.167	.108	-.031	1			
SO_4^{2-}	-.276	.339	.517*	-.278	.835**	.284	.649**	.291	.199	.483*	.674**	1		
CO_3^{2-}	.661**	-.125	-.033	.781**	-.223	-.296	-.021	.029	-.202	-.216	-.190	-.331	1	
HCO_3^-	-.600**	.612**	.596**	-.334	.681**	.504*	.558*	.661**	.191	.218	.442	1.000**	-.331	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

The Pearson Correlation matrix (Table 9) was generated with the help of the Statistical Package for Social Science software (SPSS), for the Physico-chemical parameters of the groundwater samples (N = 19). A positive correlation (r = 0.748) was observed between pH and F^-, likewise for Na^+ (r = 0.767) with respect to F^-, with $p < 0.01$. These two conditions are considered favourable for the release of F, hence increasing the level of risk for the individuals relying on the groundwater for both drinking and irrigation. On the other hand, a negative correlation was observed with $p < 0.05$ between fluoride and Ca^{2+} (r = - 0.364), Mg^{2+} (r = -0.441), SO_4^{2-} (r = -0.278) and HCO_3^- (r = -0.334) was observed. The previously mentioned 4 parameters help bring down the fluoride content, once their respective concentration is increased (Rao *et al.*, 2013; Raj and Shaji, 2017).

CHAPTER 5 CONCLUSION

Fluoride, as a natural pollutant is seen to be widely spread across the villages of North-West, Delhi. The distribution, exposure and assessment of risk allied with fluoride in groundwater was carried out based upon the methodology prescribed by USEPA. The base- exchange and the meteoric percolation were observed to be associated with the spatial distribution of fluoride in groundwater. The richness of the fluoride ions present in water could be attributed to the rock-water interaction. Further, ion-exchange reactions and alkaline pH were seen to be contributing to the solubilisation of fluoride from the parent material. Since groundwater serves for both drinking and agricultural purposes, and have a direct association with soil and the plants, the F content of the soil samples and the bioavailable F was determined in the vegetables collected in the study. The soil pH and its sandy loam nature, the presence of organic content and presence of phosphate were seen to be some of the underlying factors contributing to the presence of F. Moreover, the transfer factor exceeding unity at Mungeshpur (Location 12), highlights the risk factor camouflaged. Coming up to the bioavailable F, only spinach at location 12 (Mungeshpur) was found to be accumulating F of 0.3 mg/g fresh weight. Minimal as it may seem, it certainly encompasses health concerns. Hence, the EDI – based risk assessment was carried out. Most of the water sources (94%) fall into the high-risk category, with mostly dental fluorosis being dominant. Further classification of EDI according to age groups highlighted that children of 3-15 years were running the highest risk followed by the children of 15-18 years and lastly by adults of 19-70 years old. Retarded growth, lower IQ levels, bone deformities, stained and mottled teeth are some of the common symptoms associated, though many more health concerns could be taking place as discussed earlier. Monitoring and surveillance particularly of the children, defluoridation techniques, diet editing and treatment of symptoms are some of the suggestive measures recommended.

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