

Groundwater fluoride contamination scenario in selected sites of West Bengal and remedial measurement

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*Dedicated to
my parents*

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I, **Ayan De**, registered on **3rd January 2019**, do hereby declare that this thesis entitled **“Groundwater fluoride contamination scenario in selected sites of West Bengal and remedial measurement”** contains literature survey and original research work done by the undersigned candidate as part of doctoral studies.

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ABSTRACT

Fluorine is an abundant trace element in natural environmental conditions and usually, it manifests as fluoride (F^-). The present study evaluates the multi-dimensional aspects of F^- contamination in groundwater, along with its exposure in cultivated crops and vegetables, followed by human health risk assessment due to F^- toxicity in West Bengal, India. According to the report of the Public Health Engineering Department (PHED), Govt. of West Bengal, 43 blocks in seven districts covering 2.26 lakh people are affected by F^- toxicity. Obtaining such information from the block level of West Bengal, the present study has given importance to the extensive monitoring of groundwater, food chain entry, source of contamination and human health concerns in F^- contaminated areas. Further, studies were conducted focusing on the distribution pattern of F^- in groundwater from six districts namely South 24 Parganas, West Medinipur, Jhargram, East Bardhaman, West Bardhaman, and Murshidabad of West Bengal. A total number of 3287 groundwater samples were collected for this purpose. The presence of F^- in groundwater was found >1.5 mg/l in 10%, 11%, 4%, and 14% of samples from South 24 Parganas, Jhargram, West Bardhaman, and Murshidabad district, respectively. This study has evaluated first time the magnitude of F^- concentration in groundwater from nine newly F^- exposed blocks in West Bengal (Baruipur, Sonarpur, Binpur II, Salanpur, Baraboni, Jamuriya, Pandabeswar, Kandi, and Khargram). At present, the total number of F^- exposed blocks are 65 from 10 districts of West Bengal. About 3% of groundwater samples from West Bardhaman district significantly represented the class V toxicity level where F^- concentration was found >10 mg/l. According to the depth-wise distribution, the maximum presence of F^- was found in the depth range of 24.4 - 30.5 m in the southeastern part (South 24 Parganas) of West Bengal. One of the important studies has been evaluated to classify the role of minerals and related hydro-geochemical processes mainly responsible for releasing high concentration of F^- in groundwater from South 24 Parganas district. The distribution of cation and anion in the fluoridated groundwater samples follows the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Fe$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > CO_3^{2-} > F^-$, in Sonarpur block and $Na^+ > Ca^{2+} > Mg^{2+} > Fe > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > CO_3^{2-} > NO_3^- > F^-$, in Baruipur block respectively. Furthermore, the Piper diagram showed that all the groundwater samples have represented the Na-Cl type and cluster analysis represented a strong primary cluster formation between Na^+ and Cl^- ions. Moreover, the positive silicate weathering condition played a significant role behind low Ca^{2+} concentration in groundwater. Additionally, Gibbs plot showed that all the groundwater samples fall between the zone of evaporation dominance and rock dominance zone, which

proves the ionic interaction process occurring between groundwater and host silicate mineral. Significantly, the saturation index (SI) suggests that the groundwater is oversaturated and can be precipitated in the form of dolomite, and calcite. Where, chloro alkaline (CA) I and CA II values represent that both Mg^{2+} and Ca^{2+} ions can be absorbed on the exchangeable sites of host mineral and instantaneously, release Na^+ and K^+ ions into the groundwater. The maximum F^- concentrations were found as 767 mg/kg and 600 mg/kg in borehole sediment samples in the depth range from 3.05 m to 6.1 m and 9.14 m to 12.19 m, respectively. XRD spectra showed the intense pick of muscovite present in borehole sediment. SEM-EDX study further confirmed that the groundwater F^- contamination is mainly of geogenic origin and predominantly influenced by muscovite.

The consumption of F^- through drinking water is either beneficial or harmful to human health according to daily ingested doses. Fluoride contamination is not only limited to groundwater, but with time it has spread into the food chain. The agricultural soil and food crops from F^- contaminated regions of Bankura and Purulia districts have been evaluated and found average soil F^- concentrations were 114 ± 59 mg/kg and 126 ± 65 mg/kg from Bankura and Purulia, respectively. Maximum F^- concentrations translocated from soil to plant body part in leafy vegetables compared to cereals, pulses and non-leafy vegetables. Moreover, nonleafy vegetables contributed the highest exposure of F^- (approximately 55.5%) to estimated daily intake (EDI) cumulative among all the food crops. The lifetime non-cancerous health risk (HL_{LTNR}) of F^- with percentile doses from P5 to P95 (exploring the model of Monte Carlo simulation) in all the studied age groups (4-70 years) was found to be >1 and indicating that the inhabitants were more vulnerable for their total lifetime period of F^- exposure through consumption of food crops from Bankura and Purulia district.

Likewise, the non-cancerous health risk was found to be comparatively higher in the southwestern districts (Jhargram, West Bardhaman, and the western part of Murshidabad) than in the southeastern districts (East Bardhaman, West Medinipur, and South 24 Parganas) of West Bengal. Urine is the most reliable indicator of F^- ; however, no correlation was found between urinary F^- and groundwater F^- in contaminated areas (Ward no.6, Rajpur Sonarpur Municipality, Sonarpur block and Dhapdhapi II gram-panchayat, Baruipur block, South 24 Parganas district) and control area (Madhyabar, Pingla, West Medinipur district). The assessment of non-cancerous health risk showed a trend of infants being the most vulnerable, followed by adults, children, and teenagers among the inhabitants of these six districts. According to the probabilistic health risk at P95 dose (by Monte Carlo simulation method) for

infants were significantly more vulnerable (>1) to F^- toxicity in contaminated areas. The sensitivity analysis study has justified that oral exposure was more vulnerable than dermal exposure in the studied population.

This research focused on the investigation of the performance efficiencies of the mitigation measures made by two different materials as seashell and dolomite and their mixture (1:1). All the adsorbents have supported the Freundlich isotherm model and Pseudo 2nd order kinetic model. Seashell and dolomite mixture (1:1) contributed the maximum F^- removal percentage of 85.5% from F^- contaminated groundwater (20 mg/l groundwater from Birbhum district). After F^- removal, the generated sludge was managed by brick formation.

So, promoting awareness programs on F^- severity and proper healthy nutritional food are highly suggested for the threatened inhabitants to fight against the overwhelming calamity of F^- .

INDEX

Content no.	Chapter Name	Section no.	Section Name	Page no.
Chapter 1	Introduction			1-10
		1.1	Global water scenario	2
		1.2	Groundwater resource in India	3
		1.3	Groundwater quality in India	4
		1.4	Groundwater contamination through fluoride	4
		1.5	History of fluoride	5
		1.6	Characteristics of fluoride	5
		1.7	Source, distribution, and mobility of natural fluoride	6
		1.8	Fluoride in food chain	7
		1.9	Fluoride toxicity and its mechanism in human health	8
		1.10	Fluoride removal techniques from groundwater	9
Chapter 2	Literature review			11-22
		2.1	Fluoride contamination in groundwater: global scenario	12
		2.2	Distribution of fluoride in Indian groundwater	13
		2.3	Distribution of fluoride in groundwater from West Bengal	14
		2.4	Food chain contamination of fluoride	15
		2.5	Adverse effects of fluoride on human health	16

		2.6	Mitigation options	17
Chapter 3	Aim and objectives			23-24
Chapter 4	Materials and methods			25-55
		4.1	Systematic literature reviews of groundwater fluoride contamination in West Bengal for meta-analysis	26
		4.1.1	Searching strategy for data	26
		4.1.2	Data extraction and quality assessment	27
		4.2	Study area	27
		4.2.1	South 24 Parganas	28
		4.2.2	West Medinipur	30
		4.2.3	Jhargram	31
		4.2.4	East Bardhaman	31
		4.2.5	West Bardhaman	32
		4.2.6	Murshidabad	33
		4.2.7	Bankura	33
		4.2.8	Purulia	34
		4.3	Sample collection and preservation	35
		4.3.1	Groundwater	35
		4.3.2	Crops and vegetables	36
		4.3.3	Soil	36
		4.3.4	Urine	36
		4.3.5	Borehole sediments	37
		4.4	Sample processing	37
		4.4.1	Acidified digestion	37
		4.4.2	Alkaline digestion	38
		4.5	Estimation of chemical parameters	38
		4.5.1	Estimation of fluoride	38
		4.5.2	Estimation of total arsenic	38

		4.5.3	Physico-chemical analysis of water quality parameters	39
		4.5.4	Estimation of other parameters	39
		4.5.4.1	Moisture percentage in food crops, vegetables, and soil	39
		4.5.4.2	Bioaccumulation factor (BCF) of fluoride in plant	39
		4.5.4.3	Protein, Carbohydrate, and total Chlorophyll	39
		4.6	Chemicals, reagents and analytical instruments	40
		4.7	Accuracy and precision	41
		4.8	Statistical analysis	41
		4.9	Data interpretation and analysis	41
		4.9.1	Single factor contamination index	42
		4.9.2	Hydro-geochemical controlling factors	42
		4.9.2.1	Geochemical weathering (Gibbs diagram)	42
		4.9.2.2	Chloro-alkaline (CA) indices	42
		4.9.2.3	Geochemical modelling: saturation index (SI)	43
		4.9.2.4	Mineralogical study	43
		4.10	Human health risk assessment	44
		4.10.1	Health risk assessment model of the studied population	44
		4.10.2	Nutritional Status and exposure dose determination	45

		4.10.3	Health risk assessment study through consumption of dietary food	46
		4.10.4	Probabilistic risk assessment	47
		4.10.5	Sensitivity analysis	47
		4.11	Defluoridation process using calcium-based materials	47
		4.11.1	Selection of materials	48
		4.11.2	Pre-treatment of dolomite and seashell	48
		4.11.3	Defluoridation procedure	49
		4.11.4	Batch study for removal of fluoride	49
		4.11.5	Adsorption isotherm	50
		4.11.5.1	Langmuir adsorption isotherm	50
		4.11.5.2	Freundlich adsorption isotherm	51
		4.12	Adsorption kinetics	52
		4.12.1	Pseudo-first order kinetic	53
		4.12.2	Pseudo-second order kinetic	53
		4.13	Stability test of sludge material (Bricks)	53
Chapter 5	Results and discussion			56-168
		5.1	Groundwater quality evaluation	58
		5.2	Fluoride distribution in groundwater from different studied areas	58
		5.2.1	South 24 Parganas district	58
		5.2.1.1	Rajpur Sonarpur Municipality in Sonarpur block	58

		5.2.1.1.1	Prevalence and distribution of fluoride and arsenic in groundwater	58
		5.2.1.1.2	Spatial distribution of fluoride and arsenic	65
		5.2.1.1.3	Depth wise distribution of fluoride and arsenic	65
		5.2.1.1.4	Correlation study among the parameters (F⁻, Ca²⁺, As and Fe)	66
		5.2.1.1.5	Principal component analysis (PCA)	67
		5.2.1.1.6	Dendrogram generated through cluster analysis (CA)	68
		5.2.1.2	Gram-panchayats and municipality in Sonarpur block	69
		5.2.1.2.1	Groundwater fluoride distribution Scenario	69
		5.2.1.2.2	Spatial distribution of fluoride	71
		5.2.1.2.3	Single factor pollution index for fluoride	72
		5.2.1.2.4	Mechanism of groundwater chemistry	73
		5.2.1.2.5	Variation of fluoride concentration in groundwater (day-wise) from Sonarpur block	75
		5.2.1.3	Gram-panchayats and municipality areas in Baruipur block	76
		5.2.1.3.1	Distribution of fluoride in groundwater	76
		5.2.1.3.2	Single factor pollution index	79
		5.2.1.3.3	Groundwater chemistry of physico-chemical parameters	79

		5.2.2	West Medinipur district	82
		5.2.2.1	Block wise fluoride distribution in groundwater	82
		5.2.2.2	Spatial distribution of fluoride in groundwater from West Medinipur district	84
		5.2.3	Jhargram district	84
		5.2.3.1	Block wise fluoride distribution in groundwater from Jhargram	84
		5.2.3.2	Spatial distribution of fluoride in groundwater from Jhargram district	85
		5.2.4	East Bardhaman district	86
		5.2.4.1	Block wise fluoride distribution in groundwater from East Bardhaman	86
		5.2.4.2	Spatial distribution of fluoride at East Bardhaman district	88
		5.2.5	West Bardhaman district	89
		5.2.5.1	Block wise fluoride distribution in groundwater from West Bardhaman	89
		5.2.5.2	Spatial distribution of fluoride in groundwater from West Bardhaman district	90
		5.2.6	Murshidabad district	91
		5.2.6.1	Block wise fluoride distribution in groundwater from Murshidabad district	91

		5.2.6.2	Spatial distribution of fluoride in groundwater from Murshidabad district	93
		5.3	Hydro-geochemical facies	94
		5.3.1	Hydrogeochemical investigation in Sonarpur block	94
		5.3.1.1	Groundwater type	94
		5.3.1.2	Geochemical weathering process of fluoride behaviour	95
		5.3.1.3	Geochemical modeling in mineral phases	97
		5.3.1.4	Geochemical process and ionic interaction of fluoride	98
		5.3.2	Hydrogeochemical investigation in Baruipur block	99
		5.3.2.1	Groundwater type	99
		5.3.2.2	Mechanism of geochemical weathering processes on fluoride behaviour	101
		5.3.2.3	Geochemical modeling in mineral phases	105
		5.3.2.4	Ionic interaction of groundwater	107
		5.4	Investigation on borehole sediments from the studied areas	107
		5.4.1	Investigation on borehole sediments from Sonarpur block	108
		5.4.1.1	Geochemical variation with depth wise distribution of borehole sediments	108

		5.4.1.2	Physico-chemical parameters of borehole sediments	110
		5.4.1.3	XRD analysis study of borehole sediment	110
		5.4.1.4	SEM-EDX analysis of borehole sediment	111
		5.4.2	Investigation on borehole sediments from Baruipur block	112
		5.4.2.1	Geochemical variation with depth wise distribution of borehole sediments	112
		5.4.2.2	Cluster analysis on concentrations of Na⁺, K⁺, Ca²⁺, Fe and F⁻ for different depth layers	114
		5.4.2.3	Physico-chemical parameters of borehole sediments	115
		5.4.2.4	XRD analysis of borehole sediments	116
		5.4.2.5	SEM-EDX analysis of borehole sediment	117
		5.5	Food chain contamination scenario in fluoride contaminated sites (Bankura and Purulia)	120
		5.5.1	Groundwater and soil fluoride concentration in the studied areas	120
		5.5.2	Spatial distribution of fluoride concentration in soil	121
		5.5.3	Fluoride contamination in local crops and vegetables	122

		5.5.4	Bio-concentration factor of fluoride in crops and vegetables	124
		5.5.5	Comparison study of fluoride toxicity on different biomolecules in plant body part from fluoride exposed and control site of West Bengal	125
		5.6	Health impact of the studied population due to fluoride toxicity in different districts of West Bengal	127
		5.6.1	Health impact on the population from South 24 Parganas district	127
		5.6.1.1	Estimation of urinary fluoride from Rajpur Sonarpur Municipality in Sonarpur block	127
		5.6.1.2	Regression analysis between water and urinary fluoride from Rajpur Sonarpur Municipality	128
		5.6.1.3	Urinary arsenic from Rajpur Sonarpur Municipality	129
		5.6.1.4	Regression analysis between water and urinary arsenic from Rajpur Sonarpur Municipality	130
		5.6.1.5	Human health risk assessment due to fluoride and arsenic exposure from Rajpur Sonarpur Municipality	130

		5.6.1.5.1	Average daily dose (ADD) of fluoride and arsenic through water consumption	130
		5.3.1.5.2	Evaluation of non-cancerous health risk associated to fluoride and arsenic exposure in different age groups from Rajpur Sonarpur Municipality	132
		5.6.1.5.3	Evaluation of cancerous health risk associated to arsenic exposure in different age groups from Rajpur Sonarpur Municipality	134
		5.6.1.6	Ingestion and dermal exposure of fluoride for the inhabitants in Baruipur block	135
		5.6.1.7	Probabilistic health risk assessment of the inhabitants from Baruipur block	137
		5.6.2	Exposure dose of fluoride due to consumption of different food crops at contaminated areas (Bankura and Purulia)	138
		5.6.2.1	Potential non-cancerous health risk assessment of the studied population though foodstuffs	141
		5.6.2.2	Uncertainty analysis using Monte Carlo simulation	142
		5.6.3	Non-cancerous health risk due to fluoride toxicity in West Medinipur district	146

		5.6.3.1	Exposure dose and total hazard quotient	146
		5.6.3.2	Probabilistic health risk in the studied population	146
		5.6.4	Non-cancerous health risk due to fluoride toxicity in Jhargram district	147
		5.6.4.1	Exposure dose and total hazard quotient	147
		5.6.4.2	Probabilistic health risk in the studied population	148
		5.6.5	Non-cancerous health risk due to fluoride toxicity in East Bardhaman district	148
		5.6.5.1	Exposure dose and total hazard quotient	148
		5.6.5.2	Probabilistic health risk in the studied population of East Bardhaman	151
		5.6.6	Non- cancerous health risk due to fluoride toxicity in West Bardhaman district	152
		5.6.6.1	Exposure dose and total hazard quotient	152
		5.6.6.2	Probabilistic health risk in the studied population	153
		5.6.7	Non-cancerous health risk in Murshidabad district	154
		5.6.7.1	Exposure dose and total hazard quotient	154
		5.6.7.2	Probabilistic health risk in the studied population	155
		5.7	Adsorption process	158
		5.7.1	Adsorbent characterization	158
		5.7.1.1	XRD study	158

		5.7.1.2	Elemental characterization of adsorbents	159
		5.7.2	Effect of various optimum parameters on adsorption of fluoride using dolomite, seashell, and their mixture	159
		5.7.2.1	Effect of Adsorbent Dose for fluoride removal	160
		5.7.2.1.1	Effect of adsorbent doses by using dolomite	160
		5.7.2.1.2	Effect of adsorbent doses by using seashell	160
		5.7.2.1.3	Effect on adsorbent doses by using the mixture of seashell and dolomite (1:1)	161
		5.7.2.2	Effect of temperature on removal of fluoride	161
		5.7.2.2.1	Effect of temperature on removal of fluoride by using dolomite	161
		5.7.2.2.2	Effect of temperature on removal of fluoride by using Seashell	162
		5.7.2.2.3	Effect of temperature on removal of fluoride using the mixture of seashell and dolomite (1:1)	162
		5.7.2.3	Effect of contact time on removal of fluoride	163
		5.7.2.3.1	Effect on adsorption time of fluoride by using dolomite	163
		5.7.2.3.2	Effect on adsorption time of fluoride by using seashell	163

		5.7.2.3.3	Effect on adsorption time of fluoride by using their mixture of seashell and dolomite (1:1)	164
		5.7.3	Isotherms and kinetic models of adsorbents for removal of fluoride	164
		5.7.4	Effect of adsorbent on synthetic and groundwater sample	165
		5.7.4.1	Adsorbent on synthetic water sample	165
		5.7.4.2	Adsorbent on groundwater sample	166
		5.7.5	Water quality after treatment with adsorbent	166
		5.7.6	Sludge management	167
		5.7.7	Benefits of brick encapsulation for fluoride-contaminated flocks	168
Chapter 6	Conclusion			169-173
Chapter 7	Recommendation			174-175
	Future scopes			176
	Field images			177-178
	Reference			179-205
	Analytical instruments used			206
	Media coverage			207-211
	Research publication			212-218
	First authorship publications			219-222
	Participation in conference			223-225
	Achievement			226
	Plagiarism report			227

Chapter 1

Introduction



1.1 Global water scenario

Water is a vital and fundamental element of all facets of human existence, and it is an essential part of the world's life support system. Numerous water crises have arisen across the world as a result of the widespread scarcity, slow depletion, and severe contamination of water supplies as well as the increasing encroachment of unsustainable activities. It is believed that there are 1.37 billion cubic kilometers of water on Earth, enough to cover the globe with a layer that is roughly 3 kilometers deep (L'vovich, 1979). The water covering more than two-thirds of the earth's surface is made up with 97.5% of salt water. Just 2.5% is fresh water left. There is a very little portion of the freshwater resource that can be used by humans. A little over 70% of the fresh water on Earth is trapped in glaciers at the poles. Furthermore, less than 0.5% of all fresh water on Earth can be used by humans due to economic and technological challenges (Fig. 1.1).

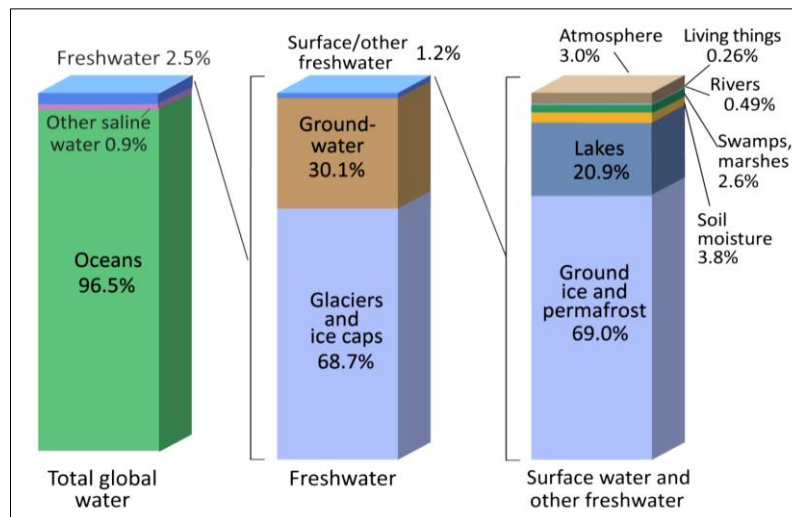


Fig. 1.1: Distribution of water (Source: U.S Geological Survey, Water Science School, <https://water.usgs.gov/edu/gallery/watercyclekids/earth-water-distribution.html>)

Fresh water consumption worldwide doubles every 20 years, growing at a rate more than twice as fast as the rate of population increase (UNFPA, 2003). In 2006, the United Nations reported that over 1 billion people did not have access to clean drinking water (WWAP, 2006). If the current pattern continues, there will be a 56% increase in the demand for fresh water by 2025, exceeding the supply (WWAP, 2014). More importantly, two-thirds of the world's population will suffer from acute shortages of water by 2025 as a result of the few freshwater supplies being diverted, drained, and contaminated so quickly (Phillips, 2001).

Global warming and climate change may have significant impacts on water resources around the globe because of the close connections between the climate and hydrological cycle. Rising temperatures are expected to boost evaporation, potentially resulting in increased precipitation, albeit with regional disparities in rainfall patterns. Consequently, droughts and floods may occur more frequently in various regions and at different times. Furthermore, mountainous areas are anticipated to experience significant shifts in snowfall and snowmelt dynamics (Mazac et al., 2022). Water pollution is widely recognized as a paramount concern in the contemporary world. According to the Sustainable Development Goals (SDGs) have been targeted to achieve universal and equitable access to safe and affordable drinking water for all by 2030.

1.2 Groundwater resource in India

Human survival hinges significantly on freshwater, crucial for drinking, agriculture, and domestic purposes. Despite India possessing only around 4 percent of freshwater resources throughout the world, it remains the leading country in groundwater utilization (World Bank, 2012). The demand for freshwater in India is rapidly increasing due to the country's fast-growing population, leading to a precarious situation regarding groundwater resources. India stands as the world's foremost consumer of groundwater globally, with approximately 90% of it being utilized for irrigation, while the remaining 10% meets around 85% of the nation's drinking water requirements in India News, 2022. Unfortunately, over usage of groundwater has rendered many aquifers unsustainable, making India into a "water-stressed region" with an average utilizable quantity per person of 1122 m³/year (Gupta and Deshpande, 2004). According to the report by the Central Groundwater Board (CGW) 2017, approximately 40% of India's 700 districts have reported critical or overexploited groundwater levels. Over the last 20 years, water levels in various regions of the country have experienced rapid decline, primarily due to heightened groundwater extraction. The proliferation of irrigation wells has surged indiscriminately, exacerbating the situation. Consequently, escalating population growth, urban expansion, and industrial development, compounded by fierce competition among agricultural, industrial, and residential sectors, are progressively depleting groundwater levels (Ahmad et al., 2007). Furthermore, as per the "NITI Aayog Report" of 2019, the water demand of India is projected to be twice the available resource by the year 2030, exacerbating the water crisis in the Statesman, in October 2022. Currently, India is experiencing population growth of approximately 1.4% per year, coupled with robust economic growth rates (Bloom, 2011). This has led to an escalated requirement and utilization of groundwater resources. Latest

studies indicate that India is withdrawing around 200 billion cubic meters of groundwater annually, the highest rate globally. Groundwater caters to approximately 80% of rural domestic water needs and 50% of urban water needs in the country (Aguilar, 2010). Inappropriately, there is currently an issue affecting both the quantity and quality of groundwater.

1.3 Groundwater quality in India

Groundwater is a necessary resource in India. More than 65% of agricultural water and 85% of drinking water sources come from it (World Bank, 2012). Concerning 33% of the country's groundwater resources are unsuitable for consumption (Times of India, March 12, 2010), and estimates about 60% of groundwater resources will be in a critical state of degradation within the next twenty years (Kumar and Raj, 2013). About 54% of the geographical region of the country faces high to extremely high stress of water (<https://www.wri.org/insights/3-maps-explain-indias-growing-water-risks>). In recent decades, a significant array of both human-made (anthropogenic) and natural (geogenic) pollutants have become a critical menace to groundwater usage. In India, sewage disposal, agriculture, and industry are the main anthropogenic sources of groundwater contamination. Astonishingly, Indian cities produce approximately 20 million m³ of sewage daily, but only a mere of 10% undergoes proper treatment before it reaches groundwater or surface water reservoirs (Chakraborti et al., 2011). Additionally, a large portion of domestic waste in India is inadequately disposed of, and these issues are further exacerbated by rapid urbanization. Industrialization is a common major problem for both surface water and groundwater contamination in Indian cities i.e. Kolkata, Mumbai, Delhi, Pune, Kanpur, and Gujarat (Bobba et al., 1997; Chakraborti et al., 2011). Various heavy metals, such as mercury (Hg), chromium (Cr), cadmium (Cd), and nickel (Ni) have been detected in the groundwater across 43 districts spanning 14 states of India (Mehta, 2006). The dumping of hazardous chemicals by some chemical factories also contaminates the local groundwater table (Chaudhary et al., 2002). Additionally, geogenic groundwater contaminants, such as fluoride (F⁻), salinity, arsenic (As), and iron (Fe), present a significant threatening to public health in the country (Chakraborti et al., 2011).

1.4 Groundwater contamination through fluoride

Groundwater F⁻ contamination has emerged as a significant global issue since its causes are natural and inevitable. Reports indicate that geogenic sources are the primary contributors to population exposure resulting from the consumption of fluoridated groundwater (Kumar et al.,

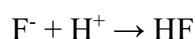
2016). In addition to this, other human activities like industrial effluent discharge, onsite sanitation systems, landfill seepage, and the use of phosphate-containing fertilizers, as well as processes like cement manufacturing, aluminum smelting, and coal combustion also contribute to groundwater contamination, as reported by Singh et al. (2008) and Sharma et al. (2017). Multiple sources and pathways exist through which F^- enters groundwater, leading to potential health effects on human health, as highlighted by Ghosh et al. (2013). Interestingly, microorganisms have been investigated to play a role in mineral weathering and F^- release, as studied by Hutchens et al. (2006). In addition, mining operations and overuse of groundwater accelerate this process of F-dissolution, as reported by Kumar et al. (2016).

1.5 History of fluoride

Fluoride is a monatomic anion of fluorine represented by the chemical expression of F^- which is usually found in white or colorless salt forms. It stands as the most basic fluorine anion. Fluorine is the 13th most abundant element in Earth's crust which is widely distributed in nature, primarily existing in the form of F^- (Wells 2008). During the initial half of the 19th century, researchers discovered that F^- is present in different concentrations in teeth, bones, and drinking water. The tale of fluoridation commences with a mysterious tooth staining, which was initially observed by dentist Dr. Frederick McKay in Colorado around 1901. Independently, in 1902, Dr. J.M. Eager, an American dentist stationed in Italy, also reported similar staining cases in Naples. As time went on, McKay encountered multiple instances that strongly indicated the water supply could be the culprit behind this staining phenomenon (Mullen 2005).

1.6 Characteristics of fluoride

Fluoride, the ionic form of fluorine, is inherently reactive due to its atomic structure (**Fig. 1.2**). Fluorine, a yellow-brown poisonous gas, is not naturally occurring and must be isolated through experimental methods. It is utilized in various forms across modern-day industries and products and occurs naturally in rock, water, and food products. Over the past two centuries, fluorine has been embroiled in controversies surrounding weapons manufacture and certain public health initiatives. Fluoride has a base-like property. It can combine with a proton (H^+):



Hydrogen fluoride (HF), the conjugate acid of F^- , is created by this neutralization process.

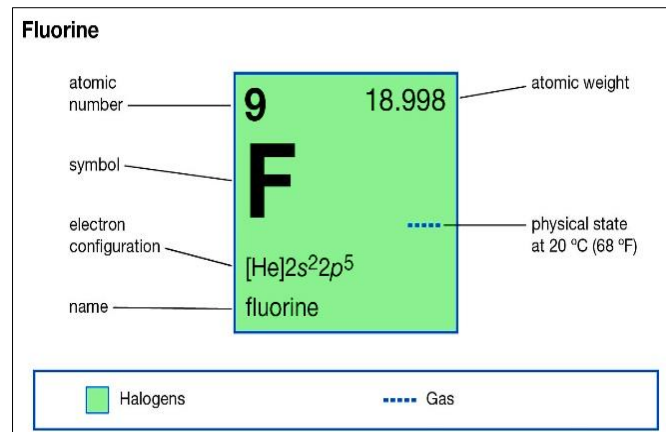
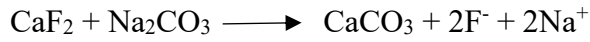


Fig. 1.2: Character of fluoride (F⁻)

1.7 Source, distribution, and mobility of natural fluoride

The weathering of F⁻ bearing minerals stands as the foremost natural source of inorganic F⁻ in groundwater, followed by volcanic eruptions and marine aerosols as the second and third main natural sources, respectively. Groundwater F⁻ is generally responsible for the geochemical behaviour into the aquifer system. Depending on several hydrogeochemical dissolution or ion exchange process with host rock or minerals to groundwater. Natural constituent in groundwater, F⁻ contamination is mostly responsible due to solubility of F⁻ bearing minerals, depth, soil porosity, soil permeability climatic condition, pH, HCO₃⁻, salinity, groundwater residence time, cation-anion exchange capacity, evapotranspiration and precipitation or complexing ions (Battaleb-Looie et al., 2012; Liu et al., 2021; Luo et al., 2018; Mamatha and Rao, 2010; Mukherjee et al., 2018; Singh et al., 2015; Thapa et al., 2018). F⁻ mobilization is generally controlled by geochemical processes, which is mostly occurring from geogenic minerals for example sellaite (MgF₂), cryolite Na₃(AlF₆), topaz (Al₂(SiO₄)F₂), fluorite (CaF₂), fluorapatite (Ca₅(PO₄)₃F), muscovite (KAl₂(AlSi₃O₁₀)(F,OH)₂) mica (K(Li,Al)₃(AlSi₃O₁₀)(O,OH,F)₂) and crystalline igneous rocks (Batabyal and Gupta, 2017; Kumar et al., 2015; Subba Rao, 2017). Due to the impact of CaF₂ dissolution by environmental conditions, high F⁻ contaminated groundwater is typically found with lower levels of Ca²⁺ ions (Adimalla, 2020; Ali et al., 2019; Su et al., 2021). Groundwater is circulated through F⁻ enriched rock/sediments resulting in the dissolution and subsequent mobilization of F⁻, recognized as geogenic activities (Chae et al., 2007; Mukherjee et al., 2018; Mukherjee and Singh, 2018). From a chemical standpoint, F⁻ and OH ions share negative charges and exhibit similar ionic sizes. This similarity enables F⁻ ions to effectively substitute OH ions in rocks during chemical reactions, leading to an enrichment of F⁻ concentration in the rocks and

minerals. When water containing high levels of carbonate and bicarbonate flows through such rocks, F^- ions are liberated through specific chemical reactions that are given below and percolate to the groundwater and increase its concentration. An alkaline environment condition with a high bicarbonate (HCO_3^-) concentration is more conducive to F^- dissolution in groundwater (Saxena and Ahmed, 2001).



High pH value indicates the alkaline character of water, which leads to ideal conditions for F^- dissolution, and alkaline water has the capacity to mobilize F^- (Salve et al., 2008). The formation of the fluoro-aluminum complex as a result of the presence of aluminum in soil increases F^- mobility (Rai et al., 2000). The figure illustrates the common mechanism of F^- arrangement in groundwater (**Fig. 1.3**), depicting hydro-chemical transformations and the precipitation of subordinate minerals as groundwater progresses from recharge areas to discharge areas.

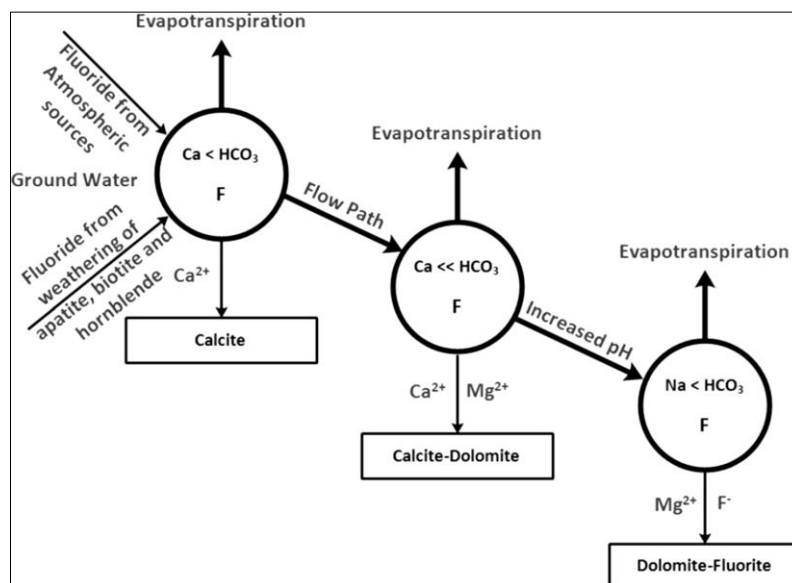


Fig. 1.3: Hydrogeochemical changes (Mukherjee and Singh, 2018)

1.8 Fluoride in food chain

Fluoride has been found to accumulate in plants at various stages via aerosol, soil, and irrigation water (Bhattacharya et al., 2017). Plant roots take F^- from the soil and carry it via xylem to various organs, especially into the leaves. The uptake of F^- by plants is enhanced in acidic soils due to its heightened solubility (Davison and Weinstein 1998; Daines et al., 1952; Ruan et al. 2004). Studies have demonstrated that the capacity and magnitude of a plant's F^- absorption are

contingent upon both the plant species and the specific F^- ionic species present in the soil solution (Okibe et al., 2010). Fluoride accumulation in plants causes chlorosis, decreased plant development, leaf tip burn, leaf necrosis damage to fruits, changes in yield, hindered germination, extreme structural abnormalities, reduced photosynthetic capacity, altered membrane permeability, lowered productivity, and phytotoxicity (Gautam et al., 2010). Consumption of plants highly contaminated with F^- has been demonstrated to induce chronic toxicity in both grazing animals and humans, resulting in issues such as bone deterioration and tooth wear (Clark and Stewart, 1983).

Fluoride-contaminated drinking water, as well as crops and vegetables cultivated in endemic zones, constitute a significant source of F^- toxicity through dietary intake, impacting human health (Bhattacharya et al., 2017; Miri et al., 2018). The dietary intake of F^- enriched crops and vegetables was found to stimulate chronic toxic effects on both the human and animal body system who feed in F^- contaminated soil (Abugri and Pelig-Ba, 2011; Saini et al., 2013; Bhattacharya and Samal, 2018). Cooking of foodstuffs with fluoridated water also assimilated additional F^- in foods (Gautam et al., 2010). However, long-term ingestion of fluoridated foodstuffs incorporated from either geogenic or anthropogenic sources of F^- ion caused adverse health effects (Okibe et al., 2010; Abugri and Pelig-Ba, 2011; Liu et al., 2014; Naik et al., 2017). Fluoride, as an essential micronutrient, exerts both beneficial and detrimental effects on human health through dietary consumption (Chavoshi et al., 2011; Kimambo et al., 2019). Some characteristics of tea such as antioxidant, antimutagenic, and anticarcinogenic properties have made it a beneficial drink. Despite its advantages, it has been noted that tea has a high level of F^- , which can be harmful (Miri et al., 2018). High doses of F^- intake can lead to various diseases, including ligament calcification, liver and kidney dysfunction, nerve weakness, developmental disorders, organ tissue damage, and pathological changes. Additionally, it can cause deleterious effects such as dental and skeletal fluorosis, as well as dense and brittle bone problems in children (Ding et al., 2011; Susheela et al., 2013; Bhattacharya et al., 2020; Mridha et al., 2021).

1.9 Fluoride toxicity and its mechanism in human health

Fluoride serves as a crucial micronutrient with effects on human health when ingested through drinking water and dietary sources, exhibiting both beneficial and detrimental impacts (Chavoshi et al., 2010). The dosage of F^- walks a fine line between necessity and harm to health. The F^- ion, highly electronegative, readily bonds with positively charged metal ions like

calcium (Ca) and sodium (Na). At even low concentrations (0.5 mg/l), F^- can bind with calcium in teeth, resulting in dental caries (Kimambo et al., 2019; Khandare et al., 2005; Dissanayake, 1991). Lower F^- levels in drinking water can promote dental fluorosis, particularly in warmer climates where water intake is higher (USEPA 1985). Several other studies stated that the damaged shape of fluorotic teeth promotes plaque buildup and food lodgment, which causes dental caries (Subba Reddy and Tewari, 1992; Dissanayake 1991). The World Health Organization has established the permissible limit of F^- at 1.5 mg/l (WHO, 2011). According to the Indian Council of Medical Research (ICMR), The highest acceptable level and maximum permitted range of F^- are 1.0 and 1.5 mg/l, respectively. However, F^- concentrations in drinking water ranging from 0.6 to 1.2 mg/l are favorable for bone and tooth growth (ICMR 1975; BIS 2003; USEPA, 2010). Drinking water minerals have been widely researched due to their relevance, health implications, and safety concerns (Rosborg 2015). Chronic absorption of excessive levels of F^- may harm human health by producing skeletal fluorosis, dental fluorosis, bone fractures, kidney stone development, reduced birth rates, thyroid dysfunction, and IQ impairment, particularly in children (Shahab et al., 2017) (**Fig. 1.4**).

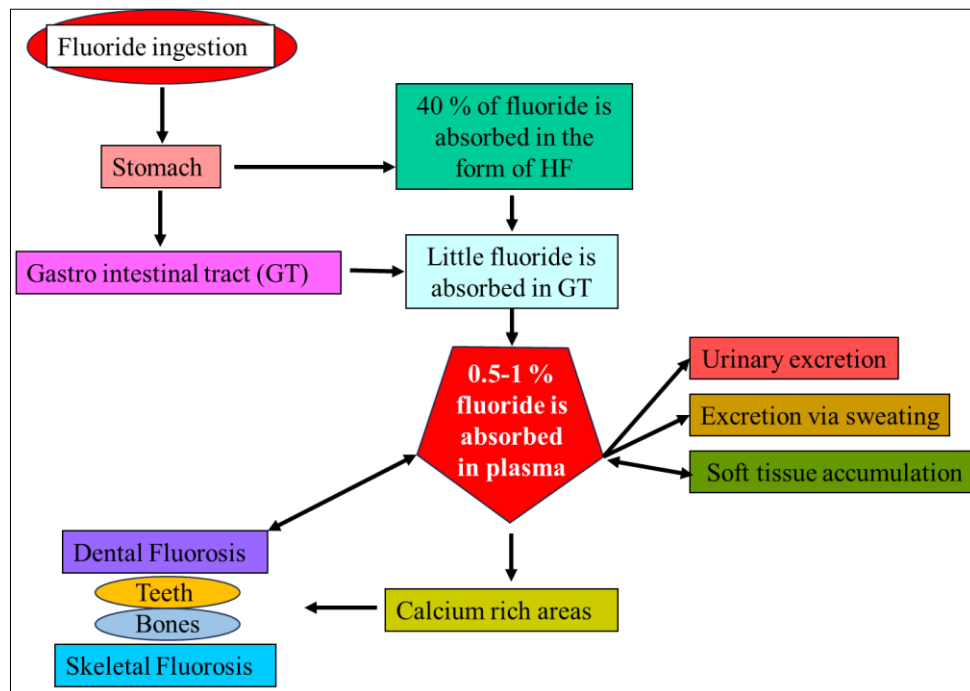


Fig. 1.4: Impact of F^- in the human body system (Kabir et al., 2020)

1.10 Fluoride removal techniques from groundwater

Keeping the view of toxic effects of F^- on human health, it is imperative to develop a reliable and efficient method for removing excess amount of F^- from the drinking water. Several

strategies have been explored to remove F^- from the contaminated groundwater and the most prevalent of which being precipitation, membrane, and adsorption (He et al., 2020). Coagulation and precipitation are commonly used to minimize excessive F^- concentrations. Precipitation yields a final F^- concentration of 10-20 mg/l. However, this process is only effective for removing F^- from water and leaves a significant residue. Electrocoagulation is an effective method for removing F^- due to its high removal rates and lack of secondary contaminants. The most important drawback is the high expense of using this approach, which requires a lot of electricity. Membrane filtration technology is effective for take away F^- from drinking water. Nanofiltration and reverse osmosis technologies may reduce F^- concentrations below WHO standards but are costly in terms of capital cost and maintenance cost. Adsorption is a popular method for eliminating F^- from drinking water due to its extraordinary highest adsorption capacity, low cost, ease of operation, and great performance (Lobo et al., 2024).

Chapter 2

Literature review



2.1 Fluoride contamination in groundwater: global scenario

Last few years the presence of F^- in groundwater has been globally labeled as one of the biggest environmental threat to the human population, reported from several countries like India, China (Li et al., 2009), Japan (Hossain et al., 2016), Sri Lanka (Dissanayake, et al., 1991), Iran (Biglari et al., 2016), Turkey (Oruc, 2003), Southern Algeria (Messaitfa, 2008), Mexico (Carrillo-Rivera et al., 2002), Korea (Chae et al., 2007), Italy (Fabiani et al., 1999), Brazil (Mirlean and Roisenberg, 2007), Pakistan (Naseem et al., 2010), Jordan (Rukah and Alsokhny, 2004), Ethiopia (Tekle-Haimanot et al., 2006), Australia (Petrides and Cartwright, 2006) Canada (Desbarats, 2009), Norway (Banks et al., 1998), Ghana (Apambire et al., 1997), Kenya (Gaciri and Davies, 1993), USA (Deering et al., 1983). F^- toxicity has recently harmed about 200 million individuals in 29 different countries, including Ethiopia, Uganda, Tanzania, Saudi Arabia, India, China, and the United States alongwith this figure is steadily rising over time (Brindha and Elango, 2013) (**Fig. 2.1**).

Fluorosis has been documented in numerous regions worldwide situated within the F^- belt. Major F^- belts on Earth extend from (i) Syria through Jordan, Egypt, Libya, Algeria, Sudan, and Kenya, and from (ii) Turkey to Iraq, Iran, Afghanistan, India, northern Thailand, and China, with similar areas in America and Japan. The highest reported F^- concentration is in Lake Nakuru, Kenya, reaching 2800 mg/l (Demelash et al., 2019). According to WHO, over 260 million people worldwide live in areas with high F^- level (>1.5 mg/l) in drinking water (Jha and Tripathi, 2021).

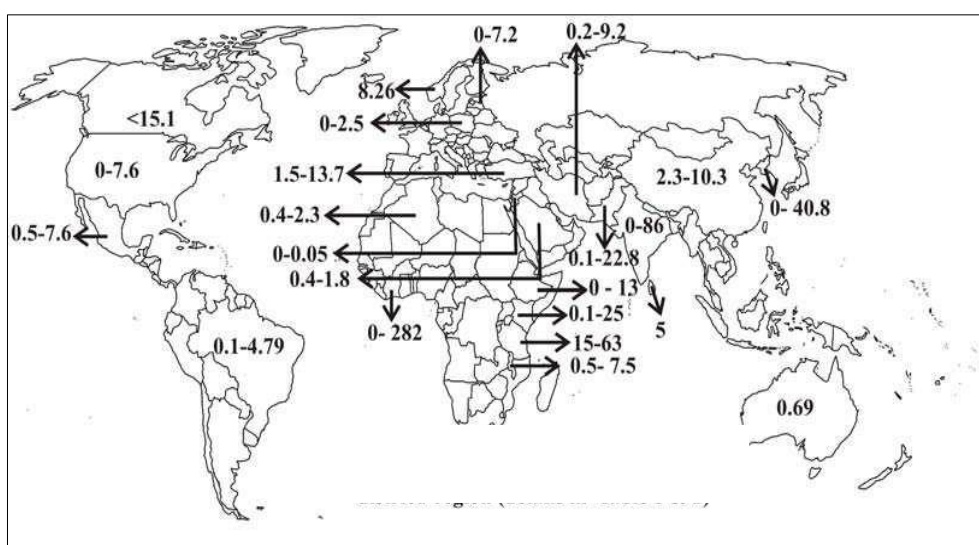


Fig. 2.1: Groundwater F^- concentration in numerous parts of the world (Brindha and Elango, 2011)

2.2 Distribution of fluoride in Indian groundwater

Fluoride was first identified in India in the Nellore area of Andhra Pradesh in 1937. Since then, extensive research has been conducted in many areas of India to investigate F^- contaminated water sources and its effects on humans and animals. Fluorosis is now considered to be widespread in 20 Indian states out of 29 states and 7 union territories. The states with fluoridated water include Assam, Bihar, Delhi, Gujarat, Haryana, Jammu Andhra Pradesh, Kashmir, Madhya Pradesh, Maharashtra, Odisha, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, Karnataka, Kerala and West Bengal (**Fig. 2.2**) (Rwenyonyi et al., 2000).

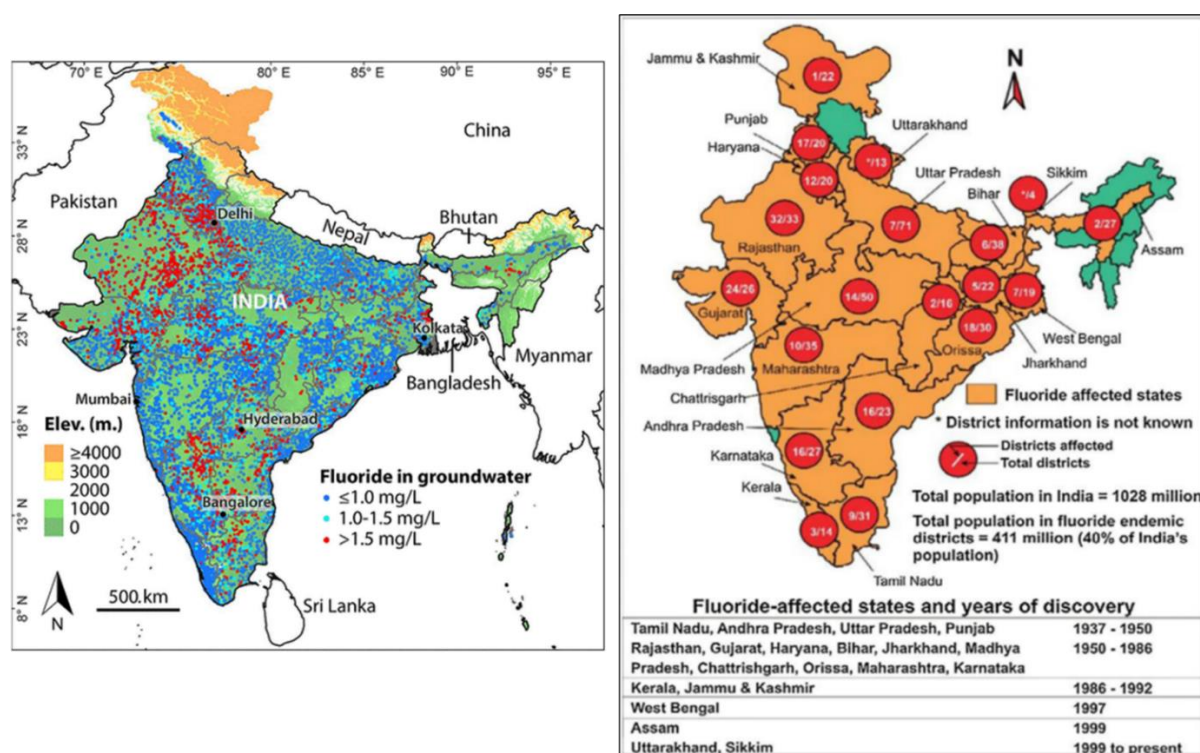


Fig. 2.2: Groundwater F^- contamination in India indicated significant F^- concentrations in many regions throughout the country (Podgorski et al., 2018; Rwenyonyi et al., 2000)

It is evident that there are both safe water and hazardous water sources in the area, yet most people are not aware of this. The intake of dangerous sources continues to exist but at a lower level. The Earth's crust holds 85 million tons of F^- deposits, with India alone accounting for 12 billion tons. The Geological Survey of India (GSI) has identified several regions in India as Red Alert zones due to elevated F^- levels. These include Nalgonda district in Andhra Pradesh; Gurgaon, Hisar, Fatehabad, Mahendergarh, and Rewari districts in Haryana; Fazilka and Jalalabad districts in Punjab; Dindigul district in Tamil Nadu; Beed district in Maharashtra; and Unnao, Rae Bareilly, Sindh district in Madhya Pradesh, and Sonbhadra districts in Uttar

Pradesh. (Gupta et al., 1993; Indu et al., 2007; Reddy et al., 2010). Fluoride contamination levels in groundwater found in India ranged from 1.0 to 48.0 mg/l (Sushila 2001).

2.3 Distribution of fluoride in groundwater from West Bengal

Due to the geographical location of West Bengal, F^- toxicity in groundwater is significantly higher in the western region covering districts like Birbhum, Purulia, and Bankura (Mondal and Nath, 2015; Samal et al., 2015) compared to the eastern zone of the state (**Fig. 2.3**).

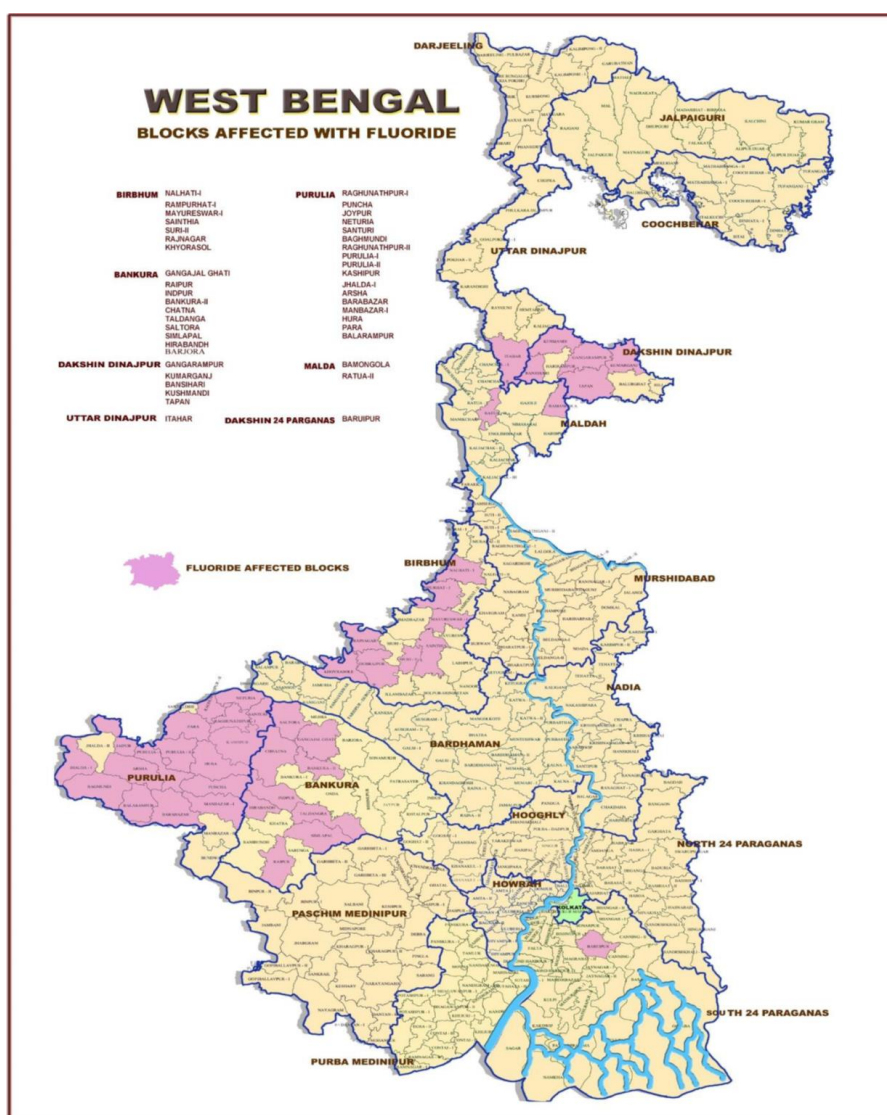


Fig. 2.3: Fluoride distribution in groundwater at West Bengal Scenario (WBPHEd)
(Source: <https://maps.wbphed.gov.in/fluoride/index.html>)

In West Bengal, F^- contamination was first detected in Bhuvanandapur village of Nalhati I block in Birbhum district in 1996 (Majumdar, 2011). Majumdar (2011) also stated Birbhum as the most critically F^- affected district among the seven affected districts of West Bengal. In the

western part of the state, maximum F^- concentrations in groundwater were reported from Birbhum, Bankura, and Purulia districts as 11.8, 12.2 and 8.16 mg/l, respectively (Chakrabarti and Ray, 2013; Mondal and Kumar, 2017; Mandal and Sanyal, 2019; Mukherjee and Singh, 2022). Moreover, the eastern side of West Bengal, the maximum F^- was found as 2.9 mg/l in Sonarpur Block, South 24 Parganas district. Basically, in the western area of West Bengal, granitic gneisses basalt rock and laterite soil characters are the responsible sources for F^- mobilization in groundwater (Gupta et al., 2006; Mondal et al., 2014; Mondal and Gupta, 2015; Rudra, 2012). Whereas, the chemical weathering of silicate minerals may insist F^- mobilization in groundwater reported from the eastern part of the lower Gangetic belt in West Bengal (Datta et al., 2000).

2.4 Food chain contamination of fluoride

Fluoride-contaminated drinking water, combined with crops and vegetables grown in endemic areas, constitutes a major source of F^- toxicity through dietary intake, impacting significantly on human health (Bhattacharya et al., 2017; Miri et al., 2018). Consequently, the ingestion of vegetables and crops is now recognized as another significant pathway for F^- entering the human food chain, alongside the consumption of drinking water. Plants absorb F^- from the soil through their roots, transporting it via the xylem primarily to the leaves, where its accumulation can have adverse effects (Davison and Weinstein, 1998). Because of its greater solubility in acidic soils, F^- uptake by plants is promoted (Daines et al., 1952; Ruan et al., 2004). However, the capacity and extent of F^- absorption by plants have been shown to vary depending on the plant species and the specific F^- ionic species present in the soil solution. (Mezghani et al. 2005; Okibe et al. 2010). Excess F^- buildup in plants causes chlorosis, impaired plant development, leaf tip burn, and leaf necrosis; Germination inhibition, ultrastructural abnormalities, reduced photosynthetic capacity, membrane permeability change, and decreased productivity (McNulty and Newman 1961; Elloumi et al. 2005; Zouari et al. 2014; Anil and Bhaskara 2008; Gautam et al. 2010). The dietary intake of F^- enriched crops and vegetables was found to stimulate chronic toxic effects on both the human and animal body systems who feed in F^- contaminated soil (Abugri and Pelig-Ba, 2011; Saini et al., 2013; Bhattacharya and Samal, 2018). Cooking of foodstuffs with fluoridated water also assimilated additional F^- in foods (Gautam et al., 2010). However, long-term ingestion of fluoridated foodstuffs incorporated from either geogenic or anthropogenic sources of F^- ion caused adverse health effects (Okibe et al., 2010; Abugri and Pelig-Ba, 2011; Liu et al., 2014; Naik et al., 2017). Fluoride is a micronutrient that

is necessary for human health and may have both positive and negative impacts on health when consumed through food chain (Chavoshi et al., 2011; Kimambo et al., 2019).

2.5 Adverse effects of fluoride on human health

Several States in our nation have reported high F^- levels, indicating that endemic fluorosis has become one of the major public health issues in the country (NPPCF 2014). **Fig. 2.4** represents the endemicity of F^- in India (UNICEF 1999).

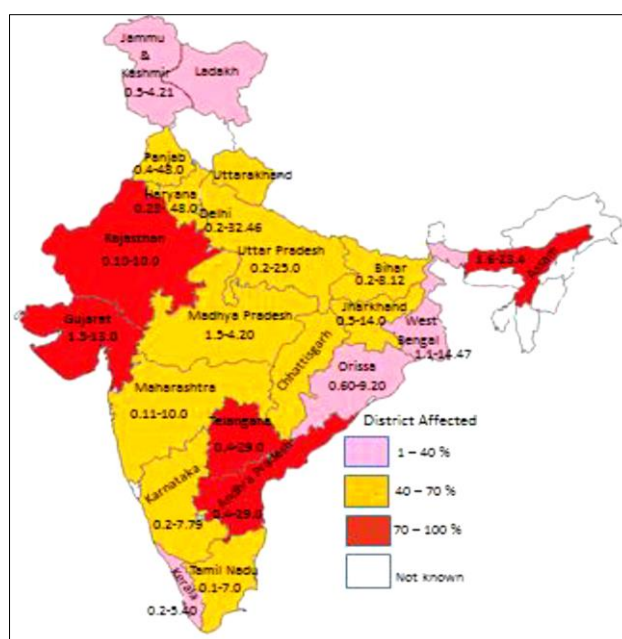


Fig. 2.4: Fluoride endemic scenario in India (UNICEF 1999)

Fluoride consumption within the recommended range of 0.5-1 mg/l has been shown to promote the development and maintenance of healthy teeth and bones in humans (Wood, 1974). However, F^- intake outside of this range may lead to dental fluorosis, bone weakening, and neurological damage (Steinberg et al., 1955). Therefore, the World Health Organization (WHO) has set the maximum allowable F^- level in drinking water at 1.5 mg/l (WHO, 2006). Consumption of F^- exceeding 2 mg/l can result in significant dental and skeletal fluorosis. (Chatterjee et al., 2008). Drinking water has historically been considered to be a primary source of fluorosis (Susheela 1999). Fluorosis is classified into two types: dental fluorosis and skeletal fluorosis. The 'Linked Disorders' are another kind of Fluorosis. The term 'Fluorosis and different linked disorders' refers to "soft tissue manifestations" (Susheela 2005). Fluoride predominantly affects teeth and bone, according to illness nomenclature. The chemical

composition of the matrices of both mineralized tissues, tooth and bone, was examined to ascertain the root cause of the disease. The tooth and bone matrices are mostly composed of collagen protein; however, two additional matrix elements that have a role in the development of fluorosis include glycosaminoglycans and sialic acid (glycoprotein) (Susheela and Sharma, 1988). Biological markers, known as biomarkers, serve as indicators of events within biological systems (such as the human body) or samples. While not diagnostic tests themselves, biomarkers signal the presence of a disease or biological change. These biomarkers are typically classified into three types: 1) Exposure; 2) Susceptibility; and 3) Biomarkers of effect. In the case of F^- biomarkers, examples include; 1) Exposure - plasma, bone, teeth, urine, saliva, dental plaque, plaque fluid, hair, and nails; 2) Susceptibility - genetic factors, acid-base disturbances, renal disturbances, bone growth, and nutritional status; 3) Biomarkers of effect - reduction in the activity and severity of dental caries, dental fluorosis, and skeletal fluorosis. Since urine serves as the main route for excreting ingested F^- , analyzing F^- concentration in urine provides a useful means of estimating the overall F^- intake of a population (Susheela et al., 1999). A portion of ingested F^- is excreted in urine. Urinary F^- concentrations reflect recent fluctuations in F^- levels in the last several hours, influenced by variations in urinary flow and pH.

2.6 Mitigation options

Various defluoridation techniques are employed to treat fluoridated water and adhere to the WHO permissible limit. These techniques are broadly categorized into two groups: physical processes and chemical processes. Physical processes encompass adsorption, ion exchange, and membrane separation techniques, while chemical processes include chemical coagulation-precipitation and electro-coagulation techniques. A brief overview of each process is provided in the following section.

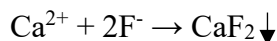
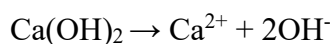
Chemical Process

Chemical processes include the chemical coagulation precipitation process which is also called the Nalgonda technique and the electrocoagulation process.

Chemical Coagulation - Precipitation Method

The chemical precipitation method is widely employed for F^- removal from water and operates through a two-step process. Initially, lime is added to induce precipitation, followed by the addition of alum to facilitate coagulation. Upon adding alum to water, two crucial reactions occur. Firstly, alum reacts with some of the alkalinity to form insoluble aluminum hydroxide

[Al(OH)₃]. Secondly, alum reacts with F⁻ ions present in the water. The most effective F⁻ removal occurs within a pH range of 5.5-7.5 (Potgeiter, 1990). The process involves the following reactions:



Electro - Coagulation Method

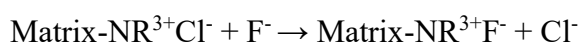
In the electrocoagulation process, a sacrificial metal anode (such as iron or aluminum) dissolves under the influence of an applied voltage, generating coagulant species in situ while hydrogen is concurrently developed at the cathode. These coagulant species aggregate suspended particles or precipitate and absorb dissolved contaminants. Tiny bubbles of hydrogen (H₂) and oxygen (O₂) formed during electrolysis of water collide with air bubbles, causing pollutant particles to float. The choice of electrode material depends on various criteria, including low cost, low oxidation potential, and inertness towards the system under consideration. Different electrode materials reported in the literature include carbon (Gallegos et al., 1999), mild steel (Golder et al., 2005), graphite, titanium (Díaz-Hernández et al., 2011), and aluminum (Ghosh et al., 2008). Aluminum has been reported to be highly effective and successful in F⁻ removal under favorable operating conditions (Ghosh et al., 2008).

Physical Process

Membrane-based technologies, ion exchange, and adsorption fall within this group. Each technique's synopsis is provided below.

Ion-Exchange Method

Ion exchange is a physical adsorption process. This method uses a strongly basic anion-exchange resin with quaternary ammonium functional groups to remove F⁻ from water supplies. The removal occurs according to the following reaction:



Fluoride ions displace chloride ions from the resin, a process that continues until all sites on the resin are occupied by F⁻. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. This leads to the replacement of F⁻ ions with chloride ions, thus recharging the resin and initiating the process anew. The driving force behind the replacement of chloride ions by F⁻ ions is the stronger electronegativity of F⁻. Meenakshi and Viswanathan (2007) studied Indian FR10 and Ceralite IRA 400 resin as defluoridating agents.

The same authors also investigated metal ion incorporation in ion exchange resin (Viswanathan and Meenakshi, 2009) for F^- removal from water.

Adsorption Method

Adsorption, being a physical process, is recognized for its cost-effectiveness and ease of handling. The selection of adsorbents should prioritize economic feasibility, availability, ease of use, and efficient F^- adsorption capabilities. A wide range of adsorbents has been investigated in the literature, including agricultural waste materials, metal oxides, encompassing biological materials, natural clay materials and hydroxides, as well as calcium and iron-based adsorbents. Among these, the plaster of Paris is a notable example. (Gopal and Elango, 2007), granular red mud (Tor et al., 2009), pyrophyllite, PCB (Viswanathan and Meenakshi, 2009), γ - alumina (Lee et al., 2010), acidic alumina (Goswami and Purkait, 2012), calcium aluminate (Sakhare et al., 2012), protonated cross-linked chitosan particles (Huang and Liu 2012), hydroxyapatite (Nie et al., 2012), granular ceramic (Chen et al., 2010) and many other adsorbents are employed for F^- removal. Apart from these adsorbents, nano-sized adsorbents such as nano alumina (Kumar et al., 2011), Fe-Al-Ce nano-adsorbent (Chen et al., 2011) and others are some of the nano adsorbents which are used in defluoridation of water. Despite numerous adsorbents reported in the literature, researchers continue to seek a better, more efficient, and cost-effective adsorbent for treating fluoridated water. Moreover, this study primarily focuses on the adsorption process for defluoridation.

Membrane Based Technologies

Membrane based techniques such as dialysis, electrodialysis, nanofiltration (NF) and reverse osmosis (RO) have become increasingly attractive in separation and purification technology. Among these, the reverse osmosis (RO) membrane process has emerged as a preferred choice for providing safe drinking water without the drawbacks associated with conventional methods. RO functions as a physical process by applying pressure to the feed water, directing it through a semipermeable membrane to remove contaminants. This process reverses natural osmosis by applying pressure to the concentrated side of the membrane, thus overcoming natural osmotic pressure. RO membranes reject ions based on size and electrical charge, resulting in water of exceptionally high purity. Various applications of reverse osmosis in water purification are discussed by Schneider and Middlebrooks (1983) and Arora et al. (2004). Ndiaye et al. (2005) studied F^- removal from effluents using the RO technique. It has been observed that the rejection of F^- ions typically exceeds 98%, assuming that the RO membrane was fully regenerated after each set of experiments. Factors influencing membrane selection include cost,

recovery, rejection, raw water characteristics, and pretreatment. The efficiency of the process is determined by various factors such as raw water characteristics, pressure, temperature, and regular monitoring and maintenance. **Table 2.1** briefly describes the advantages and disadvantages of various F^- removal techniques which vary depending on factors such as efficiency, cost, ease of operation, and environmental impact.

Table 2.1: Advantages and disadvantages of various F^- removal techniques

	Adsorption	Ion Exchange	Coagulation-Precipitation	Membrane Process
Technique/ materials	Adsorbents: activated coconut activated alumina, activated carbon, calcite, activated saw dust, activated fly ash, shell carbon, groundnut shell, coffee husk, rice husk, bone charcoal, Activated soil sorbent, etc.	Strongly basic anion- exchange resin containing quatarnary ammonium functional groups is used.	Nalgonda technique: In the first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation.	NF (Nano Filtration) and RO (Reverse Osmosis) are generally used for F^- removal
Advantages	1. Easy to operate. 2. The adsorption process is effective. 3. High efficiency in F^- removal, achieving up to 90% removal. 4. Produces high- quality water. 5. Regeneration is possible.	Removes F^- up to 90-95%. Retains the taste and color of water intact	The two-step process has been claimed as the most effective technique by NEERI under Rajiv Gandhi Drinking Water Mission several fill and hand pump attached (HPA) plant based on Nalgonda technique have come up in rural areas.	1. The technique proves highly efficient in removing F^- . 2. The RO membrane was consistently regenerated after each experimental set. 3. This method reliably removes over 90% of F^- irrespective of

	Adsorption	Ion Exchange	Coagulation-Precipitation	Membrane Process
				<p>initial concentrations.</p> <p>4. It facilitates the concurrent removal of other dissolved solids.</p> <p>5. It operates effectively across a broad pH spectrum.</p> <p>6. No interference is encountered from other ions.</p> <p>7. It entails no chemical additives, minimal labor, and low operational costs.</p> <p>8. The process enables water treatment and purification in a single step.</p> <p>9. It guarantees consistent water quality.</p>
Disadvantages	<p>1. Disposal of depleted adsorbents and concentrated regenerated materials poses an issue.</p> <p>2. Interference due to the presence of</p>	<p>1. The technique is prohibitively expensive.</p> <p>2. The treated water has a low pH and high chloride concentration.</p> <p>3. Interference arises due to the</p>	<p>1. High chemical dosages are required ($\text{Al}(\text{OH})_3$ up to 700-1200 mg/l).</p> <p>2. There is an issue with transferring sludge.</p> <p>3. The acceptable F⁻ limit cannot be achieved.</p>	<p>1. Not feasible for rural regions.</p> <p>2. The process is prohibitively expensive compared to other options.</p> <p>3. Removes valuable</p>

	Adsorption	Ion Exchange	Coagulation-Precipitation	Membrane Process
	<p>various anions in close proximity may lead to competition for active sites on the absorbent.</p> <p>3. Reduction in removal effectiveness after the regeneration step.</p> <p>4. Highly pH subordinate.</p> <p>5. Elevated concentrations of total dissolved salts (TDS) can lead to fouling of the alumina bed.</p>	<p>presence of other anions such as sulphate, carbonate, phosphate, and alkalinity.</p> <p>4. Regenerating the resin poses challenges as it leads to F⁻ rich waste, which must be managed before final disposal.</p> <p>5. It necessitates a longer reaction period.</p>	<p>3. Skilled labor is required.</p> <p>4. Release of aluminum in treated water, which may lead to Alzheimer's syndrome.</p> <p>5. The final concentration of F⁻ in treated water significantly depends on the solubility of precipitated F⁻ and calcium and aluminum salts.</p> <p>6. The use of aluminum sulfate as a coagulant significantly increases the sulfate ion concentration, leading to laxative effects in humans.</p>	<p>minerals necessary for proper development; remineralization is required after treatment.</p> <p>4. Significant water wastage occurs as saline solution and disposable saltwater pose issues.</p> <p>5. The water becomes acidic and requires pH adjustment</p>

Chapter 3

Aim and objectives



Aim and Objectives:

Fluoride exposure in groundwater has been crossed nearly 30 years after its first incidence in West Bengal. Last few years, the toxicity F^- scenario has not been eradicated, even in few cases it is magnified. Consequently, the objectives of the present research study are listed below:

1. The status of groundwater F^- contamination sites in different parts of West Bengal (South 24 Parganas, Bardhaman, Bankura, Purulia, Birbhum, Murshidabad, Jhargram and West Medinipur districts).
2. Food chain contamination scenario through irrigation of agricultural lands in F^- contaminated sites.
3. Health impact of the studied inhabitants.
4. Possible remedial options.

Chapter 4

Materials and methods



4.1 Systematic literature reviews of groundwater fluoride contamination in West Bengal for meta-analysis

A systematic review of literature studies has been conducted to comprehensively explore the landscape of F^- contamination.

4.1.1 Searching strategy for data

A systematic review of published research articles was undertaken reporting the F^- contamination in the groundwater of West Bengal. Boolean operators (e.g., “OR” and “AND”) were used to develop search terms from the keywords ‘fluoride’, ‘West Bengal’ ‘water’, and ‘contamination’. Searching ISI Web of Science and PubMed with these terms identified relevant research papers published in English from 2006 - 2024. Studies were included in the meta-analysis if a) the research paper reported F^- contamination from West Bengal, India irrespective of groundwater type, time of sampling b) proper analytical procedures were followed for F^- analysis. Initially, a total number of 121 research studies were selected. After the preliminary screening of titles and abstracts, 90 papers were excluded. Finally, 26 papers fulfilled the inclusion criteria. The Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) flow chart is presented in **Fig. 4.1**.

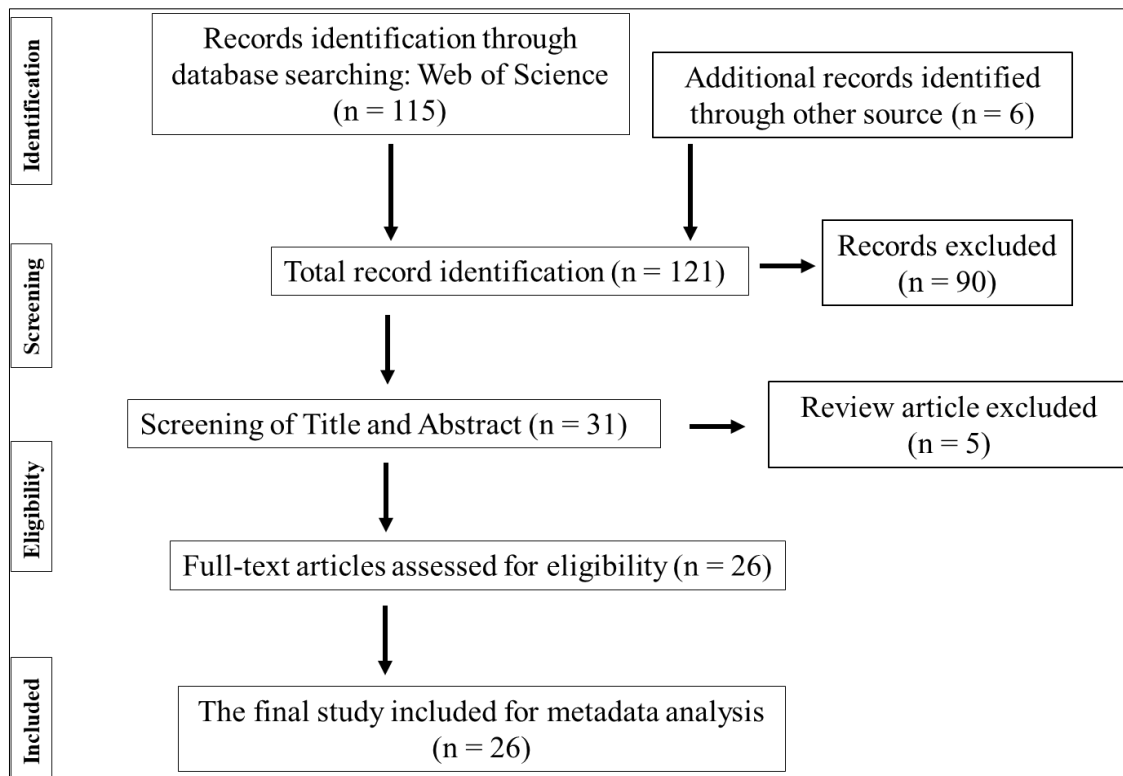


Fig. 4.1: Prisma diagram flow for meta-analysis

4.1.2 Data extraction and quality assessment

The data recorded from each paper were reviewed like author, publication year, research type, the total number of sample size, the average and standard deviation of the analysed F^- concentration in groundwater. A "Random-Effects" (RE) model was employed for the meta-analysis presented here, as it accommodates variation in effect sizes between studies, which exceeds what would be anticipated by chance. This variability stems from differences in study design, sample size, population characteristics, or other factors that may influence the measured outcome (Romano et al., 2006). The RE model is a statistical tool used in meta-analysis to aggregate data from numerous studies with a similar research issue (Romano et al., 2006). A forest plot was created using data from individual studies within the meta-analysis to visually represent the degree of heterogeneity. The plot features a vertical line at its centre, representing the absence of a difference between the study group and the marginal level, also referred to as the 'no effect' or 'zero effect' line (indicating that the mean difference was zero at this point). Within the plots, each study is represented by squares, with the square size reflecting both the estimate's effect size and the study's weight. The endpoints of each horizontal segment in the plot display 95% confidence intervals (CI) that are symmetrically positioned around the mean. When the 95% CI excludes zero, it signifies a statistically significant mean effect size. Conversely, if the CIs overlap by 95%, it indicates that There is no statistically significant distinction between the two groups (Mandal et al., 2024).

4.2 Study area

West Bengal, India, has been widely affected by groundwater pollution for the past several years. Seven districts in West Bengal i.e. Birbhum, Bankura, Purulia, North Dinajpur, South Dinajpur, Malda, and South 24 Parganas have high F^- contamination in groundwater currently. Fluoride contamination in groundwater in the western part of the Bhagirathi River is a burning public health issue so far and is well documented by a lot of researchers. The present study comprises the evaluation of groundwater quality and investigation of health exposure in several sites of West Bengal, India including South 24 Parganas, Bardhaman, Bankura, Purulia, Birbhum, Murshidabad, Jhargram, and West Medinipur. According to the acquaintance of samples, research work was carried out further on selected control sites of West Bengal (Madhyabar, a F^- unexposed agriculture-based village, Pingla block, West Medinipur district).

4.2.1 South 24 Parganas

Two blocks of South 24 Parganas district (Sonarpur and Baruipur) are covered under research work to evaluate the groundwater quality for drinking and domestic purposes. The district is based on the alluvial and deltaic plains of the south and south-eastern part of West Bengal is encompassed within the latitude: $22^{\circ} 31' 48.00''$ N and longitude: $88^{\circ} 19' 48.00''$ E. It is the 2nd largest populated district in West Bengal. Sonarpur and Baruipur blocks are investigated for groundwater F^{-} scenario located at latitude: $22^{\circ} 26' 18''$ N and longitude: $88^{\circ} 25' 55''$ E and latitude: $22^{\circ} 21' 55.6''$ N and longitude: $88^{\circ} 25' 57.01''$ E, respectively. Sonarpur block consists of 13 gram-panchayat and its municipality area. Baruipur block consists of Baruipur municipality and 19 gram-panchayat areas.

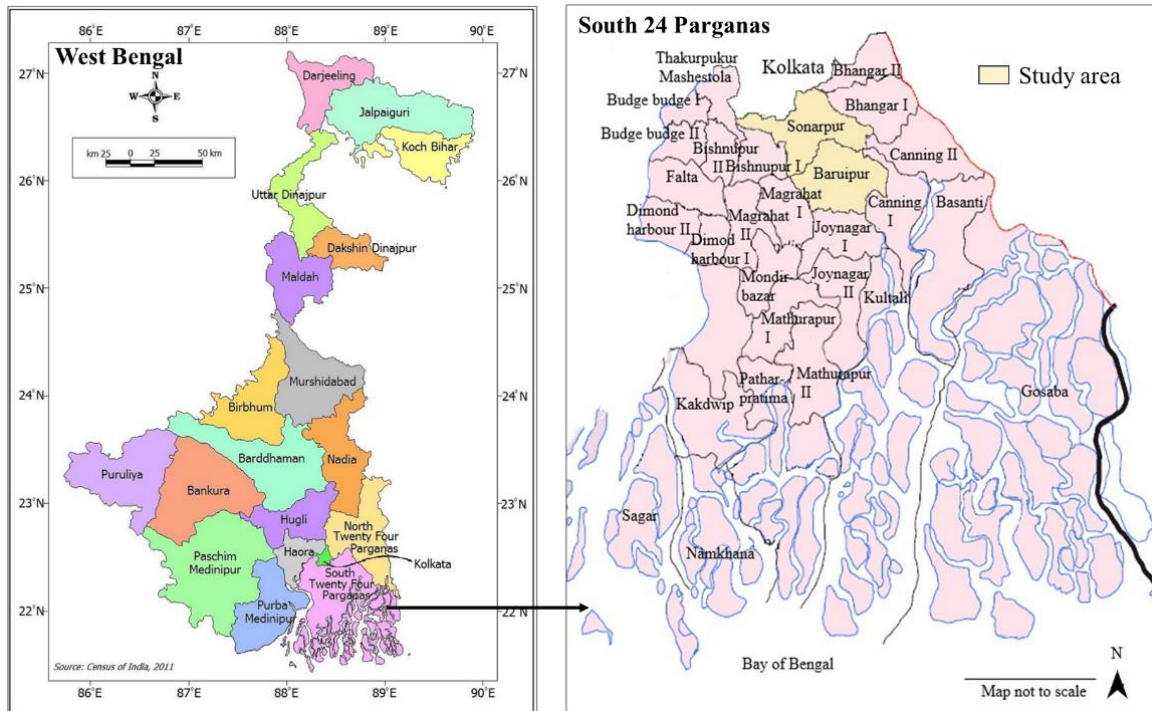


Fig. 4.2: Study area of South 24 Parganas district

The presence of high arsenic and F^{-} concentration in groundwater have been reported earlier in the lower part of Gangetic plains in West Bengal covering South 24 Parganas district (Chakrabarti and Bhattacharya, 2013; Kar et al., 2010). This district mostly belongs to the lower Ganga basin, underlain by a thick layer of unconsolidated sediments of the Quaternary age (Majumdar and Kar, 2013); where, the source of drinking water mainly comes from a confined aquifer, located at a depth of between 160 m and 335 m. Approximately, 41.9% of the collected groundwater samples ($n = 8333$), from 12 blocks in the district were identified with arsenic concentration beyond the $10 \mu\text{g/l}$ (Chakraborti et al., 2009). Based on the preliminary

investigation, Baruipur block was reported earlier as a F^- contaminated site in West Bengal (PHED, 2007). The study areas located in South 24 Parganas district have been demonstrated. The map of the studied location in Rajpur Sonarpur Municipality, Sonarpur and Baruipur blocks have been shown in **Fig. 4.3**, **Fig. 4.4** and **Fig. 4.5**, respectively.

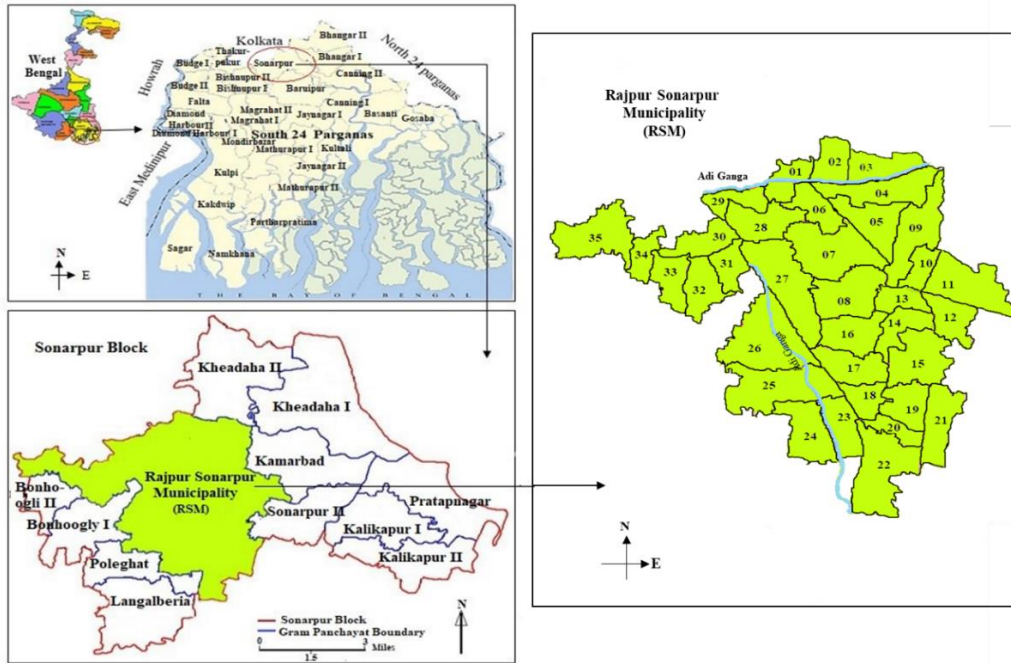


Fig. 4.3: Study area of Rajpur Sonarpur Municipality, Sonarpur block

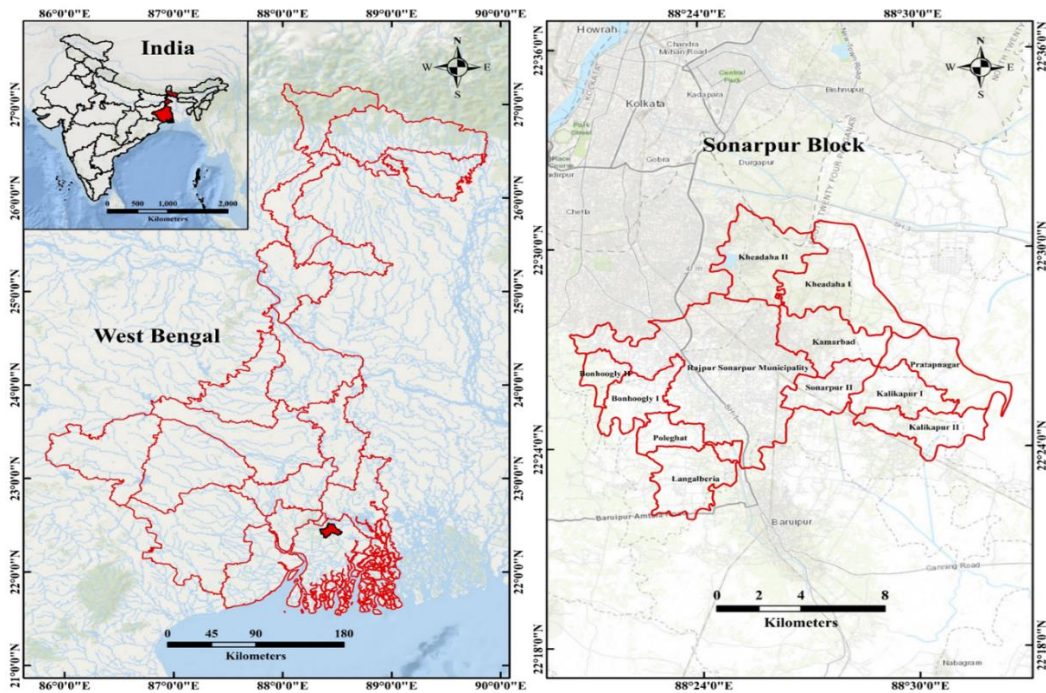


Fig. 4.4: Study area of Sonarpur block

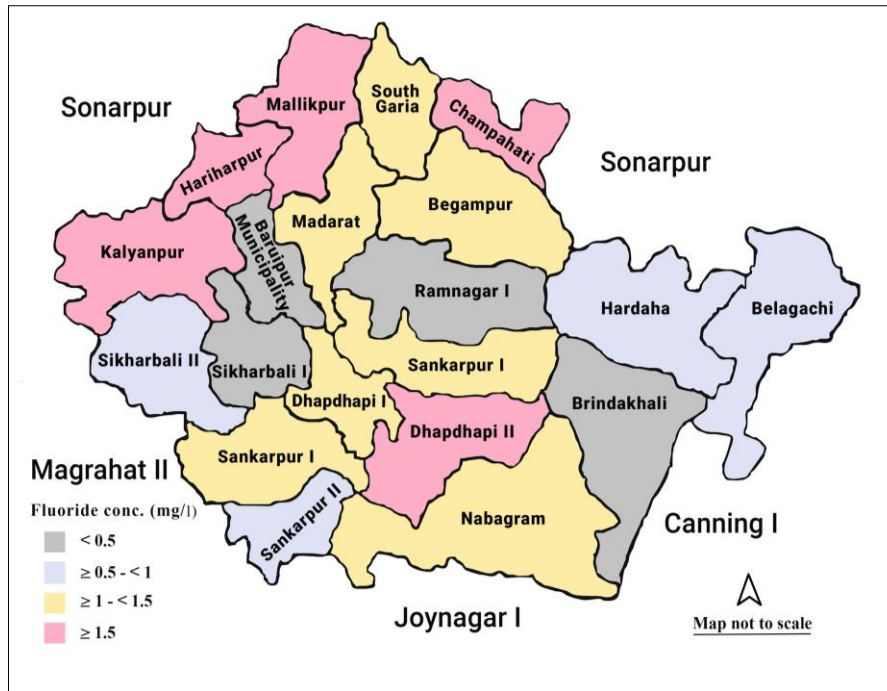


Fig. 4.5: Study area of Baruipur block

4.2.2 West Medinipur

West Medinipur district is located in the central south-western part of West Bengal within the latitude: $22^{\circ} 24' 28.93''$ N and longitude: $87^{\circ} 22' 51.86''$ E. Different geographical characteristics of the West Medinipur district are based on the alluvium and fluvio-deltaic sediment overlain by the laterite soil. Pingla, Narayanganr, Keshiyari, Garbeta I, and Garbeta II blocks have been surveyed for groundwater F^{-} scenarios in the West Medinipur district. The study areas have been demonstrated in Fig. 4.6.

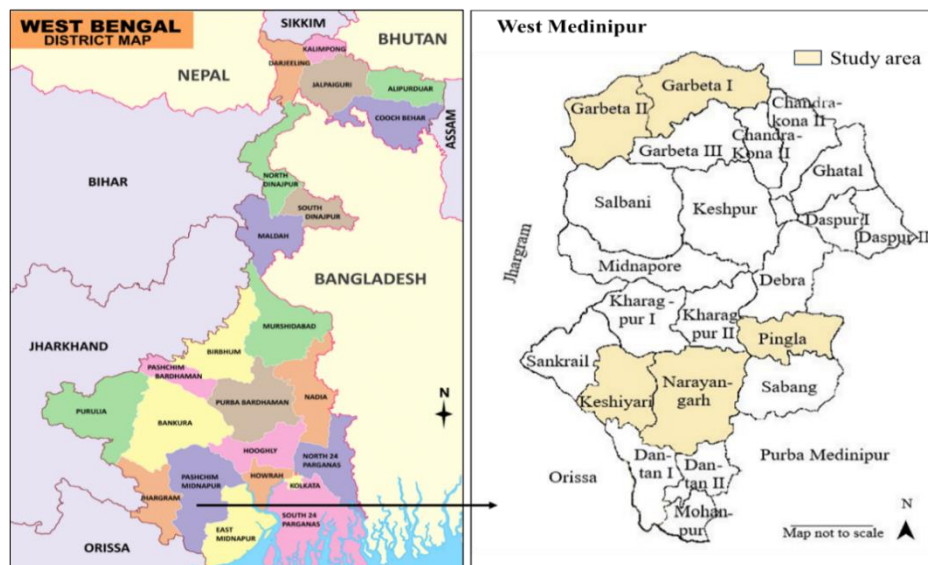


Fig. 4.6: Study area of West Medinipur district

4.2.3 Jhargram

Jhargram district is located at latitude: 22° 27' 48.98" N and longitude: 86° 58' 21.28" E. This district has one of the lowest population densities in the South-Western part of West Bengal. The Chota Nagpur Plateau progressively dips down, forming an undulating terrain with barren laterite rocks/soil. The entire area is prone to drought, with an especially severe drought scenario. Jhargram district has a total area of 3,037.64 km² and a population of 1,136,548 according to the 2011 census (Census 2011). Rural people belong to the 96.52% of the overall population, while urban people belong to only 3.48%. Gopiballavpur-I, Gopiballavpur-II, Jamboni, Nayagram, Binpur I, and Binpur II blocks have been investigated for groundwater F⁻ scenarios in Jhargram district. The study areas have been demonstrated in **Fig. 4.7**.

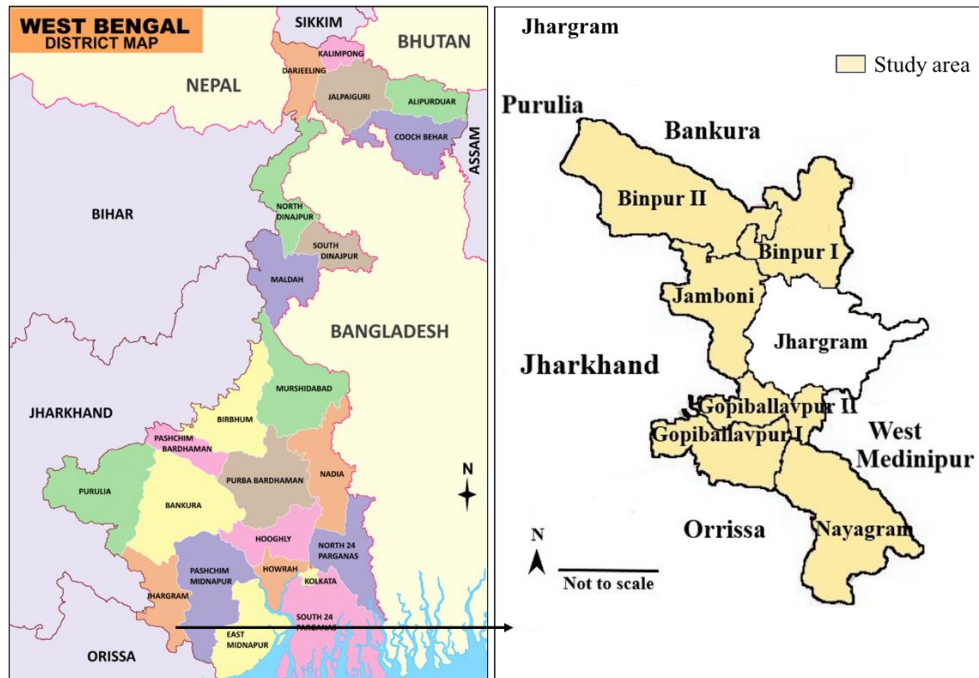


Fig. 4.7: Study area of Jhargram district

4.2.4 East Bardhaman

East Bardhaman district is located at latitude 23° 13' 57.04" N and longitude 87° 51' 48.30" E and it is the midpoint of the south part of West Bengal. The river Damodar flows to the south and southeast of the Bardhaman plain. According to the rural household survey managed by the state government in 2005, 37.14% of rural households in the East Bardhaman district were living below the poverty line (District Human Development Report, Bardhaman, 2011). A total number of 22 blocks i.e., Memari I, Memari II, Raina I, Raina II, Burdwan I, Burdwan II, Khandoghosh, Galsi I, Galsi II, Jamalpur, Manteswar, Bhatar, Mongolkote, Aushgram I, Aushgram II, Kalna I, Kanla II, Purbasthali I, Purbasthali II, Katwa I, Ketugram I, and

Ketugram II blocks have been investigated for groundwater F⁻ scenario in East Bardhaman. The study areas have been demonstrated in **Fig. 4.8**.



Fig. 4.8: Study area of East Bardhaman district

4.2.5 West Bardhaman

West Bardhaman district is located in the western part of West Bengal within latitude 23° 45' 00.00" N and longitude 87° 1' 00.00" E. This area is surrounded by urban industrial hubs and coal mining areas. The Raniganj coalfield was the site of the country's earliest coal mining operations in 1774 (Chattopadhyay 2001). This area is a sort of extension of the Chota Nagpur plateau. Kanksa, Durgapur, Asansol, Salanpur, Barabani, Andal, Pandabeswar, Jamuriya, and Raniganj blocks have been investigated for groundwater F⁻ scenarios in West Bardhaman district. The study areas have been demonstrated in **Fig. 4.9**.

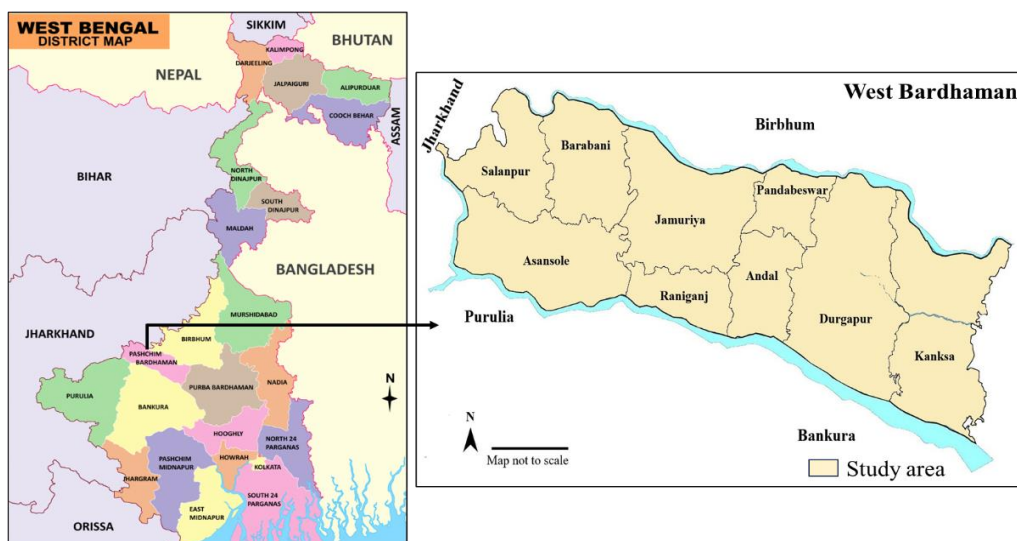


Fig. 4.9: Study area of West Bardhaman district

4.2.6 Murshidabad

Murshidabad district consists of 26 blocks, and it is situated in the western part of West Bengal within latitude $24^{\circ} 10' 33.25''$ N and longitude $88^{\circ} 16' 48.65''$ E. Bhagirathi River divides the district into two geographic regions. Bhagirathi is a branch of the Ganga, and it flows towards the south from the Farakka barrage where it originated from the Ganga. The eastern part of Murshidabad is made of an alluvial tract of the Gangetic delta and to the western part lies the Rarh zone i.e., a high, undulating continuation of the Chota Nagpur plateau. Bharatpur II, Kandi, Khargram, Nabagram, Sagardighi, Burwan, Berhaampur, Suti II, Raghunathganj I, Raghunathganj II, Farakka, Samserganj, and Jiaganj blocks have been investigated for groundwater F^{-} scenario in Murshidabad district. The study areas have been demonstrated in Fig. 4.10.

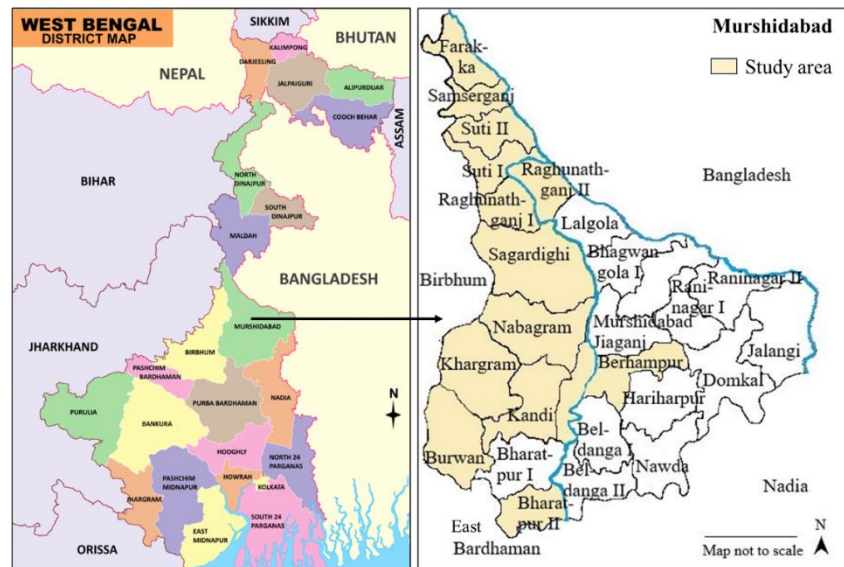


Fig. 4.10: Study area of Murshidabad district

4.2.7 Bankura

Previous studies in the Bankura district of West Bengal solely focused on the groundwater F^{-} contamination scenario and assessing the extent of fluorosis to a limited extent (Bera and Ghosh, 2019; Bhattacharya et al., 2017; Mondal and Kumar, 2017). The district is geographically divided into three distinct parts towards north-south trending zones: the hilly hard rock-dominated tract in the west (hard rock province); the sedimentary plain lands in the east (alluvial province); and the undulating tract with a mix of both rocky and alluvial formations in the central part (mixed formation province). (Chakrabarti and Bhattacharya, 2013). Groundwater was reported with contamination of F^{-} much higher than its recommended value in drinking water (range: 0.1-12.2 mg/l) (Mondal and Kumar, 2017). Out of the 22 blocks

in Bankura, 12 blocks have been reported as F^- contaminated, according to the preliminary database and documentary evidence. Of these, 5 blocks are predominately composed of hard rock, and the remaining 7 blocks are underlain by mixed rock formation (with a top veneer of softer alluvium over the substrate of hard rock) (Chakrabarti and Bhattacharya, 2013).

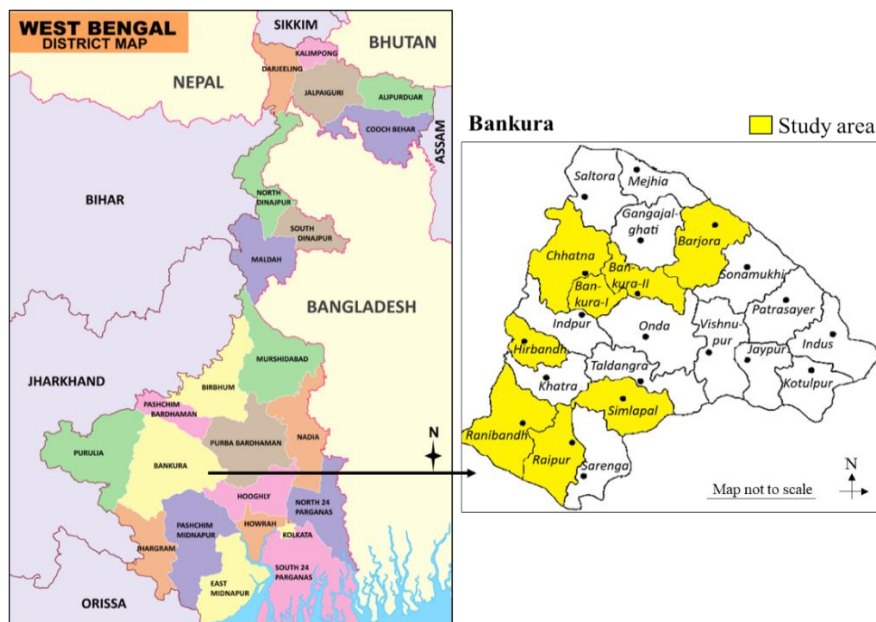


Fig. 4.11: Study area of Bankura district

Apart from the ingestion of F^- contaminated water, the crops and vegetables cultivated using F^- contaminated groundwater contribute a significant amount of F^- to the daily dietary intake of the local inhabitants (Bhattacharya et al., 2017; Pal et al., 2012). Thus, the assessment of F^- content in various food sources was estimated and health risk assessment was further investigated. Chhatna, Bankura I, Bankura II, Barjora, Hirbandh, Simlapal, Raipur and Ranibandh have been investigated for groundwater F^- scenario along with the cultivated crops and vegetables grown up by using F^- contaminated groundwater. The study areas have been demonstrated in Fig. 4.11.

4.2.8 Purulia

Purulia is located on the most western part of the state West Bengal and on the eastern side of the Chotonagpur plateau. The district has been characterized by a tropical savanna climate (Aw), where the majority of rainfall is concentrated during the monsoon season. The conditions that favor the F^- enrichment in groundwater include an extended and intense dry spell, a semi-arid climate, extensive groundwater withdrawal for irrigation, the alkaline nature of subsurface circulating water, a lengthy residence time in fractured aquifers, and a low likelihood of

dilution. The groundwater is contaminated with significant levels of F^- in 18, out of 20 blocks (Mandal and Sanyal, 2019). The magnitude of F^- in groundwater and its spatial distribution have been investigated. Additionally, the contents of F^- in crops and vegetables cultivated by using F^- contaminated groundwater have been thoroughly estimated. The study areas have been demonstrated in Fig. 4.12.

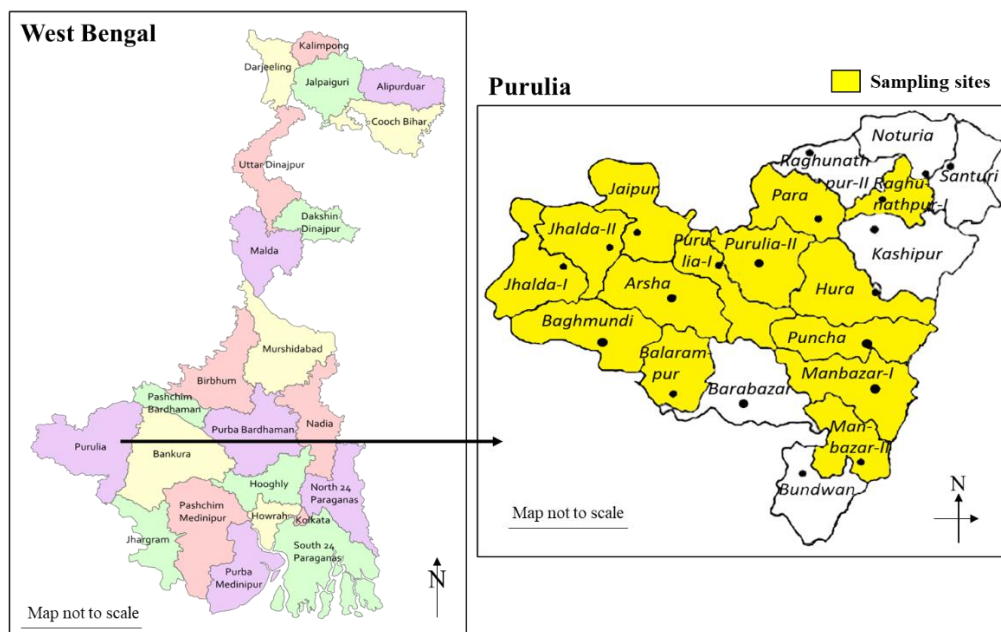


Fig. 4.12: Study area of Purulia district

4.3 Sample collection and preservation

4.3.1 Groundwater

Groundwater samples were collected from eight different districts in West Bengal. The field survey involved the collection of groundwater from the government, and private hand tube wells and pumps. All the sample locations were recorded with proper latitude and longitudes using Garmin GPS etrex 10 meters. Airtight prewashed polyethylene containers (50 ml) were used for sample collection. During sample collection, the containers were rinsed thoroughly with the same groundwater samples. A total number of 3523 groundwater samples were collected from eight districts, out of which 143, 134, 176, 574, 2096, 143, 83 and 153 from East Bardhaman, West Bardhaman, Jhargram, Murshidabad, South 24 Parganas, West Medinipur, Bankura and Purulia districts, respectively. Water samples were collected in duplicates; a part of the water samples were preserved without the addition for estimation of F^- and other water quality parameters. The other part of the water samples was preserved with addition of 0.1% HNO_3 for quantification of arsenic (As), calcium (Ca) and Iron (Fe). All the

collected water samples were transported to the laboratory and kept in a cold condition at 4 °C until further analysis.

4.3.2 Crops and vegetables

All crops and vegetables were collected from contaminated sites such as Bankura and Purulia districts. Locally cultivated fresh food crops and vegetables were collected from the agricultural fields which include cereal like rice (*Oryza sativa*) and wheat (*Triticum aestivum*); pulses like pigeon pea (*Cajanus cajan*), lentils (*Lens culinaris*), chana (*Cicer arietinum*), and lentils arhar (*Lens culinaris*); nonleafy vegetables like sweet potato (*Ipomoea batatas*), potato (*Solanum tuberosum*), turmeric (*Curcuma longa*), ginger (*Zingiber officinale*), onion (*Allium cepa*), carrot (*Daucus carota*), shim/broad beans (*Vicia faba*), beans (*Vicia faba*), radish (*Raphanus sativus*), cauliflower (*Brassica juncea*), chilli (*Capsicum frutescens*), pumpkin (*Cucurbita pepo*), brinjal (*Solanum melongena*), cucumber (*Cucumis sativus*), bitter guard (*Momordica charantia*), mustard seed (*Brassica juncea*), and tomato (*Lycopersicon esculentum*); and leafy vegetables like cabbage (*B. oleracea* var. *capitata*), coriander (*Coriandrum sativum*), spinach (*Spinacia oleracea*), and methi saag/fenugreek leaves (*Trigonella foenum-graecum*). The collected samples were individually packed into polythene zip locks and labeled, respectively. All the collected samples were stored in an icebox to prevent degradation of the organic substances and transported to the laboratory.

4.3.3 Soil

All the soil samples were collected from Bankura and Prulia districts. Soil samples were collected individually into ziplock in triplicates from the upper surface of respective agricultural fields (a distance of approximately 600 cm between each other). All the collected samples were stored in an icebox to prevent degradation of the organic substances and transported to the laboratory.

4.3.4 Urine

For the health risk assessment study of F⁻, urine samples (n = 192) were collected from the inhabitants residing in the two F⁻ endemic wards, which include 35 families from ward number 6 (n = 124) and 21 families from ward number 7 (n = 68) of Rajpur Sonarpur Municipality of Sonarpur block, South 24 Parganas. Similarly, for the health risk assessment study of arsenic, urine samples (n = 51) were collected from the inhabitants of 10 families residing in ward

number 15 where the groundwater was found with a high level of arsenic. All the urine samples were collected in 10 ml of polyethylene containers, stored in an icebox, transported to the laboratory, and kept at -20 °C until analysis.

Urine samples (n = 19) were further collected from the members of the families residing in control sites namely Madhyabar village, Pingla, West Medinipur and processed for the estimation of F⁻ and arsenic.

4.3.5 Borehole sediments

Borehole sediments (n = 30) were collected from two boreholes located in Nachangacha village, Dhaphdapi II gram-panchayat of Baruipur block (Latitude: 22°17'42.07" N, Longitude: 88°28'04.33" E) and ward number 6, Rajpur Sonarpur Municipality, Sonarpur block (22.4473° N, 88.3920° E) by the rotary drilling method in the depth range of 0 - 91.5 m with every 3.05 m interval between successive layers and kept in 250 ml of individual plastic containers. The borehole sediment samples were dried for 72 h in a hot air oven at 50 °C and preserved in a plastic zip-lock (18 × 10 cm) for further processing.

4.4 Sample processing

The collected foodstuffs were cleaned properly with distilled water and dried in hot air oven at 60 °C for 2 days. The dried foodstuff samples were processed for alkaline digestion for estimation of F⁻. The soil and borehole sediment samples were dried in hot air oven at 60 °C for 7 days. Furthermore, the dried samples were grounded in powder form and sieved to 100 µm. The sediment samples were processed for two-way digestion, first acidified digestion for estimation of iron and calcium and secondly alkaline digestion for estimation of F⁻ and potassium. No digestion protocol was followed for water and urine samples for estimation of F⁻ and arsenic.

4.4.1 Acidified digestion

About 0.02 - 0.2 g of all kinds of individual solid and semi-solid samples (dry weight) were placed in Teflon container, followed by addition of 69% concentrated HNO₃ and 30% (v/v) H₂O₂ in a ratio of 2:1. Teflon containers were kept into their particular bombs and placed in an oven at ~120 °C for 6 h. Subsequent to cooling of the bombs, the digested samples were placed on a hot plate at ~90 °C for evaporation for 1 h to achieve a final volume of 2 - 5 ml with double

distilled water, followed by filtration through a Millipore suction filter (0.45 μm). The filtered samples were stored at 4 °C for further analysis. About 50 % of the samples were digested by using the hot plate method.

4.4.2 Alkaline digestion

The collected food crops and soil samples were digested following the protocol of the alkali fusion process (Malde et al., 2001; Mridha et al., 2021). About 0.5 g of dried sample was taken in a 25 ml nickel crucible followed by the addition of 0.5 ml double distilled water to maintain the moist condition and 6 ml of 8 (M) NaOH solutions. The crucible was placed at 150°C for 2 h inside a hot air oven. The crucible was taken out and placed inside a muffle furnace initially at 400 °C, with a gradual rise in temperature up to 600 °C for 1 h. The crucible was allowed to cool at room temperature and about 10 ml of double-distilled water was added for dissolution of fusion cake and placed on a hotplate. For maintaining the pH at 7-9, concentrated HCl was added dropwise with continuous stirring and made up the volume to 25 ml with distilled water. Finally, the solution was filtrated through Whatman 42 filter paper, and the samples were stored in a cooled place for F^- estimation.

4.5 Estimation of chemical parameters

4.5.1 Estimation of fluoride

Fluoride concentration in digested soil, borehole sediment and foodstuffs were measured electrochemically using an ion-selective electrode (ISE) meter (Thermo Scientific Orion Star A214) combined with F^- ion-selective electrode (Orion ISE model no. 9609BNWP) following the recommended protocol by the American Society for Testing and Materials (ASTM, 2010). Aliquots of 0.1, 1, and 10 mg/l were prepared directly from the standard stock solution of sodium F^- (100 mg/l) through serial dilutions. A mixture solution of TISAB-III with F^- aliquot in a 1:10 ratio was used daily for calibration. Prior to the measurement of F^- , the ion meter was calibrated to a slope of -59.2 ± 2.0 . TISAB-III and digested samples in the same ratio (1:10) were used for the estimation of F^- .

4.5.2 Estimation of total arsenic

Total arsenic estimation has been carried out using an Atomic Absorption Spectrophotometer (AAS) of Model: Varian AA140, USA with software version 5.1 connected with Vapor Generation Accessory (VGA-77, Agilent Technologies, Malaysia). All the liquid (water and

urine) and digested solid samples have been analyzed for arsenic using HG-AAS i.e. Hydride Generation-Atomic Absorption Spectrometry methodology.

4.5.3 Physico-chemical analysis of water quality parameters

Different physico-chemical parameters namely pH, Electrical Conductivity (EC), temperature, Iron (Fe), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Arsenic (As), Total Hardness (TH), Total Alkalinity (TA), Chloride (Cl^-), Sulphate (SO_4^{2-}), Nitrate (NO_3^-), carbonate (CO_3^{2-}), sodium(Na^+), potassium(K^+), bicarbonate (HCO_3^-), magnesium(Mg^{2+}), and calcium (Ca^{2+}) present in the groundwater samples were quantified. The physico-chemical water quality parameters were analyzed using individual digital instruments, reagents and methodology as followed by the protocol of APHA 2005 and Das et al. (2020).

4.5.4 Estimation of other parameters

4.5.4.1 Moisture percentage in food crops, vegetables, and soil

All the samples were collected from Bankura and Purulia districts. The edible parts of crops and vegetables were thoroughly washed with laboratory tap water, followed by rinsing with double-distilled water. About 100 g of each of washed food crops, vegetables, and collected soil samples were placed into a hot air oven at 60 °C for 72 h and taken out to determine the moisture content (Bhattacharya et al., 2017). The moisture content was evaluated using the following equation:

$$\text{Moisture content (\%)} = \frac{\text{Initial fresh weight of food} \frac{\text{Stuff}}{\text{Soil}} - \text{final dry weight of food} \frac{\text{Stuff}}{\text{Soil}}}{\text{Initial fresh weight of food} \frac{\text{Stuff}}{\text{Soil}}}$$

4.5.4.2 Bioaccumulation factor (BCF) of fluoride in plant

BCF is presented to show the amount of F^- accumulated in plant systems through the soil. The BCF of F^- in the collected food crops was evaluated using the formula of Pal et al. (2012).

$$\text{BCF} = \frac{\text{Fluoride in vegetables} \left(\frac{\text{mg}}{\text{kg}} \text{ Dry weight of plant} \right)}{\text{Fluoride in soil} \left(\frac{\text{mg}}{\text{kg}} \text{ Dry weight of soil} \right)}$$

4.5.4.3 Protein, Carbohydrate, and total Chlorophyll

Protein, Carbohydrate, Total Chlorophyll and F^- concentration in cultivated plants collected from F^- exposed area (Nachangacha, South 24 Parganas) and control area (Pingla, Paschim Medinipur).

To estimate the total protein content, 10 g of dried plant material was homogenized using a mortar and pestle, and then 50 ml of phosphate buffer was added. Subsequently, 100 ml of 0.1 N NaOH (MERCK DK7D672577) was combined with the solution and incubated for 30 minutes in a water bath at 80 °C. The solution was then centrifuged at 1000 rpm (Remi, C-24BL), and the supernatant was collected to determine the total protein content using the Lowry method (1951). Following the estimation of total lipid, moisture, total proteins, total ash, and crude fiber, carbohydrate content was determined using the following equation (Raghuramulu et al., 2003):

$$\text{Carbohydrate} \left(\frac{\text{g}}{100\text{g}} \text{ sample} \right) = 100 - \left[\frac{(\text{moisture} + \text{fat} + \text{protein} + \text{ash} + \text{crude fiber})\text{g}}{100\text{g}} \right]$$

The chlorophyll content was determined from plant parts using the acetone extraction method. Approximately 0.1 g of plant leaf tissue was homogenized with 5 ml of 80% (v/v) acetone solution. The extracted solution was then filtered, and the concentration of chlorophyll a and b (mg/g FW) was measured according to the method described by Arnon (1949), by measuring the optical density of the extracted sample at 663 nm and 645 nm, respectively.

4.6 Chemicals, reagents and analytical instruments

Analytical graded chemicals, reagents and double distilled water were used all over the systematic process. Standard F^- solution (100 mg/l, Orion 940911, Thermo Scientific, USA) and Total Ionic Strength Adjusting Buffer (TISAB-III) which was used at a 1:10 ratio (buffer: sample) were procured from Thermo Fisher Scientific, (USA, Orion 940911) for the estimation of F^- . Nitrate (NO_3^-) standard solution of 1000 mg/l as nitrogen (Orion 920707, Thermo Scientific, USA) and Interference Suppressor solution (Orion 930,710, Thermo Scientific, USA) were used 1:1 ratio for estimation of nitrate. Calcium (Ca^{2+}) was measured by the Flame Photometric method, where calcium carbonate salt was used during the preparation of the standard (1000 mg/l, Merck, Mumbai, India) solution. Potassium (K^+) and sodium (Na^+) concentrations were measured using a similar method while potassium chloride (KCl) and sodium chloride (NaCl) salts (1000 mg/l, Merck, Mumbai, India) were used for the standard solution preparation. Analytical grade of NaOH (Merck, Mumbai, India) was used for alkali digestion of borehole sediments to estimate F^- . Concentrated nitric acid and H_2O_2 (30 % v/v) (Merck, Mumbai, India) were used for digesting the sediment samples for Ca^{2+} and Fe

estimation. Iron (Fe) standard solution (1000 mg/l) was used for Fe estimation. Specified information of the aforesaid methodologies was defined previously (Das et al., 2020).

4.7 Accuracy and precision

The precision and consistency of the acquired data were corroborated through the assessment of blank, inter-laboratory testing and accurate standardization (Das et al., 2020). Quality control tests were maintained by duplicate analysis ($\pm 5\%$ variation) and observing spiked recovery of some selected samples (Joardar et al., 2021). Quality control assessments were also performed by measuring the samples in duplicates and calculating spiked recovery on 15 - 20 % of the analysed samples. The average recovery showed $95 \pm 5 \%$ of spiked F^- in groundwater, urine, digested sediment, soil, crops and vegetables samples.

4.8 Statistical analysis

Sampling points of groundwater were run by Google Earth Pro 7.3.3. The longitudinal distribution of F^- in groundwater was evaluated using Arc-GIS 10.8 software application through Inverse Distance Weighing (IDW) model system. IDW model, an interpolation method that is determined using variables and the distance between points. The PHREEQC software interactive (version 2.11) was used to find mineral data in the groundwater which was useful for the determination of geochemical modelling. Gibbs diagram modelling and dendrogram cluster analysis were determined by using R 4.1.2 software version. The uncertainty of non-cancerous health risk was assessed by using Oracle Crystal Ball Fusion edition version 11.1.1.1.00 and related other statistical data were analysed by Microsoft office 2019. The principal component analysis (PCA) was performed to understand the interdependence of the four studied elements (As, F^- , Fe, and Ca) (Lima et al., 2019) where the depth ranges were set as observational levels (Fang et al., 2012). Cluster analysis (CA) was done on the same parameters to create different groups clustering among the variables and observational depth levels. A ward-algorithmic method was used to perform the CA (Facchinelli et al., 2001). The visual representation of hierarchical clustering analysis was presented in a dendrogram to show different clustering groups. All the multivariate statistical analysis and ward-wise spatial distribution plots (Lima et al., 2020) were performed using Origin Pro 2018 software.

4.9 Data interpretation and analysis

All the estimated data has been calculated and estimated by the given process.

4.9.1 Single factor contamination index

The assessment has been evaluated for groundwater contamination with special emphasis on F^- (Das et al., 2021; Rehman et al., 2018).

$$I_i = \frac{C_i}{C_o}$$

where, I_i represents the specific toxicant specifies: C_i signifies the concentration of harmful substances in the groundwater. C_o indicates the acceptable concentration of the toxic contaminant as prescribed by the standard guidelines (WHO).

The respective C_o value for F^- in drinking water is 1.5 mg/l (BIS, 2012; WHO, 2011). These contamination factors have been classified into 4 groups; 1st group: low contamination ($I_i < 1.0$), 2nd group: moderate contamination ($1.0 \leq I_i < 3.0$), 3rd group: considerable contamination ($3.0 \leq I_i < 6.0$) and 4th group: high contamination ($I_i \geq 6.0$) (Hakanson, 1980; Rehman et al., 2018).

4.9.2 Hydro-geochemical controlling factors

Different hydro-geochemical modelling was suggested to verify the responsible source of F^- leaching in groundwater in the Gangetic belt of West Bengal.

4.9.2.1 Geochemical weathering (Gibbs diagram)

Gibbs diagram is commonly used in determining the relationship between groundwater composition and host mineral/lithological characteristics of the underground aquifer systems. Gibbs (1970) explains the impact of three distinct fields like evaporation dominance, precipitation dominance and rockwater interaction dominance areas on water chemistry using major cations and anions ratio, and TDS. The hypothesis was described in the hydro-geochemical characterization by $(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$ ratio vs TDS and $Cl^- / (Cl^- + HCO_3^-)$ ratio vs TDS (Gibbs, 1970).

4.9.2.2 Chloro-alkaline (CA) indices

Chloro-alkaline indicates the relation between CA I and CA II proposed by Schoeller (1967). The calculated formulas were represented using given equations. It is widely used to assess the possible mechanism of the ion exchange process between groundwater and host minerals/rocks at the aquifer level (Feng et al., 2020; Karunanidhi et al., 2020; Marghade et al., 2012; Subba Rao, 2017). If the CA value is negative, it indicates an exchange of Ca^{2+} and Mg^{2+} of the

groundwater with K^+ and Na^+ ions from the host rock. It generally shows a cation-anion exchange reaction. If the CA value is positive, it specifies the exchange of K^+ and Na^+ ions from the groundwater with Ca^{2+} and Mg^{2+} of the host rock. This type of ion exchange is called a base exchange reaction. CA I and CA II are based on two equations given below.

$$CA\ I = (Cl^- - Na^+ + K^+)/Cl^-$$

$$CA\ II = (Cl^- - Na^+ + K^+)/(\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-)$$

4.9.2.3 Geochemical modelling: saturation index (SI)

Saturation index (SI) is performed to assess the degree of equilibrium between groundwater and minerals. Inverse geochemical modelling is a mass balance simulation, and it specifies the change in chemical characteristics and chemical reactions. The saturation index (SI) of water samples was determined using the PHREEQC software package (Parkhurst and Appelo, 1999; Xu et al., 2021a, 2021b) to infer the geochemical processes that influence the evolution of groundwater chemistry along with its flow path and characteristics (Belkhiri et al., 2011; Carucci et al., 2012; Kumar and Singh, 2015; Singh et al., 2017; Thapa et al., 2019). The saturation index (SI) with respect to fluorite, dolomite, anhydrite, calcite, halite and gypsum was calculated using analytical data of groundwater from various sources with the aid of the following equation given below:

$$SI = \log\left(\frac{IAP}{K_{eq}}\right)$$

where, IAP = the product of the concentration of dissolved species

K_{eq} = the equilibrium constant

In a system, a positive saturated index (SI) value suggests that the mineral is supersaturated or oversaturated and may be precipitated whereas negative saturated index (SI) value indicates under saturated with respect to the correspondent mineral phase (Alcaine et al., 2020; Langmuir and Melchior, 1985).

4.9.2.4 Mineralogical study

The mineralogical investigation was conducted on borehole sediment samples by using X-ray diffractometer (XRD). XRD assessment of sediment samples was conveyed in the Department of Geology, Jadavpur University, Kolkata using a Malvern P analytical X-ray diffractometer. Elemental components (mineral compositions) were determined under Scanning Electron Microscope (SEM) (Carl Zeiss, Model Number - EVO18 Special Edition) to examine the

presence of elements and morphology of minerals in sediment samples (Mridha et al., 2022). The SEM was conducted at 15 kV with a working distance of 10 mm. For Energy Dispersive X-ray spectroscopy (EDX) analysis, an accelerating voltage of 15 kV was used to obtain sufficient X-ray counts. EDX analysis of sediment samples was run in Nano Science department, University of Calcutta, Kolkata.

4.10 Human health risk assessment

4.10.1 Health risk assessment model of the studied population

This assessment determines the risk initiated by different toxic exposure on human health (USEPA, 1993, 2003). The risk assessment tool has been consigned based on F^- concentration in drinking water on four different studied age groups. Due to different behavioural and physiological attributes according to the age, the studied agegroups including infants (1 to 3 years), children (4 to 10 years), teenagers (11 to 19 years) and adults (20 to 70 years) were selected from the study area. The average daily dose (ADD) of F^- was calculated by using modelled dose exposure for the four age groups of the studied population. The ADD model was categorized in two directions, direct oral intake (ingestion) and dermal exposure (Adimalla and Qian, 2020; Ali et al., 2021; Senthilkumar et al., 2021).

$$ADD_{ing}(\text{mg/kg - body weight/day}) = (C \times IR \times EF_{ing} \times ED_{ing}) / (BW \times AT_{ing})$$

$$ADD_{der}(\text{mg/kg - body weight /day}) = (C \times SA \times KP \times F \times ET_{der} \times EF_{der} \times Ed_{der} \times 0.001) / (BW \times AT_{der})$$

$$HQ_{ing} = ADD_{ing} / RfD_{ing}$$

$$HQ_{der} = ADD_{der} / RfD_{der}$$

where HQ_{ing} and HQ_{der} are non-carcinogenic risk or hazard quotient (HQ) of F^- through ingestion and dermal exposure. Total Hazard Quotient (THQ) of non-carcinogenic risk is evaluated by the given equation below.

$$THQ_{ing+der} = HQ_{ing} + HQ_{der}$$

For non-carcinogenic risk, the acceptable limit of THQ of F^- is 1 (USEPA, 2003, 2010). $THQ > 1$ specifies that there is a severe health risk to human health. A detailed description of the parameters used for calculating the ADD and HQ for four different studied age groups are given in **Table 4.1**.

Table 4.1: Data used to calculate the exposure risk of F⁻ toxicity (EDI_{ing}, EDI_{der}, HQ_{ing} and HQ_{der}) through ingestion and dermal contact (through showering)

Parameters	Description	Units	Adopted value for population groups				Reference
			Infants	Children	Teenagers	Adults	
IR	Daily groundwater ingestion Rate	l/day	0.5	1	2.5	4	Mondal et al., 2012
BW	Average body weight of a population group	kg	6	20	52	70	Adimalla, 2020
ED_{ing}	Exposure duration through ingestion	year	2	7	8	50	Narsimha and Rajitha., 2018
EF_{ing}	Exposure frequencies for ingestion	day/year	365	365	365	365	Mukherjee and Singh, 2021
AT_{ing}	Average exposure time for ingestion	day	730	2555	2920	18250	Mukherjee et al., 2019
SA	Exposed skin area during bathing	cm ²	3229	6600	14321	18000	Mukherjee et al., 2020
Kp	Dermal permeability coefficient	cm/hour	0.001	0.001	0.001	0.001	Karunanidhi et al., 2020
ED_{der}	Dermal exposure frequency	day/year	2	7	8	50	Mukherjee and Singh, 2021
EF_{der}	Exposure duration through dermal contact	year	200	350	350	350	Mukherjee and Singh, 2021
AT_{der}	Average exposure time for dermal contact	day	400	2450	2800	17500	Mukherjee and Singh, 2021; Shil and Singh, 2019
ET	Exposure time in the shower	hour/day	0.1	0.13	0.25	0.33	Mukherjee and Singh, 2021
F	Fraction of the contact surface of the skin with the groundwater	unitless	0.65	0.65	0.65	0.65	USEPA, 2010
RfD_{oral}	Oral reference dose	mg/kg/day	0.06	0.06	0.06	0.06	IRIS, 2016
RfD_{dermal}	Dermal reference dose	mg/kg/day	0.0528	0.0528	0.0528	0.0528	Mukherjee et al., 2020

4.10.2 Nutritional status and exposure dose determination

An initial survey was supervised on food habits, food consumption patterns, and body weight of 57 households from Bankura and Purulia districts comprising different age groups. Based on the surveyed data, an average value for the consumption rates of cereals, pulses, green leafy vegetables, and nonleafy vegetables has been placed for health risk evaluation. The populations in the study area have been grouped into four categories according to their ages, i.e., children (4-8 years), adolescents (9-13 years), teenagers (14-18 years), and adults (19-70 years). The diet of the studied populations mainly depends on rice and wheat with periodical changes and alteration of pulses and vegetables. EDI of F⁻ is an indicator that expresses how much F⁻ a person ingested through the daily consumption of different food crops. The generic equation of EDI was established on the given formula by US Environmental Protection Agency (USEPA, 1993) as follows:

$$EDI = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

where C = concentration of F⁻ in foodstuff (mg/kg); IR = ingestion or intake rate of F⁻ (mg/day); EF = exposure frequency (days/year); ED = exposure duration (year); BW = average body

weight (kg); and AT = average lifetime (days) that is equal to ED times 365 days/year (Erdal and Buchanan, 2005). To calculate the exposure dose of four different aged populations in this study, average body weight was considered as 22 kg, 40 kg, 60 kg, and 70 kg for children, adolescents, teenagers, and adults, respectively (based on our preliminary survey in the studied areas). $EDI_{\text{cumulative}}$ is a summative expression of F^- exposure pathway through different dietary sources, which has been calculated with the following equation:

$$EDI_{\text{cumulative}} = EDI_{\text{Cereals}} + EDI_{\text{Pulses}} + EDI_{\text{Non-leafy vegetables}} + EDI_{\text{Leafy vegetables}}$$

4.10.3 Health risk assessment study through consumption of dietary food

Health risk assessment is a quantitative model for the evaluation of possible risk through different toxic exposure on human (USEPA, 1993). The health risk assessment of four different age groups has been carried out by comparing the exposure dose and reference dose (RfD) of F^- to determine the HI. HI represents the ratio of EDI to the oral RfD for non-carcinogenic health risk from individual food crops.

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

where the oral RfD value for F^- is 0.06 mg/kg bw/day (USEPA, 2003). It is derived from the NOAEL (no observed adverse effect level) of 0.06 mg/kg-day which is divided by the uncertainty factor (UF) and modifying factor (MF); the value of both UF and MF is 1 (USEPA, 2003). If the obtained HI value of F^- is <1 , then the chances of non-carcinogenic effects are hardly present, whereas $HI > 1$ designates potential non-carcinogenic human health effects (USEPA, 2010). The THI of the inhabitants through the dietary intake of food crops has been measured with the following equation:

$$THI = \sum_{k=0}^n HI_{\text{Cerals} + \text{Pulses} + \text{Non-leafy vegetables} + \text{Lefy vegetables}}$$

The lifetime non-carcinogenic risk (LTNR) assessment for the populations of the study areas (4-70 years) due to lifelong exposure to F^- is calculated using the following equation (USEPA, 2003):

$$HI_{\text{LTNR}} = HI_{4-8 \text{ years}} + HI_{9-13 \text{ years}} + HI_{14-18 \text{ years}} + HI_{19-70 \text{ years}}$$

4.10.4 Probabilistic risk assessment

Futuristics health risk assessment study has been computed by the Monte Carlo simulation method which is used for probabilistic health risk and uncertainty analysis. In this deterministic approach, health risk exposure assessment model input values are expressed as a point or single value. To minimize the uncertainty data, this technique is used to analyze the probabilistic health risk due to ingestion and dermal exposure of groundwater. Through this method, 10,000 iterations were run by Oracle Crystal Ball programming software in Excel 2019. To determine the THQ values and measure the probabilistic risk distribution from lower to upper boundary i.e., lower boundary: 5th percentile (P5), middle boundary: 50th percentile (P50), and upper boundary: 95th percentile (P95) (Bazeli et al., 2020).

4.10.5 Sensitivity analysis

Sensitivity analysis was carried out during the Monte Carlo simulation, to identify the input variables that have a substantial impact on the outcome of the probable risk assessment. According to their data of variables, probabilistic distribution was conducted for four different age groups. The Monte Carlo simulation and sensitivity were done in Microsoft Excel within compiled Crystal Ball software and all input parameters were established in **Table 4.8.1**.

4.11 Defluoridation process using calcium-based materials

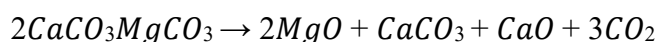
Calcium-containing compounds, including calcium hydroxide (Ca(OH)_2), calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), and quick lime (CaO), are recognized for their ability to enhance F^- removal from water due to the strong binding affinity between calcium and F^- (Jadhav et al., 2014). However, calcium (hydro)oxides present several significant limitations in practice, such as pH elevation, effectiveness only at initial fluoride concentrations exceeding 10 mg/l, and inability to reduce concentrations below WHO guidelines (Islam and Patel, 2007). Consequently, calcium-modified dairy manure-derived biochar (Ca-DM500) was investigated due to its availability, low cost, utilization of waste materials, high sorption capacity, and unique physical and chemical properties. Furthermore, the high buffering ability of biochar, as well as the addition of calcium, can improve CaF_2 precipitation. The goal of this study was to assess the efficacy and mechanism of modified calcium from natural sources for fluoride removal from water.

4.11.1 Selection of materials

Dolomite: Dolomite [$\text{CaMg}(\text{CO}_3)_2$] is a common rock-forming mineral, constituting a layer of carbonate ion (CO_3^{2-}) separated by an alternating layer of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions (**Fig. 4.13**). It is an anhydrous carbonate mineral. Dolomite is also known as dolostone. This is a sedimentary rock and found in the sedimentary rock basin worldwide. The color of dolomite is white to grey. Thermal treatment of dolomite at 800 °C led to changes in its chemical composition. In this change Calcite, Calcium Oxide and Magnesium Oxide are formed (Staszczuk et al., 1997).



Fig. 4.13: Dolomite mineral
(Source: Learning Geology)



The change in chemical composition increases the BET (Brunaur, Emmet & Teller Method) surface area of dolomite in many folds which increases the adsorption properties (Walker et al., 2005).

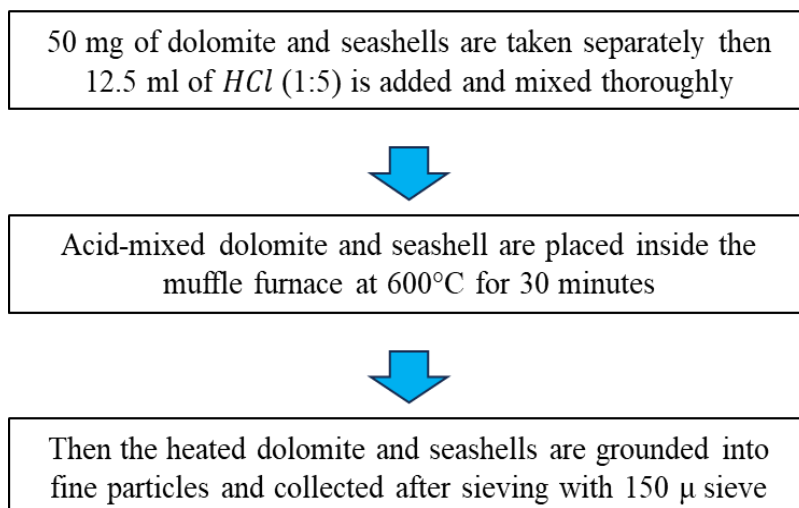
Seashell: A seashell is typically the outer skeleton of an invertebrate, lacking a backbone, and is commonly made of calcium carbonate or chitin (**Fig. 4.14**). Marine mollusk shells, primarily composed of calcium carbonate, are prevalent on beaches due to their superior durability compared to shells made of chitin. Seashells are composed of an outer layer of protein followed by an intermediate coat of calcite and a smooth inner layer of platy calcium carbonate crystal (Narayanan et al., 2006). It has important functional groups like $-\text{CH}_2$, OH , CO_2 and PO_4 which make it more effective adsorbent for the removal of both organic and inorganic pollutants (Chowdhury and Saha, 2010).



Fig. 4.14: Seashell
(Source: Printnerst)

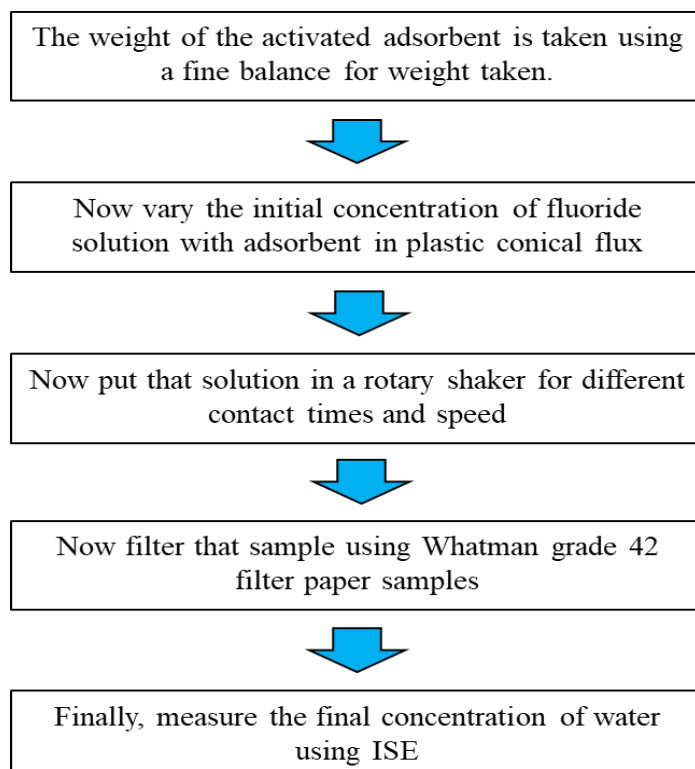
4.11.2 Pre-treatment of dolomite and seashell

The dolomite and seashell have been activated through chemically and physically before using as an adsorbent. Pre-treatment procedure for the activation process is explained below.



4.11.3 Defluoridation procedure

Activated dolomite and seashell are used for defluoridation procedure as adsorbent. The defluoridation procedure is described below.



4.11.4 Batch study for removal of fluoride

Dilution of F^- concentration varies: 20,10,5,4 and 2 mg/l

- pH varies: 3 to 11 by using $NaOH$ and HNO_3
- Adsorbent dosage varies: 5 g/l to 50 g/l
- Contact time varies: 10 to 60 min

At the end of contact time, filtrate was examined for residual F^- conc.

$$\text{Removal of } F^- (\%) = (C_0 - C_t) / C_0 \times 100\%$$

Where, C_0 = F^- concentration initially (mg/l), C_t = F^- conc. at any time (mg/l)

$$\text{Again, } q_t = (C_0 - C_t) / m_s$$

q_t = F^- adsorbed (mg) per gm of dolomite or seashell

m_s = Amount of adsorbents (g/l)

4.11.5 Adsorption isotherm

There are different types of adsorption equilibrium models exist, which differ in complexity and the number of parameters necessary. An adsorption isotherm is an equation that describes the correlation between the quantity of a substance bound to a surface and its concentration in the gas phase or solution, maintaining a constant temperature. The two models that use frequently are the Langmuir (1918) and Freundlich, (1906) isotherms.

4.11.5.1 Langmuir adsorption isotherm

The theoretical of Langmuir isotherm is the equilibrium distribution of sorbate ions between the solid and liquid phases (Kumar et al., 2011). It is assumed that the surface of the adsorbents is uniform so that all the adsorption sites are equal, adsorbed molecules will not interact, all adsorption occurs through the same mechanism, and at the maximum adsorption, only a monolayer is formed. The Langmuir isotherm model postulates homogeneous adsorption energies onto the surface and no adsorbate molecule interaction on the surface's plane where chemical bonds might form. It is also assumed that the reaction undergoes a constant free-energy change for all sites, and only one adsorbate molecule can be bound to each site, resulting in monolayer coverage. However, the Langmuir equation is typically applicable only for small concentration ranges, as it assumes a homogeneous structure of the adsorbent surface., i.e. it is assumed as all sites of adsorption energetically equal (Langmuir, 1918).

The Langmuir in its nonlinear equation is commonly expressed as follows:

$$q_e = \frac{q_e b C_e}{1 + b C_e}$$

The linear Langmuir isotherm agree with the calculation of adsorption capacities and the Langmuir isotherm in its linear form is represented by the following equation:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m} \right) + \left(\frac{1}{b q_m} \right)$$

Where, the q_m is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent, C_e is the equilibrium concentration of F^- (mg/l) and b (l/mg) is Langmuir isotherm constant that relates to the energy of adsorption and q_e is an adsorption capacity. The Langmuir constants q_m and b can be calculated from the slope and intercept of the plot C_e/q_e versus C_e respectively. The feasibility of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L (Weber and Chakkravorti, 1974) which is expressed as:

$$R_L = \frac{1}{1 + bC_0}$$

Where, b is the Langmuir isotherm constant, and C_0 is the initial concentration of F^- (mg/l). The R_L values lying between 0 and 1 indicate the conditions are favorable for adsorption, $R_L > 1$ unfavorable, $R_L = 1$ linear and $R_L = 0$ means irreversible.

Table 4.2: Favourability of Langmuir Isotherm Model

R_L	Types of Isotherms
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

4.11.5.2 Freundlich adsorption isotherm

A practical formula known as the Freundlich isotherm takes into account the energy and site heterogeneity as well as the sites' exponential distribution. The heterogeneity of the surface and the exponential distribution of sites and their energy are captured by this empirical statement. Assuming a logarithmic reduction in the enthalpy of sorption with an increase in the proportion of occupied sites, one may obtain the Freundlich isotherm. Generally, the Freundlich isotherm is more suitable for describing adsorption in aqueous solutions than the Langmuir isotherm. It has been demonstrated that the Freundlich equation can be derived from the Langmuir equation if a logarithmic decrease in the differential adsorption enthalpy with increasing solid-phase concentration is assumed, corresponding to the behaviour of a heterogeneous adsorbent surface. The Freundlich equation can only adequately represent experimental data within a certain concentration range, during which the constants hold true. Other isotherms must be constructed from tests carried out within other concentration ranges in order to describe adsorption outside of this range (Freundlich, 1906).

The Freundlich model is commonly given by the non-linear equation:

$$q_e = K_F C_{eq}^{\frac{1}{n}}$$

The Freundlich isotherm in its linear form is represented by:

$$\ln(q_e) = \ln K_f + \left(\frac{1}{n}\right) \times \ln(C_e)$$

Where q_e represents the amount of F^- adsorbed per unit weight of the sorbent (mg/g), C_e stands for the equilibrium concentration of F^- in solution (mg/l), K_F denotes a measure of adsorption capacity, and $1/n$ represents the adsorption intensity. The Freundlich isotherm constants $1/n$ and K_F can be calculated from the slope and intercept of the plot $\log q_e$ versus $\log C_e$. Values of $1/n$ ranging between 0 and 1, and n values ranging between 1 and 10, indicate favorable conditions for adsorption. The intercept of the line, K_F , roughly indicates the adsorption capacity, while the slope indicates adsorption effectiveness (Cooney, 1998).

4.12 Adsorption kinetics

To gain deeper insights into its performance and processes, adsorption should be examined from both thermodynamic and kinetic perspectives. Besides adsorption capacity, the kinetic performance of a particular adsorbent is crucial for pilot applications. The kinetic analysis may be used to calculate the solute absorption rate, which defines the residence time necessary to complete the adsorption process (Qiu et al., 2009). The kinetic information may also be used to determine the size of an adsorption equipment. Adsorption kinetics, in general, serves as the foundation for determining the performance of fixed-bed or other flow-through systems. Several mathematical models for describing adsorption data have been suggested during the last few decades, which may be broadly classed as Adsorption reaction models and adsorption diffusion models are both utilized to describe the kinetics of the adsorption process. They are, nevertheless, completely distinct in nature (Mohammed et al., 2011). Currently, adsorption reaction models have been extensively developed or utilized to describe the kinetics of adsorption (Banat et al., 2003).

Numerous adsorption methods have been researched, notably in the last fifteen years. The solute absorption rate, which determines the equilibrium time necessary to complete the adsorption reaction, may be determined using kinetic analysis. The adsorption process was characterized using three well-established kinetic models: pseudo-first order, pseudo-second order, and intraparticle diffusion (Banat et al., 2003).

4.12.1 Pseudo-first order kinetic

First-order kinetic is a chemical reaction in which the reaction rate is directly proportional to the reactants concentration. In certain conditions, the reaction rate becomes fast. The overall rate behavior of a reaction follows a first-order rate equation.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303}$$

where,

q_e = quantity for F^- adsorbed (mg/g) during equilibrium

q_t = quantity for F^- adsorbed (mg/g) at any specific time 't'

K_{ad} = Pseudo-first order kinetic constant (min^{-1})

To differentiate kinetic equations based on adsorption capacity from solution concentration, Lagergren's first-order rate equation has been termed pseudo-first order. In recent years, it has been extensively employed to describe the adsorption of pollutants from wastewater in various fields.

4.12.2 Pseudo-second order kinetic

The pseudo-second-order kinetic model is grounded on the assumption that chemical sorption or chemisorption is the rate-limiting phase and predicts behavior across the entire adsorption range. In this scenario, the adsorption rate is governed by adsorption capacity rather than adsorbate concentration (Agbovi and Wilson, 2021). In addition, the adsorption arises from the Langmuir equation. Therefore, the rate of phrase, i.e. pseudo-second order equation is

$$\frac{t}{q_t} = \frac{1}{k'_{q_e^2}} + \frac{t}{q_e}$$

Where,

q_e = quantity for F^- adsorbed (mg/g) during equilibrium

q_t = quantity for F^- adsorbed (mg/g) at any specific time 't'

K' = pseudo-second-order kinetic constant (g/mg min)

4.13 Stability test of sludge material (Bricks)

The compressive strength of bricks refers to the maximum amount of compressive load that a brick can with stand before it fails or breaks (**Fig. 4.15**). It is an essential property to consider in construction and engineering, as it indicates the brick's ability to support heavy loads without undergoing deformation or crumbling. The compressive strength of bricks can vary depending on their composition, manufacturing process, and specific use. Generally, bricks are classified

into different classes based on their compressive strength as per IS-3495:1976 (Part-1). The most common classes of bricks are based on the criteria which are given below.

First-class bricks: These bricks have a high compressive strength and are used for load-bearing structures. Their compressive strength can range from 7 to 14 N/mm² (Newtons per square millimetre) or higher.

Second-class bricks: These bricks have a lower compressive strength than first-class bricks and are used for non-load-bearing walls. Their compressive strength can range from 3.5 to 7 N/mm².

Third-class bricks: These bricks have the lowest compressive strength and are used for temporary and unimportant structures. Their compressive strength can range from 2.5 to 3.5 N/mm².



Fig. 4.15: Compressive Strength Test

It is important to note that the compressive strength of bricks is typically measured in a laboratory under controlled conditions. The bricks are subjected to a compressive force until they break, and the maximum force applied before failure is recorded as the compressive strength. Additionally, some specialized bricks, such as engineering bricks or high-strength bricks, may have even higher compressive strength, reaching values of 40 N/mm² or more. When using bricks for construction, it is crucial to consider their compressive strength and choose the appropriate class based on the specific requirements of the structure. Proper selection ensures the safety and durability of the construction project. Compressive strength has been measured by the given equation below.

$$\text{Compressive Strength} \left(\frac{\text{N}}{\text{mm}^2} \right) = \frac{\text{Applied force}}{\text{Area}}$$

The process of heating clay bricks at a high temperature is known as "firing" or "burning." This process transforms the raw clay into a durable and hardened brick. The temperature and duration of firing can significantly influence the properties of the bricks, including their strength and porosity.

Firing temperature: The firing temperature for clay bricks typically ranges between 800 to 1000 °C (1472 to 1832 °F). At this temperature range, the clay undergoes a process called vitrification, where the particles fuse together, resulting in a solid, dense structure. During the firing process, the bricks are placed inside a kiln, and the temperature is gradually raised to the

desired firing temperature. After reaching the target temperature, the bricks are held at that temperature for the required duration to ensure even firing and proper vitrification of the clay.

Firing duration: The firing duration depends on several factors, such as the type of clay used, the size of the bricks, the kiln design, and the desired properties of the final product. Generally, bricks are fired for several hours, ranging from 24 to 48 h or more placed into a heat chamber. For common clay bricks, firing for 24 h is quite common.

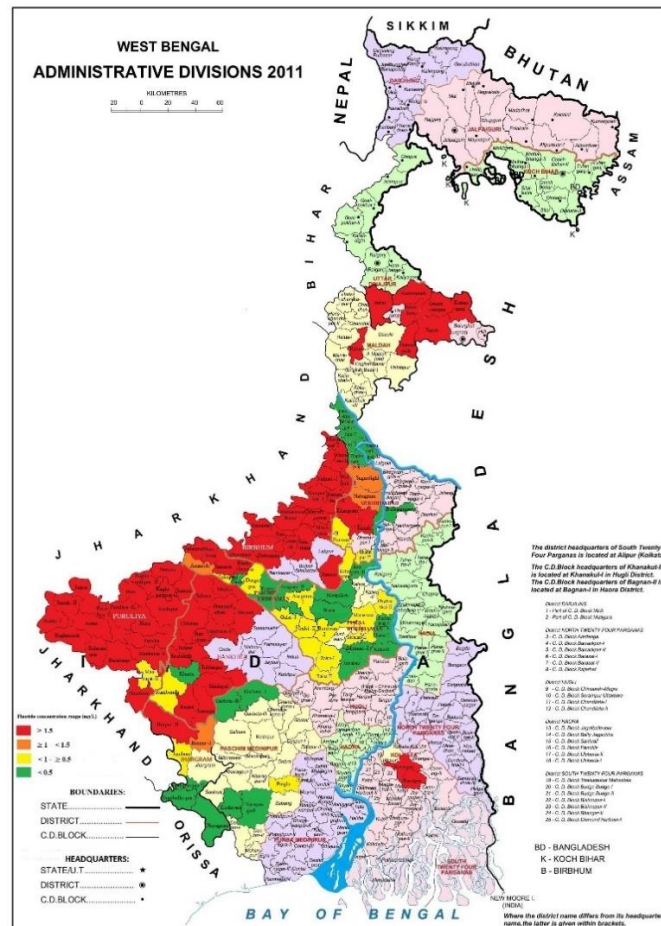
Chapter 5

Results and discussion



Objective: 1

The status of groundwater fluoride contamination sites in different parts of West Bengal



5.1 Groundwater quality evaluation

Following the Sustainable Development Goal (SDG) 6, specifically targets 6.1 and 6.4, the present study aims to support universal and equitable access to clean and inexpensive drinking water for all by 2030. Therefore, all the collected groundwater samples have been evaluated from the eight districts of West Bengal.

5.2 Fluoride distribution in groundwater from different studied areas

5.2.1 South 24 Parganas district

In South 24 Parganas district, detailed studies have been conducted in Sonarpur and Baruipur blocks to accurately assess the levels of F^- present in groundwater. These studies have been comprehensive and systematic, aiming to provide a thorough understanding of F^- concentration in these areas.

5.2.1.1 Rajpur Sonarpur Municipality in Sonarpur block

Groundwater in this area was reported as arsenic-contaminated (Rahman et al., 2003); however, the presence of a considerable amount of F^- was found in groundwater from the same region through our follow-up investigations.

5.2.1.1.1 Prevalence and distribution of fluoride and arsenic in groundwater

The distribution of F^- and arsenic along with calcium and iron in groundwater from all the 35 wards of Rajpur-Sonarpur Municipality has been depicted in **Table 5.1**. **Fig. 5.1** shows the ward-wise distribution of F^- and arsenic in groundwater ($n = 984$) with different concentration ranges (minimum to maximum) from all the studied wards. Approximately, 26% and 13% of the collected groundwater samples ($n = 984$) from all the wards contain $F^- \geq 1.0$ mg/l and ≥ 1.5 mg/l, respectively (**Fig. 5.2.a**). The F^- concentration in groundwater ≥ 1.5 mg/L has been found in 7 wards (ward numbers 6, 7, 8, 9, 21, 22 and 34) (**Table 5.1** and **Fig. 5.1**). Out of which, the presence of higher levels of F^- has been identified in four wards. Approximately, 46.5, 35.4, 35, and 33.3% of the water samples contain $F^- \geq 1.5$ mg/l in ward number 6, 7, 8, and 21, respectively. Approximately, 40.3% and 27.1% of the groundwater samples ($n = 320$) from these four wards contain $F^- \geq 1.5$ mg/l and ≥ 1.0 -1.49 mg/l, respectively (**Table 5.1**). Groundwater in seven more wards (ward numbers 1, 5, 13, 26, 32, 33, and 35) has been identified with F^- in the range of ≥ 1.0 -1.49 mg/l (**Fig. 5.1**). The maximum concentration of F^- has been found as 2.9 mg/l in ward number 21. The average concentration of iron and calcium in groundwater has been found as 3.79 ± 7.49 mg/l (range: <0.05 -50.4 mg/l, $n = 984$) and 31 ± 17.6 mg/l (range: 7.3-184 mg/l, $n = 862$), respectively.

Table 5.1: Concentrations of fluoride, calcium, arsenic, and iron in groundwater of Rajpur-Sonarpur Municipality (RSM), South 24 Parganas, West Bengal

Ward no.	Population*	Area** (km ²)	Fluoride (mg/l)			Calcium (mg/l)			Arsenic (µg/l)			Iron (mg/l)		
			No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range
1	12780	1.48	29	0.82±0.23	0.2-1.2	21	24.94±3.98	18.4-35.2	29	3.4±1.73	<3- 11.6	29	4.9±4.07	0.3-15.8
2	10389	1.21	25	0.52±0.32	0.03-0.98	14	53±13.3	40.3-84.8	25	3.8±4.28	<3- 24.4	25	6.67±10.8	<0.05-50.4
3	13208	1.53	24	0.64±0.25	0.18-0.99	20	55.8±10.7	41.3-75.3	24	4.46±4.55	<3-23.2	24	3.87±3.24	<0.05-11.1
4	15259	1.77	12	0.51±0.31	0.18-0.9	12	19.1±5.54	11.3-33.1	12	17.2±27.1	<3-97.7	12	2.52±2.91	<0.05-8.57
5	16332	1.90	24	0.81±0.29	0.07-1.2	9	25.9±7.62	14.7-42.7	24	13.3±2.74	<3-105	24	1.98±3.42	<0.05-15.4
6	11956	1.39	146	1.38±0.51	0.05-2.2	82	24.9±6.17	18.6-35.4	146	3.6±3.71	<3-44.5	146	1.15±2.05	<0.05-17.1
7	16702	1.94	96	1.18±0.67	0.02-2.5	80	20.1±7.42	14.1-46.2	96	3.34±1.33	<3-10.1	96	10.2±1.45	0.05-49.1
8	12441	1.44	57	1.09±0.62	0.3-2.5	57	29.5±8.36	19.2-49.1	57	<3	<3	57	2.78±2.9	<0.05-9.36
9	16373	1.90	21	0.75±0.38	0.26-1.5	21	27.7±7.9	16.6-50.4	21	3.36 ±0.95	<3-6.39	21	4.56±2.9	0.21-10.3
10	9404	1.09	21	0.32±0.13	0.2-0.78	21	40.4±7.26	27.6-49.2	21	10.9±8.91	<3-44	21	6.45±4.73	0.11-50.1
11	17920	2.08	21	0.42±0.15	0.23-0.69	21	38±14.6	13.2-59.7	21	14.6±12.9	<3-56.6	21	3.04±5.20	0.13-23.8
12	10837	1.26	21	0.13±0.09	0.01-0.32	21	41.6±11.7	23.6-69.2	21	6.31±6.70	<3-31.4	21	2.1±2.35	0.08-10.6
13	9363	1.09	21	0.52±0.29	0.14-1.1	21	41.3±6.58	29.6-56.2	21	3.56±2.55	<3-14.7	21	4.54±5.05	0.08-17.7
14	11500	1.33	21	0.41±0.13	0.25-0.7	21	48±4.87	39.4-56.7	21	39.9±42.8	<3-95.7	21	1.4±1.5	0.17-6.66
15	19691	2.29	21	0.42±0.14	0.2-0.64	21	51.2±5.06	38.1-58.6	21	56.3±33.5	<3-105	21	2.48±3.96	0.12-13.5
16	9014	1.05	21	0.07±0.17	0.08-0.8	21	36.7±7.55	17.4-44.7	21	3.91±2.30	<3-13.8	21	6.18±9.7	<0.05-37.8
17	10925	1.27	21	0.26±0.18	0.08-0.85	21	28.3±5.69	13.3-35.6	21	<3	<3	21	2.58±3.19	<0.05-10.4
18	7221	0.84	21	0.33±0.17	0.15-0.67	21	38.4±9.9	19.4-50.9	21	20.8±19.6	<3-65	21	4.84±7.54	<0.05-25.8
19	8363	0.97	21	0.61±0.13	0.41-0.88	21	36.9±4.8	25.8-44.8	21	28.9±24.3	<3-69.6	21	1.2±1.77	0.06-7.94

Ward no.	Population*	Area** (km ²)	Fluoride (mg/l)			Calcium (mg/l)			Arsenic (µg/l)			Iron (mg/l)		
			No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range	No. of samples (n)	Mean	Range
20	6025	0.70	21	0.37±0.23	0.03-0.9	21	25.1±15.5	7.3-40.3	21	56.8±71.7	6-213	21	6.51±8.22	<0.05-28.6
21	14672	1.70	21	1.29±0.79	0.52-2.9	21	87.8±55.5	33.1-184	21	<3	<3	21	2.81±4.67	0.09-19.6
22	15581	1.81	21	0.76±0.31	0.44-1.6	21	13.4±1.99	9.8-19.3	21	3±0.09	<3-3.43	21	5.92±9.28	<0.05-30.3
23	7738	0.90	21	0.29±0.11	0.12-0.52	21	26.3±8.66	11.3-36.5	21	37.6±53.5	<3-147	21	3.04±5.21	<0.05-18.6
24	9873	1.15	21	0.32±0.09	0.17-0.64	21	19.9±5.21	10.6-33.2	21	66.4±50.6	<3-138	21	5.56±9.7	<0.05-32.1
25	11683	1.36	21	0.51±0.14	0.32-0.94	21	16.9±4.56	8.7-23.1	21	25.7±41	<3-124	21	2.24±5.28	<0.05-22.8
26	10984	1.28	21	0.56±0.31	0.23-1.3	21	13±2.59	7.3-16.9	21	<3	<3	21	2.97±8.26	0.06-36.7
27	15856	1.84	21	0.41±0.10	0.15-0.53	21	19.5±2.55	15.2-25.1	21	<3	<3	21	0.86±1.35	<0.05-0.86
28	12511	1.45	21	0.52±0.12	0.27-0.72	21	22.5±4.49	17.7-32.2	21	3.2±1.02	<3-8.03	21	0.55±0.47	0.1-1.54
29	11118	1.29	25	0.62±0.18	0.23-0.89	21	33.7±8.55	22.4-49.3	25	4.3±4.56	<3-14	25	4.82±4.21	0.1-43.2
30	10349	1.20	21	0.28±0.20	0.03-0.72	21	32.5±11.8	18.8-53.5	21	25.9±41.6	<3-119	21	1.38	0.07-29
31	12694	1.47	21	0.53±0.18	0.21-0.81	21	27±9.86	15.3-43.3	21	14.5±26.3	<3-119	21	4.19±3.47	0.05-25.9
32	11809	1.37	21	0.82±0.36	0.26-1.4	21	27.7±6.52	18.7-44.9	21	11.7±28.4	<3-119	21	3.64±3.32	0.05-25.9
33	11603	1.35	21	0.88±0.21	0.58-1.4	21	28.1±4	21.3-38.5	21	4.72±4.19	<3-16.8	21	4.6±3.57	<0.05-27.5
34	11116	1.29	21	0.62±0.46	0.22-2.4	21	34±7.96	17.3-49.6	21	3.39±1.20	<3-7.66	21	1.87±2.35	<0.05-8.06
35	11078	1.29	21	0.39±0.33	0.06-1.4	21	29.9±5.27	19.8-38.7	21	3.71±2.39	<3-13	21	0.82±1.51	<0.05-6.45
Total	424368	49.26	984	0.75±0.55	0.01-2.9	862	31±17.6	7.3-184	984	11.3±25.9	<3-213	984	3.79±7.49	<0.05-50.4

#The detection limit of Fluoride, Calcium, Arsenic, and Iron are 0.001 mg/l, 0.3 µg/l, 3 µg/l, and 0.05 mg/l, respectively.

*Source: <https://www.censusindia2011.com/west-bengal/south-twenty-four-parganas/no-sub-district/raipur-sonarpur-m-population.html>

** the area has been calculated by this formula: (Each ward population) / (Total ward population) × Total area of 35 wards

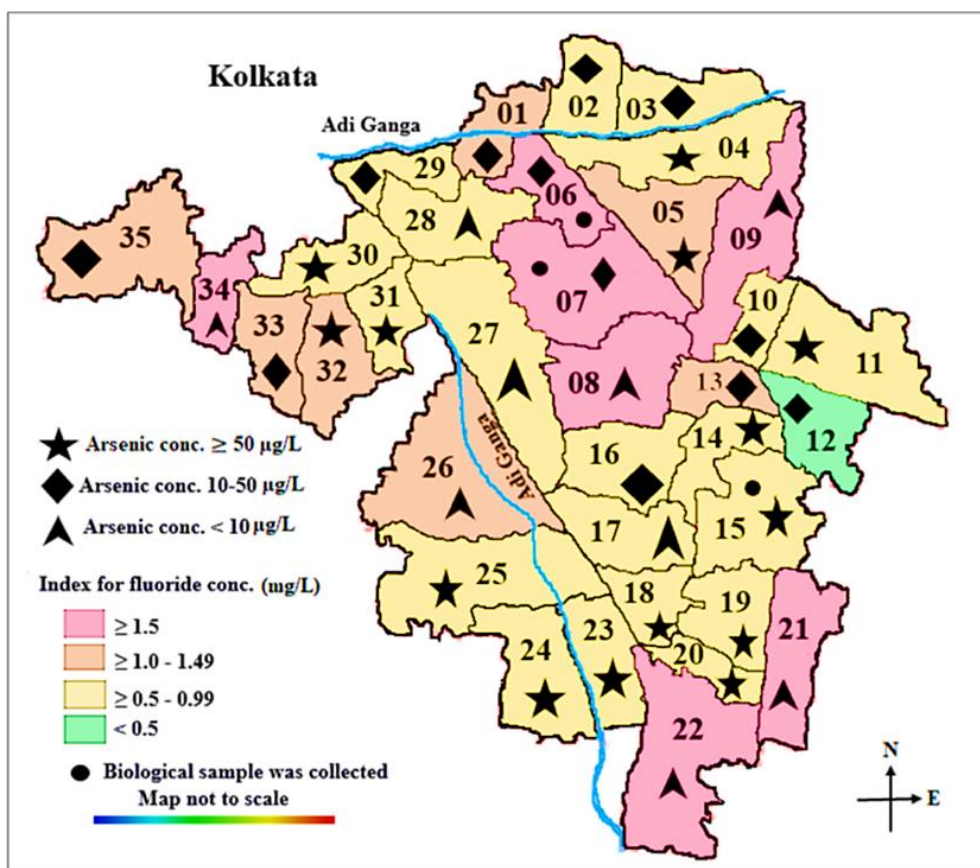


Fig. 5.1: Ward-wise distribution of fluoride (F^-) and arsenic (As) in groundwater ($n = 984$) with different concentration ranges (minimum to maximum) from all the 35 wards in Rajpur-Sonarpur Municipality (RSM)

Approximately, 16% of the groundwater samples ($n = 984$) contain arsenic $\geq 10 \mu\text{g/l}$ (Fig. 5.2.b). However, arsenic concentration in groundwater $> 10 \mu\text{g/l}$ has been found in 26 wards from the studied areas (Table 5.1 and Fig. 5.1). Approximately, 44% and 25% of the groundwater samples ($n = 288$) from 14 wards have been identified with the presence of higher levels of arsenic $\geq 10 \mu\text{g/l}$ and $\geq 50 \mu\text{g/l}$, respectively. Approximately, 62% and 57% of the groundwater samples contain arsenic $\geq 50 \mu\text{g/l}$ in ward number 15 and 24, respectively. Distribution of $F^- \geq 1.5 \text{ mg/l}$ (mean = $1.9 \pm 0.3 \text{ mg/l}$, range: 1.51-2.9 mg/l, $n = 122$) and $< 1.5 \text{ mg/l}$ (mean = $0.6 \pm 0.4 \text{ mg/l}$, range: 0.01-1.49 mg/l, $n = 862$), and arsenic $\geq 10 \mu\text{g/l}$ (mean = $56.2 \pm 43.7 \mu\text{g/l}$, range: 10.1-213 $\mu\text{g/l}$, $n = 157$) and $< 10 \mu\text{g/l}$ (mean = $3.3 \pm 1.1 \mu\text{g/l}$, range: < 3 -9.7 $\mu\text{g/l}$, $n = 827$) have been observed in groundwater ($n = 984$). Occurrence of both F^- and arsenic in groundwater has been found from only two wards (ward number 6 and 7) above their recommended values in drinking water, i.e. 1.5 mg/l and 10 $\mu\text{g/l}$, respectively (Table 5.1). Although, the mean concentration of arsenic in groundwater ($n = 242$) from these two wards has been found in lower level (mean = 3.5 $\mu\text{g/l}$, range: < 3 -44.5 $\mu\text{g/l}$), compared to the higher

level of F^- (mean = 1.3 mg/l, range: 0.02-2.5 mg/l). Groundwater (n = 137) in another six wards (ward number 1, 5, 13, 32, 33, and 35) have been found with F^- (mean = 0.72 ± 0.28 mg/l, range: 0.06-1.4 mg/l) and arsenic (mean = 6.68 ± 6.59 μ g/l, range: <3-119 μ g/l) concentration ≥ 1.0 mg/l and ≥ 10 μ g/l, respectively.

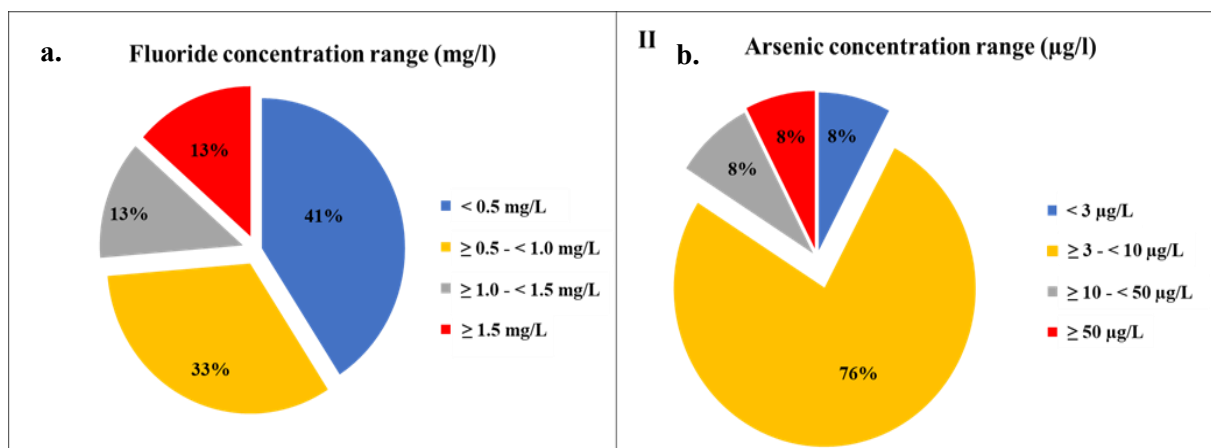


Fig. 5.2: Distribution (%) of (a) fluoride and (b) arsenic in groundwater (n = 984) with different concentration ranges (minimum to maximum) from 35 wards in Rajpur-Sonarapur Municipality

Existence of these two contaminants in groundwater has been observed in another five wards (ward number 2, 3, 4, 20, and 25) with F^- and arsenic concentration ≥ 0.9 mg/l and ≥ 10 μ g/l, respectively. Interestingly, existence of both F^- and arsenic ≥ 1.0 mg/l and ≥ 10 μ g/l has been identified only in nine groundwater samples in the depth range of 24.4-76.2 m from the four wards (ward number 1, 5, 6, and 7) in the studied areas. Mean concentrations of F^- and arsenic in these nine groundwater samples were 1.29 mg/l (range: 1.1-1.5 mg/l) and 27.7 μ g/l (range: 10.1-105 μ g/l), respectively. Considerable amounts of F^- (range: 0.02-2.5 mg/l) and arsenic (range: <3-119 μ g/l) have been observed in the collected groundwater samples (n = 295) from these four wards, which further supports the presence of these two toxic contaminants in groundwater from the studied areas. Distribution of F^- and arsenic in groundwater from the studied area is shown (Table 5.2) in comparison with other studies, reported from all over the world.

Table 5.2: World-wide scenario of F⁻ and arsenic distribution in groundwater and health risk assessment in comparison with the present study in Rajpur-Sonarpur Municipality.

Geographical location of both affected areas	Climate type/ Prevailing geological condition	No. of water sample (n)	F ⁻ (mg/l) (Range)	As (µg/l) (Range)	Correlation between F ⁻ & As (R ²)	NCR Health risk by fluoride	NCR/CR Health risk by Arsenic	References
Tabalaopa–Aldama, Aldama–Dolores and Laguna de Hornigas, Chihuahua, Mexico	Arid and oxidizing condition	37	1.06-4.55	4-39	0.72	A	NCR (A)	Reyes-Gomez et al., 2013
Laguna El Cuervo basin, northern Mexico	Arid and oxidizing condition	35	1.1-6.8	4-117	0.55	NA	NA	Reyes-Gomez et al., 2015
Northern Ningxia, Dawukou, northwest China	Alluvial and lacustrine deposition	80	0.06-2.8	0.25-22	-	A	CR (A)	Chen et al., 2011
Central-West Region, Chaco Province, northern Argentina	Semiarid and subtropical continental region	207	0.1-4.2	4-800	0.04	A	CR (A)	Buchhamer et al., 2012
Peninsula, Geumsan County, Korea	Igneous rocks, and quaternary alluvial deposits	150	<0.1-7.54	<5-113	-	NA	NA	Ahn, 2012
Brahmaputra flood plains, Assam, India	Alluvial flood plain	164	0.01-1.31	0.08-22.1	0.03	A	CR(A)	Das et al., 2018
Yuncheng Basin, China	Semiarid	73	0.31-14.1	0.24-154	0.99	NA	NA	Currell et al., 2011
Lahore and Kasur districts, Pakistan	Semiarid-condition and tropical desert	24	0.16-21.1	10-530	0.12	NA	NA	Farooqi et al., 2007a
Coronel Moldes, Argentina	Humid and Arid	40	0.5-12	0-250	0.84	NA	NA	Gomez et al., 2009
Chaco-Pampean plain, Argentina	Semiarid-arid dry climate	167	0.05-7.34	<10-5300	0.66	A	CR (A)	Nicolli et al., 2012

Geographical location of both affected areas	Climate type/ Prevailing geological condition	No. of water sample (n)	F-(mg/l) (Range)	As (µg/l) (Range)	Correlation between F & As (R ²)	NCR		NCR/CR		References
						Health risk by fluoride	Health risk by Arsenic	Health risk by fluoride	Health risk by Arsenic	
Mankyong River floodplain, Korea	Temperate and reducing floodplains environment	72	0.02-2.747	<1-100	0.39	NA	NA	NA	NA	Kim et al., 2012
Kourikasa, Rajnandgaon district, Chhattisgarh, India	Hot and Humid	20	3.7-27	148-985	0.04	A	CR (A)	CR (A)	CR (A)	Patel et al., 2017
Dhipu, Assam, India	Humid	38	0-1	0-6	0.02	NA	NA	NA	NA	Kumar et al., 2016
Tharparkar district, Pakistan	Arid and tropical desert	20	1.27-43	117-2580	0.64	A	CR (A)	CR (A)	CR (A)	Brahman et al., 2013
Brahmaputra flood plains, northeast India	Alluvial flood plain	40	ND-14.4	0.18-22.1	0.13	NA	NA	NA	NA	Das et al., 2018
Punjab province, Lahore, southeast Pakistan	Arid and Semiarid condition	147	0.38-22.8	1-2400	0.02	NA	NA	NA	NA	Farooqi et al., 2007b
Tehsil Mailsi, Pakistan	Semiarid and alluvial plain	52	5.5-29.6	5-507	0.37	A	CR (A)	CR (A)	CR (A)	Rasool et al., 2015
Chihuahua, Mexico	Semiarid and alluvial condition	1119	0.05-11.8	0.1-419	0.74	A	CR (A)	CR (A)	CR (A)	González-Horta et al., 2015
Dharmanagar region, north Tripura, India	Alluvial plain	71	<0.005-4.8	<3-44	0.6	A	NCR (A)	NCR (A)	NCR (A)	Bhattacharya et al., 2020
Rajpur-Sonarpur Municipality, South 24 Parganas, West Bengal,	Alluvial plain	984	0.01-2.9	<3-213	0.301	A	NCR (A), CR (A)	NCR (A), CR (A)	NCR (A), CR (A)	Present study

5.2.1.1.2 Spatial distribution of fluoride and arsenic

Fig. 5.3 represents the spatial distribution of fluoride (F^-) and arsenic (As) concentration in groundwater from the 35 wards through different colour gradients. The lowest concentration of F^- 0.01 mg/l (Lat: 22°26' 10.73", Long: 88°26' 15.20") is found in the groundwater from ward number 12 and the highest one is found to be 2.9 mg/l (Lat: 22°24'45.87", Long: 88°26' 19.23") from ward number 21 (**Fig. 5.3.a**). About 16% of the groundwater samples from all 35 wards have been found to exceed the permissible limit of arsenic. The highest concentration of arsenic is found to be 213 μ g/l (Lat: 22°24'36.30", Long: 88°25'22.72") from ward number 20 (**Fig. 5.3.b**), which is approximately 21 times higher than the recommended value of arsenic in drinking water.

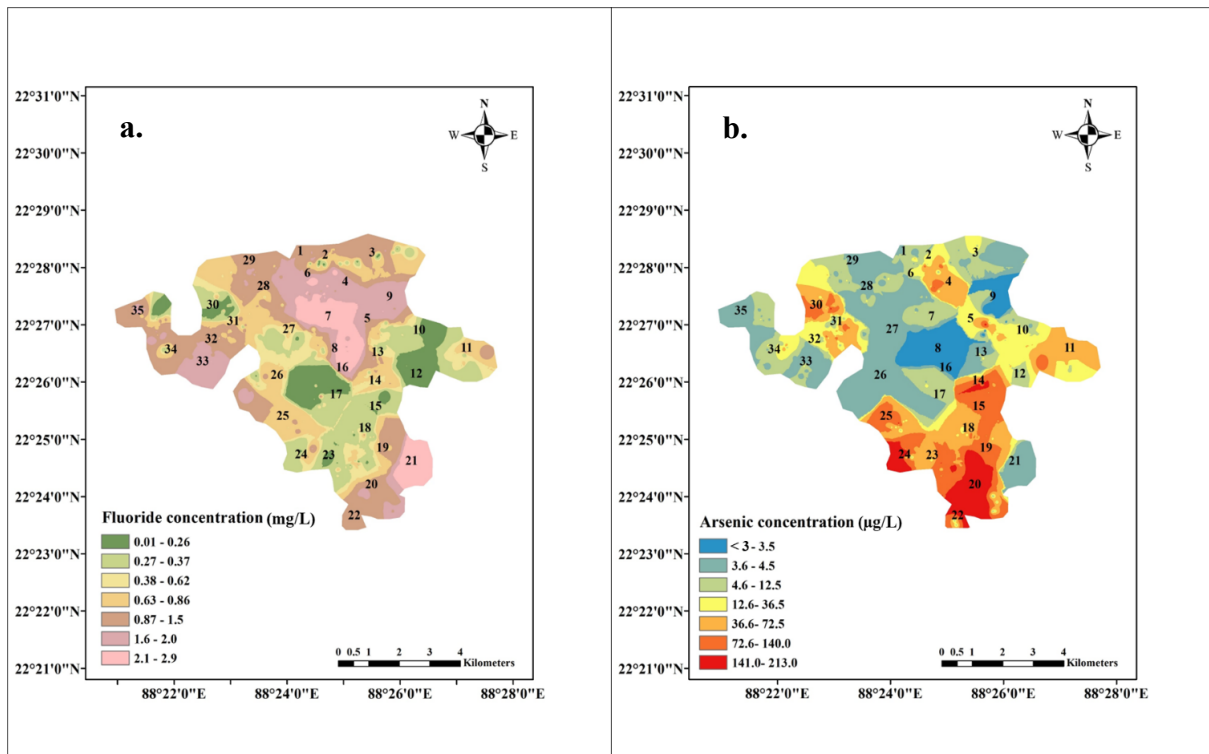


Fig. 5.3: Spatial distribution of **a.** fluoride and **b.** arsenic concentration in groundwater

5.2.1.1.3 Depth wise distribution of fluoride and arsenic

Stacked-bar distribution (%) of tube-well water samples having $F^- \geq 1.5$ mg/l and < 1.5 mg/l, and arsenic ≥ 10 μ g/l and < 10 μ g/l with different depth range and has been established in **Fig. 5.4**. About 10.1% and 1.32% of the groundwater samples ($n = 984$) have been found with $F^- \geq 1.5$ mg/l in the depth range > 24.4 -30.5 m and > 30.5 -45.7 m, respectively. About 1.33%, 2.85% and 10.5% of groundwater samples ($n = 984$) have been found with arsenic ≥ 10 μ g/l in the depth range < 15.2 m, > 15.2 -24.4 m and > 24.4 -30.5 m, respectively. So, both the F^- and

arsenic concentrations in groundwater were highest in the depth range of 24.4-30.5 m. The presence of F^- and arsenic in groundwater had been decreased considerably below 152 m. Alabdulaaly et al. (2013) reported that comparatively higher levels of F^- were found in relatively less deep wells in Saudi Arabia. About 59% and 28% of the groundwater samples with an arsenic (As) above 50 $\mu\text{g/l}$ were found in the depth zone less than 30.5 m and 33.5 m in Bangladesh ($n = 7800$) and West Bengal, India ($n = 55,000$), respectively (Roychowdhury et al., 1999). Thus, the presence of F^- and arsenic in groundwater above their recommended values from the same depth layers may possess serious health risk to the studied populations exposed through the drinking of contaminated water.

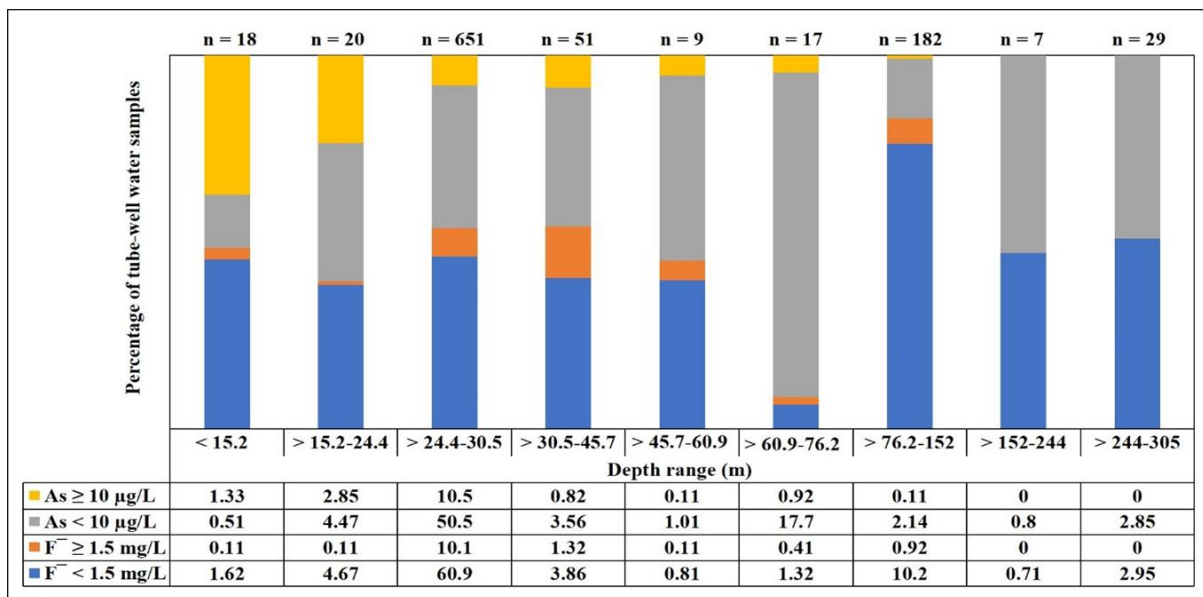


Fig. 5.4: Stacked-bar distribution (%) of tube-well water samples having F^- (≥ 1.5 and < 1.5 mg/l) and As (≥ 10 and < 10 $\mu\text{g/l}$) with depth range (< 15.2 -305 m) from Rajpur-Sonarpur Municipality.

5.2.1.1.4 Correlation study among the parameters (F^- , Ca, As, and Fe)

A strong correlation between Ca and Fe in groundwater was reported by other studies (Gebregiorgis et al., 2020). The correlation matrix of the four elements has been shown in **Fig 5.3**. The moderate positive relationship between As and Fe ($r = 0.39$) also indicates the geogenic source of As by absorption and desorption from metallic oxide (Fe hydroxide) under varying acidic and alkaline conditions, which was supported by the other studies (Alvarez and Carol, 2019; Farooqi et al., 2007a, b). The positive correlation between As and F^- ($r = 0.30$) in this study suggested the presence of these two toxic contaminants in groundwater due to their

low absorption and desorption from their respective minerals, which was supported by Das et al. (2018) and Farooqi et al. (2007a). A significant correlation between F^- and As in groundwater has been reported from other studies in Mexico ($r = 0.72, 0.55$, and 0.74) (González-Horta et al., 2015; Reyes- Gomez et al., 2013, 2015); China ($r = 0.99$ and 0.303) (Currell et al., 2011; Khair et al., 2014); Argentina ($r = 0.84$ and 0.66) (Gomez et al., 2009; Nicolli et al., 2012); Korea (0.39) (Kim et al., 2012); Pakistan (0.64 and 0.37) (Brahman et al., 2013; Rasool et al., 2015) and India ($r = 0.60$) (Bhattacharya et al., 2020) (Table 5.2). Fluoride found in groundwater aquifers primarily stems from various sources and processes, including the dissolution of calcium fluoride (CaF_2) and anthropogenic activities such as the application of fertilizers and air pollution. (Farooqi et al., 2007a). In the lower GMB flood plain (Bengal basin), dissolved F^- in groundwater comes mainly from the weathered fluorite mineral (CaF_2) (Datta et al., 2000). The negative relationship among F^- and Ca ($r = -0.33$, $p < 0.05$) (Table 5.3) indicates the increasing F^- / Ca ratio in solution due to the fluorite saturation with respect to calcite which minimizes the calcium level and allowing the entry of more F^- in groundwater. So, the interplay between F^- and Ca was mainly controlled by the presence of calcite and fluorite minerals (Brahman et al., 2013).

Table 5.3: Correlation matrix of the four elements

	F^-	Ca	As	Fe
F^-	1			
Ca	-0.329	1		
As	0.301	0.138	1	
Fe	0.482	0.604	0.394	1

5.2.1.1.5 Principal component analysis (PCA)

The data sets of F^- , As along with Ca and Fe present in groundwater from the studied areas were plotted through Principal Component Analysis (PCA). The two Principal components explained 81.5% of the total variation cumulatively, out of which PC1 and PC2 contributed 47.5% and 33.9%, respectively (Table 5.4).

Table 5.4: Eigenvalue of correlation matrix

Sl. No.	Principal component	Eigenvalue	Percentage of variance	Cumulative
1	PC 1	1.901	47.53%	47.53%
2	PC 2	1.358	33.97%	81.50%
3	PC 3	0.692	17.32%	98.82%
4	PC 4	0.047	1.18%	100%

Principal component analysis for the relationship between different elements in groundwater has been shown in **Fig. 5.5**. The biplot was constructed with nine observational levels (depth ranges) and four variables (F^- , As, Ca, and Fe). All the trace elements were clubbed into two groups (Fig. 5.5). Group 1 in PCA biplot was formed between F^- and As. Numerous additional research have observed similar types of observations in the Brahmaputra flood plain, India (Das et al., 2018) and Mexico (Alarcón-Herrera et al., 2020). Group 2 in the PCA biplot was formed between Ca and Fe. The vector lines of Ca and Fe in PCA biplot were in very close proximity indicating a strong correlation between these two elements.

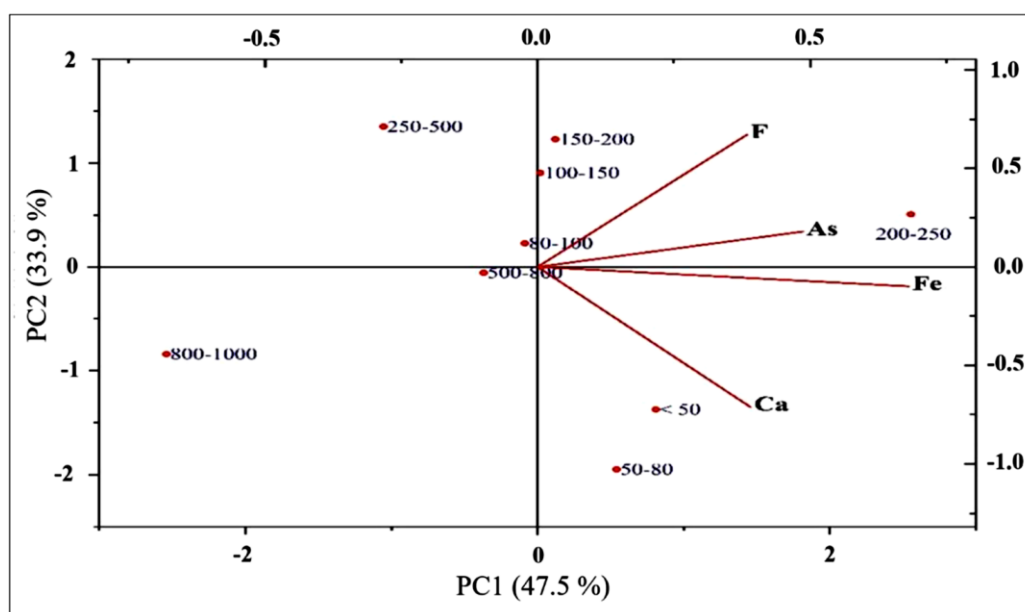


Fig. 5.5: Principal Component Analysis (PCA) showing the relationship between four different elements present in groundwater.

5.2.1.1.6 Dendrogram generated through cluster analysis (CA)

Cluster analysis (CA) was performed for four elements and nine depth ranges by Ward's method using square Euclidean distances as similarity index (Davies, 1986). The results were introduced in a dendrogram (**Fig. 5.6**), where the different depth ranges were placed in two main clusters. A similar kind of clustering was reported by Chen et al. (2008) in their study in Hangzhou, China. All these clusters were formed due to the presence of different concentrations of As, F^- , Fe, and Ca. The four elements in groundwater are likely to be concentrated mostly in the following depth ranges: 30.5-60.9 m, 60.9-152 m and 152-305 m which are shown by three consecutive clusters. Maximum number of water samples with F^- and As concentrations above their respective permissible limits in drinking water have been found in the depth range of 24.4-30.5 m; however, both the toxic contaminants were safe below

152 m (Fig. 5.6). Low concentrations of calcium are predominantly attributed to carbonate precipitation and progressive mineralization occurring as chemical facies change along the depth-wise flow path in groundwater (Tirumalesh et al., 2007). Based on the findings from PCA and CA in this study, both As and F^- might be leaching from geogenic sources. Desorption from clays, Fe-oxides, and evaporation may account for arsenic in granular aquifers (Armienta and Segovia, 2008) as well as organic content in sediments along with land-use pattern are some other possible significant factors governing the mobility of arsenic in alluvial aquifers (Bhattacharya et al., 1997). Das et al. (2018) stated that no significant relation was obtained between all the elements at different depths of the water columns in the Brahmaputra river flood plain.

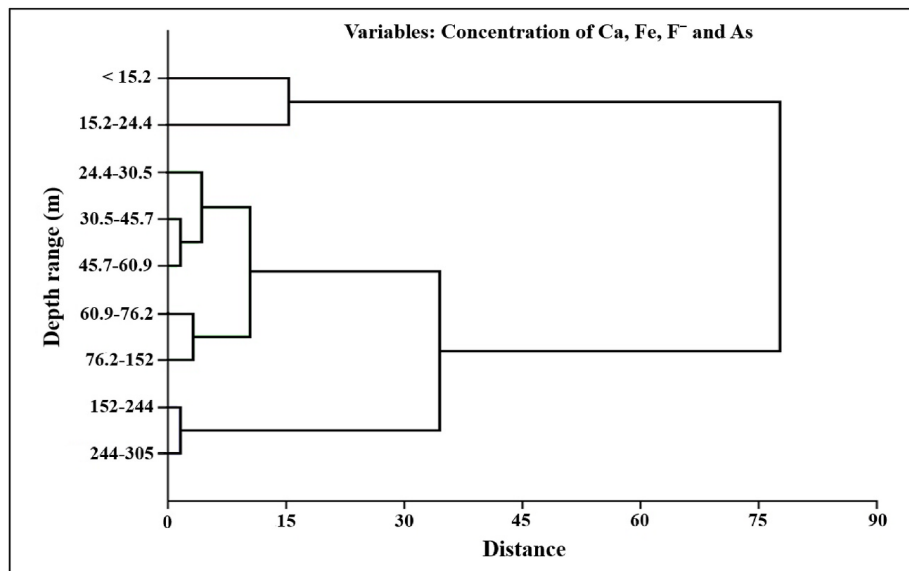


Fig. 5.6: Dendrogram generated through Cluster Analysis (CA) on concentrations of Ca, Fe, F^- and As for different depth layers (<15.2-305 m)

5.2.1.2 Gram-panchayats and municipality in Sonarpur block

All studied areas of Sonarpur block have been highlighted in this study.

5.2.1.2.1 Groundwater fluoride distribution scenario Sonarpur block

The distribution of F^- in groundwater, with a sample size of 1272, across the entire study area has been analysed to assess its suitability for drinking water. The findings are presented in **Table 5.5**.

Table 5.5: Distribution of F^- (mg/l) in groundwater from Sonarpur block, South 24 Parganas district

Gram-panchayat / Municipality	Sample Number (n)	Mean (mg/l)	Standard deviation (S. D.)	Range (mg/l)	CV%
Bonhugly I	43	0.59	0.31	0.13-1.2	52.54
Bonhugly II	9	0.45	0.21	0.16-0.78	46.66
Poleghat	11	0.17	0.11	0.06-0.44	64.70
Langalberia	22	0.35	0.06	0.23-0.49	17.14
Sonarpur II	21	0.18	0.13	0.1-0.62	72.22
Kalikapur I	35	0.48	0.19	0.22-0.76	39.58
Kalikapur II	12	0.37	0.2	0.16-0.97	54.05
Pratapnagar	46	0.51	0.25	0.11-1.16	49.01
Kamarbad	37	0.39	0.18	0.11-0.81	46.15
Kheadaha I	31	0.58	0.23	0.24-1.09	39.65
Kheadaha II	21	0.47	0.16	0.02-0.69	34.04
Rajpur-Sonarpur Municipality	984	0.75	0.55	0.01-2.9	73.33
Total	1272	0.44	0.21	0.01-2.9	47.63

Fig. 5.7.a represents the distribution percentage of F^- in groundwater from the studied area with different concentration ranges. Approximately, 10 and 20% of the collected groundwater samples contain $F^- > 1.5$ and >1 mg/l, respectively (**Fig. 5.7.b**) in the Sonarpur block. About 10% of the groundwater samples were found with $F^- > 1.5$ mg/l from Rajpur Sonarpur Municipality (Fig. 5.7.a). Moreover, 25, 8, and 3% of the groundwater samples were found in the range >1 - <1.5 mg/l from three gram-panchayats, namely Bonhugly I ($n = 43$), Pratapnagar ($n = 46$) and Kheadaha I ($n = 31$), respectively (Fig. 5.7.a). The plausible explanation behind the groundwater F^- distribution pattern in the Rajpur Sonarpur Municipality area is mainly based on the hydrogeological characteristics of the host mineral or rock. Moreover, the shallow groundwater level of the lower Gangetic belt has a significant risk of F^- mobilization in the depth zone of 0-30.5 m (Datta et al., 2000).

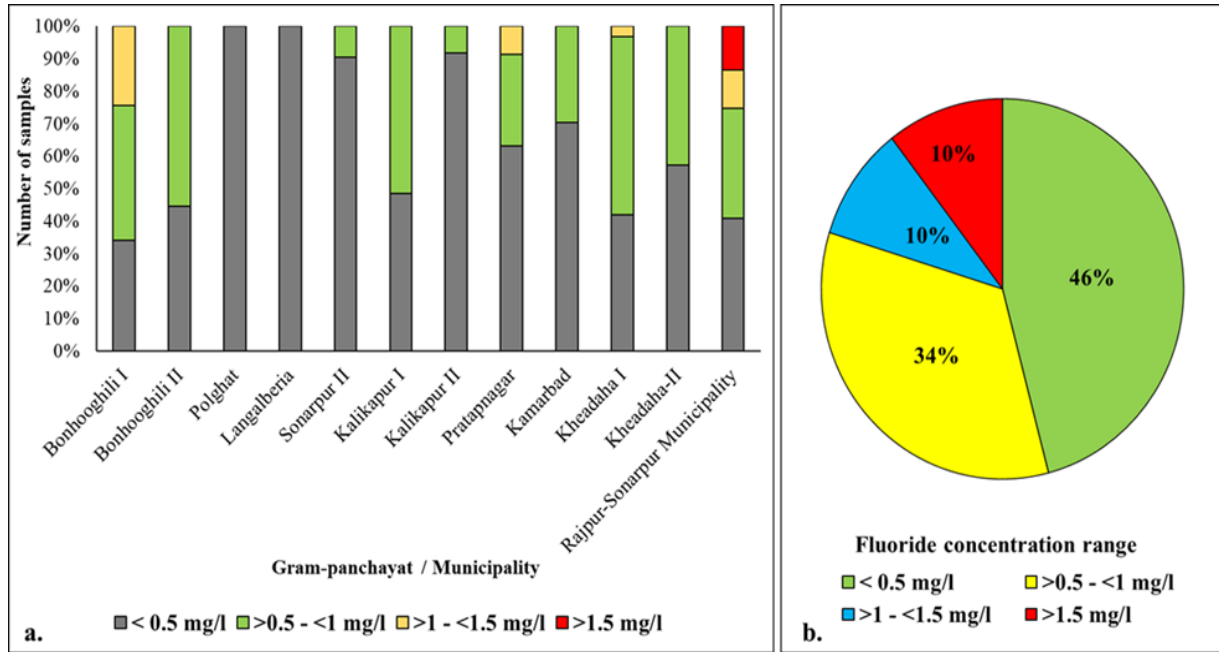


Fig. 5.7: a. Percentage of fluoride concentration in groundwater samples (n = 1272) from 11 gram-panchayats and Rajpur-Sonarpur municipality area of Sonarpur block, **b.** distribution of fluoride concentration ranges in groundwater from Sonarpur block

5.2.1.2.2 Spatial distribution of fluoride

The spatial distribution pattern of F^- concentration in groundwater from the Sonarpur block has been demonstrated in **Fig. 5.8** by using different colour gradients and a densely orange color distribution pattern highlighted the highly F^- contaminated areas in the study area. Boalia (Lat: 22°27'29", Long: 88°24'36") and Narendrapur (Lat: 22°27'16.06", Long: 88°24'40.73") were identified as the highly F^- contaminated areas in the studied areas. The average F^- in groundwater from the entire studied area was found to be 0.44 mg/l (range - 0.01-2.9 mg/l, n = 1272) (Table 5.5). Likewise, the spatial uncertainty of F^- depends on the geological conditions that play an important role in the aquifer level (Parganas et al., 2015). The alluvial and sandy loam nature of the soil in the studied area might be responsible for fluoride mobilization in groundwater which is supported by other study (Su et al., 2019).

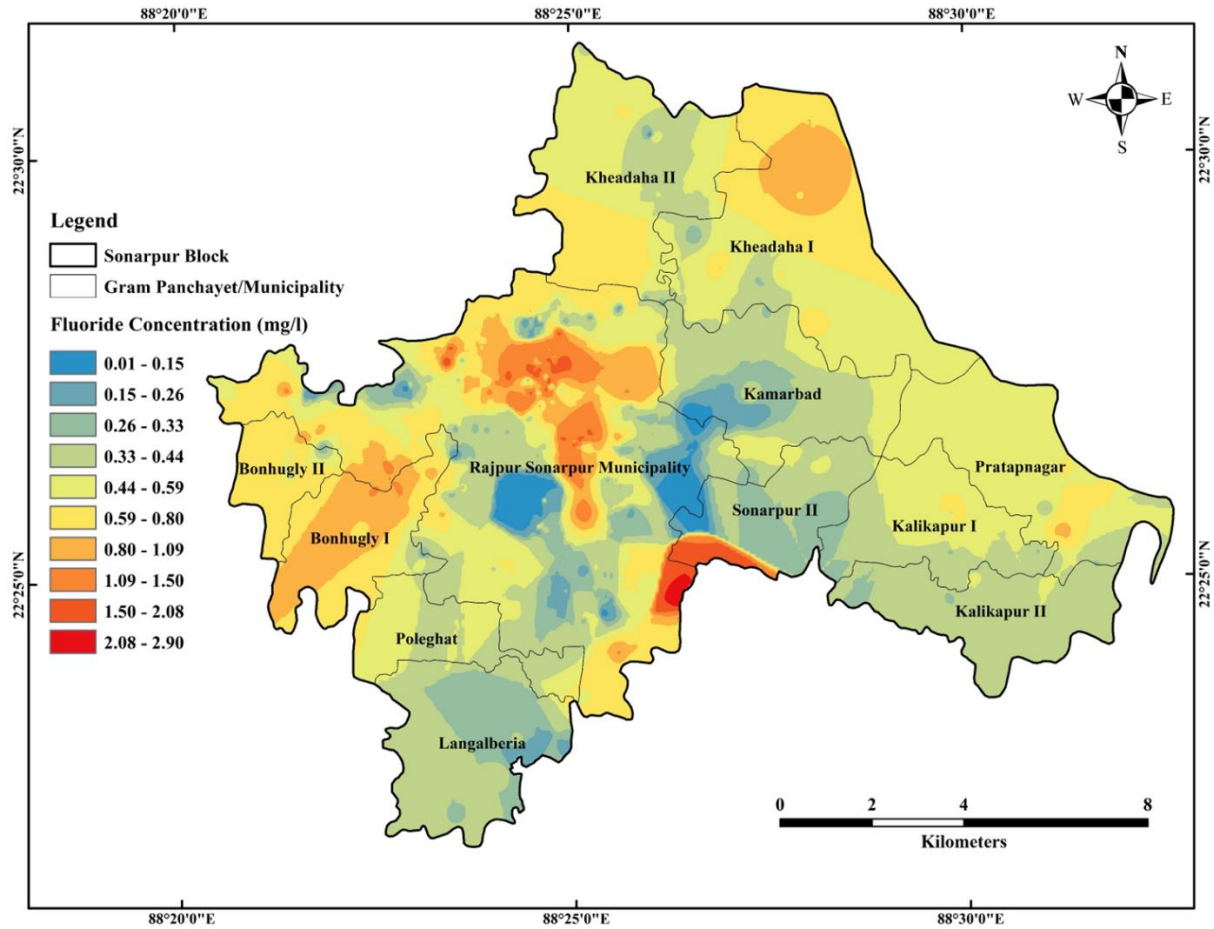


Fig. 5.8: Spatial distribution of fluoride concentration in groundwater of Sonarpur block

5.2.1.2.3 Single factor pollution index for fluoride

The contamination measurement has been conducted by using the single factor pollution index system for the groundwater quality of the Sonarpur block based on F^- concentration in groundwater allowing classification in a systematic way (**Fig. 5.9**). About, 14% of groundwater samples have been shown under the second group/class: $1.0 \leq I_i < 3.0$ (moderate contamination factor) in Rajpur-Sonarpur Municipality, and the maximum pollution index was found to be 1.9. Groundwater samples from the other gram-panchayats are classified as the first group/class: $I_i < 1.0$ (low contamination factor) (pollution index ranged from 0.01 to 0.84). About 10% of groundwater samples from the entire studied area are represented under the second group/class: $1.0 \leq I_i < 3.0$ (moderate contamination factor) (pollution index ranged from 1 to 1.9) which is well supported by other studies (Yu et al., 2018, Rehman et al., 2018). Moreover, the pollution index represents the level of F^- toxicity, which is significantly harmful to human health based on the groundwater contamination effects. The moderate contamination

class of F^- toxicity in groundwater was found to be extremely high in certain locations from the study area.

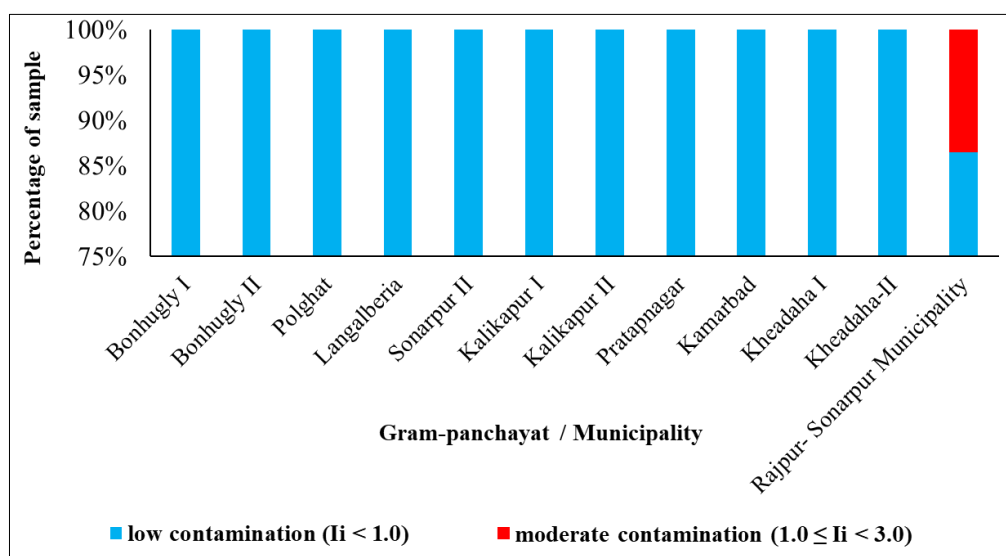


Fig. 5.9: Single factor contamination index for fluoride from 11 gram-panchayat and municipality areas of Sonarpur block

5.2.1.2.4 Mechanism of groundwater chemistry

The results of different physicochemical parameters in 20 fluoridated groundwater samples from the highly F^- exposed area (Boalia and Narendrapur) have been shown in **Table 5.6**. The mean pH value was 8.12 ranging from 7.89 to 8.43, and this suggests that the groundwater exhibited an alkaline nature. EC values ranged from 856 to 1700 $\mu S/cm$ (mean: 1051 $\mu S/cm$) which denotes the variation in total electrical capacity with different geochemical activities. The mean TDS value was 832 mg/l (range: 650-1084 mg/l) which indicates a good variation in the groundwater saline condition. The mean TDS value was 832 mg/l (range: 650-1084 mg/l) which indicates a good variation in the groundwater saline condition. Mean TDS values in groundwater were ~1.5 fold higher compared to the acceptable limit (500 mg/l) recommended by WHO. Higher TDS value influenced the significant role of groundwater quality in the studied areas. The correlation matrix of the physicochemical parameters of fluoridated groundwater samples has been shown in **Fig. 5.10**. A strong positive correlation has been observed between TDS vs EC ($r = 0.91$) and TDS vs Cl^- ($r = 0.97$) (Fig. 5.10). Multiple studies have been undertaken to establish the exact mathematical correlation between Total Dissolved Solids (TDS) and Electrical Conductivity (EC), facilitating the convenient measurement of one parameter based on the other. However, it is not necessarily linear depending on the particular

activity of the dissolved ions, but the relationship is represented by the following equation: $\text{TDS (mg/l)} = k \times \text{EC (mS/cm)}$. The factor (k) is determined as the ratio of TDS/EC, where k value varies for different types of water samples.

Table 5.6: Physico-chemical parameters in fluoridated groundwater samples from the highly fluoride exposed area (Boalia and Narendrapur) in Sonarpur block

Parameters	Mean	Standard deviation (S. D.)	Range	CV%
pH	8.12	0.14	7.89-8.43	1.82
TDS (mg/l)	832	141	650-1084	16.9
TSS (mg/l)	93	63.3	34-180	68.04
EC ($\mu\text{S/cm}$)	1051	171	856-1700	16.2
F^- (mg/l)	1.81	0.10	1.65-2.02	5.81
Cl^- (mg/l)	172	65.2	105-351	37.81
CO_3^{2-} (mg/l)	4.9	3.52	2-14	71.89
HCO_3^- (mg/l)	54.2	2.93	50-61	5.41
NO_3^- (mg/l)	5.84	3.37	2.06-13.71	57.67
SO_4^{2-} (mg/l)	10.3	6.57	0.63-20.81	63.34
Na^+ (mg/l)	227	10.2	213-243	4.49
K^+ (mg/l)	0.63	0.14	0.5-0.9	23.08
Ca^{2+} (mg/l)	23.6	4.34	18.2-33.5	18.39
Mg^{2+} (mg/l)	0.69	0.21	0.3-1.3	31.50
Fe (mg/l)	0.57	0.36	0.08-1.35	64.36

McNeil and Cox also demonstrated that the range of ratio varied from 0.5 to 1.0 in freshwater samples (McNeil and Cox, 2000). Similarly, in this study, the estimated ratio of TDS and EC in groundwater samples was found in the range of 0.69 to 0.85. The average Na^+ value was found to be 227 mg/l (range: 213-243 mg/l) and the average Cl^- value was found to be 172 mg/l (range: 105-351 mg/l) in fluoridated groundwater (Table 5.6). Cl^- plays a significant role as an influencer for TDS when groundwater becomes saline condition (Feng et al., 2020). TDS value is influenced by Cl^- ions, and it provides an indication of the salinity in groundwater. Good positive correlation was found between Na^+ and Cl^- ($r = 0.75$) which signifies the groundwater was strongly saline in condition (Fig. 5.10). Mean Na^+ and Cl^- concentrations were found higher compared to Ca^{2+} (Mean: 23.6 mg/l, range: 18.2-33.5 mg/l). The average Mg^{2+} concentration was 0.69 mg/l and ranged from 0.3 mg/l to 1.3 mg/l. The mean HCO_3^- concentration was found higher compared to the mean CO_3^{2-} concentration. Moreover, the average cationic and anionic distribution in groundwater was found in a sequence of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Fe}$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{CO}_3^{2-} > \text{F}^-$, respectively which express the groundwater quality in the studied area. The similar kind of ionic distribution was reported in other studies from lower Gangetic plain.

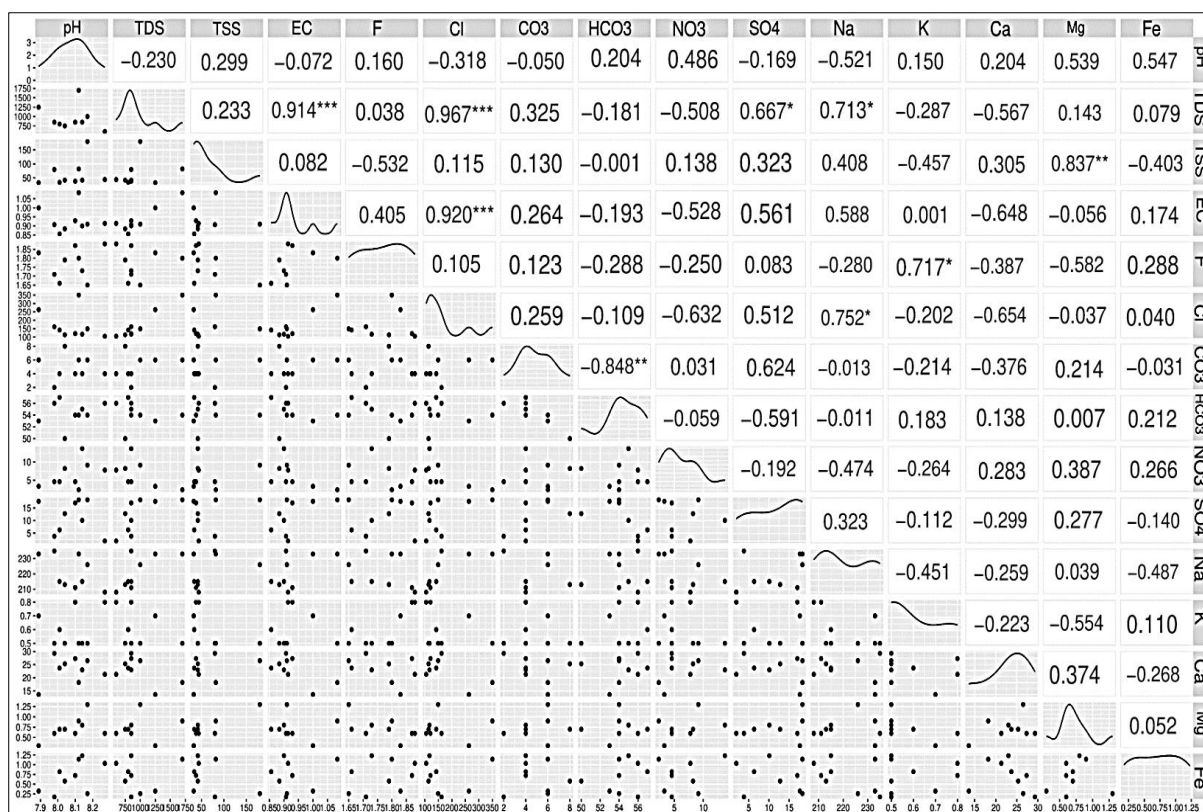


Fig. 5.10: Correlation matrix of the physicochemical parameters of fluoridated groundwater in the study area

5.2.1.2.5 Variation of fluoride concentration in groundwater (day-wise) from Sonarpur block

Two different locations have been selected to examine the variation of F^- concentration in groundwater (day-wise) from the contaminated region. The mean F^- concentrations were found 2.2 ± 0.14 mg/l (range: 1.9 - 2.4 mg/l) and 2 ± 0.17 mg/l (range: 1.7 - 2.3 mg/l) in groundwater over a period of one month and 19 days study from the domestic tube well of Billwapada Mondal and Sourav Naskar, respectively. In both cases, on an average about 2 mg/l F^- concentration was found from ward no. 6, Rajpur Sonarpur, Municipality at Sonarpur block (Fig. 5.11).

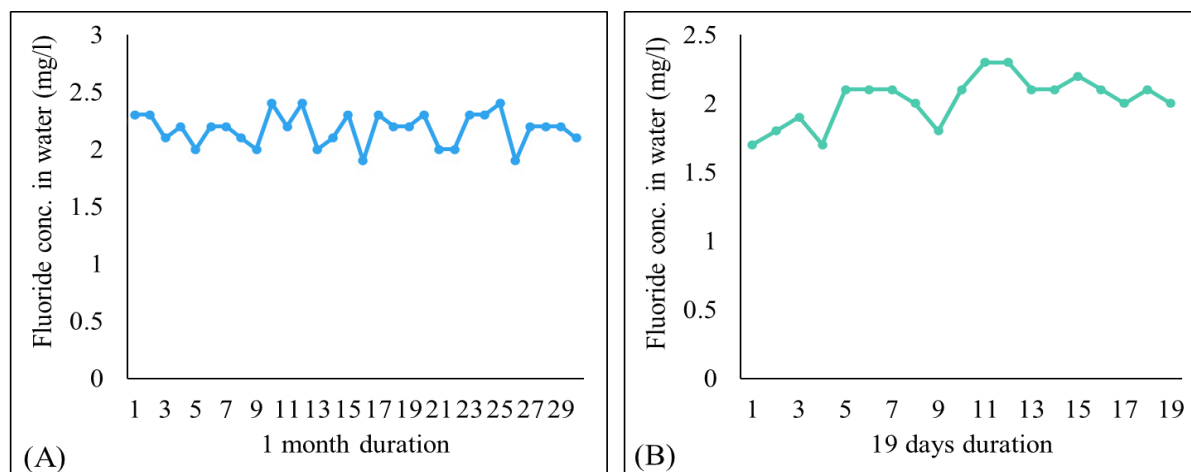


Fig. 5.11: Variation of fluoride concentration in groundwater (day-wise) from the house of (A) Billwapada Mondal and (B) Sourav Naskar.

5.2.1.3 Gram-panchayats and municipality areas in Baruipur block

5.2.1.3.1 Distribution of fluoride in groundwater

The magnitude of F^- concentration in groundwater has been shown in **Table 5.7**. The mean F^- concentration was found 0.56 mg/l (range: 0.02-2.5 mg/l; $n = 824$). The maximum level of F^- concentration was found in Dhapdhapi II gram-panchayat (average: 1.17 mg/l; range: 0.19-2.5 mg/l; $n = 167$) and the maximum concentration was found about 1.7-fold higher than the respective permissible limit. F^- distribution in groundwater within the survey area showed wide spatial heterogeneity (**Fig. 5.12**) with large variation in F^- concentration. Approximately, 10% of the groundwater samples ($n = 824$) exhibited high F^- values (**Fig. 5.13**) over the acceptable limit in drinking water (WHO, 2011). Moreover, 2.9%, 6.7%, 6.8%, 4%, and 43.7% of the groundwater samples crossed the permissible limit of F^- in 5 gram-panchayats, like Kalyanpur ($n = 34$), Mallikpur ($n = 49$), Hariharpur ($n = 15$), Champahati ($n = 58$) and Dhapdhapi II ($n = 167$), respectively among the 19 gram-panchayats and Baruipur municipality area (**Fig. 5.14**, Table 5.7). In a previous study, about 13% of groundwater samples were reported as F^- contaminated (average: 0.75 mg/l; range: 0.01-2.9 mg/l; $n = 984$) beyond its permissible limit from Sonarpur block which is adjacent to the study area. Moreover, the shallow Gangetic alluvial plain has a potential risk to groundwater F^- leachability in the aquifer zone of <30.5 m depth (Chaudhuri and Roy, 2017). Likewise, the F^- uncertainty depends on the geological condition that plays a potential role in the aquifer level.

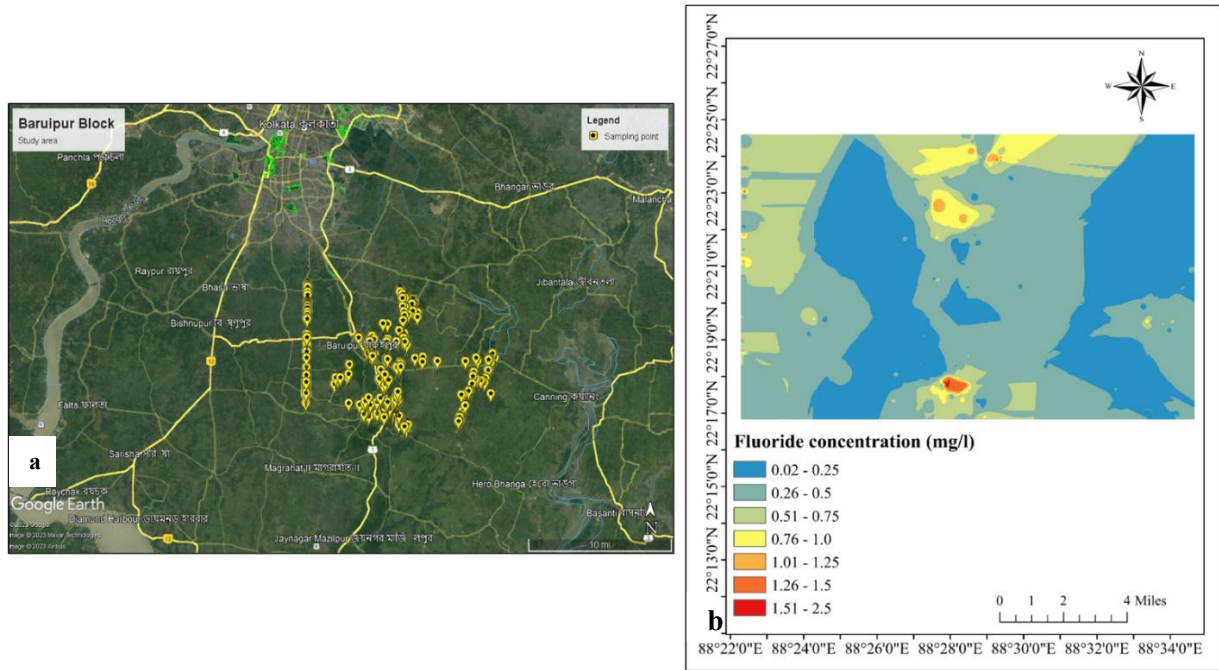


Fig. 5.12: a. Sampling point of collected groundwater samples from the studied area; b. spatial distribution of fluoride concentration in groundwater from the studied area

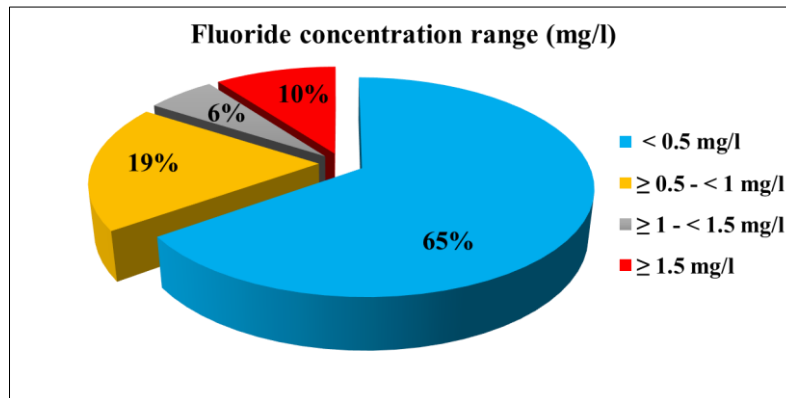


Fig. 5.13: Distribution of fluoride in groundwater (n = 824) from Baruipur block

The soil character is mainly found as clay with sandy loam entire the study area (Srinivasan et al., 2015). In alluvial plain, higher groundwater flow rate decreases the contact time between minerals and groundwater interaction which causes the low concentration of most of the contaminant solutes into the groundwater (Su et al., 2021). According to previous reports, chemical weathering of silicate minerals may be responsible and has a significant impact on F^- leachability into the groundwater from the lower Gangetic belt of South 24 Parganas district (Datta et al., 2000).

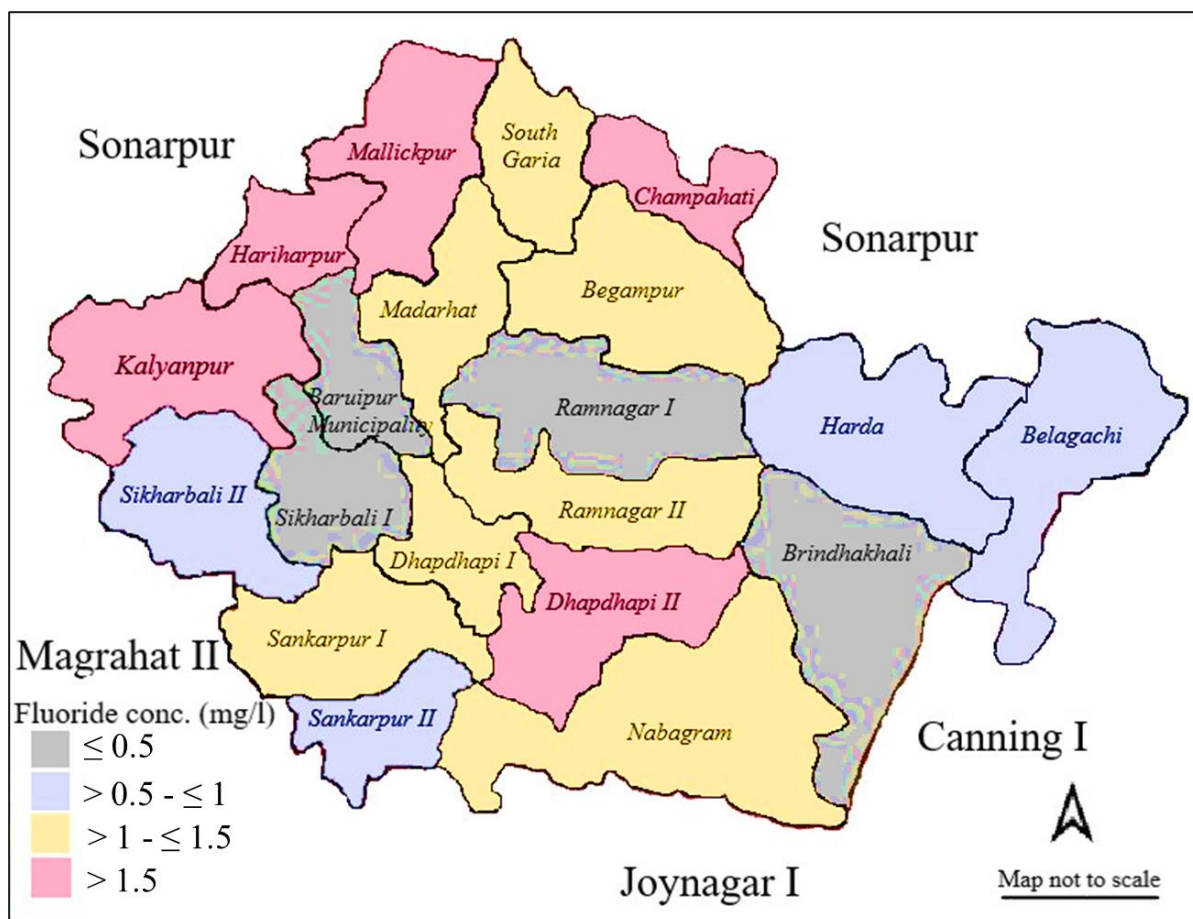


Fig. 5.14: Minimum to maximum fluoride concentration range in groundwater from 19 gram-panchayat and Baruiপুর municipality in the studied area

Table 5.7: Fluoride (mg/l) distribution in groundwater of from Baruiপুর Block (Gram-panchayat and Municipality area wise)

Gram-panchayat/ Municipality	No. of sample	Mean (mg/l)	Standard deviation (SD)	Range (mg/l)
South Garia	47	0.51	0.28	0.26 -1.35
Kalyanpur	34	0.62	0.39	0.13 - 2.06
Champahati	58	0.81	0.45	0.22 -1.76
Begampur	23	0.51	0.35	0.2 -1.25
Madarat	6	0.53	0.36	0.26 -1.16
Ramnagar I	8	0.32	0.03	0.3 - 0.4
Ramnagar II	65	0.27	0.19	0.08 -1.23
Hardaha	22	0.31	0.19	0.02 - 0.59
Hariharpur	15	0.49	0.44	0.12 - 0.59
Mallikpur	49	0.57	0.26	0.02 -1.69
Belagachi	50	0.24	0.13	0.08 - 0.8

Gram-panchayat/ Municipality	No. of sample	Mean (mg/l)	Standard deviation (SD)	Range (mg/l)
Brindakhali	34	0.26	0.07	0.12 - 0.38
Nabagram	22	0.57	0.33	0.13 - 1.22
Dhapdhapi I	80	0.43	0.2	0.08 - 0.98
Dhapdhapi II	167	1.17	0.76	0.19 - 2.5
Sankarpur I	49	0.23	0.2	0.08 - 0.44
Sankarpur II	18	0.38	0.22	0.09 - 0.89
Sikharbali I	11	0.31	0.1	0.11 - 0.44
Sikharbali II	7	0.57	0.24	0.16 - 0.77
Baruipur Municipality	59	0.14	0.07	0.05 - 0.45
Total	824	0.56	0.54	0.02 - 2.5

5.2.1.3.2 Single factor pollution index

The assessment of contamination has been conducted using the single factor pollution index system for groundwater quality of Baruipur block based on F^- concentration allowing with classification in a systematic way. The mean F^- concentration of single factor pollution index from Baruipur block is 0.37 ± 3 ($n = 824$) classified as first group ($I_i < 1.0$), thus it comes under low contamination factor. Moreover, 10% of high fluoridated groundwater samples showed $1.0 \leq I_i < 3.0$ (moderate contamination factor). The gram-panchayats like Kalyanpur, Champahati, Hariharpur, Mallikpur and Dhaphdapi II contributed moderate contamination factor. Whereas, 55 % and 45 % of groundwater samples have expressed $I_i < 1.0$ ($n = 92$) (low F^- contamination factor) and $1.0 \leq I_i < 3.0$ ($n = 75$) (moderate contamination factor) in Dhaphdapi II gram-panchayat. Comparable observations were documented in other studies as well (Das et al., 2021; Rehman et al., 2018; Yu et al., 2018).

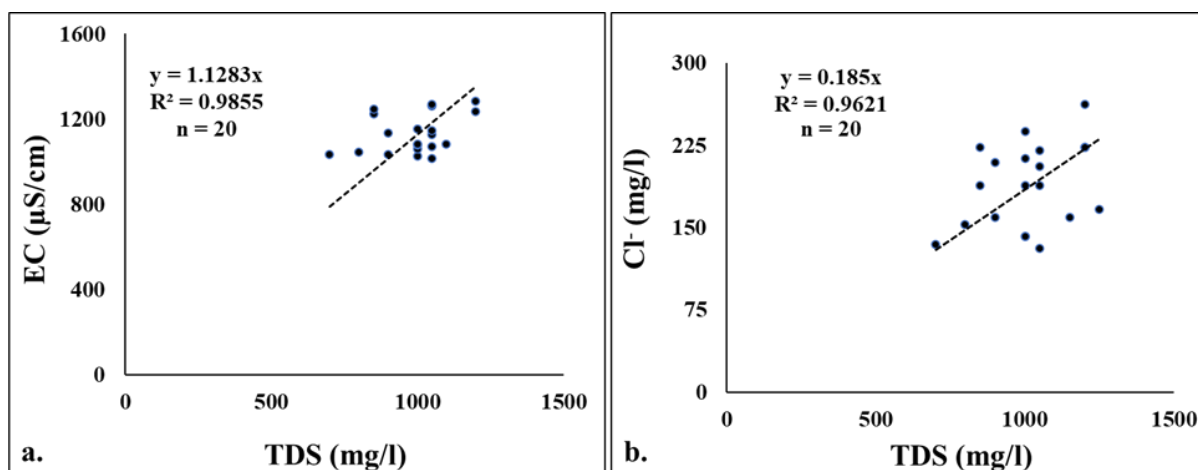
5.2.1.3.3 Groundwater chemistry of physico-chemical parameters

The various results of physico-chemical parameters in fluoridated groundwater samples ($n = 20$) collected from Dhaphdapi II gram-panchayat, Baruipur block are shown in **Table 5.8**. pH values varied in the range of 7.5-8.3 (mean: 7.74) indicates an alkaline situation in groundwater. EC has the capacity to run the electrical current of the total ions present in groundwater.

Table 5.8: Physico-chemical parameters of the fluoridated groundwater (n = 20) from Dhapdhapi II gram-panchayat in Baruipur block, South 24 Parganas district

Parameters	Mean	Standard deviation (SD)	Coefficient of variation (CV) %	Median	Range
pH	7.74	0.26	3.39	7.65	7.5 - 8.3
TDS (mg/l)	1010	146.5	14.5	1000	700 - 1250
TSS (mg/l)	114.5	33.9	29.6	105	70 - 180
EC ($\mu\text{S}/\text{cm}$)	1080	171	15.82	1103	635-1283
F ⁻ (mg/l)	1.98	0.19	10.1	1.96	1.61 - 2.36
Cl ⁻ (mg/l)	188.7	38.3	20.3	188.2	131 - 262
CO ₃ ²⁻ (mg/l)	6.7	2.17	32.5	6	4 - 12
HCO ₃ ⁻ (mg/l)	53.6	3.25	6.07	53.5	48 - 62
NO ₃ ⁻ (mg/l)	6.15	3.47	56.4	5.02	4.06 - 20
SO ₄ ²⁻ (mg/l)	15.1	8.14	54.2	16.6	1.63 - 32
Na ⁺ (mg/l)	301	11.5	3.82	303	282 - 323
K ⁺ (mg/l)	0.7	0.18	26.6	0.7	0.4 - 1.1
Ca ²⁺ (mg/l)	40.3	10.97	27.3	35.7	27.8 - 62.2
Mg ²⁺ (mg/l)	8.87	2.76	31.2	8.51	4.86-14.6
Fe (mg/l)	0.83	1.11	132.8	0.34	0.03 - 4.69

Mean EC value was found 1080 $\mu\text{S}/\text{cm}$ (varied from 635 to 1283 $\mu\text{S}/\text{cm}$) which indicates a lot of difference in geochemical activities. TDS is the most potential parameter for measuring the groundwater quality, which ranged from 700 to 1250 mg/l with a mean of 1010 mg/l, indicating good variation in the groundwater salinity. The mean TDS value is ~2 folds higher than the acceptable limit prescribed for drinking water (500 mg/l) (WHO, 2011) which influenced to recognize that groundwater in this region holds a good potential role behind the enrichment of minerals and salts. Higher TDS level in groundwater causes a slew of problems for humans, including gastrointestinal irritation, kidney stones and heart disease (Garg et al., 2009). Moreover, a strong regression association was observed between TDS vs EC ($R^2 = 0.98$) and TDS vs Cl⁻ ($R^2 = 0.96$) (Fig. 5.15).

**Fig. 5.15:** Regression analysis between a. TDS and EC and b. TDS and Cl⁻

In the present study, the ratio of TDS/EC was found in the range of 0.67-1. TDS-EC varied ratios were also found in the range of 0.52-0.67 and 0.53-0.6 in different groundwater samples worldwide (Das et al., 2020; McNeil and Cox, 2000). Cl^- ions act as an influencer for TDS, determining that the groundwater is in saline condition (Balakrishnan et al., 2011; Feng et al., 2020). It is most important for groundwater quality and the mean Cl^- value was found as 188.7 mg/l (range: 131-262 mg/l). The average Na^+ ion concentration was found 301 mg/l (range: 282-323 mg/l) in fluoridated groundwater. The correlation matrix among the different physicochemical parameters has been shown in **Table 5.9**. A good correlation has been found between Na^+ and Cl^- ($r = 0.89$) which indicates that the groundwater is supposed to be strongly saline in condition (Table 5.9). Ca^{2+} is the most significant element that is released into groundwater due to the weathering dissolution of host mineral/rock (Subba Rao et al., 2020).

Table 5.9: Correlation matrix of the physicochemical parameters of fluoridated groundwater in the studied area

Parameters	pH	TDS (mg/l)	TSS (mg/l)	EC ($\mu\text{S}/\text{cm}$)	F^- (mg/l)	Cl^- (mg/l)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Fe (mg/l)
pH	1.00														
TDS (mg/l)	0.12	1.00													
TSS (mg/l)	0.22	0.24	1.00												
EC ($\mu\text{S}/\text{cm}$)	0.48	0.23	0.17	1.00											
F^- (mg/l)	-0.12	0.20	0.18	0.15	1.00										
Cl^- (mg/l)	0.28	0.35	0.39	0.41	-0.03	1.00									
CO_3^{2-} (mg/l)	-0.14	0.29	0.18	-0.07	-0.29	0.02	1.00								
HCO_3^- (mg/l)	-0.02	0.00	0.21	-0.21	0.44	0.31	-0.44	1.00							
NO_3^- (mg/l)	0.04	-0.20	-0.21	0.26	-0.09	0.06	-0.09	-0.07	1.00						
SO_4^{2-} (mg/l)	-0.05	-0.15	-0.45	0.01	-0.18	0.15	0.05	0.05	0.08	1.00					
Na^+ (mg/l)	0.30	0.53	0.43	0.40	0.17	0.89	-0.05	0.30	0.14	-0.09	1.00				
K^+ (mg/l)	-0.31	0.22	-0.11	-0.49	-0.27	-0.37	0.16	0.03	-0.42	0.08	-0.37	1.00			
Ca^{2+} (mg/l)	0.04	-0.06	0.21	-0.05	-0.34	0.10	0.03	-0.41	0.14	-0.38	0.23	-0.21	1.00		
Mg^{2+} (mg/l)	0.13	-0.03	-0.20	0.10	-0.16	-0.08	0.06	-0.13	0.26	0.19	-0.12	-0.02	-0.12	1.00	
Fe (mg/l)	-0.37	-0.50	-0.26	-0.59	-0.13	-0.07	-0.18	0.37	0.15	0.03	-0.16	-0.09	-0.02	-0.18	1.00

Mean Ca^{2+} concentration (mean: 40.3 mg/l, range: 27.8-62.2 mg/l) was found higher than that of Mg^{2+} concentration (mean: 8.87 mg/l, range: 4.86-14.6 mg/l). The mean HCO_3^-

concentration (53.6 mg/l; range: 48-62 mg/l) was observed higher than the mean concentration of CO_3^{2-} (6.7 mg/l; range: 4-12 mg/l). Mean F^- concentration was observed as 1.98 mg/l (range: 1.61-2.36 mg/l) under alkaline environmental condition ($\text{pH} > 7$) in groundwater which was supported by Subba Rao et al. (2020). Moreover, the anionic and cationic concentration ranges were found in the order of $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^- > \text{F}^-$ and $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Fe} > \text{K}^+$, respectively which simplify the fluoridated groundwater quality of Dhapdhapi II gram-panchayat.

5.2.2 West Medinipur district

5.2.2.1 Block wise fluoride distribution in groundwater

The presence of F^- in groundwater from five blocks of West Medinipur district ($n = 143$) has been shown in **Table 5.10**. The maximum F^- of 0.85 mg/l was found at Pingla block among other blocks of the West Medinipur district (Table 5.10).

Table 5.10: Block wise fluoride distribution in groundwater from West Medinipur district

District Name	Block Name	Number of Sample	Mean F^- (mg/l)	Range (mg/l)	S.D.	C.V. %
West Medinipur ($n = 143$)	Narayangarh	19	0.13	0.01-0.45	0.15	115.3
	Keshiyari	4	0.25	0.14-0.36	0.11	44
	Garbeta I	39	0.04	0.02-0.36	0.03	75
	Garbeta II	24	0.17	0.03-0.49	0.14	82.35
	Pingla	87	0.79	0.66-0.85	0.08	11.59

Table 5.11: Block wise fluoride distribution range in groundwater from West Medinipur

District Name	Block name	F ⁻ concentration range (mg/l)			
		<0.5	≥0.5 - <1	≥1- <1.5	≥1.5
West Medinipur	Narayangarh	19			
	Keshiyari	4			
	Garbeta I	39			
	Garbeta II	24			
	Pingla		57		

Fluoride distribution pattern in groundwater has been shown in **Table 5.11** and **Fig. 5.16**. About 40% and 60% of all groundwater samples showed the distribution of F^- concentration in the ranges of ≥ 0.5 - <1 mg/l and < 0.5 mg/l, respectively from the studied areas (Fig. 5.16).

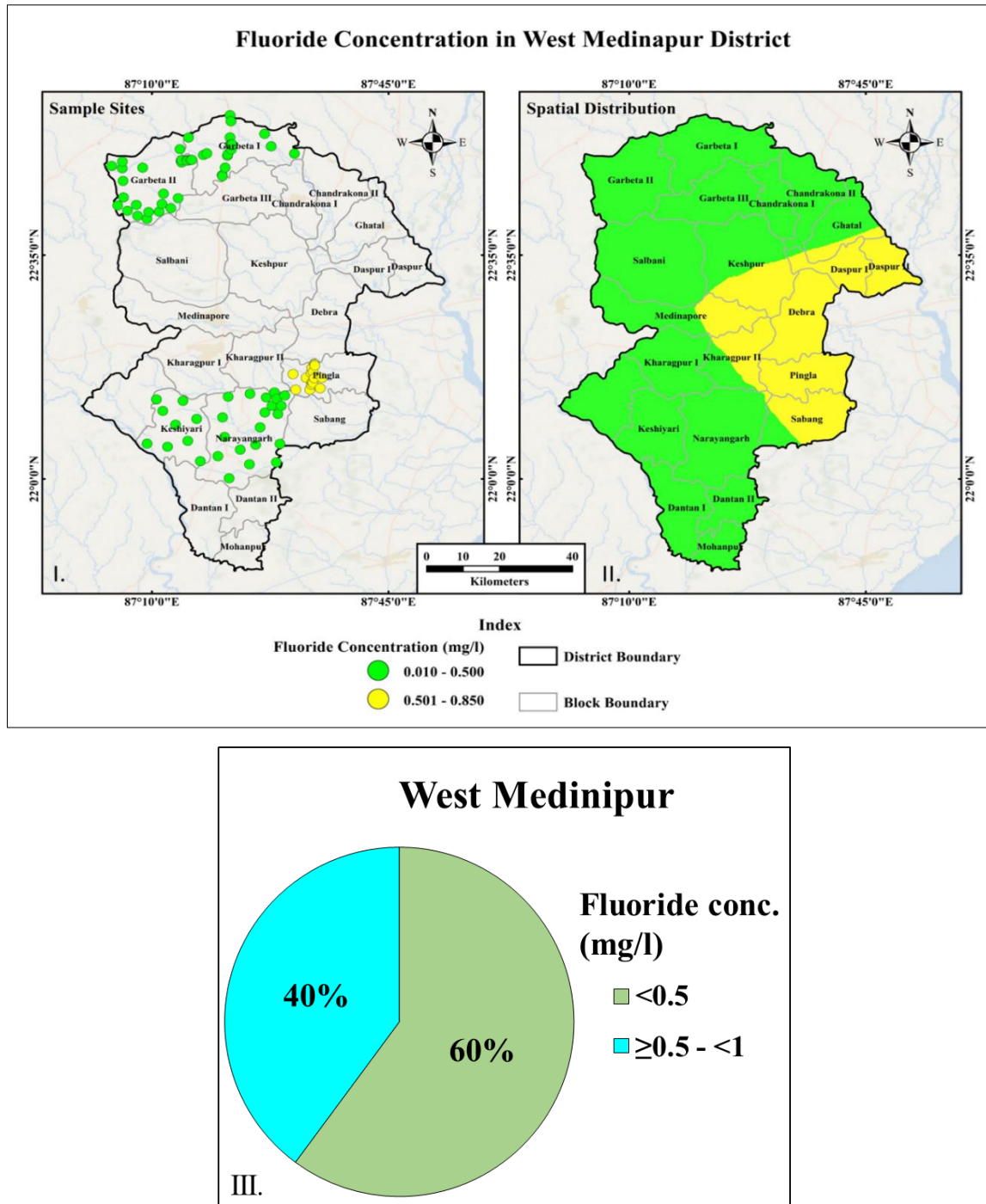


Fig. 5.16: I. Concentration wise fluoride distribution pattern in West Medinipur district, II. Spatial distribution pattern of fluoride in West Medinipur district, III. Fluoride concentration range in West Medinipur district

5.2.2.2 Spatial distribution of fluoride in groundwater from West Medinipur district

The minimum F^- concentration was found as 0.1 mg/l (latitude 22° 50' 45" N and longitude 87° 21' 15" E) at Nayangarh block and the maximum F^- concentration was found as 0.85 mg/l (latitude 22°14' 47.76" N and longitude 87°32' 50.83" E) in Pingla area of West Medinipur. The distribution pattern has been represented in **Fig. 5.16. II**.

5.2.3 Jhargram district

All the studied areas of Jhargram district have been highlighted in this study.

5.2.3.1 Block wise fluoride distribution in groundwater from Jhargram

The F^- distribution in groundwater from six blocks of Jhargram district ($n = 176$) has been displayed in **Table 5.12**. The maximum F^- concentration was found approx. 6-fold higher compared to the permissible limit in Binpur II block (Table 5.12). 22% of samples contributed F^- concentration ≥ 1.5 mg/l in Binpur II block of Jhargram district (**Table 5.13** and **Fig. 5.17.I**). All the collected groundwater samples were found 11% of ≥ 1.5 mg/l, 10% of $\geq 1 - < 1.5$ mg/l, 19% of $\geq 0.5 - < 1$ mg/l, and 60% of < 0.5 mg/l from six blocks of Jhargram district (**Fig. 5.17.II**).

Table 5.12: Block wise fluoride distribution in groundwater from Jhargram district

District Name	Block Name	Number of Sample	Average F^- (mg/l)	Range (mg/l)	S.D.	C.V.%
Jhargram ($n = 167$)	Gopiballavpur I	26	0.17	0.01-0.45	0.13	76.4
	Gopiballavpur II	17	0.15	0.1-0.38	0.1	66.6
	Binpur II	88	1.38	0.04-8.8	1.49	107.9
	Jamboni	20	0.08	0.02-0.56	0.14	175
	Binpur I	16	0.3	0.07-1.2	0.32	106.6
	Nayagram	9	0.38	0.03-0.82	0.28	73.6

Table 5.13: Block wise fluoride distribution range in groundwater from Jhargram district

District Name	Block name	F ⁻ concentration range (mg/l)			
		<0.5	$\geq 0.5 - < 1$	$\geq 1 - < 1.5$	≥ 1.5
Jhargram	Gopiballavpur I	26			
	Gopiballavpur II	17			
	Binpur II	26	26	17	19
	Jamboni	19	1		
	Binpur I	13	2	1	
	Nayagram	5	4		

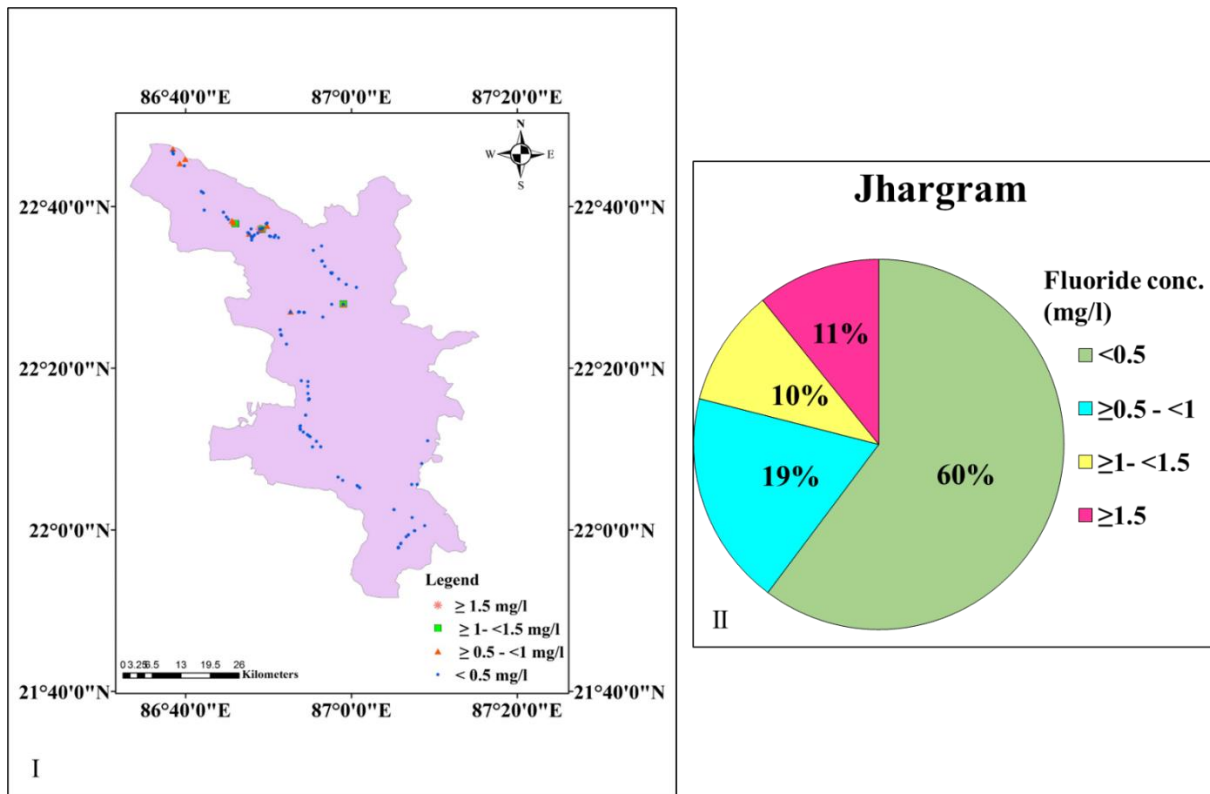


Fig. 5.17: I. Concentration wise fluoride distribution pattern in Jhargram district, II. Fluoride concentration range in Jhargram district

5.2.3.2 Spatial distribution of fluoride in groundwater from Jhargram district

Minimum F^- was found as 0.01 mg/l (latitude $21^\circ 57' 50.59''$ N and longitude $87^\circ 05' 39.64''$ E) in Gopiballavpur I area and maximum F^- was evaluated at 8.8 mg/l (latitude $22^\circ 37' 12.45''$ N and longitude $86^\circ 49' 08.25''$ E) at Binpur II block of Jhargram district (**Fig. 5.18**). These areas have arid or semiarid climate conditions. In the eastern part of West Bengal, the toxicity of F^- is less compared western part due to the alluvium sediments of the lower Gangetic plain (Farooq et al., 2018; Hossain et al., 2021; Samal et al., 2015). According to the report of CGWB (1985), the maximum F^- concentration in groundwater was found as 17.9 mg/l at 30-80 m depth from the fractured basaltic aquifer in Birbhum district (Hossain et al., 2021).

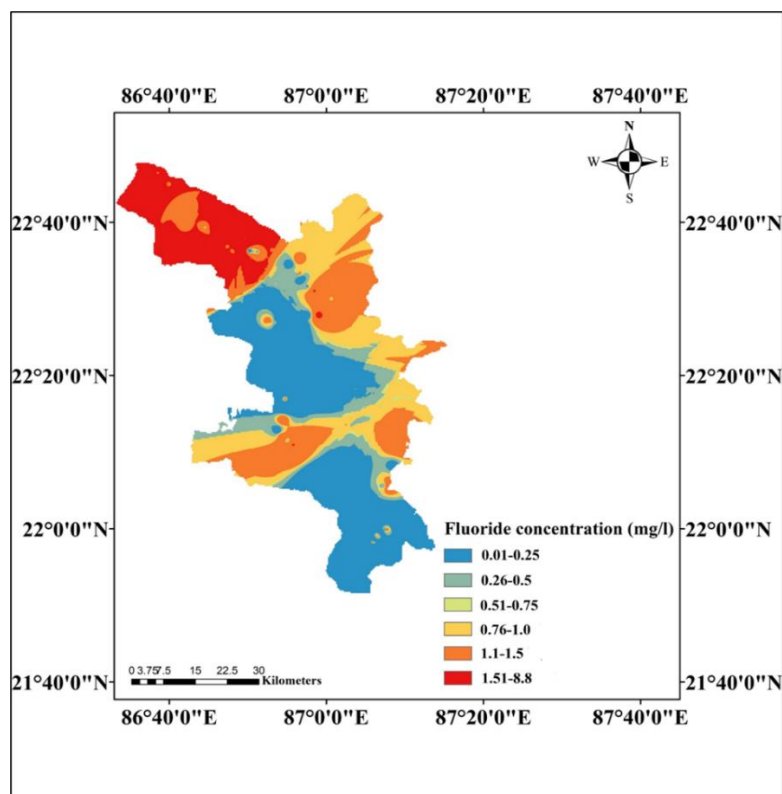


Fig. 5.18: Spatial distribution pattern of fluoride in groundwater from Jhargram district

5.2.4 East Bardhaman district

5.2.4.1 Block wise fluoride distribution in groundwater from East Bardhaman

The groundwater F^- concentration in 23 blocks of East Bardhaman district has been represented in **Table 5.14**. Maximum F^- concentration was found 0.93 mg/l in Memari II block considering the other blocks of East Bardhaman district **Table 5.14**. Sample wise F^- distribution pattern of groundwater has been highlighted in **Table 5.15** and **Fig. 5.19.I**. 23% of samples contributed to the F^- concentration range ≥ 0.5 - <1 mg/l in East Bardhaman district (**Fig. 5.19.II**).

Table 5.14: Block wise fluoride distribution in groundwater from East Bardhaman district

District Name	Block Name	Number of Sample	Mean F^- (mg/l)	Range (mg/l)	S.D.	C.V.%
East Burdhaman (n = 143)	Ausgram I	6	0.27	0.1-0.43	0.24	88.8
	Ausgram II	6	0.12	0.02-0.25	0.11	91.6
	Galsi II	6	0.48	0.37-0.58	0.09	18.7
	Galsi I	6	0.54	0.39-0.75	0.12	22.2
	Bhatar	6	0.21	0.11-0.35	0.08	38
	Mongolkote	6	0.23	0.1-0.47	0.14	60.8
	Khandaghosh	6	0.57	0.31-0.65	0.25	43.8

District Name	Block Name	Number of Sample	Mean F ⁻ (mg/l)	Range (mg/l)	S.D.	C.V.%
	Burdwan I	10	0.36	0.04-0.58	0.15	41.6
	Burdwan II	6	0.51	0.27-0.71	0.18	35.2
	Raina I	8	0.53	0.32-0.78	0.17	32.07
	Raina II	7	0.54	0.33-0.73	0.14	25.9
	Memari I	5	0.33	0.28-0.47	0.07	21.2
	Memari II	5	0.61	0.35-0.93	0.23	37.7
	Jamalpur	6	0.34	0.17-0.47	0.11	32.3
	Monteswar	6	0.46	0.31-0.89	0.21	45.6
	Kalna I	6	0.23	0.21-0.26	0.02	8.6
	Kanla II	6	0.16	0.08-0.24	0.06	37.5
	Purbasthali I	6	0.25	0.04-0.27	0.18	72
	Purbasthali II	6	0.26	0.06-0.63	0.21	80.7
	Katwa I	6	0.28	0.11-0.39	0.11	39.2
	Katwa II	6	0.15	0.1-0.3	0.08	53.3
	Ketugram I	6	0.36	0.25-0.61	0.13	36.1
	Ketugram II	6	0.48	0.15-0.48	0.12	25

Table 5.15: Block wise fluoride distribution range in groundwater from East Bardhaman district

District Name	Block name	F ⁻ concentration range (mg/l)			
		<0.5	≥0.5 - <1	≥1- <1.5	≥1.5
East Burdhaman	Memari II	3	2		
	Raina II	2	5		
	Burdwan I	8	2		
	Burdwan II	2	4		
	Raina I	3	5		
	Khandoghosh	2	4		
	Galsi II	3	3		
	Galsi I	2	4		
	Jamalpur	6			
	Manteswar	5	1		
	Memari I	5			
	Bhatar	6			
	Mongolkote	6			
	Aushgram II	6			
	Aushgram I	5	1		
	Kalna I	6			
	Kanla II	6			
	Purbasthali I	6			
	Purbasthali II	5	1		
	Katwa I	6			
	Katwa II	6			
	Ketugram I	5	1		
	Ketugram II	6			

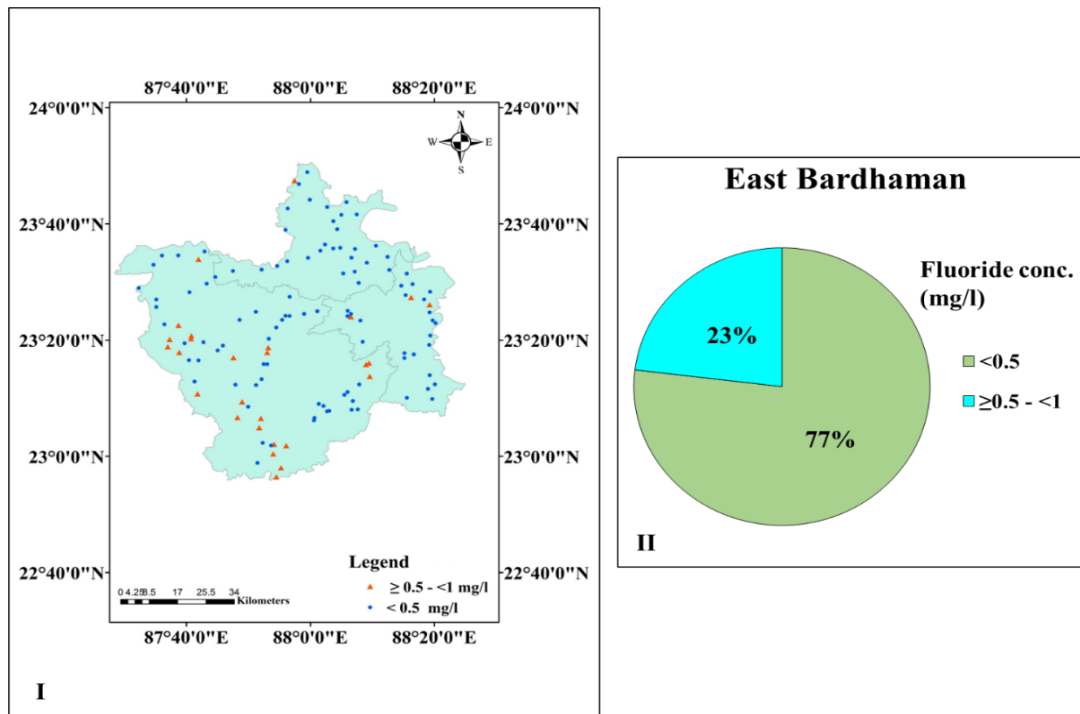


Fig. 5.19: I. Concentration wise fluoride distribution pattern in groundwater, **II.** Fluoride concentration range in East Bardhaman district

5.2.4.2 Spatial distribution of fluoride at East Bardhaman district

Minimum F^- 0.02 mg/l (latitude 23° 28' 59.39" N and longitude 87° 32' 17.20" E) was found at Ausgram II and maximum F^- 0.93 mg/l (latitude 23°13' 45.31" N and longitude 88° 09' 34.06" E) at Memari II in East Bardhaman district (**Fig. 5.20**).

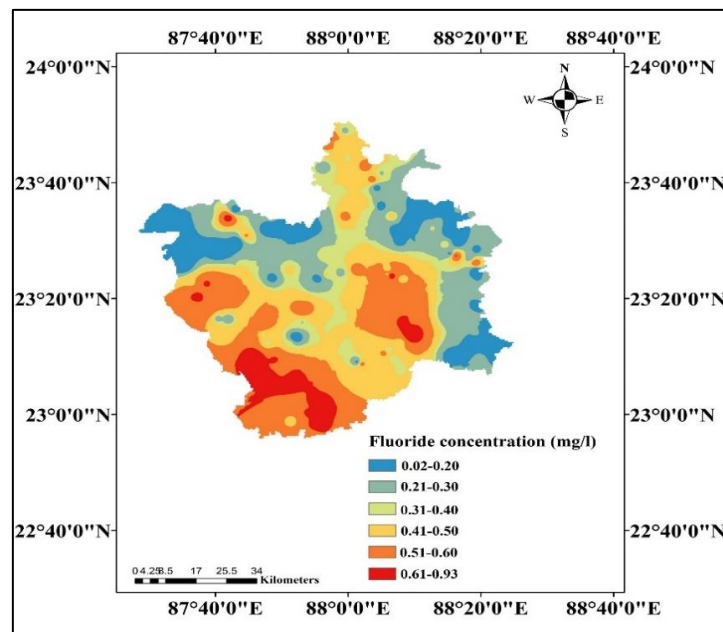


Fig. 5.20: Spatial distribution pattern of fluoride in groundwater from East Bardhaman district

According to the geological conditions and weather process is significant for F^- contamination. During the monsoonal season, the groundwater aquifer is enriched by water, that's why the concentration of F^- in the pre-monsoon season becomes high compared to post-monsoon. In the post-monsoonal season, F^- concentration may be decreased due to the dissolution of F^- in the monsoonal period from contaminated areas as previously reported by Batabyal and Gupta, 2017; Hossain et al., 2021; Mondal and Kumar, 2017; Farooq et al., 2018.

5.2.5 West Bardhaman district

5.2.5.1 Block wise fluoride distribution in groundwater from West Bardhaman

The groundwater F^- concentration in nine blocks of West Bardhaman district has been exhibited in **Table 5.16**. The maximum F^- concentration was found approx. 9-fold higher in the Barabani block among other blocks in West Bardhaman (Table 5.16). 10% and 10% groundwater samples participated for the F^- concentration range for ≥ 1 - <1.5 mg/l and ≥ 1.5 mg/l, respectively (**Table 5.17** and **Fig. 5.21.I**). 4% and 5% of all groundwater samples contributed F^- concentration ≥ 1.5 mg/l and ≥ 1 - <1.5 mg/l in West Bardhaman, respectively (**Fig. 5.21. II**).

Table 5.16: Block wise fluoride distribution in groundwater from West Bardhaman district

District Name	Block Name	Number of Sample	Mean F^- (mg/l)	Range (mg/l)	S.D.	C.V.%
West Burdhaman (n = 164)	Salanpur	42	0.65	0.11-1.01	0.29	44.6
	Barabani	30	1.21	0.06-13.4	2.63	217.3
	Jamuria	23	0.45	0.09-1.8	0.34	75.5
	Pandabeswar	16	0.55	0.03-4.1	0.98	178.1
	Asansole	20	0.62	0.27-1.38	0.34	54.8
	Ondal	6	0.48	0.35-0.69	0.12	25
	Raniganj	6	0.49	0.2-0.65	0.17	34.6
	Durgapur	15	0.34	0.02-1	0.29	85.2
	Kanksa	6	0.31	0.1-0.48	0.14	45.1

Table 5.17: Block wise fluoride distribution range in groundwater from West Bardhaman

District Name	Block name	F^- concentration range (mg/l)			
		<0.5	≥ 0.5 - <1	≥ 1 - <1.5	≥ 1.5
West Burdhaman	Durgapur	11	4		
	Asansole	9	8	3	
	Salanpur	12	26	3	1
	Barabani	21	3	3	3
	Jamuriya	17	5		1
	Pandabeswar	12	3		1
	Ondal	2	4		
	Raniganj	2	4		
	Kanksa	6			

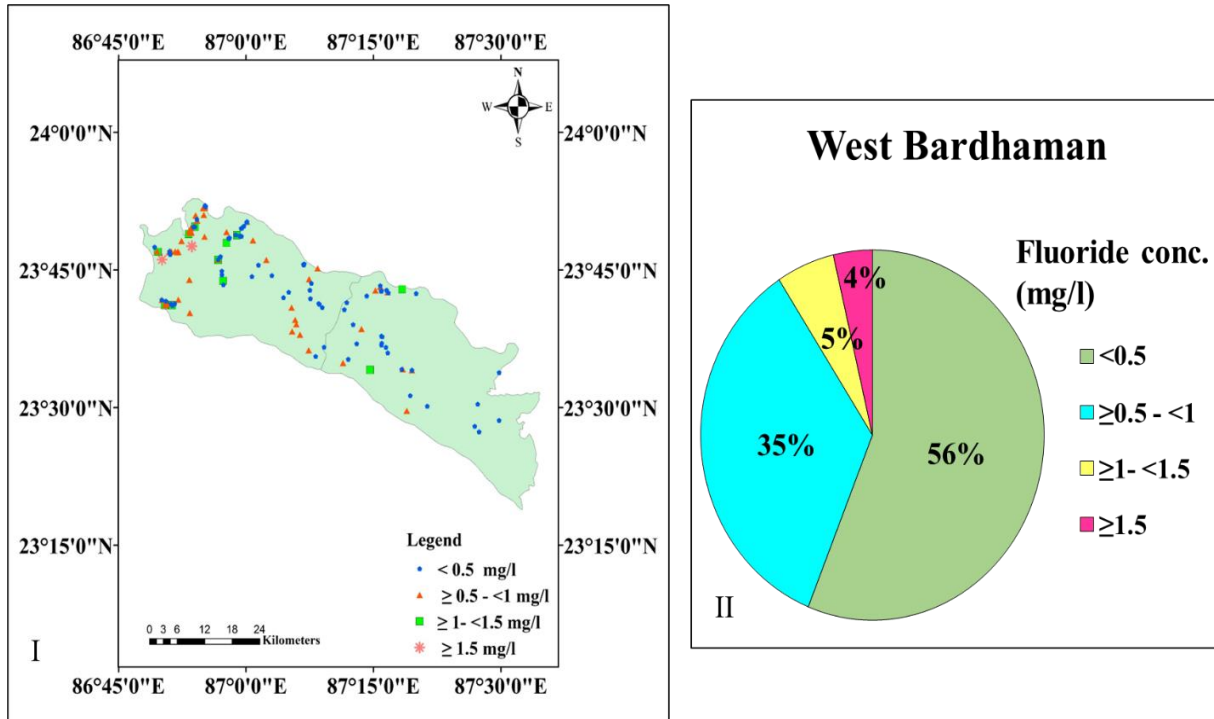


Fig. 5.21: I. Concentration wise fluoride distribution pattern in groundwater, II. Fluoride concentration range from East Bardhaman district

5.2.5.2 Spatial distribution of fluoride in groundwater from West Bardhaman district

Minimum F^- was found 0.02 mg/l at Durgapur (latitude 23°36'49.28" N and longitude 87°15' 57.14" E) and maximum F^- was found 13.4 mg/l (latitude 23°47' 34.90" and longitude 86° 53' 38.08" E) at Barabani in West Bardhaman district (**Fig. 5.22**). Furthermore, in the western part of West Bardhaman district, coal mining areas are significantly contributed to F^- leaching in groundwater at Salanpur, Baraboni, Jamuria, and Pandabeyswar areas (Gupta et al., 2012; Chatterjee et al., 2008; Ando et al., 1998). Maximum average F^- concentration in groundwater was found to be 1.2 mg/l (Chatterjee et al., 2008) and 0.72 mg/l (Gupta et al., 2012) in Raniganj area which is basically comes under the coal mining areas (Masood et al., 2022; Yadav et al., 2021).

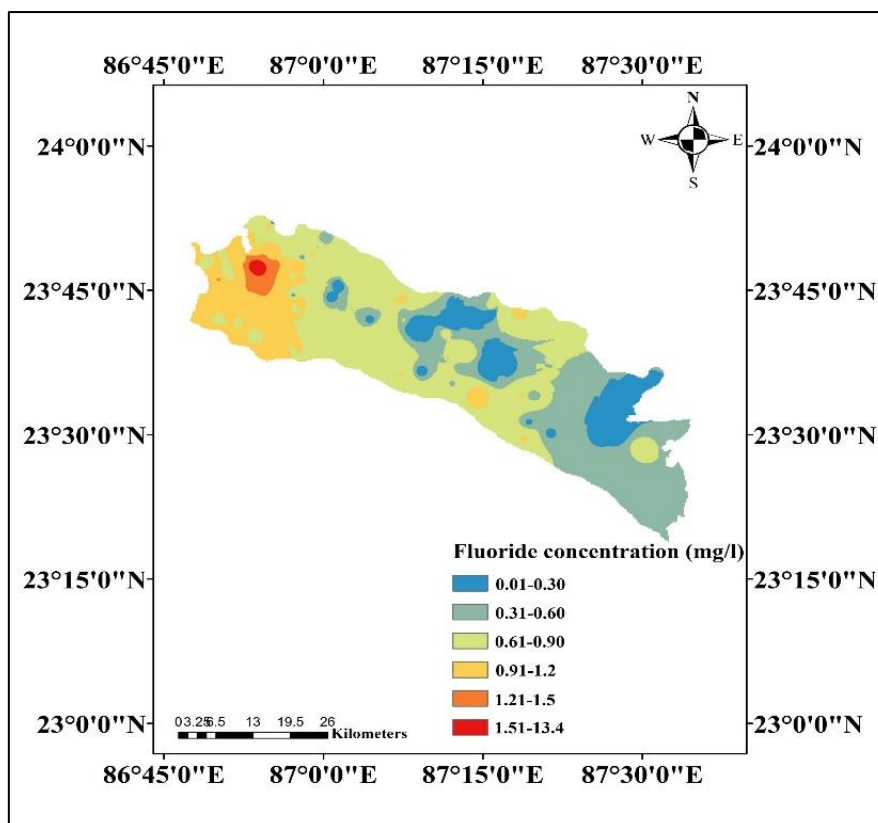


Fig. 5.22: Spatial distribution pattern of fluoride groundwater from West Bardhaman district

5.2.6 Murshidabad district

5.2.6.1 Block wise fluoride distribution in groundwater from Murshidabad district

The groundwater F^- concentration in thirteen blocks from Murshidabad district has been shown in Table 5.18. The maximum F^- concentration was found ~3.7-fold higher in the Kandi block compared to the recommended value (>1.5 mg/l) (Table 5.18). 31% and 15% of groundwater samples showed concentration of $F^- \geq 1.5$ mg/l from Kandi and Khargram blocks, respectively (Table 5.19 and Fig. 5.23.I). 14%, 8%, and 37% of overall groundwater samples contributed to the F^- concentration range ≥ 1.5 , ≥ 1 - <1.5 , and ≥ 0.5 - <1 mg/l in Murshidabad district, respectively (Fig. 5.23.II). Fluoride-containing minerals such as apatite and fluorite in the granitic rocks may be responsible for F^- leaching in the western part of Murshidabad district as Kandi and Khargram blocks (Mukherjee and Singh, 2018; Bera et al., 2021). According to the previous study, average F^- concentration was 0.28 mg/l found in Berhampur block at Murshidabad district (Datta et al., 2014).

Table 5.18: Block wise fluoride distribution in groundwater from Murshidabad district

District Name	Block Name	Number of Sample	Mean F ⁻ (mg/l)	Range (mg/l)	S.D.	C.V. %
Murshidabad (n = 574)	Bharatpur II	24	0.5	0.31-0.71	0.1	20
	Kandi	203	1.3	0.07-5.64	1.07	82.3
	Khargram	137	0.81	0.2-3.39	0.68	83.9
	Nabagram	101	0.53	0.32-1.38	0.15	28.3
	Sagardighi	43	0.39	0.06-1.01	0.17	43.5
	Burwan	38	0.42	0.22-0.81	0.11	26.1
	Berhaampur	9	0.12	0.02-0.28	0.08	66.6
	Suti II	8	0.14	0.07-0.22	0.06	42.8
	Raghunathganj I	3	0.38	0.34-0.45	0.05	13.1
	Raghunathganj II	2	0.05	0.16-0.17	0.007	14
	Farakka	1				
	Samserganj	5	0.26	0.03-0.49	0.23	88.4

Table 5.19: Block wise fluoride distribution range in groundwater from Murshidabad

District Name	Block name	F ⁻ concentration range (mg/l)			
		<0.5	≥0.5 - <1	≥1- <1.5	≥1.5
Murshidabad	Bharatpur II	10	14		
	Kandi	36	66	39	62
	Khargram	47	64	6	20
	Nabagram	47	53	1	
	Sagardighi	38	4	1	
	Burwan	28	10		
	Berhaampur	9			
	Suti II	8			
	Raghunathganj I	3			
	Raghunathganj II	2			
	Farakka	1			
	Samserganj	5			

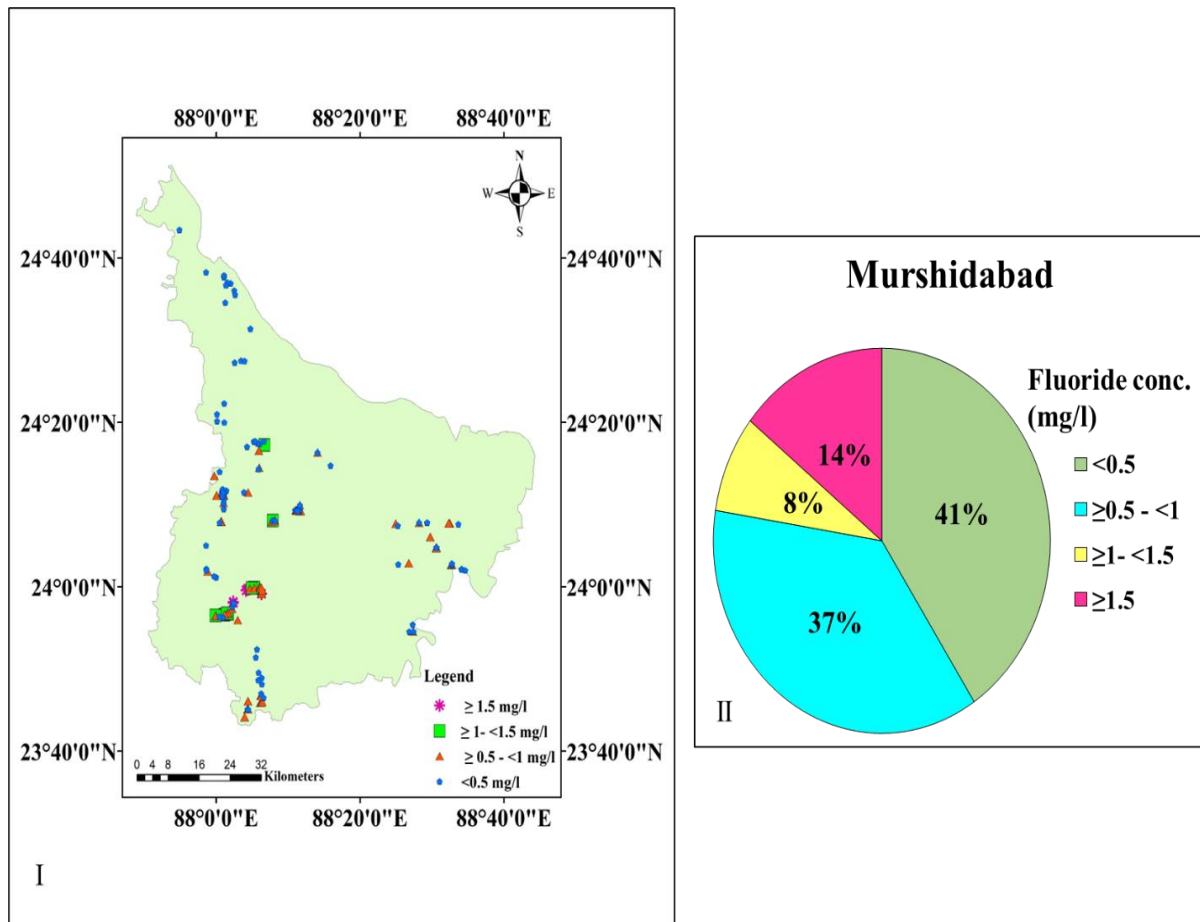


Fig. 5.23: I. Concentration wise fluoride distribution pattern in groundwater, II. Fluoride concentration range from Murshidabad district

5.2.6.2 Spatial distribution of fluoride in groundwater from Murshidabad district

Minimum F^- was found as 0.02 mg/l (latitude 24° 36' 41.00" N and longitude 88° 01' 20.87" E) and maximum F^- was found as 5.64 mg/l (latitude 23° 59' 48.35" N and longitude 88° 05' 01.91" E) at Kandi block in Murshidabad district. The distribution pattern is represented in **Fig. 5.24**. The western part of Murshidabad and Birbhum districts are situated under the region of Chota Nagpur Plateau. These areas have arid or semiarid climatic conditions.

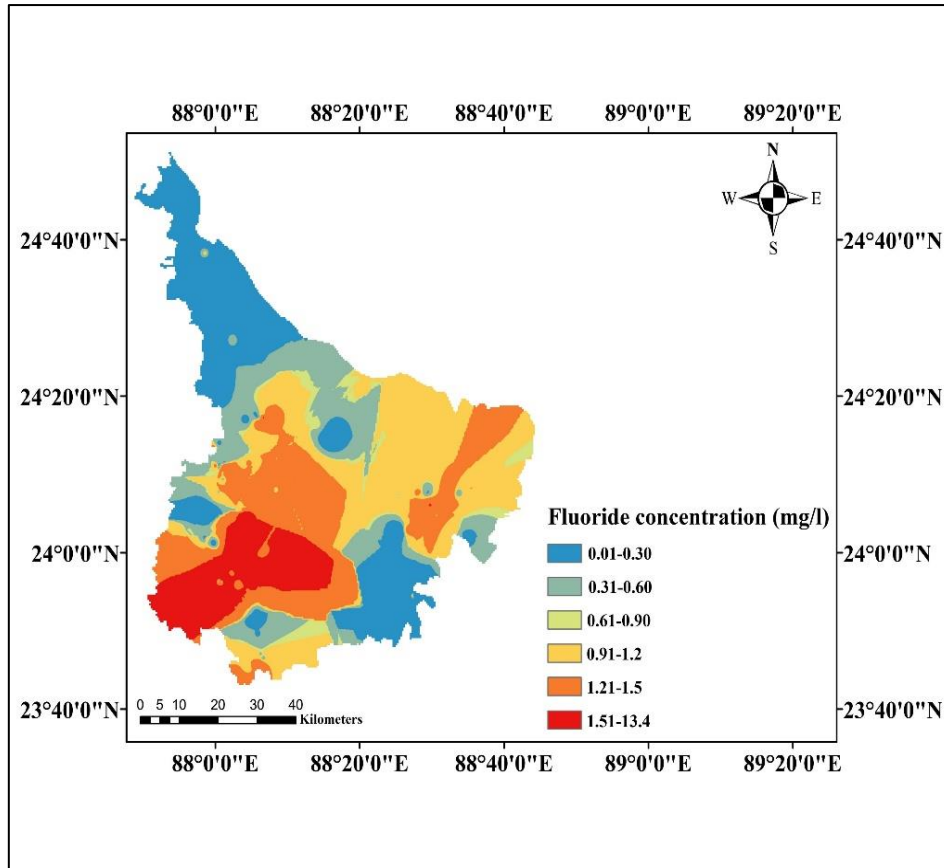


Fig. 5.24: Spatial distribution pattern of fluoride in groundwater from Murshidabad district

5.3 Hydro-geochemical facies

Different hydrogeochemical characteristics evaluate the responsible source for F^- leaching in fluoridated groundwater ($n = 20$) from Sonarpur and Baruipur blocks individually.

5.3.1 Hydrogeochemical investigation in Sonarpur block

5.3.1.1 Groundwater type

The Piper trilinear diagram has (Piper 1944) been shown in **Fig. 5.25.a** which expressed the groundwater character in the study area. The triangle plot of cations and anions revealed that all of the groundwater samples were of (D) sodium-potassium (Na-K) type and (G) chloride (Cl^-) type (Fig. 5.25.a). All the ionic concentrations were plotted in the central diamond shape of the diagram which represents sodium chloride (Na-Cl) type. The Chadha diagram corresponds to a relationship between the distribution of F^- and groundwater chemistry (Rashid et al., 2018). The Chadha diagram categorizes four types of groundwater fields by plotting the disparity between cation and anion concentrations, as $HCO_3^--(SO_4^{2-} + Cl^-)$ vs $(Ca^{2+} + Mg^{2+})-(Na^+ + K^+)$ (**Fig. 5.25.b**). It represents the overall fields as Field 1: Ca-Mg- HCO_3 (alkaline earth

> alkaline metals), Field 2: Ca-MgSO₄/Cl (alkaline metals > alkaline earth), Field 3: Na-Cl (weak acidic anion > strong acidic anion), Field 4: Na-HCO₃ (strong acidic anion > weak acidic anion) and all the groundwater samples represent under Field 3 (Na-Cl type).

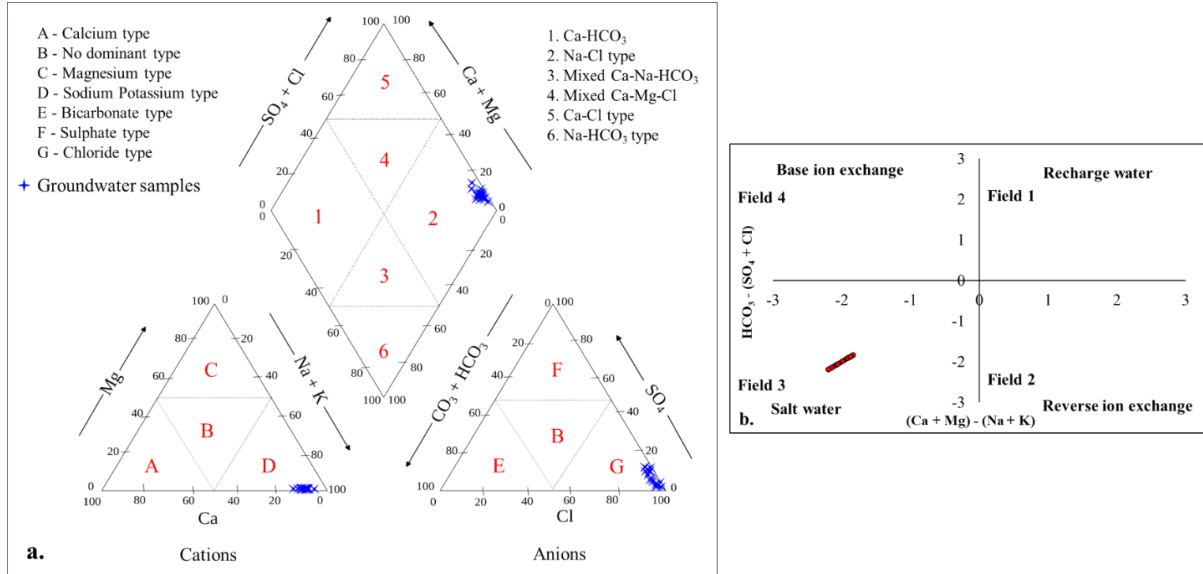


Fig. 5.25: a. Piper trilinear diagram represented the groundwater character **b.** Chadha diagram represents the classification of groundwater type

Na⁺ is present as the most dominant ion in groundwater (mean: 227 mg/l, **Table 5.6**) followed by Cl⁻ as the second most abundant ion (mean: 172 mg/l, Table 5.6). Thus, these two ions primarily formed Na-Cl type through ionic interaction in groundwater. In that situation, the favorable weathering process played a significant role behind the low Ca²⁺ concentration in groundwater (mean: 23.6 mg/l) which is directly associated with HCO₃⁻ minerals through its precipitation and formed calcium and dolomite. Thus, a strong correlation was found between Na and Cl ions in fluoridated groundwater which showed saline condition and this observation is strongly corroborated by other studies (Wang et al., 2019). Moreover, higher F⁻ dissolution in groundwater is due to silicate weathering under alkaline conditions in the lower Gangetic plain which is supported by other studies (Dehbandi et al., 2018).

5.3.1.2 Geochemical weathering process of fluoride behaviour

The groundwater chemistry is influenced by various factors, including bedrock/host minerals, flow, and climatic circumstances. According to the Gibbs plot, TDS concentrations were drawn against the ratios of a. $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ and b. $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$, respectively (**Fig. 5.26**).

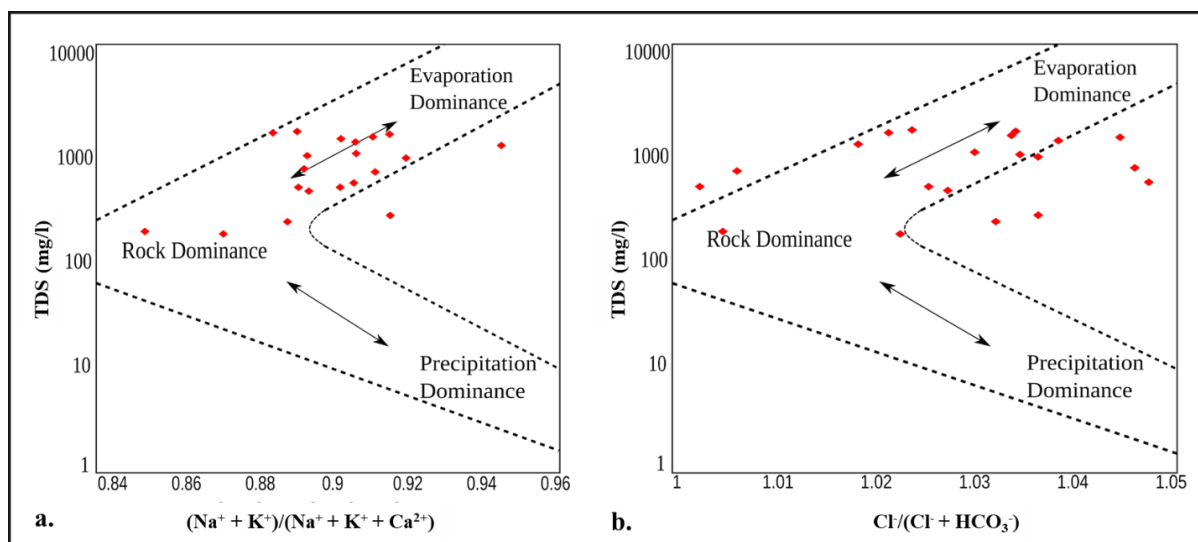
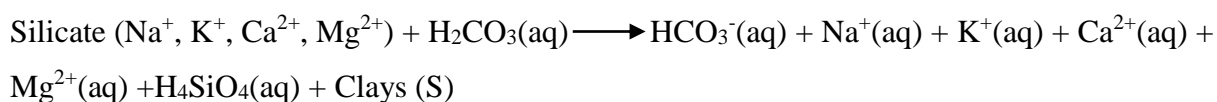


Fig. 5.26: Gibbs diagrams showing the mechanisms and controlling the groundwater interaction

The Gibbs diagrams demonstrate the three processes that regulate the chemistry of water in relation to the influence of precipitation (rainwater), rock/host mineral interaction (soil and/or lithology), and evaporation (climate). The ratio of different ions in groundwater samples fall in rock and evaporation dominance zone ($100 \text{ mg/l} < \text{TDS} < 10000 \text{ mg/l}$) (Fig. 5.26). There is not a single sample found in rock/host mineral and precipitation ($\text{TDS} < 100 \text{ mg/l}$) dominance zone. A few groundwater samples that fall into the rock domain and has been suggested that the geogenic origin is the primary cause for the increasing of ions from the evaporation domain to the rock domain zone. This process occurs when water interacts with soils and/or weathering rocks and creating minerals, before it reaches into the water table.



Above equation illustrates a general response for the water and host/rock mineral interaction. Based on this process, the predominant ions in groundwater should be Na^+ and HCO_3^- which may play potential role for F^- mobilization in groundwater. However, evaporation and/or increase of the concentrations of sodium (Na^+) and chloride (Cl^-) ions in groundwater close to the Bay of Bengal may contribute to increase the mineralization process i.e. > 1000 zone. As a result, all the points move towards the evaporation domain to rock domain zone which supports the theory. The mechanism of water and host rock/mineral interaction may have a role in controlling the chemistry of groundwater and this study is supported by Subba Rao (2017). Moreover, it is suggested that geogenic origin is a responsible factor for F^- mobilization in

groundwater from evaporation dominance area to rock dominance area and numerous additional research have observed similar types of observations (Rashid et al., 2018).

5.3.1.3 Geochemical modelling in mineral phases

The saturation indices (SI) were computed using PHREEQC interactive version 2.11 (Dehbandi et al., 2018). The negative SI values were found for halite, anhydrite, and gypsum, while the SI values of dolomite, calcite, and fluorite were found positive. Average saturation index values were -0.6 ± 0.37 for gypsum (range: -0.19 - -1.69), -0.89 ± 0.37 for anhydrite (range: -0.48 - -1.99), -3.3 ± 0.14 for halite (range: -2.99 - -3.52), 2.46 ± 0.17 for calcite (range: 2.83 - 2.01), 3.5 ± 4.24 for dolomite (range: 4.24 - -2.5), and 2.43 ± 0.1 for fluorite (range: 2.62 - 2.18). The relationship between fluorite and dolomite, calcite, anhydrite, gypsum, and halite were represented in **Fig. 5.27**. The positive saturation index indicates that the minerals, like calcite, dolomite, and fluorite are oversaturated and can be precipitated in aqueous medium and negative saturation index signifies that the minerals, like gypsum, anhydrite, and halite are under saturated state and this observation is strongly corroborated by other studies (Zhang et al., 2020). The positive saturation index value of calcite (CaCO_3) has a substantial impact on F^- dissolution into the groundwater and it is well supported by other study (Nawale et al., 2021).

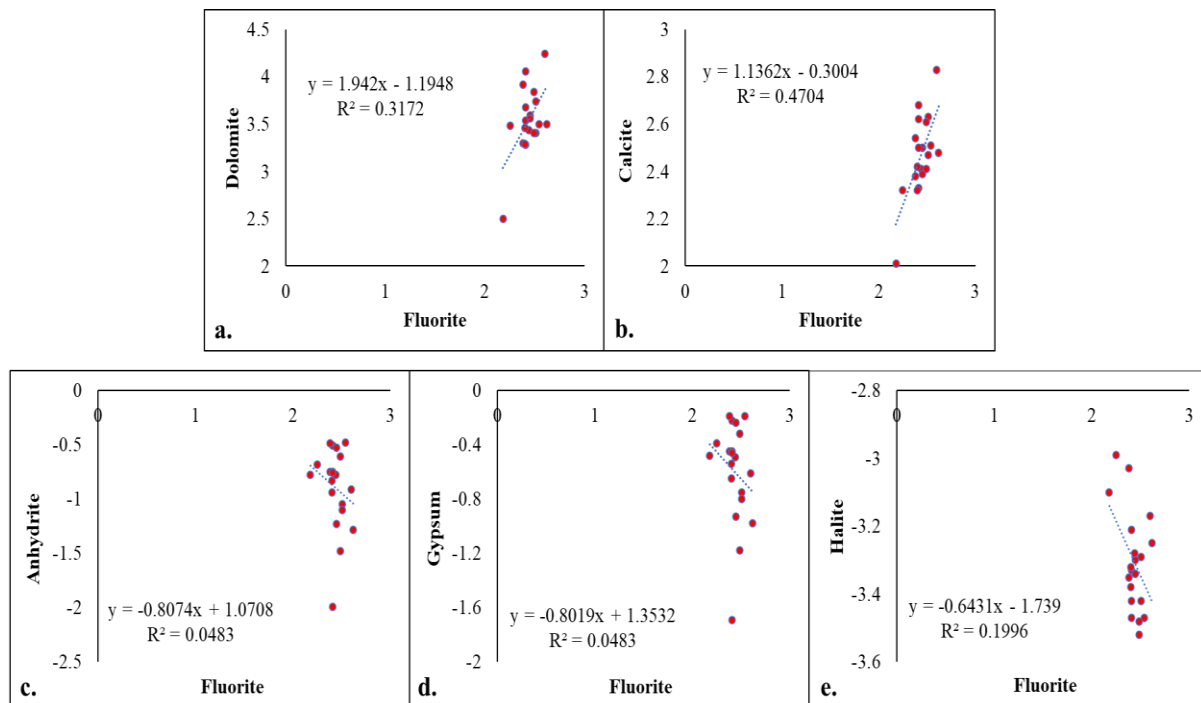
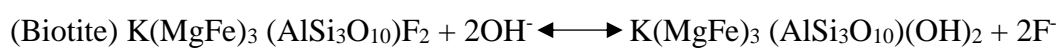


Fig. 5.27: Saturation index (SI) of scatterplot showing the relationship between fluorite and **a.** dolomite **b.** calcite **c.** anhydrite **d.** gypsum and **e.** halite.

5.3.1.4 Geochemical process and ionic interaction of fluoride

The bivariate plot suggested that groundwater tends to follow the carbonate and silicate weathering process (**Fig. 5.28**). Maximum F^- levels in groundwater samples have been shown below the 1:1 line which indicated the enrichment of Sodium (Na^+) in groundwater due to the ion exchange and salinity effect (Xu et al., 2021a). The ratio of $(HCO_3^- + SO_4^{2-})$ and $(Ca^{2+} + Mg^{2+})$ was found >1 which indicated that dolomite dissolution was dominant along with calcite precipitation caused by the dissolution of gypsum and this observation is robustly supported by a body of additional research (Xu et al., 2021b, Farid et al., 2015). The alkaline groundwater and silicate weathering aided the fluorinated host material to solubilize F^- and leach into the groundwater resulting in a high concentration of Na^+ and low Ca^{2+} (Rashid et al., 2018; Xiao et al., 2015). The solubility of F^- bearing silicate minerals such as biotite and muscovite, where, both have a substantial impact on the solubility of F^- in groundwater. However, geochemically, in alkaline circumstances, F^- and OH^- ions have the same atomic charge and ionic radius, which makes it easier for them to replace one another in biotite and muscovite. In the silicate weathering process, high Na^+ and HCO_3^- support F^- leaching in the hydrolysis condition from the host mineral (biotite, muscovite) to groundwater (Rashid et al., 2020).



Both the equations showed F^- enrichment in groundwater. Therefore, OH^- and HCO_3^- ions are concurrently released into the groundwater during the leaching or dissolution process of F^- bearing minerals. Hence, along with the lowering activity of Ca^{2+} ions, a positive and strong correlation was found between F^- and K^+ ($r = 0.71$), whereas a negative correlation was found between F^- and Mg^{2+} ($r = -0.58$) (Fig. 5.10). So, in that case, muscovite can be a responsible host mineral for mobilization of F^- in groundwater which was previously supported by other study from lower Gangetic plain. The ionic interaction between TDS vs $Na^+/(Na^+ + Cl^-)$ supports that ion-exchange process is responsible for F^- leaching (**Fig. 5.28.b**). As a result, the ratio of Na^+ and Cl^- was found more than 1, which indicated that the groundwater may contribute to ion exchange capability, as seen in other investigations (Feng et al., 2020, Marghade et al., 2012).

All the groundwater samples revealed negative values, which suggested a cation-anion exchange in chloro-alkaline (CA) disequilibrium condition (**Fig. 5.28.c**). The strong correlation between Na^+ and Cl^- was found to be 0.75 (Fig. 5.10), which favours the precipitation of Ca^{2+} and Mg^{2+} ions on the transferrable site of host silicate mineral and simultaneously releases K^+

and Na^+ during the ion-exchange reaction. The cation-anion exchange process is significantly contributed for the maximum concentration of Na^+ in groundwater and this observation was supported by other studies (Marghade et al., 2012, Xiao et al., 2015, Mondal et al., 2015, Palanisamy et al., 2023).

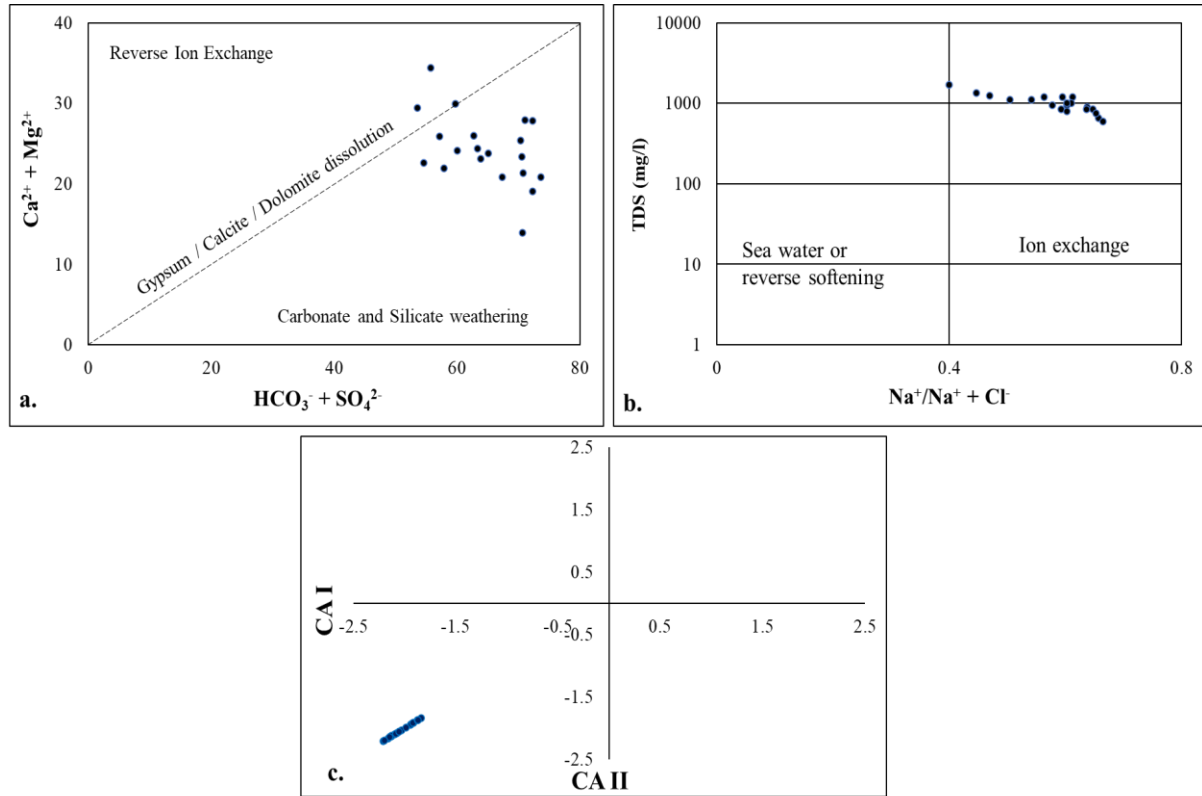


Fig. 5.28: **a.** The bivariate plot between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs $(\text{HCO}_3^- + \text{SO}_4^{2-})$, **b.** The graphical plot of TDS vs $\text{Na}^+ / (\text{Na}^+ + \text{Cl}^-)$ showing ion exchange capacity and, **c.** $\text{CA I} = [\text{Cl}^- + (\text{Na}^+ + \text{K}^+) / \text{Cl}^-]$ vs $\text{CA II} = [\text{Cl}^- + (\text{Na}^+ + \text{K}^+) / (\text{HCO}_3^- + \text{CO}_3^{2-} + \text{SO}_4^{2-} + \text{NO}_3^-)]$ showing the cation-anion exchange capacity in chloro-alkaline (CA) condition

5.3.2 Hydrogeochemical investigation in Baruipur block

5.3.2.1 Groundwater type

The Piper trilinear diagram is mostly used to evaluate groundwater type evolution (Karunanidhi et al., 2020; Piper, 1944). Ionic concentrations were plotted in the Piper trilinear plot to distinguish the groundwater quality (**Fig. 5.29**). The triangle plot of cation (on the left side of the plot) reveals that all the groundwater points fall at the right lower corner of this diagram i.e. (D) or sodium-potassium ($\text{Na}^+ - \text{K}^+$) types. Whereas, at the anion triangle (right side of the plot), it is seen that all the groundwater points represent (G) or chloride (Cl^-) type. The central diamond shape in the Piper plot differentiates 6 different kinds of water such as (1) Ca-HCO_3 ,

(2) Na-Cl, (3) mixed Ca-Na-HCO₃, (4) mixed Ca-Mg-Cl, (5) Ca-Cl and (6) Na-HCO₃ types. In the study area, all fluoridated groundwater samples (n = 20) have represented the Na-Cl type (Fig. 5.29).

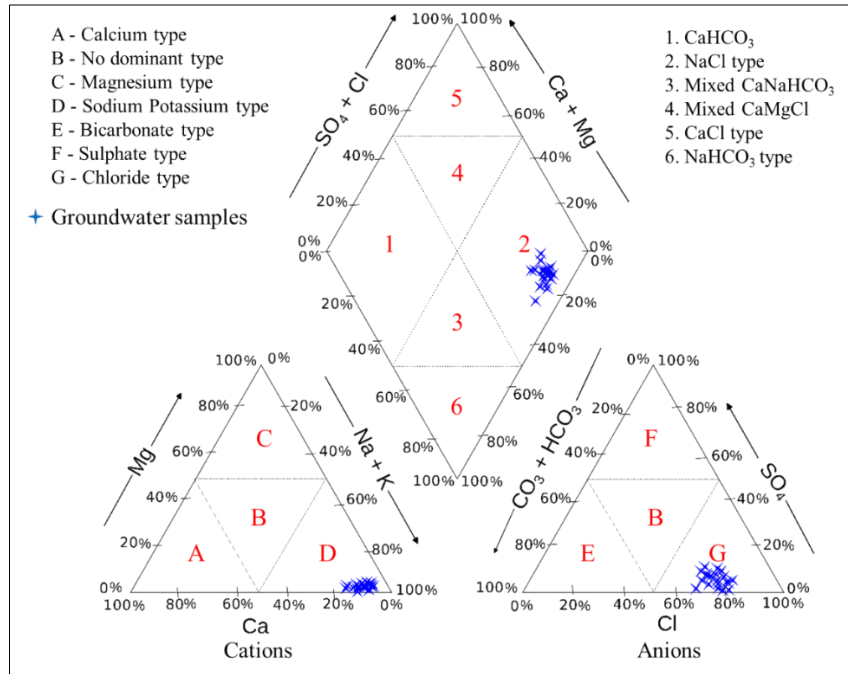


Fig. 5.29: Piper trilinear diagram display hydrogeochemical character of groundwater samples

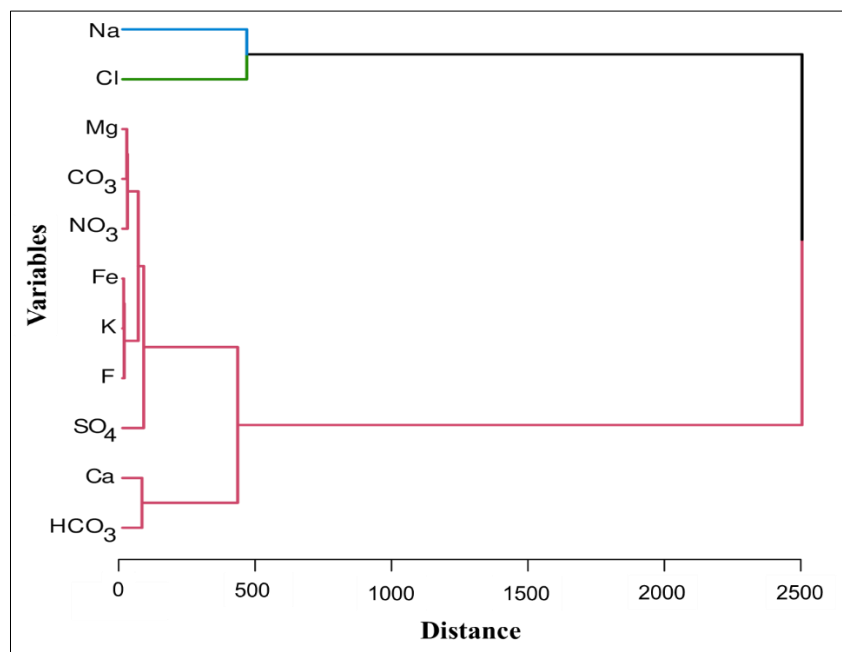


Fig. 5.30: Dendrogram generated cluster analysis showing the relation among the groundwater quality parameters

A strong correlation has been observed between Na^+ and Cl^- in groundwater (Table 5.10). These water facies indicate that similar types of water have undergone comparable geogenic interactions with host rocks, particularly intensified at shallower depths. The host rocks and minerals in the study regions exhibit enrichment in alkaline elements such as Na^+ and K^+ . The Piper plot indicated that the release of F^- into the groundwater is attributed to cation and anion exchange activities with minerals, a conclusion consistent with findings by Kashyap et al. (2020).

Fig. 5.30 represents the difference of homogeneity among the created cluster products which describe the two main clusters found among the different ions (Das et al., 2018; Das et al., 2020; Wang et al., 2019; Zhang et al., 2014). The colored branches of the dendrogram show close interaction and inter-ionic relationships. Blue and green branches indicate the separate cluster formed between Na^+ and Cl^- ions due to their abundance in those samples and distinct origin as shown in the black-coloured branch-root. Other branches are associated together forming a different origin of the cluster in red colour, having multiple sister branches of closely related ions. These different coloured branches are important to show the different origins of ionic species and their mineralogical forms. The cluster analysis suggested that the primary cluster is formed between Na^+ and Cl^- ions (Fig. 5.30) which proves that both are closely interrelated. Other part of cluster, F^- ion is closely related to the K^+ and Fe ions as all are found in a single cluster. Mg^{2+} , CO_3^{2-} and NO_3^- fall under different small clusters and SO_4^{2-} ion is directly dependent on other ions. Secondary cluster is strongly formed between Ca^{2+} and HCO_3^- ions. The ratio of $\text{HCO}_3^-/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ were found much higher than 1 which suggested that the favourable silicate weathering condition played a significant role behind low Ca^{2+} concentration in groundwater (Adimalla et al., 2020; Naderi et al., 2020). Devi et al. (2021) supported that low concentration of Ca^{2+} in groundwater is directly associated with HCO_3^- minerals (such as calcite and dolomite) and its precipitation.

5.3.2.2 Mechanism of geochemical weathering processes on fluoride behaviour

The Gibbs plot is widely utilized for assessing the correlation between groundwater composition and diverse lithological/aquifer characteristics. Geogenic weathering and human involvements have a significant impact on groundwater quality. The Gibbs diagram explained three different mechanisms with respect to influencing the groundwater quality such as evaporation dominance (climate), rock dominance (soil or lithology) and precipitation

dominance (rainwater) (Gibbs, 1970). The mechanisms controlling of groundwater chemistry in studied area have been shown through Gibbs diagrams (**Fig. 5.31**).

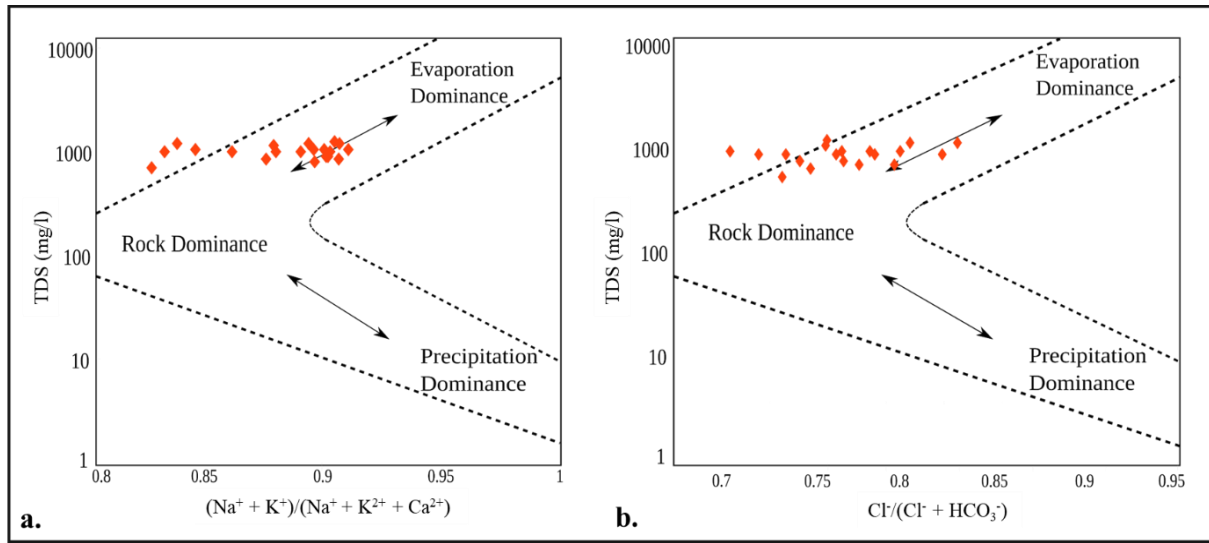


Fig. 5.31: Gibbs diagrams representing the mechanisms controlling groundwater chemistry **a.** TDS vs $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$; **b.** TDS vs $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$

All the groundwater samples fall between the zone of evaporation dominance and rock dominance which further support that the mechanism of water interaction is treated as a potential role for regulating groundwater chemistry (Feng et al., 2020; Zhang et al., 2020). There is not a single sample found into the precipitation domain area ($\text{TDS} < 100 \text{ mg/l}$), a similar observation was previously reported by Subba Rao et al. (2017). As a result, the geogenic origin is the main responsible aspect for the increase of ions from the rock dominance area to evaporation dominance area ($\text{TDS}: 100\text{-}10,000 \text{ mg/l}$). Moreover, this study indicates that groundwater interacts with soil or clay minerals into the groundwater aquifer table.

The bivariate plot of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs $(\text{Ca}^{2+} + \text{Mg}^{2+})$ (**Fig. 5.32**) suggests a potential role of carbonate and/or silicate weathering mineral in groundwater, which was further supported by other studies (Dedzo et al., 2017; Srinivasamoorthy et al., 2014; Thapa et al., 2019). Fig. 5.32 explains the presence of maximum fluoridated groundwater samples below the 1:1 line indicating Na^+ enrichment in groundwater due to the salinity effect or cation exchange process (Xu et al., 2021a).

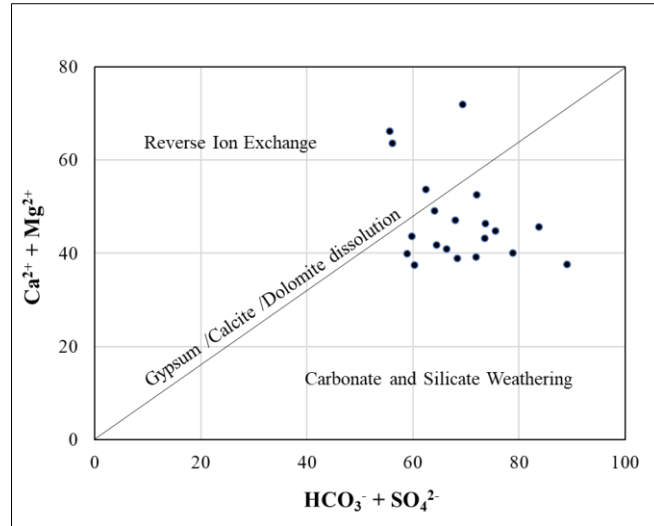
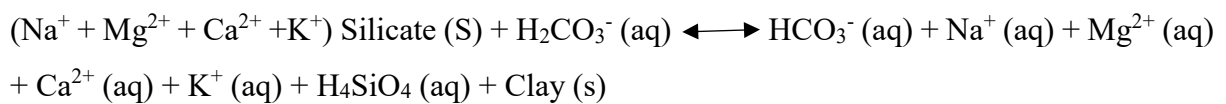


Fig. 5.32: Bivariant plot between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs $(\text{HCO}_3^- + \text{SO}_4^{2-})$

Consequently, the ratio of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ and $(\text{Ca}^{2+} + \text{Mg}^{2+})$, being >1 , suggests that dolomite dissolution is dominant along with calcite precipitation caused by the dissolution of gypsum, and Numerous additional research have observed similar types of observations (Farid et al., 2015; Xu et al., 2021a). Xu et al. (2021a) also showed the dissolution of carbonate, such as dolomite and calcite minerals in groundwater with $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio being >1 . The Ca^{2+} concentration in groundwater is also affected by dissolution or precipitation of dolomite and calcite or cation exchange process, discussed earlier in Farid et al. (2015) and Dehbandi et al. (2018). Rock-water interaction has been shown in the equation below where HCO_3^- and Na^+ act as the major dominant ions (Mrazovac et al., 2013).



Silicate minerals via weathering activity can result in the formation of clay minerals. The elevated concentration of Na^+ usually increases in a geogenic weathering environment, resulting in the solubility of fluorinated mineral leaching F^- into the groundwater (Feng et al., 2020; Li et al., 2020; Rashid et al., 2020; Xiao et al., 2015). Geochemically, in alkaline conditions, F^- ion has the same atomic charge and ionic radius as that of OH^- ion, so, thereby facilitating the replacement to each other. Moreover, F^- concentration in groundwater significantly depends on the solubility of F^- bearing silicate minerals (biotite and muscovite) and depends on the ionic conversation ability of aquifer minerals (OH^- for F^-). With the amount of time, the size and type of geological formation traversed by water interaction with host rock or mineral (Kumar et al., 2017; Saxena and Ahmed, 2003; Su et al., 2019; Thapa et al., 2019).

The equation is given below and describes the possible mechanisms involved in the release of F^- from biotite and muscovite into groundwater (Nawale et al., 2021; Su et al., 2019; Thapa et al., 2019).



High Na^+ and low Ca^{2+} levels facilitate F^- dissolution in groundwater due to the presence of silicate weathering (**Table 5.8**) (Marghade et al., 2020; Nawale et al., 2021). It has been established further through the mild positive relationship found between Na^+ and F^- ($r = 0.17$) in groundwater (**Fig. 5.33** and Table 5.8). OH^- and HCO_3^- ions are instantaneously released into the groundwater during the leaching or dissolution of F^- bearing minerals/host rocks (Kumar et al., 2017). However, a negative relation was found between SO_4^{2-} and F^- ($r = -0.18$), and NO_3^- and F^- ($r = -0.09$) (**Table 5.9**) which confirms the geogenic origin contributed to F^- leachability in groundwater (Karunanidhi et al., 2020). Apart from dissolved oxygen, both SO_4^{2-} and NO_3^- ions thermodynamically favoured the reducing conditions to influence the F^- mobilization in groundwater and this assertion finds support in corroborating studies (Dehbandi et al., 2018; Nawale et al., 2021).

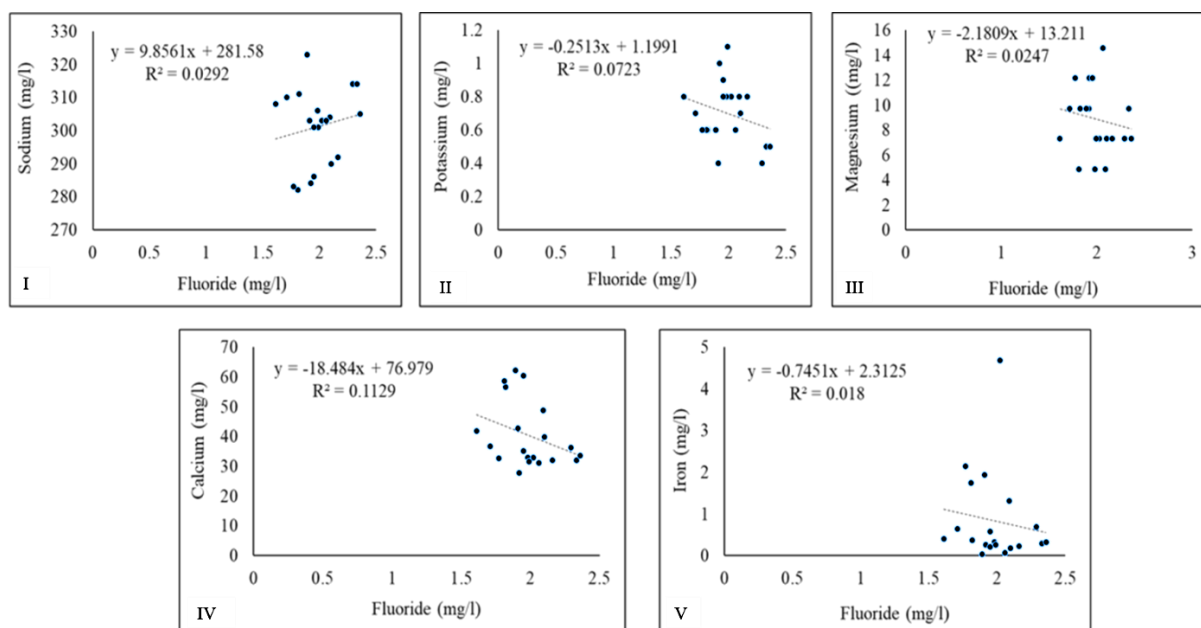


Fig. 5.33: Regression between Fluoride (mg/l) and **I.** Sodium (mg/l), **II.** Potassium (mg/l), **III.** Magnesium (mg/l), **IV.** Calcium (mg/l) and **V.** Iron (mg/l) of fluoridated groundwater ($n = 20$)

The poor negative correlation was observed between F^- and Mg^{2+} ($r = -0.16$), K^+ ($r = -0.27$), Ca^{2+} ($r = -0.34$), Fe ($r = -0.13$) except Na^+ ($r = 0.17$) (Table 5.9 and Fig. 5.33), which indicates

the significant role of ion-exchange in groundwater. A similar kind of observation was reported by Dehbandi et al. (2018). Mostly, evaporation and rock dominance processes in semiarid and arid climate conditions are responsible for F^- enhancement in groundwater (Raju, 2017). Moreover, higher levels of F^- in groundwater are due to the F^- dissolution through silicate weathering under alkaline condition (Dehbandi et al., 2018).

5.3.2.3 Geochemical modeling in mineral phases

According to Schoeller (1967), the ionic interaction in groundwater was widely used to better understand by chloro-alkaline (CA) study. Average CA I and CA II values are -0.64 (range: -1.15 to -0.22) and -0.008 (range: -0.016 to -0.002), respectively. All the groundwater samples showed negative values which indicate cation-anion exchange (chloro-alkaline disequilibrium condition) (Fig. 5.34). Thus, both Mg^{2+} and Ca^{2+} ions can be adsorbed onto the exchangeable sites of the host mineral, while concurrently releasing Na^+ and K^+ ions into the groundwater. This study exhibited the participation of silicate weathering in the geochemical processes, which delivers mainly Na^+ ion to the groundwater which was supported by Mondal and Gupta (2015). During this system, the host silicate minerals are the responsible source of dissolved ions into the groundwater. According to Marghade et al. (2012), Cation-anion exchange primarily accounts for the highest concentration of Na^+ ions in groundwater. In the present study, concentration of Na^+ dominates over the other ions. It is confirmed that the host silicate mineral is a responsible contributor for the excess amount of Na^+ in groundwater.

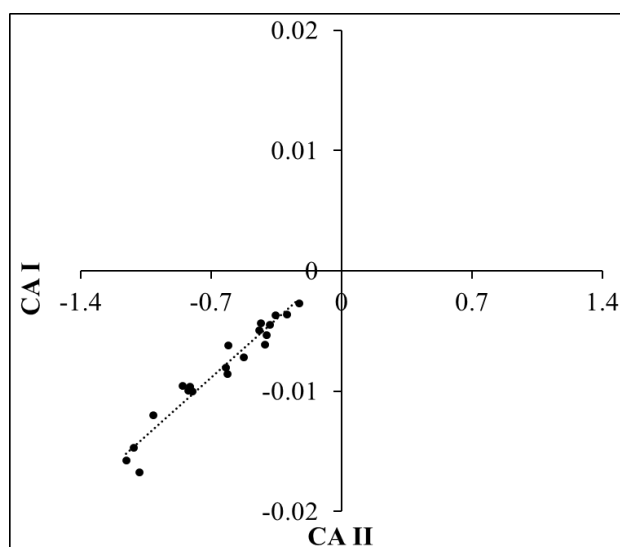


Fig. 5.34: CA I vs CA II showing the cation-anion exchange capacity

Saturation index (SI) is a tool to the mineral stability between solid mineral phase and aqueous phase of groundwater that indicates the tendency of dissolution or precipitation (Marghade et al., 2020; Nawale et al., 2021; Subba Rao et al., 2017; Yadav et al., 2021). Average SI values for anhydrite (CaSO_4), halite (NaCl), calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), fluorite (CaF_2) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), have been observed as 4.71 (range: 3.9 to 5.3), 2.83 (range: 2.57 to 3.12), -0.29 (range: -1.32 to -0.01), -0.52 (range: -1.32 to -0.28), 2.64 (range: 2.39 to 2.91) and -3.14 (range: -2.97 to -3.3), respectively. The positive SI values were found for dolomite, calcite, and fluorite; while the SI values of halite, anhydrite and gypsum were found negative.

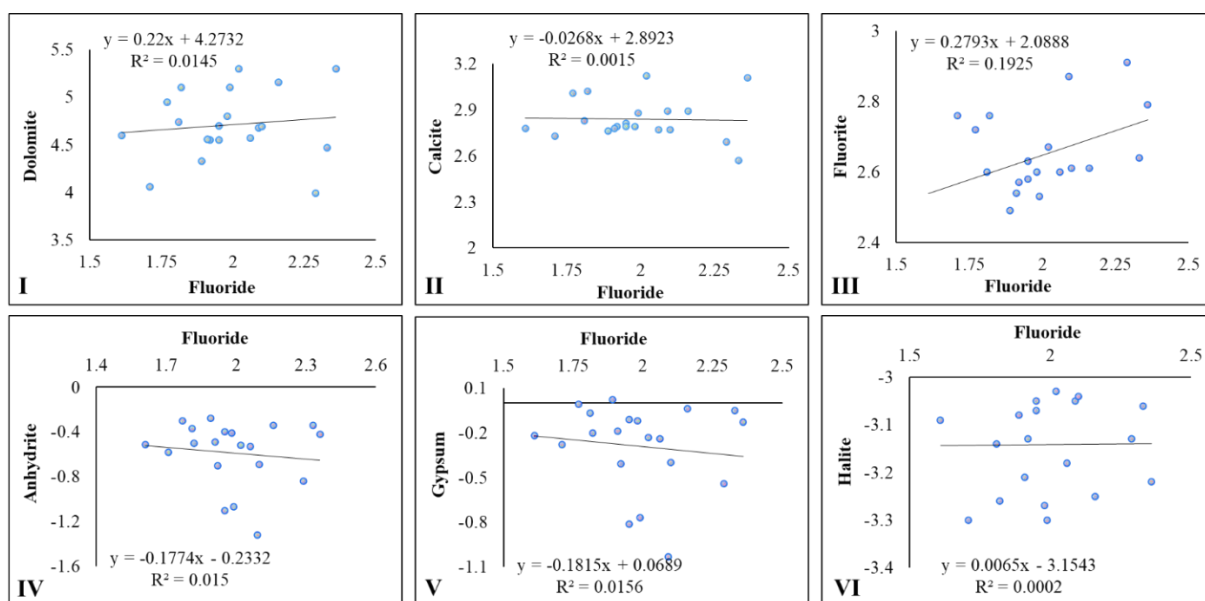


Fig. 5.35: Correlation study between Saturation Index of **I.** dolomite vs fluoride, **II.** calcite vs fluoride, **III.** fluorite vs fluoride **IV.** anhydrite vs fluoride, **V.** gypsum vs fluoride and **VI.** halite vs fluoride

The correlation between positive and negative SI values with respective F^- concentration has been shown in **Fig. 5.35**. Due to positive SI values and the high solubility product, an inverse correlation has been found between Ca^{2+} and F^- which is attributed to precipitate CaF_2 as HCO_3^- type (Kumar et al., 2017; Singaraja, 2017). The positive saturation indicates that the minerals ($\text{CaMg}(\text{CO}_3)_2$, CaCO_3 , and CaF_2) are oversaturated and can be precipitated in aqueous medium (Subba Rao, 2017; Zhang et al., 2020). Negative SI values of halite imply that the mineral is under saturated condition, which is supported by Zhang et al. (2020). The positive SI value of calcite (CaCO_3) has a potential role for F^- leaching into the groundwater (Nawale et al., 2021; Srivastava et al., 1998). As a result, the lowering activity of Ca^{2+} ion which enables more F^- enriched silicate weathering minerals to dissolve by ionic interaction and mixed into the

aquifer (Feng et al., 2020; Karunanidhi et al., 2020). Moreover, these observations support that none of the above minerals justify the leaching of F^- into the groundwater of studied area. Therefore, the most plausible reason behind the presence of F^- has been studied further.

5.3.2.4 Ionic interaction of groundwater

The ionic relation between TDS vs $Na^+/(Na^+ + Cl^-)$ with respect to the two plot areas like seawater or reverse softening and ion-exchange areas has been presented in **Fig. 5.36**. All the collected groundwater samples fall into the field of ion-exchange area which supports that ionic interaction is responsible for F^- mobilization into the aquifer. Na^+ and Cl^- concentrations ranged from 282-323 mg/l and 131-262 mg/l, respectively (**Table 5.8**). The average ratio of Na^+ and Cl^- concentration was found as 1.65 (range: 1.23-2.61). So, the ratio of Na^+ and $Cl^- > 1$ suggested that the groundwater samples can contribute to ion exchange capacity, which was observed by previous studies (Karunanidhi et al., 2020; Marghade et al., 2012).

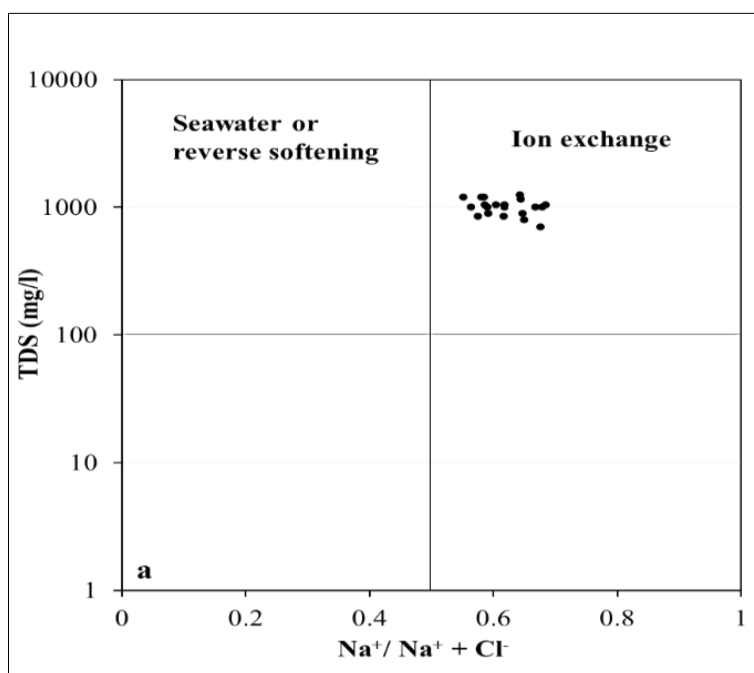


Fig. 5.36: Graphical plots of TDS vs $Na^+/(Na^+ + Cl^-)$ showing ion exchange.

5.4 Investigation on borehole sediments from the studied areas

Borehole sediments samples have been collected from individual sampling sites like ward no. 6, Rajpur Sonarpur Municipality, Sonarpur block (n = 30) and Dhaphdapi II gram-panchayat, Baruipur block (n = 30).

5.4.1 Investigation on borehole sediments from Sonarpur block

5.4.1.1 Geochemical variation with depth wise distribution of borehole sediments

Lithological description of the borehole sediments ($n = 30$) in the studied area has been shown in **Fig. 5.37**. The depth-wise sediment character was found in the order i) clay (depth ranged from 0 to 12.2 m) ii) clay mixed with fine sand (depth ranged from 12.2 to 21.4 m), iii) fine sand (light blackish) (depth ranged from 21.4 to 48.8 m), iv) fine sand (light yellow) (depth ranged from 48.8 to 79.3 m), and v) clay mixed with fine sand (depth ranged from 79.3 to 91.5 m). Physicochemical parameters of borehole sediments and depth wise allocation of F^- , sodium, potassium, iron, and calcium concentrations have been exhibited in **Table 5.20** and **Fig. 5.38**, respectively.

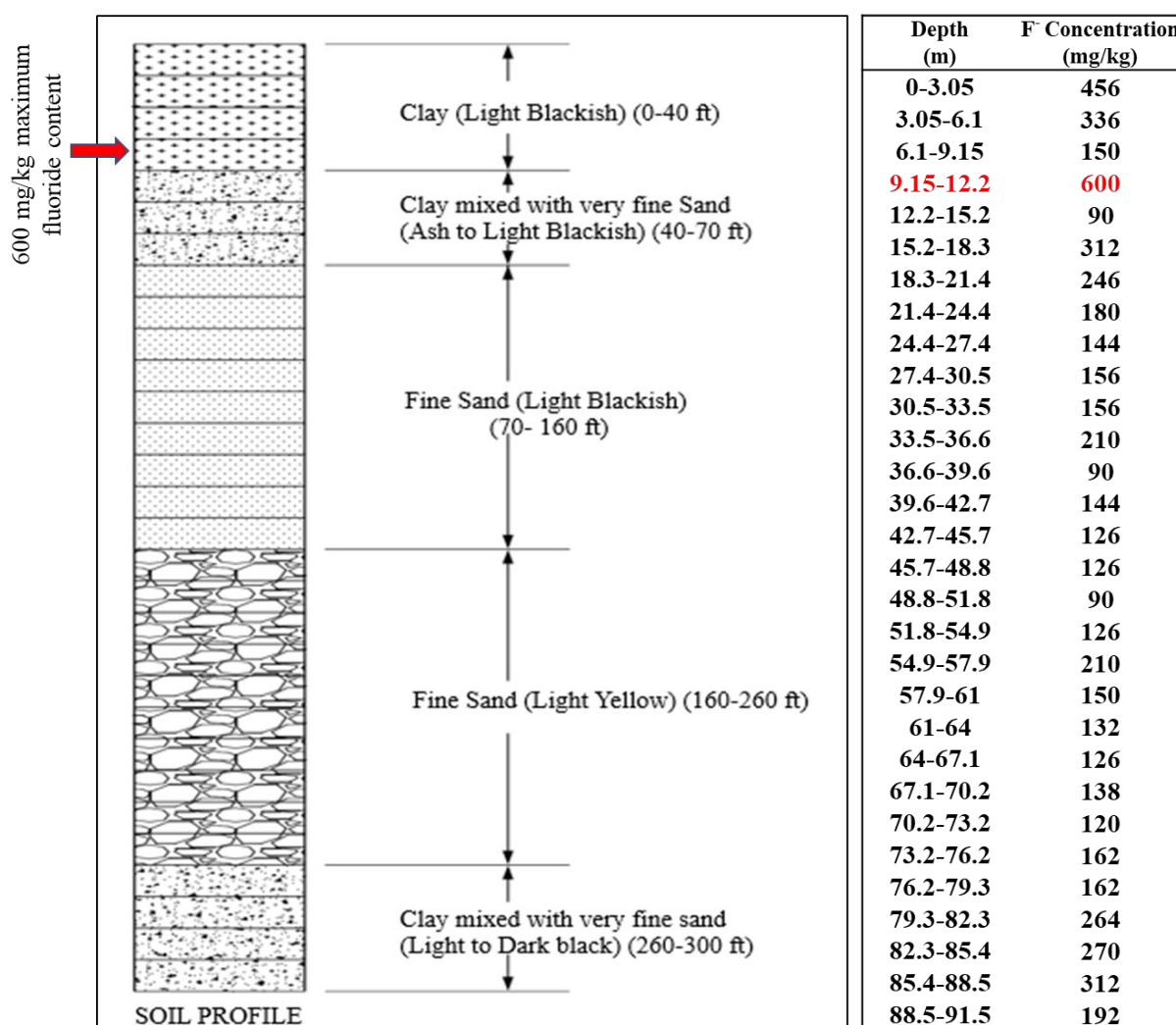
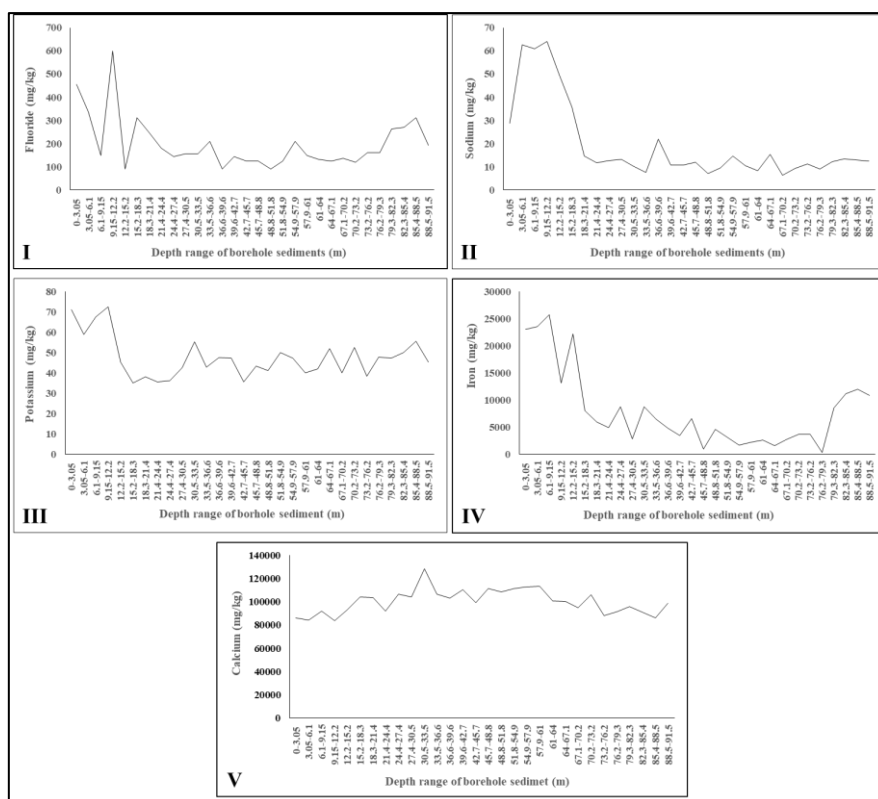


Fig. 5.37: Lithological description of borehole sediments (0-91.5 m) from ward no. 6, Rajpur Sonarpur Municipality in Sonarpur block

Table 5.20: Physico-chemical parameters of borehole sediments (n = 30) samples from ward no. 6, Rajpur Sonarpur Municipality, Sonarpur block

Parameters	Mean	SD	Minimum	Maximum
pH	7.92	0.34	6.45	8.56
EC ($\mu\text{S}/\text{cm}$)	262	220	100	982
Na^+ (mg/kg)	19	17	6.4	64
K^+ (mg/kg)	47	10	35	73
Ca^{2+} (mg/kg)	102377	15991	83748	166800
Fe (mg/kg)	7973	7251	247	25735
F^- (mg/kg)	199	113	90	600

Fluoride concentrations in sediments decreased with depth (**Fig. 5.38**). The maximum F^- concentration (600 mg/kg) was found in the depth range of 9.15-12.2 m (Fig. S5a). The majority of the domestic tube-wells in the surveyed area were installed at <30.5 m depth zone and the mean F^- concentration in groundwater was observed as 1.81 mg/l from Rajpur Sonarpur Municipality (**Table 5.6**). The clay minerals were found <24.4 m depth followed by the presence of very fine sand in deeper zones up to 90.5 m (Fig. 5.37). The maximum density of F^- ions was found in 0-12.2 m depth, then gradually decreased with depth (**Fig. 5.38**). Similar trend was identified in the case of distribution of Na^+ (**Fig. 5.38 II**), K^+ (**Fig. 5.38 III**), Fe (**Fig. 5.38 IV**) and Ca^{2+} (**Fig. 5.38 V**) ions.

**Fig. 5.38:** Depth wise distribution of I. fluoride, II. sodium, III. potassium, IV. iron and V. calcium concentration in borehole sediments from Sonarpur

5.4.1.2 Physico-chemical parameters of borehole sediments

Correlation matrix of the physico-chemical parameters of borehole sediments has been revealed in **Table 5.21**. A good positive relationship was found between F^- and K^+ ($r = 0.59$). Also, strong to moderate correlations have been observed for Na^+ ($r = 0.51$), Ca^{2+} ($r = -0.32$) and Fe ($r = 0.45$) with F^- and it is in the order of $K^+ > Na^+ > Fe > Ca^{2+}$. Moreover, EC holds a very strong interrelation with Na^+ and K^+ which signifies the likelihood of salinity in groundwater. According to Feng et al. (2020) and Li et al. (2020), the salinity of groundwater influences the release of F^- from K^+ enriched clay mineral.

Tables 5.21: Correlation matrix of the physico-chemical parameters of borehole sediments in the study area

Parameters	pH	EC	Na^+	K^+	Ca^{2+}	Fe	F^-
pH	1						
EC	-0.25	1					
Na^+	-0.219	0.950	1				
K^+	-0.193	0.596	0.587	1			
Ca^{2+}	0.026	-0.488	-0.408	-0.21	1		
Fe^{2+}	-0.110	0.703	0.785	0.605	-0.362	1	
F^-	-0.119	0.604	0.517*	0.591*	-0.326	0.452*	1

**It denotes a good correlation between sodium and potassium with fluoride*

5.4.1.3 XRD analysis of borehole sediments

The mineralogical study of the F^- enriched sediment sample was performed to understand the impact of hydro-geochemical evolution on F^- mobilization. The XRD spectra of the highest F^- enriched sediment (600 mg/kg) found in the depth range of 9.15-12.2 m has been shown in **Fig. 5.39**.

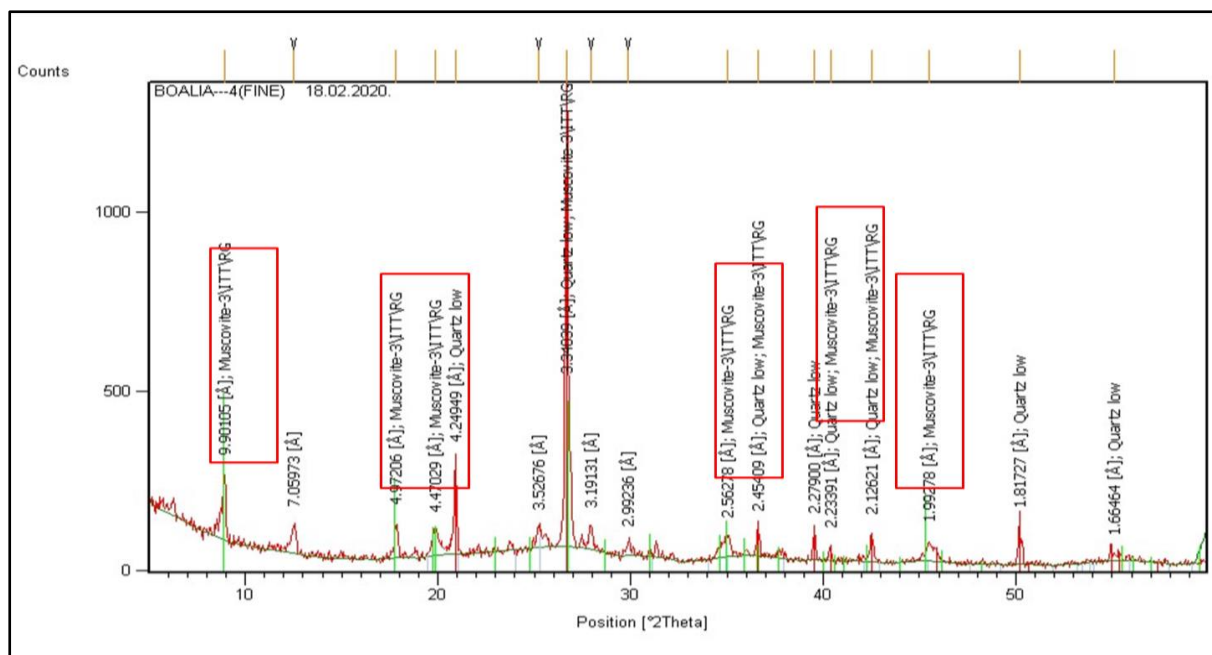


Fig. 5.39: XRD spectra of F^- enriched sediment sample found at 9.15-12.2 m depth zone

5.4.1.4 SEM-EDX analysis of borehole sediments

The SEM-EDX analysis was done considering samples from each sample site and after revising all the SEM-EDX images, a sample with common elements encountered in most of the samples was selected. The study is provided with only one such field-scan to avoid large and repetitive data sets. Generally, in sediment, any mineral-bound element shows a discrete and scattered concentration range, hence, the SEM-EDX was used for the identification of fluorine, instead of quantitative assessment. **Fig. 5.40** presents the scanned area showing a prominent F^- peak. The methods of SEM-EDX data representation were followed by Majumdar et al. (2023). SEM-EDX study showed the presence of responsible elemental composition, where the weight percentages of F^- , Al, Si, Ca and K were found as 1.12%, 15.15%, 27.94%, 0.82%, and 4%, respectively (Fig. 5.40). This suggests the leaching of F^- from clay minerals rich in F^- (such as muscovite) into the aquifer with geochemical process and aligning with findings from previous studies (Aravinthasamy et al., 2020; Liu et al., 2021b; Onipe et al., 2021; Su et al., 2021). This indicates that groundwater F^- contamination is mainly of geogenic origin and predominantly influenced by muscovite. It was observed in a previous study that silicate weathering minerals such as, muscovite is responsible for leaching of F^- in groundwater in Sonarpur block at South 24 Parganas district which comes under the lower Gangetic plain (Datta et al., 2000).

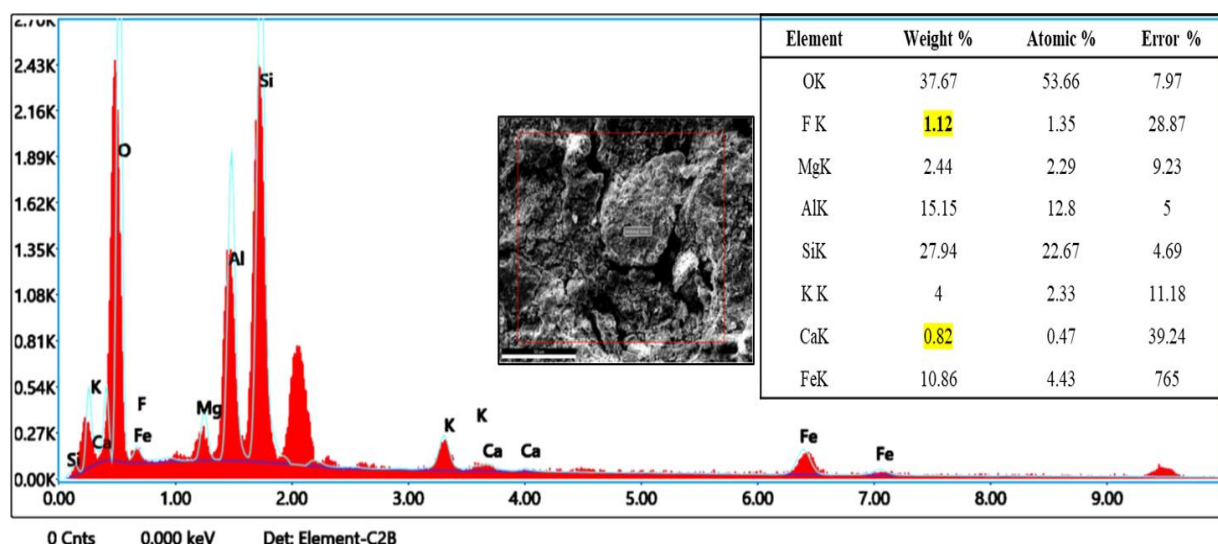


Fig. 5.40: SEM-EDX study with area scan of fluoride enriched sediment sample

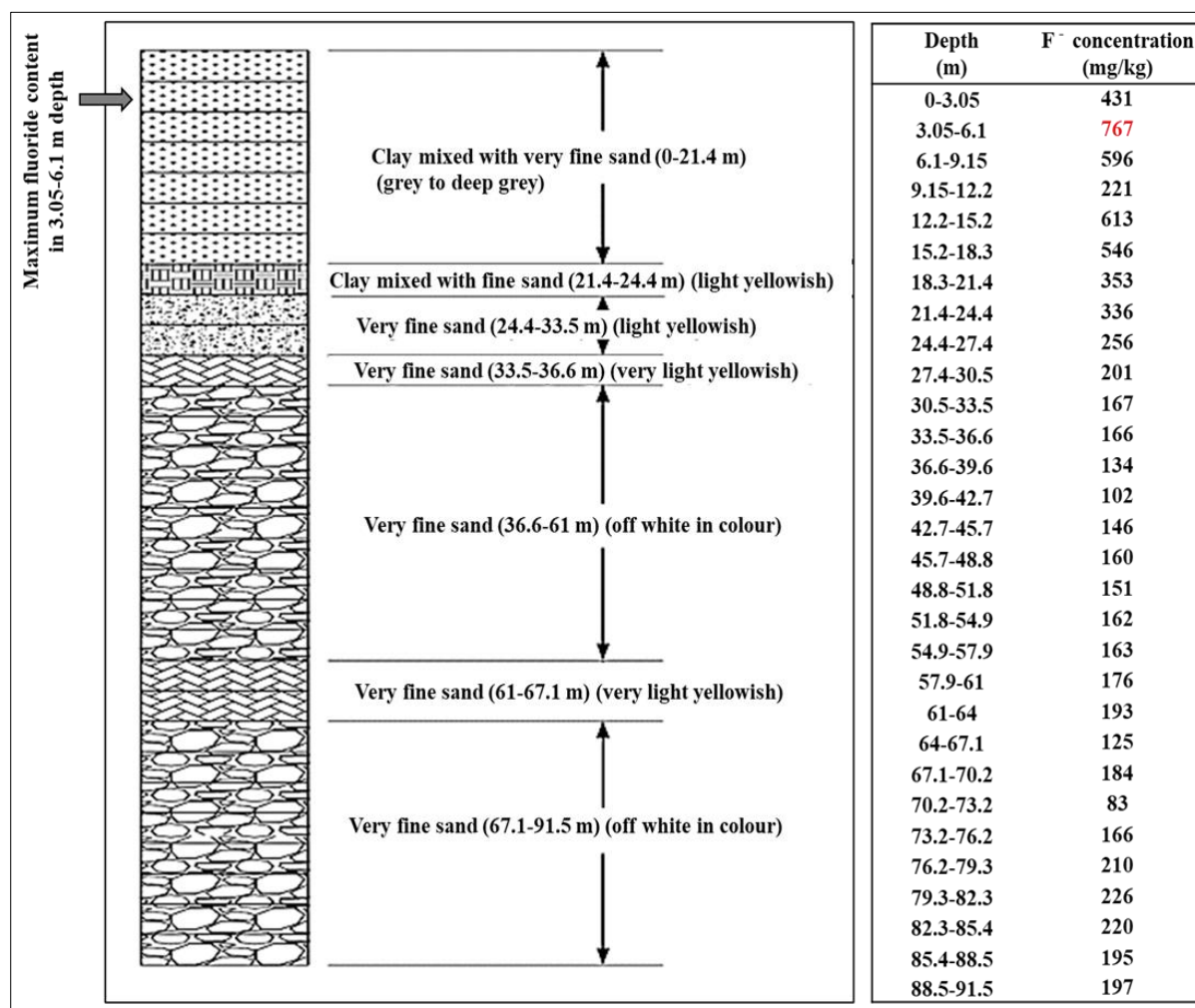
5.4.2 Investigation on borehole sediments from Baruipur block

5.4.2.1 Geochemical variation with depth wise distribution of borehole sediments

Lithological description of the borehole sediments ($n = 30$) in the studied area has been shown in **Fig. 5.41**. The depth-wise sediment character was found in the order i) clay mixed with very fine sand (depth ranged from 0 to 21.4 m) ii) clay mixed with fine sand (depth ranged from 21.4 to 24.4 m) and iii) very fine sand (depth ranged from 24.4 to 91.5 m). Physicochemical parameters of borehole sediments and depth wise allocation of F^- , sodium, potassium, iron, and calcium concentrations have been shown in **Table 5.22** and **Fig. 5.42**, respectively. Fluoride concentrations in sediments decreased with depth (Fig. S5a). The maximum F^- concentration (767 mg/kg) was found in the depth range of 3.05-6.1 m (Fig. 5.41). The majority of the domestic tube-wells in the surveyed area were installed at <30.5 m depth zone and the mean F^- concentration in groundwater was observed as 1.98 mg/l in Nachangacha village, Dhapdhapi II gram-panchayat (**Table 5.8**). The clay minerals were found <24.4 m depth followed by the presence of very fine sand in deeper zones up to 90.5 m (Fig. 5.41). The similar kind of lithological distribution was found in alluvium aquifer of F^- endemic Birbhum district, West Bengal (Mondal et al., 2014).

Table 5.22: Physico-chemical parameters of borehole sediments (n = 30) samples

Parameters	Mean	SD	Median	CV%	Minimum	Maximum
pH	7.41	0.19	7.40	2.58	7.12	7.85
EC	962	752	669	78.1	360	3770
Na ⁺ (mg/kg)	151	98	104	94.3	48	422
K ⁺ (mg/kg)	222	61	199	28	146	381
Ca ²⁺ (mg/kg)	32411	2572	32720	7.93	27280	36600
Fe (mg/kg)	9318	7398	6497	79.4	505	26418
F ⁻ (mg/kg)	255	169	194	67	82	767

**Fig. 5.41:** Lithological description of borehole sediments (0-91.5 m) in the studied area.

The maximum density of F⁻ ions was found in 0-24.4 m depth, then gradually decreased with depth (Fig. 5.41). Analogous pattern was identified in the case of distribution of Na⁺ (Fig. 5.42.II), K⁺ (Fig. 5.42.III), Fe (Fig. 5.42.IV) and Ca²⁺ (Fig. 5.42.V) ions. Low concentration of Ca²⁺ is mainly found in groundwater due to HCO₃⁻ precipitation and the depth-wise ionic

interaction of water with silicate mineral regulates the chemical facies into the groundwater of the lower Gangetic plain in West Bengal (Aravinthasamy et al., 2020; Datta et al., 2000).

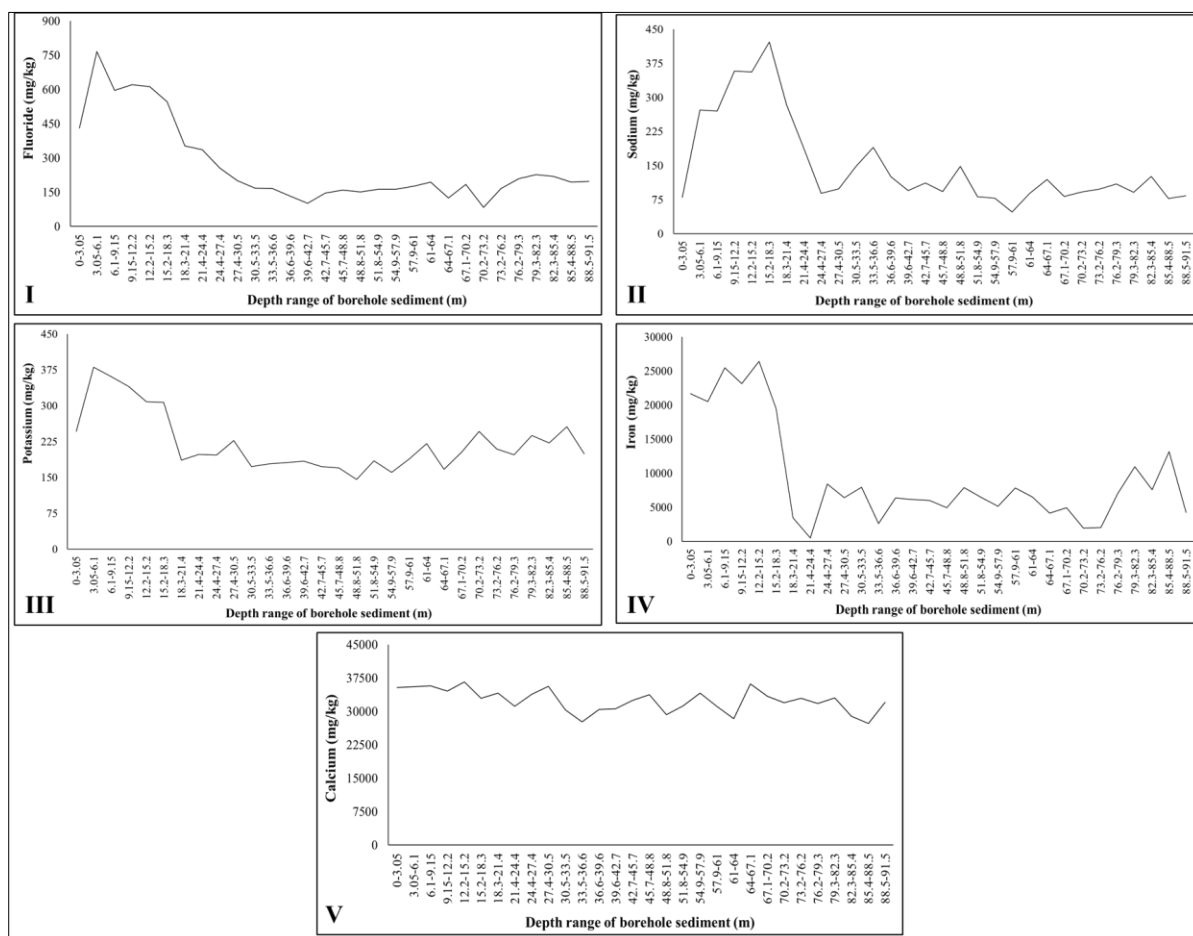


Fig. 5.42: Depth wise distribution of I. fluoride, II. sodium, III. potassium, IV. iron and V. calcium concentration in borehole sediments from Baruipur

5.4.2.2 Cluster analysis on concentrations of Na^+ , K^+ , Ca^{2+} , Fe and F^- for different depth layers

The multitude concentrations of Na^+ , K^+ , Ca^{2+} , Fe , and F^- ions for different depth layers have been presented through a dendrogram, where the different depth ranges were placed in two main clusters by different colour gradients (**Fig. 5.43**). Five ions are likely to be concentrated in two depth ranges; mostly in the depth range of 0 - 18.3 m, followed by 18.3 - 91.5 m, which are demonstrated by two consecutive clusters. The distance of two sister branches from their roots determine the strong interaction of the concerned ions. From Fig. 5.43, the red-coloured cluster group of ions shows a significant branch of length from 0 to 18.3 m which indicates a potential high inter-species (cations) interaction, adopted by strong soil/lithological character.

The next depth from 18.3 to 91.5 m has been represented with a green-coloured non-consecutive branch resulting due to the different sedimentary characteristics of soil. This depth range indicates an active redox potential fluctuation which determines the ionic interaction in the host silicate minerals or the lithological characters, which was supported by Kim et al. (2012). It is suggested that the lithological character of soil is a significant factor for holding the responsible ions at different concentration in different depth ranges and this finding is reinforced by additional studies (Mashal et al., 2022).

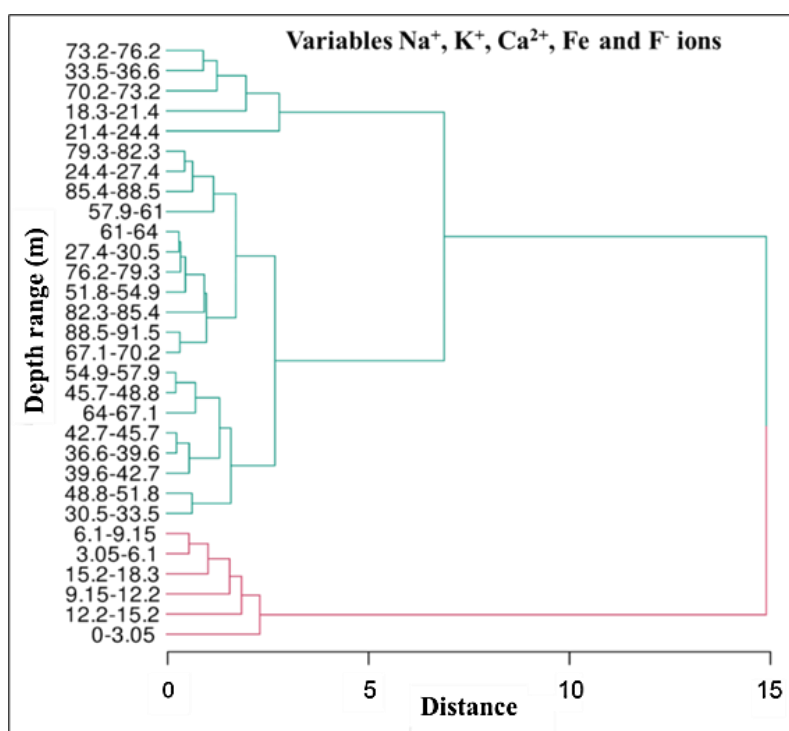


Fig. 5.43: Dendrogram generated through cluster analysis on concentrations of Na^+ , K^+ , Ca^{2+} , Fe and F^- for different depth layers (0 - 91.5 m)

5.4.2.3 Physico-chemical parameters of borehole sediments

Correlation matrix of the physico-chemical parameters of borehole sediments has been revealed in **Table 5.23**. A good positive relationship was found between F^- and K^+ ($r = 0.78$). Also, strong to moderate correlations have been observed for Na^+ ($r = 0.69$), Ca^{2+} ($r = 0.49$) and Fe ($r = 0.75$) with F^- and it is in the order of $\text{K}^+ > \text{Fe} > \text{Na}^+ > \text{Ca}^{2+}$. Moreover, EC holds a very strong interrelation with Na^+ and K^+ which signifies the likelihood of salinity in groundwater. According to Feng et al. (2020) and Li et al. (2020), the salinity of groundwater influences the release of F^- from K^+ enriched clay mineral.

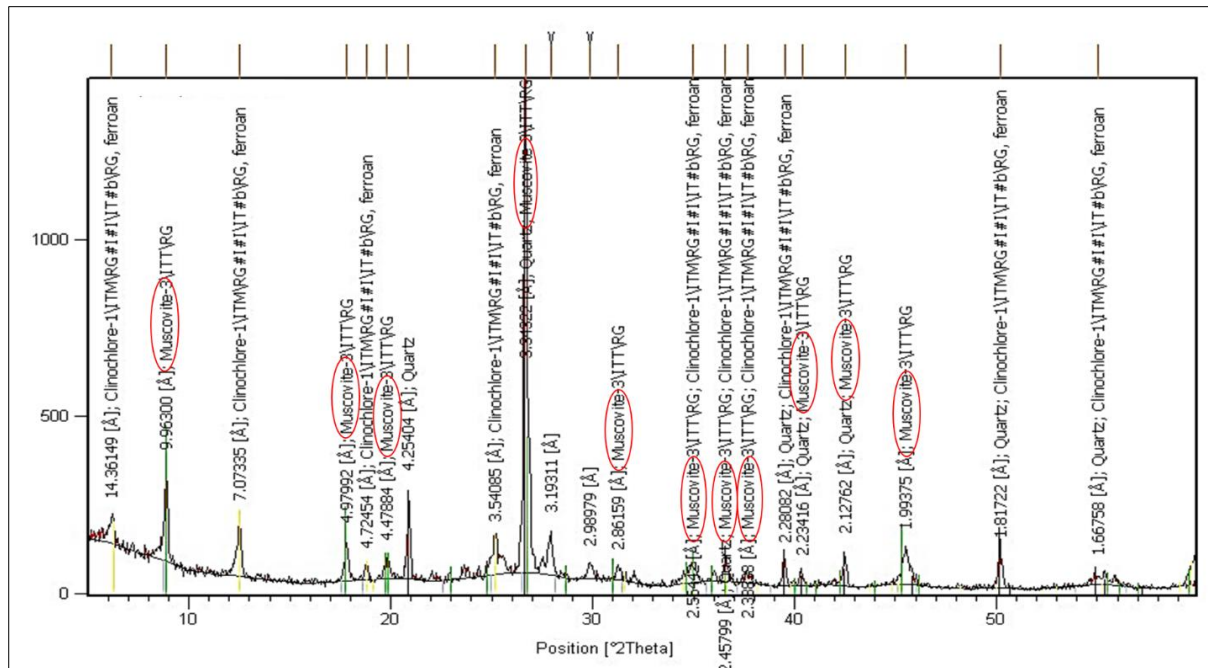
Tables 5.23: Correlation matrix of the physico-chemical parameters of borehole sediments in the study area

Parameters	pH	EC	Na ⁺	K ⁺	Ca ²⁺	Fe	F ⁻
pH	1						
EC	-0.109	1					
Na ⁺	0.053	0.895	1				
K ⁺	-0.063	0.653	0.654	1			
Ca ²⁺	-0.010	0.305	0.337	0.410	1		
Fe	-0.032	0.673	0.627	0.829	0.441	1	
F ⁻	0.044	0.631	0.694*	0.782*	0.498	0.757	1

*It denotes a good correlation between sodium and potassium with fluoride

5.4.2.4 XRD analysis of borehole sediments

The mineralogical study of the F⁻ enriched sediment sample was performed to understand the impact of hydro-geochemical evolution on F⁻ mobilization. The XRD spectra of the highest F⁻ enriched sediment (767 mg/kg) found in the depth range of 3.03-6.1 m has been shown in Fig. 5.44.

**Fig. 5.44:** XRD spectra of fluoride enriched sediment sample found at 3.03 - 6.1 m depth zone

Intense pick of muscovite in the sediment was detected in most of the cases. The muscovite peaks in the samples using powder XRD has been identified using the Crystallography Open

Database (COD) with card entry no. (COD - 1100007). This identified mineral has similar structural and crystal plane features as described by Liang and Hawthorne (1996). It shows the Hermann-Mauguin space group $C12/c1$ with the crystal plane lengths a ($5.18 \pm 0.004 \text{ \AA}$), b ($8.993 \pm 0.006 \text{ \AA}$) and c ($20.06898 \pm 0.013 \text{ \AA}$) while the angles between these planes are α (90°), β ($95.69 \pm 0.06^\circ$) and γ (90°). These combinations make this mineral a monoclinic crystal with $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ$ but $\beta \neq 90^\circ$. The XRD identification using this database provides insight into this mineral with accurate elemental analysis with quantitative and qualitative measurements.

5.4.2.5 SEM-EDX analysis of borehole sediments

The SEM-EDX analysis was done considering samples from each sample site and after revising all the SEM-EDX images, a sample with common elements encountered in most of the samples was selected. Each sediment sample was scanned five times for better accuracy of F^- identification and the best one was selected as a representative of the site. The study is provided with only one such field-scan to avoid large and repetitive data sets.

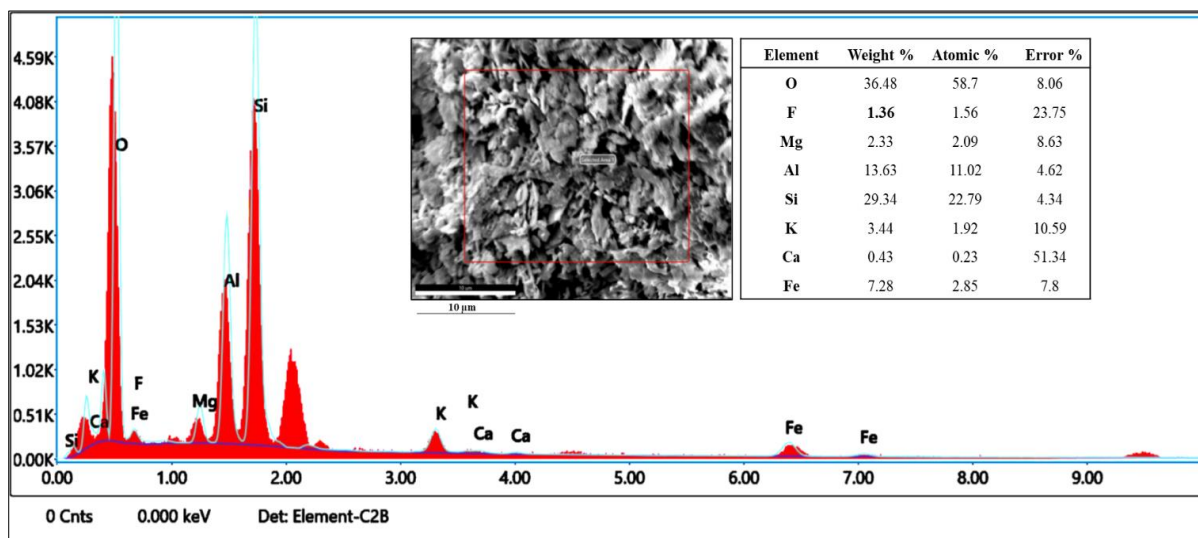


Fig. 5.45: SEM-EDX study with area scan of fluoride enriched sediment sample

Generally, in sediment, any mineral-bound element shows a discrete and scattered concentration range, hence, the SEM-EDX was used for the identification of fluorine, instead of quantitative assessment. **Fig. 5.45** presents the scanned area showing a prominent F^- peak. The methods of SEM-EDX data representation were followed by Majumdar et al. (2023). SEM-EDX study showed the presence of responsible elemental composition, where the weight percentages of F^- , Al, Si, Ca and K were found as 1.36 %, 13.63 %, 29.34%, 0.43%, and 3.44

%, respectively (Fig. 5.45). This indicates the dissolution of F^- from F^- bearing clay mineral (muscovite) into the aquifer due to the geochemical process which was carried out by the earlier reports (Aravinthasamy et al., 2020; Liu et al., 2021; Onipe et al., 2021; Su et al., 2021). Moreover, it can be postulated that under flooded conditions or throughout the rainy season, the salt/mineral becomes dissolved, percolates down and contaminates the groundwater on the top aquifer level (Kashyap et al., 2020). This indicates that groundwater F^- contamination is mainly of geogenic origin and predominantly influenced by muscovite. It was observed in a previous study that silicate weathering minerals such as, muscovite is responsible for leaching of F^- in groundwater in Baripur blocks at South 24 Parganas district which comes under the lower Gangetic plain (Datta et al., 2000).

Objective: 2

*Food chain contamination scenario
through irrigation of agricultural lands
in fluoride contaminated sites*



5.5 Food chain contamination scenario in fluoride contaminated sites (Bankura and Purulia)

This portion is highlighted as a F⁻ contaminated sites in West Bengal which is previously reported. In this study, the food chain F⁻ contamination scenario in Bankura and Purulia district is represented here.

5.5.1 Groundwater and soil fluoride concentration in the studied areas

Groundwater F⁻ concentration was studied in 8 and 14 blocks from Bankura and Purulia districts, respectively. Mean F⁻ concentration was observed as 0.38 ± 0.48 (0.1- 4.1) mg/l and 0.66 ± 0.41 (0.1- 3.3) mg/l, respectively. About 3% and 5% groundwater samples crossed the WHO permissible limit >1.5 mg/l from Bankura (n: 83) and Purulia (n: 153), respectively (**Fig. 5.46**). Fluoride concentration status in the studied agricultural field soil from same blocks of Bankura and Purulia districts was shown in **Table 5.24**. Average F⁻ concentrations in soil samples observed from Bankura and Purulia were 114 ± 59 mg/kg (range: 22.8 - 267 mg/kg, n = 41) and 126 ± 65 mg/kg (range: 47.9 - 297 mg/kg, n = 47), respectively.

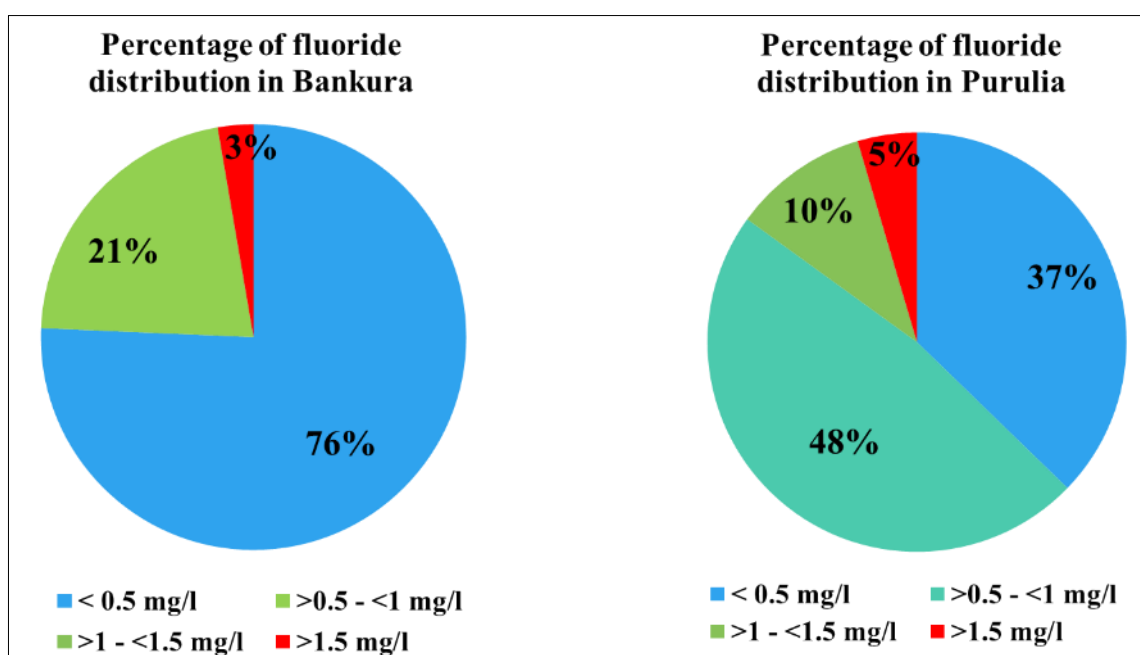


Fig. 5.46: Concentration wise groundwater fluoride distribution in Bankura and Purulia

Table 5.24: Concentration of fluoride in agricultural field soil from the studied areas of Bankura and Purulia districts

District	Block Name	n	Mean \pm SD (mg/kg)	Range (mg/kg)
Bankura	Barjora	5	45 \pm 57	22.8-89.7
	Bankura-II	12	139 \pm 56	96.4-267.4
	Chhatna	1	92	
	Bankura-I	10	95 \pm 57	24.3-208.7
	Simlapal	7	139 \pm 57	60.7-245
	Raipur	2	108 \pm 64	62.7-152.9
	Ranibandh	2	83 \pm 29	62.6-104
	Hirbandh	2	134 \pm 63	89.2-178.4
Total		41	114\pm59	22.8-267.4
Purulia	Manbazar-I	2	67 \pm 13	57.8-76
	Manbazar-II	5	94 \pm 33	68.9-152.3
	Puncha	8	147 \pm 45	76.5-219.6
	Hura	1	128	
	Puruliya-I	2	86 \pm 12	94.9-77
	Arsha	2	54 \pm 5	49.9-57.47
	Balarampur	7	87 \pm 24	59.7-124.3
	Bagmundi	3	164 \pm 91	86.3-247.7
	Jhalda-I	3	133 \pm 72	50.1-183.8
	Jhalda-II	2	114 \pm 62	105.7-121
	Jaipur	2	261 \pm 51	224.5-297.4
	Puruliya-II	3	143 \pm 96	47.9-241
	Para	4	115 \pm 75	55.2-221
	Raghunathpur-I	3	201 \pm 58	136.5-248.4
Total		47	126\pm65	47.9-297.4

5.5.2 Spatial distribution of fluoride concentration in soil

The spatial distribution of F⁻ concentration in soil from Bankura and Purulia was depicted in the **Fig. 5.47**. According to the interpolation mapping, the soil surrounding the area of Bankura-II (267 mg/kg) (Lat: 23°17'58.42" N and long: 87°11'45.50" E) and Jaipur (297 mg/kg) (Lat: 23°18'13.64" N and Long: 87°11'35.88" E) in Bankura and Purulia districts, respectively, may have been heavily lodged with higher amount of F⁻ (Fig. 5.47). Similarly, the lowest concentration of F⁻ in the soil of Bankura and Purulia was found in Barjora (22.8 mg/kg) (Lat: 23°31'35.60"N and Long: 86°37'52.25" E) and Purulia-II (47.9 mg/kg) (Lat: 23°30'11.70" N and Long: 86°31'04.94" E), respectively (Fig. 5.47). The mean F⁻ concentration in soil from Purulia district was found to be 4% higher than that of Bankura district. The interpolation map shows that distribution characteristics of F⁻ in the soil of Purulia varied significantly. The concentration and diverse distribution of F⁻ in the soils of Purulia and Bankura mainly occurred

due to the geogenic (mineral composition of rocks) and anthropogenic activities. IDW method suggested that the magnitude of F^- contamination in soils of Purulia and Bankura mainly existed between Lat: $23^{\circ}18'13.64''$ N and Long: $87^{\circ}11'35.88''$ E and Lat: $23^{\circ}18'13.64''$ N and Long: $87^{\circ}11'35.88''$ E, respectively.

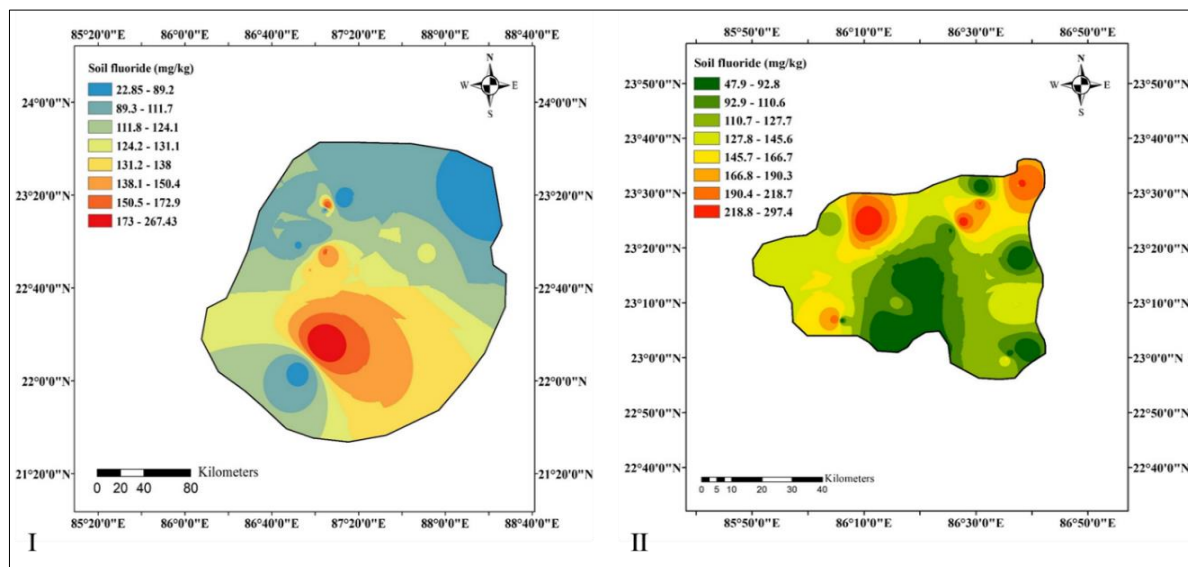


Fig. 5.47: Spatial distribution of fluoride concentration in soil from I. 8 blocks of Bankura district and II. 14 blocks of Purulia district

5.5.3 Fluoride contamination in local crops and vegetables

The concentration of F^- in cereal, pulses, and nonleafy and leafy vegetables cultivated in the studied area was shown in **Table 5.25**. The concentration of F^- in collected food crops ranged between 0.68-54 mg/kg (n: 79) and 0.31-58.9 mg/kg (n =108) in Bankura and Purulia district, respectively (Table 5.25). Among all the collected food crops, the maximum F^- concentration was found in onion from both Bankura (mean: 43 ± 7 mg/kg dw, range: 2.11-54 mg/kg, n = 8) and Purulia (mean: 40.3 ± 1.08 mg/kg dw, range: 3.02-58.9 mg/kg, n = 9). Moreover, the least amount of F^- concentrations was observed in rice compared to any other foodstuff from both the studied districts, Bankura (range: 0.68-1.71 mg/kg, n = 3) and Purulia (range: 0.48-3.31 mg/kg, n = 4). The concentration of F^- in rice cultivated in Purulia district was found to be ~2 times higher than that in Bankura district. The cultivated nonleafy and leafy vegetables in Purulia district contributed to higher F^- (range: 0.31- 58.9 mg/kg, n= 66 and 0.33-48 mg/kg, n= 23) than that of Bankura district (range: 1.2-54 mg/kg, n = 50 and 0.78-19.11 mg/kg, n = 19). The mean concentration of F^- in pigeon pea, lentils, chana, potato, turmeric, chilli, cucumber, tomato, cabbage, coriander, spinach, and fenugreek leaves cultivated in Purulia district was found to be higher than that in Bankura district. Comparatively, F^- concentration in wheat, lentils (arhar), ginger, onion, carrot, shim/broad beans, cauliflower, pumpkin, brinjal, bitter guard, and mustard seed was found to be much higher in Bankura than in Purulia district.

Table 5.25: Concentration of fluoride in cereals, pulses, non-leafy vegetables and leafy vegetables grown in studied areas of Bankura and Purulia districts

Items	Cultivated crops	Bankura			Purulia		
		n	Mean±SD (mg/kg)	Range (mg/kg)	n	Mean±SD (mg/kg)	Range (mg/kg)
Cereals	Rice (<i>Oryza sativa</i>)	3	1.05±0.57	0.68-1.71	4	1.82±0.38	0.48-3.31
	Wheat (<i>Triticum aestivum</i>)	1	2.94		2	1.84±0.64	1.39-2.29
Total		4	2±1.05	0.68-2.94	6	2.01±1.1	0.48-3.31
Pulses	Pigeon Pea (<i>Cajanus cajan</i>)	3	4.1±0.7	3.42-4.73	3	15.42±1.12	14.3-16.78
	Lentils (<i>Lens culinaris</i>)	1	0.9		7	3.32±2.15	0.63-6.52
	Chana (<i>Cicer arietinum</i>)	1	3.78		1	5.63	
	Lentils arhar (<i>Lens culinaris</i>)	1	4.68		2	2.58±0.65	1.92-3.25
Total		6	3.35±1.42	0.9-4.73	13	4.82±1.9	0.63-16.7
Nonleafy Vegetables	Sweet Potato (<i>Ipomoea batatas</i>)	1	6.24		1	13.43	
	Potato (<i>Solanum tuberosum</i>)	8	7.8±11.3	2.4-35.6	9	10.7±2.14	0.74-13.9
	Turmeric (<i>Curcuma longa</i>)	2	3.52±1.02	2.8-4.24	1	4.22	
	Ginger (<i>Zingiber officinale</i>)	1	4.47		1	2.89	
	Onion (<i>Allium cepa</i>)	8	43±7	2.11-54	9	40.3±1.08	3.02-58.9
	Carrot (<i>Daucus carota</i>)	3	42.4±11.8	31.15-53.71	2	28.23±1.24	27.02-30
	Shim/Broad beans (<i>Vicia faba</i>)	2	1.23±0.04	1.20-1.3	1	0.69	
	Beans (<i>Vicia faba</i>)	2	2.03±0.58	1.45-2.61	5	3.37±2.3	0.89-5.87
	Radish (<i>Raphanus sativus</i>)	4	28.02±6.9	21.16-34.9	6	32.9±15.41	1.4-39.37
	Cauliflower (<i>Brassica juncea</i>)	3	7.12±2.6	4.52-9.42	9	6.75±3.05	1.05-9.75
	Chilli (<i>Capsicum frutescens</i>)	1	4.96		8	7.52±5.32	0.31-12.6
	Pumpkin (<i>Cucurbita pepo</i>)	3	22.7±6.5	16.2-29.18	1	9.73	
	Brinjal (<i>Solanum melongena</i>)	3	22.36±3.2	19.16-25.6	1	7.29	
	Cucumber (<i>Cucumis sativus</i>)	1	9.23		1	13.26	
	Bitter guard (<i>Momordica charantia</i>)	1	22.7		1	19.52	
	Mustard seed (<i>Brassica juncea</i>)	5	4±1.87	1.46-6.49	3	2.59±1	1.78-4
	Tomato (<i>Lycopersicon esculentum</i>)	2	11.94±1	11.3-12.6	7	14.01±6.04	0.31-16.5
Total		50	18.1±6.51	1.2-54	66	15.6±5.93	0.31-58.9
Leafy Vegetable	Cabbage (<i>B. oleracea</i> var. capitata)	9	11.71±3	8.89-15	8	12.59±5.18	0.33-16.95
	Coriander (<i>Coriandrum sativum</i>)	1	19.11		6	38.57±18.43	1.07-48
	Spinach (<i>Spinacea Oleracea</i>)	5	10.51±2.6	7.98-13.21	5	13.15±8.77	0.6-21.42
	Fenugreek leaves (<i>Trigonella foenum-graecum</i>)	4	3.11±3	0.78-7.44	4	6.187±3.93	1.74-9.75
Total		19	12.8±2.8	0.78-19.11	23	18.4±6.33	0.33-48

5.5.4 Bio-concentration factor of fluoride in crops and vegetables

Bio-concentration factor (BCF) values of F^- concentration in various crops and vegetables collected from the studied areas are presented in the **Fig. 5.48**. The observed BCF values for all the collected food crops were found to be <1 , which indicates that none of the crops and vegetables were hyper- or good accumulator of F^- .

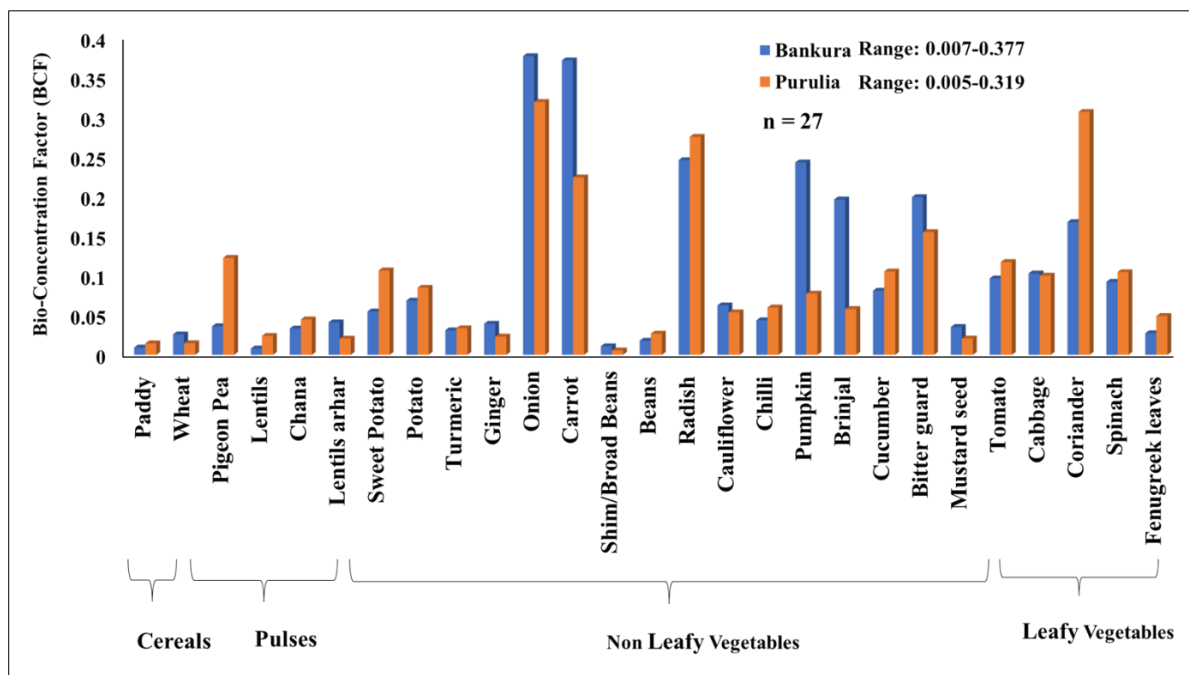


Fig. 5.48: Average bioconcentration factor (BCF) of fluoride in cereals, pulses, nonleafy and leafy vegetable items from Bankura and Purulia districts

The highest BCF of F^- was found in onion, i.e., 0.37 and 0.31 in Bankura and Purulia, respectively. The minimum BCF was observed in lentils (0.007) and shim/broad beans (0.005) from Bankura and Purulia districts, respectively. However, among the cereals, the BCF of F^- was found to be more in rice than in wheat in Purulia and vice versa in Bankura district (Fig. 5.48). Among the pulses, the order of BCF of F^- was found to be lentils arhar > pigeon pea > chana > lentils in Bankura and pigeon pea > chana > lentils > lentils arhar in Purulia. Nonleafy vegetables showed the sequence of BCF in the order of onion > carrot > radish > bitter guard > pumpkin > brinjal > tomato > cucumber > potato > cauliflower > sweet potato > chilli > ginger > mustard seed > turmeric > beans > shim/ broad beans and onion > reddish > carrot > bitter guard > tomato > sweet potato > cucumber > potato > pumpkin > chilli > brinjal > cauliflower > turmeric > beans > ginger > master seed > shim/broad beans in Bankura and Purulia, respectively. Among the leafy vegetables, the BCF of F^- was found in the order of

coriander > cabbage > spinach > fenugreek leaves and coriander > spinach > cabbage > fenugreek leaves in Bankura and Purulia, respectively. The estimated BCF of F^- was found in the order of nonleafy vegetables > leafy vegetables > pulses > cereal in both the studied areas (Table 5.25).

5.5.5 Comparison study of fluoride toxicity on different biomolecules in plant body part from fluoride exposed and control site of West Bengal

Two different locations have been selected as comparative study to understand the variation from F^- toxicity in plant body. Other than F^- concentration, several biomolecules like protein, carbohydrate, total chlorophyll have been analysed in cultivated plants collected from F^- exposed (Nachangacha, Baruipur block, South 24 Parganas) and control area (Pingla, Paschim Medinipur). Protein, carbohydrate and total chlorophyll concentration in most of the leafy vegetables (like Amaranthus, Spinach, Coriander) were found higher in control area compared to F^- exposed area (Fig. 5.49) and this observation was well supported by other studies (Arnesen, 1997; Gadi et al., 2021; Panda, 2015).

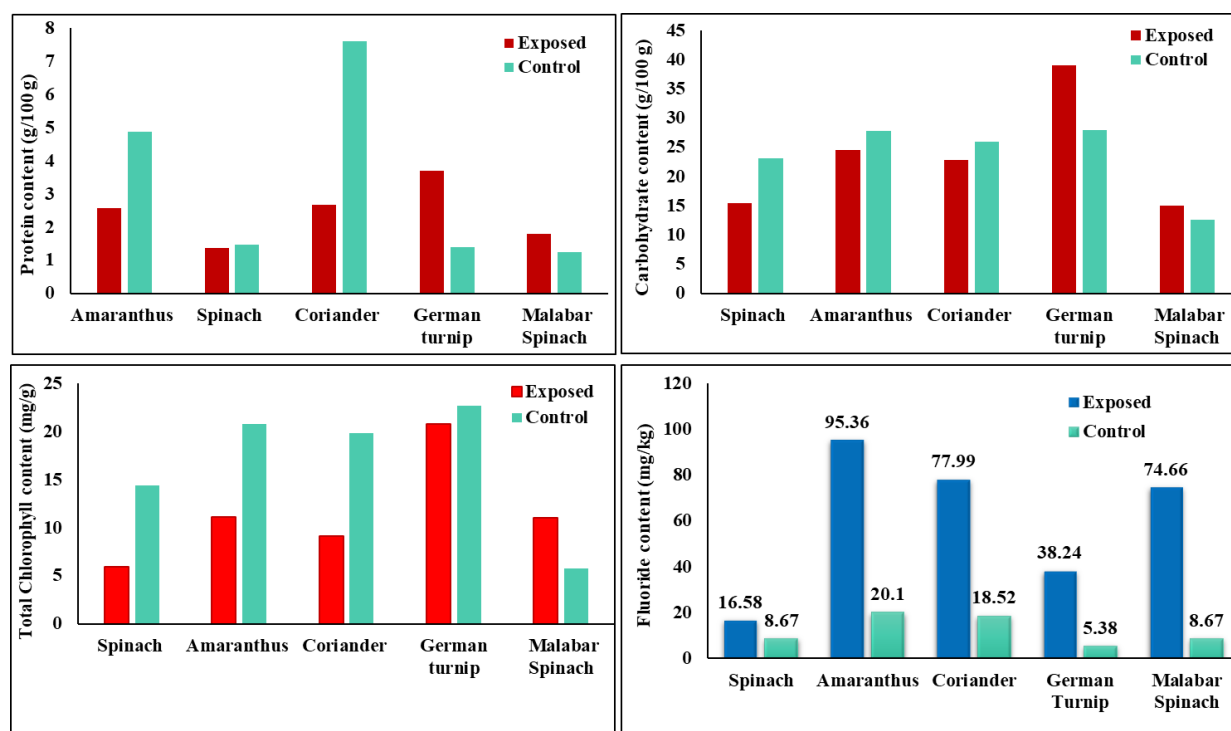


Fig. 5.49: Protein, Carbohydrate content, Total Chlorophyll and fluoride concentration in leafy and non-leafy vegetables from fluoride exposed and control areas

Objective: 3

Health impact of the studied inhabitants



5.6 Health impact of the studied population due to fluoride toxicity in different districts of West Bengal

The health effects on the studied population stemming from F^- toxicity through consumption of F^- contaminated water and foodstuffs have been studied.

5.6.1 Health impact on the population from South 24 Parganas district

5.6.1.1 Estimation of urinary fluoride from Rajpur Sonarpur Municipality in Sonarpur block

Presence of F^- in urine is a well-established pathological indicator and contemporary biomarker of F^- toxicity (Singh et al., 2007; Villa et al., 2000, 2010). Average urinary F^- concentrations in children ($n = 11$), teenagers ($n = 12$), and adults ($n = 101$) of ward number 6 were 2.01 ± 0.85 mg/l (range: 0.79 - 3.26 mg/l), 2.36 ± 1.2 mg/l (range: 0.73 - 4.5 mg/l), and 2.1 ± 1.21 mg/l (range: 0.32 - 7.02 mg/l), respectively. In the case of the studied populations from ward number 7, the mean urinary F^- concentrations in children ($n = 9$), teenagers ($n = 9$) and adults ($n = 50$) were 2.1 ± 1.16 mg/l (range: 0.39 - 3.9 mg/l), 2.56 ± 1.5 mg/l (range: 0.28 - 4.66 mg/l) and 1.84 ± 1.01 mg/l (range: 0.38 - 4.98 mg/l), respectively. Urinary F^- concentration for all the studied age groups from ward number 6 (mean = 2.12 ± 1.18 mg/l; range: 0.32 - 7.02 mg/l; $n = 124$) and 7 (mean = 1.97 ± 1.09 mg/l; range: 0.28 - 4.98 mg/l; $n = 68$) was found quite similar. This might be due to the fact that the studied population from the two wards was exposed to apparently similar concentration of F^- through drinking water (mean = 1.38 ± 0.51 mg/l; range: 0.05 - 2.2 mg/l; $n = 146$ and mean = 1.18 ± 0.67 mg/l; range: 0.02 - 2.5 mg/l; $n = 96$, respectively) (Table 5.1). The observed values of urinary F^- in exposed populations were quite high compared to the studied control populations. The average urinary F^- concentration in the control population exposed with low concentration of F^- through drinking water (mean = 0.64 ± 0.12 mg/l; range: 0.36 - 0.7 mg/l, $n = 7$) was found to be 1.29 ± 0.43 mg/l (range: 0.52 - 1.7 mg/l, $n = 19$). Compared to the children in this study, the F^- excretion through urine was higher for teenagers (from both the ward numbers 6 and 7) and adults (from ward number 6). This might be due to the saturation of F^- absorption in the calcified tissues (bones and teeth) with growing age, resulting rapid excretion of ingested F^- through urine on later stage (Myers, 1978). However, F^- is absorbed more rapidly into calcified tissues during the developmental phase in young individuals compared to older ones (Rango et al., 2014; Whiteford, 1999). Several other studies on Indian population reported the urinary F^- concentration in the range of 0.1-17 mg/l when level of water F^- was 1.6-3.3 mg/l (Bhattacharya et al., 2020; Das and Mondal, 2016;

Haritash et al., 2018; Kumar et al., 2017; Singh et al., 2007). Higher levels of urinary F^- were reported from several other studies in Mexico, Ethiopia, Chile, China and Pakistan, exposed with F^- contaminated water (Carmen et al., 2016; Rango et al., 2014; Villa et al., 2010; Xiang et al., 2003; Zulfiqar et al., 2019).

5.6.1.2 Regression analysis between water and urinary fluoride from Rajpur Sonarpur Municipality

The regression analysis between water and urinary F^- concentrations among the studied populations has been shown in **Fig. 5.50**, where found maximum density of F^- . The R^2 values in both cases (0.1078 and 0.0555) showed poor correlations between water and urinary F^- for two studied populations in ward number 6 and 7, respectively (**Fig. 5.50 I and II**).

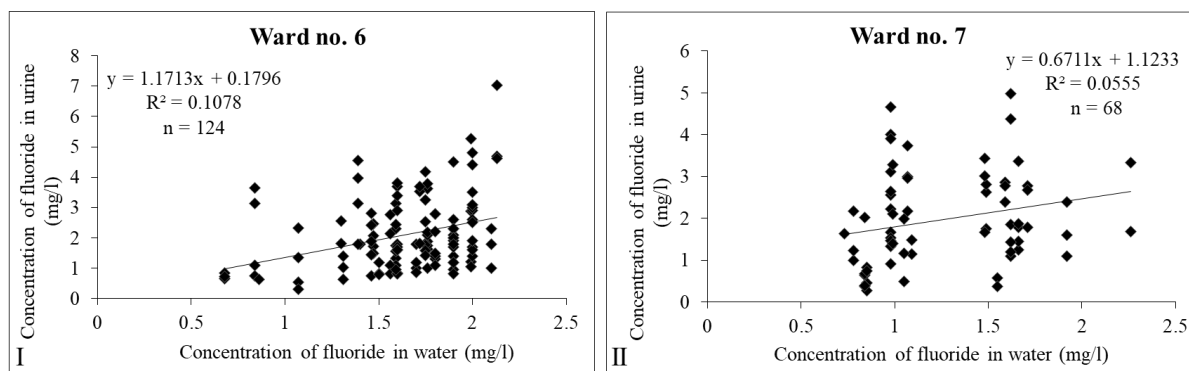


Fig. 5.50: Regression analysis between fluoride (F^-) concentrations in water and urine among the studied populations in **I.** ward number 6 and **II.** ward number 7

A parallel study found no notable correlation between urinary F^- levels and drinking water F^- concentrations, with F^- concentration in urine (mean = 1.10 mg/l; range: 0.10–2.67 mg/l), which might be due to inhalation of F^- contaminated dust particles and through their daily diet (Czarnowski et al., 1996). A study report showed that urinary F^- concentration was not always positively correlated with F^- level in drinking water (Bhowmik et al., 2019). However, an apparent increasing trend of urinary F^- concentration was observed in this study with increasing water F^- concentration which was supported by other studies (Idowu et al., 2019; Khanoranga and Khalid, 2019; Kumar et al., 2017; Rango et al., 2017). In a recent study, a positive correlation was observed ($r = 0.46$) between water and urinary F^- concentration of the studied populations in Dharmanagar region, north Tripura, India (Bhattacharya et al., 2020).

5.6.1.3 Urinary arsenic from Rajpur Sonarpur Municipality

In Rajpur Sonarpur Municipality, approximately, 44% and 25% of the groundwater samples ($n = 288$) from 14 wards have been identified with presence of higher levels of As with $\geq 10 \mu\text{g/l}$ and $\geq 50 \mu\text{g/l}$, respectively. Likewise, approximately, 62% and 57% of the groundwater samples contain As with $\geq 50 \mu\text{g/l}$ in ward number 15 and 24, respectively.

Urine serves as the most dependable indicator of recent exposure to inorganic arsenic since it is the primary route for excreting most arsenic species (ATSDR, 1993; Buchet et al., 1981; Vahter, 1994). The half-time of inorganic arsenic subjects about 4 days in human body system. Approximately, 60-75% of the ingested dose of arsenic is excreted through urine within a few days and arsenic species contribute as 10-15% of inorganic arsenic, 10-15% monomethyl arsenic acid (MMA) and 60-80% dimethylarsonic acid (Hopenhayn-Rich et al., 1996). Elevated level of urinary arsenic (mean = $46.5 \pm 30.8 \mu\text{g/l}$; range: 4-120 $\mu\text{g/l}$, $n = 51$) from the studied population of ward number 15 was due to intake of considerable amount of arsenic through drinking water (mean = $56.3 \pm 33.5 \mu\text{g/l}$; range: 3-105 $\mu\text{g/l}$; $n = 21$) (Table 5.1). The average urine arsenic concentration in the control population exposed with low concentration of arsenic ($< 3 \mu\text{g/l}$) through drinking water was found to be $3.3 \pm 0.6 \mu\text{g/l}$ (range: < 3 -5.14 $\mu\text{g/l}$, $n = 19$) and this value was much lower compared to urinary arsenic level for exposed populations. In this study, the populations have been exposed to either F^- or arsenic depending on the groundwater quality status in the particular geographical location. As a result, potential health risk must exist there due to F^- and arsenic toxicity. Roychowdhury (2010) reported the presence of high concentrations of arsenic in urine samples (mean = 292 $\mu\text{g/l}$; range: 8.35-1024 $\mu\text{g/l}$; $n = 193$) of the exposed populations from an arsenic endemic area of North 24 Parganas district, West Bengal. Elevated concentration of arsenic (mean = $74.7 \pm 34.9 \mu\text{g/l}$; $n = 68$) was reported in urine samples from the studied children (5-15 years) in Murshidabad district of West Bengal who were exposed to higher concentration of arsenic through drinking water (mean = $50.8 \pm 30.8 \mu\text{g/l}$) (Chatterjee et al., 2018). In a recent study (Joardar et al., 2021b), the urine samples obtained from school children exposed in North 24 Parganas district, West Bengal, exhibited elevated levels of arsenic (mean = $64.6 \pm 48.6 \mu\text{g/l}$; range: 15-212 $\mu\text{g/l}$; $n = 43$). Higher levels of urinary arsenic were also reported from the inhabitants exposed with contaminated drinking water in several other studies from Bangladesh, USA and China (Kippler et al., 2016; Watanabe et al., 2007; Welch et al., 2018; Zhang et al., 2018).

5.6.1.4 Regression analysis between water and urinary arsenic from Rajpur Sonarpur Municipality

The R^2 value (0.8476) in regression analysis between water and urinary arsenic concentration among the studied populations showed strong correlation between these two (**Fig. 5.51**). This finding is supported by several other studies in West Bengal, India (Joardar et al., 2021b; Maity et al., 2012; Roychowdhury, 2010; Uchino et al., 2006) and Korea (Sun Bae et al., 2013). Strong correlation was observed ($r = 0.69$) between water and urinary arsenic concentration of the investigated inhabitants in north Tripura, India (Bhattacharya et al., 2020).

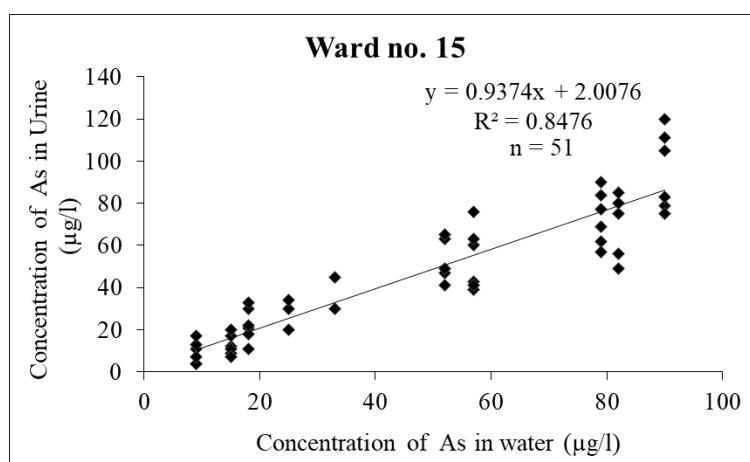


Fig. 5.51: Regression analysis between arsenic concentrations in water and urine among the studied populations in ward number 15

5.6.1.5 Human health risk assessment due to fluoride and arsenic exposure from Rajpur Sonarpur Municipality

The estimated risk from Rajpur Sonarpur Municipality has been evaluated and represented by different model.

5.6.1.5.1 Average daily dose (ADD) of fluoride and arsenic through water consumption

The average daily dose (ADD) of F^- and arsenic through consumption of water is the ultimate tool to analyse the toxicological effects on human health. The ADD of F^- and arsenic in the studied populations was presented in **Table 5.26** and **5.27**. Among the different age groups, adults had been experienced the highest daily dose of F^- and arsenic as assessed to the other two age groups. In most of the cases, the average daily dose of F^- and arsenic calculated for all the age groups in the studied area was in the order adults > teenagers > children (Table 5.26

and 5.27). The exposure dose value obtained from this area was based on daily water consumption; however, intake of F^- and arsenic from other foodstuffs (cereals and vegetables) and the use of F^- and arsenic-contaminated water in cooking were not accounted in this study. Due to the higher consumption of water and exposure duration, adults had high ADD of arsenic and F^- as compared to teenagers and children.

Table 5.26: Modelled average daily dose (ADD) of fluoride for children, teenagers and adults from the studied areas

ADD (F^-) (mg/kg bw/day)							
Ward No.	Children	Teenagers	Adults	Ward No.	Children	Teenagers	Adults
1	0.041	0.045	0.047	19	0.031	0.034	0.035
2	0.026	0.028	0.03	20	0.018	0.02	0.021
3	0.032	0.036	0.037	21	0.064	0.071	0.072
4	0.026	0.028	0.029	22	0.038	0.042	0.043
5	0.041	0.045	0.046	23	0.014	0.015	0.017
6	0.069	0.076	0.079	24	0.016	0.017	0.018
7	0.059	0.065	0.067	25	0.026	0.028	0.029
8	0.055	0.059	0.062	26	0.028	0.031	0.032
9	0.038	0.041	0.043	27	0.021	0.022	0.023
10	0.016	0.018	0.018	28	0.026	0.028	0.03
11	0.021	0.023	0.024	29	0.031	0.034	0.035
12	0.006	0.007	0.007	30	0.014	0.015	0.016
13	0.026	0.028	0.03	31	0.027	0.029	0.03
14	0.021	0.022	0.023	32	0.041	0.045	0.047
15	0.021	0.023	0.024	33	0.044	0.048	0.05
16	0.003	0.003	0.004	34	0.031	0.034	0.035
17	0.013	0.014	0.015	35	0.019	0.021	0.022
18	0.017	0.018	0.019				

Table 5.27: Modelled average daily dose (ADD) of arsenic for children, teenagers and adults from the studied areas

ADD (As) (mg/kg bw/day)							
Ward No.	Children	Teenagers	Adults	Ward No.	Children	Teenagers	Adults
1	0.000059	0.000124	0.00048	19	0.000293	0.00062	0.00239
2	0.000090	0.000189	0.00073	20	0.000398	0.00084	0.00324
3	0.000101	0.000213	0.00082	21	0.000021	0.00004	0.00017
4	0.000260	0.000551	0.00212	22	0.000021	0.00004	0.00017
5	0.000232	0.000494	0.0019	23	0.000403	0.00085	0.00329
6	0.000270	0.000572	0.0022	24	0.000465	0.00098	0.00379
7	0.000057	0.000122	0.00047	25	0.000389	0.00083	0.00318
8	0.000021	0.000043	0.00017	26	0.000021	0.00004	0.00017
9	0.000022	0.000049	0.00019	27	0.000021	0.00004	0.00017
10	0.000202	0.000427	0.00165	28	0.000022	0.00005	0.00018
11	0.000172	0.000365	0.0014	29	0.000071	0.00015	0.00058
12	0.000183	0.000389	0.0015	30	0.000321	0.00068	0.00262
13	0.000024	0.000051	0.0002	31	0.000381	0.00081	0.00311
14	0.000279	0.000591	0.00228	32	0.000291	0.00062	0.00238
15	0.000393	0.000834	0.00321	33	0.000088	0.00019	0.00072
16	0.000069	0.000147	0.00056	34	0.000022	0.00005	0.00019
17	0.000021	0.000045	0.00017	35	0.000081	0.00017	0.00066
18	0.000230	0.000487	0.00187				

5.6.1.5.2 Evaluation of non-cancerous health risk associated to fluoride and arsenic exposure in different age groups from Rajpur Sonarpur Municipality

The exposure through different hazardous materials is of major importance to evaluate the adverse human health effects and potential health risk evaluation. The investigation on potential health risk based on the estimation of targeted hazard quotient (THQ) due to the consumption of F⁻ and arsenic through water was presented in **Table 5.28**. The tolerable level of any non-carcinogenic risk is considered when THQ <1 and THQ >1 indicates high non-carcinogenic risk may exist among the exposed populations (USEPA, 2003, 2009). THQ value of arsenic was found >1 for adults, teenagers and children in 24, 17 and 7 wards, respectively and observed >1 for all the age groups in 7 wards from the studied areas (ward number 15, 20, 23, 24, 25, 30 and 31) (**Table 5.29**). The observed mean THQ_{As} values for adults, teenagers and children from these 7 wards were 10.7, 2.77, and 1.31, respectively. The THQ_{As} values for teenagers (mean = 1.21; range: 0.14-3.28) and children (mean = 0.57; range: 0.07-1.55) were much lower compared to the adults (mean = 4.66; range: 0.57-12.63) in the entire studied areas.

The trend in THQ value of F^- was same as that of THQ_{As} i.e. adults had the highest THQ value followed by the teenagers and children (Table 5.28 and 5.29). The ward numbers 6 and 21 in the studied area were found with $THQ_{F^-} > 1$ for all the studied age groups. THQ value of F^- was found >1 for adults and teenagers in 4 wards (6, 7, 8, and 21); whereas, for children in two wards (6 and 21). The observed mean THQ_{F^-} value for adults and teenagers from these 4 wards was 1.17 (range: 1.03-1.32) and 1.13 (range: 1.00 -1.26), respectively. The THQ_{F^-} values for teenagers (mean = 0.53; range: 0.06-1.26) and children (mean = 0.49; range: 0.06-1.15) were found lower compared to the adults (mean = 0.55; range: 0.07-1.32) in the entire studied areas. Out of 35 wards, 25 wards showed $THQ_{As} > 1$, whereas 4 wards showed $THQ_{F^-} > 1$ in case of adults. High non-carcinogenic risk of both F^- (1.32 and 1.12) and arsenic (7.33 and 1.57) were observed in the case of adults from ward number 6 and 7, respectively.

Table 5.28: Targeted hazard quotient (THQ) of fluoride for the studied populations through dietary intake of groundwater

THQ _{F⁻}							
Ward No.	Children	Teenagers	Adults	Ward No.	Children	Teenagers	Adults
1	0.68	0.75	0.78	19	0.51	0.56	0.58
2	0.43	0.48	0.50	20	0.31	0.34	0.35
3	0.53	0.59	0.61	21	1.08*	1.18*	1.20*
4	0.43	0.47	0.48	22	0.63	0.70	0.72
5	0.68	0.74	0.77	23	0.24	0.27	0.28
6	1.15*	1.26*	1.32*	24	0.27	0.29	0.30
7	0.98	1.08*	1.12*	25	0.43	0.47	0.48
8	0.91	1.00*	1.03*	26	0.47	0.51	0.53
9	0.63	0.69	0.72	27	0.34	0.38	0.38
10	0.27	0.29	0.30	28	0.43	0.48	0.50
11	0.35	0.38	0.40	29	0.52	0.57	0.58
12	0.11	0.12	0.12	30	0.23	0.26	0.27
13	0.43	0.48	0.50	31	0.44	0.49	0.50
14	0.34	0.38	0.38	32	0.68	0.75	0.78
15	0.35	0.38	0.40	33	0.73	0.81	0.83
16	0.06	0.06	0.07	34	0.52	0.57	0.58
17	0.22	0.24	0.25	35	0.33	0.36	0.37
18	0.28	0.30	0.32				

*Non-carcinogenic risk >1

Table 5.29: Targeted hazard quotient (THQ) of arsenic for the studied populations through dietary intake of groundwater

THQ _{As}							
Ward No.	Children	Teenagers	Adults	Ward No.	Children	Teenagers	Adults
1	0.20	0.41	1.60*	19	0.98	2.07*	7.97*
2	0.30	0.63	2.43*	20	1.33*	2.81*	10.8*
3	0.34	0.71	2.73*	21	0.07	0.14	0.57
4	0.87	1.84*	7.07*	22	0.07	0.14	0.57
5	0.77	1.65*	6.33*	23	1.34*	2.84*	10.97*
6	0.90	1.91*	7.33*	24	1.55*	3.28*	12.63*
7	0.19	0.41	1.57*	25	1.30*	2.75*	10.6*
8	0.07	0.14	0.57	26	0.07	0.14	0.57
9	0.07	0.16	0.63	27	0.07	0.14	0.57
10	0.67	1.42*	5.50*	28	0.07	0.15	0.60
11	0.57	1.22*	4.67*	29	0.24	0.50	1.93*
12	0.61	1.30*	5.00*	30	1.07*	2.27*	8.73*
13	0.08	0.17	0.67	31	1.27*	2.69*	10.37*
14	0.93	1.97*	7.60*	32	0.97	2.06*	7.93*
15	1.31*	2.78*	10.70*	33	0.29	0.62	2.40*
16	0.23	0.49	1.87*	34	0.07	0.16	0.63
17	0.07	0.15	0.57	35	0.27	0.58	2.20*
18	0.77	1.62*	6.23*				

*Non-carcinogenic risk > 1

5.6.1.5.3 Evaluation of cancerous health risk associated to arsenic exposure in different age groups from Rajpur Sonarpur Municipality

The cancer risk (CR) assessment due to arsenic exposure among the studied populations is presented in **Table 5.30**. The studied populations might be exposed to serious threat of cancer risk (CR) as the values of carcinogenic health risk were high for all the age groups. The CR values for children (mean = 2.57×10^{-4} ; range: 3.15×10^{-5} - 6.97×10^{-4}), teenagers (mean = 5.44×10^{-4} ; range: 6.48×10^{-5} - 1.47×10^{-3}) and adults (mean = 2.10×10^{-3} ; range: 2.55×10^{-4} - 5.69×10^{-3}) were much higher compared to the recommended threshold level of carcinogenic health risk of arsenic (1×10^{-6}) (USEPA, 2005). The mean CR values due to arsenic toxicity among all the studied age groups in ward number 6 and 7 were 15.2×10^{-4} and 3.24×10^{-4} , respectively (Table 5.30). The highest cancer risk can be presumed among the populations in 7 wards (15, 20, 23, 24, 25, 30, and 31) (Table 5.30) due to the presence of higher level of arsenic in groundwater (Table 5.1). The existence of F^- (range: 0.05 - 2.2 mg/l and 0.02 - 2.5 mg/l) and As (range: <3 - 44 μ g/l and <3 - 10.1 μ g/l) in groundwater above their recommended values in drinking water increased the health risk of the local inhabitants in ward number 6 and 7, respectively compared to the other studied wards in Rajpur-Sonarpur Municipality.

Table 5.30: Cancer risk (CR) among the different age groups due to arsenic toxicity through groundwater

Ward No.	Children	Teenagers	Adults	Ward No.	Children	Teenagers	Adults
1	8.82×10^{-5}	1.86×10^{-4}	7.20×10^{-4}	19	4.39×10^{-4}	9.32×10^{-4}	3.59×10^{-3}
2	1.34×10^{-4}	2.84×10^{-4}	1.10×10^{-3}	20	5.96×10^{-4}	1.26×10^{-3}	4.86×10^{-3}
3	1.51×10^{-4}	3.20×10^{-4}	1.23×10^{-3}	21	3.15×10^{-5}	6.48×10^{-5}	2.55×10^{-4}
4	3.91×10^{-4}	8.26×10^{-4}	3.18×10^{-3}	22	3.15×10^{-5}	6.48×10^{-5}	2.55×10^{-4}
5	3.49×10^{-4}	7.41×10^{-4}	2.85×10^{-3}	23	6.05×10^{-4}	1.28×10^{-3}	4.94×10^{-3}
6	4.05×10^{-4}	8.59×10^{-4}	3.30×10^{-3}	24	6.97×10^{-4}	1.47×10^{-3}	5.69×10^{-3}
7	8.61×10^{-5}	1.82×10^{-4}	7.05×10^{-4}	25	5.84×10^{-4}	1.24×10^{-3}	4.77×10^{-3}
8	3.15×10^{-5}	6.48×10^{-5}	2.55×10^{-4}	26	3.15×10^{-5}	6.48×10^{-5}	2.55×10^{-4}
9	3.36×10^{-5}	7.29×10^{-5}	2.85×10^{-4}	27	3.15×10^{-5}	6.48×10^{-5}	2.55×10^{-4}
10	3.02×10^{-4}	6.40×10^{-4}	2.48×10^{-3}	28	3.36×10^{-5}	6.89×10^{-5}	2.70×10^{-4}
11	2.58×10^{-4}	5.47×10^{-4}	2.10×10^{-3}	29	1.07×10^{-4}	2.27×10^{-4}	8.70×10^{-4}
12	2.75×10^{-4}	5.83×10^{-4}	2.25×10^{-3}	30	4.81×10^{-4}	1.02×10^{-3}	3.93×10^{-3}
13	3.57×10^{-5}	7.70×10^{-5}	3.00×10^{-4}	31	5.71×10^{-4}	1.21×10^{-3}	4.67×10^{-3}
14	4.18×10^{-4}	8.87×10^{-4}	3.42×10^{-3}	32	4.37×10^{-4}	9.27×10^{-4}	3.57×10^{-3}
15	5.90×10^{-4}	1.25×10^{-3}	4.82×10^{-3}	33	1.32×10^{-4}	2.79×10^{-4}	1.08×10^{-3}
16	1.03×10^{-4}	2.21×10^{-4}	8.40×10^{-4}	34	3.36×10^{-5}	7.29×10^{-5}	2.85×10^{-4}
17	3.15×10^{-5}	6.68×10^{-5}	2.55×10^{-4}	35	1.22×10^{-4}	2.59×10^{-4}	9.90×10^{-4}
18	3.44×10^{-4}	7.30×10^{-4}	2.81×10^{-3}				

5.6.1.6 Ingestion and dermal exposure of fluoride for the inhabitants in Baruipur block

A significant amount of F^- ingestion through drinking water can have a lot of negative health impacts on the human body. This study investigated the health risk measurement by the ingestion and dermal exposure of F^- toxicity from the drinking water source. The results of the health risk assessment revealed variations in non-carcinogenic effects among the four age groups studied. The results of HQ_{ing} and HQ_{der} for different studied age groups are represented in **Table 5.31**. Computed HQ_{ing} and HQ_{der} values range from 1.94×10^{-1} to 1.62 , 1.17×10^{-1} to 9.75×10^{-1} , 1.12×10^{-1} to 9.38×10^{-1} , and 1.33×10^{-1} to 1.11 and 9.28×10^{-5} to 7.75×10^{-4} , 7.39×10^{-5} to 6.18×10^{-4} , 1.19×10^{-4} to 9.92×10^{-4} , and 1.46×10^{-4} to 1.22×10^{-3} for infants, children, teenagers and adults, respectively. These results indicate that HQ_{der} is lower than HQ_{ing} in the studied region irrespective of the four different studied age groups. THQ values have been ranged from 1.95×10^{-1} to 1.63 , 1.17×10^{-1} to 9.76×10^{-1} , 1.12×10^{-1} to 9.38×10^{-1} and 1.33×10^{-1} to 1.12 for infants, children, teenagers and adults, respectively (Table 5.31).

THQ value of F^- was found >1 for infants in two gram-panchayats like Champahati and Dhaphdhabi II, whereas, for adults only from Dhaphdhabi II gram-panchayat. According to THQ values, the health risk for the four studied age groups was found in the order of infants $>$ adults $>$ children $>$ teenagers. Thus, the results revealed that infants were the most vulnerable inhabitants showed to F^- contaminated water due to their body weight (BW). This observation signifies that infants of two gram-panchayat areas have high risk of dental fluorosis, which was reported by other study (Mridha et al., 2021). According to the reports of Bhattacharya et al. (2020) and Kaur et al. (2020), the maximum hazard quotient due to F^- exposure was found 3 and 5.75 in Tripura and Haryana, respectively. Similarly, the hazard quotient in the range of 0.09-6.78 was observed by Karunanidhi et al. (2020). The toxicity of high F^- also has a negative impact on brain development and causes different fluorosis with developing age (National Research Council, 2007; Zhang et al., 2020).

Table 5.31: HQ values of non-carcinogenic risk of fluoride toxicity for the four studied age groups

Location	HQ _{ing}				HQ _{der}				Total exposure THQ			
	Infants	Children	Teenagers	Adults	Infants	Children	Teenagers	Adults	Infants	Children	Teenagers	Adults
South Garia	7.08×10^{-1}	4.25×10^{-1}	4.09×10^{-1}	4.86×10^{-1}	3.38×10^{-4}	2.69×10^{-4}	4.32×10^{-4}	5.33×10^{-4}	7.09×10^{-1}	4.25×10^{-1}	4.09×10^{-1}	4.86×10^{-1}
Kalyanpur	8.61×10^{-1}	5.17×10^{-1}	4.97×10^{-1}	5.90×10^{-1}	4.11×10^{-4}	3.27×10^{-4}	5.26×10^{-4}	6.48×10^{-4}	8.62×10^{-1}	5.17×10^{-1}	4.97×10^{-1}	5.91×10^{-1}
Champahati	1.13	6.75×10^{-1}	6.49×10^{-1}	7.71×10^{-1}	5.37×10^{-4}	4.28×10^{-4}	6.87×10^{-4}	8.46×10^{-4}	1.13*	6.75×10^{-1}	6.50×10^{-1}	7.72×10^{-1}
Begampur	7.08×10^{-1}	4.25×10^{-1}	4.09×10^{-1}	4.86×10^{-1}	3.38×10^{-4}	2.69×10^{-4}	4.32×10^{-4}	5.33×10^{-4}	7.09×10^{-1}	4.25×10^{-1}	4.09×10^{-1}	4.86×10^{-1}
Madarat	7.36×10^{-1}	4.42×10^{-1}	4.25×10^{-1}	5.05×10^{-1}	3.51×10^{-4}	2.80×10^{-4}	4.49×10^{-4}	5.54×10^{-4}	7.36×10^{-1}	4.42×10^{-1}	4.25×10^{-1}	5.05×10^{-1}
Ramnagar I	4.44×10^{-1}	2.67×10^{-1}	2.56×10^{-1}	3.05×10^{-1}	2.12×10^{-4}	1.69×10^{-4}	2.71×10^{-4}	3.34×10^{-4}	4.45×10^{-1}	2.67×10^{-1}	2.57×10^{-1}	3.05×10^{-1}
Ramnagar II	3.75×10^{-1}	2.25×10^{-1}	2.16×10^{-1}	2.57×10^{-1}	1.79×10^{-4}	1.43×10^{-4}	2.29×10^{-4}	2.82×10^{-4}	3.75×10^{-1}	2.25×10^{-1}	2.17×10^{-1}	2.57×10^{-1}
Hardaha	4.31×10^{-1}	2.58×10^{-1}	2.48×10^{-1}	2.95×10^{-1}	2.05×10^{-4}	1.64×10^{-4}	2.63×10^{-4}	3.24×10^{-4}	4.31×10^{-1}	2.58×10^{-1}	2.49×10^{-1}	2.96×10^{-1}
Hariharpur	6.81×10^{-1}	4.08×10^{-1}	3.93×10^{-1}	4.67×10^{-1}	3.25×10^{-4}	2.59×10^{-4}	4.15×10^{-4}	5.12×10^{-4}	6.81×10^{-1}	4.09×10^{-1}	3.93×10^{-1}	4.67×10^{-1}
Mallikpur	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}	3.78×10^{-4}	3.01×10^{-4}	4.83×10^{-4}	5.95×10^{-4}	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}
Belagachi	3.33×10^{-1}	2.00×10^{-1}	1.92×10^{-1}	2.29×10^{-1}	1.59×10^{-4}	1.27×10^{-4}	2.03×10^{-4}	2.51×10^{-4}	3.33×10^{-1}	2.00×10^{-1}	1.93×10^{-1}	2.29×10^{-1}
Brindakhali	3.61×10^{-1}	2.17×10^{-1}	2.08×10^{-1}	2.48×10^{-1}	1.72×10^{-4}	1.37×10^{-4}	2.20×10^{-4}	2.72×10^{-4}	3.61×10^{-1}	2.17×10^{-1}	2.09×10^{-1}	2.48×10^{-1}
Nabagram	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}	3.78×10^{-4}	3.01×10^{-4}	4.83×10^{-4}	5.95×10^{-4}	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}
Dhaphdhabi I	5.97×10^{-1}	3.58×10^{-1}	3.45×10^{-1}	4.10×10^{-1}	2.85×10^{-4}	2.27×10^{-4}	3.64×10^{-4}	4.49×10^{-4}	5.98×10^{-1}	3.59×10^{-1}	3.45×10^{-1}	4.10×10^{-1}
Dhaphdhabi II	1.63	9.75×10^{-1}	9.38×10^{-1}	1.11	7.75×10^{-4}	6.18×10^{-4}	9.92×10^{-4}	1.22×10^{-3}	1.63*	9.76×10^{-1}	9.38×10^{-1}	1.12*
Sankarpur I	3.19×10^{-1}	1.92×10^{-1}	1.84×10^{-1}	2.19×10^{-1}	1.52×10^{-4}	1.21×10^{-4}	1.95×10^{-4}	2.40×10^{-4}	3.20×10^{-1}	1.92×10^{-1}	1.84×10^{-1}	2.19×10^{-1}
Sankarpur II	5.28×10^{-1}	3.17×10^{-1}	3.04×10^{-1}	3.62×10^{-1}	2.52×10^{-4}	2.01×10^{-4}	3.22×10^{-4}	3.97×10^{-4}	5.28×10^{-1}	3.17×10^{-1}	3.05×10^{-1}	3.62×10^{-1}
Sikharbali I	4.31×10^{-1}	2.58×10^{-1}	2.48×10^{-1}	2.95×10^{-1}	2.05×10^{-4}	1.64×10^{-4}	2.63×10^{-4}	3.24×10^{-4}	4.31×10^{-1}	2.58×10^{-1}	2.49×10^{-1}	2.96×10^{-1}
Sikharbali II	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}	3.78×10^{-4}	3.01×10^{-4}	4.83×10^{-4}	5.95×10^{-4}	7.92×10^{-1}	4.75×10^{-1}	4.57×10^{-1}	5.43×10^{-1}
Baruipur Municipality	1.94×10^{-1}	1.17×10^{-1}	1.12×10^{-1}	1.33×10^{-1}	9.28×10^{-5}	7.39×10^{-5}	1.19×10^{-4}	1.46×10^{-4}	1.95×10^{-1}	1.17×10^{-1}	1.12×10^{-1}	1.33×10^{-1}

*Where, THQ value > 1 showed non-carcinogenic health risk

5.6.1.7 Probabilistic health risk assessment of the inhabitants from Baruipur block

The probabilistic health risk assessment of fluoride toxicity has been observed by Monte Carlo simulation methods (Pirsaheb et al., 2021). The non-carcinogenic effects depend on independent variables like HQ_{ing} and HQ_{der} for THQ. The probable THQ values of four studied age groups were found in the order of infants > adults > children > teenagers (Table 5.32). Moreover, among the 19 gram-panchayats and Baruipur municipality, the combined effect of probable THQ value was found >1 at P95 for four studied age groups in Dhaphdapi II gram-panchayat (Table 5.32). Long term exposure to fluoridated drinking water may result in chronic F^- related problems among the inhabitants in Dhaphdapi II gram-panchayat. In another study from Haryana, India, the estimated probable non-carcinogenic health risk was 2.44 at 95th percentile (Kaur et al., 2020). This finding corroborates with all the previous studies reported by Bhattacharya et al. (2020), Karunanidhi et al. (2020), Pirsaheb et al. (2021), and Zhang et al. (2020).

Table 5.32: The uncertainty upper bound (P95), uncertainty lower bound (P5) and average uncertainty (P50) of THQ for the four studied age groups

Location	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
South Garia	5.96×10^{-1}	7.09×10^{-1}	8.26×10^{-1}	3.55×10^{-1}	4.26×10^{-1}	4.94×10^{-1}	3.41×10^{-1}	4.08×10^{-1}	4.76×10^{-1}	4.07×10^{-1}	4.87×10^{-1}	5.66×10^{-1}
Kalyanpur	7.25×10^{-1}	8.62×10^{-1}	1.00	4.32×10^{-1}	5.18×10^{-1}	6.01×10^{-1}	4.14×10^{-1}	4.96×10^{-1}	5.78×10^{-1}	4.94×10^{-1}	5.92×10^{-1}	6.88×10^{-1}
Champahati	9.47×10^{-1}	1.13*	1.31*	5.64×10^{-1}	6.77×10^{-1}	7.85×10^{-1}	5.41×10^{-1}	6.49×10^{-1}	7.55×10^{-1}	6.46×10^{-1}	7.73×10^{-1}	8.99×10^{-1}
Begampur	5.96×10^{-1}	7.09×10^{-1}	8.26×10^{-1}	3.55×10^{-1}	4.26×10^{-1}	4.94×10^{-1}	3.41×10^{-1}	4.08×10^{-1}	7.76×10^{-1}	4.07×10^{-1}	4.87×10^{-1}	5.66×10^{-1}
Madarat	6.20×10^{-1}	7.36×10^{-1}	8.58×10^{-1}	3.69×10^{-1}	4.43×10^{-1}	5.14×10^{-1}	3.54×10^{-1}	4.24×10^{-1}	4.94×10^{-1}	4.23×10^{-1}	5.06×10^{-1}	5.88×10^{-1}
Ramnagar I	3.74×10^{-1}	4.45×10^{-1}	5.18×10^{-1}	2.23×10^{-1}	2.67×10^{-1}	3.10×10^{-1}	2.57×10^{-1}	2.57×10^{-1}	2.57×10^{-1}	2.55×10^{-1}	3.05×10^{-1}	3.55×10^{-1}
Ramnagar II	3.16×10^{-1}	3.75×10^{-1}	4.37×10^{-1}	1.88×10^{-1}	2.26×10^{-1}	2.62×10^{-1}	1.81×10^{-1}	2.16×10^{-1}	2.52×10^{-1}	2.15×10^{-1}	2.58×10^{-1}	3.00×10^{-1}
Hardaha	3.62×10^{-1}	4.31×10^{-1}	5.02×10^{-1}	2.16×10^{-1}	2.59×10^{-1}	3.00×10^{-1}	2.07×10^{-1}	2.48×10^{-1}	2.89×10^{-1}	2.47×10^{-1}	2.96×10^{-1}	3.44×10^{-1}
Hariharpur	5.73×10^{-1}	6.09×10^{-1}	7.94×10^{-1}	3.41×10^{-1}	4.09×10^{-1}	4.75×10^{-1}	3.28×10^{-1}	3.92×10^{-1}	4.57×10^{-1}	3.91×10^{-1}	4.68×10^{-1}	5.44×10^{-1}
Mallikpur	6.66×10^{-1}	7.92×10^{-1}	9.23×10^{-1}	3.97×10^{-1}	4.76×10^{-1}	5.52×10^{-1}	3.81×10^{-1}	4.56×10^{-1}	5.31×10^{-1}	4.54×10^{-1}	5.44×10^{-1}	6.33×10^{-1}
Belagachi	2.81×10^{-1}	3.34×10^{-1}	3.89×10^{-1}	1.91×10^{-1}	2.29×10^{-1}	2.66×10^{-1}	1.60×10^{-1}	1.92×10^{-1}	2.24×10^{-1}	1.67×10^{-1}	2.00×10^{-1}	2.33×10^{-1}
Brindakhali	3.04×10^{-1}	3.61×10^{-1}	4.21×10^{-1}	1.81×10^{-1}	2.17×10^{-1}	2.52×10^{-1}	1.74×10^{-1}	2.08×10^{-1}	2.42×10^{-1}	2.07×10^{-1}	2.48×10^{-1}	2.89×10^{-1}
Nabagram	6.66×10^{-1}	7.92×10^{-1}	9.23×10^{-1}	3.97×10^{-1}	4.76×10^{-1}	5.52×10^{-1}	3.18×10^{-1}	4.56×10^{-1}	5.31×10^{-1}	4.54×10^{-1}	5.44×10^{-1}	6.33×10^{-1}
Dhaphdapi I	5.03×10^{-1}	5.98×10^{-1}	6.96×10^{-1}	2.99×10^{-1}	3.59×10^{-1}	4.17×10^{-1}	2.87×10^{-1}	3.44×10^{-1}	4.01×10^{-1}	3.43×10^{-1}	4.12×10^{-1}	4.78×10^{-1}
Dhaphdapi II	1.37*	1.63*	1.90*	8.15×10^{-1}	9.77×10^{-1}	1.13*	7.82×10^{-1}	9.37×10^{-1}	1.09*	9.33×10^{-1}	1.12*	1.30*
Sankarpur I	2.69×10^{-1}	3.20×10^{-1}	3.73×10^{-1}	1.60×10^{-1}	1.92×10^{-1}	2.23×10^{-1}	1.54×10^{-1}	1.84×10^{-1}	2.14×10^{-1}	1.83×10^{-1}	2.20×10^{-1}	2.55×10^{-1}
Sankarpur II	4.44×10^{-1}	5.28×10^{-1}	6.15×10^{-1}	2.65×10^{-1}	3.17×10^{-1}	3.68×10^{-1}	2.54×10^{-1}	3.04×10^{-1}	3.54×10^{-1}	3.03×10^{-1}	3.63×10^{-1}	4.22×10^{-1}
Sikharbali I	3.62×10^{-1}	4.31×10^{-1}	5.02×10^{-1}	2.16×10^{-1}	2.59×10^{-1}	3.00×10^{-1}	2.07×10^{-1}	2.48×10^{-1}	2.89×10^{-1}	2.47×10^{-1}	2.96×10^{-1}	3.44×10^{-1}
Sikharbali II	6.66×10^{-1}	7.92×10^{-1}	9.23×10^{-1}	3.97×10^{-1}	4.76×10^{-1}	5.52×10^{-1}	3.81×10^{-1}	4.56×10^{-1}	5.31×10^{-1}	4.54×10^{-1}	5.44×10^{-1}	6.33×10^{-1}
Baruipur Municipality	1.63×10^{-1}	1.95×10^{-1}	2.27×10^{-1}	9.36×10^{-2}	1.12×10^{-1}	1.31×10^{-1}	9.75×10^{-2}	1.17×10^{-1}	1.36×10^{-1}	1.12×10^{-1}	1.34×10^{-1}	1.55×10^{-1}

*Where, THQ value > 1 showed non-carcinogenic health risk

5.6.2 Exposure dose of fluoride due to consumption of different food crops at contaminated areas (Bankura and Purulia)

Exposure dose helps to measure the health risk assessment in the studied populations. EDI value was evaluated based on the food crops consumed by different age groups and their respective F^- concentrations from both the studied areas. The relevant EDI value from different food crops for the different age groups in the studied populations was presented in **Table 5.33** and **5.34**. Due to the highest accumulation pattern of F^- (Table 5.33 and 5.34), maximum EDI value was observed in onion. Average EDI (mg/kg bw/day) for onion was found to be 0.00678, 0.00609, 0.00564, and 0.00658 and 0.00636, 0.00571, 0.00529, and 0.00617 in children, adolescents, teenagers, and adults in Bankura and Purulia, respectively. Among the cereals, rice was a major food item that was consumed daily, and the EDI was found to be ~1.5 to ~2 times higher than wheat in Purulia and vice versa in Bankura. Minimum EDI value was observed in beans from all the age groups in the studied districts. The pie chart diagram shown in **Fig. 5.52** depicts that nonleafy vegetables were the major contributor to F^- exposure among all the groups of food crops in both the studied districts Bankura (60 - 63%) and Purulia (48 - 52%) and the observed EDI was in the order of nonleafy vegetables > cereal > pulses > leafy vegetables. The cumulative EDI value showed that the children from both the studied districts were exposed to the highest dietary intake of F^- compared to other age groups (**Table 5.52 a and b**) and observed $EDI_{cumulative}$ for the studied populations was in the order of children > adults > adolescents > teenagers from both districts.

Table 5.33: Average estimated daily intake (mg/kg bw/day) of fluoride through consumption of cultivated food crops by the different age groups in the studied populations of Bankura*

Food Items	Cultivated crops	Bankura			
		EDI (mg/kg bw/day)			
		Children (4-8 years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
Cereals	Rice	0.003393	0.002169	0.001633	0.002256
	Wheat	0.005126	0.004348	0.003926	0.005029
$\Sigma EDI_{Cereals}$		0.008518	0.006517	0.005558	0.007284
Pulses	Pigeon Pea	0.000589	0.000494	0.000442	0.00052
	Lentils	0.000876	0.000723	0.000642	0.00085
	Chana	0.000375	0.00031	0.000275	0.000364
	Lentils arhar	0.000044	0.000037	0.000033	0.000043
ΣEDI_{Pulses}		0.001885	0.001562	0.001392	0.001778
Non-leafy Vegetables	Sweet Potato	0.00003	0.000024	0.000022	0.000029
	Potatoo	0.002404	0.001982	0.001763	0.002334
	Turmeric	0.000032	0.000026	0.000024	0.000032
	Ginger	0.000146	0.000107	0.00009	0.000143
	Onion	0.006789	0.006094	0.005644	0.006589
	Carrot	0.000439	0.000362	0.000322	0.000426

Food Items	Cultivated crops	Bankura			
		EDI (mg/kg bw/day)			
		Children (4-8 years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
	Shim/Broad beans	0.000016	0.000013	0.000012	0.000015
	Beans	0.000005	0.000004	0.000003	0.000005
	Radish	0.000163	0.000134	0.00012	0.000159
	Cauliflower	0.000062	0.000051	0.000045	0.00006
	Chilli	0.00023	0.000169	0.000141	0.000223
	Pumpkin	0.000343	0.000283	0.000252	0.000333
	Brinjal	0.000176	0.000145	0.000129	0.000171
	Cucumber	0.000054	0.000045	0.00004	0.000052
	Bitter guard	0.000227	0.000187	0.000166	0.00022
	Mustard seed	0.005973	0.004927	0.00438	0.005797
	Tomato	0.000375	0.000275	0.000231	0.000357
Σ EDI _{Non-leafy vegetables}		0.017462	0.014829	0.013383	0.016945
Leafy Vegetables	Cabbage	0.000054	0.000045	0.00004	0.000056
	Coriander	0.000591	0.000487	0.000433	0.000574
	Spinach	0.000196	0.000162	0.000144	0.00019
	Fenugreek leaves	0.000297	0.000267	0.000247	0.000289
Σ EDI _{Leafy vegetables}		0.001138	0.000961	0.000864	0.001108
EDI _{cumulative}		0.029004	0.02387	0.021198	0.02712

*EDI has been calculated with respect to average consumption (g dw/day)

Table 5.34: Average estimated daily intake (mg/kg bw/day) of F⁻ through consumption of cultivated food crops by the different age groups in the studied populations of Purulia*

Food Items	Cultivated crops	Purulia			
		EDI (mg/kg bw/day)			
		Children (4-8years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
Cereals	Rice	0.005998	0.003834	0.002886	0.003988
	Wheat	0.003204	0.002718	0.002454	0.003144
Σ EDI _{Cereals}		0.009201	0.006552	0.005341	0.007131
Pulses	Pigeon Pea	0.002233	0.00187	0.001675	0.00197
	Lentils	0.002972	0.002451	0.002179	0.002884
	Chana	0.000558	0.00046	0.000409	0.000541
	Lentils arhar	0.000025	0.00002	0.000018	0.000024
Σ EDI _{Pulses}		0.005787	0.004802	0.004281	0.00542
Non-leafy Vegetables	Sweet Potato	0.000064	0.000053	0.000047	0.000062
	Potato	0.003273	0.002699	0.002401	0.003178
	Turmeric	0.000038	0.000032	0.000029	0.000039
	Ginger	0.000095	0.00007	0.000058	0.000093
	Onion	0.006365	0.005714	0.005291	0.006178
	Carrot	0.000292	0.000241	0.000214	0.000284

Food Items	Cultivated crops	Purulia			
		EDI (mg/kg bw/day)			
		Children (4-8years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
	Shim/Broad beans	0.000009	0.000007	0.000006	0.000009
	Beans	0.000008	0.000006	0.000005	0.000008
	Radish	0.000202	0.000166	0.000148	0.000196
	Cauliflower	0.000059	0.000048	0.000043	0.000057
	Chili	0.000349	0.000256	0.000213	0.000339
	Pumpkin	0.000147	0.000122	0.000108	0.000143
	Brinjal	0.000057	0.000047	0.000042	0.000056
	Cucumber	0.000078	0.000064	0.000057	0.000075
	Bitter guard	0.000195	0.000161	0.000143	0.000189
	Mustard seed	0.003873	0.003196	0.00284	0.003759
	Tomato	0.000463	0.00034	0.000286	0.000441
Σ EDI _{Non-leafy vegetables}		0.015568	0.01322	0.011933	0.015105
Leafy Vegetables	Cabbage	0.000058	0.000048	0.000043	0.00006
	Coriander	0.001195	0.000985	0.000876	0.001159
	Spinach	0.000245	0.000202	0.00018	0.000238
	Fenugreek leaves	0.000591	0.000531	0.000491	0.000573
Σ EDI _{Leafy vegetables}		0.002088	0.001766	0.001589	0.002031
EDI_{cumulative}		0.032645	0.026341	0.023144	0.029687

*EDI has been calculated with respect to average consumption (g dw/day)

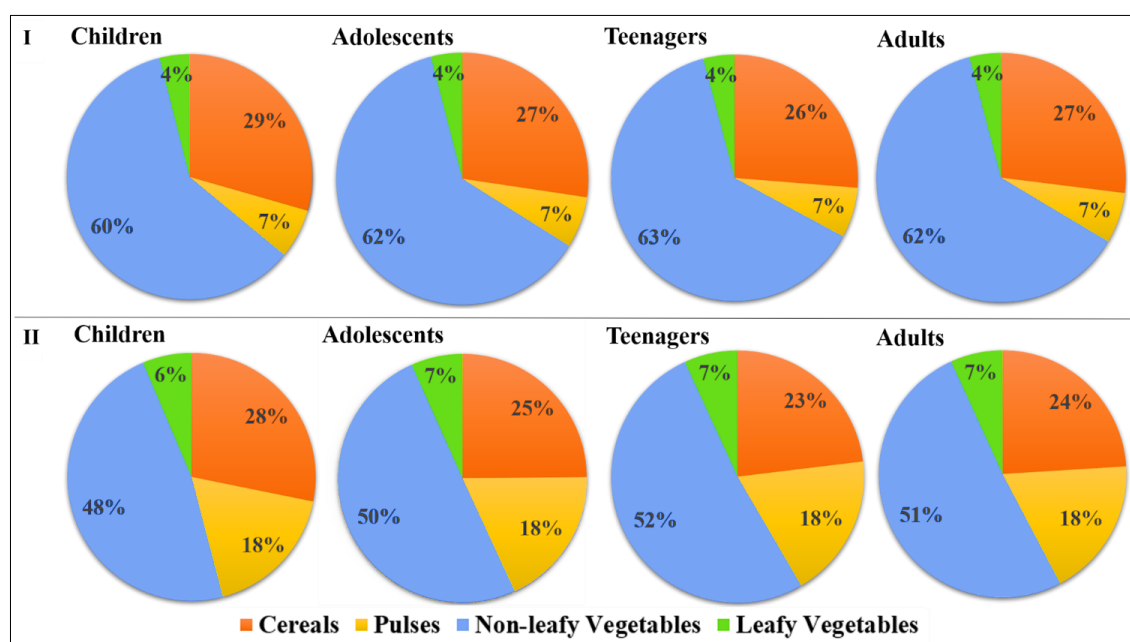


Fig. 5.52: Fluoride exposure through dietary intake of cereals, pulses, and nonleafy and leafy vegetables in the studied age group from **I. Bankura** and **II. Purulia** districts

5.6.2.1 Potential non-cancerous health risk assessment of the studied population through foodstuffs

The current study uncovered that the calculated HI values of all the age groups from cultivated food crops were less than 1 in both Bankura and Purulia (Table 5.35 and 5.36). The HI values of the children in both districts were found to be the highest compared to adolescents, teenagers, and adults. However, the calculated values of the HI_{LTNR} in both districts were greater than 1 (Table 5.35 and 5.36). The HI_{LTNR} value comparatively higher in Purulia district compared with Bankura district.

Table 5.35: Hazard index (HI), total hazard index (THI) and lifetime non-carcinogenic risk (HI_{LTNR}) of fluoride from cultivated food crops for four different age groups in Bankura

Hazard index HI (Bankura)					
Food Items	Cultivated crops	Children (4-8 years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
Cereals	Rice	5.66×10^{-2}	3.62×10^{-2}	2.72×10^{-2}	3.76×10^{-2}
	Wheat	8.54×10^{-2}	7.25×10^{-2}	6.54×10^{-2}	8.38×10^{-2}
Pulses	Pigeon Pea	9.82×10^{-3}	8.23×10^{-3}	7.37×10^{-3}	8.67×10^{-3}
	Lentils	1.46×10^{-2}	1.20×10^{-2}	1.07×10^{-2}	1.42×10^{-2}
	Chana	6.25×10^{-3}	5.16×10^{-3}	4.59×10^{-3}	6.07×10^{-3}
	Lentils arhar	7.40×10^{-4}	6.10×10^{-4}	5.40×10^{-4}	7.20×10^{-4}
Non-leafy Vegetables	Sweet Potato	4.90×10^{-4}	4.10×10^{-4}	3.60×10^{-4}	4.80×10^{-4}
	Potato	4.01×10^{-2}	3.30×10^{-2}	2.94×10^{-2}	3.89×10^{-2}
	Turmeric	5.30×10^{-4}	4.40×10^{-4}	4.10×10^{-4}	5.40×10^{-4}
	Ginger	2.44×10^{-3}	1.79×10^{-3}	1.50×10^{-3}	2.39×10^{-3}
	Onion	1.13×10^{-1}	1.02×10^{-1}	9.41×10^{-2}	1.10×10^{-1}
	Carrot	7.31×10^{-3}	6.03×10^{-3}	5.36×10^{-3}	7.10×10^{-3}
	Shim/Broadbeans	2.60×10^{-4}	2.20×10^{-4}	1.90×10^{-4}	2.50×10^{-4}
	Beans	8.00×10^{-5}	6.00×10^{-5}	5.00×10^{-5}	8.00×10^{-5}
	Radish	2.72×10^{-3}	2.24×10^{-3}	2.00×10^{-3}	2.64×10^{-3}
	Cauliflower	1.03×10^{-3}	8.50×10^{-4}	7.60×10^{-4}	1.00×10^{-3}
	Chilli	3.84×10^{-3}	2.81×10^{-3}	2.34×10^{-3}	3.72×10^{-3}
	Pumpkin	5.71×10^{-3}	4.72×10^{-3}	4.20×10^{-3}	5.55×10^{-3}
	Brinjal	2.93×10^{-3}	2.41×10^{-3}	2.15×10^{-3}	2.85×10^{-3}
	Cucumber	9.00×10^{-4}	7.40×10^{-4}	6.60×10^{-4}	8.70×10^{-4}
	Bitter guard	3.78×10^{-3}	3.12×10^{-3}	2.77×10^{-3}	3.67×10^{-3}
	Mustard seed	9.95×10^{-2}	8.21×10^{-2}	7.30×10^{-2}	9.66×10^{-2}
	Tomato	6.24×10^{-3}	4.58×10^{-3}	3.85×10^{-3}	5.94×10^{-3}
Leafy Vegetables	Cabbage	9.00×10^{-4}	7.40×10^{-4}	6.60×10^{-4}	9.40×10^{-4}
	Coriander	9.85×10^{-3}	8.12×10^{-3}	7.22×10^{-3}	9.56×10^{-3}
	Spinach	3.26×10^{-3}	2.69×10^{-3}	2.39×10^{-3}	3.17×10^{-3}
	Fenugreekleaves	4.95×10^{-3}	4.45×10^{-3}	4.12×10^{-3}	4.81×10^{-3}
THI		4.83×10^{-1}	3.98×10^{-1}	3.53×10^{-1}	4.52×10^{-1}
HI_{LTNR}		1.686			

Table 5.36 Hazard index (HI), total hazard index (THI) and lifetime non-carcinogenic risk (HI_{LTNR}) of fluoride from cultivated food crops for four different age groups in Purulia

Hazard index HI (Purulia)					
Food Items	Cultivated crops	Children (4-8 years)	Adolescents (9-13 years)	Teenagers (14-18 years)	Adults (19-70 years)
Cereals	Rice	1.00×10^{-1}	6.39×10^{-2}	4.81×10^{-2}	2.58×10^{-3}
	Wheat	5.34×10^{-2}	4.53×10^{-2}	4.09×10^{-2}	5.24×10^{-2}
Pulses	Pigeon Pea	3.72×10^{-2}	3.12×10^{-2}	2.79×10^{-2}	3.28×10^{-2}
	Lentils	4.95×10^{-2}	4.09×10^{-2}	3.63×10^{-2}	4.81×10^{-2}
	Chana	9.30×10^{-3}	7.67×10^{-3}	6.82×10^{-3}	9.02×10^{-3}
	Lentils arhar	4.10×10^{-4}	3.40×10^{-4}	3.00×10^{-4}	4.00×10^{-4}
Non-leafy Vegetables	Sweet Potato	1.06×10^{-3}	8.80×10^{-4}	7.80×10^{-4}	1.03×10^{-3}
	Potato	5.46×10^{-2}	4.50×10^{-2}	4.00×10^{-2}	5.30×10^{-2}
	Turmeric	6.40×10^{-4}	5.30×10^{-4}	4.90×10^{-4}	6.50×10^{-4}
	Ginger	1.58×10^{-3}	1.16×10^{-3}	9.70×10^{-4}	1.55×10^{-3}
	Onion	1.06×10^{-1}	9.52×10^{-2}	8.82×10^{-2}	1.03×10^{-1}
	Carrot	4.87×10^{-3}	4.02×10^{-3}	3.57×10^{-3}	4.73×10^{-3}
	Shim/Broad beans	1.50×10^{-4}	1.20×10^{-4}	1.10×10^{-4}	1.40×10^{-4}
	Beans	1.30×10^{-4}	1.00×10^{-4}	8.00×10^{-5}	1.30×10^{-4}
	Radish	3.37×10^{-3}	2.77×10^{-3}	2.47×10^{-3}	3.27×10^{-3}
	Cauliflower	9.80×10^{-4}	8.10×10^{-4}	7.20×10^{-4}	9.50×10^{-4}
	Chilli	5.82×10^{-3}	4.26×10^{-3}	3.55×10^{-3}	5.64×10^{-3}
	Pumpkin	2.45×10^{-3}	2.03×10^{-3}	1.80×10^{-3}	2.38×10^{-3}
	Brinjal	9.60×10^{-4}	7.90×10^{-4}	7.00×10^{-4}	9.30×10^{-4}
	Cucumber	1.29×10^{-3}	1.07×10^{-3}	9.50×10^{-4}	1.26×10^{-3}
	Bitter guard	3.25×10^{-3}	2.68×10^{-3}	2.38×10^{-3}	3.16×10^{-3}
	Mustard seed	6.46×10^{-2}	5.33×10^{-2}	4.73×10^{-2}	6.27×10^{-2}
	Tomato	7.72×10^{-3}	5.66×10^{-3}	4.76×10^{-3}	7.35×10^{-3}
Leafy Vegetables	Cabbage	9.70×10^{-4}	8.00×10^{-4}	7.10×10^{-4}	1.01×10^{-3}
	Coriander	1.99×10^{-2}	1.64×10^{-2}	1.46×10^{-2}	1.93×10^{-2}
	Spinach	4.08×10^{-3}	3.37×10^{-3}	3.00×10^{-3}	3.96×10^{-3}
	Fenugreek leaves	9.84×10^{-3}	8.84×10^{-3}	8.18×10^{-3}	9.55×10^{-3}
THI		5.44×10^{-1}	4.39×10^{-1}	3.86×10^{-1}	4.95×10^{-1}
HI_{LTNR}		1.864			

5.6.2.2 Uncertainty analysis using Monte Carlo Simulation

The uncertainty upper boundary (P95), lower boundary (P5), and average uncertainty (P50) of HI and THI using the Monte Carlo simulation model for estimation of probabilistic health risk assessment of fluoride at four different age groups in different cultivated crops from Bankura and Purulia were shown in **Table 5.37** and **5.38** and **Fig. 5.53**, respectively.

Table 5.37: The uncertainty upper boundary (P95), lower boundary (P5) and average uncertainty (P50) of HI at four different age groups in different cultivated crops from sampling sites of Bankura

Items	P5				P50				P95			
	Children	Adolescents	Teenagers	Adults	Children	Adolescents	Teenagers	Adults	Children	Adolescents	Teenagers	Adults
Cereals												
Paddy	4.47×10^{-2}	2.86×10^{-2}	2.16×10^{-2}	2.96×10^{-2}	5.67×10^{-2}	3.62×10^{-2}	2.73×10^{-2}	3.77×10^{-2}	7.18×10^{-2}	4.56×10^{-2}	3.44×10^{-2}	4.77×10^{-2}
Pulses												
Wheat	6.73×10^{-2}	5.73×10^{-2}	5.15×10^{-2}	6.65×10^{-2}	8.54×10^{-2}	7.25×10^{-2}	6.54×10^{-2}	8.38×10^{-2}	1.08×10^{-1}	9.16×10^{-2}	8.34×10^{-2}	1.06×10^{-1}
Pigeon Pea	7.77×10^{-3}	6.49×10^{-3}	5.81×10^{-3}	6.85×10^{-3}	9.85×10^{-3}	8.22×10^{-3}	7.36×10^{-3}	8.65×10^{-3}	1.25×10^{-2}	1.04×10^{-2}	9.39×10^{-3}	1.09×10^{-2}
Lentils	1.15×10^{-2}	9.53×10^{-3}	8.46×10^{-2}	1.13×10^{-2}	1.46×10^{-2}	1.21×10^{-2}	1.07×10^{-2}	1.41×10^{-2}	1.84×10^{-2}	1.52×10^{-2}	1.35×10^{-2}	1.79×10^{-2}
Chana	4.94×10^{-3}	4.07×10^{-3}	3.63×10^{-3}	4.81×10^{-3}	6.23×10^{-3}	5.15×10^{-3}	4.58×10^{-3}	6.08×10^{-3}	7.85×10^{-3}	6.56×10^{-3}	5.81×10^{-3}	7.68×10^{-3}
Lentilsarhar	5.87×10^{-4}	4.82×10^{-4}	4.29×10^{-4}	5.69×10^{-4}	7.45×10^{-4}	6.10×10^{-4}	5.44×10^{-4}	7.19×10^{-4}	9.42×10^{-4}	7.75×10^{-4}	6.89×10^{-4}	9.09×10^{-4}
Sweet Potato	3.91×10^{-4}	3.23×10^{-4}	2.87×10^{-4}	3.77×10^{-4}	4.94×10^{-4}	4.08×10^{-4}	3.61×10^{-4}	4.78×10^{-4}	6.24×10^{-4}	5.11×10^{-4}	4.60×10^{-4}	6.07×10^{-4}
Non leafy Vegetables												
Potato	3.16×10^{-2}	2.62×10^{-2}	2.32×10^{-2}	3.08×10^{-2}	4.00×10^{-2}	3.31×10^{-2}	2.95×10^{-2}	3.89×10^{-2}	5.05×10^{-2}	4.19×10^{-2}	3.73×10^{-2}	4.91×10^{-2}
Turmeric	4.22×10^{-4}	3.48×10^{-4}	3.21×10^{-4}	4.24×10^{-4}	5.34×10^{-4}	4.40×10^{-4}	4.08×10^{-4}	5.39×10^{-4}	6.78×10^{-4}	5.58×10^{-4}	5.14×10^{-4}	6.82×10^{-4}
Ginger	1.93×10^{-3}	1.41×10^{-3}	1.19×10^{-3}	1.89×10^{-3}	2.44×10^{-3}	1.79×10^{-3}	1.50×10^{-3}	2.38×10^{-3}	3.09×10^{-3}	2.27×10^{-3}	1.91×10^{-3}	3.01×10^{-3}
Onion	8.96×10^{-2}	8.07×10^{-2}	7.45×10^{-2}	8.67×10^{-2}	1.13×10^{-1}	1.02×10^{-1}	9.42×10^{-2}	1.09×10^{-1}	1.44×10^{-1}	1.29×10^{-1}	1.19×10^{-1}	1.39×10^{-1}
Carrot	5.78×10^{-3}	4.76×10^{-3}	4.25×10^{-3}	5.61×10^{-3}	7.30×10^{-3}	6.03×10^{-3}	5.37×10^{-3}	7.11×10^{-3}	9.24×10^{-3}	7.66×10^{-3}	6.81×10^{-3}	9.00×10^{-3}
Shim/Broadbeans	2.07×10^{-4}	1.71×10^{-4}	1.51×10^{-4}	2.01×10^{-4}	2.61×10^{-4}	2.16×10^{-4}	1.92×10^{-4}	2.54×10^{-4}	3.32×10^{-4}	2.73×10^{-4}	2.43×10^{-4}	3.19×10^{-4}
Beans	6.29×10^{-5}	4.67×10^{-5}	3.93×10^{-5}	6.26×10^{-5}	7.96×10^{-5}	5.92×10^{-5}	4.97×10^{-5}	7.90×10^{-5}	1.01×10^{-4}	7.48×10^{-5}	6.28×10^{-5}	9.98×10^{-5}
Radish	2.16×10^{-3}	1.77×10^{-3}	1.58×10^{-3}	2.09×10^{-3}	2.72×10^{-3}	2.24×10^{-3}	1.99×10^{-3}	2.64×10^{-3}	3.46×10^{-3}	2.84×10^{-3}	2.52×10^{-3}	3.34×10^{-3}
Cauliflower	8.13×10^{-4}	6.67×10^{-4}	5.97×10^{-4}	7.88×10^{-4}	1.03×10^{-3}	8.47×10^{-4}	7.56×10^{-4}	1.00×10^{-3}	1.30×10^{-3}	1.08×10^{-3}	9.60×10^{-4}	1.26×10^{-3}
Chilli	3.01×10^{-3}	2.22×10^{-3}	1.85×10^{-3}	2.95×10^{-3}	3.83×10^{-3}	2.81×10^{-3}	2.34×10^{-3}	3.73×10^{-3}	4.83×10^{-3}	3.53×10^{-3}	2.96×10^{-3}	4.73×10^{-3}
Pumpkin	4.51×10^{-3}	3.73×10^{-3}	3.32×10^{-3}	4.39×10^{-3}	5.70×10^{-3}	4.7×10^{-3}	4.20×10^{-3}	5.55×10^{-3}	7.23×10^{-3}	5.94×10^{-3}	5.30×10^{-3}	7.03×10^{-3}
Brinjal	2.31×10^{-3}	1.91×10^{-3}	1.70×10^{-3}	2.26×10^{-3}	2.94×10^{-3}	2.40×10^{-3}	2.15×10^{-3}	2.84×10^{-3}	3.71×10^{-3}	3.05×10^{-3}	2.72×10^{-3}	3.61×10^{-3}
Cucumber	7.15×10^{-4}	5.87×10^{-4}	5.18×10^{-4}	6.91×10^{-4}	9.01×10^{-4}	7.41×10^{-4}	6.59×10^{-4}	8.73×10^{-4}	1.14×10^{-3}	9.45×10^{-4}	8.35×10^{-4}	1.10×10^{-3}
Bitter guard	3.00×10^{-3}	2.47×10^{-3}	2.20×10^{-3}	2.90×10^{-3}	3.79×10^{-3}	3.12×10^{-3}	2.78×10^{-3}	3.67×10^{-3}	4.78×10^{-3}	3.95×10^{-3}	3.53×10^{-3}	4.63×10^{-3}
Mustardseed	7.81×10^{-2}	6.46×10^{-2}	5.76×10^{-2}	7.63×10^{-2}	9.97×10^{-2}	8.18×10^{-2}	7.30×10^{-2}	9.62×10^{-2}	1.26×10^{-1}	1.04×10^{-1}	9.23×10^{-2}	1.22×10^{-1}
Tomato	4.93×10^{-3}	3.61×10^{-3}	3.03×10^{-3}	4.74×10^{-3}	6.24×10^{-3}	4.57×10^{-3}	3.85×10^{-3}	5.96×10^{-3}	7.90×10^{-3}	5.78×10^{-3}	4.87×10^{-3}	7.54×10^{-3}
Leafy Vegetables												
Cabbage	7.09×10^{-4}	5.83×10^{-4}	5.20×10^{-4}	7.39×10^{-4}	8.99×10^{-4}	7.40×10^{-4}	6.58×10^{-4}	9.37×10^{-4}	1.14×10^{-3}	9.38×10^{-4}	8.32×10^{-4}	1.18×10^{-3}
Coriander	7.76×10^{-3}	6.40×10^{-3}	5.75×10^{-3}	7.54×10^{-3}	9.85×10^{-3}	8.12×10^{-3}	7.24×10^{-3}	9.55×10^{-3}	1.24×10^{-2}	1.03×10^{-2}	9.11×10^{-3}	1.21×10^{-2}
Spinach	2.57×10^{-3}	2.13×10^{-3}	1.88×10^{-3}	2.51×10^{-3}	3.26×10^{-3}	2.68×10^{-3}	2.40×10^{-3}	3.17×10^{-3}	4.13×10^{-3}	3.42×10^{-3}	3.04×10^{-3}	4.00×10^{-3}
Fenugreek	3.90×10^{-3}	3.52×10^{-3}	3.26×10^{-3}	3.80×10^{-3}	4.95×10^{-3}	4.46×10^{-3}	4.12×10^{-3}	4.81×10^{-3}	6.29×10^{-3}	5.64×10^{-3}	5.22×10^{-3}	6.09×10^{-3}
leaves												

Table 5.38: The uncertainty upper boundary (95th percentile: P95), lower boundary (5th percentile: P5) and average uncertainty (50th percentile: P50) of HI at four different age groups in different cultivated crops from sampling sites of Purulia

Items	Cultivated crops	P5					P50					P95				
		Children	Adolescents	Teenagers	Adults	Children	Adolescents	Teenagers	Adults	Children	Adolescents	Teenagers	Adults	Children	Adolescents	Teenagers
Cereals	Paddy	7.94×10^{-2}	5.07×10^{-2}	3.80×10^{-2}	5.25×10^{-2}	1.00×10^{-1}	6.42×10^{-2}	4.80×10^{-2}	6.65×10^{-2}	1.27×10^{-1}	8.11×10^{-2}	6.08×10^{-2}	8.41×10^{-2}	1.27×10^{-1}	8.11×10^{-2}	6.08×10^{-2}
	Wheat	4.21×10^{-2}	3.57×10^{-2}	3.25×10^{-2}	4.12×10^{-2}	5.34×10^{-2}	4.53×10^{-2}	4.10×10^{-2}	5.24×10^{-2}	6.77×10^{-2}	5.72×10^{-2}	5.18×10^{-2}	6.64×10^{-2}	6.77×10^{-2}	5.72×10^{-2}	5.18×10^{-2}
Pulses	Pigeon Pea	2.93×10^{-2}	2.62×10^{-2}	2.21×10^{-2}	2.59×10^{-2}	3.72×10^{-2}	3.11×10^{-2}	2.78×10^{-2}	3.28×10^{-2}	4.71×10^{-2}	3.93×10^{-2}	3.55×10^{-2}	4.16×10^{-2}	4.71×10^{-2}	3.93×10^{-2}	3.55×10^{-2}
	Lentils	3.91×10^{-2}	3.24×10^{-2}	2.87×10^{-2}	3.80×10^{-2}	4.95×10^{-2}	4.09×10^{-2}	3.62×10^{-2}	4.82×10^{-2}	6.26×10^{-2}	5.15×10^{-2}	4.59×10^{-2}	6.08×10^{-2}	6.26×10^{-2}	5.15×10^{-2}	4.59×10^{-2}
Non leafy Vegetables	Chana	7.38×10^{-3}	6.06×10^{-3}	5.38×10^{-3}	7.1×10^{-3}	9.31×10^{-3}	7.66×10^{-3}	6.82×10^{-3}	9.00×10^{-3}	1.18×10^{-2}	9.69×10^{-3}	8.65×10^{-3}	1.13×10^{-2}	1.18×10^{-2}	9.69×10^{-3}	8.65×10^{-3}
	Lentilsarhar	3.22×10^{-4}	2.66×10^{-4}	2.39×10^{-4}	3.13×10^{-4}	4.09×10^{-4}	3.38×10^{-4}	3.01×10^{-4}	3.95×10^{-4}	5.17×10^{-4}	4.26×10^{-4}	3.79×10^{-4}	5.01×10^{-4}	5.17×10^{-4}	4.26×10^{-4}	3.79×10^{-4}
Non leafy Vegetables	Sweet Potato	8.41×10^{-4}	6.93×10^{-4}	6.19×10^{-4}	8.15×10^{-4}	1.06×10^{-3}	8.74×10^{-4}	7.79×10^{-4}	1.03×10^{-3}	1.34×10^{-3}	1.11×10^{-3}	9.86×10^{-4}	1.30×10^{-3}	1.34×10^{-3}	1.11×10^{-3}	9.86×10^{-4}
	Potato	4.30×10^{-2}	3.55×10^{-2}	3.15×10^{-2}	4.20×10^{-2}	5.44×10^{-2}	4.51×10^{-2}	4.01×10^{-2}	5.30×10^{-2}	6.89×10^{-2}	5.70×10^{-2}	5.09×10^{-2}	6.7×10^{-2}	6.89×10^{-2}	5.70×10^{-2}	5.09×10^{-2}
Non leafy Vegetables	Turnmeric	5.06×10^{-4}	4.17×10^{-4}	3.86×10^{-4}	5.08×10^{-4}	6.39×10^{-4}	5.27×10^{-4}	4.87×10^{-4}	6.44×10^{-4}	8.10×10^{-4}	6.64×10^{-4}	6.19×10^{-4}	8.12×10^{-4}	8.10×10^{-4}	6.64×10^{-4}	6.19×10^{-4}
	Ginger	1.25×10^{-3}	9.14×10^{-4}	7.65×10^{-4}	1.22×10^{-3}	1.58×10^{-3}	1.16×10^{-3}	9.71×10^{-4}	1.55×10^{-3}	2.01×10^{-3}	1.47×10^{-3}	1.23×10^{-3}	1.96×10^{-3}	2.01×10^{-3}	1.47×10^{-3}	1.23×10^{-3}
Non leafy Vegetables	Onion	8.37×10^{-2}	7.54×10^{-2}	6.95×10^{-2}	8.16×10^{-2}	1.06×10^{-1}	9.50×10^{-2}	8.84×10^{-2}	1.03×10^{-1}	1.34×10^{-1}	1.20×10^{-1}	1.12×10^{-1}	1.30×10^{-1}	1.34×10^{-1}	1.20×10^{-1}	1.12×10^{-1}
	Carrot	3.85×10^{-3}	3.18×10^{-3}	2.82×10^{-3}	3.75×10^{-3}	4.87×10^{-3}	4.04×10^{-3}	3.57×10^{-3}	4.73×10^{-3}	6.15×10^{-3}	5.09×10^{-3}	4.53×10^{-3}	5.94×10^{-3}	6.15×10^{-3}	5.09×10^{-3}	4.53×10^{-3}
Non leafy Vegetables	Shim/Broadbeans	1.16×10^{-4}	9.64×10^{-5}	8.56×10^{-5}	1.13×10^{-4}	1.48×10^{-4}	1.22×10^{-4}	1.08×10^{-4}	1.43×10^{-4}	1.87×10^{-4}	1.37×10^{-4}	1.81×10^{-4}	1.80×10^{-4}	1.87×10^{-4}	1.37×10^{-4}	1.81×10^{-4}
	Beans	1.05×10^{-4}	7.76×10^{-5}	6.52×10^{-5}	1.04×10^{-4}	1.33×10^{-4}	9.84×10^{-5}	8.26×10^{-5}	1.31×10^{-4}	1.68×10^{-4}	1.25×10^{-4}	1.05×10^{-4}	1.65×10^{-4}	1.68×10^{-4}	1.25×10^{-4}	1.05×10^{-4}
Non leafy Vegetables	Radish	2.66×10^{-3}	2.20×10^{-3}	1.95×10^{-3}	2.58×10^{-3}	3.36×10^{-3}	2.78×10^{-3}	2.47×10^{-3}	3.25×10^{-3}	4.24×10^{-3}	3.51×10^{-3}	3.13×10^{-3}	4.11×10^{-3}	4.24×10^{-3}	3.51×10^{-3}	3.13×10^{-3}
	Cauliflower	7.74×10^{-4}	6.38×10^{-4}	5.69×10^{-4}	7.54×10^{-4}	9.73×10^{-4}	8.04×10^{-4}	7.17×10^{-4}	9.49×10^{-4}	1.23×10^{-3}	1.02×10^{-3}	9.07×10^{-4}	1.20×10^{-3}	1.23×10^{-3}	1.02×10^{-3}	9.07×10^{-4}
Non leafy Vegetables	Chilli	4.60×10^{-3}	3.37×10^{-3}	2.81×10^{-3}	4.47×10^{-3}	5.80×10^{-3}	4.27×10^{-3}	3.57×10^{-3}	5.66×10^{-3}	7.35×10^{-3}	5.44×10^{-3}	4.51×10^{-3}	7.16×10^{-3}	7.35×10^{-3}	5.44×10^{-3}	4.51×10^{-3}
	Pumpkin	1.93×10^{-3}	1.59×10^{-3}	1.42×10^{-3}	1.89×10^{-3}	2.45×10^{-3}	2.03×10^{-3}	1.81×10^{-3}	2.39×10^{-3}	3.09×10^{-3}	2.56×10^{-3}	2.29×10^{-3}	3.02×10^{-3}	3.09×10^{-3}	2.56×10^{-3}	2.29×10^{-3}
Non leafy Vegetables	Brinjal	7.55×10^{-4}	6.22×10^{-4}	5.54×10^{-4}	7.34×10^{-4}	9.55×10^{-4}	7.86×10^{-4}	7.00×10^{-4}	9.26×10^{-4}	1.21×10^{-3}	9.93×10^{-4}	8.90×10^{-4}	1.18×10^{-3}	1.21×10^{-3}	9.93×10^{-4}	8.90×10^{-4}
	Cucumber	1.02×10^{-3}	8.42×10^{-4}	7.52×10^{-4}	9.83×10^{-4}	1.30×10^{-3}	1.07×10^{-3}	9.51×10^{-4}	1.26×10^{-3}	1.64×10^{-3}	1.35×10^{-3}	1.20×10^{-3}	1.59×10^{-3}	1.64×10^{-3}	1.35×10^{-3}	1.20×10^{-3}
Non leafy Vegetables	Bitter guard	2.57×10^{-3}	2.12×10^{-3}	1.89×10^{-3}	2.50×10^{-3}	3.25×10^{-3}	2.68×10^{-3}	2.39×10^{-3}	3.16×10^{-3}	4.10×10^{-3}	3.40×10^{-3}	3.01×10^{-3}	4.00×10^{-3}	4.10×10^{-3}	3.40×10^{-3}	3.01×10^{-3}
	Mustardseed	5.09×10^{-2}	4.18×10^{-2}	3.76×10^{-2}	4.94×10^{-2}	6.47×10^{-2}	5.31×10^{-2}	4.74×10^{-2}	6.28×10^{-2}	8.16×10^{-2}	6.75×10^{-2}	6.00×10^{-2}	7.90×10^{-2}	8.16×10^{-2}	6.75×10^{-2}	6.00×10^{-2}
Non leafy Vegetables	Tomato	6.13×10^{-3}	4.48×10^{-3}	3.74×10^{-3}	5.80×10^{-3}	7.70×10^{-3}	5.66×10^{-3}	4.76×10^{-3}	7.34×10^{-3}	9.72×10^{-3}	7.15×10^{-3}	6.03×10^{-3}	9.38×10^{-3}	9.72×10^{-3}	7.15×10^{-3}	6.03×10^{-3}
	Cabbage	7.62×10^{-4}	6.29×10^{-4}	5.59×10^{-4}	7.94×10^{-4}	9.67×10^{-4}	7.97×10^{-4}	7.11×10^{-4}	1.01×10^{-3}	1.23×10^{-3}	1.01×10^{-3}	8.93×10^{-4}	1.27×10^{-3}	1.23×10^{-3}	1.01×10^{-3}	8.93×10^{-4}
Non leafy Vegetables	Coriander	1.57×10^{-2}	1.30×10^{-2}	1.16×10^{-2}	1.53×10^{-2}	1.99×10^{-2}	1.64×10^{-2}	1.46×10^{-2}	1.93×10^{-2}	2.51×10^{-2}	2.08×10^{-2}	1.86×10^{-2}	2.45×10^{-2}	2.51×10^{-2}	2.08×10^{-2}	1.86×10^{-2}
	Spinach	3.23×10^{-3}	2.67×10^{-3}	2.38×10^{-3}	3.13×10^{-3}	4.09×10^{-3}	3.38×10^{-3}	3.00×10^{-3}	3.98×10^{-3}	5.18×10^{-3}	4.26×10^{-3}	3.79×10^{-3}	5.03×10^{-3}	5.18×10^{-3}	4.26×10^{-3}	3.79×10^{-3}
Non leafy Vegetables	Fenugreek leaves	7.79×10^{-3}	7.00×10^{-3}	6.43×10^{-3}	7.57×10^{-3}	9.84×10^{-3}	8.85×10^{-3}	8.16×10^{-3}	9.55×10^{-3}	1.25×10^{-2}	1.11×10^{-2}	1.04×10^{-2}	1.21×10^{-2}	1.25×10^{-2}	1.11×10^{-2}	1.04×10^{-2}

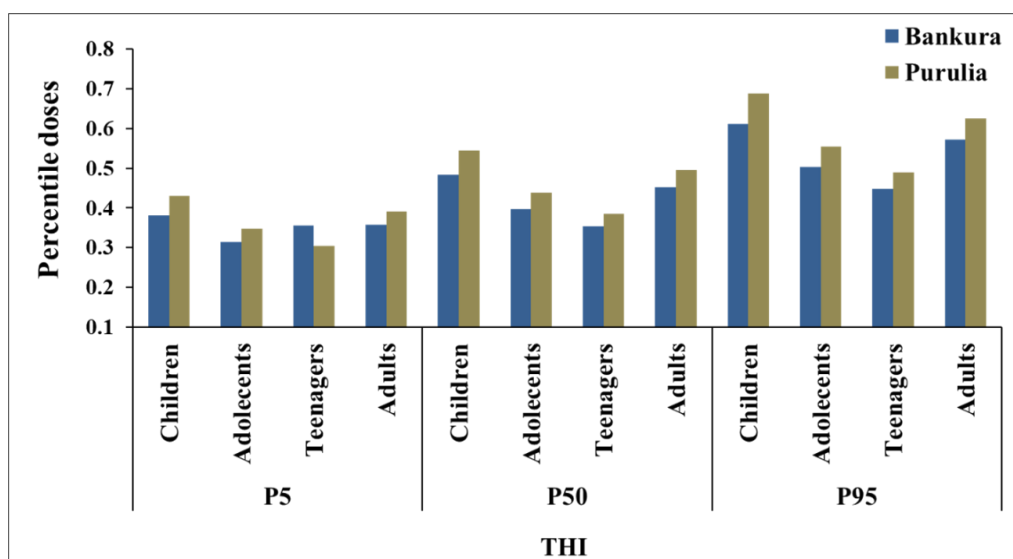


Fig. 5.53: Total hazard index (THI) determined at P5, P50, and P95 doses by a probabilistic health risk assessment of fluoride exposure at four different age groups in different cultivated crops from Bankura and Purulia

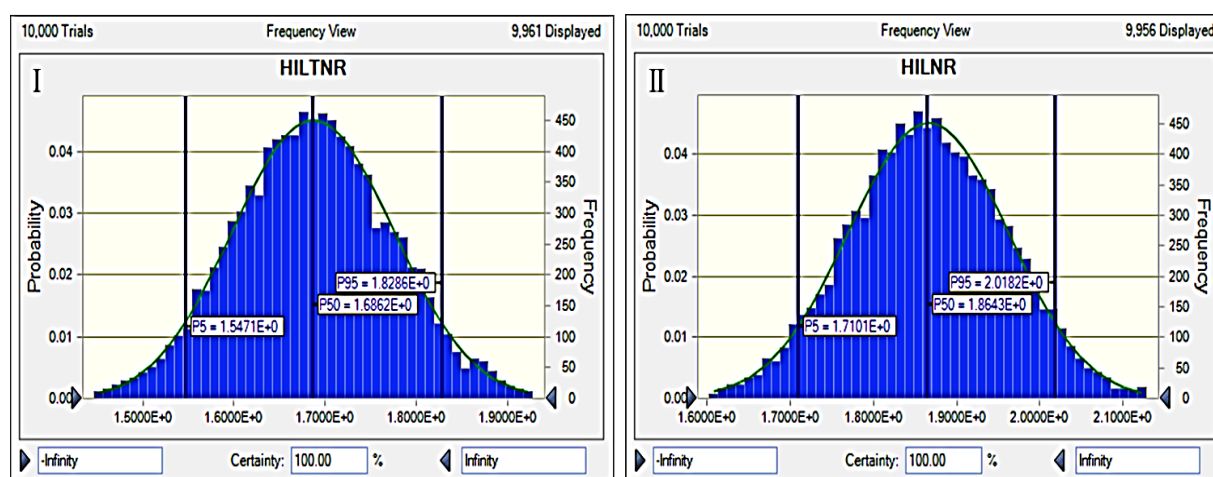


Fig. 5.54: Probabilistic health risk assessment of fluoride for lifetime exposure (HILNR) for percentile doses from P5 to P95 in **I.** Bankura and **II.** Purulia

The HI and THI values remained within the allowable limit of less than 1 even at the uncertainty upper bound (P95) for all the age groups in Bankura and Purulia. It is evident from Table 5.37 and 5.38 that the children were shown to a greater amount of non-carcinogenic risk in both districts. A similar result was noticed in the case of THI (Fig. 5.53). However, the uncertainty analysis of lifetime non-carcinogenic risk (HI_{LTNR}) yielded values greater than 1 at P5, P50, and P95 in both districts (Fig. 5.54). The HI_{LTNR} values at Purulia were around 11% greater than those in Bankura (Fig. 5.54).

5.6.3 Non-cancerous health risk due to fluoride toxicity in West Medinipur district

Health risk assessment of the studied population through consumption of F^- contaminated water has been evaluated and observed by two different ways in West Medinipur district.

5.6.3.1 Exposure dose and total hazard quotient

The health risk assessment of the studied population from West Medinipur district was found the maximum hazard quotient value of 3.47×10^{-1} and 2.61×10^{-4} for oral and dermal exposure for infants and adults, respectively (Table 5.39). According to the studied age group, THQ was found in order of infants > adults > children > teenagers (Table 5.39).

Table 5.39: Health risk assessment through oral and dermal exposure of fluoride toxicity

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	THQ
West Medinipur	Nayagram	Infants	1.81×10^{-1}	8.61×10^{-5}	1.81×10^{-1}
		Children	1.08×10^{-1}	6.87×10^{-5}	1.08×10^{-1}
		Teenagers	1.04×10^{-1}	1.10×10^{-4}	1.04×10^{-1}
		Adults	1.24×10^{-1}	1.36×10^{-4}	1.24×10^{-1}
	Keshiyari	Infants	3.47×10^{-1}	1.66×10^{-4}	3.47×10^{-1}
		Children	2.08×10^{-1}	1.32×10^{-4}	2.08×10^{-1}
		Teenagers	2.00×10^{-1}	2.12×10^{-4}	2.01×10^{-1}
		Adults	2.38×10^{-1}	2.61×10^{-4}	2.38×10^{-1}
	Garbeta I	Infants	5.56×10^{-2}	2.65×10^{-5}	5.56×10^{-2}
		Children	3.33×10^{-2}	2.11×10^{-5}	3.34×10^{-2}
		Teenagers	3.21×10^{-2}	3.39×10^{-5}	3.21×10^{-2}
		Adults	3.81×10^{-2}	4.18×10^{-5}	3.81×10^{-2}
	Garbeta II	Infants	2.36×10^{-1}	1.13×10^{-4}	2.36×10^{-1}
		Children	1.42×10^{-1}	8.98×10^{-5}	1.42×10^{-1}
		Teenagers	1.36×10^{-1}	1.44×10^{-4}	1.36×10^{-1}
		Adults	1.62×10^{-1}	1.78×10^{-4}	1.62×10^{-1}
	Pingla	Infants	9.58×10^{-1}	4.57×10^{-4}	9.59×10^{-1}
		Children	5.75×10^{-1}	3.64×10^{-4}	5.75×10^{-1}
		Teenagers	5.53×10^{-1}	5.85×10^{-4}	5.53×10^{-1}
		Adults	6.57×10^{-1}	7.21×10^{-4}	6.58×10^{-1}

5.6.3.2 Probabilistic health risk in the studied population

The combined effect of THQ values was found >1 at P95 for infants in Pingla block in West Medinipur district. This probabilistic health risk assessment study was evaluated by Monte Carlo simulation methods. The THQ values for four age groups were found in a trend of infants > adults > children > teenagers (Table 5.40).

Table 5.40: Probabilistic non-cancerous health risk (THQ) value for four age groups in different blocks of West Medinipur

Block name	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
Nayagram	1.52×10^{-1}	1.81×10^{-1}	2.11×10^{-1}	9.12×10^{-1}	1.08×10^{-1}	1.26×10^{-1}	8.77×10^{-1}	1.04×10^{-1}	1.22×10^{-1}	1.04×10^{-1}	1.24×10^{-1}	1.44×10^{-1}
Keshiyari	2.90×10^{-1}	3.47×10^{-1}	4.04×10^{-1}	1.74×10^{-1}	2.08×10^{-1}	2.42×10^{-1}	1.68×10^{-1}	2.01×10^{-1}	2.33×10^{-1}	1.99×10^{-1}	2.38×10^{-1}	2.78×10^{-1}
Garbeta I	4.68×10^{-2}	5.56×10^{-2}	6.48×10^{-2}	2.81×10^{-2}	3.34×10^{-2}	3.89×10^{-2}	2.68×10^{-2}	3.21×10^{-2}	3.74×10^{-2}	3.18×10^{-2}	3.81×10^{-2}	4.43×10^{-2}
Garbeta II	1.97×10^{-1}	2.36×10^{-1}	2.75×10^{-1}	1.18×10^{-1}	1.42×10^{-1}	1.65×10^{-1}	1.15×10^{-1}	1.36×10^{-1}	1.59×10^{-1}	1.35×10^{-1}	1.62×10^{-1}	1.88×10^{-1}
Pingla	7.99×10^{-1}	9.59×10^{-1}	1.11	4.81×10^{-1}	5.75×10^{-1}	6.70×10^{-1}	4.66×10^{-1}	5.53×10^{-1}	6.45×10^{-1}	5.53×10^{-1}	6.58×10^{-1}	7.67×10^{-1}

5.6.4 Non-cancerous health risk due to fluoride toxicity in Jhargram district

Health risk assessment of the studied population through consumption of F^- contaminated water has been evaluated and observed by two different ways in Jhargram district.

5.6.4.1 Exposure dose and total hazard quotient

The health risk assessment of the studied population from Jhargram district was found the maximum hazard quotient value of 1.92 and 1.44×10^{-3} for oral and dermal exposure in infants and adults, respectively (Table 5.41). According to the total health risk assessment, the THQ values were found > 1 in infants from four block as; Binpur II. According to the studied age group was found THQ values in range in order of infants $>$ adults $>$ children $>$ teenagers (Table 5.41).

Table 5.41: Health risk assessment through oral and dermal exposure of fluoride toxicity

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	Total HQ
Jhargram	Gopiballavpur I	Infants	2.36×10^{-1}	1.13×10^{-4}	2.36×10^{-1}
		Children	1.42×10^{-1}	8.98×10^{-5}	1.42×10^{-1}
		Teenagers	1.36×10^{-1}	1.44×10^{-4}	1.36×10^{-1}
		Adults	1.62×10^{-1}	1.78×10^{-4}	1.62×10^{-1}
	Gopiballavpur II	Infants	2.08×10^{-1}	9.94×10^{-5}	2.08×10^{-1}
		Children	1.25×10^{-1}	7.92×10^{-5}	1.25×10^{-1}
		Teenagers	1.20×10^{-1}	1.27×10^{-4}	1.20×10^{-1}
		Adults	1.43×10^{-1}	1.57×10^{-4}	1.43×10^{-1}
	Binpur II	Infants	1.92	9.14×10^{-4}	1.92
		Children	1.15	7.29×10^{-4}	1.15
		Teenagers	1.11	1.17×10^{-3}	1.11
		Adults	1.31	1.44×10^{-3}	1.32
	Jamboni	Infants	1.11×10^{-1}	5.30×10^{-5}	1.11×10^{-1}
		Children	6.67×10^{-2}	4.23×10^{-5}	6.67×10^{-2}
		Teenagers	6.41×10^{-2}	6.78×10^{-5}	6.42×10^{-2}
		Adults	7.62×10^{-2}	8.36×10^{-5}	7.63×10^{-2}

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	Total HQ
	Binpur I	Infants	4.17×10^{-1}	1.99×10^{-4}	4.17×10^{-1}
		Children	2.50×10^{-1}	1.58×10^{-4}	2.50×10^{-1}
		Teenagers	2.40×10^{-1}	2.54×10^{-4}	2.41×10^{-1}
		Adults	2.86×10^{-1}	3.13×10^{-4}	2.86×10^{-1}
	Nayagram	Infants	5.28×10^{-1}	2.52×10^{-4}	5.28×10^{-1}
		Children	3.17×10^{-1}	2.01×10^{-4}	3.17×10^{-1}
		Teenagers	3.04×10^{-1}	3.22×10^{-4}	3.05×10^{-1}
		Adults	3.62×10^{-1}	3.97×10^{-4}	3.62×10^{-1}

5.6.4.2 Probabilistic health risk in the studied population

Moreover, the THQ value in Binpur II block of Jhargram district, the combined values were found >1 at P50 and P95 for all the age groups, and at P5 doses, infants and adults were found more susceptible compared to children, and teenagers (Table 5.42).

Table 5.42: Probabilistic non-cancerous health risk (THQ) value for studied four age groups in different blocks of Jhargram district

Block name	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
Gopiballavpur I	1.99×10^{-1}	2.36×10^{-1}	2.75×10^{-1}	1.18×10^{-1}	1.42×10^{-1}	1.65×10^{-1}	1.14×10^{-1}	1.36×10^{-1}	1.59×10^{-1}	1.36×10^{-1}	1.62×10^{-1}	1.88×10^{-1}
Gopiballavpur II	1.75×10^{-1}	2.08×10^{-1}	2.43×10^{-1}	1.04×10^{-1}	1.25×10^{-1}	1.45×10^{-1}	1.01×10^{-1}	1.20×10^{-1}	1.40×10^{-1}	1.01×10^{-1}	1.43×10^{-1}	1.40×10^{-1}
Binpur II	1.61	1.92	2.24	9.61×10^{-1}	1.15	1.34	9.23×10^{-1}	1.11	1.29	1.1	1.32	1.53
Jamboni	9.35×10^{-2}	1.11×10^{-1}	1.30×10^{-1}	5.57×10^{-2}	6.67×10^{-2}	7.75×10^{-2}	5.38×10^{-2}	6.42×10^{-2}	7.46×10^{-2}	6.38×10^{-2}	7.63×10^{-2}	8.88×10^{-2}
Binpur I	3.51×10^{-1}	4.17×10^{-1}	4.86×10^{-1}	2.09×10^{-1}	2.50×10^{-1}	2.91×10^{-1}	2.01×10^{-1}	2.41×10^{-1}	2.80×10^{-1}	2.39×10^{-1}	2.86×10^{-1}	3.33×10^{-1}
Nayagram	4.44×10^{-1}	5.28×10^{-1}	6.15×10^{-1}	2.65×10^{-1}	3.17×10^{-1}	3.68×10^{-1}	2.54×10^{-1}	3.05×10^{-1}	3.54×10^{-1}	3.03×10^{-1}	3.62×10^{-1}	4.22×10^{-1}

5.6.5 Non-cancerous health risk due to fluoride toxicity in East Bardhaman district

Health risk assessment of the studied population through consumption of F^- contaminated water has been evaluated and observed by two different ways in East Bardhaman district.

5.6.5.1 Exposure dose and total hazard quotient

The maximum hazard quotient value of the computed data was found of 8.47×10^{-1} in infants for oral exposure and 6.37×10^{-4} in adults for dermal exposure from East Bardhaman (Table 5.43). According to the studied age group was found THQ values in range in order of infants $>$ adults $>$ children $>$ teenagers (Table 5.43).

Table 5.43: Health risk assessment through oral and dermal exposure of fluoride toxicity

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	Total HQ
East Bardhaman	Ausgram I	Infants	3.75×10^{-1}	1.79×10^{-4}	3.75×10^{-1}
		Children	2.25×10^{-1}	1.43×10^{-4}	2.25×10^{-1}
		Teenagers	2.16×10^{-1}	2.29×10^{-4}	2.17×10^{-1}
	Ausgram II	Adults	2.57×10^{-1}	2.82×10^{-4}	2.57×10^{-1}
		Infants	1.67×10^{-1}	7.95×10^{-5}	1.67×10^{-1}
		Children	1.00×10^{-1}	6.34×10^{-5}	1.00×10^{-1}
	Galsi II	Teenagers	9.62×10^{-2}	1.02×10^{-4}	9.63×10^{-2}
		Adults	1.14×10^{-1}	1.25×10^{-4}	1.14×10^{-1}
		Infants	6.67×10^{-1}	3.18×10^{-4}	6.67×10^{-1}
	Galsi I	Children	4.00×10^{-1}	2.54×10^{-4}	4.00×10^{-1}
		Teenagers	3.85×10^{-1}	4.07×10^{-4}	3.85×10^{-1}
		Adults	4.57×10^{-1}	5.01×10^{-4}	4.58×10^{-1}
	Bhatar	Infants	7.50×10^{-1}	3.58×10^{-4}	7.50×10^{-1}
		Children	4.50×10^{-1}	2.85×10^{-4}	4.50×10^{-1}
		Teenagers	4.33×10^{-1}	4.58×10^{-4}	4.33×10^{-1}
	Mongolkote	Adults	5.14×10^{-1}	5.64×10^{-4}	5.15×10^{-1}
		Infants	2.92×10^{-1}	1.39×10^{-4}	2.92×10^{-1}
		Children	1.75×10^{-1}	1.11×10^{-4}	1.75×10^{-1}
	Khandaghosh	Teenagers	1.68×10^{-1}	1.78×10^{-4}	1.68×10^{-1}
		Adults	2.00×10^{-1}	2.19×10^{-4}	2.00×10^{-1}
		Infants	3.19×10^{-1}	1.52×10^{-4}	3.20×10^{-1}
	Burdwan I	Children	1.92×10^{-1}	1.21×10^{-4}	1.92×10^{-1}
		Teenagers	1.84×10^{-1}	1.95×10^{-4}	1.84×10^{-1}
		Adults	2.19×10^{-1}	2.40×10^{-4}	2.19×10^{-1}
	Burdwan II	Infants	3.19×10^{-1}	1.52×10^{-4}	3.20×10^{-1}
		Children	1.92×10^{-1}	1.21×10^{-4}	1.92×10^{-1}
		Teenagers	1.84×10^{-1}	1.95×10^{-4}	1.84×10^{-1}
	Raina I	Adults	2.19×10^{-1}	2.40×10^{-4}	2.19×10^{-1}
		Infants	5.00×10^{-1}	2.39×10^{-4}	5.00×10^{-1}
		Children	3.00×10^{-1}	1.90×10^{-4}	3.00×10^{-1}
	Raina II	Teenagers	2.88×10^{-1}	3.05×10^{-4}	2.89×10^{-1}
		Adults	3.43×10^{-1}	3.76×10^{-4}	3.43×10^{-1}
		Infants	7.08×10^{-1}	3.38×10^{-4}	7.09×10^{-1}
	Memari I	Children	4.25×10^{-1}	2.69×10^{-4}	4.25×10^{-1}
		Teenagers	4.09×10^{-1}	4.32×10^{-4}	4.09×10^{-1}
		Adults	4.86×10^{-1}	5.33×10^{-4}	4.86×10^{-1}
		Infants	7.36×10^{-1}	3.51×10^{-4}	7.36×10^{-1}
		Children	4.42×10^{-1}	2.80×10^{-4}	4.42×10^{-1}
		Teenagers	4.25×10^{-1}	4.49×10^{-4}	4.25×10^{-1}
		Adults	5.05×10^{-1}	5.54×10^{-4}	5.05×10^{-1}
		Infants	7.50×10^{-1}	3.58×10^{-4}	7.50×10^{-1}
		Children	4.50×10^{-1}	2.85×10^{-4}	4.50×10^{-1}
		Teenagers	4.33×10^{-1}	4.58×10^{-4}	4.33×10^{-1}
		Adults	5.14×10^{-1}	5.64×10^{-4}	5.15×10^{-1}
		Infants	4.58×10^{-1}	2.19×10^{-4}	4.59×10^{-1}
		Children	2.75×10^{-1}	1.74×10^{-4}	2.75×10^{-1}

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	Total HQ
		Teenagers	2.64×10^{-1}	2.80×10^{-4}	2.65×10^{-1}
		Adults	3.14×10^{-1}	3.45×10^{-4}	3.15×10^{-1}
	Memari II	Infants	8.47×10^{-1}	4.04×10^{-4}	8.48×10^{-1}
		Children	5.08×10^{-1}	3.22×10^{-4}	5.09×10^{-1}
		Teenagers	4.89×10^{-1}	5.17×10^{-4}	4.89×10^{-1}
		Adults	5.81×10^{-1}	6.37×10^{-4}	5.82×10^{-1}
	Jamalpur	Infants	4.72×10^{-1}	4.04×10^{-4}	2.25×10^{-4}
		Children	2.83×10^{-1}	3.22×10^{-4}	1.80×10^{-4}
		Teenagers	2.72×10^{-1}	5.17×10^{-4}	2.88×10^{-4}
		Adults	3.24×10^{-1}	6.37×10^{-4}	3.55×10^{-4}
	Monteswar	Infants	6.39×10^{-1}	3.05×10^{-4}	2.25×10^{-4}
		Children	3.83×10^{-1}	2.43×10^{-4}	1.80×10^{-4}
		Teenagers	3.69×10^{-1}	3.90×10^{-4}	2.88×10^{-4}
		Adults	4.38×10^{-1}	4.81×10^{-4}	3.55×10^{-4}
	Kalna I	Infants	3.19×10^{-1}	1.52×10^{-4}	2.25×10^{-4}
		Children	1.92×10^{-1}	1.21×10^{-4}	1.80×10^{-4}
		Teenagers	1.84×10^{-1}	1.95×10^{-4}	2.88×10^{-4}
		Adults	2.19×10^{-1}	2.40×10^{-4}	3.55×10^{-4}
	Kalna II	Infants	2.22×10^{-1}	1.06×10^{-4}	2.25×10^{-4}
		Children	1.33×10^{-1}	8.45×10^{-5}	1.80×10^{-4}
		Teenagers	1.28×10^{-1}	1.36×10^{-4}	2.88×10^{-4}
		Adults	1.52×10^{-1}	1.67×10^{-4}	3.55×10^{-4}
	Purbasthali I	Infants	3.47×10^{-1}	1.66×10^{-4}	2.25×10^{-4}
		Children	2.08×10^{-1}	1.32×10^{-4}	1.80×10^{-4}
		Teenagers	2.00×10^{-1}	2.12×10^{-4}	2.88×10^{-4}
		Adults	2.38×10^{-1}	2.61×10^{-4}	3.55×10^{-4}
	Purbasthali II	Infants	3.61×10^{-1}	1.72×10^{-4}	2.25×10^{-4}
		Children	2.17×10^{-1}	1.37×10^{-4}	1.80×10^{-4}
		Teenagers	2.08×10^{-1}	2.20×10^{-4}	2.88×10^{-4}
		Adults	2.48×10^{-1}	2.72×10^{-4}	3.55×10^{-4}
	Katwa I	Infants	3.89×10^{-1}	1.86×10^{-4}	2.25×10^{-4}
		Children	2.33×10^{-1}	1.48×10^{-4}	1.80×10^{-4}
		Teenagers	2.24×10^{-1}	2.37×10^{-4}	2.88×10^{-4}
		Adults	2.67×10^{-1}	2.93×10^{-4}	3.55×10^{-4}
	Katwa II	Infants	2.08×10^{-1}	9.94×10^{-5}	2.25×10^{-4}
		Children	1.25×10^{-1}	7.92×10^{-5}	1.80×10^{-4}
		Teenagers	1.20×10^{-1}	1.27×10^{-4}	2.88×10^{-4}
		Adults	1.43×10^{-1}	1.57×10^{-4}	3.55×10^{-4}
	Ketugram I	Infants	5.00×10^{-1}	2.39×10^{-4}	2.25×10^{-4}
		Children	3.00×10^{-1}	1.90×10^{-4}	1.80×10^{-4}
		Teenagers	2.88×10^{-1}	3.05×10^{-4}	2.88×10^{-4}
		Adults	3.43×10^{-1}	3.76×10^{-4}	3.55×10^{-4}
	Ketugram II	Infants	6.67×10^{-1}	3.18×10^{-4}	2.25×10^{-4}
		Children	4.00×10^{-1}	2.54×10^{-4}	1.80×10^{-4}
		Teenagers	3.85×10^{-1}	4.07×10^{-4}	2.88×10^{-4}
		Adults	4.57×10^{-1}	5.01×10^{-4}	3.55×10^{-4}

5.6.5.2 Probabilistic health risk in the studied population

All the THQ values were found <1 for all the age groups in East Bardhaman district. So, the overall futuristic health risk for different studied age groups is considerably safe from F⁻ toxicity (Table 5.44).

Table 5.44: Probabilistic non-cancerous health risk (THQ) value for studied four age groups in different blocks of East Bardhaman district

Block name	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
Ausgram I	3.16×10^{-1}	3.75×10^{-1}	4.37×10^{-1}	1.88×10^{-1}	2.25×10^{-1}	2.62×10^{-1}	1.81×10^{-1}	2.17×10^{-1}	2.52×10^{-1}	2.11×10^{-1}	2.57×10^{-1}	3.00×10^{-1}
Ausgram II	1.40×10^{-1}	1.67×10^{-1}	1.94×10^{-1}	8.36×10^{-2}	1.00×10^{-1}	1.16×10^{-1}	8.22×10^{-2}	9.63×10^{-2}	1.12×10^{-1}	9.57×10^{-2}	1.14×10^{-1}	1.33×10^{-1}
Galsi II	5.61×10^{-1}	6.67×10^{-1}	7.77×10^{-1}	3.34×10^{-1}	4.00×10^{-1}	4.65×10^{-1}	3.21×10^{-1}	3.85×10^{-1}	4.48×10^{-1}	3.83×10^{-1}	4.58×10^{-1}	5.33×10^{-1}
Galsi I	6.31×10^{-1}	7.50×10^{-1}	8.75×10^{-1}	3.76×10^{-1}	4.50×10^{-1}	5.23×10^{-1}	3.61×10^{-1}	4.33×10^{-1}	5.04×10^{-1}	4.30×10^{-1}	5.15×10^{-1}	5.99×10^{-1}
Bhatar	2.45×10^{-1}	2.92×10^{-1}	3.40×10^{-1}	1.46×10^{-1}	1.75×10^{-1}	2.04×10^{-1}	1.40×10^{-1}	1.68×10^{-1}	1.96×10^{-1}	1.67×10^{-1}	2.00×10^{-1}	2.33×10^{-1}
Mongolkote	2.69×10^{-1}	3.20×10^{-1}	3.73×10^{-1}	1.60×10^{-1}	1.92×10^{-1}	2.23×10^{-1}	1.54×10^{-1}	1.84×10^{-1}	2.14×10^{-1}	1.83×10^{-1}	2.19×10^{-1}	2.55×10^{-1}
Khandaghosh	6.61×10^{-1}	7.92×10^{-1}	9.21×10^{-1}	3.96×10^{-1}	4.75×10^{-1}	5.53×10^{-1}	3.82×10^{-1}	4.57×10^{-1}	5.32×10^{-1}	4.56×10^{-1}	5.43×10^{-1}	6.33×10^{-1}
Burdwan I	4.89×10^{-1}	5.00×10^{-1}	5.82×10^{-1}	2.51×10^{-1}	3.00×10^{-1}	3.49×10^{-1}	2.41×10^{-1}	2.89×10^{-1}	3.36×10^{-1}	2.88×10^{-1}	3.43×10^{-1}	4.00×10^{-1}
Burdwan II	5.92×10^{-1}	7.09×10^{-1}	8.24×10^{-1}	3.54×10^{-1}	4.25×10^{-1}	4.96×10^{-1}	3.42×10^{-1}	4.09×10^{-1}	4.76×10^{-1}	4.05×10^{-1}	4.86×10^{-1}	5.65×10^{-1}
Raina I	6.20×10^{-1}	7.36×10^{-1}	8.58×10^{-1}	3.69×10^{-1}	4.42×10^{-1}	5.15×10^{-1}	3.55×10^{-1}	4.25×10^{-1}	4.96×10^{-1}	4.23×10^{-1}	5.05×10^{-1}	5.88×10^{-1}
Raina II	6.28×10^{-1}	7.50×10^{-1}	8.71×10^{-1}	3.76×10^{-1}	4.50×10^{-1}	5.25×10^{-1}	3.61×10^{-1}	4.33×10^{-1}	5.05×10^{-1}	4.31×10^{-1}	5.15×10^{-1}	5.99×10^{-1}
Memari I	3.83×10^{-1}	4.59×10^{-1}	5.35×10^{-1}	2.29×10^{-1}	2.75×10^{-1}	3.20×10^{-1}	2.21×10^{-1}	2.65×10^{-1}	3.08×10^{-1}	2.62×10^{-1}	3.15×10^{-1}	3.66×10^{-1}
Memari II	7.06×10^{-1}	8.48×10^{-1}	9.89×10^{-1}	4.24×10^{-1}	5.09×10^{-1}	5.92×10^{-1}	4.09×10^{-1}	4.89×10^{-1}	5.68×10^{-1}	4.84×10^{-1}	5.82×10^{-1}	6.76×10^{-1}
Jamalpur	3.93×10^{-1}	4.73×10^{-1}	5.51×10^{-1}	2.39×10^{-1}	2.84×10^{-1}	3.31×10^{-1}	2.28×10^{-1}	2.73×10^{-1}	3.18×10^{-1}	2.75×10^{-1}	3.24×10^{-1}	3.78×10^{-1}
Monteswar	5.35×10^{-1}	6.39×10^{-1}	7.44×10^{-1}	3.21×10^{-1}	3.84×10^{-1}	4.45×10^{-1}	3.08×10^{-1}	3.69×10^{-1}	4.30×10^{-1}	3.65×10^{-1}	4.39×10^{-1}	5.11×10^{-1}
Kalna I	2.67×10^{-1}	3.20×10^{-1}	3.72×10^{-1}	1.61×10^{-1}	1.92×10^{-1}	2.24×10^{-1}	1.54×10^{-1}	1.84×10^{-1}	2.14×10^{-1}	1.83×10^{-1}	2.19×10^{-1}	2.55×10^{-1}
Kalna II	1.86×10^{-1}	2.22×10^{-1}	2.60×10^{-1}	1.12×10^{-1}	1.33×10^{-1}	1.55×10^{-1}	1.07×10^{-1}	1.28×10^{-1}	1.50×10^{-1}	1.27×10^{-1}	1.53×10^{-1}	1.78×10^{-1}
Purbasthali I	2.91×10^{-1}	3.47×10^{-1}	4.05×10^{-1}	1.74×10^{-1}	2.08×10^{-1}	2.43×10^{-1}	1.67×10^{-1}	2.01×10^{-1}	2.33×10^{-1}	1.99×10^{-1}	2.38×10^{-1}	2.78×10^{-1}
Purbasthali II	3.02×10^{-1}	3.61×10^{-1}	4.21×10^{-1}	1.81×10^{-1}	2.17×10^{-1}	2.53×10^{-1}	1.74×10^{-1}	2.09×10^{-1}	2.42×10^{-1}	2.07×10^{-1}	2.48×10^{-1}	2.89×10^{-1}
Katwa I	3.27×10^{-1}	3.89×10^{-1}	4.54×10^{-1}	1.95×10^{-1}	2.33×10^{-1}	2.72×10^{-1}	1.87×10^{-1}	2.25×10^{-1}	2.62×10^{-1}	2.23×10^{-1}	2.67×10^{-1}	3.11×10^{-1}
Katwa II	1.74×10^{-1}	2.08×10^{-1}	2.42×10^{-1}	1.05×10^{-1}	1.25×10^{-1}	1.46×10^{-1}	1.00×10^{-1}	1.20×10^{-1}	1.40×10^{-1}	1.20×10^{-1}	1.43×10^{-1}	1.66×10^{-1}
Ketugram I	4.18×10^{-1}	5.00×10^{-1}	5.84×10^{-1}	2.50×10^{-1}	3.00×10^{-1}	3.49×10^{-1}	2.41×10^{-1}	2.89×10^{-1}	3.36×10^{-1}	2.86×10^{-1}	3.43×10^{-1}	4.00×10^{-1}
Ketugram II	5.55×10^{-1}	6.67×10^{-1}	7.78×10^{-1}	3.34×10^{-1}	4.00×10^{-1}	4.65×10^{-1}	3.22×10^{-1}	3.85×10^{-1}	4.47×10^{-1}	3.81×10^{-1}	4.58×10^{-1}	5.32×10^{-1}

5.6.6 Non- cancerous health risk due to fluoride toxicity in West Bardhaman district

Health risk assessment of the studied population through consumption of F^- contaminated water has been evaluated and observed by two different ways in West Bardhaman district.

5.6.6.1 Exposure dose and total hazard quotient

The health risk assessment of the studied population from West Bardhaman district was found the maximum hazard quotient value of 1.68 and 1.26×10^{-3} for oral and dermal exposure in infants and adults, respectively (Table 5.45). According to the total health risk assessment, the THQ values were found > 1 for all the studied age groups (other than teenagers) in Barabani block. According to the studied age group, the THQ was found in order of infants $>$ adults $>$ children $>$ teenagers (Table 5.45).

Table 5.45: Health risk assessment through oral and dermal exposure of fluoride toxicity

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	THQ
West Bardhaman	Salanpur	Infants	9.03×10^{-1}	4.31×10^{-4}	9.03×10^{-1}
		Children	5.42×10^{-1}	3.43×10^{-4}	5.42×10^{-1}
		Teenagers	5.21×10^{-1}	5.51×10^{-4}	5.21×10^{-1}
		Adults	6.19×10^{-1}	6.79×10^{-4}	6.20×10^{-1}
	Barabani	Infants	1.68	8.02×10^{-4}	1.68
		Children	1.01	6.39×10^{-4}	1.01
		Teenagers	9.70×10^{-1}	1.03×10^{-3}	9.71×10^{-1}
		Adults	1.15	1.26×10^{-3}	1.15
	Jamuria	Infants	6.25×10^{-1}	2.98×10^{-4}	6.25×10^{-1}
		Children	3.75×10^{-1}	2.38×10^{-4}	3.75×10^{-1}
		Teenagers	3.61×10^{-1}	3.81×10^{-4}	3.61×10^{-1}
		Adults	4.29×10^{-1}	4.70×10^{-4}	4.29×10^{-1}
	Pandabeswar	Infants	7.64×10^{-1}	3.64×10^{-4}	7.64×10^{-1}
		Children	4.58×10^{-1}	2.90×10^{-4}	4.59×10^{-1}
		Teenagers	4.41×10^{-1}	4.66×10^{-4}	4.41×10^{-1}
		Adults	5.24×10^{-1}	5.75×10^{-4}	5.24×10^{-1}
	Asansole	Infants	8.61×10^{-1}	4.11×10^{-4}	8.62×10^{-1}
		Children	5.17×10^{-1}	3.27×10^{-4}	5.17×10^{-1}
		Teenagers	4.97×10^{-1}	5.26×10^{-4}	4.97×10^{-1}
		Adults	5.90×10^{-1}	6.48×10^{-4}	5.91×10^{-1}
	Ondal	Infants	6.67×10^{-1}	3.18×10^{-4}	6.67×10^{-1}
		Children	4.00×10^{-1}	2.54×10^{-4}	4.00×10^{-1}
		Teenagers	3.85×10^{-1}	4.07×10^{-4}	3.85×10^{-1}
		Adults	4.57×10^{-1}	5.01×10^{-4}	4.58×10^{-1}

District Name	Block Names	Population	HQ _{oral}	HQ _{dermal}	THQ
	Raniganj	Infants	6.81×10^{-1}	3.25×10^{-4}	6.81×10^{-1}
		Children	4.08×10^{-1}	2.59×10^{-4}	4.09×10^{-1}
		Teenagers	3.93×10^{-1}	4.15×10^{-4}	3.93×10^{-1}
		Adults	4.67×10^{-1}	5.12×10^{-4}	4.67×10^{-1}
	Durgapur	Infants	5.28×10^{-1}	2.52×10^{-4}	5.28×10^{-1}
		Children	3.17×10^{-1}	2.01×10^{-4}	3.17×10^{-1}
		Teenagers	3.04×10^{-1}	3.22×10^{-4}	3.05×10^{-1}
		Adults	3.62×10^{-1}	3.97×10^{-4}	3.62×10^{-1}
	Kanksa	Infants	4.31×10^{-1}	2.05×10^{-4}	4.31×10^{-1}
		Children	2.58×10^{-1}	1.64×10^{-4}	2.58×10^{-1}
		Teenagers	2.48×10^{-1}	2.63×10^{-4}	2.49×10^{-1}
		Adults	2.95×10^{-1}	3.24×10^{-4}	2.96×10^{-1}

5.6.6.2 Probabilistic health risk in the studied population

In Barabani block of West Bardhaman district, all the THQ_{ing+der} values were found > 1 at P5, P50 and P95 doses for infants. Children and adults were found more susceptible to F⁻ toxicity (THQ_{ing+der} > 1) at P50 and P95 doses. Even, the probable THQ_{ing+der} values were found ≥ 1 for infants at P95 dose from two other blocks namely, Salanpur and Asansole in West Bardhaman district (Table 5.46).

Table 5.46: Probabilistic non-cancerous health risk (THQ) value for studied four age groups in different blocks of West Bardhaman

Block name	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
Salanpur	7.60×10^{-1}	9.03×10^{-1}	1.05	4.53×10^{-1}	5.42×10^{-1}	6.30×10^{-1}	4.35×10^{-1}	5.21×10^{-1}	6.06×10^{-1}	5.18×10^{-1}	6.20×10^{-1}	7.21×10^{-1}
Barabani	1.41	1.68	1.96	8.43×10^{-1}	1.01	1.17	8.09×10^{-1}	9.71×10^{-1}	1.13	9.65×10^{-1}	1.15	1.34
Jamuria	5.26×10^{-1}	6.25×10^{-1}	7.29×10^{-1}	3.13×10^{-1}	3.75×10^{-1}	4.36×10^{-1}	3.01×10^{-1}	3.61×10^{-1}	4.20×10^{-1}	3.59×10^{-1}	4.29×10^{-1}	4.99×10^{-1}
Pandabeswar	6.43×10^{-1}	7.64×10^{-1}	8.91×10^{-1}	3.83×10^{-1}	4.59×10^{-1}	5.33×10^{-1}	3.68×10^{-1}	4.41×10^{-1}	5.13×10^{-1}	4.38×10^{-1}	5.24×10^{-1}	6.10×10^{-1}
Asansole	7.25×10^{-1}	8.62×10^{-1}	1	4.32×10^{-1}	5.17×10^{-1}	6.01×10^{-1}	4.14×10^{-1}	4.97×10^{-1}	5.78×10^{-1}	4.94×10^{-1}	5.91×10^{-1}	6.88×10^{-1}
Ondal	5.61×10^{-1}	6.67×10^{-1}	7.77×10^{-1}	3.34×10^{-1}	4.00×10^{-1}	4.65×10^{-1}	3.28×10^{-1}	3.85×10^{-1}	4.48×10^{-1}	3.83×10^{-1}	4.58×10^{-1}	5.33×10^{-1}
Raniganj	5.73×10^{-1}	6.81×10^{-1}	7.93×10^{-1}	3.41×10^{-1}	4.09×10^{-1}	4.75×10^{-1}	3.28×10^{-1}	3.93×10^{-1}	4.57×10^{-1}	3.91×10^{-1}	4.67×10^{-1}	5.44×10^{-1}
Durgapur	4.44×10^{-1}	5.28×10^{-1}	6.15×10^{-1}	2.65×10^{-1}	3.17×10^{-1}	3.68×10^{-1}	2.55×10^{-1}	3.05×10^{-1}	3.55×10^{-1}	3.02×10^{-1}	3.62×10^{-1}	4.21×10^{-1}
Kanksa	3.62×10^{-1}	4.31×10^{-1}	5.02×10^{-1}	2.16×10^{-1}	2.58×10^{-1}	3.00×10^{-1}	2.07×10^{-1}	2.49×10^{-1}	2.89×10^{-1}	2.47×10^{-1}	2.96×10^{-1}	3.44×10^{-1}

5.6.7 Non-cancerous health risk due to fluoride toxicity in Murshidabad district

Health risk assessment of the studied population through consumption of F^- contaminated water has been evaluated and observed by two different ways in Murshidabad district.

5.6.7.1 Exposure dose and total hazard quotient

The health risk assessment of the studied population from Murshidabad district was found the maximum hazard quotient value of 1.8 and 1.36×10^{-3} for oral and dermal exposure in infants and adults, respectively. According to the total health risk assessment, the THQ values were found > 1 for infants from two blocks namely Kandi and Khargram. The THQ values for all the studied age groups were found > 1 in Kandi block. According to the studied age group was found in range in order of infants $>$ adults $>$ children $>$ teenagers (**Table 5.47**).

Table 5.47: Health risk assessment through oral and dermal exposure of fluoride toxicity

District Name	Block Names	Population	HQ _{ing}	HQ _{dermal}	Total HQ
Murshidabad	Bharatpur II	Infants	6.94×10^{-1}	3.31×10^{-4}	6.95×10^{-1}
		Children	4.17×10^{-1}	2.64×10^{-4}	4.17×10^{-1}
		Teenagers	4.01×10^{-1}	4.24×10^{-4}	4.01×10^{-1}
		Adults	4.76×10^{-1}	5.22×10^{-4}	4.77×10^{-1}
	Kandi	Infants	1.81	8.61×10^{-4}	1.81
		Children	1.08	6.87×10^{-4}	1.08
		Teenagers	1.04	1.10×10^{-3}	1.04
		Adults	1.24	1.36×10^{-3}	1.24
	Khargram	Infants	1.13	5.37×10^{-4}	1.13
		Children	6.75×10^{-1}	4.28×10^{-4}	6.75×10^{-1}
		Teenagers	6.49×10^{-1}	6.87×10^{-4}	6.50×10^{-1}
		Adults	7.71×10^{-1}	8.46×10^{-4}	7.72×10^{-1}
	Nabagram	Infants	7.36×10^{-1}	3.51×10^{-4}	7.36×10^{-1}
		Children	4.42×10^{-1}	2.80×10^{-4}	4.42×10^{-1}
		Teenagers	4.25×10^{-1}	4.49×10^{-4}	4.25×10^{-1}
		Adults	5.05×10^{-1}	5.54×10^{-4}	5.05×10^{-1}
	Sagardighi	Infants	5.42×10^{-1}	2.58×10^{-4}	5.42×10^{-1}
		Children	3.25×10^{-1}	2.06×10^{-4}	3.25×10^{-1}
		Teenagers	3.13×10^{-1}	3.31×10^{-4}	3.13×10^{-1}
		Adults	3.71×10^{-1}	4.07×10^{-4}	3.72×10^{-1}

District Name	Block Names	Population	HQ _{ing}	HQ _{dermal}	Total HQ
	Burwan	Infants	5.83×10^{-1}	2.78×10^{-4}	5.84×10^{-1}
		Children	3.50×10^{-1}	2.22×10^{-4}	3.50×10^{-1}
		Teenagers	3.37×10^{-1}	3.56×10^{-4}	3.37×10^{-1}
		Adults	4.00×10^{-1}	4.39×10^{-4}	4.00×10^{-1}
	Berhaampur	Infants	1.67×10^{-1}	7.95×10^{-5}	1.67×10^{-1}
		Children	1.00×10^{-1}	6.34×10^{-5}	1.00×10^{-1}
		Teenagers	9.62×10^{-2}	1.02×10^{-4}	9.63×10^{-2}
		Adults	1.14×10^{-1}	1.25×10^{-4}	1.14×10^{-1}
	Suti II	Infants	1.94×10^{-1}	9.28×10^{-5}	1.95×10^{-1}
		Children	1.17×10^{-1}	7.39×10^{-5}	1.17×10^{-1}
		Teenagers	1.12×10^{-1}	1.19×10^{-4}	1.12×10^{-1}
		Adults	1.33×10^{-1}	1.46×10^{-4}	1.33×10^{-1}
	Raghunathganj I	Infants	5.28×10^{-1}	2.52×10^{-4}	5.28×10^{-1}
		Children	3.17×10^{-1}	2.01×10^{-4}	3.17×10^{-1}
		Teenagers	3.04×10^{-1}	3.22×10^{-4}	3.05×10^{-1}
		Adults	3.62×10^{-1}	3.97×10^{-4}	3.62×10^{-1}
	Raghunathganj II	Infants	6.94×10^{-2}	3.31×10^{-5}	6.95×10^{-2}
		Children	4.17×10^{-2}	2.64×10^{-5}	4.17×10^{-2}
		Teenagers	4.01×10^{-2}	4.24×10^{-5}	4.01×10^{-2}
		Adults	4.76×10^{-2}	5.22×10^{-5}	4.77×10^{-2}
	Samserganj	Infants	3.61×10^{-1}	1.72×10^{-4}	3.61×10^{-1}
		Children	2.17×10^{-1}	1.37×10^{-4}	2.17×10^{-1}
		Teenagers	2.08×10^{-1}	2.20×10^{-4}	2.09×10^{-1}
		Adults	2.48×10^{-1}	2.72×10^{-4}	2.48×10^{-1}

5.6.7.2 Probabilistic health risk in the studied population

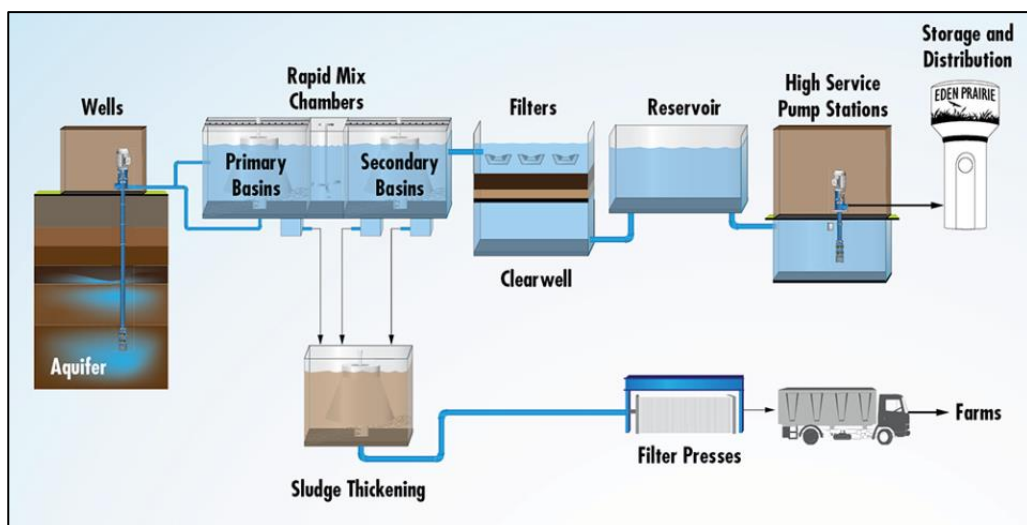
In Kandi block of Murshidabad district, the probable THQ_{ing+der} values were found > 1 for infants and adults at P5, P50 and P95 doses; whereas the children and teenagers were more susceptible to F⁻ toxicity at P50 and P95 doses. Moreover, the THQ_{ing+der} values were found > 1 for infants at P50 and P95 doses in Khargram block of Murshidabad district (**Table 5.48**).

Table 5.48: Probabilistic non-cancerous health risk (THQ) value for studied four age groups in different blocks of Murshidabad district

Block name	Infants			Children			Teenagers			Adults		
	5%	50%	95%	5%	50%	95%	5%	50%	95%	5%	50%	95%
Bharatpur II	5.84×10^{-1}	6.95×10^{-1}	8.10×10^{-1}	3.48×10^{-1}	4.18×10^{-1}	4.85×10^{-1}	3.34×10^{-1}	4.00×10^{-1}	4.66×10^{-1}	3.99×10^{-1}	4.77×10^{-1}	5.55×10^{-1}
Kandi	1.52	1.81	2.11	9.05×10^{-1}	1.09	1.26	8.69×10^{-1}	1.04	1.21	1.04	1.24	1.44
Khargram	1.47×10^{-1}	1.13	1.31	5.65×10^{-1}	6.77×10^{-1}	7.88×10^{-1}	5.63×10^{-1}	6.76×10^{-1}	7.86×10^{-1}	6.43×10^{-1}	7.74×10^{-1}	8.98×10^{-1}
Nabagram	6.20×10^{-1}	7.36×10^{-1}	8.58×10^{-1}	3.69×10^{-1}	4.42×10^{-1}	5.15×10^{-1}	3.55×10^{-1}	4.25×10^{-1}	5.96×10^{-1}	4.23×10^{-1}	5.06×10^{-1}	5.88×10^{-1}
Sagardighi	4.56×10^{-1}	5.42×10^{-1}	6.32×10^{-1}	2.72×10^{-1}	3.25×10^{-1}	3.79×10^{-1}	2.61×10^{-1}	3.13×10^{-1}	3.65×10^{-1}	3.10×10^{-1}	3.72×10^{-1}	4.33×10^{-1}
Burwan	4.91×10^{-1}	5.84×10^{-1}	6.80×10^{-1}	2.92×10^{-1}	3.51×10^{-1}	4.08×10^{-1}	2.81×10^{-1}	3.37×10^{-1}	3.93×10^{-1}	3.35×10^{-1}	4.01×10^{-1}	4.66×10^{-1}
Berhaampur	1.40×10^{-1}	1.67×10^{-1}	1.90×10^{-1}	1.40×10^{-1}	1.67×10^{-1}	1.94×10^{-1}	8.03×10^{-2}	3.62×10^{-2}	1.12×10^{-1}	9.57×10^{-2}	1.14×10^{-1}	1.33×10^{-1}
Suti II	1.63×10^{-1}	1.95×10^{-1}	2.26×10^{-1}	9.76×10^{-1}	1.17×10^{-1}	1.36×10^{-1}	9.45×10^{-2}	1.12×10^{-1}	1.31×10^{-1}	1.11×10^{-1}	1.34×10^{-1}	1.56×10^{-1}
Raghunathganj I	4.44×10^{-1}	5.28×10^{-1}	6.15×10^{-1}	2.65×10^{-1}	3.17×10^{-1}	3.69×10^{-1}	2.54×10^{-1}	3.05×10^{-1}	3.55×10^{-1}	3.03×10^{-1}	3.63×10^{-1}	4.22×10^{-1}
Raghunathganj II	5.84×10^{-2}	6.95×10^{-2}	8.05×10^{-2}	3.48×10^{-2}	4.17×10^{-2}	4.86×10^{-2}	3.37×10^{-2}	4.01×10^{-2}	4.67×10^{-2}	3.98×10^{-2}	4.77×10^{-2}	5.56×10^{-2}
Samserganj	3.02×10^{-1}	3.61×10^{-1}	4.21×10^{-1}	1.81×10^{-1}	2.97×10^{-1}	2.52×10^{-1}	1.74×10^{-1}	2.09×10^{-1}	2.42×10^{-1}	2.07×10^{-1}	2.48×10^{-1}	2.89×10^{-1}

Objective: 4

Possible remedial options



5.7 Adsorption process

Adsorption is a physical or chemical process in which ions enter a bulk phase, involving both liquid and solid materials.

5.7.1 Adsorbent characterization

The characterization of the adsorbents has been studied by XRD analysis.

5.7.1.1 XRD study

The adsorbent materials have been characterized by the XRD study and showed the chemical purity of the used adsorbent materials.

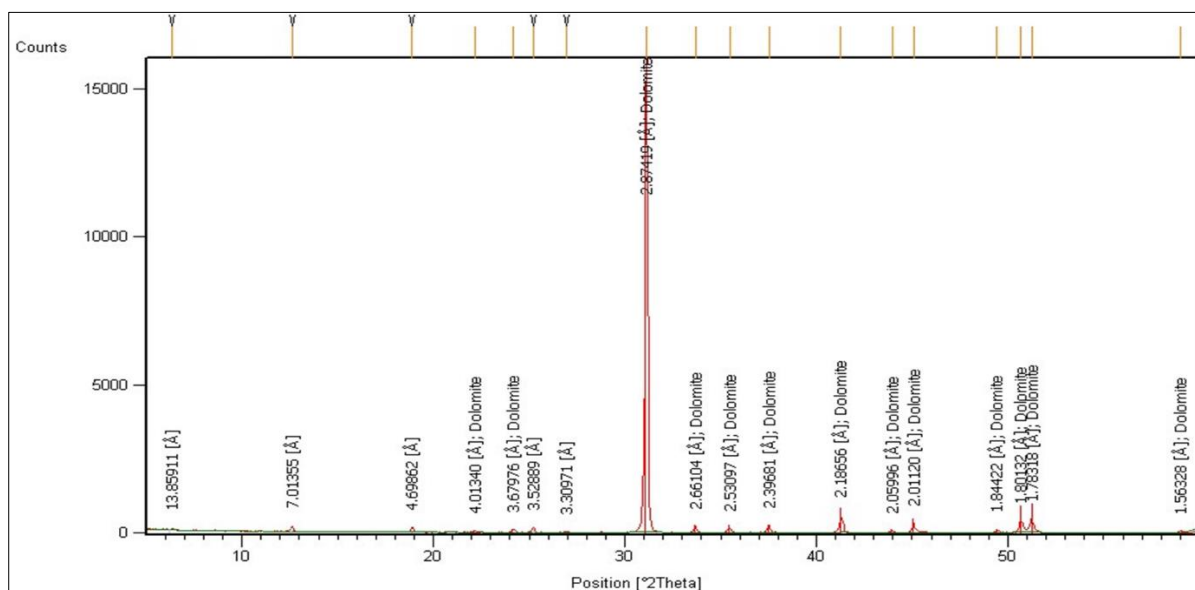


Fig. 5.55: X-ray diffraction (XRD) study of dolomite

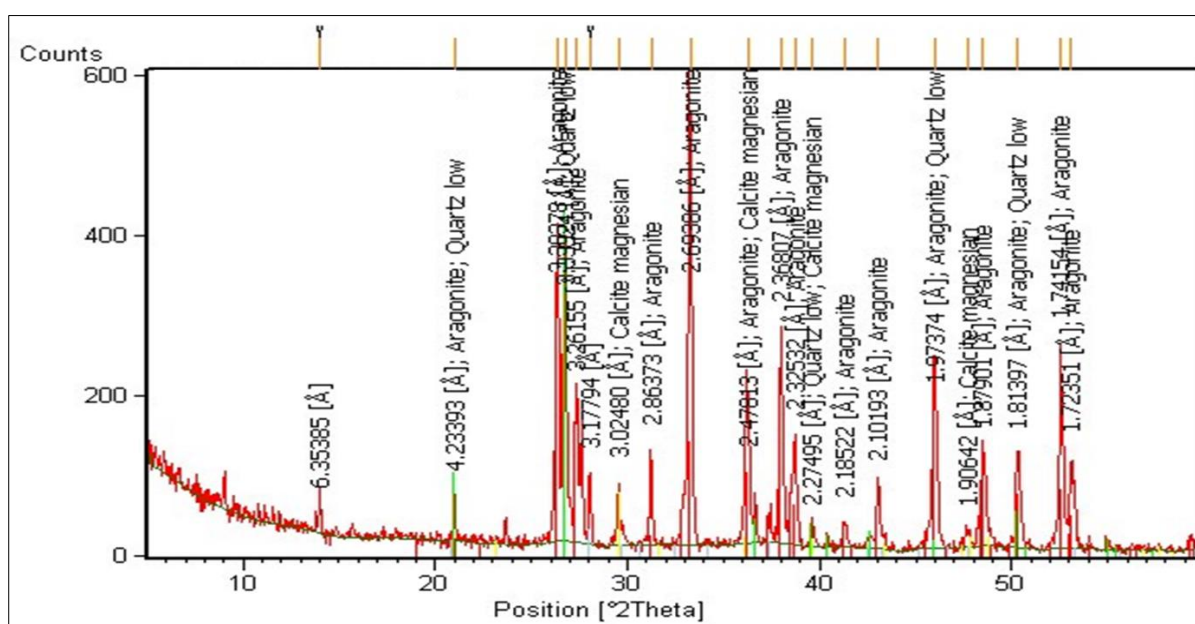


Fig. 5.56: X-ray diffraction (XRD) study of seashell

5.7.1.2 Elemental characterization of adsorbents

Both adsorbent materials have been characterized by alkaline and acid digestion process. Main adsorbent element is calcium presence in dolomite and seashell. The calcium concentration in dolomite and seashell are 142 mg/kg and 260 mg/kg, respectively. Iron concentration in seashell and dolomite are 7145 mg/kg and 2034 mg/kg, respectively. Dolomite is primarily a ubiquitous sedimentary rock-forming mineral. It basically consists of the layers of carbonate ions (CO_3^{2-}), calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}). Thermally activated and treated dolomite at higher temperature (600 °C or 800 °C) leads to change its original chemical composition and formed calcium oxide, magnesium oxide and calcite as shown in the below equation (Staszczuk et al., 1997).



This change of chemical composition increased in the BET surface area of the dolomite (Staszczuk et al., 1997). It has been reported that subjecting dolomite to thermal treatment at 800°C leads to a substantial increase in its surface area, consequently enhancing its adsorption properties manifold (Walker et al., 2003). From the XRD and elemental distribution it is also clear that this adsorbent are highly calcium and iron enriched and calcite is in the maximum and dominating proportion which also increases the adsorption. Seashell usually consists of an outer layer of protein followed by an intermediate layer of calcite and a smooth inner layer of platy calcium carbonate crystal (Narayanan et al., 2006). It has important functional groups like $-\text{CH}_2$, $-\text{OH}$, $-\text{CO}_2$ and $-\text{PO}_4$ which make its more effective adsorbent for removal both organic and inorganic pollutants. (Chowdhury and Saha, 2010). The temperature plays a vital role on the calcination process of seashell. It has been reported that thermally activated seashell (mainly at 750 - 800 °C) has the higher amount of CaO and this calcination process also increased the amount of calcium and oxygen which reduced the carbon content (Nordin et al., 2015; Dampang et al., 2021). Hence thermally activated (at higher temperature like 600 °C or 800 °C) adsorbents are found most appropriate for its rapid increasing of BET surface area, pore size distribution and pore volume. (Chaudhary and Prasad, 2015).

5.7.2 Effect of various optimum parameters on adsorption of fluoride using dolomite, seashell, and their mixture

Various adsorbent techniques have been occupied to eliminate F^- from F^- contaminated water, aiming to optimize different parameters (doses, temperature, contact time). At initial condition

the adsorbent materials were prepared pH at 7-8 and F^- concentration prepared as synthetic contaminated water 20 mg/l.

5.7.2.1 Effect of adsorbent doses for fluoride removal

5.7.2.1.1 Effect of adsorbent doses by using dolomite

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 5-50 g/l

F^- concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature ($^{\circ}C$): 600 $^{\circ}C$

Rotational speed of shaker (RPM): 40 rpm

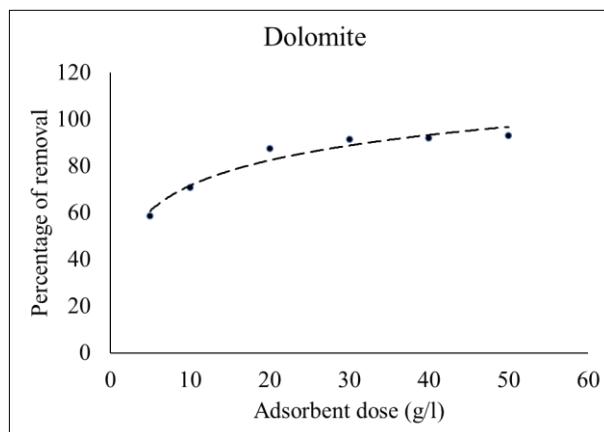


Fig. 5.57: Removal (%) vs. Adsorbent dose

Experimental results showed that percentage of F^- removal varied at different adsorbent doses of dolomite range from 5- 50 g/l. The removal of F^- was increased from 58.8% to 93.1% with increase of adsorbent dosage at 5 to 50 g/l. The maximum removal of F^- ions can be obtained by using 50 g/l of dolomite.

5.7.2.1.2 Effect of adsorbent doses by using seashell

Experiment process:

Initial pH: 7-8

Dolomite dose (g/l): 5-50 g/l

F^- concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature ($^{\circ}C$): 600 $^{\circ}C$

Rotational speed of shaker (RPM): 40 rpm

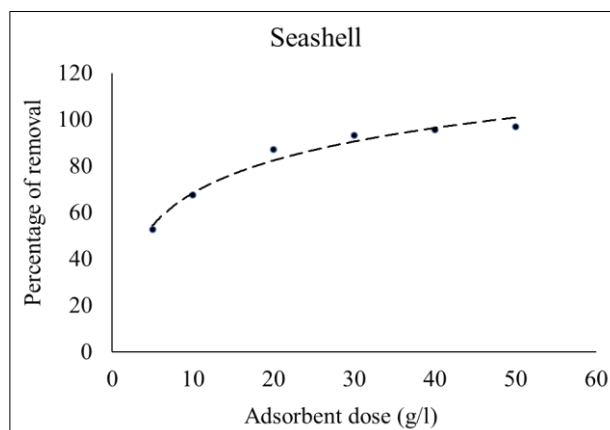


Fig. 5.58: Removal (%) vs. Adsorbent dose

Experimental results showed that percentage of F^- removal varied at different adsorbent dosage of seashell range from 5 to 50 g/l. The removal of F^- was increased from 52.7% to 97.1% with increase of adsorbent dosage at 5 to 50 g/l. The maximum removal of F^- ions can be obtained by using 50 g/l of seashell.

5.7.2.1.3 Effect of adsorbent doses by using the mixture of seashell and dolomite (1:1)

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 5-50 gm/l

F⁻ concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature (°C): 600 °C

Rotational speed of shaker (RPM): 40 rpm

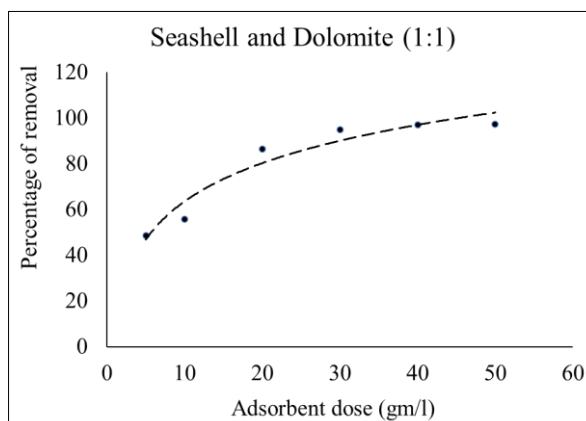


Fig. 5.59: Removal (%) vs. Adsorbent dose

Experimental results showed that percentage of F⁻ removal varied at different adsorbent dosage of seashell and dolomite mixture range from 5 to 50 g/l. The removal of F⁻ was increased from 48.7% to 97.3% with increase of adsorbent dosage at 5 to 50 g/l. The maximum removal of F⁻ ions can be obtained by using 50 gm/l of seashell and dolomite.

5.7.2.2 Effect of temperature on removal of fluoride

5.7.2.2.1 Effect of temperature on removal of fluoride by using dolomite

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 50 g/l

F⁻ concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature (°C): 100 to 800 °C

Rotational speed of shaker (RPM): 40 rpm

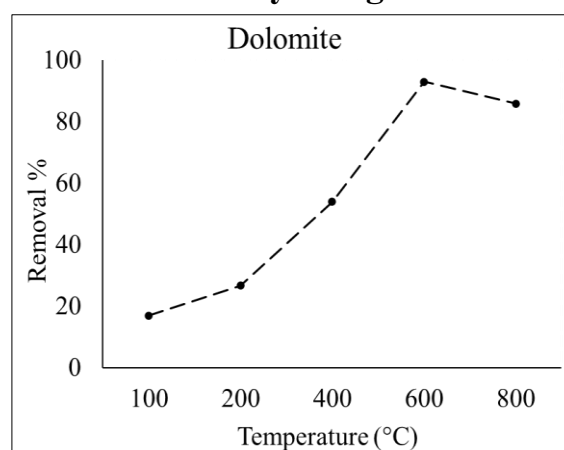


Fig. 5.60: Removal (%) vs. temperature

Experimental result showed that percentage of F⁻ removal varied at different adsorbent activation temperature range from 100°C to 800°C for dolomite. The removal of F⁻ was increased from 17% to 93% at 100°C to 800°C of dolomite activation temperature. The maximum removal of F⁻ ions can be obtained by using 600°C of temperature.

5.7.2.2.2 Effect of temperature on removal of fluoride by using seashell

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 50 g/l

F⁻ concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature (°C): 100 to 800 °C

Rotational speed of shaker (RPM): 40 rpm

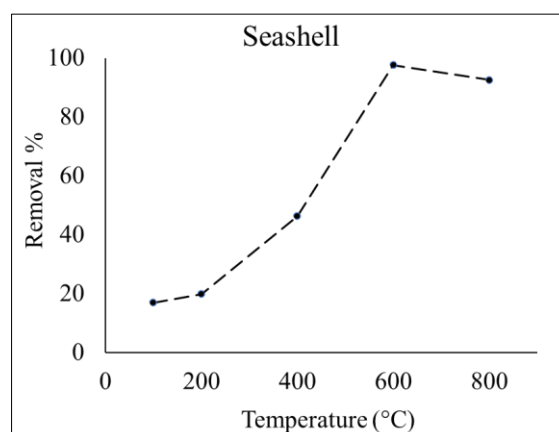


Fig. 5.61: Removal (%) vs. Temperature

Experimental result showed that percentage of F⁻ removal varied at different adsorbent activation temperature range from 100°C to 800°C for seashell. The removal of F⁻ was increased from 16.9% to 97.6% at 100°C to 800°C of seashell activation temperature. The maximum removal of F⁻ ions can be obtained by using 600°C of temperature.

5.7.2.2.3 Effect of temperature on removal of fluoride using the mixture of seashell and dolomite (1:1)

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 50 g/l

F⁻ concentration (mg/l): 20 mg/l

Contact time (min): 60 min

Temperature (°C): 100 to 800 °C

Rotational speed of shaker (RPM): 40 rpm

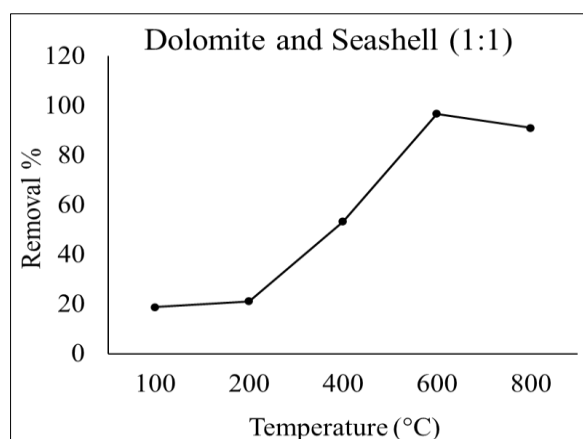


Fig. 5.62: Removal (%) vs. Temperature

Experimental result showed that percentage of F⁻ removal varied at different adsorbent activation temperature range from 100°C to 800°C for mixture. The removal of F⁻ was increased from 18.8% to 96.7% at 100°C to 800°C of mixture activation temperature. The maximum removal of F⁻ ions can be obtained by using 600°C of temperature.

5.7.2.3 Effect of contact time on removal of fluoride

5.7.2.3.1 Effect on adsorption time of fluoride by using dolomite

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): **50 g/l**

F⁻ concentration (mg/l): **20 mg/l**

Contact time (min): **10-60 min**

Temperature (°C): **600 °C**

Rotational speed of shaker (RPM): **40 rpm**

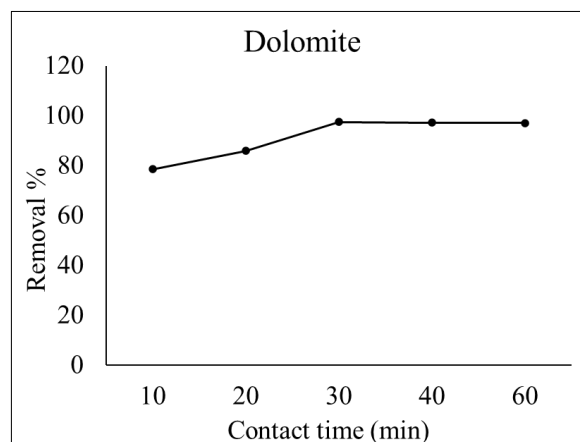


Fig. 5.63: Removal (%) vs. contact time

Experimental result showed that percentage of F⁻ removal varied at different contact time range from 10 min to 60 min by using dolomite. The removal of F⁻ was increased from 78.5% to 97.5% at 10 min to 60 min of contact time of dolomite. Maximum removal of F⁻ ions can be obtained by using within 30 min of contact time.

5.7.2.3.2 Effect on adsorption time of fluoride by using seashell

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): **50 g/l**

F⁻ concentration (mg/l): **20 mg/l**

Contact time (min): **10-60 min**

Temperature (°C): **600 °C**

Rotational speed of shaker (RPM): **40 rpm**

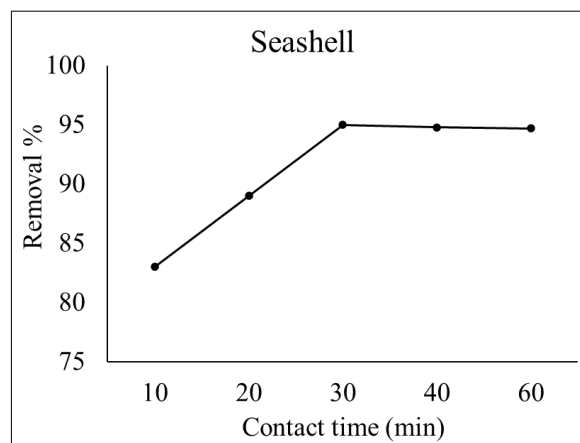


Fig. 5.64: Removal (%) vs. contact time

Experimental result showed that percentage of F⁻ removal varied at different contact time range from 10 min to 60 min by using seashell. The removal of F⁻ was increased from 83% to 95.5% at 10 min to 60 min of contact time of seashell. Maximum removal of F⁻ ions can be obtained by using within 30 min of contact time.

5.7.2.3.3 Effect on adsorption time of fluoride by using the mixture of seashell and dolomite (1:1)

Experiment process:

Initial pH: 7-8

Dolomite dose (gm/l): 50 g/l

F⁻ concentration (mg/l): 20 mg/l

Contact time (min): 10-60 min

Temperature (°C): 600 °C

Rotational speed of shaker (RPM): 40 rpm

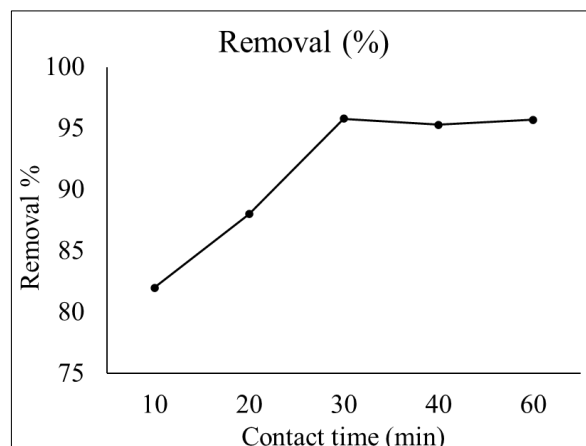


Fig. 5.65: Removal (%) vs. contact time

Experimental result showed that percentage of F⁻ removal varied at different contact time range from 10 min to 60 min by using mixture (1:1). The removal of F⁻ was increased from 82% to 95.8% at 10 min to 60 min of contact time of mixture (1:1). Maximum removal of F⁻ ions can be obtained by using within 30 min of contact time.

5.7.3 Isotherms and kinetic models of used adsorbents for removal of fluoride

After optimization of adsorbent technique, the intercept of the plot C_e/q_e versus C_e of the Langmuir isotherm, the r^2 values of dolomite, seashell and mixture of dolomite and seashell (1:1) are 0.98, 0.67 and 0.98, respectively. Moreover, from intercept of the plot $\log q_e$ vs $\log C_e$ of Freundlich isotherm, the r^2 values of dolomite, seashell and mixture of dolomite and seashell (1:1) are 0.99, 0.38 and 0.99, respectively. According to Kinetic models of Pseudo-first order kinetic r^2 values for dolomite, seashell and mixture of dolomite and seashell (1:1) are 0.94, 0.84 and 0.95, respectively. In Pseudo-second order kinetic r^2 values for dolomite, seashell and mixture of dolomite and seashell (1:1) are 0.99, 0.99 and 0.99, respectively. **Table 5.49** represents the relevant isotherm and kinetic models of adsorbents used in this study for removal of F⁻.

Table 5.49: Relevant isotherm and kinetic models of adsorbents followed in the study

Name of the adsorbent	Suitable adsorption isotherm	Suitable adsorption kinetics	Remarks
Dolomite	Freundlich	Pseudo 2nd order	This isotherm signifies that surface of dolomite dust is monolayer and heterogeneous in nature. This kinetics supports that the adsorbent particles are heterogeneous, and the adsorption process is chemical.
Seashell	Freundlich	Pseudo 2nd order	This isotherm signifies that the surface of seashell dust is monolayer and heterogeneous in nature. This kinetics supports that the adsorbent particles are heterogeneous, and the adsorption process is chemical.
Dolomite and seashell mixture (1:1)	Freundlich	Pseudo 2nd order	This isotherm signifies that surface of mixture of dolomite and seashell (1:1) of dust is monolayer and heterogeneous in nature. This kinetics supports that the adsorbent particles are heterogeneous, and the adsorption process is chemical.

5.7.4 Effect of adsorbent on synthetic and groundwater sample

Fluoride concentration in both the water samples were maintained as 20 mg/l. The F^- concentration in synthetic water was prepared from NaF salt at laboratory scale. The concentration of F^- in groundwater collected from Nalhathi, Birbhum district was also 20 mg/l. After optimization using different adsorbents, the F^- concentration in treated water represented the removal efficiency.

5.7.4.1 Adsorbent on synthetic water sample

The fluoride removal efficiency is shown in **Table 5.50** under the optimum conditions of Adsorbent dose: **50 g/l**, pH: **7-8**, Temperature: **600 °C**, Time: **30 min**.

Table 5.50: Optimized conditions for fluoride removal from the synthetic water sample

Adsorbent	Initial concentration (mg/l)	Final Concentration (mg/l)	Percentage of Removal
Dolomite	20	2.3	88.5
Seashell	20	2.1	89.5
Mixture	20	1.7	91.5

Here all the experimental materials followed the optimum condition and the mixture of dolomite and seashell (1:1) contributed maximum removal percentage of fluoride.

5.7.4.2 Adsorbent on groundwater sample

The fluoride removal efficiency is shown in **Table 5.51** under the optimum conditions of Adsorbent dose: **50 g/l**, pH: **7-8**, Temperature: **600 °C**, Time: **30 min**.

Table 5.51: Optimized conditions for fluoride removal from the fluoridated groundwater sample

Adsorbent	Initial concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage of Removal
Dolomite	20	3.8	16.2	81
Seashell	20	3.7	16.3	81.5
Mixture	20	2.9	17.1	85.5

According to the optimized condition, the mixture of dolomite and seashell (1:1) contributed maximum removal percentage of F⁻.

5.7.5 Water quality after treatment with adsorbent

After optimized condition, the mixture of seashell and dolomite (1:1) acted nicely as a suitable adsorbent for F⁻ removal from synthetic fluoridated water. The fluoridated groundwater sample (20 mg/l) was treated with the mixture of dolomite and seashell (1:1) under optimum conditions to check the removal efficiency of F⁻ and other water quality parameters recommended for drinking water by Bureau of Indian Standard (BIS) (**Table 5.52**).

Table 5.52: Concentrations of different physico-chemical parameters in groundwater before and after the treatment with adsorbent under optimum conditions

Sl. No.	Parameter	Unit	Acceptable limit	Permissible limit	Before treatment	After treatment
1	pH		6.5-8.5	No relaxation	6.8	7.4
2	Turbidity	NTU	1	5	2	3
3	Total Dissolved Solids	mg/l	500	2000	170	230
4	Calcium	mg/l	75	200	48	180
5	Chloride	mg/l	250	1000	27	42
6	Fluoride	mg/l	1	1.5	20	2.9
7	Magnesium	mg/l	30	100	12	87
8	Nitrate	mg/l	45	No relaxation	16	14
9	Total Alkalinity	mg/l	200	600	56	120
10	Sulphate	mg/l	200	400	14	17
11	Total Hardness	mg/l	200	600	84	194
12	Sodium	mg/l			27	34
13	Potassium	mg/l			8	12
14	Iron	mg/l	0.3	No relaxation	0.08	0.07

5.7.6 Sludge management

The generated sludge produced through adsorption process during defluoridation of water was properly managed and used for modified brick production. Proper selection ensures the safety and durability of the construction project. Compressive strength of bricks has been measured and given in **Table 5.53**.

Table 5.53: Compressive strength of bricks

Bricks (Waste Materials)	Weight (g)	Strength Reading (kN)	Compressive Strength (N/mm ²)	Brick Class
Seashell	160	18	7.2	First Class
Dolomite	155	14.2	5.6	Second Class
Mixture	155	15.6	6.2	Second Class

**Note: All the bricks are 5mm×5mm size.*

The bricks are kept at the desired temperature for the required time after achieving uniform burning and appropriate clay vitrification. During the firing process, the bricks are placed inside a kiln, and the temperature is gradually raised to the desired firing temperature.

5.7.7 Benefits of brick encapsulation for fluoride-contaminated flocks

Brick encapsulation offers numerous benefits for managing F⁻ contaminated flocks, some of which are listed below:

1. **Waste Diversion:** Brick encapsulation diverts F⁻ contaminated flocks from disposing them in landfills, reducing the environmental impact and promoting a more sustainable waste management approach.
2. **Reduced Environmental Contamination:** By encapsulating the F⁻ contaminated flocks within bricks, the risk of leaching and secondary contamination is minimized, safeguarding soil and water quality.
3. **Eco-Friendly Construction Material:** The brick encapsulation process yields bricks with enhanced properties, making them suitable for various construction applications. These eco-friendly bricks reduce the demand for traditional clay bricks, conserving natural resources.
4. **Cost-Effective:** The use of F⁻ contaminated flocks in brick manufacturing lowers the production cost, resulting in a cost-effective building material option.
5. **Community Development:** Brick encapsulation projects can contribute to community development by creating employment opportunities and supporting local industries.
6. **Contribution to Circular Economy:** By converting waste into a valuable resource, brick encapsulation associates with the principles of the circular economy, where materials are recycled and repurposed, minimizing waste and maximizing resource efficiency.

Chapter 6

Conclusion



The meta-analysis of these studies supports the fact that substantial research on groundwater F^- contamination in West Bengal has been undertaken. Given the diverse range of outcomes observed in the current meta-analysis, it can be inferred that there is a consistent and increasing trend in daily groundwater F^- contamination in West Bengal. This present study has represented the groundwater F^- concentration in groundwater from six districts from West Bengal. Overall, 10 % of groundwater samples ($n = 984$) crossed the recommended value of F^- from the Sonarpur block of South 24 Parganas district. Ward no 6. of Rajpur Sonarpur Municipality (RSM), Sonarpur block is mostly substantially F^- contaminated area. The study investigated the spatial uncertainties surrounding F^- distribution in groundwater and elucidated potential sources of F^- in the Baruipur block. About 10 % of groundwater samples ($n = 824$) crossed the permissible limit of F^- . Dhapdhapi II gram-panchayat is the worst F^- endemic zones in the study area where 43.7 % of groundwater samples ($n = 167$) were identified with $F^- \geq 1.5$ mg/l. 45 % of groundwater samples showed moderate contamination factor ($1.0 \leq I_i < 3.0$). Moreover, in the West Medinipur district, all the groundwater samples from the other five districts were found < 1 mg/l. In Jhargram district, basically, Binpur II block found the concentration of F^- in groundwater exceeds the permissible limit (1.5 mg/l). 10% and 4% of groundwater samples crossed the permissible limit of WHO in West Bardhaman district (Salanpur, Baraboni, Jamuriya, Pandabeswar) and Murshidabad district (Kandi and Khargram), respectively. This study has evaluated the magnitude of F^- concentration in groundwater and for the first time 9 new F^- contaminated blocks (Baruipur, Sonarpur, Binpur II, Salanpur, Baraboni, Jamuriya, Pandabeswar, Kandi and Khargram) in West Bengal has been described.

Moreover, the overall mean cationic and anionic distribution in groundwater was found in a sequence of $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Fe$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > CO_3^{2-} > F^-$, respectively which express the groundwater (drinking water) quality in Sonarpur block. The distribution of cations and anions in the fluoridated groundwater samples adheres to the following order of $Na^+ > Ca^{2+} > Mg^{2+} > Fe > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > CO_3^{2-} > NO_3^- > F^-$, respectively in Dhapdhapi II gram-panchayat at Baruipur block. A strong correlation was found among Na^+ and Cl^- which suggested that groundwater is highly saline in nature and groundwater contributed high TDS value in both areas (Sonarpur and Baruipur blocks). The maximum presence of F^- was found at a depth layer of 24.4-30.5 m. The existence of both the toxic contaminants (F^- and As) in groundwater had decreased considerably below 152 m of depth, which is relatively safe for daily use.

The rock/mineral-water interaction and ionic-interaction between weathering of silicate mineral and groundwater were found the main significant factor for F^- leaching into the groundwater aquifer. The silicate dissolution dominates carbonate dissolution which influences the groundwater chemistry. The groundwater in this zone was found to be oversaturated and precipitated with calcite, fluorite and dolomite and under-saturated with gypsum, anhydrite and halite. Muscovite is identified as the primary potential source of groundwater F^- contamination in both studied blocks (Sonarpur and Baruipur blocks) of South 24 Parganas district.

This study evaluated the degree of F^- contamination in surface soil from two F^- endemic districts, Bankura and Purulia, in West Bengal, India. The crops and vegetables grown in F^- intoxicated agricultural fields also accumulated a substantial amount of F^- in their edible parts and F^- accumulation in food crops was found to be higher in Purulia than in Bankura district. Fluoride accumulation was observed to be higher in vegetables (both leafy and non-leafy) compared to pulses and cereals in both studied districts. Among the vegetables, onion exhibited the highest accumulation, while rice showed the lowest. The calculated BCF values for all the crops and vegetables were found to be <1 which indicated that none of the food crops were hyper or good accumulator of F^- . Protein, carbohydrate and total chlorophyll content in leafy vegetables have been decreased in F^- exposed area (Baruipur, South 24 Parganas) compared to the control area (Pingla, West Medinipur) due to stress of F^- . The lower BCF value of F^- was found in cereal, pulses, leafy and nonleafy vegetables. The nonleafy vegetables were the major contributor of F^- exposure among all the groups of food crops and the observed EDI was in the order of nonleafy vegetables $>$ cereals $>$ pulses $>$ leafy vegetables in both the studied districts.

As population and urbanization rapidly increase in Rajpur-Sonarpur Municipality, located in the South 24 Parganas district, the demand for freshwater is escalating each day. As a result, the inhabitants in this area are dependent on groundwater to serve their daily needs. The adults and teenagers in the studied area have comparatively higher THQ values of F^- and arsenic compared to the children. THQ_{fluoride} was found >1 for adults and teenagers in four wards through consumption of drinking water in the Rajpur Sonarpur Municipality of Sonarpur block, South 24 Parganas district. The non-carcinogenic risk of both F^- and arsenic for adults exceeded the tolerable level ($THQ > 1$) in 4 and 25 wards, respectively. Urine as a contemporary biomarker suggested the toxicity level in the contaminated sites of Rajpur Sonarpur Municipality in Sonarpur block. Additionally, the non-carcinogenic risk (THQ) for infants exceeded the tolerable limit of >1 in Champahati and Dhapdhapi II gram-panchayat. THQ values for the studied four age groups were found in the order of infants $>$ adults $>$ children $>$

teenagers. The probabilistic health risk assessment found $THQ > 1$ for all the age groups with P95 percentile dose in Dhapdhapi II gram-panchayat which indicates that all the inhabitants were more vulnerable of both F^- exposure through ingestion and dermal pathway. According to the $THQ_{oral+dermal}$ values for infants were found > 1 and more vulnerable due to the toxicity of F^- in Binpur, Barabani, Kandi and Khargram blocks. The non-carcinogenic health risk (THQ) was found in range in order of infants $>$ adults $>$ children $>$ teenagers from all districts. The probable health risk at P95 percentile dose in infants significantly crossed the tolerable limit of > 1 through both F^- exposure in Pingla, Salanpur and Asansole blocks. Only Barabani block from West Bardhaman district which signifies the class V fluoride risk where F^- concentration above > 10 mg/l. The eight blocks are (Sonarpur, Pingla, Binpur II, Salanpur, Barabani, Asansole, Kandi and Khargram blocks) significantly crossed the suggested level 1 at P95 dose of F^- .

The cumulative EDI values ($EDI_{cumulative}$) of F^- through cultivated food crops for all the studied age groups were found to be lower than the recommended limit 1 and children were exposed to the highest dietary intake of F^- compared to the other studied age groups in the order of children $>$ adults $>$ adolescents $>$ teenagers from Bankura and Purulia districts. The Hazard Index (HI) values for the four different age groups studied were significantly lower than 1, which indicating no potential health risk of fluorosis among the exposed populations through consumption of individual food crops. The HI of F^- for the inhabitants of Purulia was higher than that of Bankura and the children were exposed more to F^- toxicity compared to adults, adolescents, and teenagers from both the studied districts. The probabilistic health risk assessment of F^- , focusing on lifetime non-carcinogenic risk (HI_{LTNR}) with percentile doses ranging from P5 to P95 using Monte Carlo simulation, revealed values exceeding 1 for all studied age groups (4-70 years). This suggests that the inhabitants are more vulnerable to F^- exposure throughout their lifetime via consumption of food crops. The health risk assessment of this study appeared to be alarming, and these newly exposed areas need regular water quality monitoring.

In the southern part of West Bengal, there is uncertainty surrounding the consumption and use of raw groundwater. Despite implementing several mitigation strategies, the quality of drinking water in the studied area remains poor, posing a significant health risk to the population due to prolonged consumption of contaminated water. Following all the issues, an adsorption process is promoted in my research at community and domestic level for removal of F^- (removal efficiency~90%) from contaminated drinking water with application of dolomite and seashell

mixture (1:1) at 50 mg/l of minor dose. After generated sludge produced by the adsorption process has been properly managed through modified brick production.

In 2024, groundwater is not the only place where F^- poisoning is exposed; it has permeated all tropical levels of our environment. Therefore, community involvement and administrative intervention should go hand in hand for a F^- free healthy environment.

Chapter 7

Recommendation

The major suggestions for the affected population are:

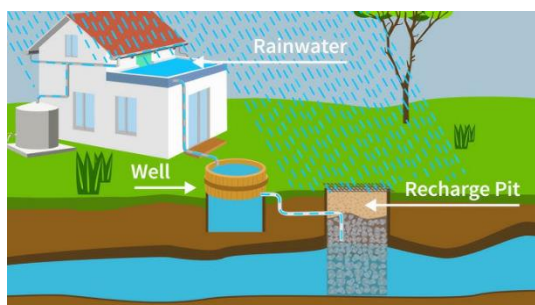
Groundwater, as an intermediate solution: Groundwater, serving as an intermediary solution is required to maintain the drinking water quality and through monitoring round the year.



Restoration and recycling of the existing surface water sources: Restoration and recycling of the existing surface water bodies are badly required to supply potable water through pipeline supply after its proper treatment. The surface water can be used preferably during pre-monsoonal (summer season) cultivation by the policy makers.



Rainwater harvesting: To collect a substantial amount of rainfall through rooftop water harvesting and establish wells to capture rainwater during the rainy seasons, thereby replenishing the groundwater table and reducing F^- concentration in the groundwater. These techniques should be strictly implemented in the F^- endemic areas.



The most important issue that needs to be addressed by the administrations is the routine monitoring of the pipeline's water quality before it reaches to the mass population, Finally, I strongly believe that this entire research will substantially contribute to the society and may draw attention of the policy makers to prevent 'groundwater exploitation'.



Future Scopes

- Groundwater monitoring and evaluation of its quality are important continuous processes for the inhabitants rely on groundwater sources.
- Evaluation of the quality of irrigational water used for agricultural practices are further required.
- To suggest alternative crop practices in F⁻ exposed areas.
- A modelled-based health evaluation study is required to understand the importance of the primary determinants regulating the F⁻ toxicity and related health risk in F⁻ exposed and unexposed population.
- For defluoridation of water, the present study mainly deals with the adsorbents used for synthetic water samples and only limited cases for groundwater samples. More field-based investigations are required for the purpose.
- The leaching of F⁻ needs further investigation after transformation of generated sludge in brick formation.

Field Images





Groundwater sample collection from different water sources in West Bengal; (a) Baruipur; (b) Ward no. 6, Rajpur Sonarpur Municipality; (c) Jhargram; (d) Murshidabad; (e) West Bardhaman; (f) East Bardhaman; (g) West Bardhaman; (h) Murshidabad; (i) Bankura; (j) Sonarpur; (k) Jhargram; (l) West Medinipur

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Analytical Instruments Used



UV-Vis Spectrophotometer
Thermo Scientific
Orion Aqamate -800



GPS Meter
Garmin etrex 10



Microcontroller
Flame Photometer G-301



pH Meter, Toshcon
Industries Pvt. Ltd. Ajmer
Model-CL 46+



Muffle furnace



Atomic Absorption Spectro
Photometer
Varian- AA140



Digital Turbidity Meter
Model-331



Thermo Scientific pH/ISE meter
Orion Star A214



Conductivity Meter, Labtronics
Model-LT16

Media Coverage

NEWS

Current Science Reports

Tarnishing the Taj Mahal *Acid rain not to blame?*

Acid rain, due to air pollution from industries and vehicles, is commonly blamed for the yellowing of the Taj Mahal. However, the process of discolouration is slow and difficult to simulate. And exposure for a short period fails to give a clear idea. So, how do we study the phenomenon?



Image: Joel Gordon via Wikimedia Commons

Researchers from the National Metallurgical Laboratory, Jamshedpur, the Central Pollution Control Board and the Indira Gandhi National Center for Arts, Delhi used metals as proxies to study how air pollutants affect corrosion. They took samples of carbon steel, zinc and copper and exposed them to the environment of the Taj Mahal from 2006 to 2010. To track the environment conditions during this period, the researchers used meteorological data from the India Meteorological Department and pollution data from the Central Pollution Control Board. Sulphur dioxide, nitrogen oxides and particulate matter were the major pollutants in the atmosphere.

Contrary to expectation, the pH of the rain was between 5.6 to 7.2, which does not fall under the category of acid rain. The rainwater had high concentrations of sulphates and ammonium ions, which mainly come from human activities.

The researchers analysed corrosion products on the metals using Raman spectroscopy and X-ray diffraction. Oxides and sulphides were the main constituents. Oxides form when metals are exposed to oxygen in the air. Reaction with acid rain forms sulphates and nitrates, but not sulphides, say the researchers.

The rate of corrosion was higher for copper than for zinc. This was unusual

as zinc corrodes faster than copper in an industrial environment.

If not industrial pollutants, what could be corroding the metals to form sulphides? The researchers attribute the corrosion and the formation of sulphides to hydrogen sulphide. The gas could come from the Yamuna flowing beside the Taj Mahal. The river has low flow and is full of effluents from industries and sewage. The sewage is decomposed by bacteria, releasing hydrogen sulphide, whose foul smell wafts down to the Taj Mahal.

'The gas corroding the experimental metals can also affect other building materials,' argues Jitendra Kumar Singh, National Metallurgical Laboratory.

To study the direct effect on Taj Mahal marble, exposure of at least 10 years is required. However, if hydrogen sulphide is the real culprit, municipal authorities will need to re-examine regulations on dumping sewage into the river to keep the Taj Mahal untarnished for the next generation.

DOI: 10.1007/s13762-021-03613-7

Fluoride Exposure in West Bengal

Cropping the risk

About one-third of the districts in West Bengal are affected by fluoride contamination. There is high fluoride content in groundwater and soil there. Soil types, geographical conditions and arid to semi-arid climatic conditions in the western parts of the state encourage high accumulation of fluoride in soil. The high soil fluoride, compounded with the fluoridated groundwater used for irrigation, facilitates fluoride accumulation in crops.

Recently, Tarit Roychowdhury and others from Jadavpur University, Kolkata assessed fluoride health risk in different crops grown in the region.

For analysis, they collected fresh food crops and soil samples from the highly fluoride-contaminated Purulia and Bankura districts. The crops consisted of cereals, pulses and non-leafy and leafy vegetables. Non-leafy and leafy vegetables, the team found, accumulated more fluoride than cereals and pulses. About 56% fluoride intake

from food came from non-leafy vegetables.

'The bioavailability of fluoride in root crops is very high. Onions have the highest fluoride accumulation,' says Tarit Roychowdhury.

The team carried out a health risk assessment for all age groups. They analysed the risk to children, adolescents and adults. The result indicates that there is no risk of fluorosis through individual food crops. But inhabitants in the region are vulnerable to fluoride exposure over their lifetime and are at risk for fluorosis, though not as much as to lead to cancer.

Proper watershed management for retaining fresh water, and limiting cultivation of crops to those that accumulate less fluoride, can help reduce long-term exposure to fluorides and related health risks.

DOI: 10.3389/fenvs.2021.713148

Asansol, West Bengal

Groundwater contamination

Asansol covers a vast spectrum of coalfield and industrial activities. To understand how industrial activity impacts groundwater quality, Gourisankar Panda and team from the Asansol Engineering College collaborated with researchers from other institutes.

They collected groundwater samples, pre- and post-monsoon. Groundwater there is neutral to slightly alkaline. After the monsoon, dissolved solids increase due to dissolved minerals, leaching and runoff water.

Atomic absorption spectrophotometry revealed lead and copper within permissible limits. Concentrations of other metals such as iron, cadmium and chromium were higher than safe before and after the monsoon.

Chromium, cadmium and lead levels can increase the chances of kidney damage. There is also a risk of cancer due to exposure to cadmium and lead.

Statistical analysis revealed that heavy metals in groundwater are derived primarily from industrial discharge, mining activities and leachate from solid waste disposal sites. Geogenic sources such as weathering of

BARUIPUR

‘10% of groundwater samples contain fluoride beyond permissible limit’

SOUMITRA NANDI

KOLKATA: A study by the School of Environmental Studies of Jadavpur University to ascertain spatial distribution of fluoride in groundwater with respect to hydro-geo-chemical characteristics and associated probabilistic health risk in Baruiপুর block in South 24-Parganas district of Bengal has found that 10 per cent of groundwater samples have crossed the permissible limit of fluoride. The research team led by has also delineated mitigation strategies in its report.

Dhapdhabi II Gram-Panchayat has been identified as the worst endemic zone with 43.7 per cent of the groundwater samples identified with over permissible fluoride limit of 1.5 mg/L in drinking water. A strong correlation was found among sodium and chlorine which further suggested that groundwater is highly saline in nature.

The study assumes significance in the backdrop of a report by the state Public Health Engineering Department stating, 2.26 lakhs people are affected by fluoride toxicity in 43 blocks consisting of the seven districts (Birbhum, North Dinajpur, South Dinajpur, Malda, Purulia, Bankura and South 24-Parganas districts).

Fluoride concentration in drinking water, if it crosses the limit causes human health hazards such as dental and skeletal fluorosis. Approximately, 61 million people are suffering from fluoride toxicity caused by groundwater in 230 districts from 20 states of India

In the study, the rock/mineral-water interaction and ionic-interaction between weathering of silicate mineral and groundwater were found

the main significant factor for fluoride leaching into the groundwater aquifer, said the first author of the study Ayan De. The silicate dissolution dominates carbonate dissolution which influences the groundwater chemistry. The groundwater in this zone was found to be oversaturated and precipitated with calcite, fluorite and dolomite and under-saturated with gypsum, anhydrite and halite. Muscovite is observed as the major possible source of groundwater fluoride contamination in the studied area.

“The mitigation strategies like installation of fluoride removal plants, treatment of surface water, boring of deep tube-wells and rainwater harvesting are needed to supply safe water used for cooking and drinking purposes in the studied area,” Tarit Roy Chowdhury of School of Environmental Studies, JU who led the study said.

The study has recommended awareness campaign through frequent medical camps and administrative involvements for ensuring better health of the inhabitants.

The research findings have been published in the highly reputed Elsevier journal “Science of the Total Environment”

Fluorine is an abundant trace element in the natural environmental condition and it generally occurs in the form of fluoride in groundwater that is used for household, industrial and irrigational purposes by approximately one-third of the world’s populace.

According to WHO report, about 80 per cent of the water-borne diseases enter from the contaminated water source, where fluoride contaminated water contributes to 65 per cent for human diseases.

Date 30.05.2023

আনন্দবাজার পত্রিকা

দক্ষিণ ২৪ পরগনায় ভূগর্ভস্থ জলে বাড়ছে ফ্লোরাইড, উদ্বেগ

সামসুল হুদা

ভাঙড়া: আসেনিকের পাশাপাশি দক্ষিণ ২৪ পরগনা জেলার ভূগর্ভস্থ জলে উদ্বেগজনক হারে বাড়ছে ফ্লোরাইডের পরিমাণ। সম্প্রতি যাদবপুর বিশ্ববিদ্যালয়ের স্কুল অব এনভায়রনমেন্টাল স্টাডিজের গবেষণায় এই তথ্য উঠে এসেছে।

তথ্য অনুযায়ী দেখা যাচ্ছে, বারুইপুর গ্রামের ১৯টি গ্রাম পঞ্চায়েতের মধ্যে পাঁচটি এলাকায় জলে উচ্চ মাত্রায় ফ্লোরাইড পাওয়া গিয়েছে। বিশেষ করে ধপধপি ২ গ্রাম পঞ্চায়েত এলাকায় ৪৫.৭ শতাংশ পানীয় জলের নমুনায় প্রতি লিটারে জলে ১.৫ মিলিগ্রাম ফ্লোরাইড মিলেছে। এ ছাড়াও, সোনারপুর গ্রামের রাজপুর সোনারপুর পুরসভা এলাকায় রক্ত জনসংখ্যা বৃদ্ধি ও নগরায়নের সঙ্গে সঙ্গে জলের চাহিদা দিন দিন বৃদ্ধি পাচ্ছে। এই এলাকায় বাসিন্দারা দৈনন্দিন জীবনে মেঝেতে ভূগর্ভস্থ জলের উপরে নির্ভরশীল। ফ্লোরাইড এবং আসেনিকের সর্বাধিক উপস্থিতি ২৪.৪ থেকে ৩০.৫ মিটার গভীরতায় স্তরে পাওয়া গেছে। ১৫২ মিটারের নীচে উল্লেখযোগ্য ভাবে হ্রাস পেয়েছে সেগুলির উপস্থিতি। ওই জব থেকে তেঁলা জল ব্যবহারের জন্য নিরাপদ। বেশি ফ্লোরাইডযুক্ত জল ব্যবহারের ফলে শরীরে একধিক বসারপ প্রভাব পড়তে পারে বলে জানা যাচ্ছে। বিশ্বায়িত মান প্রকৃতি হ্রাসে ‘সয়েম অফ দ্য টেটাল এনভায়রনমেন্ট’ এবং ‘ব্রাউড ওয়াটার ফর সাস্টেনেবল ডেভেলপমেন্ট’ জার্নালে।

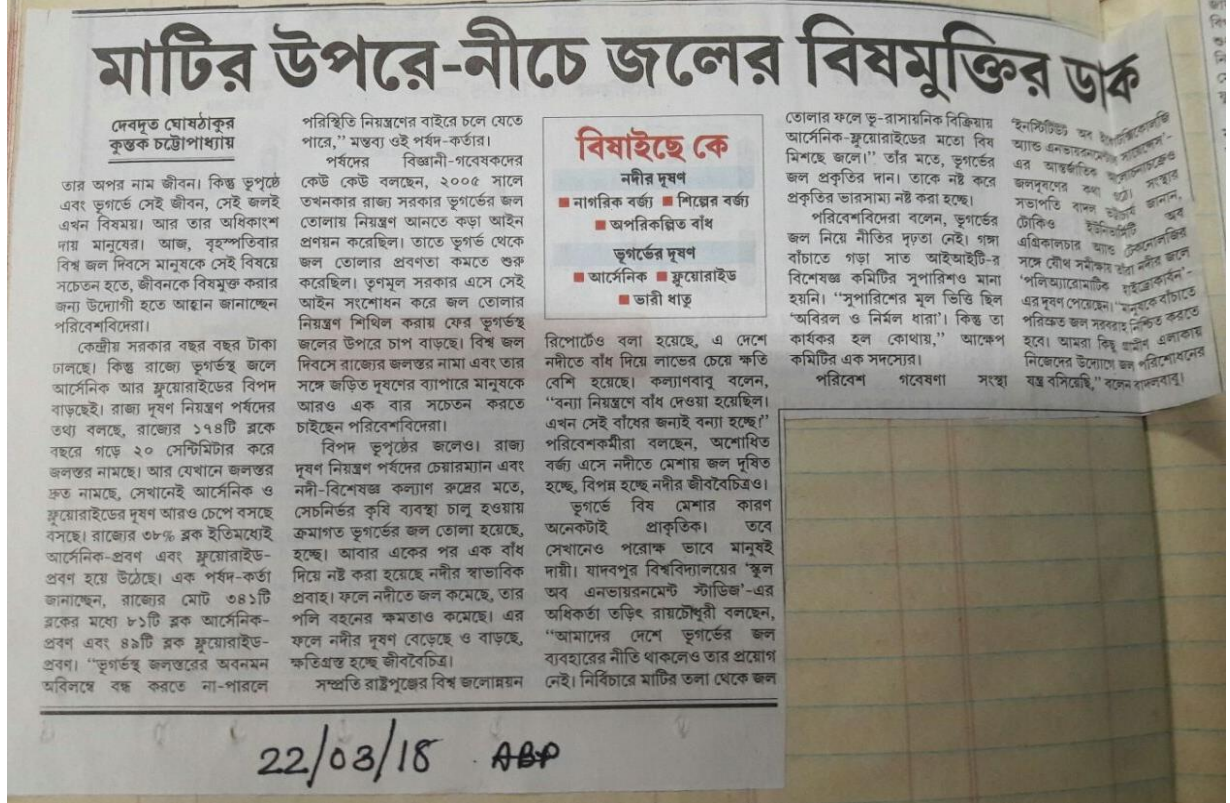
যাদবপুর বিশ্ববিদ্যালয়ের স্কুল অব এনভায়রনমেন্টাল স্টাডিজের পক্ষ থেকে জানানো হয়েছে, বিশ্ব স্বাস্থ্য সংস্থার সুপারিশ অনুযায়ী প্রতি লিটার পানীয় জলে সর্বাধিক ১.৫ মিলিগ্রাম ফ্লোরাইড থাকা উচিত। মানবদেহে ফ্লোরাইড দুর্যকম ভাবে কাজ করে। সেটির মাত্রা প্রতি লিটারে জলে ১.৫ মিলিগ্রামের নীচে থাকলে তা উপকারী। দাঁত, হাড় শক্তিশালী করার কাজে নাগে ফ্লোরাইড। তবে সেই মাত্রা প্রতি লিটারে ১.৫

মিলিগ্রামের বেশি থাকলে তা ক্ষতিকর। শরীরে থাকা ফ্লোরাইডের ভাঙতে শুরু করে। এ ক্ষেত্রে ফ্লোরাইড তুরোসিন (দাঁত ভাঙতে শুরু করা, হস্ত জ্ঞাপ পত্র, হাঁড়ের স্থানান্তরিত হওয়া), হাড় চূর্ণ-বিশৃঙ্খল হওয়ার মতো রোগ দেখা দেয়। পশ্চিমবঙ্গের বাকুড়া, পুরুলিয়া, খীরকুদ জেলার অনেক আগেই ভূগর্ভস্থ জলে ফ্লোরাইড পাওয়া গিয়েছে। ফ্লোরাইড আক্রান্ত রোগীও রয়েছে সেখানে।

কী কারণে ভূগর্ভস্থ জলে ফ্লোরাইডের পরিমাণ বৃদ্ধি পাচ্ছে? এর কারণ জনসংখ্যার গবেষণায় একাধিক পরিসংখ্যান মডেল প্রয়োগ করা হয়েছিল। গবেষণার ফলাফলে, অতিরিক্ত মাত্রায় ভূগর্ভস্থ জল তুলে নেওয়ার ফলেই সমস্যা তৈরি হচ্ছে। শূন্য থেকে ১৮.৫ মিটার গভীরতায় দ্রুত মানুষের হাট নামে একটি খনিজ পদার্থের প্রবীণত্ব হচ্ছে বেশি মাত্রায়। ওই খনিজ থেকে দিয়ে ফ্লোরাইড বেরিয়ে জলে মিশে যাচ্ছে। ফ্লোরাইড মুক্ত জলের চরিত্র অতিরিক্ত লবণাক্ত জলের মতো। ওই জল ব্যবহারের আগে ফ্লোরাইড মুক্ত করার ওজারি প্রাচীর তৈরির প্রয়োজন আছে বলে গবেষণার ফলাফলে। এ ছাড়া, বুটের জল সংরক্ষণ করে তা ব্যবহার করা যেতে পারে। গভীর নলকূপের জল ব্যবহারও নিরাপদ। বিশ্বায়িত নিয়ে মানুষের মধ্যে সচেতনতা বৃদ্ধি, প্রশাসনিক স্তরে পর্যবেক্ষণ প্রয়োজন বলেও জানাচ্ছেন গবেষকরা।

গবেষক তর্কিং রায়চৌধুরী বলেন, “যে ভারে ভূগর্ভস্থ পানীয় জলে আসেনিকের পাশাপাশি ফ্লোরাইড পাওয়া যাচ্ছে, তা উদ্বেগের। এ ক্ষেত্রে সরকারি ভাবে ফ্লোরাইড দূরীকরণ ওয়াটার প্রাচীর মসকরা। বুটের জল সংরক্ষণ করারও প্রয়োজনীয়তা বাড়ছে।” গবেষক অজয় দে বলেন, “ফ্লোরাইডের যে সমস্যা দেখা দিয়েছে, তা আংশিক ভাবে প্রাকৃতিক। আমরা এই অঙ্কনে গবেষণা করে দেখছি, মাটিতে মাসকোলাইট নামে ফ্লোরাইড খনিজ রয়েছে। অতিরিক্ত মাত্রায় ভূগর্ভস্থ জল তুলে নেওয়ার ফলে সেখান থেকে ফ্লোরাইড বেরিয়ে মিশেছে জলে।”

Ananda Bazar Patrika 22.03.2018



Ei Somoi 03.05.2023

আন্তর্জাতিক পত্রিকায় বঙ্গসন্তানদের কাজ

এই সময়: ভূগর্ভের জলে মিশে থাকা বিপজ্জনক ফ্লোরিন যৌগ শোষণ করে নিতে পারে বিশেষ এক ধরনের ব্যাক্টেরিয়া। ভৌম জলের পরিশোধনে কী ভাবে এই ব্যাক্টেরিয়ার প্রয়োগ করা যেতে পারে, সেই সম্পর্কেই নতুন দিশা দেখালেন বর্ধমান বিশ্ববিদ্যালয়ের উদ্ভিদবিদ্যা বিভাগের মাইক্রোবায়োলজি শাখার গবেষক মৈত্রী লেটা। বিভাগের অধ্যাপক রাজীব বন্দ্যোপাধ্যায়ের তত্ত্বাবধানে এবং যাদবপুর বিশ্ববিদ্যালয়ের স্কুল অফ এনভায়রনমেন্ট স্টাডিজের সহযোগিতায় এই গবেষণার কাজ এগিয়েছে। সেই গবেষণার খবরই প্রকাশ হয়েছে এলসেভিয়ারের জার্নাল অফ এনভায়রনমেন্টাল কেমিক্যাল ইঞ্জিনিয়ারিং পত্রিকায়।

আপনার টুথপেস্টে কি ফ্লোরিন-ঘটিত যৌগ রয়েছে? যদি না থাকে

তাহলে এমন টুথপেস্ট ব্যবহার না করাই ভালো। কারণ দাঁত ও হাড়ের গঠন মজবুত করতে হলে নির্দিষ্ট পরিমাণ ফ্লোরিন আবশ্যিক। টুথপেস্টে প্রস্তুতকারী একাধিক জনপ্রিয় সংস্থা এমন ভাবেই মানবদেহে ফ্লোরিনের উপকারিতার প্রচার করে।

ফ্লোরাইড দূষণ রুখতে ব্যাক্টেরিয়া

কিন্তু ফ্লোরিনের পরিমাণ যদি মাত্রার চেয়ে বেশি হয়? তাহলে ঘোর বিপদ। দাঁত ও হাড়ের ক্ষয় থেকে শুরু করে পক্ষাঘাত এমনকি কিডনিতে পাথর — অনেক কিছুই হতে পারে। গত কয়েক বছর ধরে পৃথিবীর বিভিন্ন দেশের গবেষকদের গবেষণায় দেখা গিয়েছে আর্সেনিকের পাশাপাশি ভূগর্ভস্থ জলে আন্তর্জাতিক ভাবে বাড়ছে ফ্লোরিন-ঘটিত যৌগের পরিমাণ। দক্ষিণ-পূর্ব

এশিয়ার যে দেশগুলোতে ভৌম জলে ফ্লোরিনের পরিমাণ খুব বেশি তার মধ্যে রয়েছে ভারতও। দেশের মধ্যে অন্তত ২৩টি রাজ্যে ভৌম জলস্তরে অতিরিক্ত ফ্লোরিনের সন্ধান পাওয়া গিয়েছে। ব্যতিক্রম নয় বাংলাও। রাজ্যের বীরভূম, পুরুলিয়া, বাঁকুড়া,

মুর্শিদাবাদ, দুই দিনাজপুর ছাড়াও কলকাতা-সংলগ্ন দক্ষিণ ২৪ পরগনার বিস্তীর্ণ এলাকা এই দলে পড়ে।

বর্ধমান ও যাদবপুর বিশ্ববিদ্যালয়ের গবেষণায় অবশ্য মারাত্মক ফ্লোরিন বিক্রিয়া থেকে মুক্তির সম্ভাব্য উপায় দেখানো হয়েছে। পরিবেশবান্ধব উপায়ে বিশেষ একধরনের ব্যাক্টেরিয়া প্রোটোপ্লাস্ট কলানিহর সাহায্য নিয়ে কী ভাবে ফ্লোরিন

যৌগ থেকে ফ্লোরিন আলাদা করে ফেলা যায় এবং ওই ব্যাক্টেরিয়াই কী ভাবে বিচ্ছিন্ন ফ্লোরিনকে নিজের শরীরে জমিয়ে জলকে বিশুদ্ধ করে ফেলে — সেই পদ্ধতিই প্রকাশিত হয়েছে এলসেভিয়ারের জার্নাল অফ এনভায়রনমেন্টাল কেমিক্যাল ইঞ্জিনিয়ারিংয়ে।

এই গবেষণা প্রসঙ্গে বর্ধমান বিশ্ববিদ্যালয়ের রাজীব বন্দ্যোপাধ্যায় ও যাদবপুর বিশ্ববিদ্যালয়ের তড়িৎ রায়চৌধুরী বলছেন, 'গবেষণা এখানেই থেমে থাকবে না। এখনও পর্যন্ত দেখা গিয়েছে এক লিটার জল থেকে অন্তত ৫ মিলিগ্রাম পর্যন্ত ফ্লোরিনকে মুক্ত করতে পারে এই ব্যাক্টেরিয়া। এটা যথেষ্ট আশাব্যঞ্জক। সবচেয়ে বড় কথা এই ব্যাক্টেরিয়ার কার্বনেট মোটোবোলাইট পরিবেশের কোনও ক্ষতি করে না।'

এই সময়: টান পড়তে শুরু করেছে
মহানগরের ভূগর্ভস্থ জলের তড়াবে।
নগরদেবের সঙ্গে পলা দিয়ে কয়েক মাইল
দূরে জলের তড়। ফলে বাড়ছে ভূমিস্থে
মাটি ধসে যাওয়ার আশঙ্কা। আর শুধু
আংশিক নয়, দক্ষিণ ককটাতা এবং
লাগোয়া বিস্তীর্ণ অঞ্চলে মাটির ন্যূনতর জলে
মিশিয়ে নানা ধরনের স্ফেরাইড বলাও
কলে প্রতিদিনই একটি করে অবনতি ঘটছে
অস্বাভাবিক। ফলি জল বিশেষ এনেই আশঙ্কার
ব্যাধী শোনাচ্ছে বিশেষজ্ঞ ও পরিবেশবিদগণ।
বাড়ছে শব্দ, কয়েক গজ কক্ষিত ও
মাটির সম্পর্কও তাই। এইই অবিনাশ পরিণতি
বিশেষে ভাব্যে জলসম্পদকে দিলে গোথোঁচ
ককটাতের বাসিন্দা। ভূগর্ভস্থ জলের নিচে
সেবারত একটি কয়েক বিশাল রিসার্ভ কয়েক,

প্রতি বছর গড়ে প্রায় দু'শুটি করে কর্মহীন
কল্যাণতার নীচে থাকে মানুষের প্রাণ। এই ব্যব-
বসায় থাকলে সকল দেশে এক দশকে তুর্গতারা
জলের দর নেমে যাবে প্রায় ২০ শতাংশ।
“পানীয় জলের জন্য গভীর জল ব্যবহার
না-করে যদি তুর্গতদের জল তোলা অস্বাভাবিক
দুখক, তাহলে জল দ্রুত ভয়ানকতর কপালে
থাকে, আছে,” স্যাক জুনালিসম বায়বীয়
বিশ্ববিদ্যালয়ের স্কুল অফ এনভায়রনমেন্টের
গবেষক ডিভি রায়চৌধুরী। তিনি বলেন,
“আমাদের বিশ্ব বাহ্যে দিন দিন কল্যাণতার
জল নিয়ে বিভাগ্য করছে। কল্যাণের
রিপোর্ট বহুদৈ টালিগঞ্জ, রানিকুটি,
নন্দকটা, নেতাজি পুর, এবং বায়বীয়ের
বহু ছাত্রদের পানীয় জলে আশ্রয়িত
হয়ে। জাড়াও বায়বীয়। সোনাপুর



নগরায়নের সঙ্গে পাশ্চা দিয়ে কমছে মাটির নীচের
জলের স্তর। ফলে বাড়ছে ভূমিকম্পে মাটি ধসে
যাওয়ার আশঙ্কা। আর শুধু আঙ্গিনিক নয়, দক্ষিণ
কলকাতা এবং লাগোয়া বিস্তীর্ণ অঞ্চলে মাটির নীচের
জলে মিলছে নানা ধরনের ফ্লোরাইড লবণও

জনকল্যাণকর সংস্থার মুখপাত্র। তড়িৎ ও
অমৃতা— দু'জনেই বৃষ্টির জল সংরক্ষণের
উপর জোর দিয়েছেন।

গোটা কলকাতার মধ্যে সবচেয়ে বারপা
অবস্থা ইস্টার্ন মেট্রোপলিটান বাইপাস সল্য
অঞ্চলে। এক কয়েক বছরে এই এলাকার
আমূল গতিবর্তন হয়েছে। ক্রত নগরায়নের
ফলে মাইলের পর মাইল এলাকার গাছ
ফেটে সাফ করে ফেলা হয়েছে। গড়ে
উঠছে বহু আবাসন। ফলে এই অঞ্চলে
ভূগর্ভস্থ জলস্রোতের পাতল সবচেয়ে বেশি।
কলকাতা পুরভার এক আয়িকারিক
জানিয়েছেন, এই অঞ্চলে এক দশকে
জলস্রোত নামে গিয়েছে প্রায় ১০-১৫ ফুট
নীচে। এই কারণেই ভূমিকম্প বলে এই
অঞ্চল হসি নামের আশঙ্কা বহু বেশি।

ও গড়িয়া অঞ্চলের জলে মিলেছে
ফ্লোরাইডের নমুনা।'
কলকাতা কর্পোরেশন থেকে প্রতিদিন
শহরের বিভিন্ন প্রান্তে প্রায় ৪০০ মিলিয়ন
গ্যালন জলের জোগান দেওয়া হয়। শহরের
বিভিন্ন প্রান্তে যে বহু কোটি টাকার আবাসন
প্রকল্পগুলো তৈরি হয়েছে এবং হয়ে চালাচ্ছে

প্রধানত এই আবাসনগুলোর বাসিন্দাদের চাহিদা মেটাতেই প্রতিদিন মাটি থেকে বেহিসেবি ভাবে পাম্প করে জল তোলা হয়। এই কারণেই কমছে ভূগর্ভস্থ জলের ভাণ্ডার—জানালেন অমৃত চট্টোপাধ্যায়। তিনি সাউথ এশিয়ান ফোরাম ফর এনভায়রনামেন্ট নামে পরিবেশ সংকোশ এক



Research Publication

First Authorship

1. **De, A.,** Mridha, D., Ray, I., Joardar, M., Das, A., Chowdhury, N. R. & Roychowdhury, T. (2021). Fluoride Exposure and Probabilistic Health Risk Assessment Through Different Agricultural Food Crops from Fluoride Endemic Bankura and Purulia Districts of West Bengal, India. *Frontiers in Environmental Science*, 282.
2. **De, A.,** Mridha, D., Joardar, M., Das, A., Chowdhury, N. R. & Roychowdhury, T. (2022). Distribution, prevalence and health risk assessment of fluoride and arsenic in groundwater from lower Gangetic plain in West Bengal, India. *Groundwater for Sustainable Development*, 100722.
3. **De, A.,** Das, A., Joardar, M., Mridha, D., Majumdar, A., Das, J., & Roychowdhury, T. (2023). Investigating spatial distribution of fluoride in groundwater with respect to hydro-geochemical characteristics and associated probabilistic health risk in Baruipur block of West Bengal, India. *Science of The Total Environment*, 886, 163877.
4. **De, A.,** Das, A., Joardar, M., Majumdar, A., Dey, A., Das, J., Thakur, B.K. & Roychowdhury, T. (2024). Investigation of Groundwater Fluoride Dynamics in the Lower Gangetic Plain Including Natural Influences with Economic and Health Issues. *ACS ES&T Water*, 4, 4, 1356-1370.
5. **De, A.,** Mridha, D., Bandopadhyay, B., Roychowdhury, T. & Panja, A.S. (2021). Arsenic and its effect on nutritional properties of oyster mushrooms with reference to health risk assessment. *Biological Trace Element Research*, 199(3), 1170-1178.
6. **De, A.,** Mridha, D., Roychowdhury, T., Bandyopadhyay, B., & Panja, A. S. (2023). Substrate level optimization for better yield of oyster mushroom (*Pleurotus ostreatus*) production, using different ratio of rice straw and sugarcane bagasse. *World Journal of Microbiology and Biotechnology*, 39(10), 270.
7. **De, A.,** et al., (2024). A systematic study of meta-analysis and present groundwater fluoride contamination scenario in West Bengal, India emphasize with health risk assessment. *Groundwater for Sustainable Development* (Under communication)

Co-authorship publication

1. Mridha, D., Priyadarshni, P., Bhaskar, K., Gaurav, A., **De, A.**, Das, A., Joardar, M., Chowdhury N. R. & Roychowdhury, T. (2021). Fluoride exposure and its potential health risk assessment in drinking water and staple food in the population from fluoride endemic regions of Bihar, India. *Groundwater for Sustainable Development*, 13, 100558.
2. Mridha, D., Paul, I., **De, A.**, Ray, I., Das, A., Joardar, M., Chowdhury, N.R., Bhadoria, P.B.S. & Roychowdhury, T. (2021). Rice seed (IR64) priming with potassium humate for improvement of seed germination, seedling growth and antioxidant defense system under arsenic stress. *Ecotoxicology and Environmental Safety*, 219, p.112313.
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Fluoride Exposure and Probabilistic Health Risk Assessment Through Different Agricultural Food Crops From Fluoride Endemic Bankura and Purulia Districts of West Bengal, India

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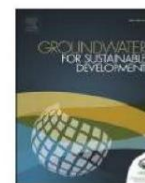
The present study investigates the magnitude of fluoride (F^-) contamination in agricultural land soil and food crops from F^- endemic regions of Bankura and Purulia districts in West Bengal. Mean fluoride level in agricultural soil was 114 ± 59 mg/kg ($n = 41$) and 126 ± 65 mg/kg ($n = 47$) in Bankura and Purulia districts, respectively. Considering the food crops cultivated in Bankura ($n = 79$) and Purulia ($n = 108$), the mean fluoride concentration in nonleafy vegetables (18.1 ± 6.51 mg/kg and 15.6 ± 5.93 mg/kg) and leafy vegetables (12.8 ± 2.8 mg/kg and 18.4 ± 6.33 mg/kg) from the two studied districts was comparatively higher than that in the cereal (2 ± 1.05 mg/kg and 2.01 ± 1.01 mg/kg) and pulses (3.35 ± 1.42 mg/kg and 4.82 ± 1.19 mg/kg). The BCF values of fluoride in food crops ($n = 27$) from Bankura (range: 0.007–0.377) and Purulia (range: 0.005–0.319) were much lower than the optimum value of 1. Estimated daily intake (EDI) of fluoride was the highest for children in both Bankura ($EDI_{cumulative} = 0.0291$ mg/kg bw/day) and Purulia ($EDI_{cumulative} = 0.0326$ mg/kg bw/day) among all the studied age groups. The nonleafy vegetables contributed the highest exposure of fluoride (approximately 55.5%) to $EDI_{cumulative}$ among all the food crops. The uncertainty analysis for assessment of probabilistic health risk was carried out for all the studied age groups through hazard index (HI), total hazard index (THI), and lifetime noncarcinogenic risk (HL_{LTNR}). However, HI value was found to be <1 for all the age groups resulting in no such kind of potential health risk of fluorosis through consumption of individual food crops, and the trend of THI from all the food crops was found in the order of children $>$ adults $>$ adolescents $>$ teenagers from both districts. The lifetime noncarcinogenic risk (HL_{LTNR}) of fluoride with percentile doses from P5 to P95 (exploring the model of Monte Carlo simulation) in all the studied age groups (4–70 years) was found to be >1 indicating that the inhabitants were more vulnerable for their total lifetime period of fluoride exposure through consumption of food crops.

Keywords: fluoride, agricultural land soil and spatial variation, food crops, bio-concentration factor, estimated daily intake, probabilistic health risk



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Distribution, prevalence and health risk assessment of fluoride and arsenic in groundwater from lower Gangetic plain in West Bengal, India

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ABSTRACT

Distribution pattern of fluoride and arsenic in groundwater ($n = 984$) from 35 wards of Rajpur-Sonarpur Municipality and its associated health risk have been evaluated. Presence of fluoride ≥ 1.5 mg/L (mean = 1.9 mg/L, range: 1.51–2.9 mg/L) and < 1.5 mg/L (mean = 0.6 mg/L, range: 0.01–1.49 mg/L), whereas, for arsenic ≥ 10 $\mu\text{g/L}$ (mean = 56.2 $\mu\text{g/L}$, range: 10.1–213 $\mu\text{g/L}$) and < 10 $\mu\text{g/L}$ (mean = 3.3 $\mu\text{g/L}$, range: < 3 –9.7 $\mu\text{g/L}$) have been observed in the studied groundwater samples. Simultaneous occurrence of fluoride and arsenic above their permissible limit in drinking water were found from two wards (ward number 6 and 7). About 13% and 16% of the collected groundwater samples ($n = 984$) have been found beyond the permissible limit of fluoride and arsenic, respectively. Mean concentrations of calcium and iron in groundwater were 31 mg/L (range: 7.3–184 mg/L) and 3.79 mg/L (range: < 0.05 –50.4 mg/L), respectively. The distribution of both fluoride and arsenic was established with a moderate positive correlation value ($r = 0.30$) and their relationship is dependent on the interrelationship between Ca and Fe. While the negative correlation between F^- and Ca ($r = -0.33$) designates the increasing F^-/Ca ratio in solution. Cluster analysis showed that calcium, iron and the two above contaminants are likely to be highly concentrated in the depth ranges 30.5–60.9 m, 60.9–152 m and 152–305 m. The highest concentration of both the toxicants has been observed in the depth range of 24.4–30.5 m. Weak (fluoride) to strong (arsenic) correlation between water & urine showed exposure of two toxic contaminants. Modelled Average Daily Dose (ADD) and Targeted Hazard Quotient (THQ) of fluoride and arsenic were found maximum for adults followed by teenagers and children. Cancer risk of arsenic was estimated higher than the threshold value among all the age groups.

1. Introduction

Presence of fluoride and arsenic in groundwater has affected more than 300 million people all over the world (Bhattacharya et al., 2020; Bibi et al., 2017). Groundwater from deep and shallow tube-wells is mainly used for drinking purposes, agricultural production, and industrial processing (Mishra and Bhatt, 2008). About 110 million people residing in south Asia are majorly affected by fluoride and arsenic through groundwater (Ain et al., 2017; Brammer and Ravenscroft, 2009). The Indo-Gangetic and Brahmaputra flood plain

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Investigating spatial distribution of fluoride in groundwater with respect to hydro-geochemical characteristics and associated probabilistic health risk in Baruipur block of West Bengal, India

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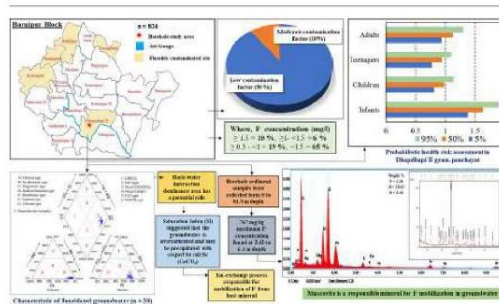
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HIGHLIGHTS

- Groundwater F^- distribution has wide spatial heterogeneity (range: 0.02–2.5 mg/l).
- Ionic distribution pattern is $Cl^- > HCO_3^- > SO_4^{2-} > CO_3^{2-} > NO_3^- > F^-$ and $Na^+ > Ca^{2+} > Mg^{2+} > Fe > K^+$.
- Geogenic activities are responsible behind groundwater F^- mobilization.
- Muscovite is most responsible silicate mineral for F^- leaching.
- Adequate THQ was observed in the order infants > adults > children > teenagers.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluoride (F^-) enrichment in groundwater of the lower Gangetic plain in West Bengal, India is a major concern. Fluoride contamination and its toxicity were reported earlier in this region; however, limited evidence was available on the precise site of contamination, hydro-geochemical attributions of F^- mobilization and probabilistic health risk caused by fluoridated groundwater. The present study addresses the research gap by exploring the spatial distribution and physico-chemical parameters of fluoridated groundwater along with the depth-wise sedimental distribution of F^- . Approximately, 10 % of the groundwater samples ($n = 824$) exhibited high $F^- \geq 1.5$ mg/l from 5, out of 19 gram-panchayats and Baruipur municipality area and the maximum F^- was observed in Dhapdhap-II gram-panchayat with 43.7 % of samples showed ≥ 1.5 mg/l ($n = 167$). The distribution patterns of cations and anions in fluoridated groundwater were $Na^+ > Ca^{2+} > Mg^{2+} > Fe > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > CO_3^{2-} > NO_3^- > F^-$. Different statistical models like Piper and Gibbs diagram, Chloro Alkaline plot, Saturation index were applied to better understand the hydro-geochemical characteristics for F^- leaching in groundwater. Fluoridated groundwater is of Na-Cl type which implies strong saline character. The intermediate zone between evaporation and rock dominance area controls F^- mobilization along with ion-exchange process occurring between groundwater and host silicate mineral. Furthermore, saturation index proves geogenic activities related to groundwater F^- mobilization. All cations present in sediment samples are closely interlinked with F^- in the depth range of 0–18.3 m. Mineralogical analyses revealed that muscovite is the most responsible mineral for F^- mobilization. The probabilistic health risk assessment disclosed severe

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Investigation of Groundwater Fluoride Dynamics in the Lower Gangetic Plain Including Natural Influences with Economic and Health Issues

Ayan De, Antara Das, Madhurima Joardar, Arnab Majumdar, Archita Dey, Jagyashila Das, Barun Kumar Thakur, and Tarit Roychowdhury*



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ABSTRACT: The lower Gangetic Plain in West Bengal, India, has previously been reported to have groundwater fluoride (F^-) contamination and its hazard; however, more information was needed about the precise location of contamination. The current study highlighted these knowledge gaps covering the toxicity of F^- through groundwater by emphasizing the role of hydrogeochemical attributions in F^- mobilization, people's socioeconomic behavior, and assessing the possible health risks of the local population. Approximately, 10% of groundwater samples exceeded the recommended value of F^- with a moderate contamination factor. The groundwater is highly saline (Na–Cl type) in nature. The intermediate zone between the area of 'rock dominance' and 'precipitation dominance' controlled the leaching of F^- from host silicate minerals to groundwater. The saturation index established geogenic activity as the responsible factor and found silicate weathering mineral muscovite for F^- leaching in groundwater. The average utility cost for 20 L of safe drinking water was US\$ 7.58 per month from affordable households. Total hazard quotient (THQ) was observed maximum for infants and significant ingestion rate (IR), body weight (BW), and body surface area (SA) were the responsible factors for the studied age groups. Fluoride-safe drinking water supply strategies are a necessary step in the studied area.

KEYWORDS: groundwater, fluoride, contamination factor, hydrogeochemical attributions, silicate mineral, utility cost, total hazard quotient (THQ)

1. INTRODUCTION

The Sustainable Development Goals (SDGs) 6 and 3 of the United Nations call for achieving universal and equitable access to safe and affordable drinking water for everyone along with reducing death and illness. SDGs 6 and 3 aim to substantially increase the water-use efficiency across all sectors by ensuring sustainable withdrawals and supply of freshwater to address water scarcity and reduce the number of people suffering from water-related issues by 2030.¹ However, without forceful guiding principle interventions, these goals appear to be difficult to reach in the territories affected by groundwater fluoride (F^-) contamination. It has been a major hazard concern for more than 200 million people in almost 35 countries throughout the world.¹ Twenty, out of 29 states across the southern and western parts of India have been reported as fluoride-endemic regions.² Most of the inhabitants in these endemic states rely on groundwater from different water sources for their everyday needs.³

Different techniques are effective to remediate F^- -contaminated water in both rural and urban regions.⁴ Moreover,

several researchers investigated how various factors impact people's willingness to accept fluoride-free services (through 20 L jerrycan water or safe pipeline supply water).^{1,5} Based on the topographical location, the western region of West Bengal experiences elevated groundwater fluoride toxicity compared to its eastern region.⁶

The present study emphasized the research gap on the toxicity of F^- in groundwater, focusing on the hydro-stratigraphy for F^- mobilization and magnifying the economic behavior along with evaluating the health risks of the studied population. This study has been conducted on the exposure of F^- in Sonarpur block, South 24 Parganas district of West Bengal. Henceforth, this study has performed a geospatial

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