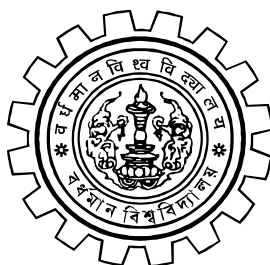


**FLUORIDE POLLUTION AND ITS EFFECT ON WATER AND
VEGETATION IN BIRBHUM DISTRICT, WEST BENGAL**

**THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN SCIENCE (ENVIRONMENTAL SCIENCE)
OF THE UNIVERSITY OF BURDWAN**



BY

KARTICK CHANDRA PAL, M.Sc. (Chem)

**THE UNIVERSITY OF BURDWAN
BURDWAN-713104
WEST BENGAL, INDIA**

2013

Dedicated to

My parents

**Sri Baidyanath Pal,
Smt. Annapurna Pal**

and

Grand Father

Late Madan Mohan Pal

ACKNOWLEDGEMENT

It fills my heart with joy to express my deepest sense of gratitude and regards to Dr. N.K. Mondal, Head of the Department, Department of Environmental Science, The University of Burdwan for his kind consent to take the huge responsibility to supervise my research work ignoring his herculean academic, administrative work load. Without his encouragement, guidance and fatherly attitude, this thesis would not have materialized.

I do also acknowledge my deep sense of gratitude and indebtedness to Dr. J.K. Datta, Professor and founder Head, Dept. of Environmental Science, University of Burdwan, West Bengal, for his valuable suggestions and constant encouragement during the entire research work.

It is indeed, a great pleasure for me to express my heartfelt gratitude to Prof. A.R. Ghosh, Department of Environmental Science, Dr. S. Gupta, Department of Environmental Science and Miss. S. Dutta, Department of Environmental Science, for their kind cooperation during the course work.

I acknowledge with thanks the help rendered by my research colleagues Sri. G. Paul, C. R. Das, R. Bhounick, B. Das, P. Roy, S. Kabi, S. Chattaraj, B. Sadhukhan, U. Dey, K. Das and P. Aditya while carrying out laboratory experiments and analysis. I do also express my sincere thanks to all the Staff and Students of the Department of Environmental Science, The University of Burdwan.

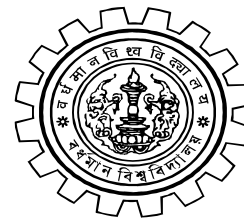
Apart from the self efforts, the success of this work would not have come out without blessings, generosity and encouragement of my parents. I really feel proud for them. I take the opportunity to express my gratitude to my brother Animesh Pal who has been instrumental in the successful completion of this thesis. During course of study many well wishers like my sister Chandana Pal, brother-in-law Subhasis Nath, preceptor Santiram Chakraborty constantly inspired me to complete the study. I also express my deepest sense of gratitude and regards to them. I am also lucky enough to have the encouragement from the brothers of Akhil Bharat Vivekananda Yuva Mahamandal. I am grateful for their constant support.

Date: 18th September, 2013

Place: Burdwan

(KARTICK CHANDRA PAL)

Department of Environmental Science
The University of Burdwan
GOLAPBAG, BURDWAN-713104
WEST BENGAL, INDIA
Phone No. : (0342)2559255



From:
Dr N.K. Mondal
Assistant Professor

Date : 18th September, 2013

To whom it may concern

It is certified that Sri Kartick Chandra Pal, a registered candidate for Ph.D degree in Science (Environmental Science) has carried out research work on a topic “FLUORIDE POLLUTION AND ITS EFFECT ON WATER AND VEGETATION IN BIRBHUM DISTRICT, WEST BENGAL” under my supervision. He has delivered seminar lecture on 09/07/2013 on his research topic as part of his Ph.D. criteria. Sri Pal has not submitted this work elsewhere for any degree or diploma.

(Dr N. K. Mondal)

CONTENTS

(i)

Chapter	Particular	Page No.
1	Introduction	1-26
1.1	Basic chemical description of fluoride	1
1.2	Fluoride pollution	1
1.3	Fluoride pollution scenario in the world	3
1.4	Fluoride pollution in India and West Bengal	5
1.5	Sources of fluoride	6
1.5.1	Natural source	6
1.5.1.1	Rock, Minerals	6
1.5.1.2	Soil	7
1.5.1.3	Aquifer	8
1.5.1.4	Air	9
1.5.2	Anthropogenic sources	10
1.5.2.1	Industrial activities	10
1.5.2.2	Fertilizers	10
1.5.2.3	Fly ash	11
1.6	Water fluoridation and other water parameters	11
1.7	Safe limit of fluoride	13
1.7.1	Recommendations	13
1.7.2	Lethal dose	14
1.8	Source of fluoride in human body	14
1.8.1	Fluoride in water, food and vegetables	14
1.8.2	Fluoride in beverages	15
1.8.3	Fluoride in other sources	15
1.9	Health impact of fluoride	16
1.9.1	Metabolism of fluoride	16

Chapter	Particular	Page No.
1.9.2	Effect of fluoride	18
1.9.2.1	Dental fluorosis	18
1.9.2.2	Skeletal fluorosis	20
1.9.2.3	Non-Skeletal fluorosis	22
1.10	Effect of fluoride on other animals	24
1.11	Accumulation of fluoride and its effect on plants	25
1.11.1	Accumulation	25
1.11.2	Effect	26
2	Review of Literature	27-63
3	Objectives	64
4	Materials and Method	65-87
4.1	Materials	65
4.1.1	Study Area	65
4.1.2	Sampling	65
4.2	Methods	66
4.2.1	Physico-chemical analysis of the water samples	66
4.2.1.1	Estimation of fluoride	66
4.2.1.2	Estimation of pH	67
4.2.1.3	Estimation of electrical conductivity	68
4.2.1.4	Estimation of total dissolved solid	68
4.2.1.5	Estimation of total alkalinity and bicarbonate	69
4.2.1.6	Estimation of total hardness	70
4.2.1.7	Estimation of Calcium	71
4.2.1.8	Estimation of Magnesium	72
4.2.1.9	Estimation of Sodium	72
4.2.1.10	Estimation of Potassium	73

Chapter	Particular	Page No.
	4.2.1.11 Estimation of Chloride	73
	4.2.1.12 Estimation of Sulphate	74
	4.2.1.13 Estimation of Phosphate	74
	4.2.1.14 Estimation of Iron	75
	4.2.1.15 Estimation of Silica	76
4.2.2	Estimation of fluoride in soil	77
4.2.3	Biochemical parameters	78
	4.2.3.1 Estimation of fluoride in vegetable	78
	4.2.3.2 Estimation of total soluble sugar	79
	4.2.3.3 Estimation of chlorophyll (Chl <i>a</i> , Chl <i>b</i> , Total Chl)	80
	4.2.3.4 Estimation of total ascorbic acid	81
	4.2.3.5 Estimation of protein	82
	4.2.3.6 Estimation of amino acid	83
4.2.4	Statistics and diagrams	84
4.2.5	Other calculations	85
	4.2.5.1 Water quality index (WQI)	85
	4.2.5.2 Percent sodium (%Na)	86
	4.2.5.3 Sodium adsorption ratio (SAR)	86
	4.2.5.4 Permeability index (PI)	86
	4.2.5.5 Magnesium hazard (MH)	87
	4.2.5.6 Percent Biochemical Change (PBC)	87
	4.2.5.7 Bio-concentration factor (BCF)	87
5	Results and Discussion	88-180
5.1	Water	88
5.1.1	Fluoride	88

Chapter	Particular	Page No.
5.1.2	Other physico-chemical parameters	89
5.1.3	Hydrochemical facies	91
5.1.4	Correlation between physico-chemical parameters	93
5.1.5	Principal component analysis	95
5.1.6	Cluster analysis	98
5.1.7	Water Quality Index (WQI)	99
5.1.8	Irrigational quality parameters	101
5.1.8.1	Sodium percentage (% Na)	101
5.1.8.2	Sodium Adsorption Ratio (SAR)	103
5.1.8.3	Permeability Index (PI)	104
5.1.8.4	Magnesium Hazard (MH)	105
5.2	Vegetables	107
5.2.1	Bio chemical parameters	107
5.2.1.1	Sugar	108
5.2.1.2	Chlorophyll	109
5.2.1.3	Ascorbic acid	112
5.2.1.4	Protein	113
5.2.1.5	Amino acid	115
5.2.2	Fluoride concentration and Bio concentration Factor (BCF)	117
6	Conclusion	181-185
7	References	186-227
8	Publications	

List of Tables

Table No.	Particular	Page No.
1	Average rainfall, population and exact location of study area	119
2	Physico- chemical parameters of groundwater samples of Nalhati -I block in PRM	120
3	Physico- chemical parameters of groundwater samples of Nalhati -I block in POM	121
4	Physico- chemical parameters of groundwater samples of Rampurhat -II block in PRM	122
5	Physico- chemical parameters of groundwater samples of Rampurhat -II block in POM	123
6	Physico- chemical parameters of groundwater samples of Khoyrasol block in PRM	125
7	Physico- chemical parameters of groundwater samples of Khoyrasol block in POM	128
8	Physico- chemical parameters of groundwater samples of Mahammad Bazar block in PRM	131
9	Physico- chemical parameters of groundwater samples of Mahammad Bazar block in POM	133
10	Statistical summary of various physico-chemical parameters for groundwater samples of Nalhati-I block	135
11	Statistical summary of various physico-chemical parameters for groundwater samples of Rampurhat-II block	136
12	Statistical summary of various physico-chemical parameters for groundwater samples of Khoyrasol block	137
13	Statistical summary of various physico-chemical parameters for groundwater samples of Mahammad Bazar block	138
14	Correlation matrix of different physico-chemical parameters in the ground water of Nalhati-I in PRM	139
15	Correlation matrix of different physico-chemical parameters in the ground water of Nalhati-I in POM	139
16	Correlation matrix of different physico-chemical parameters in the ground water of Rampurhat – II in PRM	140
17	Correlation matrix of different physico-chemical parameters in the ground water of Rampurhat – II in POM	140
18	Correlation matrix of different physico-chemical parameters in the ground water of Khoyrasol in PRM	141
19	Correlation matrix of different physico-chemical parameters in the ground water of Khoyrasol in POM	141
20	Correlation matrix of different physico-chemical parameters in the ground water of Mahammad Bazar in PRM	142
21	Correlation matrix of different physico-chemical parameters in the ground water of Mahammad Bazar in POM	142

Table No.	Particular	Page No.
22	Percent sample exceeding the BIS (2009) permissible of water parameters limit in the four blocks during PRM and POM	143
23	The weight and relative weight of each of the physico-chemical parameters used for WQI determination	143
24	Computed values of %Na, SAR, PI, MH and WQI in Nalhati- I Block	144
25	Computed values of %Na, SAR, PI, MH and WQI in Rampurhat-II Block	145
26	Computed values of %Na, SAR, PI, MH and WQI in Khoyrasol block	146
27	Computed values of %Na, SAR, PI, MH and WQI in Mahammad Bazar block	148
28	Percent sample with different water category according to WQI in the four blocks during PRM and POM	149
29	Biochemical constituents in different vegetable plants collected from Nalhati-I block	149
30	Biochemical constituents in different vegetable plants collected from Rampurhat-II block	150
31	Biochemical constituents in different vegetable plants collected from Khoyrasol block	150
32	Biochemical constituents in different vegetable plants collected from Mahammad Bazar block	151
33	Biochemical constituents in different vegetable plants collected from control area (Jagdhari)	151
34	Percent biochemical change with respect to control in different vegetable plants collected from Nalhati -I block	152
35	Percent biochemical change with respect to control in different vegetable plants collected from Rampurhat-II block	152
36	Percent biochemical change with respect to control in different vegetable plants collected from Khoyrasol block	153
37	Percent biochemical change with respect to control in different vegetable plants collected from Mahammad Bazar block	153
38	Fluoride concentration levels of different types of vegetable samples and BCF in Nalhati-I block	154
39	Fluoride concentration levels of different types of vegetable samples and BCF in Rampurhat-II block	154
40	Fluoride concentration levels of different types of vegetable samples and BCF in Khoyrasol block	155
41	Fluoride concentration levels of different types of vegetable samples and BCF in Mahammad Bazar block	155

List of Figures

Figure No.	Particular	Page No.
1	Birbhum District in West Bengal	156
2	Study locations in Nalhati -I block	156
3	Study locations in Rampurhat	157
4	Study locations in Khoyrasol	157
5	Study locations in Mohammad Bazar	158
6	Study location of Control area (Jagdhari)	158
7	Comparison of water parameters values of Nalhati I Block in PRM and POM	159
8	Comparison of water parameters values of Rampurhat-II Block in PRM and POM	159
9	Comparison of water parameters values of Khoyrasol Block in PRM and POM	160
10	Comparison of water parameters values of Mahammad Bazar Block in PRM and POM	160
11	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Nalhati-I in PRM	161
12	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Nalhati-I in POM	161
13	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Rampurhat-II in PRM	162
14	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Rampurhat-II in POM	162
15	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Khoyrasol in PRM	163
16	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Khoyrasol in POM	163
17	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Mahammad Bazar in PRM	164
18	Piper trilinear diagram showing hydrogeochemical facies for groundwater of Mahammad Bazar in POM	164
19	PCA loading plot of the water parameters in PRM season of Nalhati –I block	165
20	PCA loading plot of the water parameters in POM season of Nalhati –I block	165
21	PCA loading plot of the water parameters in PRM season of Rampurhat -II block	166
22	PCA loading plot of the water parameters in POM season of Rampurhat -II block	166

Figure No.	Particular	Page No.
23	PCA loading plot of the water parameters in PRM season of Khoyrasol block	167
24	PCA loading plot of the water parameters in POM season of Khoyrasol block	167
25	PCA loading plot of the water parameters in PRM season of Mahammad Bazar block	168
26	PCA loading plot of the water parameters in POM season of Mahammad Bazar block	168
27	Cluster Analysis Dendrogram of the water parameters in PRM season of Nalhati-I Block	169
28	Cluster Analysis Dendrogram of the water parameters in POM season of Nalhati-I Block	169
29	Cluster Analysis Dendrogram of the water parameters in PRM season of Rampurhat-II Block	170
30	Cluster Analysis Dendrogram of the water parameters in POM season of Rampurhat-II Block	170
31	Cluster Analysis Dendrogram of the water parameters in PRM season of Khoyrasol Block	171
32	Cluster Analysis Dendrogram of the water parameters in POM season of Khoyrasol Block	171
33	Cluster Analysis Dendrogram of water parameters in PRM season of Mahammad Bazar Block	172
34	Cluster Analysis Dendrogram of water parameters in POM season of Mahammad Bazar Block	172
35	Comparison of average of %Na, SAR, PI , MH and WQI values in Nalhati I Block during PRM and POM	173
36	Comparison of average of %Na, SAR, PI , MH and WQI values in Rampurhat-II Block during PRM and POM	173
37	Comparison of average of %Na, SAR, PI , MH and WQI values in Khoyrasol Block during PRM and POM	173
38	Comparison of average of %Na, SAR, PI , MH and WQI values in Mahammad Bazar Block during PRM and POM	173
39	Water Quality Index (WQI) in Nalhati - I block	174
40	Water Quality Index (WQI) in Rampurhat- II block	174
41	Water Quality Index (WQI) in Khoyrasol block	174
42	Water Quality Index (WQI) in Mahammad Bazar block	174
43	Average Fluoride level in different four blocks during PRM and POM in Birbhum district	175
44	Comparison between average Fluoride level and average WQI/25 in different four blocks of Birbhum district during PRM and POM	175

Figure No.	Particular	Page No.
45	Percent biochemical change with respect to control in Cabbage collected from different blocks	176
46	Percent biochemical change with respect to control in Onion collected from different blocks	176
47	Percent biochemical change with respect to control in Spinach collected from different blocks	176
48	Percent biochemical change with respect to control in Radish collected from different blocks	176
49	Percent biochemical change with respect to control in Potato collected from different blocks	177
50	Percent biochemical change with respect to control in Cauliflower collected from different blocks	177
51	Percent biochemical change with respect to control in Papaya collected from different blocks	177
52	Percent biochemical change with respect to control in Squash collected from different blocks	177
53	Percent biochemical change with respect to control in Kundri collected from different blocks	178
54	Percent biochemical change with respect to control in Brinjal collected from different blocks	178
55	Percent biochemical change with respect to control in Seem collected from different blocks	178
56	Percent biochemical change with respect to control in Korola collected from different blocks	178
57	BCF of different vegetables and Fluoride in soil in Nalhati-I block	179
58	BCF of different vegetables and Fluoride in soil in Rampurhat-II block	179
59	BCF of different vegetables and Fluoride in soil in Khoyrasol block	180
60	BCF of different vegetables and Fluoride in soil in Mahammad Bazar block	180

ABBREVIATIONS AND NOTATIONS USED

PRM	Pre Monsoon
POM	Post Monsoon
EC	Electrical Conductivity
TH	Total Hardness
TA	Total Alkalinity
TDS	Total dissolved solid
Min	Minimum
Max	Maximum
SE Mean	Standard Error Mean
SD	Standard Deviation
BIS	Bureau of Indian Standard
WQI	Water Quality Index
% Na	Percent Sodium
SAR	Sodium Adsorption Ratio
PI	Permeability Index
MH	Magnesium Hazard ratio
Chl <i>a</i>	Chlorophyll <i>a</i>
Chl <i>b</i>	Chlorophyll <i>b</i>
Total Chl	Total Chlorophyll
PBC	Percent Biological Change
BCF	Bio Concentration Factor

CHAPTER - 1

INTRODUCTION

1.1 BASIC CHEMICAL DESCRIPTION OF FLUORIDE

Fluoride (F^-) is a uni-negative ion of fluorine (F). Fluorine is the lightest halogen in the halogen family (Group 17 in periodic table) and the most chemically reactive non-metal with atomic weight 18.998 and atomic number 9. Fluorine is highly toxic, corrosive diatomic light yellow-green colored gas, with a pungent smell. French scientist Henri Moissan was awarded the Nobel Prize in 1906 for the discovery fluorine in 1886. It is the most electronegative and the most reactive compared to all chemical elements in the periodic table (Greenwood and Earnshaw, 1984; Gillespie et al., 1989). It has an oxidation state of -1(F^-) and occurs as both organic and inorganic compounds. It has the ability to make strong hydrogen bonds. The small size enables it to form strong covalent bonds and to have high coordination numbers in molecular fluorides. Of all metal ions, Al^{3+} makes the strongest bonds to F^- , but also beryllium (Be) and calcium (Ca) binds with high affinity (Li, 2003). The bonds in $AlFx$ -complexes are mostly ionic, and the coordination number and configuration can be different depending on fluoride concentration (Schlichting and Reinstein, 1999, Strunecka et al., 2002). F^- and OH^- ions have nearly the same size and same negative charge, which means that they have the same ionic potential. Therefore they can easily replace each other in many rock forming processes (Jones and Atkins, 1999; Saxena and Ahmed, 2001). Fluoride does not exhibit any color, taste or smell when dissolved in water and therefore is not easy to determine it through physical examination.

1.2 FLUORIDE POLLUTION

Fluoride is recognized to be physiologically essential nutrient for the normal development and growth of human beings (Dhar and Bhatnagar, 2009). To a certain extent (as per WHO; 0.6 ppm) fluoride ingestion is useful for bone and teeth development, but excessive ingestion causes a disease known as Fluorosis. Fluoride intake through drinking water and food or through the occupational exposure in those engaged in aluminium production, magnesium foundries, fluorspar processing, and superphosphate, chronic fluoride intoxication may lead to various health hazards (Hodge and Smith, 1977).

Drinking water is typically the largest single contributor to daily fluoride intake (Murray, 1986). Enhanced fluoride intake through drinking water along with dietary intake significantly substantiates the total fluoride accumulation in body tissue (Pandey and Pandey, 2011). 1 ppm of fluoride in drinking water leads to a reduction in dental caries, with minor side effects such as dental fluorosis (da Cunha and Tomita, 2006; Pizzo et al., 2007). Dental fluorosis is a hypoplasia or hypomineralization of tooth enamel or dentin indicated by barely noticeable whitish striations to confluent pitting and staining produced due to the chronic ingestion of excessive amounts fluoride during the developing period of teeth (Horo-witz, 1986). Increased bioaccumulation of fluoride in bone causes skeletal fluorosis which leads to severe and permanent bone and joint deformities with pain and stiffness in the joints. WHO (World Health Organisation) (1984) has prescribed the range of fluoride from 0.6 to 1.5 mg/L in drinking water as suitable for human consumption. BIS (Bureau of Indian Standards) (1992) has set a desirable range of 0.6 to 1.2 mg/L fluoride in drinking water with the maximum permissible limit of 1.5 mg/L. But in areas with warm climate, the fluoride concentration in drinking water should remain below 1.0 mg/L, whereas in cooler climates, the recommended limit may increase up to 1.2 mg/L (WHO, 1991). This is due to higher water consumption in warmer climates as a result of higher perspiration (Yadav et al., 2009). In tropical countries, the places like Ghana, people consume 3 to 4 liters of water which is higher than the WHO estimate of 2 l/adult/day (Apambire et al., 1997). Therefore fluoride intake and its harmful effects are more relevant in the context of India compared to Western countries, where the fluoridation of water is, instead, recommended to help prevent dental caries (Teotia and Teotia, 1991). Depending upon the source of fluoride contamination, there are two types of water pollution: artificial and natural. When fluoride contamination is caused by anthropological activities and/or industrial effluents, it is referred to as artificial fluoride pollution while significant presence of the chemical in water, soil and air is referred to as natural fluoride pollution.

1.3 FLUORIDE POLLUTION SCENARIO IN THE WORLD

Worldwide, more than 200 million people (including 70 million in India and 45 million in China) from 28 tropical countries are suffering from dental, skeletal and/or non-skeletal fluorosis (Yang et al., 2003). According to UNICEF, fluorosis is endemic in at least 25 countries around the world with the highest prevalence rates in India, China and Africa (Mahapatra, 2007). The following studies on fluoride in different part of the world visualize the fluoride pollution scenario.

Dean (1933) reported the prevalence of fluorosis in Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Nevada, New Mexico, North Carolina, North Dakota, Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah and Virginia. High concentration of fluoride (>3.5 mg/L) was noticed in South Carolina where 40% of the people depend on groundwater for their needs (South Carolina Ambient Groundwater Quality Report, 2003). The volcanic ash deposits in Texas which was the reason behind high fluoride in groundwater up to 6.27 mg/L showed better correlation with well depth (Hudak and Sanmanee, 2003). Emission from phosphate fertilizer production factory which was the cause of high fluoride in groundwater in southern Brazil was found to be influenced by vegetation cover (Mirlean and Roisenberg, 2007). In Belgium, drinking water contains fluoride below 0.3 mg/L. However, cases of dental fluorosis have been reported by Carvalho et al., (1998) in Belgium. In 1984, the National Survey of Children's Dental Health in Ireland examined people until 15 years and found that they had fluorosis from mild to questionable level but higher levels were absent (Whelton et al., 2004). Schwartz and Friedrich (1973) assessed the concentration of fluoride in spring and stream waters to determine occurrences of fluorite in Osor district, Spain. It was observed that dental fluorosis was detected in parts of Norway which are related to the bedrock source (Banks et al., 1998). Czarnowski et al., (1996) studied the groundwater quality in Poland with respect to fluoride and found that they were well below limits in most places. Even then fluoride concentrations of about 7 mg/L occur naturally in western Estonia which is due to Silurian-Ordovician aquifer system (Indermitte et al., 2009). Alumina production plants had increased the fluoride concentration in Greece

(Haidouti, 1991). Oruc (2008) stated that in Turkey endemic fluorosis related to high fluoride ranging from 1.5 to 4 mg/L in drinking water was observed since 1955. North Jordan has very low fluoride concentration (Rukah and Alsokhny, 2004) where it becomes necessary to provide fluorinated water to meet the daily requirement of fluoride by the human body. Moghaddam and Fijani (2008) found that groundwater occurring almost everywhere in basaltic rocks in north western Iran contain fluoride beyond the suitable range. Messaïtfa (2008) reported the concentration of fluoride up to 2.3 mg/L in groundwater in Algeria. Fluoride contents in some rivers (12-26 mg/L), springs (15-63 mg/L) and alkaline ponds and lakes (60-690 mg/L) were found to be very high in Tanzania (Nanyaro et al., 1984). Gaciri and Davies (1993) noticed that in natural waters of Kenya, fluoride concentration was greater in lake water than groundwater and springs which was greater than river water. Groundwater studies on fluoride in South Korea show that the concentration of fluoride depends on the residence time (Kim and Jeong, 2005) due to geogenic source of fluoride (Chae et al., 2006; Kim et al., 2010). Ash from volcanic explosion of Sakurajima volcano, Japan was found to contain average fluoride concentration of 788.1 mg/Kg (Nogami et al., 2006). This forms a potential source of threat to groundwater around this area. Abdelgawad et al., (2009) found that weathering and alteration of granitic rocks was the factor affecting oversaturation of fluoride ion in groundwater in Mizunami area, Japan. The incidence of mottled enamel was first reported in 1930 by Anderson and Stevenson (1930) in China. Fluoride problems in China occur through drinking water, indoor coal combustion and brick tea in Taiyuan basin of China (Guo et al., 2007). Fertilizer containing leachable fluoride ranging from 53 to 255 mg/Kg and coal containing fluoride ranging from 5 to 20 mg/Kg were reported to pollute groundwater with high fluoride in east Punjab, Pakistan by Farooqi et al., (2007). The granitic rocks with average fluoride concentration of 1939 mg/Kg in Nagar Parkar area, Pakistan, contain fluoride in kaolin deposits between 468 and 1722 mg/Kg and secondary kaolin deposits have 270 mg/Kg which are the source of fluoride up to 7.85 mg/L in groundwater in this area (Naseem et al., 2010). Studies on fluoride in groundwater in

Sri Lanka carried out by Dissanayake (1991) and Young et al., (2010) shows that the condition has not changed even after about two decades with fluoride above 4 mg/L in groundwater. It was found that high fluoride areas lie within low plains and low fluoride areas were usually highlands. This was because the contact time with the geological material was longer in the plains and there exists slow groundwater movement compared to highlands (Dharmagunawardhane and Dissanayake, 1993).

1.4 FLUORIDE POLLUTION IN INDIA AND WEST BENGAL

Endemic fluorosis is prevalent in India since 1937 (Shortt et al., 1937). Of the 85 million tons of fluoride deposits on the earth's crust, the contribution of India is 12 million (Teotia and Teotia, 1994). Naturally, in India fluoride contamination is widespread and intensive. Indians are living in about 200 districts of 20 states in endemic areas of fluorosis and are at risk of developing fluorosis (Susheela, 2005). Over 66 million of the total populations in India are consuming drinking water containing elevated levels of fluoride (FRRDF, 1999). More and more fluoride affected areas are being discovered regularly in different parts of the country (Fluoride and fluorosis, 2012). In India, fluoride level in ground water varies substantially in different areas (Dhar and Bhatnagar, 2009). Fluoride concentration as high as 86 mg/L, has been reported from Motipura village of Haryana, India (Garg et al., 2009). 50-100% districts of various states like Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat and Rajasthan are fluoride affected (RGNDWM, 1993). Some regions in north western and southern India are affected with fluorosis (Agarwal et al., 1997; Yadav et al., 1999). In Delhi, about 50% of the groundwater exceeds the maximum permissible limit for fluoride in drinking water (Datta et al., 1996). Evapo-transpiration of groundwater with residual alkalinity raises the fluoride concentration in many parts of India (Jacks et al., 2005). Due to long residence time higher fluoride content was observed in deeper aquifers of Maharashtra than shallow groundwater (Madhnure et al., 2007). The granitic rocks in Nalgonda district of Andhra Pradesh contain average fluoride concentration of 1440 mg/Kg which is much higher than the world average fluoride concentration of 810 mg/Kg (Wedepohl, 1969). The mean fluoride content in

Hyderabad granites is 910 mg/Kg (Rao et al., 1993). In West Bengal, excess fluoride in groundwater has been detected so far in 43 blocks spread over seven districts, viz. Purulia, Birbhum, Bankura, Malda, South Dinajpur, North Dinajpur and South 24-Parganas (PHED report, 2009). Fluoride contamination of ground water in the State of West Bengal was first detected during 1996 at Nasipur area of Nalhati-I Block in the district of Birbhum. Basaltic rocks are the source of fluoride in this region (Patra et al., 2010). There after many reports on fluoride contamination came forth from different parts of West Bengal (Gupta et al., 2006; Chatterjee et al., 2008; Kundu and Mandal, 2009 and Ghosh et al., 2010). According to the report of Geological Survey of India (GSI), Precambrian terrain with fractured/shear zones are the possible locale for elevated level of fluoride in ground water in parts of Purulia and Bankura Districts. GSI also reported that the fluoride contamination occurs mostly within tube wells tapping ground water in the basaltic rocks of Rajmahal trap. The dug wells, ponds and tube wells tapping water from alluvium sediments generally contain fluoride beyond 1.50 mg/L.

1.5 SOURCES OF FLUORIDE

1.5.1 Natural source

1.5.1.1 Rock, minerals

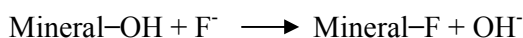
Surface rocks, deposits and the oceans are the main sources of fluoride in the biosphere. According to Smith and Hodge (1979), fluoride is the 13th and according to Bell et al., (1970), 17th most abundant element in the earth's crust in igneous and sedimentary rocks. Its natural concentration is estimated to be 0.06 to 0.09% in the upper layer of lithosphere (Fawell et al., 2006) and the average crustal abundance is 300 mg/Kg (Tebutt, 1983). Hundreds of minerals are known to contain fluoride. The fluoride content in these minerals varies from as high as 73% in the rare mineral griceite (LiF) to many others with less than 0.2% (Weinstein and Davison, 2004). Fluoride occurs in the form of minerals such as biotite, muscovite and hornblende etc. which usually originate from micas, apatite and tourmaline. Fluorite (fluorspar) (CaF₂), fluorapatite [3Ca₃(PO₄)₂ Ca(F,Cl₂)], fluormica (phlogopite) [KMg₃(Si₃Al)O₁₀(F,OH)₂],

apatite $[\text{CaF}_2.3\text{Ca}_3(\text{PO}_4)]$, cryolite $[\text{Na}_3\text{AlF}_6]$, epidote $[\text{Ca}_2\text{Al}_2(\text{Fe}^{3+};\text{Al})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})]$, sellaite $[\text{MgF}_2]$, topaz $[\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2]$, phosphorite $[\text{Ca}_3(\text{PO}_4)_2]$, tremolite $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$, biotite $[\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2]$, hornblende $[\text{Ca}_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Al},\text{Si})_8\text{O}_{22}(\text{OH})_2]$, phosphorite $[\text{Ca}_3(\text{PO}_4)_2]$, certain varieties of mica etc. are the fluoride bearing minerals (Raju et al., 1979; Matthess, 1982; Hem, 1985; Handa, 1988; Gaumat et al, 1992; Gaciri and Davies, 1993; ; Datta et al., 1996; Apambire et al., 1997; Kundu et al., 2001; Mohapatra et al., 2009). Similar occurrence of fluoride both in igneous and sedimentary rocks is reported (Deer et al., 1983). Fluoride content varies from 0.8 to 3.6% in apatite rocks of the Singhbhum district of Bihar, the Vizianagaram district of Andhra Pradesh and the Purulia district of West Bengal (Sinha, 1986; Narasayya 1970).

1.5.1.2 Soil

Soil fluoride is derived from the minerals by weathering and actions of microorganisms, plants and animals. Deposition on the surface from atmosphere by rainfall or by flooding soil fluoride is also derived (Weinstein and Davison, 2004). Fluoride content in soil may vary from under 20 to several thousand mg/Kg (Davison, 1983). The higher level of fluoride is found in areas with sedimentary phosphate or fluorite deposits but the level may also range up to 700 mg/Kg in absence of such sedimentation or deposits (McLaughlin et al., 1996; Cronin et al., 2000). Heavier soils tend to have higher concentration of fluoride than sandy soils as most of the fluoride is associated with clay fraction (Weinstein and Davison, 2004). . Fluoride content in the soil concentration can vary over a short distance due to variation in underlying parent rocks (Geeson et al., 1998). The fluoride content of soil is dependent mainly on the mineralogical composition of the soil, inorganic fraction, the extent of clay and pH. Mobility of fluoride in soil is influenced mainly by pH and formation of aluminium and calcium complexes (Pickering, 1985). It has been found from most of the researches that in soils with $\text{pH} < 6$ fluoride is mainly bound in complexes with either aluminium or iron (e.g. AlF_2^+ , AlF_3 , AlF_4^- , FeF_2^+ , FeF_3) (Elrashidi and Lindsay, 1985). Al is the most abundant metal in the soil (Rayner-Canham and Overton, 2003)

and is present in free hydrous oxides, aluminosilicates. Adsorption and availability of fluoride is determined by the anion exchange of fluoride with minerals (Huang and Jackson, 1965) can be represented as:



ZPC (Zero Point Charge), the pH at which the surface charge is equal to zero is an important parameter which determines the adsorption and availability of fluoride in soil. At a pH below ZPC, surface are charged positive and the adsorption of fluoride become more feasible. As the aluminium hydroxide has a ZPC of 7.1 to 9.5 and alumina has a ZPC of 8 (Müller, 2005), fluoride has a high affinity to be absorbed on these minerals in the neutral pH range.

1.5.1.3 Aquifer

Fluoride comes to the aqueous solution due to the weathering process of rocks and minerals through anthropogenic activities and leaching. The fluoride concentration in ground water depends on geology, chemistry, physical characteristics and climate of the area. As evaporative concentration, change in water chemistry and leaching concentrates the fluoride, higher fluoride concentrations tend to occur in arid regions (Weinstein and Davison, 2004).

Although the solubility of fluoride bearing minerals are low under normal conditions but the slow kinetics for a long time often enhances leaching and enhancement of fluoride in ground water (Hem, 1989). Dissolution rates of fluorite minerals increase under alkaline condition in the range of specific conductivity between 750 and 1750 $\mu\text{S/cm}$ (Saxena and Ahmed, 2001).

Granitic rocks contain fluoride ranging between 500 and 1400 mg/Kg (Koritnig, 1978; Krauskopf and Bird, 1995), which is much higher than any other rock type. The weathering of these rocks results in increased fluoride content in groundwater. Laboratory studies conducted by Chae et al., (2006) showed that leaching of fluoride from granitic rocks contributed 6 to 10 mg/L of fluoride to water. Enhancement fluoride levels in the groundwater occur due to longer residence time in aquifers with fractured fluoride rich rocks. Granite and granitic gneisses in Nalgonda, India contain

fluoride rich minerals such as fluorite (0 to 3.3%), biotite (0.1 to 1.7%) and hornblende (0.1 to 1.1%) (Ramamohana Rao et al., 1993) where 460 to 1706 mg/Kg of fluoride containing rocks are reported Mondal et al., (2009).

Sea water has an average fluoride level of 1.3 mg/L (Carpenter, 1969). Undersea volcano and vents increases the fluoride level in sea water which in turn entering into the river water increases the fluoride level. Another way of fluoride input in water is through the deposition of gases and particulate materials from the atmosphere to a little extent (Weinstein and Davison, 2004).

1.5.1.4 Air

Air borne fluoride arises both from natural and anthropogenic sources. However, a small fraction of the total fluoride exposure arises from air (USNRC, 1993). Fluoride is released into the atmosphere on a large scale due to volcanic ash, dust, industrial production of phosphate fertilizers, coal ash from the burning of coal, smoke in the brick field and volcanic activities. Amongst these aerial fluoride sources, volcanic activities have long been known to be the largest natural source as volcanic rocks are often enriched in fluoride. Magma soluble Hydrogen fluoride gas comes out partially during eruptive activity (D'Alessandro, 2006). During volcanic eruption the aerial emission of fluoride in the form of volcanic ash is deposited on the surface by fall out of particulate fluorides and during rainfall. Due to the high solubility of volcanic ash in rain water the risk of fluoride contamination in groundwater is very high. Percolating rainwater carries this fluoride from the soil surface the groundwater zone. Fluorosis in livestock and humans was identified long ago in 1978 from the Laki eruption (Fridriksson, 1983; Steingrímsson, 1998). Hekla eruption in 2010 contained 23-35 mg/Kg of fluoride (Matvælastofnun, 2010). Fluoride contaminations in groundwater of Kenya have been found to be caused by volcanic eruption (Gaciri and Davies, 1993).

Volcanoes are important source of organo fluorides including some CFCs. These have been shown to contain gaseous fluoride compounds like hydrogen fluoride (HF), ammonium fluoride (NH_4F), silicon tetrafluoride (SiF_4), ammonium fluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$), sodium fluorosilicate (Na_2SiF_6), potassium fluorosilicate (K_2SiF_6) and

potassium fluoroborate (KBF_4) (Weinstein and Davison, 2004). In addition volcanoes erupt some solid fluorides like sodium fluoride (NaF), potassium fluoride (KF), magnesium fluoride (MgF_2) and calcium fluoride (CaF_2) (Roholam, 1937).

1.5.2 Anthropogenic sources

1.5.2.1 Industrial activities

Many types of anthropogenic activities result in the emission and deposition of gaseous and particulate fluorides in the environment. Drying, grinding and calcining of fluoride containing minerals, their reactions with acids, smelting and electrochemical reduction of metals using fluoride containing fluxes or electrolytes, firing of brick or ceramic materials, high temperature melting of raw materials in glass manufacture and the use of fluoride containing chemicals for cleaning, electroplating and etching in various process etc. are the basic industrial activities that results in fluoride pollution (Weinstein and Davison, 2004). Aluminium smelting (Haidouti, 1991), cement production and ceramic firing (WHO, 2002), HF alkylation in petroleum refining (Weinstein and Davison, 2004) releases a high amount of fluoride into the environment. Fluorspar [CaF_2], fluorapatite [$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{F}, \text{Cl}_2)$] and cryolite [Na_3AlF_6] are the major minerals exploited commercially. Fluorspar is as source of hydrofluoric acid, which is a feed chemical for the production of thousands of organic and inorganic fluorine compounds, including insecticides, pharmaceutical and fabric conditioners. For example, about 80% is used for hydrofluoric acid production and the rest is used as a flux in a variety of industries in USA (Weinstein and Davison, 2004). The deposits of apatite mineral that are contained in the rock phosphates are mined for the production of phosphorus and phosphate fertilizers.

1.5.2.2 Fertilizers

Phosphate containing fertilizers enhances the fluoride content in soil and groundwater (Motalane and Strydom, 2004; Farooqi et al., 2007). Phosphatic fertilizers contain remarkable amount of fluoride for example superphosphate (2750 mg of F/Kg), potash

(10 mg of F /Kg) and NPK (Nitrogen Phosphorous Potassium) (1675 mg of F /Kg) (Srinivasa Rao, 1997). In agricultural areas successive use of these fertilizers results in higher fluoride concentration in groundwater (Young et al., 2010). If an agriculture field of 1 ha receives 10 cm of irrigation water containing 10 mg/L of fluoride, then the soil can obtain 10 Kg of fluoride (Datta et al., 1996).

1.5.2.3 Fly ash

Fly ash from the combustion of fossil fuels emits high fluoride in atmosphere. Due to the combustion of coal especially from power plants more than 100 to 150 million tons of fly ash is produced worldwide annually (Prasad and Mondal, 2006; Piekos and Paslawska, 1998). Inappropriate disposal of this fly ash ultimately leaches the fluoride into groundwater. Beside these, the combustion of coal is also a potential source of fluoride emissions in industrial processes (Weinstein and Davison, 2004). Brick kilns which use coal for burning is source of fluoride (Jha et al., 2008), but the amount of pollution depends on the type of coal being burnt as the fluoride content in coal may vary from 40 to 295 mg /Kg (Churchill et al., 1948).

1.6 WATER FLUORIDATION AND OTHER WATER PARAMETERS

Drinking water is typically the largest single contributor to daily fluoride intake (Murray, 1986). Groundwater contributes only 0.6% of the total water resources on earth which is major and preferred source of drinking water particularly in India (Sharma et al., 2011). The chief sources of fluoride ion in the natural waters are fluorite, fluoroapatite as well as fluoride replacing hydroxyl in the ferromagnesium silicates. Presence of fluoride bearing minerals, amount of leachable F^- in a terrain and the degree of weathering are the deciding factors for the fluoride content in water (Ramesam and Rajagopalan, 1985).

Physicochemical parameters as well as hydrochemistry were studied by many researchers to assess the characteristics of groundwater (Sanchez Martos et al., 1999; Subba Rao et al., 2002; Bhardwaj and Singh, 2010). Amongst these parameters some play a vital role in fluoride dissolution and fluoride concentration in water.

The solubility of fluorite in water increases with increasing concentration of sodium (Kundu et al., 2001) indicating an important role of sodium content in water. During the process of chemical weathering, the minerals change to montmorillonite phase and sodium is released into the ground water (Patra et al., 2010). Therefore the degree of weathering is indicated by the sodium acquired by the ground waters.

Water quality parameters such as alkalinity, pH and hardness have high impact on water fluoride levels due to the release of fluoride from fluoride-containing minerals by carbonates and dissolved solids (Viswanathan et al., 2009). High alkalinity of water containing high bicarbonate activity promotes leaching of fluoride and thus affects the concentration of fluoride in groundwater (Salve et al., 2008). Alkaline pH where bicarbonate activity is high, promotes the fluoride dissolution represented as (Salve et al., 2008): $\text{CaF}_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + 2\text{Na}^+ 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2$

The ionic radius of fluoride (0.136 nm) is the same as that of hydroxyl ion, which can be easily substituted from water at high pH (Sreedevi et al., 2006; Gupta et al., 2006). In acidic medium, fluoride is absorbed in clay, whereas high pH, alkalinity of the draining solution favors the leaching of fluoride from the rocks (Patra et al., 2010). Calcium and magnesium sometimes show positive correlation with fluoride (Alagumuthu et al., 2010). The positive correlation with calcium observed may be attributed to the presence of limestone in those areas (Taher and Ahmed, 2001). High fluoride and very low Ca in water may also arise in some cases due to prior precipitation of CaCO_3 from water with limited incorporation of F^- in CaCO_3 structure or due to replacement of calcium by sodium in cation exchange reactions (Patra et al., 2010).

Few other water quality parameters show both positive and negative correlation with fluoride depending on the rock minerals and weathering processes. For example, chloride shows negative correlation with fluoride (Mondal et al., 2012) as well as positive correlation (Dutta et al., 2010; Karthikeyan and Shunmugasundarraaj, 2000). Iron and sulfate had a significant positive correlation with fluoride in some case (Ramakrishnaiah et al., 2009) but showed insignificant negative (iron) or insignificant positive (sulphate) in the study of Mondal et al., (2012).

1.7 SAFE LIMIT OF FLUORIDE

1.7.1 Recommendations

As water is the major source of daily fluoride intake (Murray, 1986), assigning the safe limit of fluoride in water is so important. Fluoride intake and its harmful effects are more relevant in the context of India compared to Western countries, where the fluoridation of water is, instead, recommended to help prevent dental caries (Teotia and Teotia, 1991). There is a risk of endemic fluorosis where the fluoride level is more than 1.0 mg/L in drinking water (Bo et al., 2003). The guidelines published by the World Health Organization (WHO, 1984) suggested that in areas with a warm climate, the optimum concentration of fluoride in drinking water should remain below 1 mg/L, while in cooler climate the recommended limit may increase up to 1.2 mg/L. This is due to higher water consumption in warmer climates as a result of higher perspiration (Yadav et al., 2009). Enhanced fluoride intake through drinking water coupled with dietary intake could significantly substantiate the total fluoride accumulation in body tissue to cross the risk limit (Pandey and Pandey, 2011). The permissible upper limit for fluoride in drinking water recommended by WHO (1997) was 1.5 mg/L, considering this threshold limit to there, where the benefit of resistance to tooth decay did not yet shade in to a significant task of dental fluorosis. The WHO guideline value for water is not universal as the climate and other factors deviate in different habitation. In India, for example, the permissible upper limit was lowered from 1.5 ppm to 1.0 ppm in 1998. For human consumption, Bureau of Indian Standards (BIS) permitted 1.5 mg/L as a safe limit of fluoride in drinking water (BIS, 2009). But more than 1 ppm of fluoride in drinking water can be positively dangerous to human health leading to dental and skeletal fluorosis, calcification of ligaments, crippling bone deformities and many other physiological disorders that might ultimately result in death. These diseases have no cure; prevention is the only means of controlling the disease. Scientists working on the issue of lowering the upper limit of fluoride to at least 1 ppm in India as there is enough evidence to prove that constant exposure to fluoride even at the level of 0.7 mg/L could lead to fluorosis and other allied diseases (Mahapatra, 2007).

The Food and Nutrition Board at the Institute of Medicine recommended a safe limit of dietary intake for fluoride. According to this recommendation, infants of 0-6 months can intake 0.01 milligrams of fluoride per day and infants of 7 - 12 months age can intake fluoride up to 0.5 mg/day. The recommended limit of fluoride intake for the children of the age 1-3 years, 4-8 years and 9-13 years are 0.7 mg/day, 1.0 mg/day and 2.0 mg/day respectively. The limit of fluoride that can be ingested to the adolescents and adults are - males of ages 14 to 18 years: 3.0 mg/day, males over 18 years of age: 4.0 mg/day and females over 14 years of age: 3.0 mg/day.

1.7.2 Lethal dose

The probable toxic dose has been set to 5 mg/Kg and acute toxicities of fluoride have symptoms as nausea, vomiting, diarrhea and cardiac arrhythmia. (Hayes, 2001; Gazzano et al., 2010).

1.8 SOURCE OF FLUORIDE IN HUMAN BODY

1.8.1 Fluoride in Water, Food and vegetables

As discussed before, water is the main source of daily fluoride ingestion in human body. Permissible upper limit for fluoride in drinking water recommended by WHO (2011) is 1.5 mg/L. Food is the next important source of fluoride in human body. Most food derived from plant or animal, contain fluoride ion at least in minute amounts. Local food habit determines the contribution of food to the total daily intake. Fluoride enters into the food stuffs from soil and water used for irrigation. Some foods concentrate additional fluoride from boiling, processing or contamination. Fluoride levels may vary widely even between samples of the same kind of food. Foodstuffs like vegetables and fruits normally contain fluoride at low concentration (0.1-0.4 mg/Kg). Higher levels (up to 2 mg/Kg) of have been found in barley and rice (WHO, 1986). Diets with high fat level increase deposition of fluoride in bone enhancing the toxicity (USDHHS, 1991). There is a little difference between fluoride contents of leaf or root vegetables and cereals with the exception of spinach which is unusually

enriched in fluoride (Gautam et al., 2010). Potato peelings can contain up to 75% of the total fluoride in the whole tuber. The food items carrying high levels of fluorides are rice, wheat, cereal, maize, pulses, cabbage, cucumber, tomato, brinjal, lady's finger, beetroot, potato, onion and sweet potato, banana, grapes, mango, apple, coconut, ground nut, mustard, mutton, beef, pork, fish, egg etc. Food Fluoride concentration in % given in the parentheses are (Mahapatra, 2007):

Banana (2.9 - 4.58), Grapes (0.84 - 1.74), Mango (3.7 - 8.18), Apple (5.7 - 5.22), Vegetables (9.0 - 45.0), Cereals (16.0 - 52.0), Pulses (6.0 - 22.0), Mutton (3.0 - 3.5), Fish (1.0 - 6.5), Wheat (5.9), Rice (1.7 - 2.23), Maize (5.6), Cabbage (3.3), Tomato (3.4), Brinjal (1.2), Lady's finger (4.0), Potato (2.8), Onion (3.7).

1.8.3 Fluoride in Beverages

Tea, coffee, coconut water, beer and wine etc. contain higher levels of fluoride. Tea is enriched with fluoride and about two thirds of the fluoride in leaves is soluble in the beverage (Fung et al., 1999). Each cup of tea may contain 0.3 - 0.5 mg of fluoride. Bottled beverages, have a variable and some have high content of fluoride. Fluoride concentrations in different beverages are (Mahapatra, 2007):

Tea (Dry leaves) 39.8-68.5, Tea infusion 18.13-56.19 (1 gm boiled for 5 min. in 125 ml. water), Tea infusion (1 gm in 125 ml of hot water) 11.13-37.34, Aerated drinks 0.77-1.44, Coconut Water 0.43-0.60.

1.8.4 Fluoride in other sources

Spices like Almond, Garlic, Ginger, Coriander, Cumin Seeds, Garlic, Turmeric, Black Salt etc contain fluoride. Fluoride concentrations (%) in Coriander, Cumin Seeds, Ginger, Garlic, Turmeric are 2.3, 1.8, 2.0, 5.0 respectively (Mahapatra, 2007). Nuts and oilseeds such as almond, coconut, mustard oil and groundnut also have higher concentration of fluoride. Fluoride concentrations in % in Almond, Coconut, Mustard Seeds, and Groundnut are 4.0, 4.4, 5.7, and 5.1 respectively (Mahapatra, 2007). Significant sources of ingested fluoride are toothpaste in very young children (who tend to swallow most of their toothpaste). The fluoride content in raw material used for the

manufacture of toothpaste can be as high as 800-1000 ppm which may range from 1,000 to 4,000 ppm in fluoridated brands (Mahapatra, 2007). Prolonged use of certain drugs leads to chronic adverse effects of fluoride, e.g., sodium fluoride for treatment of osteoporosis, Niflumic acid for the treatment of rheumatoid arthritis, fluoride mouth rinse (Proflo) for the stronger tooth etc. (Kadu et al., 2012).

1.9 HEALTH IMPACT OF FLUORIDE

Fluoride is said to be the greatest scientific fraud of this century. It has been used for many years in carries prevention, mainly as community water fluoridation, whereby 1 ppm of fluoride in drinking water leads to reduction in dental carries with minor side effects such as dental fluorosis (Clarkson and McLoughlin, 2000; da Cunha and Tomita, 2006; Pizzo et al., 2007). Metabolism of ingested fluoride distributed in the organs, bone and teeth shows it adverse effect after long time exposure. Therefore it is important to know the metabolism process for better understanding of health impact of fluoride on human body.

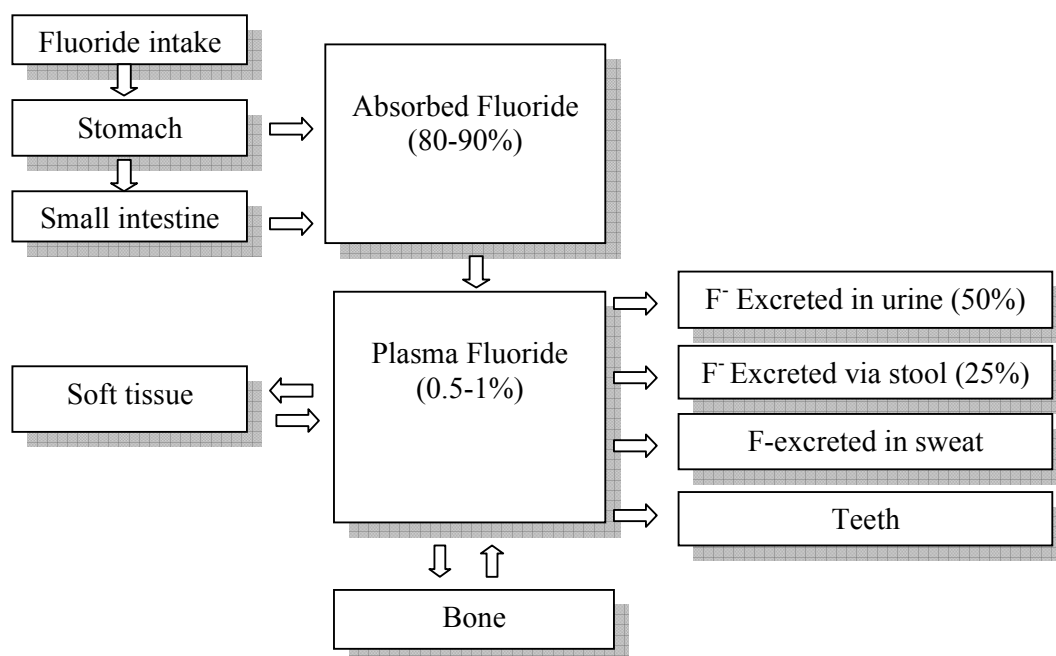
1.9.1 Metabolism of Fluoride

Fluoride can be incorporated in human body through gastrointestinal tract after ingestion, following inhalation, and through the skin. Inhalation and skin absorption are not so important except some occupational exposure situations.

The overall metabolism of fluoride is a three steps process, namely, absorption, distribution, and excretion. In absorption process, the majority of the ingested fluoride is absorbed from the stomach and small intestine into blood stream (Whitford, 1990). This absorption process depends mainly on the solubility of the ingested fluorides, the pH in the digestive system and the presence of compounds in the diet that can complex fluoride (Ekstrand, 1996; Whitford, 1996; WHO, 2002; Weinstein and Davison, 2004; Buzalaf and Whitford, 2011). Just after absorption the fluoride levels increase quickly to reach a peak concentration within 20-60 min. as the ions pass the central component,

plasma, before being distributed and eliminated (Buzalaf and Whitford, 2011). Usually within 3-6 hours fluoride level decline rapidly due to the uptake of fluoride by hard tissue and efficient removal of fluoride by the kidneys (Whitford, 1994). Fluoride is removed from plasma by urinary excretion or by incorporation into mineralized tissues. The distribution process is understood by Tissue-water to plasma-water ratio (T/P) index. An agent with T/P higher than 0.4 means that it can penetrate cells and $T/P > 1$ indicates that it can be accumulated in the tissue. T/P ratio of fluoride is 0.4-0.9 in most organs, such as in liver, lung, heart, salivary gland. It indicates that fluoride is able to penetrate cells but is not accumulated intracellularly (as T/P is less than 1). Exceptionally high T/P ratio of fluoride in kidney (4.16) does not indicate accumulation but is related to the excretion of fluoride by kidney (Buzalaf and Whitford, 2011). Fluoride exists largely in bound forms in plasma, with ionic form (Dhar, 2009). Fluoride in calcified tissues may be released during normal remodeling of bone (Buzalaf and Whitford, 2011). The biological half-life of bound fluoride is several years and for this reason fluorosis persists for a long time. The excretion of fluoride occurs through urine and roughly 50% of the absorbed fluoride is excreted during the following 24 hours (Kadu et al., 2012). Approximately 50% of the fluoride absorbed is deposited in the bones and teeth and the remaining is excreted in urine storing about 99 % of the fluoride retained in the mineralized bones and teeth due to its affinity for calcium phosphate (Teotia et al., 2003, Robinson et al., 1996; Whitford, 1996; Buzalaf and Whitford, 2011). Soluble forms of fluoride, such as fluoride water, have been found to be absorbed at an efficiency of 90 percent or greater. Fluoride intoxication is much effective in case of children as in children less than three years of age only about 50% of total absorbed amount is excreted, where as in adults and children over 3 years about 90% is excreted (Kadu et al., 2012). Fluoride may also pass through the placenta and a minute amount of it is present in saliva, sweat, and milk (Buzalaf and Whitford, 2011).

The metabolism of fluoride can be represented as (Mahapatra, 2007):



1.9.2 Effect of fluoride

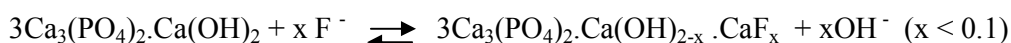
Excessive amount of fluoride ingestion for a long period leads to a dreaded, crippling, incurable disease known as Fluorosis. Fluorosis is a result of abnormal deposition of fluoride in hard tissues. Dental fluorosis or mottled teeth in children is the first indication of fluorosis (Mahapatra et al., 2005). Long-term exposure to fluoride causes skeletal fluorosis (IPCS, 2002). There are basically three types of fluorosis namely, (i) Dental Fluorosis, (ii) Skeletal fluorosis (iii) Non-skeletal fluorosis.

1.9.2.1 Dental fluorosis

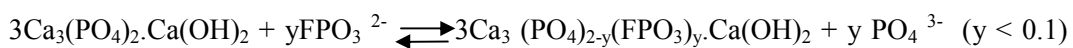
Dental fluorosis, a hypoplasia or hypomineralization of tooth enamel or dentin produced due to the chronic ingestion of excessive amounts fluoride during period when teeth are developing ranges in intensity from barely noticeable whitish striations to confluent

pitting and staining (Horowitz, 1986). The severity of dental fluorosis depends on when and for how long the over exposure of fluoride occurs (Den Besten, 1994).

Teeth are composed of a protein matrix (poly-proline) intimately mixed with an inorganic mineral hydroxy-apatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$). Fluoride ion (F^-) forms small amounts of fluorapatite through an ion-exchange with the hydroxyl ion (OH^-) in the mineral phase according to the reaction (NHMRC, 1999):



As a result of the substitution of fluoride for hydroxyl ion, the volume of the unit cell decreases due to more efficient ionic packing resulting in denser lattice leading to stronger, acid resistant tooth surface supporting the anti-caries effect of fluoride in drinking water (Aoba, 1997). Disodium monofluorophosphate (MFP = Na_2FPO_3), the most commonly used fluoride dentifrice, may ion-exchange the FPO_3^{2-} ion with the isostructural phosphate ion (PO_4^{3-}) according to the reaction (NHMRC, 1999):



But MFP can also behave as an indirect fluoride source as it is degraded to fluoride ion by oral bacteria utilising general purpose phosphatases present in dental plaque (Whitford, 1990). Both the ion-exchange processes lead to the incorporation of fluoride in teeth, principally in the outer enamel layer.

But at the time of tooth and enamel development, chronic exposure to fluoride causes increased mineralization with the loss of matrix proteins resulting in dose-related disruption of enamel mineralization, excessive retention of enamel proteins, and increased porosity (Aoba and Fejerskov, 2002). Although it has not yet been confirmed, some researchers have suggested that chronic fluoride exposure causes aged dentin to crack more easily (Doull et al., 2006).

The appearance of white horizontal striations on the tooth surface or opaque patches of chalky white discolorations indicates a mild dental fluorosis (WHO, 1999; Susheela, 2003; Rao, 2003). The opaque patches can become stained yellow to brown or even black, and increased tooth porosity leads to structural damages, such as pitting or chipping in case of moderate to severe forms of fluorosis (Rao, 2003). Drinking water is the most important factor of dental fluorosis and it has been reported that at least 60

percent of the population are affected where drinking water contains more than 2 mg/L fluoride (Fordyce et al., 2007) reaching upto 100% of the population where fluoride content is 6 mg/L in drinking water (Apambire et al., 1997). The symptoms of dental fluorosis that appears in different stages are – (i) Dull white or yellow patches and loss of shine; (ii) Yellow white spots turning brown in horizontal streaks; (iii) Brown streak at the tip, in the middle or in the upper part of teeth indicating a child to be exposed to high fluoride in food or water or both up to the age of 2 years, from the age of 2 years up to 4 years and from the age of 4 years up to 6 years and after respectively; (iv) Teeth turning black with pitting and even to be flaked and disfigured (v) Teeth loss at an early age; (vi) Delayed eruption of teeth.

1.9.2.2 Skeletal Fluorosis

Increased in bioaccumulation of fluoride in bone due to prolong fluoride exposure with the advancement of age, there are chances of appearance of skeletal fluorosis. Skeletal fluorosis leads to severe and permanent bone and joint deformities causing pain and stiffness in the joints and cripples a person. Skeletal fluorosis occurs due to the consumption of drinking-water containing high levels of fluoride. Exposure to additional sources of fluoride such as high-fluoride coal can also be a potential reason for it. Climate, water consumption, nutritional status and diet, additional sources of fluoride and exposure to other substances that modify the absorption of fluoride into the body etc. are the determining factor of skeletal fluorosis. Occupational exposure to higher concentrations of fluoride in the air may also be a cause of skeletal fluorosis. Crippling skeletal fluorosis can result in osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity.

Skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4–8 mg/L (Teotia and Teotia, 1988). Although the threshold level of fluoride in ground water to cause skeletal fluorosis varies depending on water intake, water quality, and other dietary factors (Jolly et al., 1969; Raja Reddy et al., 1985). In the U.S. there is no evidence of skeletal fluorosis occurrence in the general population when fluoride level in drinking water is less than 4 mg/L; but in some cases renal

deficiencies were observed who ingest large volumes of water at 2–8 mg/L (Kaminsky et al., 1990; Juncos and Donadio, 1972). Crippling skeletal fluorosis can occur when the drinking water contains more than 10 mg/L of fluoride (Boyle and Chagnon, 1995; Reddy and Prasad, 2003).

Skeletal fluorosis is characterized by increase in bone density leading to thickness of long bones and calcification of ligaments. Fluoride accumulated in bone has a biological half-life of several years in this tissue. It is well established that fluoride exposure disrupts the synthesis of collagen and leads to the breakdown of collagen in bone (Susheela and Jha, 1981; Sharma, 1982a; Susheela and Mukerjee, 1981; Sharma, 1982b). Fluoride stimulates bone growth, although it does not directly stimulate osteoblastic activity, and in vivo, there is a lag time (months to years) before the onset of osteoblastic activity (NHMRC, 1999). The enhanced stability due to replacement of hydroxyl ion by fluoride ion renders the skeletal structures more resistant to osteoblastic resorption, which alters the normal bone remodeling cycle. Because bone remodeling is an integral part of skeletal health, the two properties of fluoride, increased formation of bone and a greater resistance to resorption and remodeling leads to the production of abnormal bone (NHMRC, 1999). In an acute case, fluoride promotes the development of bone cancer (Hrudey et al., 1990; Mahoney, 1991).

Although the mechanism that leads to skeletal fluorosis are little understood, the stages of development are well-documented (Hil-eman, 1988; WHO, 1999; Rao, 2003; Susheela, 2003; Edmunds and Smedley, 2005). In early stages, the symptoms include pain and stiffness in the backbone, hip region, and joints, along with increased bone density (osteosclerosis). With progress of this condition, various ligaments of the spine can also become calcified and ossified and in advanced stages, fluorosis produces neurological defects, muscle wasting, paralysis, crippling deformities of the spine and major joints, and compression of the spinal cord (Ozsvath, 2009). Severe pain and stiffness in the backbone, stiffness in joints, rigidity in the hip region, increased thickening and density of bone, besides calcification of ligaments, constriction of vertebral canal and inter-vertebral foramen pressure on nerves, deformities in limbs, hunch back, paralysis, muscular wasting and premature aging are the symptoms of skeletal fluorosis.

1.9.2.3 Non-skeletal Fluorosis

This kind of fluorosis is often disregarded due to the wrong prevailing perception that fluoride affects only bone and teeth. Other non-skeletal health disorders that occur due to high fluoride intake through drinking water are muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, depression, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, male sterility, etc (Meenakshi and Maheshwari, 2006).

As fluoride is excreted in urine through the kidneys, it may affect the functioning of kidneys. A few studies reported that chronic ingestion of fluoride can have non-carcinogenic effects on the kidney with the incidence of kidney stones (Doull et al., 2006).

Several researchers studied the effects of fluoride on the endocrine system found a relation between endemic goiter and fluoride exposure in human populations (e.g., Steyn, 1948; Day and Powell-Jackson, 1972; Obel, 1982; Desai et al., 1993; Jooste et al., 1999) although the exact causal mechanism for effect of fluoride on the thyroid has not yet been established (Doull et al., 2006).

According to the report of Li et al., (1988) fluoride might have genotoxic effects. Several studies supported these effects on humans and animals (Sheth et al., 1994; Joseph and Gadhia, 2000; Tripathi et al., 2009).

A number of studies conducted in China have suggested that dietary fluoride ingestion has an adverse effect on the intelligence of children (e.g., Li et al., 1995; Zhao et al., 1996; Lu et al., 2000; Xiang et al., 2003; Wang et al., 2007). Trivedi et al., (2007) found a statistically significant inverse relationship between the intelligence quotient (IQ) and urinary fluoride levels of school-aged children. Although the actual mechanism occurring in human brain is not known but, according to the suggestion of Guan et al., (1999), changes in the membrane lipids may be the cause of alteration of phospholipids and ubiquinone in the brain of rats due to chronic fluoride ingestion. Several other studies also comply with this fact (Trivedi et al., 2007; Ge et al., 2010).

Fluorides are known to cause chromosome damage and mutations and are therefore considered possible carcinogens. Several studies have found evidence for a relationship between fluoride exposure and specific cancers prevalence, for example, uterine cancer (Tohyama, 1996; Yang et al., 2000) and colon cancer (Yang et al., 2000; Takahashi et al., 2001). The studies by Grandjean et al., (1990), Grandjean et al., (1992) and Grandjean and Olsen (2004) found that cryolite workers are in the risk of lung cancer.

Although the human exposure is uncertain, the effect of fluoride on reproductive structure or function involving animals have been studied to find out the relationship (Doull et al., 2006). According to the study of Freni (1994), there is a association between increasing fluoride concentrations and decreasing birth rates in human being. The results of other studies suggest that high fluoride ingestion on males have an effect on the morphology and mobility of sperm (Chinoy and Narayana, 1994), or the levels of testosterone, follicle-stimulating hormones and inhibin-B (Susheela and Jethanandani, 1996; Ortiz-Perez et al., 2003).

In cases of acute fluoride toxicity, a variety of gastrointestinal effects, including nausea, vomiting, diarrhea and abdominal pain have been reported (Gessner et al., 1994; Penman et al., 1997; Sidhu and Kimmer, 2002). Studies involving animal reveal that fluoride can stimulate the secretion of stomach acid, reduce blood flow away from the stomach lining, and even cause the death of gastrointestinal tract epithelium cells (Doull et al., 2006). Adverse gastrointestinal symptoms are common in areas of endemic fluorosis with poor nutrition (Gupta et al., 1992; Susheela et al., 1993; Dasarathy et al., 1996).

There is a possible link between fluoride ingestion and the prevalence of Down's syndrome (Whiting et al., 2001), especially for children born to mothers under the age of 30 (Takahashi, 1998). Two small-scale studies conducted by Gupta et al., (1994, 1995) in India have raised the possibility of being spina bifida occulta abnormally high in fluorosis-prone regions.

1.10 EFFECT OF FLUORIDE ON OTHER ANIMALS

Along with human being, chronic fluoride toxicity in the environment imposes a harmful effect on animals. Chronic exposure to F in water can develop fluorotoxycosis in any animal and the severity varies among species, animals, and their habitat (Choubisa et al., 2011). Many studies dealt with bones and the teeth examination of wild and domesticated animals for indirect assessment of the fluoride contamination hazards. The bioaccumulation fluoride in mammals generally increases with age. Many studies have done to identify good bioindicators of fluoride pollution collecting the bone samples from herbivorous ungulates, like, European red deer (*Cervus elaphus*), white-tailed deer (*Odocoileus virginianus*), roe deer (*Capreolus capreolus*), sheep (*Ovis aries*) and horse (*Equus caballus*) etc. (Suttie et al., 1987; Kierdorf et al., 1996; Boulton et al., 1999; Tataruch and Kierdorf, 2004; Weinstein and Davison, 2004; Choubisa, 2008; Macicek and Krook, 2008; Telesiński and Śnioszek, 2009; Jelenko and Pokorny, 2010). Several studies have done on the fluoride concentration in teeth and bone of deer from the family Cervidae in north-west Poland, where a major producer of phosphatic fertilizers is located (Dabkowska et al., 1995; Zakrzewska, 1996; Gutowska et al., 2004; Zakrzewska et al., 2005). But a few ecotoxicological analyses of fluoride were conducted taking omnivorous wild mammals and rarely performed on carnivores and canids (Walton, 1988; Kierdorf et al., 2000; Weinstein and Davison, 2004).

In India, the effects of fluoride have been studied mainly among domestic animals and mostly in cattle (*Bos taurus*) and buffaloes (*Bubalus bubalis*) (Choubisa, 1999, 2008, 2007). There are a few reports of ecotoxicological effects of fluoride on other animals like, horses (*Equus caballus*), donkeys (*E. asinus*), camels (*Camelus dromedarius*), goats (*Capra hircus*), and sheep (*Ovis aries*), (Choubisa, 2010c; 1999; 2008; 2007; 2010a). Although A recent study also indicated a contributory role of food and its nutrient composition in ameliorating F toxicity in goats and sheep (Choubisa, 2010 b).

1.11 ACCUMULATION OF FLUORIDE AND ITS EFFECT ON PLANTS

1.11.1 Accumulation

The fluoride concentration in plant leaves varies from <1 to several thousand mg/Kg (Weinstein and Davison, 2004). Plants usually have from <2 to about 20mg/Kg fluoride in the leaves growing in soils containing about 600 to 800 mg/Kg fluoride (Weinstein, 1977). Leaf concentration may reach several thousand mg/ Kg where the soil fluoride content is much higher such as in fluospar mine waste. Cooke et al., (1976) reported concentrations from 280 to over 4000 mg/Kg in arrange of grass and legume species.

The controlling influence of concentration of fluoride in the soil solution has been established by growing plants in aqueous culture media. When groundwater is used in irrigation, the vegetables grown also incorporate fluoride. Fluoride is absorbed by plant roots (Kamaluddin and Zwiazek, 2003; Pant et al., 2008) and then transported via xylematic flow to the transpiratory organs, mainly leaves, where it can be accumulated with adverse effects. The fluoride content of the leaves increases approximately in proportion to the concentration bathing the roots in aqueous culture media (Cooke et al., 1978). The concentration of fluoride in plant increases with time and is highest in the roots and is progressively lower in younger leaves that are more distant from the root (Weinstein and Davison, 2004).The concentrations differ from species to species.

Plant may also uptake fluoride from air when gases containing fluoride (mainly HF) deposited on leaf surfaces. Cuticular uptake of plant leaves is important in the case of plants in dry habitats (Areas et al., 1980). Boundary layers, nature of the surfaces and stomatal apertures of plant leaves determines the uptake of fluoride by plant. The quantitative relationship between exposure to HF and the fluoride content of vegetation were examined by Hitchcock et al., (1971) and McCune and Hitchcock (1971). The simplified dose rate equation (NAS, 1971; Weinstein, 1977) is:

$$\Delta F = KCT$$

Where ΔF is the change in fluoride concentration (mg/Kg), K = an accumulation coefficient, C = the concentration of hydrogen fluoride ($\mu\text{g}/\text{m}^3$) and T = duration of exposure (days). The hydrophilic pores of cuticles through which low molecular weight

solutes in water solutions permeate are lined with fixed negative charges, and therefore cations can permeate but not the anions like fluoride (F^-) (Marschner, 1995). But probably after weathering or insect damage fluoride penetrate cuticles (Davison, 1982). Spray of NaF solution applied to leaves can cause necrosis identical to that caused by HF. Heavy particulate deposits on wet leaf surface may also cause visible injury (McCune et al., 1965, 1977).

1.11.2 Effect

Certain physiological processes are known to be markedly affected by fluoride, including decreased plant growth, chlorosis, leaf tip burn and leaf necrosis (Miller et al., 1999; Elloumi et al., 2005; McNulty and Newman, 1961) This fluoride may affect the biochemical ratio of the plant body (Yang and Miller, 1963). The toxic effect of fluoride on pigments like chlorophyll and some secondary metabolites like sugar, ascorbic acid, amino acids and proteins are well documented (Elloumi et al., 2005; McNulty and Newman, 1961; Yang and Miller, 1963; Horvath et al., 1978; Verma and Dubey, 2001; Kim et al., 2003; Kundu and Mondal, 2010). Fluoride causes reduction in photosynthetic pigment concentration (Lal and Ambasht, 1981), inhibition of photosynthesis (Darral, 1989) and changes in carbohydrate metabolism (Asthir et al., 1998). Some plant species have a very low tolerance to atmospheric fluorides (Szokolay et al., 1960; Lovelace et al., 1968; Oelschläger et al., 1967; Garber, 1967). The symptoms of fluoride injury is manifested by an initial chlorosis of the leaves (Hitchcock et al., 1962) which is characterized by a yellow to brown bleaching of the tips and upper margins of plant leaves, with subsequent tissue collapse, cupping, and other distortions (Hitchcock et al., 1962; MacLean et al., 1968). Although the precise mechanisms by which fluorides induce injury in plants is not known but the affects concerning the alteration of plant cell ultrastructure and physiological processes by fluoride is well studied (Wei and Miller, 1972; Thomas and Alther, 1966). Effects of fluoride on photosynthesis, respiration, RNA structure, and on cellular metabolites involved in the reactions of certain enzymes are well documented (Brandt and Heck, 1968; Lee et al., 1965; Chang, 1968; Yang and Miller, 1963).

CHAPTER - 2

REVIEW OF LITERATURE

Saini et al., (2013) made a mapping of F^{-1} endemic area of Newai Tehsil, Tonk district, Rajasthan, India. For the study, water, soil (0–45 cm), and vegetation samples were collected from 17 villages. Fluoride concentration in water samples ranged from 0.3 to 9.8 mg/l. Out of 17 villages studied, the amounts of F^{-1} content of eight villages were found to exceed the permissible limits. Labile F^{-1} content and total F^{-1} content in soil samples ranges 11.00–70.05 mg/l and 50.3–179.63 $\mu\text{g g}^{-1}$, respectively. F^{-1} content in tree species was found in this order *Azadirachta indica* 47.32–55.76 $\mu\text{g g}^{-1}$ > *Prosopis juliflora* 40.16–49.63 $\mu\text{g g}^{-1}$ > *Acacia tortilis* 34.39–43.60 $\mu\text{g g}^{-1}$ while in case of leafy vegetables, F^{-1} content order was *Chenopodium album* 54.23–98.42 $\mu\text{g g}^{-1}$ > *Spinacea oleracea* 30.41–64.09 $\mu\text{g g}^{-1}$ > *Mentha arvensis* 35.48–51.97 $\mu\text{g g}^{-1}$. The order of F^{-1} content in crops was found as 41.04 $\mu\text{g g}^{-1}$ *Pennisetum glaucum* > 13.61 $\mu\text{g g}^{-1}$ *Brassica juncea* > 7.98 $\mu\text{g g}^{-1}$ *Triticum sativum* in Krishi Vigyan Kendra (KVK) farms. Among vegetation, the leafy vegetables had more F^{-1} content. From the results, it was suggested that the people of KVK farms should avoid the use of highly F^{-1} containing water for irrigation and drinking purpose and to grow more F^{-1} hyperaccumulator plants in F^{-1} endemic areas to lower the F^{-1} content of the soils.

Routroy et al., (2013) studied the seasonal variation of ground water in Nayagarh district, Odisha, analysing both pre and post monsoon water samples. The high fluoride content was an endemic problem in the area and special attention was attached to the point. The chemical compositions of the ground water of the area were dominated by Ca-Cl, Na-Cl and mixed Ca-Mg-Cl types in pre-monsoon and Ca-HCO₃-mixed Ca-Mg-Cl type in post-monsoon. This was largely due to chemical weathering of Eastern Ghats Mobile Belt rock types. Increasing alkalinity vis-a-vis F concentration in pre-monsoon was associated with sodium-bicarbonate water types having high pH (>7) and low calcium and magnesium contents. The percentage of total high fluoride containing water samples was nearly double in pre-monsoon than in post-monsoon. During both the seasons, pH values indicate mildly alkaline to weakly acidic nature of the water samples. Fluoride concentration had good correlation with pH in pre-monsoon whereas in post-monsoon it shows good correlation with Fe. Facies analysis indicated that water

is becoming predominantly Ca-Na cation and Cl-SO₄-HCO₃ anion type in premonsoon than Ca-Mg type and HCO₃-Cl-SO₄ type in post-monsoon. The seasonal variations in concentrations of anthropogenic components demonstrated that the groundwater system is very less liable to pollution by human activities.

The ground water quality of drinking water of tube well, ring well and PHE of Hojai sub-division of Nagaon, district, Assam, had been studied by Mitra and Kumar (2013) with special reference to the presence of fluoride. Most of Fluoride levels were within permissible limits, whereas a ten water samples has higher concentration of fluoride than permissible limit (1 mg/L, WHO). Fluoride content had positive correlation with Na⁺ and K⁺ and negative correlation with Mg²⁺, Ca²⁺ and total hardness (TH). Fluoride showed fairly good positive correlation with depth of sources. The main source of fluoride came into contact with ground water from its source of origin, the rock minerals. They concluded that the concentration of fluoride in groundwater basically depends on easily weathered fluoride bearing minerals, the accessibility of circulating water to fluoride bearing minerals, extent of fresh water exchange in an aquifer, evaporation and evapotranspiration, formation of ionic compound such as CaSO₄, CaHCO₃ etc. and complexing of F with Al, Be, Ferric ions.

Florence et al., (2013) studied on ground water samples of open wells, bore wells and hand pumps collected from 15 different locations in Gangavalli Taluk in Salem District during the Pre-Monsoon (PM1) period (June-July 2010) and Post-Monsoon (PM2) period (December 2010-January 2011) and were analyzed for their physico-chemical characteristics. Each parameter was compared with the standard permissible limit of the parameter as prescribed by World Health Organization (WHO). The multivariate statistical tools such as Correlation Coefficient Analysis (CCA), Factor Analysis (FA) and Cluster Analysis (CA) were also used for the interpretation of water quality data and its spatial variations. Most of the physico-chemical parameters measured for groundwater samples were within the limits set by the World Health Organization. The study revealed that in few villages, water had high hardness and fluoride content. Correlation analysis indicated that the water quality parameters viz., EC, TDS, salinity,

CH and F were significantly correlated with one another. FA showed high loading of physical parameters viz., Temperature, TS, TDS and TS in the PM1 season while high loading of Temperature, EC, Salinity, TS, TDS and TSS in the PM2 season indicated that the contamination of ground water may be due to agricultural runoff, solid waste disposal and surface water pollution from industrial discharges. FA showed high loading of chemical parameters F and TA in the PM1 season indicating the presence of carbonates and bicarbonates added to water when it passed through the soil and rocks. Factors showing high loading of TH, CH and F indicated soil /rock containing Fluorospars (CaF_2) in the study area. Thus the factors extracted reduced the overall complexity of the data. Ward's method of CA indicated four clusters in the PM1 season and three clusters in the PM2 season that represented specific patterns of trends in groundwater quality. This study demonstrated the application of multivariate statistical methods in assessing the hydro chemical characteristics of the Gangavalli Taluk and also provided preliminary assessment of the ground water quality that can serve as a database for future investigations and monitoring of groundwater quality in the study area.

Sajil Kumar et al., (2013) investigated the physicochemical properties of the groundwater in Thirupathur region in Tamil Nadu, India to understand the status of water quality and also detect the sources of contamination. A wide seasonal variation was showed for the majority of the samples; higher concentration was observed in the pre-monsoon season. Concentration of fluoride was quite alarming in many locations. Groundwater is found to be dominated by Na^+ , Ca^{2+} , HCO_3^- and Cl^- . Four types of water were identified, which are Ca-Cl, Na-Cl, Ca-Na- HCO_3 and mixed Ca-Mg-Cl in which Na-Cl type was observed in 50 % of the samples. All the samples were alkaline in nature and a higher value was shown in 38 % of the samples. In general, all the parameters showed a higher concentration in the pre-monsoon season except F^- . High fluoride concentration (up to 2.75 mg/l) exceeding the guideline value 1.5 mg/L was observed in 62.5 % of the post-monsoon season. A lower F^- concentration in the pre-monsoon season may be due to the precipitation of F^- as CaF_2 . High TDS values

are observed in the pre-monsoon season, with 50 % of samples exceeding the permissible limit 1,000 mg/l in the case of Na; 50 % of the post-monsoon and 75 % of the pre-monsoon samples were exceeded the drinking water guideline 200 mg/L. K and Ca concentrations were under the permissible limit, except three samples during pre-monsoon season exceeding the permissible level of Ca 75 mg/l. Mg concentration in the study area with exceeded in the 62.5 % of pre- and 75 % in post-monsoon season. Since the study area does not have carbonate rocks in the geological formations, the origin of Ca and Mg may be attributed to the weathering of silicate minerals. Bicarbonate was the dominant anion that imparting alkalinity to groundwater, this is supporting the alkaline pH in the study area. Chloride concentration was within the limit during post-monsoon and showed higher concentration with 50 % samples exceeded the permissible limit during pre-monsoon. Sulphate was under the guideline value and nitrate was higher in one sample near the agricultural field. Fluoride posing serious problems especially in the post-monsoon season with 62.5 % of the samples exceeded the permissible limit 1.5 mg/l. Evaluation of the source of ions and controlling process were carried out initially with Gibbs plot and later with bivariate plots of ionic ratios. Rock–water interaction was identified as the major process in the study area. Further investigation on the rock–water interaction was to indicate the dominance of silicate weathering on the other processes in contributing the ions such as Na, Ca, Mg, HCO_3^- , etc. The odd behavior of few samples from the normal silicate weathering process was attributed to the cation exchange process in the study area. However, the origin of fluoride was largely controlled by the fluoride rich minerals in the hard rock's of the study area.

Chakrabarti et al., (2013) studied the accumulation of fluoride in roots, leaves and seeds of two paddy varieties (i.e. *Oryza sativa* L. var. *IR-36* and *Oryza sativa* L. var. *Swarno*) when treated with different concentrations of fluoridated water. The translocation pattern of fluoride was also observed. The water soluble fluoride ($\text{F}_{\text{H}_2\text{O}}$) in the soil and plant parts increased substantially with increasing fluoride concentration in treated water. The Swarno variety showed a slight but consistent higher uptake of fluoride than the IR-36 variety. Fluoride uptake by the germinated seedlings was many

folds higher than the uptake by mature plants. At 30 mg l⁻¹ fluoride exposure, the mean F_{H₂O} accumulation (mg kg⁻¹ dry weight) in root, leaves, and seeds of Swarno was 54.1, 51.4 and 42.3, whereas the corresponding values in IR-36 were 50.9, 48.5 and 39.2. For the same exposure, the fluoride accumulation in root and shoot of Swarno and IR-36 seedlings were 3,480, 3,463 and 3,386, 3,360 mg kg⁻¹, respectively. Normally, the fluoride accumulation followed the order of soil > root > shoot > grain. However, at early stage of fluoride contamination (5 mg l⁻¹ NaF) roots tended to hyper accumulate fluoride from the soil. They concluded that paddy had an alarmingly high efficiency in translocation of fluoride to the rice grains through the root and leaves enhancing the risk of increased dietary intake of fluoride in fluorosis endemic areas.

The work of Ravikumar et al., (2013) aimed at assessing the water quality index (WQI) in the surface water of Sankey tank and Mallathahalli lake situated in Bangalore Urban district by monitoring three sampling locations within Sankey tank (viz., A, B and C) and Mallathahalli lake (viz., Inlet, Centre and outlet) for a period of 3 months from March to May 2012. The surface water samples were subjected to comprehensive physico-chemical analysis involving major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe²⁺), anions (HCO₃⁻, Cl⁻, SO₄²⁻, NO₃⁻, F⁻, PO₄³⁻) besides general parameters (pH, EC, TDS, alkalinity, total hardness, DO, BOD, COD, CO₂, SiO₂, color, turbidity). For calculating the WQI, 14 parameters namely, pH, electrical conductivity, total dissolved solids, total hardness, alkalinity, calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate, fluorides and iron were considered. SAR values indicated that both Sankey tank and Mallathahalli lake waters are excellent (S1) for irrigation, while electrical conductivity values classified these lake waters, respectively under medium salinity (C2) and high (C3) salinity category. Correlation between SAR and electrical conductivity revealed that Sankey tank water is C2S1 (medium salinity-low sodium) type while Mallathahalli lake water was C3S1 (high salinity-low sodium) type. Sankey tank and Malla-thahalli lake water were, respectively hard and very hard in nature. Further, it was apparent from WQI values that Sankey tank water belongs to good

water class with WQI values ranging from 50.34 to 63.38. The Mallathahalli lake water with WQI value ranging from 111.69 to 137.09, fell under poor water category.

Brahman et al., (2013) worked on fluoride ion (F^-), total arsenic (tAs) and inorganic arsenic (iAs) species contamination in underground water of Mithi and Nangarparkar subdistricts of Tharparkar, Pakistan. In this study, different multivariate statistical techniques, SI and SAR were used to evaluate variations in underground water quality in sub districts Mithi and Nangarparkar of the Tharparkar. It was concluded that As and F^- concentration in most of the underground water samples were higher than the permissible limits proposed by WHO. The alkaline environment further sustains high F^- and promotes the replacement of OH^- with F^- in the underground water of study area. The granite and mica of the study area contains abundant F bearing minerals, which upon weathering, leached out and dissolved in underground water. The calcite and fluorite are the two main minerals abundantly available and controlling the aqueous geochemical changes. Cluster analysis grouped fourteen sampling sites into three clusters of similar water quality characteristics. Based on obtained information, it is possible to design a future, optimal sampling strategy, which could reduce the number of sampling sites and associated cost. Principle component analysis helped in identifying the factors or sources responsible for water quality variations. PCA results may convincingly be presumed that the contamination in underground water samples might be geologic and climatic but not anthropogenic. The multivariate techniques of analysis of study area clearly showed the high, medium and less polluted sites for underground water.

Borah (2013) worked on fluoride concentration and some other parameters of the ground water of Tengakhat circle of Dibrugarh district, Assam was measured. 35 water samples were collected from different villages of the circle. The sources of all the water samples were hand tube wells, motor pumps and deep tube wells. Ground water of the region was found slightly acidic in nature. Fluoride level varied from 0.0785 mg/L to 0.8152 mg/L. Calcium and magnesium concentration were found quite low. His

conclusion about his study was that, due to low level of fluoride concentration in ground water there is a possibility of occurring dental caries among the children.

Parikh and Parikh (2013) made a research on fluoride endemic villages of Kheralu taluka of Mehsana district which is rich in agricultural production but is largely dependent on groundwater, both for irrigation and drinking water requirements. In their study, the ground water samples of 60 villages of the taluka were collected and were analyzed for fluoride concentration along with other potable parameters during winter months of the year 2012. Out of total villages surveyed, 33 villages (i.e. 55%) are in the range of 1 - 1.5 ppm of which 16 villages(i.e. 27 %) had fluoride content below permissible limit i.e. below 1 ppm. 27 Villages (i.e. 45%) had Fluoride concentration beyond permissible limit i.e. beyond 1.5 ppm. It is envisaged that the sedimentary rock basin, semi-arid climate and high loss of surface water due to extreme evaporation in the study area might have lead to fluoride enrichment in the ground water.

Abdulrahman et al., (2013) undertook a survey of wells (n = 1,060) in all the 13 regions of the Kingdom of Saudi Arabia to assess the contained fluoride (F) levels. The results indicated variation in fluoride levels from 0.10 to 5.4 mg/L as F throughout the kingdom. The average fluoride levels in milligrams per liter as F were as follows in descending order: 1.80 (Hadwood Shamalyah), 1.37 (Hail), 1.33 (Eastern Province), 1.16 (Al Jouf), 1.11 (Qassim), 1.01 (Riyadh), 0.90 (Madina Al Munnawara), 0.81 (Tabouk), 0.74 (Makkah Al- Mukaramma), 0.73 (Jizan), 0.66 (Asir), 0.64 (Najran), and 0.60 (Al Baha). The results indicated that fluoride levels exceeded the USEPA maximum contaminant limits for drinking water (4 mg/L) in several wells (n = 7) in different regions of the kingdom and that 13.96 % of the wells exceeded the World Health Organization recommended levels (1.5 mg/L). The results were also compared with the secondary USEPA contaminant standards of 2.0 mg/L for fluorides.

A work was undertaken by Mazhar Nazeeb Khan and Ravikumar (2013) to study the specific relationship between alkalinity and presence of fluoride ion in groundwater. Groundwater samples were collected from 24 different stations in Tiruchengode taluk,

Namakkal district, Tamilnadu, India during the month of December 2011 and July 2012. The samples were stored in sterilized 2 L polythene containers and used to carry out the analysis of various physicochemical parameters. The alkalinity values were found to be more than the permissible limit. It plays an important role for the release of fluoride ion from its ore to the groundwater. It was observed that an increase in the alkalinity value made a similar increase in the amount of fluoride. In alkaline environment, the fluoride ion can be easily liberated from their ore because OH⁻ and F⁻ ions have similar radii. Hence they easily exchange with each other. They concluded that the increased fluoride level in the groundwater of Tiruchengode taluk was due to some geological process such as dissolution of fluoride rich mineral (Fluorspar) in the environment of alkaline pH, excess of bicarbonates, evaporation, semi aridity and high temperature. Geochemical behavior of groundwater from the study area suggested that the high fluoride content groundwater contains low levels of Ca and has high alkalinity.

Chakrabarti and Patra (2013) conducted a study on four common plants to understand the effect of fluoride on them focusing mainly on superoxide dismutase activity. Radish (*Raphanus sativa*), coriander (*Coriandrum sativum*), mustard (*Brassica juncea*), and spinach (*Spinacea oleracea*) plants were grown in earthen pots watered with aqueous solutions containing 0, 5, and 10 mg F/L. Fluoride (F) uptake and superoxide dismutase (SOD) activity (unit/mg protein/min) were estimated from the edible plant parts following harvest after 60 days. The values of both entities rose with increasing F exposure in the order radish > coriander > spinach > mustard. The results indicated that plant species tolerant to F toxicity induce higher antioxidant SOD activity, which may be an adaptive reaction in plant cells to attenuate the damaging effect of reactive oxygen species (ROS) generated during F stress. Their study concluded on the fact that F exposure possibly increases SOD activity through enhanced metabolism or SOD biosynthesis in the crop plants, which can be considered as a positive feedback mechanism.

Chen et al., (2012) conducted successive surveys in 1984, 2006 and 2007, of all villages in Yuanmou County, China, highlighting 40 villages with groundwater fluoride levels higher than 1.0 mg/L and related cases of human fluorosis. Using the data from these surveys and by employing geographic information system (GIS) techniques, high fluoride levels and fluorosis cases were mapped. The results show high fluoride concentrations and fluorosis hotspots were found to be predominately located in the lowlands of central Yuanmou County. Spatial distribution of high fluoride levels was found to be primarily determined by geology, arid climate, and topography. Both dental and skeletal fluorosis had dramatically decreased due to a program of low-fluoride drinking water supply supported by local governments. The prevalence of dental fluorosis in children had dropped from 43.26% in 1984 to 21.97% in 2006, and the number of skeletal fluorosis cases had decreased from 327 in 1984 to 148 in 2006, respectively. Despite a decline in fluorosis cases, the emergence of fluorosis in new areas indicates the need for both continuous monitoring of drinking water in affected areas and increased public awareness. Mapping showed that 70% of all townships were affected by fluorosis, and helped to identify hotspots of fluorosis in the central areas of the county, especially in the 3 townships of the basin area. Fluoride concentration in drinking water has decreased over the period between 1984 and 2007, in terms of extent of the fluoride levels and number of villages with fluoride levels exceeding the national standard. Severity of dental and skeletal fluorosis in humans had been reduced during the same period regarding to prevalence of dental fluorosis and number of cases of skeletal fluorosis.

This study of Rango et al., (2012) aimed to assess the link between fluoride content in groundwater and its impact on dental health in rural communities of the Ethiopian Rift. A total of 148 water samples were collected from two drainage basins within the Main Ethiopian Rift (MER). In the Ziway – Shala basin in particular, wells had high fluoride levels (mean: 9.4 ± 10.5 mg/l; range: 1.1 to 68 mg/l), with 48 of 50 exceeding the WHO drinking water guideline limit of 1.5 mg/l. Total average daily intake of fluoride from drinking groundwater (calculated per weight unit) was also found to be six times

higher than the No-Observed-Adverse-Effects-Level (NOAEL) value of 0.06 mg/kg/day. The highest fluoride levels were found in highly-alkaline (pH of 7 to 8.9) groundwater characterized by high salinity; high concentrations of sodium (Na^+), bicarbonate (HCO_3^-), and silica (SiO_2); and low concentrations of calcium (Ca^{2+}). A progressive Ca^{2+} decrease along the groundwater flow path was associated with an increase of fluoride in the groundwater. The groundwater quality problem was also coupled with the presence of other toxic elements, such as arsenic (As) and uranium (U). The health impact of fluoride was evaluated based on clinical examination of dental fluorosis (DF) among local residents using the Thylstrup and Fejerskov index (TFI). In total, 200 rural inhabitants between the ages of 7 and 40 years old using water from 12 wells of fluoride range of 7.8 – 18 mg/l were examined. Signs of DF (TF score of ≥ 1) were observed in all individuals. Most of the teeth (52%) recorded TF scores of 5 and 6, followed by TF scores of 3 and 4 (30%), and 8.4% had TF scores of 7 or higher. Sixty percent of the teeth exhibited loss of the outermost enamel. They did not find any correlation between fluoride content and DF. Preliminary data suggested that milk intake reduces the severity of DF. The study highlighted the apparent positive role of milk on DF, and emphasized the importance of nutrition in management efforts to mitigate DF in the MER and other parts of the world.

Investigation done by Dey et al., (2012), reported the assessment of hydro chemical and geochemical processes controlling the concentration of fluoride in groundwater of a village in India (Boden block, Orissa). The study elucidated the relations between high fluoride concentration in groundwater and geology. From the investigation, it has been concluded that 36.60% water samples of the study area exceed the WHO prescribed limit of 1.5 mg/l. Based on total hardness values, 90% of the water samples of the study area fall under “very hard” category. Whereas, based on TDS value, majority, i.e., 95% of water samples belonged to fresh water type. The groundwater with high HCO_3^- , Na^+ , and higher pH value under the control of water–rock interactions could be responsible for the release of F^- from the aquatic matrix into groundwater level. The study of hydro geochemical facies revealed a strong association exists between high fluoride content

and soft alkaline groundwater depleted in calcium content. Calcite and fluorite are main minerals controlling the aqueous geochemistry with respect to elevated fluoride contamination of the groundwater. The R, calculated as a function of fluoride level in drinking water. Geochemical classification of groundwater based on Chadha rectangular diagram showed that most of the groundwater samples having fluoride concentration more than 1.5 mg/l belonged to the Na-K-HCO₃ type. The saturation index values evaluated for the groundwater of the study area indicated that it is oversaturated with respect to calcite, whereas the same is under saturated with respect to fluorite content. The deficiency of calcium ion concentration in the groundwater from calcite precipitate ion favored fluorite dissolution leading to excess of fluoride concentration. The risk index was calculated as a function of fluoride level in drinking water and morbidity of fluorosis categorized high risk for villages of Amera and Karlakote panchayat of Boden block.

The study of Mangukiya et al., (2012) aimed at assessing the water quality index (WQI) for the groundwater of Surat city. This had been determined by collecting 125 groundwater samples from 39 areas of Surat city and subjecting the samples to a comprehensive physicochemical analysis. For calculating the WQI, the following 13 parameters have been considered: pH, total hardness, calcium, magnesium, chloride, nitrate, sulphate, total dissolved solids, iron, boron, and fluorides, COD and DO. The WQI for these samples ranged from 15.93 to 977.86. The high value of WQI had been found to be mainly from the higher values of iron, nitrate, total dissolved solids, hardness, fluorides, and boron in the groundwater. The results of analyses had been used to suggest models for predicting water quality.

Gupta et al., (2012) undertook a research work on the hydro-geochemical characterization as well as demarcation of fluoride (F⁻) contaminated area by means of GIS modeling. F⁻ Concentration in the study area ranged from 0.20 mg/l to 1.67 mg/l with a mean of 0.72 mg/l. Among the twenty six (26) collected samples from water table sedimentary aquifer of study area 54 % samples had F⁻ concentration < 0.6 mg/l;

and 8% of the samples have concentration > 1.5 thereby unsuitable for drinking purpose. Majority of the water samples fall under the category of Ca-Mg-Cl followed by Ca-HCO₃ type hydro facies. Fluoride had a significant ($p < .05$) positive correlation with bicarbonate (HCO₃⁻) ion and it also shows a positive correlation with sodium (Na⁺) but higher negative correlation with calcium (Ca²⁺). This was attributed to ion-exchange process where Ca²⁺ ions in water may react with clay minerals (sodium-montmorillonite) to release Na⁺ ion in groundwater. All the groundwater samples had $\text{Ca}^{2+} \ll \text{HCO}_3^-$ thereby reflects its precipitation as carbonate. Ion exchange between Ca²⁺ and Na⁺ due to the movement of groundwater in the weathering zone may also result in high F⁻ associated with high Na⁺ and low Ca²⁺ concentration. Gibb's ratio suggested that majority of high-fluoride groundwater samples were mainly attributed to weathering of rocks. Activity diagram between Ca²⁺ vs. F⁻ suggested that all the water samples were unsaturated with respect to fluorite. Raniganj sandstone, containing 248 mg/kg of total F⁻ may be the major contributor of F⁻ in the water-table aquifer of the study area. Output of GIS based thematic map revealed that fluoride distribution might also be structurally controlled. Their study concluded that ion-exchange within Raniganj Sandstone and to some extent evaporation is the major contributing factors of fluoride contamination in the Raniganj coal field area.

The quality of groundwater in the coastal aquifer of eastern Niger Delta had been assessed by Amadi et al., (2012) using Geostatistical techniques. The range, standard deviation and variance of the dataset showed that multi-chemical processes controlled the groundwater quality/facies and their spatial distributions. The result of the multivariate statistical analysis provided an insight into the underlying factors controlling hydro geochemical processes in the area. Six Factors, accounting for 91.18% of the total variance were identified. Factors 1 (Conductivity, Cl⁻, TH, TSS, TDS, Na and Mg), factor 2 (Ca, Fe, pH, NO₃⁻, K and SO₄²⁻), factor 3 (BOD, COD, PO₄²⁻, EC and TC), factor 4 (Cu, F, Mn and Zn), factor 5 (Cr, Pb and Ni) and factor 6 (Ar and Hg) represented the signatures of saltwater intrusion, chemical weathering, leaching and various human activities domiciled in the area. The observed wide range,

high standard deviation and variance in some of the parameters indicated that there were substantial differences in the groundwater quality within the study area. The WQI value was 285.20, which suggested that the groundwater in the area was very poor in quality. The high value of WQI obtained was due to the high concentration of copper, iron, lead, nitrate, TC, EC, COD, chromium, nickel and zinc in the groundwater which can be attributed to both natural and anthropogenic sources. Factors analysis reduced the dataset into six major components representing the different sources of the contaminant. Major contributors to factor 1 and 2 are natural phenomenon while those of factors 3 to 6 were of anthropogenic origin. The water in the area was Calcium-Chloride type from Piper diagram, which suggested that the water might be from a marine source. The effectiveness of Geostatistical techniques (WQI and FA) in groundwater quality studies had been demonstrated in the study.

Shyam and Kalwania (2012) identified the controlling factors of groundwater chemistry, including chemical leaching and fluoride contaminations. The geochemical processes were identified using characterization of the major physico-chemical parameters of ground water from northern part of Sikar city. For this purpose, 15 ground water samples were collected and analyzed for different water quality parameters, such as pH, EC, TDS, TH, TA, DO, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, sulfate and fluoride with the help of standard methods recommended by American Public Health Association. The analysis indicated that fluoride concentrations in four samples are at alarming state as compared to the World Health Organization standards for drinking purposes, thereby suggesting the need for treatment and precautionary measures for use of the particular ground water. To classify the ground water ability for different purposes various graphical plots like Piper tri-linear, Durov, Schoeller, Bar, Scatter diagrams had been drawn. The analysis revealed that most of the samples in the western part of Sikar city were slightly alkaline. Some of the samples showed the value of TDS, EC, nitrate and chloride more than the permissible limit prescribed by WHO. The other water quality parameters such as pH, K^+ , Mg^{2+} , CO_3^{2-} , HCO_3^- , SO_4^{2-} and DO were within permissible

limit. The fluoride ion concentration in four samples was more than 1.5 mg/l. Sample no S-58 and S-71 contains this concentration more than 2.5 mg /l. Most of the samples showed the negative value of CAI-I index suggesting a exchange between sodium and potassium (Na^+ , K^+) in water with calcium and magnesium (Ca^{2+} , Mg^{2+}) in the rocks through a type of base-exchange reaction. The increased fluoride level in the ground water of Sikar city was due to the some geological process such as dissolution of fluoride rich mineral (fluorspar) in the environment of alkaline pH, excess of bicarbonates, evaporation, semi aridity and high temperature.

High fluoride contents in the water supply of the city of Ponta Delgada, located in the volcanic island of São Miguel (Azores, Portugal) had been reported by Cordeiro et al., (2012). The study was carried out in order to characterize the natural F-pollution of a group of springs (30) and wells (3) that were associated to active central volcanoes of a trachytic nature. Two springs known for their high content in fluoride were sampled, both located in the central volcano of Furnas. The sampled waters were cold, ranging from slightly acidic to slightly alkaline (pH range 6.53–7.60), exhibiting a low electrical conductivity (springs range 87–502 $\mu\text{S}/\text{cm}$; wells range 237–1761 $\mu\text{S}/\text{cm}$), and were mainly from the $\text{Na}-\text{HCO}_3$, $\text{Na}-\text{HCO}_3-\text{Cl}$ and $\text{Na}-\text{Cl}-\text{HCO}_3$ water types. Results suggested two main trends of geochemical evolution: silicate weathering, enhanced by CO_2 dilution, and seawater spraying. Fluoride contents range between 0.17 mg/l and 2 mg/l, and no seasonal variations were detected. Results in the sources of the water supply system were lower than those of the Furnas volcano, which reached 5.09 mg F/l demonstrating the effect of F-rich gaseous emanations in this area. Instead, the higher fluoride contents in the water supply were mainly due to silicate weathering in aquifers made of more evolved volcanic rocks. The composition of the groundwater sampled during the study was modified by two main geochemical processes: CO_2 dissolution and water–rock interaction and marine airborne salts. Considering the fluoride content in groundwater, it was possible to establish a closer positive relation between F and Na in the more F-enriched samples. The relation between F and Ca content, with the former suggested a contribution from leaching of more evolved rocks

of acidic nature, such as pumice pyroclastic deposits. In fact, results gathered showed that the higher F contents are associated to Na in aquifers made of trachytic rocks due to silicate weathering, and not from a direct volcanic input, which influenced the waters of Furnas.

The hydro-geochemical study by Sarath Prasanth et al., (2012) was confined to the coastal belt of Alappuzha district, which lies in the coastal lowland division of Kerala. Groundwater quality and its suitability for irrigation and domestic purpose were examined by various physico-chemical parameters such as pH, electrical conductivity, total dissolved solids, total hardness, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, and chloride. These parameters were used to assess the suitability of ground-water for domestic purpose by comparing with the WHO and Indian standards. TDS, sodium adsorption ratio (SAR), and permeability index were used for irrigation suitability assessment. The sample analysis revealed that the ground-water was not entirely fit for drinking with respect to pH, EC, Ca, Mg, Na, and Cl^- . In some of the collected samples, the concentrations of these parameters exceed the permissible limits of WHO and ISI standards. Based on TDS and SAR almost all samples were suitable for irrigation purpose except a few locations, which showed values beyond the permissible limits. They found that Ca-Mg-HCO_3 is the dominant water type in the study area. The sequence of the abundance of the major cations and anions was $\text{Ca} > \text{Na} > \text{Mg} > \text{K} = \text{HCO}_3 > \text{Cl} > \text{SO}_4$. Based on the total hardness and TDS, 96 % of groundwater samples were found suitable for drinking purpose.

The study of Gupta et al., (2011) reports fluoride (F) accumulation in vegetables and a cultivated crop together with dietary F intake among a selected group of adults in Junitpur, an F-endemic area of the Birbhum district, West Bengal. Variable F accumulation occurred in a cultivated crops (mustard) and vegetables (spinach, coriander, marcellia, potato, tomato, brinjal, onion, and beans). The fluoride content of leafy vegetables was found to be higher [transfer factor (TF)>1] than that of fruiting and tuber vegetables as well as seed crops. Analysis of the diet of eight adults in four

families (4 males and 4 females, age 30–40 and 25–35, respectively), revealed that drinking water contributed 43%, rice meal 26%, and vegetables 30% to the total mean F intake. They suggested that to reduce the risk of human exposure to F, the use of F-contaminated irrigation water, especially for crops that tend to accumulate F, should be reduced as much as possible. They advised to grow crops with relatively low capabilities to enrich F, such as those with seeds or tubers as the main edible parts.

An extensive geochemical study was performed by Gautam et al., (2011) taking 27 villages of eastern, south-eastern and southern zone of Nawa tehsil was done. Total 46 ground water samples were collected and analyzed for various physicochemical parameters as well as fluoride content. The ground water samples collected in clean polyethylene plastic containers were analyzed for pH, electrical conductivity, total dissolved salts, calcium, magnesium, total hardness, chloride and alkalinity. The fluoride concentration in the three different zones ranged from 0.64 to 14.62 mg/l where 13.04% samples were found within permissible limit while 86.96% had fluoride beyond permissible limit (> 1.5 mg/l). It was found that among the three different zones south-eastern zone was under serious fluoride contamination where fluoride concentration ranged between 1.10 to 14.62 mg/l. In the eastern zone fluoride concentration was recorded from 1.52 to 5.13 mg/l whereas in the southern zone it was found between 0.64 to 3.63 mg/l.

Borah (2011) made a study collecting the ground water samples from different locations of the Dibrugarh district. He measured for fluoride concentration and some other physico-chemical properties. Water samples were collected from tea gardens and brick industry areas of the district in the month of January-February of 2011. Ground water of the study area was found slightly acidic in nature with pH range 5.3-7.3. Ion selective electrode method was employed for measuring the fluoride concentration. Fluoride level was found in the range from 0.0222 to 0.5789 mg/l, which is quite below the maximum permissible level, 1.5 mg/l. No case of fluorosis was found in the study area. He concluded that low level of fluoride in the study area may be attributed to the absence of fluoride bearing minerals. He assumed that due to the adsorption of fluoride

by acidic soil and dilution because of heavy rain inhibited the increase of fluoride level in spite of using huge amount of fertilizers and pesticides containing fluoride impurities in the tea gardens.

Paul et al., (2011) estimated fluoride levels of water, soil and vegetables from four irrigation farms at the bank of Basawa River, Zaria, Nigeria using Alizarin red spectrometric method. The soil samples from the four farms had a mean soil leachable fluoride in the range of 0.091 mg/Kg to 0.135 mg/Kg, while the river water had mean fluoride levels in the range 0.081 to 0.191 mg/Kg. The mean concentration of soil leachable fluorides for soils from the farms, at 95% confidence limit, were 0.110 ± 0.011 , 0.108 ± 0.001 , 0.114 ± 0.012 and 0.108 ± 0.001 mg/Kg for farms A, B, C and D respectively. At the same confidence limit, the mean fluoride concentration for the river water Upstream, Midstream and Downstream were 0.148 ± 0.027 , 0.152 ± 0.036 and 0.137 ± 0.013 mg/Kg, respectively. T-test was used to evaluate and compare mean values of fluoride in the different vegetables. At 95% confidence interval ($p = 0.05$) and 18 degrees of freedom, with critical value of 2.26, the $|t_{\text{exp}}|$ were 0.600, 1.986, 2.649, 1.924, 2.858 and 0.772 for Cabbage and Garden Egg, Cabbage and Onion, Cabbage and Tomato, Garden Egg and Onion, Garden Egg and Tomato and Onion and Tomato respectively. The only significant difference was observed for the fluoride levels of Cabbage and Tomato, and Garden Egg and Tomato where $t_{\text{exp}} > \text{Critical value}$. The fluoride values obtained were all below the toxic limit of 2.57 to 16.44 mg/Kg for soil and maximum contaminant level of 4.0 mg/Kg for water, food and vegetables as stipulated by the joint EPA, FAO, and WHO Standard limit for fluoride. The implications of the results are discussed. The results showed that the use of the Basawa river water for irrigation had no deleterious effect on the soil and vegetables cultivated at the precinct of the river. Also, the contribution of fluoride to the soil, river water and vegetables from anthropogenic sources within and around the Basawa river area was not ultimately damaging to human health. But they suggested to employ caution in the utilization of the crops as continuous ingestion may result in considerable increase in the daily dietary intake leading to deleterious bioaccumulation in the human body.

A study was carried out by Jha et al., (2011) to assess toxicological risk from the fluoride (F) exposure due to ingestion of vegetables and cereal crops such as rice and wheat grown in potentially fluoridated area (brick kiln and sodic areas), of different age groups in Unnao district, Uttar Pradesh, India. Fluoride contents in vegetables and cereal were found to be in the order brick kiln sites > sodic sites > normal sites. Among vegetables maximum F concentration was found in spinach and mint, whereas in cereal crops, wheat accumulated more F than rice. The exposure dose of F was determined using estimated daily intake (EDI) and bio-concentration factor (BCF) of F. The children of age group 3–14 years in the potentially fluoridated area were found to be at the risk of fluorosis. The mean BCF value of F was the highest in mint (36.6 mg/kg_{dwt} plant/mg/kg_{dwt} soil), followed by spinach (33.99 mg/kg_{dwt} plant/mg/kg_{dwt} soil). The exposure doses of F from the consumption of vegetables and cereal crops in children (3–14 years of age) were found to be higher than the limits laid down by IOM. This means the children in this age group were more likely at the risk of fluorosis from consumption of vegetables and cereal grown in the fluoridated areas. They concluded that in children (15–18 years) and adults the exposure dose did not exceed the toxicity threshold limits prescribed by ATSDR and IOM but when the dietary intake from all other sources such as water used in cooking food, drinking water, tooth paste, etc. are considered, it may exceed the limits and will be having toxic effects on human health. The bio-concentration factors calculated in this study clearly indicated that the F accumulation in vegetables and cereal crops is mainly due to soluble F present in the soil, taken by the plant.

According to Sharma et al., (2011) high concentration of fluoride is present in groundwater in Agra district in Uttar Pradesh, India and weathering of rocks and evaporation of groundwater are responsible for the high fluoride concentration. The study was carried out to understand the status of groundwater quality in Agra and also to assess the possible causes for high concentration of fluoride in groundwater. The fluoride concentration in groundwater of this region ranged from 0.1 to 14.8 mg/l.

Fluoride in groundwater of this region was mainly due to dissolution from fluoride bearing minerals like Fluorspar, Fluorite etc. 71% Samples were found exceeding permissible limit in the study area and local people ingested the groundwater without any medical attention.

Brindha et al., (2011) conducted a study to find out the status of groundwater in parts of Nalgonda district. Samples from 45 wells were collected once every 2 months and analyzed for fluoride concentration using an ion chromatograph. The fluoride concentration in groundwater of this region ranged from 0.1 to 8.8 mg/l with a mean of 1.3 mg/l. About 52% of the samples collected were suitable for human consumption. However, 18% of the samples were having less than the required limit of 0.6 mg/l, and 30% of the samples possessed high concentration of fluoride, i.e., above 1.5 mg/l. Weathering of rocks and evaporation of groundwater were responsible for high fluoride concentration in groundwater of this area apart from anthropogenic activities including irrigation which accelerated weathering of rocks.

Borah and Saikia (2011) monitored the quality of ground water of Tinsukia town master plan area of the Tinsukia district, Assam. In their study fluoride concentration along with metals-calcium and magnesium and some physico-chemical properties were measured. 30 water samples were collected from different locations of the study area. All the water samples were collected from hand tube wells, motor pumps and public water supply schemes. Ground water of the study area was found slightly acidic in nature. Fluoride level varied from 0.0912 mg/l to 0.2283 mg/l. In all the water samples fluoride concentration was found quite below than the acceptable range 0.6 mg/l to 1.2 mg/l.

The study of Arveti et al., (2011) examines the fluoride content of well water in different parts of Talupula area of Anantapur district, Andhra Pradesh. It also focused on fluorides and their relationship to water-quality parameters and their impacts on humans through groundwater resources. Most parts of the area covered in this region

were inherently enriched with fluorides threatening several ecosystems. The fluoride concentration ranged between 0.78 and 6.10 mg/l. Large percentage of the groundwater samples possessed fluoride concentrations greater than 1.5 mg/l. The water samples in the study area showed enrichment of sodium, magnesium, and calcium among cations and bicarbonate among anions. They concluded that the alkaline pH and high bicarbonate were responsible for release of fluoride-bearing minerals into groundwater. The arid climate of the region, the granitic rocks and the low freshwater exchange due to periodical drought conditions are the factors responsible for the higher incidence of fluorides in the ground- water resources.

Vinod et al., (2011) assessed the groundwater quality for drinking, domestic and irrigation in the village Lutfullapur Nawada, Loni, district Ghaziabad, U.P., India. Groundwater samples were collected, processed and analyzed for temperature, pH, conductivity, salinity, total alkalinity, carbonate alkalinity, bicarbonate alkalinity, total hardness, calcium hardness, magnesium hardness, total solids, total dissolved solids, total suspended solids, nitrate-nitrogen, chloride, fluoride, sulfate, phosphate, silica, sodium, potassium, calcium, magnesium, total chromium, cadmium, copper, iron, nickel, lead and zinc. A number of groundwater samples showed levels of electrical conductivity (EC), alkalinity, chloride, calcium, sodium, potassium and iron exceeding their permissible limits. Except iron, the other metals (Cr, Cd, Cu, Ni, Pb, and Zn) were analyzed below the permissible limits. The correlation matrices for 28 variables were performed. EC, salinity, TS and TDS had significant positive correlations among themselves and also with NO_3^- , Cl^- , alkalinity, Na^+ , K^+ , and Ca^{2+} . Fluoride was not significantly correlated with any of the parameters. NO_3^- was significantly positively correlated with Cl^- , alkalinity, Na^+ , K^+ and Ca^{2+} . Chloride also correlated significantly with alkalinity, Na^+ , K^+ and Ca^{2+} . Sodium showed a strong and positive correlation with K^+ and Ca^{2+} . pH was negatively correlated with most of the physicochemical parameters. This groundwater was classified as a normal sulfate and chloride type. Base-exchange indices classified 73% of the groundwater sources as the $\text{Na}^+ - \text{SO}_4^{2-}$ type. Meteoric genesis indices demonstrated that 67% of groundwater sources belong

to a deep meteoric water percolation type. Hydro chemical groundwater evaluations revealed that most of the ground waters belong to the $\text{Na}^+ - \text{K}^+ - \text{Cl}^- - \text{SO}_4^{2-}$ type followed by $\text{Na}^+ - \text{K}^+ - \text{HCO}_3^-$ type. Salinity, chlorinity and SAR indices indicated that majority of groundwater samples can be considered suitable for irrigation purposes.

Hydro geochemical investigation of fluoride contaminated groundwater samples from Kolar and Tumkur Districts in Karnataka were undertaken by Mamatha and Rao (2010) to understand the quality and potability of groundwater from the study area, the level of fluoride contamination, the origin and geochemical mechanisms driving the fluoride enrichment. Majority of the groundwater samples did not meet the potable water criteria as they contained excess (1.5 mg/l) fluoride, dissolved salts (500 mg/l) and total hardness (75–924 mg/l). Hydro geochemical facies of the groundwater samples suggested that rock weathering and evaporation–crystallization control the groundwater composition in the study area with 50–67% of samples belonging to the Ca-HCO_3 type and the remaining falling into the mixed Ca-Na-HCO_3 or Ca-Mg-Cl type. The saturation index values indicated that the groundwater in the study area is oversaturated with respect to calcite and under-saturated with respect to fluorite. They concluded that the deficiency of calcium ion concentration in the groundwater from calcite precipitation favors fluorite dissolution leading to excess fluoride concentration.

Ghosh et al., (2010) assessed the health risks associated with fluoride- contaminated groundwater in Birbhum district of West Bengal, India. They analyzed the fluoride-induced oxidative stress damage parameters of the male inhabitants and to mitigate such impact by antioxidant vitamin supplementation. Seventy-five male dwellers residing at Noapara, Nasipur, Zunitpur, Bhabanandapur, Chakpara, and Atla of Birbhum district within the age group of 25-35 years were selected. From the physiological and clinical point of view, almost 95% of the subjects were found to suffer from dental and skeletal fluorosis. Some of the photographs taken ensured the fact. They were randomly divided into three groups of 25 men each. Vitamin E (clinical dose); a mixture of vitamin E, vitamin C, β -carotene and reduced glutathione were

supplemented in the three groups for 21 days along with peppermint lozenges as placebo. The hemoglobin levels, body mass index, glucose-6-phosphate dehydrogenase level, and malondialdehyde status were assessed before and after supplementation. Standard methods were used to analyze the groundwater samples from these areas for their chloride, fluoride, and iron concentrations. The acute fluoride toxicity had been established in the groundwater samples. Results indicated that vitamin mixture and glutathione supplementation together may be treated as an important detoxification technique against detrimental effects of fluoride toxicity to male inhabitants, at least partially.

Fluoride concentrations in water samples (surface and ground) were determined by Dutta et al., (2010) in fifteen small tea gardens of Sonitpur district, Assam, India. Forty-five samples were collected and analyzed for Fluoride content along with pH, electrical conductivity (EC), total hardness (TH), sulphate (SO_4^{2-}), nitrate (NO_3^-), phosphate (PO_4^{2-}), chloride (Cl^-), calcium (Ca^{++}) and magnesium (Mg^{++}). Fluoride concentration varied from 0.17 ppm to 5.602 ppm. Fluoride concentration was not uniform of all the tea gardens area. Physicochemical conditions like decomposition, dissociation, subsequent dissolution and agrochemicals might be responsible for leaching of fluoride in to the drinking water sources. From the correlation analysis F^- contents was found to be negatively correlated with Ca^{2+} , Mg^{2+} and Total hardness and positively correlated with pH, SO_4^{2-} and Cl^- .

Groundwater in Keta strip of Keta basin was assessed by Yidana et al., (2010) for its quality for use for both domestic and irrigation purposes. A groundwater classification scheme had been developed for groundwater in the area using a robust water quality index (WQI) modified for the case of the Keta basin. On the basis of the WQI so computed, groundwater in the area had been spatially classified into 'good', 'fair', and 'marginal' water types using ordinary kriging developed from a well fitted linear semivariogram function. The analysis of the data suggested that 51.5% of the wells sampled provided water of good quality for drinking purposes. Thirty eight and a half

percent (38.5%) and 10% of the wells deliver groundwater of fair and marginal quality respectively for human consumption. They concluded that the poor performance of most of the samples on the WQI is attributable to high concentrations of the F^- , NO_3^- , and TDS. Multivariate analysis of the hydrochemical parameters suggested that groundwater quality is attributed largely to the weathering of silicate and accessory minerals as well as seawater effects. This study found that the salinity of groundwater in the basin is largely attributed to mineral weathering and seawater intrusion. Groundwater is stable within kaolinite and Na-smectite field, suggesting the predominance of Na-rich silicate minerals over the high temperature Ca-rich minerals. Four groundwater clusters had been distinguished: clusters 1 and 4 are low salinity Ca- HCO_3 waters distinguished by differences in pH, whereas clusters 2 and 3 represented high and intermediate salinity Na-Cl waters respectively. The study found that clusters 1 and 4 present the best water types for irrigation purposes in the Keta basin. On account of high salinity, cluster 2 members were not suitable for irrigation of any crop in the basin. Sodium adsorption ratio (SAR) appears to display weak seasonal variations. During dry seasons when the water table became low, saline water intrusion elevated the content of sodium in groundwater.

The work of Avishek et al., (2010) involved the assessment of water quality with special reference to fluoride in Majhiaon block of Garwa district in Jharkhand. Iron, nitrate and arsenic were also tested for the water samples collected from site. Eight hundred forty samples were tested for fluoride on site using colorimetric method, and one tenth of the samples were brought to laboratory for iron, nitrate, and arsenic and fluoride analysis. Results showed that 402 samples were having fluoride above permissible limit. Iron and nitrate were found to be beyond permissible limits in 302 and 286 water samples, respectively. More than 50% of samples collected from school had fluoride levels above permissible limits. Arsenic was well within the limits. However, few samples shown were excessive of iron and nitrate. It was also observed that more than 50% samples collected from schools had non-permissible limits of fluoride concentration. Dental fluorosis was widely seen in the study area; however there were cases of skeletal fluorosis. But the cases of skeletal fluorosis were

mainly identified in families that were malnourished. It could be attributed to the lower intake of calcium-based products like milk. Cases of dental fluorosis had been observed in all age groups of population. Eighty percent of samples surveyed from 12 villages (Fig. 7) had shown non-permissible limits of fluoride.

Gautam and Bhardwaj (2010) illustrated the groundwater quality of randomly selected villages of Nawa tehsil. Fluoride in ground water showed positive correlation with alkalinity in their study. A positive correlation had also been observed between fluoride and pH ($r = 0.75$), Total Dissolved Solids ($r = 0.14$), Total Alkalinity ($r = 0.82$), Na ($r = 0.62$) and SO_4^{2-} ($r = 0.56$). This positive correlation of fluoride with pH and alkalinity explained on the basis that high bicarbonate concentration in water at relatively higher pH can replace fluoride from minerals surfaces. In the study area hardness varied from 20 mg/L (Shimbhupura village) to 4560 mg/l (Rulaniyo ki Dhani in Govindi village). The study revealed a negative correlation between total hardness and fluoride concentration. Calcium content ranged from 3.20 mg/l (Shimbhupura village) to 769.53 mg/l (Rulaniyo ki Dhani in Govindi village) whereas magnesium contents were recorded between 2.93 mg/l (Shimbhupura village) to 643.79 mg/l (Rulaniyo ki Dhani in Govindi village). Chloride was recorded minimum 38.34 mg/l in Kukanwali and maximum 4245.8 mg/l in Rulaniyo ki dhani in Govindi village. Discharge of domestic sewage is the most important source of chloride in water. Electrical conductivity ranged between 1062 $\mu\text{mho/cm}$ (Motipura ki dhani in Anandpura village) to 9760 $\mu\text{mho/cm}$ (Rulaniyo ki dhani in Govindi village), while TDS varied from 760 mg/l in Deosar village to 6420 mg/l in Rulaniyo ki dhani in Govindi village.

Patra et al., (2010) studied on the occurrence of fluoride rich groundwater in Asanjola, Madhabpur and Narayanpur villages of Birbhum District in West Bengal, India and its relation with major chemical constituents of the ground water. High concentration (1.3 to 20.9 mg/L) of fluoride was detected in 6 out of the total 43 sampled tube wells. Fluoride content was found to exhibit considerable variation within short distances.

Fluoride enriched tube wells appeared to follow a linear tract; however, no relation with topography could be ascertained. Fluoride concentration showed a significant (>0.389 at probability level <0.01) positive relation to pH, sodium and carbonate whereas a negative relation to magnesium and calcium. The degree of weathering of the silicate minerals as indicated by the sodium acquired by the ground waters seems to have a decisive role in fluoride enrichment process. According to their study, during the process of chemical weathering, sodium was released into the ground waters, as the minerals change to montmorillonite phase. Thus the degree of weathering is indicated by the sodium acquired by the ground waters. High fluoride and very low Ca in water may be due to prior precipitation of CaCO_3 from water with limited incorporation of F^- in CaCO_3 structure. Alternatively, Ca might have replaced by Na in cation exchange reactions. In acidic medium, fluoride was absorbed in clay, whereas high pH, alkalinity (CO_3^{2-}) of the draining solution favours the leaching of fluoride from the rocks. They concluded that the availability of F^- in leachable state in a soil horizon is more important in deciding the fluoride in water rather than the mere presence of fluoride rich minerals.

Veeraputhiran and Alagumuthu (2010) analyzed the most extensive database on fluoride and other chemical constituent distribution in arid tract of Ottapidaram block, Tamilnadu, India where it is the only source of drinking water. The study was conducted in the summer season (May – June, 2010). The water samples of 61 village panchayats were tested; 81.97% had injurious fluoride level above than 1.5 mg/l. The fluoride concentration in drinking waters varied from 0.936 to 4.34 mg/L in the study area. Due to the high concentration of fluoride, dental fluorosis was also identified. Majority of the samples do not comply with Indian as well as WHO standards for most of the water quality parameter. In addition, Fluoride concentration was not correlated with other physicochemical parameters significantly in ground water. Overall water quality was found as unsatisfactory for drinking purposes without any prior treatment except at eleven locations out of 61.

Kundu and Mandal (2010) reported the fluoride concentration in groundwater in the north 24-paraganas district of west bengal, india. In their study one hundred and sixty samples of ground source drinking water were collected at different depths in the 24-Paraganas District of West Bengal and analysed for pH, electrical conductivity (EC), and fluoride (F). Nearly all the samples had pH \sim 7.0, low salinity ($EC < 1.0$ ds/m), and low F (0.01–1.18 mg/l). While exhibiting little dependence on location or depth of sampling, only 2.5% of the samples contained more than 1.0 mg F/L that might pose a potential threat of endemic fluorosis. On the other hand, the F content in the water had a significant positive correlation ($r = 0.16$, $p < 0.05$) with the amount of phosphate fertilizer use, thereby indicating its possible role in F enrichment of the groundwater. The threat of F toxicity existed for a few villages in the district.

In 2010, Alagumuthu and Rajan made Chemometric studies of water quality parameters of Sankarankovil block of Tirunelveli, Tamilnadu. They determined the fluoride concentration in ground water in Sankarankovil block of Tirunelveli district of Tamilnadu (India) where it is the only source of drinking water. Various other water quality parameters such as pH, electrical conductivity, total hardness and total alkalinity as well as calcium, magnesium, carbonate, bicarbonate and chloride concentrations were also measured. A systematic calculation of correlation co-efficient among different physico-chemical parameters was performed. The analytical results indicated considerable variations among the analyzed samples with respect to their chemical composition. Majority of the samples do not comply with Indian as well as WHO water quality standards. The fluoride concentration in the ground water of these villages varied from 0.66 to 3.84 mg/l, causes dental fluorosis among people especially children of these villages. The high and low fluoride containing areas were located using isopleth mapping technique. Overall water quality was found unsatisfactory for drinking purposes without any prior treatment except at few locations out of 50 villages.

Okibe et al., (2010) reported the fluoride Content of Soil and Vegetables from Irrigation Farms on the Bank of RiverGalma, Zaria, Nigeria. Fluoride content of the soils and some vegetables from three farms near the bank of river Galma, Zaria, Nigeria were estimated by Alizarin red spectrometric method. The mean soil leachable fluorides for all the soils were in the 0.075 - 0.200 mg/Kg range. At 95 % confidence limit ($p=0.05$), the mean concentration of soil leachable fluoride for soils from the farms A, B, and C investigated were 0.139 ± 0.030 , 0.115 ± 0.041 , and 0.080 ± 0.005 mg Kg⁻¹ respectively. The mean fluoride content in vegetable at the same confidence limit was Cabbage: 0.054 ± 0.0093 mg Kg⁻¹, Carrot: 0.035 ± 0.01 mg Kg⁻¹, and Lettuce: 0.096 ± 0.0199 mg Kg⁻¹. The t_{exp} evaluated to compare the averages of fluoride levels in the vegetables using t-test at 95% confidence level ($p=0.05$) for 18 degrees of freedom, 2.10 critical value, were 1.62, 5.77, and 1.84 for lettuce and cabbage, carrot and cabbage, and carrot and lettuce respectively. Significant difference only exists in the fluoride levels of carrot and cabbage with $t_{exp} >$ the critical value. All the values obtained were well below the toxic limit of 2.57-16.44 mg/Kg in soil and maximum contaminant level of 4.0 mg/Kg in food and vegetable stipulated by EPA, FAO, and WHO Joint Standard limit for fluoride. The implication of the results was that the use of the Galma river water for irrigation, and the contribution of fluoride to the soil and vegetables from anthropogenic sources within and around the Galma river area, had no deleterious effect on the soil and some vegetables cultivated in farms at the river bank.

Gautam and Bhardwaj (2010) investigated bioaccumulation of fluoride in different plant parts of *Hordeum vulgare* (barley) var. rd-2683 from irrigation water. Investigation of fluoride (F) accumulation in *Hordeum vulgare* (barley) var. RD-2683 and its effect on the growth and crop yield was conducted in a pot experiment. Six different concentrations of F in the water were used for irrigation ranging from 4 to 20 ppm with distilled water as the control. Potentiometric determinations of the F content in different parts of the plant were made 45, 90, and 135 days after sowing the seeds (first, second, and third harvest, respectively). At the third harvest the highest mean plant part concentrations of F were recorded with 20 ppm F in the irrigation water and

17.36 µg/g in the roots, 13.06 µg/g in the shoots, 11.74 µg/g in the leaves, and 14.44 µg/g in the crop (grain).

Bhargava et al., (2010) studied the effect of sodium fluoride on seed germination and Seedling growth of *Triticum aestivum* var. Raj. 4083. They studied the effects of 4, 8, 12, 16 and 20 mg/l sodium fluoride (NaF) were studied on *Triticum aestivum* var. Raj. 4083 seeds and seedling growth. After 7 days of treatment with control, 100% germination occurred, but at 20 mg NaF/L, germination was reduced to 88%. Physiological parameters, viz., root length, shoot length and dry weight decreased with increasing NaF concentration. At 20mg NaF/L, the average root length, shoot length and dry weight were reduced by 36.6%, 24% and 20.54% respectively. At 20 mg NaF/L, Vigor index was reduced by 37.20% compared to control. The chlorophyll content of the leaves was also reduced monotonically. At 20mg NaF/L, it was 0.074 mg/g which was 27.45% lesser compared to control. Ascorbic acid content initially decreased and then increased with increasing concentration of NaF (20 mg/l). So our study concludes that sodium fluoride has significant impact on seed germination and seedling growth of wheat.

Dave et al., (2010) studied the status of fluoride in ground water of several villages of Modasa Taluka, North Gujarat for drinking purpose. Fluoride concentration of ground water samples from several villages of Modasa taluka, Dist-Sabarkantha (N.G.) was determined. Out of 88 sources of 23 villages 34 sources were found to have fluoride concentration 1.0 mg / l. 52 sources were found to have fluoride concentration 1.0 to 1.5 mg/l. which is maximum desirable limit of drinking water standards. 2 sources were found to have fluoride concentration between 1.5 to 3.0 mg/l. In these villages there are maximum possibilities of dental and skeletal fluorosis.

Paya and Bhatt (2010) reported fluoride contamination in groundwater of Patan district, Gujarat, India. They found that the major source for drinking and irrigation water in North Gujarat is groundwater. High concentration of fluoride in the groundwater

posing health hazard has been observed in Patan district. The upper unconfined aquifers consisting of weathered mantle represents the main source for fluoride in groundwater of this region. Study was conducted to work out seasonal variation in fluoride content of ground water from different sites in Patan district of North Gujarat region. Water samples were collected from dug well bore well and water-harvesting structures of selected sites during different seasons. Seasonal variations in fluoride concentration in groundwater had been studied during the period from December 2006 to November 2007. Maximum value of fluoride was recorded during summer (May-June) and minimum during post monsoon (September-November) period. The physicochemical and microbiological analysis of groundwater was performed by employing standard water analysis methods. The physico-chemical parameters tested were DO, BOD, COD, pH, conductivity, TDS, nitrate, nitrite, sodium, potassium etc and the results of physico-chemical analysis of water were discussed.

Raju and Das (2009) reported Fluoride contamination in groundwaters of Sonbhadra District, Uttar Pradesh, India Preliminary investigations indicated that severe health disorders had been identified in parts of the Kachnarwa region, which was in the upper Panda river basin, Sonbhadra District, Uttar Pradesh, due to excess intake of fluoride through drinking water. The lithological units of the study area mainly consisted of granite and gneissic complex rocks of the Chota-Nagpur Plateau. In order to understand the probable source of fluoride and its concentration, 17 groundwater samples mostly from granite and phyllite regions were collected for fluoride estimation during May 2006. The concentration of fluoride in the groundwater of the study area varied from 0.483 to 6.7 mg/l. Among the 17 samples analyzed, 8 exceeded the maximum permissible limits of fluoride in the study area. The source of fluoride in the groundwater of the study area was mainly from geological occurrence (i.e. fluoride bearing minerals, viz. apatite and biotitic mica). Microscopic analysis of the rock samples showed 5–10% apatite and 20–25% biotite, but other fluoride-bearing minerals like fluorite and hornblende were characteristically absent. X-ray diffraction studies showed that apatite mineral peak profile of the rock samples corroborated with the

fluorapatite of the standard set by the JCPDS. Most people in these villages suffered from dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments, bending of spinal column and ageing problem.

Ramakrishnaiah et al., (2009) assessed the Water Quality Index for the Groundwater in Tumkur Taluk, Karnataka State, India. They aimed at assessing the water quality index (WQI) for the groundwater of Tumkur taluk. This had been determined by collecting groundwater samples and subjecting the samples to a comprehensive physicochemical analysis. For calculating the WQI, the following 12 parameters had been considered: pH, total hardness, calcium, magnesium, bicarbonate, chloride, nitrate, sulphate, total dissolved solids, iron, manganese and fluorides. The WQI for these samples ranged from 89.21 to 660.56. The high value of WQI had been found to be mainly from the higher values of iron, nitrate, total dissolved solids, hardness, fluorides, bicarbonate and manganese in the groundwater. The results of analyses had been used to suggest models for predicting water quality.

Gupta et al., (2009) made study on the phytotoxicity of fluoride in the germination of paddy (*oryza sativa*) and its effect on the physiology and biochemistry of germinated seedlings. The study reported the influence of 0, 10, 20, and 30 mg/l sodium fluoride (NaF) on paddy (rice, *Oryza sativa*) seeds and seedlings. After 15 days of treatment with 0 and 10 mg NaF/L, 100% germination occurred, but at 20 and 30 mg NaF/L, germination reduced to 96 and 92%, respectively. Physiological parameters (root length, shoot length, and dry weight) decreased monotonically with increasing NaF concentration. At 30 mg NaF/L the average root length, shoot length, and dry weight were reduced to 50%, 27%, and 29%, respectively. The chlorophyll content of the leaves also decreased monotonically, but the reducing sugar and ascorbic acid content initially decreased and then increased with increasing concentration of NaF. Uptake of fluoride in the whole plant body increased with increasing levels of NaF; at 10 mg NaF/L. The accumulation was less than 75 mg/kg dry mass, but at 20 mg/l NaF it increased to 2000 mg/kg and doubled this level at 30 mg/l NaF.

Kundu et al., (2009) found a functional relationship between nitrate and fluoride contamination in groundwater of an intensively managed agroecosystem. They conducted a study to assess the potential hazards of nitrate-nitrogen ($\text{NO}_3\text{-N}$) and fluoride (F) contamination in drinking groundwater as a function of lithology, soil characteristics and agricultural activities in an intensively cultivated district in India. Two hundred and fifty two groundwater samples were collected at different depths from various types of wells and analyzed for pH, electrical conductivity (EC), $\text{NO}_3\text{-N}$ load and F content. Database on lithology, soil properties, predominant cropping systems, fertilizer and pesticide uses were also recorded for the district. The $\text{NO}_3\text{-N}$ load in groundwater samples were low ranging from 0.12 to 6.58 $\mu\text{g/ml}$ with only 8.7% of them contained greater than 3.0 $\mu\text{g/ml}$ well below the 10 $\mu\text{g/ml}$, the threshold limit fixed by WHO for drinking purpose. Samples from the habitation areas showed higher $\text{NO}_3\text{-N}$ content over the agricultural fields. The content decreased with increasing depth of wells ($r = -0.25$, $P \leq 0.01$) and increased with increasing rate of nitrogenous fertilizer application ($r = 0.90$, $P \leq 0.01$) and was higher in areas where shallow- rather than deep-rooted crops ($r = -0.28$, $P \leq 0.01$, with average root depth) are grown. The $\text{NO}_3\text{-N}$ load also decreased with increasing bulk density ($r = -0.73$, $P \leq 0.01$) and clay content ($r = -0.51$, $P \leq 0.01$) but increased with increasing hydraulic conductivity ($r = 0.68$, $P \leq 0.01$), organic C ($r = 0.78$, $P \leq 0.01$) and potential plant available N ($r = 0.82$, $P \leq 0.01$) of soils. Fluoride content in groundwater was also low (0.02 to 1.15 $\mu\text{g/ml}$) with only 4.0% of them exceeding 1.0 $\mu\text{g/ml}$ posing a potential threat of fluorosis. On average, its content varied little spatially and along depth of sampling aquifers indicating little occurrence of F containing rocks/minerals in the geology of the district. The content showed a significant positive correlation ($r = 0.234$, $P \leq 0.01$) with the amount of phosphatic fertilizer (single super phosphate) used for agriculture. Results thus indicated that the groundwater of the study area was safe for drinking purpose but some anthropogenic activities associated with intensive cultivation had a positive influence on its loading with $\text{NO}_3\text{-N}$ and F.

Chunlei Li et al., (2009) reported the effect of fluoride on chemical constituents of tea leaves. Seedlings of the tea plant, *Camellia sinensis* (L.), were grown hydroponically for 30 days to study the effect of fluoride (F) on the chemical composition and minerals in the leaves. Polyphenols, total catechins, and protein decreased significantly with increasing exposure to F. Except for epigallocatechin, most of the monomeric catechins also decreased significantly. These changes are not considered beneficial. On the other hand, the content of amino acids and soluble sugars increased significantly, but the differences in caffeine and water-soluble extracts were not statistically significant. Except for magnesium and manganese, the uptake of most of minerals was inhibited, whereas the content of F increased markedly. These results suggested that the main chemical constituents of tea leaves decreased under F treatment and that individuals who consume these teas may ingest excessive amounts of F.

Fluoride accumulation in paddy (*oryza sativa*) irrigated with fluoride-contaminated groundwater in an endemic area of the birbhum district, west bengal was investigated by Gupta and Banerjee (2009). Substantial accumulation of fluoride (F) was observed in different parts of paddy (rice, *Oryza sativa*) irrigated with F-contaminated groundwater (0.62–4.06 mg/L) grown in soil containing 1.45–3.80 mg water-extractable (F_{H_2O}) and 140–144 mg total (F_{TOTAL}) F/kg dry wt. Statistically significant correlations ($p < 0.05$ and 0.01) were found in the irrigation water between F, TH, Mg^{2+} , and Na^+ . The mean F_{H_2O} and F_{TOTAL} accumulation (mg/kg dry wt) in paddy decreased in the order: root (F_{H_2O} 6.28, F_{TOTAL} 80.83) > leaf (F_{H_2O} 5.88, F_{TOTAL} 50.30) > stem (F_{H_2O} 3.26, F_{TOTAL} 19.57) > seeds (F_{H_2O} 2.88, F_{TOTAL} 12.31). The transfer factor (TF) with respect to water-extractable soil F and in different parts of paddy also showed a high translocation pattern similar to the accumulation pattern.

Jha et al., (2009) conducted a study in Nagar of Unnao district, Uttar Pradesh (India), and estimated fluoride concentration along with other physico-chemical parameters in ground water samples where it was the only source of drinking water for the villagers. The fluoride concentration in the water varied from 0.8 to 13.9 $mg\ l^{-1}$ with a mean of 4.02 $mg\ l^{-1}$. The correlation analysis revealed that fluoride had a positive correlation

with pH, CO_3 , HCO_3 , and sodium adsorption ratio (SAR), whereas a negative correlation with Ca and Mg was found. A soil profile was also dug in the area to assess depth-wise fluoride content in the soil. The soil samples and underneath calcium carbonate (CaCO_3) concretion were analyzed for fluoride content. The percent of soluble fluoride to total fluoride in the soil varied from 25.15 to 4.76% down the soil profile. The soluble fluoride was found to decrease with the increase in the clay content in the soil. The total leachable fluoride in CaCO_3 concretions was found to be 6.08%. It was inferred from this study that the soil and underneath layer of CaCO_3 concretions may be the potential source of fluoride contamination in the shallow drinking water sources of the area.

Kumar et al., (2009) investigated the effect of fluoride on catalase, guaiacol peroxidase and ascorbate oxidase activities in two varieties of mulberry leave (*Morus alba* L.). They stated that regulated balance between oxygen radical production and destruction is required of metabolic efficiency and function is to be maintained either in normal or toxic conditions. A continually high anti oxidant capacities under toxicity conditions can present the damage correlated with resistance to that of particular toxicity. Hence the mechanisms that reduce oxidative stress are expected to play an important role in imparting toxicity tolerance in plant. A significant alleviation in activities of peroxidase, catalase and ascorbic acid oxidase was recorded on both cultivars on exposure to fluoride. Further the degree of increase was found to be dependent on severity and duration of exposure. Further degree of elevation in enzyme activity was relatively high in fluoride tolerant cultivar M when compared to sensitive cultivar V_1 . Mulberry cultivar M on the whole, 5 1 5 exhibited more fluoride toxic tolerance than mulberry cultivar V_1 .

Kundu and Mandal (2009) assessed the potential hazards of fluoride contamination in drinking groundwater of an intensively cultivated district in West Bengal, India. They assessed the potential of fluoride (F) contamination in drinking groundwater of an intensively cultivated district in India as a function of its lithology and agricultural activities. Three hundred and eight groundwater samples were collected at different

depths from various types of wells and analyzed for pH, EC, NO₃-N load and F content. A typical lithology was constructed and database on fertilizer and pesticide uses were also recorded for the district. The water samples were almost neutral in reaction and non-saline in nature with low NO₃-N content (0.02 to 4.56 µg/ml). Fluoride content in water was also low (0.01 to 1.18 µg/ml) with only 2.27% of them exceeding 1.0 µg/ml posing a potential threat of fluorosis. On average, its content varied little spatially and along depth of sampling aquifers because of homogeneity in lithology of the district. The F content in these samples showed a significant positive correlation ($r=0.12$, $P \leq 0.05$) with the amount of phosphatic fertilizer (single super phosphate) used for agriculture but no such relation either with the anthropogenic activities of pesticide use or NO₃-N content, pH and EC values of the samples was found. The results suggest that the use of phosphatic fertilizer may have some role to play in F enrichment of groundwater.

Salve et al., (2008) conducted a study in the summer season (April–May 2007). The fluoride concentration along with physico-chemical parameters in ground water samples was determined in various villages of Kadi tehsil at Mehsana district of Gujarat state (India), since in most of the villages it is the only source of drinking water. The fluoride concentrations in these villages varied from 0.94 to 2.81 mg/L (1.37 ± 0.56) with highest fluoride level at Visalpur (2.08 mg/L) and lowest at Adaraj (0.91 mg/L). There was found a positive correlation of pH with fluoride and a negative relationship of fluoride with bicarbonate which is generally observed in deep ground water. They concluded that correlation of Ca and Mg indicates a possible ion-exchange process in the ground water system. The HCO₃, Cl, Na, SO₄ ions constituted 92% of major ions indicating the active secondary geochemical process controlling the ground water chemistry.

Kumar and Rao (2008) performed the study of photosynthetic capacity, chlorophyll a and b concentrations and leaf area showing differences in the responses of two cultivars of mulberry growing in high fluoride content of soil. Mulberry variety (S54) is believed

to be sensitive to fluoride, showed reduction in all of these parameters which are significantly, correlated with leaf fluoride contents and fluoride in soil. The same parameters in mulberry variety kanva (M5) which is believed to be tolerant to fluoride showed no significant differences in high fluoride containing soil. The results of this study suggested that the physical and biochemical changes may be manifested as a reduction in leaf chlorophyll content and may influence photosynthetic capacity under chronic fluoride exposure conditions. Therefore significant correlations were found in the present study between fluoride flux in the soil, foliar fluoride concentrations in both leaf chlorophyll concentration and photosynthetic rate. They concluded that correlations do not necessarily employ a casual relationship, but they may add support to the hypothesis that fluoride effects on leaf chlorophyll concentrations in S54 and M5 may result in a reduced photosynthetic capacity. Further, the lesser inhibition in the parameters like leaf area, chlorophylls and photosynthetic rates with fluoride concentrations reflects the fluoride tolerance nature of M5.

Nitrate-N and Fluoride concentrations were analyzed by Sankararamakrishnan et al., (2008) in shallow and unconfined groundwater aquifers of Kanpur district along the Ganges Alluvial Plain of Northern India. Kanpur district was divided into three zones namely, Bithore, Kanpur City and Beyond Jajmau and sampling was carried out three seasons (summer, monsoon and winter). The data set consisted of the results of water samples from around 99 India Mark II hand Pumps, which were analyzed for summer monsoon and winter seasons. In Bithore zone, 19% of the samples exceeded the BIS (Bureau of India Standards) limit 10.2 mg/l as nitrate-N and as high as 166 mg/l as nitrate - N was observed. 10% and 7% samples in Kanpur city and beyond Jajmau zone respectively, exceeded the BIS limit. The Frequency distribution histogram of nitrate - N revealed a skewed (non-normal) distribution. Both point and non-point sources contributed to the ground water contamination. Especially in Bithore zone, the point sources could be attributed to the animal wastes derived from cows and buffaloes and nonpoint sources could be due to the extensive agricultural activity prevalent in that area. Fluoride level in most samples were within the BIS maximum permissible level of

1.5 mg/ l. No significant seasonal variation in water quality parameters was observed.

Bishnoi and Arora (2007) performed a study in ten villages of Rohtak district of Haryana state (India). The fluoride concentration in the underground water of these villages varied from 0.034-2.09 mg/l. Various other water quality parameters, viz., pH, electrical conductivity, total dissolved salts, total hardness, total alkalinity, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride and sulfate were also measured. A systematic calculation of correlation coefficients among different physicochemical parameters indicated considerable variations among the analyzed samples with respect to their chemical composition. Majority of the samples do not comply with Indian as well as WHO standards for most of the water quality parameters measured. Overall water quality was found unsatisfactory for drinking purposes. Fluoride content was higher than permissible limit in 50% samples. On the basis of physicochemical analysis of the studied water sources in ten villages of Rohtak district (India), it had been concluded that the groundwater and dug well water quality varied spatially and at most of the locations was not suitable for drinking purposes as per WHO guidelines.

The concentration of fluoride ion (F) in groundwater samples from different sites in Nalhati-1 block of the Birbhum district, West Bengal, was determined by Gupta et al., (2006). Most of the F levels were within permissible limits, whereas a significantly higher concentration of 1.95 mg/L was found in artesian well samples of Nasipur village. The F in groundwater appears to be controlled by the distribution of Ca^{2+} and to some extent SO_4^{2-} , ionic strength, and the presence of complex ions. From correlation coefficient analysis, F was found to be inversely related to Ca^{2+} and positively related to Na^+ . Basaltic rock and water interaction with it may be responsible for the increased F in the artesian well samples from the study area.

Fluoride concentrations in surface and ground water samples were determined by Ramanaiah et al., (2006) in eight villages of Prakasham district in India. Thirty-eight

samples were collected and analyzed for fluoride content along with pH, electrical conductivity, and total dissolved solids (TDS), total hardness, total alkalinity, chlorides (Cl^-), sulfates (SO_4^{2-}) and nitrates (NO_3^-). Fluoride concentrations in surface and ground water samples of these villages varied between 0.5 and 9.0 mg/L. Groundwater samples contained high concentrations of fluorides compared to open well and pond water samples, which could be a major source of fluoride in water since the geological formation of this area consists of fluorite and fluorapatite. From the data, it is evident that the population in the study area is severely affected by fluorosis. Dental and skeletal fluorosis and deformation of bones in children as well as adults were observed in the study area indicating the consequences of excess fluoride concentration. Fluoride concentrations showed good correlation with TDS concentrations (R^2 of 0.61) compared to other physico-chemical parameters [EC (R^2 - 0.36), nitrate (R^2 - 0.24), total hardness (R^2 - 0.12), chloride (R^2 - 0.06) and sulfate (R^2 - 4×10^{-5})]. They concluded that the excess fluoride concentration in the study area may be attributed to the geological formation of that particular area and rapid ground water depletion.

CHAPTER - 3

AIMS AND OBJECTIVES

To encounter the prevalence of fluoride and its deleterious effect on human being, the foremost necessity is to find out the main sources of fluoride in ground water through which fluoride is ingested directly in human body when used in drinking purpose and indirectly via vegetables when used in irrigation purpose. In Birbhum district, West Bengal, many ground water sources have been identified containing fluoride and the study revealed new locations where the people residing there are not aware of the problem.

Focusing on the fluoride in ground water and its probable effect on vegetation, the research work was framed on the basis of the following objectives:

- To find out new locations containing high level of fluoride in Birbhum district
- To substantiate the ground water quality used for drinking in the locality
- To justify the validity of the ground water used for irrigation
- To find out the probable relations between physico-chemical parameters of water
- To pursue the probable seasonal variation of water quality
- To find out the transportation of fluoride from soil to edible parts of locally grown vegetables
- To estimate the biochemical parameters from vegetables available in fluoride affected area of Birbhum district
- To find out a relation between fluoride level in ground water and changes in biochemical parameters of the vegetables
- To make aware the local people where fluoride is detected during the study

CHAPTER - 4

MATERIALS AND METHODS

4.1 MATERIALS

4.1.1 Study area

The study area is in the Birbhum district, which is located between 23°32'30" and 24°35'0" N and 87°05'25" and 87°01'40" E having an area of 4,545 km². Geographically, this district lies at the north eastern end of Chota Nagpur Plateau, as it slopes down and merges with alluvial plains of the Ganges. The climate on the western side is dry and extreme, but it is relatively milder on the eastern side. During the summer, the temperature can shoot to well above 40°C and, in the winter, it can drop to around 10°C with an annual average rainfall of 1,405 mm. It has been observed that rainfall is higher in the western areas as compared to the eastern areas and the rainfall mostly occurs in the monsoon months (June to October). Ground water is the main source of drinking and irrigation in most of the part of this district. The present cross sectional study was conducted among twenty two villages, viz., Nasipur, Vabanandapur, Deshnabagram (under Nalhati I block); Kamdebpur, Chalk Atla, Nowapara, Junitpur (under Rampurhat II block); Loha Bazar, Kaijuli, Chak Sehara, Seharakuri, Sankarpur (Mahammad Bazar block); Gostho Dungal, Sarsa, Tithikapur, Lauberia, Tarapur, Nowpara, Bhadulia, Paschim Sibpur, Rasa (Khoyrasole block) and control area of Hazratpur (Nalhati-I block) of Birbhum district, West Bengal, India (Fig.1-4). The population, average rainfall and GPS readings are listed in Table 1. The most interesting part of the geology of this area stems from the gradient of red soil. A kind of sandy hard red soil of the alfisol type and laterite soil of this area give rise to potential aquifers at depth. Open wells and bore wells are the main source of water supply for domestic and agricultural purposes in this arid region.

4.1.2 Sampling

Samples were picked up from randomly chosen 220 sites of 22 villages from 4 blocks namely, Nalhati I, Rampurhat II, Khoyrasole and Mahammad Bazar in Birbhum district (Fig. 1) during pre monsoon (PRM) and post monsoon (POM) seasons. The month of April- May (in a few cases, Feb- March) was designated as PRM and September-October as POM. The sample spots were marked at the time of sampling during PRM.

All the water samples were collected in 500 ml sterilized polypropylene (Turson made) bottles and stored in freezing condition (temperature $<10^{\circ}\text{C}$), by following standard protocols. Geographical positions of all the sampling sites are recorded during the sampling by using GPS (Model: GARMIN GPS 12). Vegetable samples were also collected depending on its availability from the aforesaid areas in zippered polyethene packets and refrigerated immediately after collection and analyses were done as quickly as possible. 114 soil samples were collected from the vegetable fields near each collected vegetables plants in the polluted area and stored in zippered polyethene packets for fluoride analysis. Thirty six soil samples from the control area were also collected from the fields where the vegetables grown, to check the availability of fluoride.

4.2 METHODS

4.2.1 Physico-chemical analysis of the water samples

4.2.1.1 Estimation of fluoride (Tokalioğlu, 2004)

Principle: The fluoride is analyzed using ion-meter in conjunction with a combination fluoride electrode. Total ionic strength adjustment buffer TISAB (4g 1,2-cyclohexanedi-amine-N,N,N',N'-tetraacetic acid (CDTA) + 57 g NaCl and 57 g glacial CH_3COOH in 1 L of distilled water adjusted to pH 5-5.5 with 6 N NaOH) solution is used to regulate the ionic strength of samples or standard solutions and to adjust the pH, to avoid interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV), which are able to complex or precipitate with fluoride resulting in reduction of free fluoride concentration in the solution. CDTA forms stable complexes with polyvalent metal cations (e.g., Al (III), Fe (III) and Si (IV)), which are more stable than metal-fluoride complexes (AlF_6^{3-} , FeF_6^{3-} etc.) in solution. The CDTA preferentially complexes with polyvalent cations present in aqueous solution (e.g., Si^{4+} , Al^{3+} and Fe^{3+}). There are 6 complexing groups in CDTA and it forms metal-CDTA complexes in a metal-ligand ratio of 1:1 (Christian, 1986), freeing the fluoride ion from its complexes

with the cations. The electrode used for the estimation is selective for the fluoride ion over other common anions by several orders of magnitude; only the hydroxide ion appears to offer some interference.

Equipments:

- (i) Instrument: Jenway 3040 model ion-meter in conjunction with a combination fluoride electrode (Orion ISE 940900).
- (ii) Analytical-reagent grade NaF for standard preparation
- (iii) TISAB buffer (4g 1,2-cyclohexanedi-amine-N,N',N'-tetraacetic acid (CDTA) + 57 g NaCl and 57 g glacial CH_3COOH in 1 L of distilled water adjusted to pH 5-5.5 with 6 N NaOH)

Procedure: Distilled water was used throughout the experiments. The use of glass ware was avoided. Fluoride stock solution ($1000 \mu\text{gml}^{-1}$) was prepared from sodium fluoride and stored in polyethene labware. 25 ml of the water sample and 25 ml of TISAB solution (1:1 ratio) were mixed with a magnetic stirrer for 3 min. The electrode potentials of the sample solutions were directly compared with those of fluoride standard solutions and the concentration of fluoride in samples were obtained. The limit of detection (LOD) of the method was 0.01 mg/L.

4.2.1.2 Estimation of pH (APHA, 1998)

Principle: The pH of a solution is defined as negative logarithm of hydrogen ion activity to the base 10 i.e., $\text{pH} = -\log_{10}a_{\text{H}^+}$

When the solution is very dilute $a_{\text{H}^+} = c_{\text{H}^+}$, i.e., $\text{pH} = -\log_{10}c_{\text{H}^+}$

Equipments:

- (i) pH meter (Orion Thermo)
- (ii) Standard pH buffer solutions (Orion)

Procedure: At first the digital pH meter was calibrated by standard pH solutions (pH 4, pH 7 and pH 10). After calibration, the pH of water samples was measured at a room temperature (27°C). During sampling, pH was measured by using hand analyzer (HANNA-HI 98121).

4.2.1.3 Estimation of Electrical Conductivity (APHA, 1998)

Principle: Electrical conductivity (EC), also called specific conductance is a measure of the ability of water samples to convey electrical current, and it is related to the total concentration of ionized substances in water. Organic compounds have little influence on the conductivity. The water conductivity increases with temperature owing to a decrease in viscosity and increasing dissociation. Normally EC value of distilled water range from 1 to 5 μmho or μS conveniently measured at 25° C.

Equipments:

- (i) Standard KCl solution (0.01 M) which has a conductivity of 1412 $\mu\text{S}/\text{cm}$ at 25°C
- (ii) Conductivity meter (Eutech CON 510)

Procedure: Digital conductivity meter (Systronics) was calibrated with standard KCl solutions (1N, 0.1N and 0.01N). The EC values of water samples were analyzed taking sample (50 mL) in a 100 ml beaker and immersing the probe into it.

During field study, EC of onsite samples were measured by using hand analyzer (HI-98301).

4.2.1.4 Estimation of Total Dissolved Solids (APHA, 1998)

Principle: The inorganic and organic solid compounds dissolved in water remaining in the solution phase is the measure of total dissolved solid (TDS). When the water (solvent) is evaporated to dryness the remaining solid represents the TDS which can be measured gravimetrically.

Equipments:

- (i) Hot water bath
- (ii) Dish, Glass goods

Procedure: An evaporating dish of appropriate size is heated in an oven at 180°C for 1hr, cooled in desiccators and weighed. 100 ml of accurately measured water samples is filtered with slight suction. The filtrate is then transferred to a pre weighed evaporating dish and evaporated to dryness. It is dried for at least 1hr at 180°C, cooled in room temperature and weighed again.

Calculation:

Total dissolved solid (TDS) in mg/L = $1000 \times (Y - X) / V$

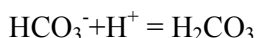
Where V = volume of water sample taken, X = Weight of empty dish (mg), Y = Weight of the dish after evaporation of water taken (mg).

4.2.1.5 Estimation of Total Alkalinity (TA) and Bicarbonate by titrimetric method (APHA, 1998)

Principle: Alkalinity is the quantitative capacity of an aqueous medium to react with hydrogen ions to pH 8.3 and then to pH 3.7. The equation in its simplest form is as follows:



From pH 8.3 - 3.7, the following reaction may occur:



Reagents:

- (i) Standard sulfuric acid (0.02N)
- (ii) Phenolphthalein indicator
- (ii) Methyl Orange indicator

Procedure: Samples were analyzed in the laboratory after collection. 10 ml of sample were taken in a flask and add 2-3 drops of phenolphthalein indicator. If a slight pink color appears, phenolphthalein alkalinity is present. Solution was titrated against sulphuric acid until the solution becomes color less (end point). The reading was noted, after that, 2-3 drops of methyl orange indicator was added in the same flask and continue to titrate against sulfuric acid until yellow color of solution turn orange (end point). The reading was noted as 't' which is the total volume of titrant used for both the titrations.

Calculations:

Phenolphthalein alkalinity (P) as CaCO_3 (mg/L) = $p \times N \times 50000 / s$

Total alkalinity (T) as CaCO_3 (mg/L) = $t \times N \times 50000 / s$

Where, p = Volume of titrant (standard acid) used against phenolphthalein indicator (ml); s = Volume of sample (ml); and t = Total volume of titrant (standard acid) used for the two titrations (ml), N = normality of the titrant (standard acid).

The value of different forms of alkalinities (hydroxide, carbonate and bicarbonate) in terms of CaCO_3 (mg/L) is computed using following table:

Result of Titration	Hydroxide alkalinity as CaCO_3	Carbonate alkalinity as CaCO_3	Bicarbonate concentration as CaCO_3
P=0	0	0	T
$P < \frac{1}{2} T$	0	2P	T-2P
$P = \frac{1}{2} T$	0	2P	0
$P > \frac{1}{2} T$	2P-T	2(T-P)	0
P=T	0	0	0

P = Phenolphthalein alkalinity; T= Total alkalinity

4.2.1.6 Estimation of Total Hardness (TH) by titrimetric method (APHA, 1998)

Principle: The total hardness of water is generally due to dissolved Ca and Mg salts, and may be determined by complexometric titration using EDTA and Eriochrome Black T indicator. A buffer (pH = 10) is used to keep the acid groups deprotonated.

Reagents:

- Standard ethylenediaminetetra-acetate (EDTA) solution (0.01 M): 3.723 g of EDTA was dissolved in distilled water and diluted to 1 litre.
- Eriochrome Black T indicator: 0.2 g of the dyestuff was dissolved in 15 ml of triethanolamine and 5 ml of absolute ethanol.
- Buffer solution (pH = 10): 142 ml of concentrated ammonia solution was added to 17.5 g A.R. ammonium chloride and diluted to 250 ml with distilled water.

Procedure: To 50 ml of the sample water 1 ml of the buffer solution and 3 -4 drops of Eriochrome Black T indicator was added. The solution was titrated with 0.01 M EDTA solution until the color changed from wine red to violet to pure blue (end point) with no reddish tinge remaining.

Calculation:

Total hardness (mg/L, as CaCO_3) = $T \times B \times 1000 / V$

Where, T= Volume of titrant (ml); V= Volume of sample (ml) and B= mg CaCO₃ equivalent to 1.00 ml EDTA titrant (for 0.01 M EDTA, B = 1 as 1 ml 0.01 M EDTA \equiv 1.00 mg of CaCO₃).

4.2.1.7 Estimation of Calcium by titrimetric method (APHA, 1998)

Principle: In a solution containing both calcium and magnesium, calcium can be determined directly with EDTA when the pH is made sufficiently high (12 - 13) so that the magnesium is largely precipitated as the hydroxide and an indicator is used which combines, only with calcium.

Reagents:

- (i) Sodium hydroxide solution (8%)
- (ii) Murexide indicator
- (iii) EDTA solution (0.01M)

Procedure: 50 ml of the sample was taken in an Erlenmeyer flask and 1 ml of sodium hydroxide solution and a pinch of murexide indicator were added. Then it was titrated against EDTA solution until the pink color turned into purple (end point).

Calculation:

$$\text{Calcium (mg/L)} = T \times B \times 400.8 / V$$

where, T= Volume of titrant (ml); V= Volume of sample (ml) and B= mg CaCO₃ equivalent to 1.00 ml EDTA titrant at the calcium indicator end point.

To determine the calcium hardness expressed as mg CaCO₃/ liter, following formula was used.

$$\text{Calcium hardness (mg/L, as CaCO}_3\text{)} = T \times B \times 1000 / V$$

where, T= Volume of titrant (ml); V= Volume of sample (ml) and B= mg CaCO₃ equivalent to 1.00 ml EDTA titrant at the calcium indicator end point (for 0.01 M EDTA, B = 1 as 1 ml 0.01 M EDTA \equiv 1.00 mg of CaCO₃).

4.2.1.8 Estimation of Magnesium titrimetric method (APHA, 1998)

Method and calculation: Total hardness and calcium hardness of water as CaCO_3 are determined using the methods described above (4.2.1.6 and 4.2.1.7). From these values magnesium content is calculated as given below:

$$\text{Magnesium (mg/L)} = (T - C) \times 0.244$$

Where, T = Total hardness (as CaCO_3); and C = Calcium hardness (as CaCO_3)

4.2.1.9 Estimation of Sodium by flame photometric method (APHA, 1998)

Principle: Trace amounts of sodium can be determined by flame emission photometry at 589 nm. Sample is nebulised into a gas flame under carefully controlled, reproducible excitation conditions. The sodium resonant spectral line at 589 nm is isolated by interference filters or by light-dispersing devices such as prisms or gratings. Emission light intensity is measured by a phototube, photomultiplier, or photodiode. The light intensity at 589 nm is approximately proportional to the sodium concentration. The appropriate wavelength setting, which may slightly more or less than 589 nm, can be determined from the maximum emission when aspirating a sodium standard solution, and then used for emission measurements.

Reagents

- (i) Double distilled water
- (ii) Standard stock sodium solution (1000 mg/L)
- (iii) Intermediate standard sodium solution (100 mg/L).

Procedure: Different standard sodium solution of following concentrations (for calibration curve) was prepared from intermediate standard sodium solution (100 mg/L) such as 2, 4, 6, 8, 10 mg/L. A blank solution was also prepared. The intensity of the different standard solutions was measured with a flame photometer (Systronics-128) using a Na-filter. The intensity of the sodium in the unknown sample was measured in a similar manner by taking 5 ml sample water in 50 ml volumetric flasks and then diluted it up to the mark.

4.2.1.10 Estimation of Potassium by flame photometric method (APHA, 1998)

Principle: Trace amounts of potassium can be determined in either a direct reading or internal standard type of flame photometer at a wavelength of 766.5 nm. Because much of the information pertaining to sodium applies equally to the potassium determination, careful study of entire discussion is required dealing with the flame photometric determination of sodium before making a potassium determination.

Reagents:

- (i) Double distilled water
- (ii) Standard stock potassium solution
- (iii) Intermediate standard potassium solution (100 mg/L)

Procedure: Different standard potassium solutions (for calibration curve) of following strength (2, 4, 6, 8, and 10 mg/L) were prepared from the intermediate standard potassium solution. A blank solution was also prepared. Intensity of the different standard solutions was measured with a flame photometer (Systronics-128) with a K-filter. The sample waters were analyzed in the same procedure.

4.2.1.11 Estimation of Chloride by titrimetric method (APHA, 1998)

Principle: In a natural or slightly alkaline medium K_2CrO_4 can indicate the end point in chloride titration. $AgCl$ is precipitated quantitatively before red silver chromate is formed.

Reagents:

- (i) 0.0141 (N) $AgNO_3$ (Silver nitrate)
- (ii) K_2CrO_4 (Potassium Chromate) indicator

Procedure: 5 ml. samples was taken in a conical flask, then 2-3 drops of K_2CrO_4 indicator was added to it and solution was titrated against 0.0141 (N) $AgNO_3$. The end point was marked by a brick red precipitate. The titrant volume was noted and the chloride content was calculated. A blank titration is performed in the same procedure using same volume of distilled water in place of the sample.

Calculation:

$$Cl^-(mg/L) = (V-B) \times N \times 35.45/S$$

Where, V = Volume of titrant (ml) needed for the sample; B = Volume of titrant (ml) needed for the blank; N = Normality of titrant (ml); S = Volume of Sample (ml).

4.2.1.12 Estimation of Sulfate by turbidimetric method (APHA, 1998)

Principle: Sulphate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride (BaCl_2) so as to form barium sulphate (BaSO_4) crystals of uniform size. Light absorbance of the BaSO_4 suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

Reagents:

- (i) Buffer solution: 30 gm $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 1g KNO_3 , 0.111g Na_2SO_4 and 20 ml acetic acid (99%) is dissolved in 500 ml distilled water and made up to 1000 ml.
- (ii) Barium chloride
- (iii) Standard sulphate solution

Procedure: 100 ml of clear sample (not containing more than 40 of SO_4^{2-}) or a suitable aliquot diluted to 100 ml in a 250 ml conical flask is taken. 5.0 ml of buffer reagent was added to it. Care should be taken not to add the conditioning reagent in all the samples simultaneously. This is to be added to each sample just prior to the further processing. The sample was stirred using a magnetic stirrer and during stirring a spoonful of BaCl_2 crystals is added to the solution and after addition of BaCl_2 stirring is continued for 1 minute. Then after 4 minutes, the optical density reading on a spectrophotometer at 420nm was taken. Same procedure described above is applied for the standards of different concentrations. Framing the standard curve using Microsoft excel, the concentrations of sulphate in water samples were determined.

4.2.1.13 Estimation of Phosphate by Spectrophotometric Method (APHA, 1998)

Principle: Molybdophosphoric acid is formed when phosphate reacts with ammonium molybdate and reduced by stannous chloride to intensely coloured molybdenum blue. This method is more sensitive than others and makes feasible measurements down

to 100 µg /L by use of increased light path length. Below 100 µg /L an extraction step may increase reliability and lessen the interference.

Reagents:

- (i) Stannous chloride solution (2.5%)
- (ii) Ammonium molybdate solution (2.5%)
- (iii) Conc. H₂SO₄ (Sulfuric acid)
- (iv) Standard Phosphate Solution of anhydrous potassium hydrogen phosphate (KH₂PO₄)

Procedure: To each 50 ml volumetric flask containing different samples, 4 ml ammonium molybdate solution and 2 - 4 drops of stannous chloride solution were added. A blue colour appeared. The volume was made up to the mark with distilled water and absorbance was measured at 690 nm in spectrophotometer (Systronics-169). Standard solutions of different concentrations were made. Standard solutions were analyzed in the same procedure mentioned above and the standard calibration curve was prepared to estimate the concentration of phosphate in the samples.

4.2.1.14 Estimation of Iron by Spectrophotometric Method (APHA, 1998)

Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1, 10 phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange colored complex which is stable and the intensity is independent of pH from 3 to 9. Measuring the color intensity (optical density or absorbance), the concentration of iron can be estimated.

Reagents:

- (i) Concentrated HCl
- (ii) Hydroxylamine (NH₂OH.HCl) solution: 10 g Hydroxylamine was dissolved 100ml water.
- (iii) Ammonium acetate buffer solution: 250 g ammonium acetate was dissolved in 150 ml water. 700ml concentrated glacial acetic acid was added to it.
- (iv) Sodium acetate solution: 200 g of sodium acetate was dissolved in 800 ml water.

(v) Phenthroline solution: 100mg 1, 10- Phenathroline monohydrate was dissolved in 10 ml water by stirring and heating to 80 ° C.

(vi) 0.1 M Potassium permanganate (KMnO₄)

(vii) Stock iron solution for standard: 20 ml of concentrated H₂SO₄ was slowly added to 50 ml water and 1.404 g ferrous ammonium sulphate was dissolved. 0.1 M KMnO₄ was added drop wise until a faint pink color persisted. The solution was diluted and the volume was made up to 1000 ml with distilled water. Standard solutions of different concentrations were prepared from the stock solution.

Procedure: 2 ml of concentrated HCl and 1 ml NH₂OH.HCl solution were added to 50 ml sample and was heated to boiling until the volume reduced to 20 ml. Then after cooling, 10 ml ammonium acetate buffer solution and 4 ml phenanthroline solution was added. The solution was kept for 10 minutes after dilution up to the mark for the color development and the optical density was measured at 510 nm in the spectrophotometer (Systronics). The same procedure was performed to find out the absorbance of standard solutions. The standard curve was then drawn by plotting concentration vs. absorbance using MS Excel and concentrations of the samples were calculated.

4.2.1.15 Estimation of Silica by Spectrophotometric Method (APHA, 1998)

Principle: Ammonium molybdate at low pH reacts with silica and any phosphate present to produce molybdosilicate giving a yellow color. Oxalic acid is added to destroy the molybdophosphoric acid. The intensity of the color can be measured at 410 nm.

Reagents:

- (i) Ammonium molybdate reagent
- (ii) Oxalic acid solution
- (iii) Hydrochloric acid solution (HCl: Water =1:1)
- (iv) Standard solution of Sodium metasilicate nonahydrate (Na₂SiO₃.9H₂O)

Procedure: 100 ml of each sample or a suitable aliquot diluted to 100 ml in a 250 ml in a conical flask was taken. 1.0 ml of 1:1 HCl and 2 ml ammonium molybdate solution was added to it and shaken well. After 5-10 minutes, 2 ml of oxalic acid was added and

mixed thoroughly. Then the optical absorbance was recorded after 2 minutes but before 20 minutes in spectrophotometer (Systronics, 169) at 410 nm. Standard solutions of different concentrations were made. Standard solutions were analyzed in the same procedure mentioned above and the standard calibration curve was prepared to estimate the concentration of silica in the samples.

4.2.2 Estimation of fluoride in soil

Principle: The fluoride in soil is estimated after bringing the soil fluoride in solution phase using the method indicated by Lori (1987). The fluoride is analyzed using ion-meter in conjunction with a combination fluoride ion selective electrode.

Materials:

- (iv) Instrument: Jenway 3040 model ion-meter in conjunction with a combination fluoride electrode (Orion ISE 940900).
- (v) Analytical-reagent grade NaF for standard preparation
- (vi) TISAB buffer (4g 1,2-cyclohexanedi-amine-N,N,N',N'-tetraacetic acid (CDTA) + 57 g NaCl and 57 g glacial CH_3COOH in 1 L of distilled water adjusted to pH 5-5.5 with 6 N NaOH)

Procedure: The method of partial leaching described by Lori (1987) was applied in the preparation of the soil extract for analysis. The air dried soil samples were crushed to powder. 10g each of the oven dried powdered soil samples were separately weighed into a 100 ml plastic beaker (Turson made) and 20 ml of distilled water was added. The mixtures were stirred and allowed to stand for six hours. They were filtered into a 100 ml volumetric flask. The residues were leached slowly over a two-hour period with distilled water on to the same filter paper and the leachate going into the same beaker containing the filtrate. The filtrates and the leachate mixture were made up to the mark with distilled water. 25 ml of this extract was used for the detection. The samples and fluoride standard solutions were diluted 1:1 with the TISAB. The solutions, which contained 25 mL of the sample and 25 mL of TISAB solutions, were mixed with a magnetic stirrer for three minute. The electrode potentials of the sample solutions were

directly compared with those of fluoride standard solutions and the concentration of fluoride in samples were obtained. The limit of detection (LOD) of the method was 0.02 mg/L.

4.2.3 Biochemical Parameters

4.2.3.1 Estimation of Fluoride in Vegetable Samples (McQuaker and Gurney, 1977)

Principle: Fluoride in the vegetable samples are extracted by the alkali fusion method described below and then analyzed using the same ion selective electrode used for water and soil samples.

Equipments:

- (i) 16.8 N NaOH solution
- (ii) 37% HCl solution
- (iii) Ni crucible
- (iv) Whatman No. 40 filter paper
- (v) Polythene labwares

Procedure: After thorough washing with water, the leaves and fruits of the fresh vegetables harvested from the contaminated and control area were dried at 105°C and crushed into powder so as to pass through a 40 mesh sieve. About 0.5 g each of the powdered samples was transferred into a 150 ml nickel crucible and moistened with a small amount of de-ionized water. Six mL of 16.8 N NaOH was added and the crucible was placed in an oven (150°C) for 1.5-2.0 hr until NaOH was solidified. The crucible was placed in a muffle furnace set at 300°C, then raised to 600°C and kept at 600°C for 30 min in order to fuse the sample in the crucible. The crucible was placed in a hood and allowed to cool, and 10 mL distilled water was added. Then, 37% HCl solution (about 7 mL) was added slowly to adjust the pH to 7-9. The sample solution was transferred to a 100 mL plastic volumetric flask, made up to volume with distilled water and filtered through a Whatman No. 40 filter paper. The filtrate was used for

analysis of fluoride with the same procedure with the same ion selective electrode used for water analysis.

4.3.3.2 Estimation of total soluble sugar (Mc. Cready et al., 1950)

Principle: The method of Mc. Cready et al., (1950) was followed where the reagent anthrone gives a blue-green coloration with sugar solution. The sugar is estimated calorimetrically measuring its intensity at an absorbance maximum of 630 nm and comparing with standard curve of D-glucose.

Reagents:

- (i) 0.2% anthrone solution
- (ii) Standard D-glucose

Procedure:

Extraction: About 0.1 g of fresh leaves weighted and crushed with a pestle in a mortar first with 3 ml and then with 7 ml distilled water. This was transferred into a centrifuge tube and centrifuged for 10 minutes at 10,000 rpm. The supernatant was collected. From this, 1 ml extracted solution was pipetted out in a test tube, 4 ml freshly prepared 0.2 % anthrone reagent was added in it and incubated for 10 minutes at 100 °C. This was allowed to cool at room temperature. Blank is prepared in the same process taking distilled water in place of extract. The absorbances were measured at 630 nm wave length.

Standard: Standard solution is prepared using D-glucose by diluting with water at different concentrations. Adding 4 ml of anthrone reagent to 1 ml of each standard of different concentrations were heated for 10 minutes in a boiling water bath at 100° C temperature. Standard curve was prepared measuring absorbance at 630 nm.

Calculation: A plot of the absorbance against the concentration is drawn using Microsoft excel and from the calibration curve, the concentration of soluble sugar was calculated.

4.2.3.4. Estimation of Total chlorophyll (Arnon, 1949)

Principle: For the estimation of chlorophyll content Aron's(1949) method was employed. Chlorophyll is extracted in 80% acetone and the absorption at 645nm; 652nm and 663nm are read in spectrophotometer. Using the absorption co-efficient, the amount of chlorophyll is calculated.

Reagents:

- (i) 80% acetone
- (ii) 0.1g of fresh leaf sample

Procedure:

0.1g of fresh leaf sample was taken. 5ml of 80% acetone is added to the sample in test tube in the ratio of 2:1. The test tube is plugged with cotton and is kept in refrigeration for 24 hours. The test tube containing green solution taken out and the supernatant is collected in another test tube. The leaves are finally washed with 5ml of 80% acetone to extract further chlorophyll from the leaves. The supernatant liquid is again collected. The absorbance of the solution was read at 645,652,663 nm against the solvent (80% acetone) blank.

Calculation:

Calculation of the amount of chlorophyll (mg) present in extract per g of tissue was determined using the following equations.

$$\text{Chlorophyll-a (mg g}^{-1} \text{ FW)} = [12.7 \times D_{663} - 2.69 \times D_{645}] \times V/1000 \times W$$

$$\text{Chlorophyll-b (mg g}^{-1} \text{ FW)} = [22.9 \times D_{645} - 4.68 \times D_{663}] \times V/1000 \times W$$

$$\text{Total Chlorophyll (mg g}^{-1} \text{ FW)} = D_{652} \times 1000/34.5 \times V/1000 \times W$$

Where, D = Optical density,

V = Final volume of 80% acetone (10ml),

W = Fresh wt. Sample taken (0.1 g),

FW = Fresh weight.

4.2.3.5 Estimation of total ascorbic acid (Sadasivam and Manickam, 1996)

Principle:

Ascorbic acid is first dehydrogenated by bromination. The dehydro ascorbic acid is then reacted with 2, 4- Dinitrophenyl hydrazine to form osazone and dissolved in sulphuric acid to give an orange red color solution which is measured at 540 nm.

Material:

- (i) 4 % oxalic acid solution
- (ii) 0.5 N H₂SO₄
- (iii) 2% 2,4- Dinitrophenyl hydrazine (DNPH) reagent: 2 g DNPH in 100 ml 0.5 N H₂SO₄ is dissolved by heating and filtered to use.
- (iv) 10% Thiourea solution
- (v) 80 % H₂SO₄
- (vi) Bromine water: 1-2 drops of of liquor bromine in approximately 100 ml cool water.
- (vii) Stock standard solution: 100mg ascorbic acid is dissolved in 100 ml of 4% oxalic acid solution (1mg/ml). Working standard solutions of different concentrations were prepared from this stock solution.

Procedure:

Extraction: 0.5-5 g of sample material was grinded using a mortar pestle in 25- 50 ml 4% oxalic acid solution and centrifuged.

A 10 ml aliquot was transferred to conical flask and bromine water was added drop wise with constant stirring. The enolic H atoms in ascorbic acid are removed by bromine. When the extract turned orange yellow due to excess bromine expelled it by blowing in air. The volume was made up to 100 ml with 4% oxalic acid solution.

10-100 µg standard dehydro ascorbic solution was pipetted out into the tubes. Different amount of aliquots (0.1 ml to 2 ml) of brominated sample extract were pipetted out depending upon the probable concentrations. The volume was made up to 3 ml by adding distilled water. 1 ml of DNPH reagent was added followed by 1-2 drops of thiourea to each tube. A blank was set with water ion place ascorbic acid solution. The contents were mixed thoroughly and incubated at 37° C for 3 hrs. After incubation the

orange red osazone crystals formed by adding 7 ml of 80% H_2SO_4 was dissolved. Then the absorbance was measured at 540 nm. The ascorbic acid contents of the samples were calculated using the standard curve obtained by plotting ascorbic acid concentration vs. absorbance.

4.2.3.6 Estimation of protein (Lowry et al., 1951)

Principle:

Estimation of protein was performed by following the method of Lowry *et al.*, (1951). The blue color developed by the reaction of the phosphomolybdic- phosphotungstic components in the Folin-Ciocalteu reagent by the amino acids tyrosine and tryptophan present in the protein plus the color developed by the biuret reaction of the protein with the alkaline cupric tartarate are measured in the Lowry's method.

Reagent:

- (i) Reagent A: 2 gm of Na_2CO_3 and 400 mg of NaOH were dissolved in 100 ml of distilled water.
- (ii) Reagent B: 0.5 % of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1 % sodium-potassium-tartarate.
- (iii) Reagent C: 50 ml of reagent A is mixed with 1 ml of reagent to prepare reagent C.
- (iv) Reagent D (Folin-Ciocalteu reagent): A mixture containing 100 g Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), 25 g sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), 700 ml water, 50 ml 85% H_3PO_4 and 100 ml concentrated HCl is refluxed in a 1.5 liter flask. After adding 150 g lithium sulphate, 50 ml water and a few drops of bromine water the mixture is boiled for 15 min without condenser to remove excess bromine. Then it is cooled and filtered after dilution to 1 liter. The reagent should not have the greenish tint. The purchased Folin-phenol solution may also be used after preparation of 1: 1 solution with distilled water.

- (v) Standard protein solution: After making 1mg/ml Bovine Serum Albumin (Fraction V) as stock solution working standards of different concentrations are made.

Procedure:

Extraction: 10 mg of the plant material was weighed out and crushed first with 3 ml and then 7 ml of distilled water. This was transferred into a centrifuge tube and centrifuged for 10 minutes at 1000 rpm. 0.2 ml from the supernatant liquid was pipette out in a test tube and added all the protein reagents.

Standard: A set of standard solutions including the blank was prepared into test tubes with different aliquots of stock solution (protein) along with water using micro and macro pipettes respectively 0.9 ml of reagent a was added to each test tube and incubated for 15 minutes at room temperature. Then 0.1 ml of reagent B was added and allowed to stand for 30 minutes. After some time 5 ml of distilled water was added to each test tube and mixed well.

Calculation: A plot of the absorbance against the concentration is drawn using micro-soft excel and from the calibration curve, the concentration of protein was calculated.

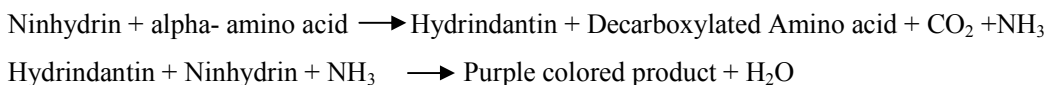
4.2.3.7 Estimation of amino acid (Moore and Stein, 1948)

The amino acids are colorless ionic compounds that form the basic building blocks of proteins. Apart from being bound as protein, amino acid can exist in free form mostly of which is water soluble and known as free amino acid. Measurement of free amino acid content indicates the physiological and health status of the plant.

Principle

Amino acids are decarboxylated by a powerful oxidizing agent, Ninhydrin to yield an intensely colored bluish purple colored compound. Measuring the intensity of the color at the wave length 570 nm, amino acid content can be measured.

The reaction can be represented as:



Materials

- (i) 0.2 M Citrate Buffer (pH 5.0)
- (ii) Ninhydrin solution: 0.8 gm of Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) is dissolved in 500 ml of 0.2 M citrate buffer (pH 5.0) and added to 20 g of ninhydrin in 500 ml of methyl cellosolve (2-Methoxyethanol).
- (iii) Diluent solvent: Equal volume of water and n- Propanol mixed to prepare the diluents solvent.

Procedure:

Extraction: 500 mg of plant sample is ground in mortar- pestle with a small quantity of acid washed sand. 5-10 ml of 80 % ethanol is added to it. After repeated extraction (twice) of the residue after centrifugation with ethanol, all the supernatant was collected and the volume of the extract is reduce by evaporation. For tough tissues boiling 80% ethanol is used for extraction.

Examination: 1 ml of ninhydrin is added to 0.1 ml of extract and the volume is made up to 2 ml with distilled water. Keeping this solution in boiling water bath for 20 minute, 5 ml of the diluents is mixed. After 15 min. colorimetric estimation is done at an wave length of 570 nm. The color is stable for 1h, therefore lingering should be avoided. Blank reagent is prepared by the same process by taking 0.1 ml 80% ethanol in the place of the extract.

Standard: Standard solutions of different concentrations are prepared by dissolving leucine in distilled water. The same procedure is maintained as for the sample to estimate the standard.

Calculation: Using the absorbance vs. concentration standard curve concentration of the total free amino acid is determined and expressed as percentage equivalent of leucine.

4.2.4 Statistics and diagrams

The results were statically analyzed (Mean, Median, Standard Deviation, Standard error mean and correlation analysis among various parameters) with the help of Minitab 16 and SPSS 7.5 software package. Gw_chart software was used to draw the Piper diagrams.

4.2.5 Other Calculations

4.2.5.1 Water Quality Index (WQI):

For calculating the WQI in the present study, 13 parameters namely, pH, electrical conductivity, total dissolved solids, total hardness, alkalinity, calcium, magnesium, sodium, potassium, iron, chloride, sulphate, phosphate and fluorides have been considered (Table 23). There were three steps for computing WQI of a water sample.

- Each of the chemical parameters was assigned a weight (w_i) based on their perceived effects on primary health and relative importance in the overall quality of water for drinking purposes (Table 23). The highest weight of 5 was assigned to parameters which have the major effects on water quality (e.g., F^- and TDS) and a minimum of 2 was assigned to parameters which are considered as not harmful (Ca^{2+} , Mg^{2+} , K^+).
- Computing the relative weight (W_i) of each parameter using Eq. 1. Table 23 present the weight (w_i) and calculated relative weight (W_i) values for each parameter.
- A quality rating scale (q_i) for each parameter is computed by dividing its concentration in each water sample by its respective standard according to the guidelines laid down by BIS (2009) and then, the result was multiplied by 100 using Eq. 2. Finally, for computing the WQI, the water quality sub-index (SI_i) for each chemical parameter is first determined, which is then used to determine the WQI as per the Eqs. 3 and 4.

$$W_i = \frac{w_i}{\sum_{n=1}^n w_i} \quad (1)$$

Where W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters.

$$q_i = \left(\frac{C_i}{S_i} \right) \times 100 \quad (2)$$

where q_i = quality rating, C_i = concentration of each chemical parameter in each water

sample in mg/L, S_i = Indian drinking water standard (BIS 2009) for each chemical parameter in mg/L except for conductivity (mS/cm) and pH.

$$SI_i = W_i \times q_i \quad (3)$$

$$WQI = \sum_{i=1}^n SI_i \quad (4)$$

Where SI_i is the sub-index of i th parameter; q_i is the rating based on concentration of i^{th} parameter and n is the number of parameters.

4.2.5.2 Percent Sodium (% Na)

Percent sodium in water is a parameter computed to evaluate the suitability for irrigation (Wilcox 1955) and is expressed as follows:

$$\% \text{ Na} = \frac{\text{Na} \times 100}{(\text{Ca} + \text{Mg} + \text{Na} + \text{K})}$$

where all the ions are expressed in meq/L.

4.2.5.3 Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio (SAR) is an important parameter for determination of suitability of irrigation water (Todd 1980) and is expressed as below:

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca} + \text{Mg})/2}}$$

where all the ions are expressed in meq/L.

4.2.5.4 Permeability index (PI)

Doneen (1964) evolved a criterion for assessing the suitability of water for irrigation based on permeability index (PI).

$$\text{PI} = \frac{(\text{Na} + \sqrt{\text{HCO}_3^-}) \times 100}{(\text{Ca} + \text{Mg} + \text{Na})}$$

where all the ions are expressed in meq/L.

4.2.5.5 Magnesium hazard (MH)

A ratio namely index of magnesium hazard was developed by Paliwal (1972). According to this, high magnesium hazard value (>50 %) has an adverse affect on the crop yield as the soil becomes more alkaline. Magnesium hazard ratio can be computed using the following equation:

$$MH = \frac{Mg \times 100}{(Ca + Mg)}$$

where all the ions are expressed in meq/L.

4.2.5.6 Percent biochemical change (PBC)

Percent change in biochemical constituents with respect to control area were calculated for better perception of the effect of fluoride on them. Percent Biochemical Change (PBC) was calculated using the following formula:

$$PBC = \frac{(S - C) \times 100}{S}$$

where S = amount of biochemical constituent (sugar, chlorophyll, ascorbic acid, protein and amino acid) in vegetable samples collected from fluoride affected area; C = amount of biochemical constituent (sugar, chlorophyll, ascorbic acid, protein and amino acid) in vegetable samples collected from control area.

4.2.5.7 Bioconcentration Factor (BCF)

For estimating fluoride concentrations in vegetables the common parameter is the Bio concentration Factor (BCF). BCF is the ratio of F concentration in the vegetable and F concentration in soil, and is computed using the following equation:

$$BCF = \frac{\text{F concentration in vegetable (mg /kg of vegetable)}}{\text{F concentration in soil (mg/Kg soil)}}$$

CHAPTER - 5

RESULTS AND DISCUSSION

5.1 WATER

5.1.1 Fluoride

Fluoride along with other water parameters were estimated in 220 sites of 22 villages from 4 blocks, namely, Nalhati I, Rampurhat II, Khoyrasole and Mahammad Bazar in Birbhum district during pre monsoon (PRM) and post monsoon (POM) seasons (Table 2-9). Thorough investigations regarding the water parameters showed that mean fluoride levels in Nalhati I block during PRM and POM were 3.15 mg/L and 2.98 mg/L respectively (Table 10) which are much higher than the recommended level of fluoride (F^-) in drinking water of 1.5 mg/L (WHO, 2011; BIS, 2009). About 90 % of the water samples exceeded the recommended value (WHO, 2011; BIS, 2009) during both PRM and POM (Table 2, 3) in Nalhati- I block. In Rampurhat -II block during PRM and POM the mean fluoride concentration in ground water were 3.96 mg/L and 3.57 mg/L respectively (Table 11) which are much higher than the aforesaid recommended level of fluoride in drinking water. In this block, all the samples (Table 4) collected during PRM and 97.5 % of the samples collected during POM (Table 5) exceeded the recommended value indicating high health and environmental hazards. Although the other two blocks investigated namely, Khoyrasol and Mahammad Bazar showed relatively lower fluoride level in comparison to these two blocks of Nalhati- I and Rampurhat –II. Khoyrasol block is in alarming position where some cases of dental fluorosis were observed. This block had the mean fluoride level of 2.26 mg/L and 2.06 mg/L during PRM and POM seasons respectively (Table 12). Water analysis results indicated (Table 6, 7) that 69.5 % and 66 % water examined had the fluoride level above the recommended value of 1.5 mg/L during PRM and POM respectively in Khoyrasol block. The mean fluoride levels in examined waters were 0.97 mg/L and 0.9 mg/L during PRM and POM respectively in Mahammad Bazar block indicating lower risk. But in few cases, fluoride levels were greater than the recommended value of 1.5 mg/L during PRM (6 % of the total samples examined) and POM (4 % of the total sample examined) in Mahammad Bazar block (Table 8, 9). The highest level of fluoride observed in the whole study considering all the four blocks was observed in

Nowapara village (9.98 mg/L) of Rampurhat-II block during PRM season (Table 4). An overview of the results indicates that the average fluoride level in all four blocks decreased slightly during POM season in comparison to PRM season. A comparative status of fluoride concentration during PRM and POM season in all the four blocks is illustrated in Fig. 43. This type of decreasing tendency of fluoride level during POM with respect to PRM was noticed before by Vasanthavigar et al., (2010). The lowering of fluoride concentration in POM with respect to PRM in all the four blocks supported the fact of high fluoride incidence in the arid region. The cause of decreasing tendency of fluoride level during POM with respect to PRM may be attributed to the fact of higher weathering and leaching of fluoride bearing minerals during PRM. The rain fall during the monsoon may cause the dilution effect, which in turn decreases normally the concentration of fluoride in water during POM (Vasanthavigar et al., 2010).

5.1.2 Other physico-chemical parameters

Along with F^- , other physico-chemical water-parameters, such as, pH, EC, TH, TA, Cl^- , HCO_3^- , Ca, Mg, SO_4^{2-} , Fe, PO_4^{3-} , TDS, Na, K and SiO_2 of each water sample collected from four blocks of Birbhum district during PRM and POM were measured and the values were listed (Table 2-9). From Table 2 and 3, the measured values of these parameters of water samples collected during PRM and POM in different villages (Nasipur, Vabanandapur and Deshnabagram) of Nalhati-I block can be inspected explicitly. The aforesaid physico-chemical parameters of ground water collected from Kamdebpur, Chak Atla, Nowapara and Junidpur villages in Rampurhat-II block during PRM and POM are listed in Table 4 and Table 5 respectively. Table 6 and Table 7 comprises of the estimated values of various physico-chemical parameters (F^- , pH, EC, TH, TA, Cl^- , HCO_3^- , Ca, Mg, SO_4^{2-} , Fe, PO_4^{3-} , TDS, Na, K and SiO_2) of ground water samples collected from the ten villages, namely, Gostho Dungal, Sarsa, Tithikapur, Lauberia, Tarapur, Nowpara, Bhadulia, Paschim Sibpur, Rasa and Hazratpur of Khoyrasol block during PRM and POM respectively. The estimated values of the same physico-chemical parameters of the ground water samples collected during PRM and

POM seasons from the villages of Chak Sehara, Kaijuli, Lohabazar, Seharakuri and Sankarpur in Mahammad Bazar block are listed in the Table 8 and Table 9 respectively. Going over the computed statistical values listed in Table 10, Table 11, Table 12 and Table 13, interpretations can be done explicitly regarding minimum (min), maximum (max), mean, standard deviation (SD) and standard error mean (SE Mean) values of the aforesaid water parameters collected from the Nalhati-I, Rampurhat- II, Khoyrasol and Mahammad Bazar block respectively. The percent sample exceeding the water parameter limit of BIS (2009) can be viewed from Table 22. From the table it is evident that most of the samples collected showed EC values higher than the permissible limit. As EC value denotes the presence of high concentration of cation and anion, it can be inferred that high amount of minerals are dissolved in the water through leaching process. Most of the water parameters in Nalhati- I block during both PRM and POM (7 parameters, viz., pH, EC, TH, Mg, K, Fe, PO_4^{3-}) exceeded the BIS (2009) permissible limit. Eight parameters, viz., pH, EC, Mg, Na, K, SO_4^{2-} , Fe, and PO_4^{3-} in water samples of Rampurhat-II during both PRM and POM exceeded the BIS (2009) permissible limit. In Khoyrasol and Mahammad Bazar block, all the water parameters of the water samples were below the BIS (2009) permissible limit during both in PRM and POM except six parameters, viz., pH, EC, Mg, K, Fe and PO_4^{3-} . Therefore from the above results it can be concluded that much concentration of fluoride in water makes the other physico-chemical parameters to go beyond the desirable limit in ground water.

Comparative approaches were made to relate the effect of seasonal variation with water parameters and are illustrated in the Fig. 7, Fig. 8, Fig. 9 and Fig. 10 for Nalhati-I, Rampurhat- II, Khoyrasol and Mahammad Bazar block respectively. A throughout inspection of these figures revealed that mean of Na and K level in all four blocks decreased in POM in comparison to PRM. The higher level of Na during PRM may be ascribed to the fact of weathering from plagioclase bearing rocks and over exploitation (Hem, 1985) and the higher level of K in PRM may also arise from weathering of potassium bearing rocks along with the dilution effect in POM. Average concentrations of HCO_3^- , Fe and TA also showed such decreasing tendency indicating a dilution effect

except in Mahammad Bazar block where increasing propensity were noticed in case of these parameters. The mean value of SiO_2 also showed this trend except in the case of Nalhati -I block.

Elevation of mean Mg and Cl level were noticed in POM in comparison to PRM in all four blocks. Increase in Cl level during POM may be due to leaching from upper soil layers derived from industrial and domestic activities and dry climates (Srinivasamoorthy et al., 2008). Higher level of Mg during POM might have been derived from dissolution of magnesium calcite, gypsum, and dolomite from the source rocks (Garrels and Christ, 1965). The mean level of Ca was observed to be higher in magnitude in POM in comparison to PRM in all the blocks except Mahammad Bazar. Ca was higher during POM due to probable dissolution of precipitates of CaCO_3 and $\text{Ca Mg}(\text{CO}_3)_2$ during recharge of ground water in monsoon season (Datta and Tyagi, 1996; Lakshmanan et al., 2003). The mean values of TDS, SO_4^{2-} , TH and pH showed the same trend during POM in Nalhati-I and Rampurhat- II block where high mean fluoride levels were noticed. SO_4^{2-} was higher in POM due to probable action of leaching and anthropogenic activities in a metamorphic environment by release of sulfur gases from industries that get oxidized and enter into the groundwater system (Saxena, 2004). These parameters (TDS, SO_4^{2-} , TH and pH) showed the reversed propensity in Khoyrasol and Mahammad Bazar block. In Khoyrasol and mahammad Bazar the mean values of PO_4^{3-} were same in PRM and POM but the elevated level was observed in Nalhati-I and Rampurhat- II during POM in comparison to PRM. The increase may be attributed to the fact of leaching from phosphate fertilizers used in these agriculture based areas.

5.1.3 Hydrochemical facies

Hydrochemical concepts may become helpful for the explication of the mechanisms of flow and transport in groundwater systems (Pierre et al., 2005) as the hydrochemical facies of groundwater depends on lithology, resident time and regional flow pattern of water (Domenico, 1972). Piper plot (Piper, 1944; 1953) is used for the conjecture of hydrogeochemical facies of groundwater. The interpretation of the results of the

chemical analyses of water samples were done using Piper diagrams to discriminate the type of waters in terms of the major constituent cations (Na, K, Ca, and Mg) and anions (Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-}) of the water samples fetched from the four blocks of the study area (Figure 6- 9).

On the basis of the explanation after Piper (1944) and Walton's classification (Walton 1970), 46.67 % of the water samples of Nalhati I block during PRM (Fig. 11), the carbonate hardness (secondary alkalinity) exceeded 50 %, i.e., alkaline earths (Ca + Mg) and weak acids ($\text{HCO}_3^- + \text{CO}_3^{2-}$) dominated. No one cation – anion pair > 50 % was observed in 40 % (mixed Ca- Na- HCO_3^- facies: 26.67 % and mixed Ca-Mg- Cl^- facies: 13.33 %) samples of this block during PRM. 43.33 % (mixed Ca- Na- HCO_3^- facies: 30 % and mixed Ca-Mg- Cl^- facies: 13.33 %) samples of this block during POM exhibited both no one cation - anion pair > 50 % and the carbonate hardness (secondary alkalinity) > 50 % (Fig. 12).

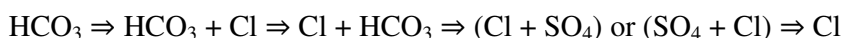
In Rampurhat II block, 40 % and 45 % of the water samples collected during PRM and POM respectively showed non carbonate alkalinity to be greater than 50 %, i.e., an excess of alkaline earth with respect to alkalis (Na + K) (Fig. 13, 14). In both PRM and POM, 40 % of the water samples showed no one cation – anion pair > 50 % (mixed Ca-Mg- Cl^- facies) in this block.

Non-carbonate hardness > 50 % were observed in 48 % sample of Khoyrasol block in both PRM and POM (Fig. 15, 16). Non carbonate alkali exceeding 50 %, i.e. alkali and strong acid dominance were observed in 28 % and 36 % of the samples in this block collected during PRM and POM respectively. The rest of the samples of this block collected in two different seasons showed no one cation – anion pair to exceed 50 % (mixed Ca- Na- HCO_3^- facies).

In Mahammad Bazar block, non carbonate alkali exceeding 50 %, i.e. alkali and strong acid dominance were noticed in 36 % and 32 % samples collected during PRM and POM respectively (Fig. 17, 18). Non-carbonate hardness > 50 % were observed in 34 % and 36 % of the samples in PRM and POM respectively. In this block, 30 % and 32 % of the water samples collected during POM and POM respectively showed no one cation – anion pair > 50 % (mixed Ca- Na- HCO_3^- facies).

The concentrations of major constituent cations and anions taken in account of the Piper diagram varied widely throughout the study areas as they mainly depends upon the metamorphism of groundwater geochemistry which is a function of salinity concentration and depth below the Earth's surface (Chebotarev, 1955). The Chebotarev sequence, which explicates transformation of water chemistry with depth, expressed in simpler terms as follows (Chebotarev, 1955):

Bicarbonate waters \Rightarrow Sulfate waters \Rightarrow Chloride waters



According to Chebotarev (1955) bicarbonate waters occur near the Earth's surface, while chloride waters occur in the deeper geologic strata. The region of active exchange between these two water types varies widely. The deepest ground waters belong to the chloride type, at depths over 11,000 ft while bicarbonate waters occur at shallower depths, with sulfate waters of a transitional type.

5.1.4 Correlation between physico-chemical parameters

An attempt was taken to correlate the fluoride and other water parameters of the four blocks during both PRM and POM season and the correlation values with level of significance are indicated in the tables attached (Table 14 -21).

All the parameters showed positive correlation with fluoride except pH, iron (Fe), phosphate (PO_4^{3-}), total alkalinity (TA), silica (SiO_2) and potassium (K) in Nalhati I block during both PRM (Table 14) and POM (Table 15), although the magnitude of correlation were different. pH (PRM: $r = -0.552$, POM: $r = -0.480$) and PO_4^{3-} (PRM: $r = -0.418$, POM: $r = -0.413$) had a significant negative correlation with fluoride during PRM and POM.

In Rampurhat II block, all the parameters were positively correlated with fluoride except pH, chloride (Cl^-), calcium (Ca), and phosphate (PO_4^{3-}) during both PRM (Table 16) and POM (Table 17) with different correlation coefficients. pH (PRM: $r = -0.509$, POM: $r = -0.546$), PO_4^{3-} (PRM: $r = -0.410$, POM: $r = -0.371$) had a negative and HCO_3^- (PRM: $r = 0.504$, POM: $r = 0.373$), TDS (PRM: $r = 0.358$, POM: $r = 0.424$), Na (PRM:

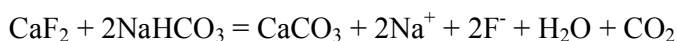
$r = 0.614$, POM: $r = 0.592$) had a positive correlation with fluoride in this block during both PRM and POM. There were significant positive correlation in this block between SO_4^{2-} and F^- ($r = 0.321$), negative correlation between Ca and F^- ($r = -0.436$) during PRM. But during POM, Mg showed a significant positive correlation ($r = 0.356$) with fluoride in this block.

Mg, SO_4^{2-} , Fe, PO_4^{3-} , Na, K and SiO_2 had the negative correlation with fluoride in Khoyrasole block in both PRM (Table 18) and POM season (Table 19). Amongst the other parameters, namely, pH, EC, TH, TA, Cl^- , HCO_3^- and Ca were positively correlated with fluoride in this block in both PRM and POM. EC (PRM: $r = 0.23$, POM: $r = 0.226$), TA (PRM: $r = 0.279$, POM: $r = 0.304$) and HCO_3^- ($r = 0.356$, POM: $r = 0.351$) had significant correlation with fluoride in PRM and POM.

In Mahammad Bazar block all the parameters showed a positive correlation with fluoride except TA, HCO_3^- and K during PRM (Table 20). During POM, there were positive correlation between all the parameters and fluoride except TA, HCO_3^- , Fe and K in this block (Table 21). But only pH had a significant correlation with F^- ($r = 0.566$) during PRM.

Although all the parameters did not show any consistent correlation with fluoride in all the four blocks during two seasons but a few were very significant in the blocks with high fluoride level. Positive correlations of Ca and Mg with fluoride in some cases as were observed in the study to comply with the report of Alagumuthu and Rajan (2010). The positive correlation with calcium observed in some of the cases stated above, may be attributed to the presence of limestone in those areas (Taher and Ahmed, 2001). But the negative correlation of fluoride with Ca indicates that it has higher affinity for sodium than calcium, and this may be due to the dominance of ion exchange between Na and Ca ions (Singh et al., 2011). All the fluoride prone blocks (Nalhati- I, Rampurhat-II and Khoyrasol) showed a positive correlation between F^- and HCO_3^- (significant in Rampurhat-II and Khoyrasol block) during both PRM and POM. According to Saxena and Ahmed (2003), high concentration of HCO_3^- and alkaline pH are the favorable conditions for the dissolution of fluorite (CaF_2) minerals.

The chemical process of fluoride dissolution according to Salve et al., (2008) can be represented as:



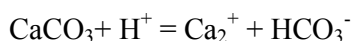
Elaborate discussion may provide better understanding of chemical process involved in fluoride dissolution. The solubility product (K_{sp}) of fluorite mineral (CaF_2) is determined according to the following equation as:



$$K_{sp} = (a_{\text{Ca}^{2+}}) \times (a_{\text{F}^-})^2 = 10^{-9.4} \text{ (at } 25^\circ \text{ C)}$$

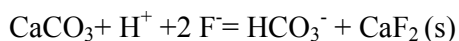
Where $a_{\text{Ca}^{2+}}$ and a_{F^-} are the activities of the concerned ions.

Due to the low solubility of CaF_2 (low K_{sp}) the occurrence of aqueous fluoride is predominantly governed by availability of free Ca^{2+} ion in water (Jacks, 1973). But the solubility product of CaCO_3 is much larger than that of fluorite (CaF_2):



$$K_{sp} = a_{\text{Ca}^{2+}} \times a_{\text{HCO}_3^-} / a_{\text{H}^+} = 0.97 \times 10^2$$

As the solubility product (K_{sp}) for fluorite is constant, the activity of fluoride is directly proportional to HCO_3^- , if the pH is constant. A combined equation is derived to compute the thermodynamic equilibrium in the ground water system in contact with both Calcite (CaCO_3) and Fluorite (CaF_2) (Handa, 1975).



$$K_{sp} = (a_{\text{HCO}_3^-}) / [(a_{\text{H}^+}) \times (a_{\text{F}^-})^2] = 1.06 \times 10^{-11} \text{ (Helgeson, 1969)}$$

From above equation, it can be concluded that aqueous fluoride concentrations are proportional to bicarbonate concentrations and pH values. High bicarbonate level in water increases the dissolution of fluoride in water and for this reason high bicarbonate concentration was noticed in the fluoride contaminated water.

5.15 Principal component analysis

Principal component analysis (PCA) represents the original dataset in a new reference system characterized by new orthogonal variables called Principal Components. The first principal component (PC) explains the maximum possible amount of residual variance in the overall data while the second one explains the residual variance.

The coefficients of the linear combination describing each PC, i.e. the weights of the original variables on each PC, are called loadings. The loading plots help the identification of groups of samples showing similar behaviors (samples close one to the other in the graph) or different characteristics (samples far from each other). The most important variables in the plot are found on the periphery, whereas non-influential variables are encountered around the origin of plot. Furthermore, the direction of each vector has an importance as a constituent of the samples lying in the direction in which the vector points. Therefore the analogies or the differences between the water parameters can be detected easily from the corresponding loading plots.

Speculation of PCA loading plot of all four blocks during PRM and POM can depict the dominant parameters ranking the water bodies (Fig. 19-26). According to Ayoko et al., (2007), most important variables are those with first component loadings > 0.20 or < 0.20 and second component loadings > 0.35 or < 0.35 .

The PCA loading plot of the water parameters in PRM season of Nalhati-I block portrayed the first principal component loading vector to have fairly large positive coefficients for Cl^- , Mg, SO_4^{2-} , TH, EC, TDS, Na, K and relatively large negative coefficients for PO_4^{3-} (Fig. 19). The second principal component loadings vector had relatively large positive coefficients for Fe and large negative coefficients for HCO_3^- and TA. The same findings were obtained for the water parameters in POM season of this block from the PCA loading plot (Fig. 20). Parameters having significant influences on fluoride have been found to make clusters among themselves. The relationship of fluoride with chloride (Cl^-) can explicitly be visualized in the upper right quadrant of the graph plot with a slight relation with Mg, SO_4^{2-} and TH (Fig. 19) for the parameters of this block during PRM. Fluoride showed a relationship with Cl^- in addition to a slight relation with Mg, SO_4^{2-} , TH and SiO_2 in POM (Fig. 20) in PRM. The above facts can be corroborated with the correlation values.

The loading plot of the water parameters in PRM season of Rampurhat-II depicted that the first principal component loading vector had large positive coefficients for Mg, TH, EC, TDS, F⁻, Na and relatively large negative coefficients for pH, PO_4^{3-} (Fig. 21). The second principal component loadings vector had relatively large positive coefficients

for SO_4^{2-} and large negative coefficients for Fe, HCO_3^- and TA. In this block during PRM, the water parameters Na, Fe, TH, TDS, EC and Mg were associated with fluoride in lower right quadrant of the graph plot indicating influences on fluoride; although TDS, EC and Mg depict the nearest association. In POM season the PCA loading plot rendered that first principal component loading vector had large positive coefficients for Mg, TH, EC, TDS, F^- , Na, Fe and relatively large negative coefficients for pH, PO_4^{3-} (Fig. 22). The second principal component loadings vector had relatively large positive coefficients for SO_4^{2-} and large negative coefficients for HCO_3^- and TH in POM. In this plot fluoride is associated with TDS, Mg, TH, EC, Na, Fe and K in lower right quadrant indicating TDS as the nearest association.

From the loading plot of the water parameters in PRM season of Khoyrasol block it is evident that the first principal component loading vector had large positive coefficients for Mg, TH, EC, TDS, Ca, Cl^- and relatively large negative coefficients for pH (Fig. 23). The second principal component loadings vector had large negative coefficients for F, HCO_3^- and TA. In this block during PRM, the water parameter EC is associated with fluoride in lower right quadrant of the graph plot indicating influences on fluoride. In POM season the PCA loading plot rendered the same findings as in the PRM season except the nearest association of fluoride to be with TA and EC (Fig. 24).

The first principal component loading vector of PCA loading plot of water parameters during PRM season in Mahammad Bazar block had large positive coefficients for Mg, TH, EC, Ca, Cl^- and relatively large negative coefficients for SO_4^{2-} , PO_4^{3-} (Fig. 25). The second principal component showed large negative coefficients for F, Fe, TDS, pH and SiO_2 . In this block during PRM, the water parameters Fe and TDS were closely associated with fluoride in lower right quadrant of the graph plot indicating influences on fluoride. In POM season the PCA loading plot depicted that first principal component loading vector had large positive coefficients for PO_4^{3-} and SO_4^{2-} and relatively large negative coefficients for Mg, TH, EC, Ca, Cl^- (Fig. 26). The second principal component loadings vector had relatively large positive coefficients for SiO_2 and large negative coefficients for HCO_3^- and TA in POM. In this plot fluoride is

closely associated with TDS in upper left quadrant. All these findings are very consistent with the hierarchical cluster analysis that can be found elsewhere.

5.1.6 Cluster analysis

Cluster analysis technique is used for the investigation of the relations between the objects or the variables for the recognition of the existence of groups. The clustering algorithm in agglomerative hierarchical method determines the defined similarity between multiple-member clusters (Roy et al., 2012). The most similar objects or groups of objects are linked and the result of such analyses graphically represented as dendrogram, where the objects along X axis are connected at decreasing levels of similarity (Y axis). The height of the node is depicted as the distance value between the sub-branch clusters. The distance measure between two clusters is calculated by the equation, $D = 1 - C$; where D = Distance and C = correlation between spot clusters.

Plot of hierarchical cluster regarding the water parameters collected from all the four blocks with Ward's linkage is portrayed in Fig. 27-34.

From the component analysis (CA) dendrogram of the water parameters during PRM season in Nalhati- I block (Fig. 27) portrayed that EC and TDS had the close similarity (96.92). This fact is inevitable as the dissolved solids or ions are responsible for the conductance. Electrical conductivity of water is a direct function of its total dissolved salts (Harilal et al., 2004) representing the total concentration of soluble salts in water (Purandara et al., 2003; Gupta et al., 2008). But if the branching of fluoride is focused, a little similarity (56.93) is seen with Fe and SiO_2 . All other parameters had similarity of 63.15 with fluoride. Close inspection of the dendrogram during POM revealed that F^- shows highest similarity (63.51) with all the parameters except phosphate and iron (Fig. 28).

In the case of Rampurhat-II block in PRM, the CA dendrogram (Fig. 29) showed that fluoride had the highest similarity with sodium (78.65) and potassium (77.31). This similarity may be attributed to the fact that fluoride comes to the solution phase being bound with the alkali metals (Na and K). During POM, CA dendrogram (Fig. 30) also depicted that fluoride has the nearest similarity with Na and K (79.62).

Fluoride showed the closest similarity (82.75) in dendrogram (Fig. 31) with TA and bicarbonate during PRM in Khoyrasol block ascertaining high concentration of HCO_3^- and alkalinity to be the favorable conditions for the dissolution of fluorite (CaF_2) minerals (Saxena and Ahmed, 2003). About the same type of dendrogram is obtained during POM (Fig. 32) indicating the closest similarity of both TA and HCO_3^- with fluoride (84.4).

Dendrogram obtained from CA with water parameters of Mahammad Bazar block during PRM (Fig. 33) indicated the closest relation between fluoride and pH (78.32) due to higher dissolution of fluorite minerals at higher pH. In POM, the CA dendrogram (Fig. 34) predicted no close similarity of fluoride with other parameters, only a distance of 60.33 was observed with all the parameters.

Although the similarity of fluoride was the only matter of attention other close similarity and relation can be depicted with the other parameters from the dendograms.

5.1.7 Water Quality Index (WQI)

The Water Quality Index (WQI) was computed for each water samples collected from the villages of four blocks to assess the quality of water that the dwellers intake as drinking water. The computed WQI values are classified into five types namely, excellent water ($\text{WQI} < 50$), good water ($50 < \text{WQI} < 100$), poor water ($100 < \text{WQI} < 200$), very poor water ($200 < \text{WQI} < 300$) and water unsuitable for drinking ($\text{WQI} > 300$) (Ravikumar et al., 2013).

The WQI value computed in Nalhathi-I block during PRM (Feb 2011) was found to be 117.58 ± 45.89 (expressed as mean \pm SD) with the minimum and maximum value of 59.36 and 342.52 respectively (Table 24). The maximum percentage (46.67 %) of water samples collected during this season was found to be of poor quality (Table 28). The samples collected during POM (Sep 2010) showed the WQI value 116 ± 45.1 with the minimum and maximum value of 59.1 and 336.6 respectively (Table 24). The maximum percentage (46.67 %) of the samples was poor in quality during this season also. The WQI values during both PRM and POM are graphically represented in the

Fig. 39. The poor water quality in this block originated mainly from high fluoride concentration.

Computed WQI value in Rampurhat-II block during PRM (Feb 2011) was found to be 122.1 ± 39.72 and the range of WQI value was 66.02 to 226.67 (Table 25). The maximum percentage (60 %) of water samples collected during this season was found to be of poor quality (Table 28). The samples collected during POM (Sep 2010) showed the WQI value 116.5 ± 35.25 with the minimum and maximum value of 64.04 and 218.67 respectively (Table 25). The maximum percentage (62.5 %) of the samples was poor in quality during this season also. The graphical representation in the Fig. 40 of WQI values during both PRM and POM gives us an overview of the water quality. The poor water quality in this block also instigated from high fluoride concentration as most of the other water parameters remain in the BIS (1998) permissible limit.

The WQI value in Khoyrasol block during PRM (April 2011) was 100.5 ± 25.9 with the minimum and maximum value of 39.81 and 165.41 respectively (Table 26). The maximum percentage (53 %) of water samples collected during this season was found to be of poor quality (Table 28). The samples collected during POM (Sep 2012) showed the WQI value 95.1 ± 24 with the minimum and maximum value of 37.9 and 155.28 respectively (Table 26). The maximum percentage (55 %) of the samples was good in quality during this season. Here in this block, the water quality changed abruptly with the seasonal variation. Most of the water samples turned to good water during POM from poor water during PRM. The recharge of good water during monsoon in ground water may have led the change with the dilution effect. The graphical representation in the Fig. 41 of WQI values during both PRM and POM gives us an overview of the water quality.

The average WQI values in Mahammad Bazar block during PRM (May 2011) was found to be 80.84 (SD = 20.75) and the range of WQI value was 36.58 to 124.56 (Table 27). The maximum percentage (70 %) of water samples collected during this season was found to be of good quality (Table 28). The samples collected during POM (Oct 2012) showed the WQI value 79.29 ± 19.67 with the minimum and maximum value of 38.85 and 122.91 respectively (Table 27). The maximum percentage (56 %) of the

samples was good in quality during this season also. In this block, a seasonal effect on WQI was observed like Khoyrasol block with a reversed trend. Here the water quality depleted during POM in comparison to PRM. This may be due to leaching of weathered minerals in to the ground water during monsoon season. An overview of the water quality can be depicted from the graphical representation in Fig. 42.

The summarized indication of comparative study regarding the average WQI and fluoride level of all four blocks during PRM and POM can be rendered in Fig. 44. To frame this diagram, WQI was divided with a numerical figure 25 to reduce the value comparable to the value of fluoride concentration (mg/L). The same pattern of peak and trough of WQI/25 and fluoride level (mg/L) indicated the vital role of fluoride in determining the WQI. The highest mean WQI/25 was observed (5.26) parallel to the highest mean level of fluoride (3.96 mg/L) in Rampurhat- II during POM and the lowest mean WQI/25 was observed (3.17) parallel to the lowest mean level of fluoride (0.9 mg/L) in Mahammad Bazar block during POM.

5.1.8 Irrigational quality parameters

Irrigational quality parameters were computed from the value obtained estimating the water parameters. Irrigational quality parameters deserve great importance when the study deals with the study of vegetation.

5.1.8.1 Sodium percentage (% Na)

The percentage of sodium (% Na) was calculated to depict the water classification both for drinking and irrigation. The widely recommended value of percentage of sodium in irrigation water should not exceed 50–60, to avoid its deleterious effects on soil. When the percent sodium exceeds 60, the water can be considered unsuitable for irrigational purposes. It is considered that water is of class I quality if the % sodium is less than 30 %, class II quality if the % sodium is between 30 and 75, and of class III quality if it is more than 75 (Ravikumar et al., 2013). Water quality reflected by sodium percentage values can be categorized according to Wilcox (1995) as < 20: Excellent, 20–40: Good, 40–60: Permissible, 60–80: Doubtful, >80: Unsuitable.

Computed % Na value in Nalhati- I block during PRM was found to be 33.04 ± 11.75 (expressed as mean \pm SD) and the range was 11.74 to 60.66 (Table 24). Therefore in view of mean value of percent sodium the water of Nalhati- I block during PRM can be categorized as class I quality for irrigation and good for drinking.

The samples collected during POM showed the % Na value 31.6 ± 11.45 with the minimum and maximum value of 11.08 and 58.74 respectively (Table 24). The mean % Na value during POM indicated the water to be good in quality (according to Wilcox categorization) and class I category for irrigation. From the lower mean value of % Na in comparison to fluoride corroborates the negative correlation of fluoride with sodium in this block.

Percentage of sodium value in Rampurhat-II block during PRM was 58.71 ± 14.36 with minimum and maximum value of 24.74 and 91.13 (Table 25). In view of mean % Na value the water of Rampurhat-II block during PRM can be categorized as class II quality for irrigation and permissible for drinking. The samples collected during POM showed the % Na value 57.5 ± 14.53 with the minimum and maximum value of 23.54 and 90.35 respectively (Table 25). The mean % Na value during POM indicated the water to be permissible in quality according to Wilcox categorization and class II category for irrigation. In Rampurhat-II block during both PRM and POM, the elevated level of sodium was observed in correlation to higher level of fluoride; which in turn gave rise to higher % Na with respect to the other blocks.

In Khoyrasol block during PRM, the % Na value was found to be 43.33 ± 18.16 with minimum and maximum value of 12.18 and 84.29 respectively (Table 26). Therefore, considering the mean % Na value, the water of Khoyrasol block during PRM can be categorized as class II quality for irrigation and permissible for drinking. The samples collected during POM showed the % Na value 41.46 ± 18.47 with the minimum and maximum value of 11 and 84.11 respectively (Table 26). The mean % Na value during POM indicated the water to be permissible in quality according to Wilcox categorization and class II category for irrigation.

Mahammad Bazar block during PRM had the % Na value of 42.51 ± 16.47 with minimum and maximum value of 12.19 and 83.06 respectively (Table 27). Therefore,

with respect to mean % Na value, the water of Mahammad Bazar block during PRM can be categorized as class II quality for irrigation and permissible for drinking. The samples collected during POM showed the % Na value 41.23 ± 16.1 with the minimum and maximum value of 11.15 and 81.11 respectively (Table 27). The mean % Na value during POM indicated the water to be permissible in quality (according to Wilcox categorization) and class II category for irrigation.

5.1.8.2 Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio (SAR) measures the suitability of water for use in agricultural irrigation due to its ability of reducing soil permeability and soil structure (Todd 1980). SAR is also a measure of alkali or sodium hazard to crops as it has a significant relationship with the extent to which sodium is absorbed by the soils when the water is used in irrigation. Sodium in the water can displace the calcium and magnesium in the soil causing a decrease in the ability of the soil to form stable aggregates and loss of soil structure (Sarath Prasanth, 2012). Problems with crop production also arise due to high SAR value leading to a decrease in infiltration and permeability of the soil to water. The groundwater based on SAR values can be classified in to four types (Todd 1959; Richards 1954): Excellent ($SAR < 10$), Good ($10 < SAR < 18$), Doubtful ($18 < SAR < 26$) and Unsuitable ($SAR > 26$).

The calculated values of SAR in Nalhati –I block during PRM had the mean value of 1.71 (SD = 0.78) and the values varied between 0.32 and 3.7 (Table 24). All the water samples had the SAR value well below 10. Therefore, classification of groundwater samples based on mean SAR values depicted the water samples to be excellent for irrigation purpose. During POM the SAR value was 1.61 ± 0.73 (mean \pm SD) with the minimum and maximum value of 0.3 and 3.48 indicating the excellence of all the water samples (Table 24).

The values of SAR in Rampurhat - II block during PRM was 5.11 ± 2.96 and the values varied between 1.11 and 12.47 (Table 25). The classification of groundwater samples based on mean SAR values depicted the water samples to be excellent for irrigation purpose. Only two water samples (one ($R_{pr} 5$) from Kamdevpur and the other ($R_{pr} 30$))

from Nowapara) had the SAR value greater than 10 indicating their goodness (instead of excellence) for irrigation. During POM the SAR value was 4.77 ± 2.76 with the minimum and maximum value of 1.04 and 11.6 respectively (Table 25). The SAR values of all the water samples during POM were of the excellent category except 3 samples (one (R_{pr} 5) from Kamdevpur and two (R_{pr} 26, R_{pr} 30) from Nowapara).

In Khoyrasole block during PRM had the mean SAR value of 3.1 (SD = 1.99) and the values varied between 0.67 and 9.9 (Table 26). All the water samples had the SAR value well below 10. Therefore, classification of groundwater samples based on mean SAR values depicted the water samples to be excellent for irrigational purpose. During POM the SAR value was 2.88 ± 1.88 (mean \pm SD) with the minimum and maximum value of 0.63 and 9.72 indicating the excellence of all the water samples (Table 26).

The mean SAR value of 2.94 (SD = 1.99) was observed with the range of 0.68 to 8.9 in Mahammad Bazar block during PRM (Table 27). All the water samples had the SAR value well below 10. Therefore, the groundwater samples based on SAR values can be classified as excellent for irrigation purpose. During POM the SAR value was 2.76 ± 1.57 (mean \pm SD) with the minimum and maximum value of 0.61 and 7.9 indicating the excellence of all the water samples (Table 27).

5.1.8.3 Permeability Index (PI)

The permeability index (PI) values in the study area of Nalhati-I block varied from 28.19 to 85.7 during the PRM period with an average value of 56.11 (Table 24). According to the classification based on PI proposed by World Health Organization (WHO) for assessing suitability of groundwater for irrigation purpose, 76.67 % of the samples fitted in the class 2 ($25 < PI < 75$) and 23.3 % belonged to class 1 ($PI > 75$) during PRM in this block. During POM, the mean value of PI was 54.57 with the minimum and maximum value of 27.01 and 84.13 respectively. In this season also 76.67 % samples belonged to the class 2 and the rest belonged to class 1.

The average permeability index (PI) values calculated in the study area of Rampurhat-II block varied from 43.6 to 139.03 during the PRM period with an average value of 90.99 (Table 25). According WHO proposition of classification regarding PI, 70 % of

the samples were of class 1 category and the rest 30 % belonged to class 2 during PRM in this block. During POM, the mean value of PI was 90.18 with the minimum and maximum value of 42.34 and 141.02 respectively. In this season also 70 % of the total samples belonged to the class 1 and the rest 30 % belonged to class 2.

In the study area of Khoyrasol block, the PI varied from 16.98 to 97.43 during the PRM period with an average value of 53.61 (Table 26). Going over the PI values revealed that 70 % of the water samples had the class 2 category, 21 % belonged to class 1 and rest 9 % was of class 3 category ($PI < 25$) during PRM in this block. During POM, the mean value of PI was 51.52 with the minimum and maximum value of 15.70 and 97.37 respectively. In this season 70 % samples belonged to the class 2, the 20 % belonged to class 1 and the rest 10 % were of class 3 category.

The permeability index (PI) values in the study area of Mahammad Bazar block varied from 16.64 to 96.76 during the PRM period with an average value of 53.28 (Table 27). According WHO classification based on PI, 76 % of the samples were under the class 2, 16 % belonged to class 1 ($PI < 75$) during PRM in this block. During POM, the average value of PI was 52.03 and the value ranged from 15.69 to 94.85. In this season 74 % of the samples were of the class 2 category, 16 % class 1 and the rest 10 % belonged to class 3.

An overview of all the results obtained from four blocks revealed that Rampurhat-II block during both PRM and POM had the highest percentage of class 1 category samples according to WHO classification based on PI. Because, the water samples of Rampurhat-II had high fluoride levels and in correlation had high Na and HCO_3^- level which resulted in higher permeability index.

5.1.8.4 Magnesium Hazard (MH)

In most waters calcium and magnesium maintains a state of equilibrium and maintains a ratio (Sarath Prasanth, 2012). Paliwal (1972) developed an index of magnesium hazard (MH) to understand the ratio. According to this, soil becomes more alkaline with high magnesium hazard value ($MH > 50$) of water which in turn implies an adverse affect on the crop yield.

The calculated values of magnesium hazard index (MH) in Nalhati –I block during PRM was found to be 51.26 ± 21.40 (mean \pm SD) and the values varied between 20.3 and 95.25 (Table 24). During POM, the MH value was 50.77 ± 21.4 with the minimum and maximum value of 10.21 and 95.21 (Table 24). In both the seasons, 43.3 % of the water samples had the MH value above 50 indicating only 56.7 % of the water samples to be suitable for irrigation.

In Rapurhat- II block, the MH ratio had the value of 57.45 ± 27.96 (mean \pm SD) and fell in the range of 8.19 to 94.37 during PRM season (Table 25). During POM, the MH value was 57.02 ± 27.95 with the minimum and maximum value of 7.88 and 94.73 (Table 25). In both the seasons, evaluation illustrated that 60 % of the samples can cause adverse effect on the agricultural yield due to the elevated MH ratio (> 50).

Magnesium hazard index (MH) in Khoyrasol block during PRM was found to be 46.14 ± 16.99 (mean \pm SD) and the values varied between 22.27 and 88.20 (Table 26). In this season, 43 % of the samples collected showed MH ratio > 50 (unsuitable for irrigation) although the average value lied below the limit of 50 (suitable for irrigation). During POM, the MH value was 46.35 ± 17.07 with the minimum and maximum value of 21.67 and 88.74 (Table 26). Only 55 % of the water samples were distinguished to be suitable for irrigation (MH < 50) during this season.

In Mahammad Bazar block, the MH ratio had the value of 47.07 ± 17.41 (mean \pm SD) and fell in the range of 22.29 to 89.23 during PRM season (Table 27). During POM, the MH value was 47.76 ± 17.50 with the minimum and maximum value of 22.34 and 88.82 (Table 27). In both the seasons, evaluation illustrated that 46 % samples can cause adverse effect on the agricultural yield due to the elevated MH ratio (> 50) although the average value of MH indicated them to be suitable for irrigation.

The study rendered an overview that in Rampurhat -II block had the highest percentage of water samples unsuitable for irrigation. Here, the average value of MH was also the highest amongst the blocks. This fact might have been originated from high level of fluoride present there.

The overall observation regarding the mean values of all the irrigational parameters (% Na, SAR, PI, MH) and water quality index of water samples collected from the four

blocks during PRM and POM depicted that about all the parameters and WQI decreased during POM (Fig. 35-38). Only MH showed a reverse trend in Khoyrasol and Mahammad Bazar block (Fig. 37, 38). The effect of dilution on sodium (Na), calcium (Ca) and magnesium (Mg) encounters the problem of higher % Na, SAR, PI, MH and WQI in the ground water during POM.

5.2 VEGETABLES

Along with the water study, some vegetables were also collected depending on their availability from selected spots in these four blocks and control area to find out the stress effect of fluoride on them. The vegetables namely, Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea*) leaf, Papaya (*Carica papaya*) fruit, Kundri (*Coccinia grandis*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit, Korola (*Momordica charantia*) fruit, Squash (*Cucurbita maxima*) fruit were selected for the study and collected during harvesting seasons. The edible parts of the vegetables were considered for the study through which fluoride can be ingested in human body. The biochemical parameters namely, chlorophyll, amino acids, proteins, soluble sugars, ascorbic acid in those vegetable leaves and fruits were estimated to find the probable effects of fluoride on them. The bio concentration factors (BCF) were also determined in each vegetable by measuring the fluoride concentrations in the vegetable parts and in the field soils collected.

5.2.1 Bio chemical parameters

Biochemical constituents (chlorophyll, amino acids, proteins, soluble sugars, ascorbic acid) in different vegetable plants collected from Nalhati-I, Rampurhat-II, Khoyrasol, Mahammad Bazar block and control area are listed in Table 29, Table 30, Table 31, Table 32 and Table 33 respectively. Mere the biochemical data gathered did not have any significance about measuring the stress effect of fluoride, therefore the percent biochemical change with respect to control area were counted taking the mean values

of biochemical constituents. Table 34, Table 35, Table 36 and Table 37 represent the percent biochemical change (PBC) calculated with respect to control in different vegetable plants collected from Nalhathi-I, Rampurhat-II, Khoyrasol, Mahammad Bazar block respectively. The positive values of PBC indicate the decrement of that particular biochemical constituent of that particular vegetable collected from the specified fluoride affected area with respect to the control area and the reverse is indicated by the negative value.

5.2.1.1 Sugar

From the Table 34, it can clearly be designated that the reducing sugar contents of Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Nalhathi-I block decreased with respect to the control area and the reduction was found to be maximum in papaya fruit (PBC = 8.7) and minimum in seem fruit (PBC = 2.2). But in Cauliflower (*Brassica oleracea* var. *botrytis*) leaf (PBC = -1.5) and Brinjal (*Solanum melongena*) fruit (PBC = -2.5) increment in sugar content were noticed.

In Rampurhat-II block, the reducing sugar contents in all the vegetable samples namely, Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Papaya (*Carica papaya*) fruit, Kundri (*Coccinia grandis*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit, Korola (*Momordica charantia*) fruit decreased consistently with respect to the control area (Table 35). The maximum reduction was found in papaya fruit (PBC = 10.65) and minimum in cauliflower leaf (PBC = 1.17).

Table 36, clearly indicates that the reducing sugar contents of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Squash (*Cucurbita maxima*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Khoyrasol block decreased with respect to

the control area and the highest reduction was found in Korola fruit (PBC = 4.00) and the lowest in Seem fruit (PBC = 2.05). But in Cauliflower (*Brassica oleracea* var. *botrytis*) leaf (PBC = -1.4) and Brinjal (*Solanum melongena*) fruit (PBC = -2.32) increment in sugar content were noticed.

Sugar content in Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Mahammad Bazar block showed a steady decrease in comparison to the control area (Table 37). The maximum reduction was found in Papaya fruit (PBC = 6.40) and minimum in Seem fruit (PBC = 0.87). An increment in sugar content was noticed only in Brinjal (*Solanum melongena*) fruit (PBC = -3.12).

The sugar levels in plants are directly related to stress factors (Verma and Dubey, 2001). From the previous description it is evident that the reducing sugar in most of the vegetable leaves and fruits collected from fluoride-affected area decreased considerably in comparison to the control area. This may be due to a lower level of photosynthesis leading to lower accumulation of photo assimilate in leaves and fruits under fluoride stress, decreasing the sensitivity of different crop plants (Elloumi et al., 2005). Since formation of reducing sugars such as glucose, fructose, and mannose is thought to be inhibited by F, the tendency of plants exposed to F to decrease the concentrations of such sugars indicated the possible conversion of these sugars to non-reducing sugars, such as sucrose and raffinose or sugar alcohols. Under these conditions, increased levels of non-reducing sugars in tissues might be a mechanism adopted by plants to reduce F toxicity (Kim et al., 2003).

5.2.1.2 Chlorophyll

The chlorophyll *a*, chlorophyll *b* and total chlorophyll contents of all the vegetable samples namely, Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos*

lablob) fruit and Korola (*Momordica charantia*) fruit collected from Nalhati-I block showed a steady decrease with respect to the control area (Table 34). The decrement in Chl *a* was found to be maximum in Cauliflower leaf (PBC = 57.81) and minimum in squash fruit (PBC = 1.35) collected from this block. The highest reduction in Chl *b* was found in cabbage leaf (PBC = 72.89) and the least in squash fruit (PBC = 1.21). In potato leaf (PBC = 59.16) and in squash fruit (PBC = 1.59), the highest and lowest decrease in total chl were observed respectively.

In Rampurhat-II block, the chlorophyll (Chl *a*, Chl *b* and total Chl) contents in all the vegetable samples namely, Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Papaya (*Carica papaya*) fruit, Kundri (*Coccinia grandis*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit, Korola (*Momordica charantia*) fruit decreased compatibly with respect to the control area (Table 35). The decrement in Chl *a* was found to be maximum in Cauliflower leaf (PBC = 61.9) and minimum in Kundri fruit (PBC = 4.17) collected from this block. The highest reduction in Chl *b* was found in cabbage leaf (PBC = 96.73) and the least in radish leaf (PBC = 5.19). In cabbage leaf and (PBC = 126.89) and seem fruit (PBC = 2.97), the highest and lowest decrease in total chl were observed respectively.

Table 36, clearly indicates that the Chlorophyll (Chl *a*, Chl *b*, total Chl) contents of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Khoyrasol block decrease consistently in comparison to the samples collected from control. The decrement in Chl *a* was found to be maximum in Cauliflower leaf (PBC = 53.85) and minimum in squash fruit (PBC = 1.22) collected from this block. The highest reduction in Chl *b* was found in potato leaf (PBC = 64.2) and the least in squash fruit (PBC = 0.76). In potato leaf and (PBC = 55.09) and squash fruit (PBC = 1.33), the highest and lowest decrease in total Chl were observed respectively.

Chlorophyll *a* content of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit samples collected from Mahammad Bazar block reduced with respect to the samples collected from control area (Table 37). The highest reduction was observed in potato leaf (PBC = 44.52) and the lowest in seem (PBC = 2.06). A reverse trend was noticed in case of Squash (*Cucurbita maxima*) fruit (PBC = -3.49) and Brinjal (*Solanum melongena*) fruit (PBC = -1.03). Steady decrements were noticed in Chlorophyll *b* content of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from this block in comparison to the control area (Table 37) with the maximum reduction in potato (PBC = 46.54) and minimum in radish (PBC = 0.62). All the vegetables except seem (PBC = -1.39) had the decreased total chlorophyll content in comparison to the vegetables collected from control. The maximum and minimum decrement were observed in potato (PBC = 48.1) and squash (PBC = 1.67).

An overview of the PBC in chlorophyll content (Chl *a*, Chl *b*, total Chl) rendered that about in all vegetables there were lesser amount of chlorophyll in the fluoride affected areas with respect to control area. The highest reduction in chlorophyll content (Chl *a*, Chl *b*, total Chl) were found mainly the leafy vegetables namely, cauliflower, potato and cabbage. It is reported that tuberous vegetables such as potato appear to accumulate relatively higher levels of fluoride (Ravichandran et al., 2007) and a high stress effect is observed. Reduction in the Chl *a*, Chl *b* and total Chl content may be due to the breakdown of chlorophyll under stress or due to inhibition of chlorophyll biosynthesis (Gupta et al., 2009). Magnesium is a central component of chlorophyll; it traps fluoride as MgF_2 in a detoxification mechanism (Abdallah et al., 2006) and this may cause decrease in the chlorophyll content in the plant body. Decrease in chlorophyll content may also be due to the disruption of chloroplast membranes as described by Horvath et al., (1978). Earlier studies confirm that fluoride causes a reduction in the chlorophyll content of foliage (McNulty and Newman, 1961). The biochemical basis of this effect

may be a consequence of inhibition by fluoride of incorporation of γ -aminolevulinic acid into chlorophyll synthetic pathway (Wallis et al., 1974).

5.2.1.3 Ascorbic acid

Ascorbic acid as an antioxidant plays an important role in protection against physiological stress (Guo et al., 2005). The assessed ascorbic acid content of the vegetables namely, Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit showed a decreasing tendency in Nalhati- I with respect to those of Control area (Table 34). The highest decrement was found in onion leaf (PBC = 55.63) and lowest in squash fruit (PBC = 2.76). Brinjal (*Solanum melongena*) fruit (PBC = -17.38), Seem (*Dolichos lablob*) fruit (PBC = -7.41) and Korola (*Momordica charantia*) fruit (PBC = -10.55) showed a reverse trend.

In Rampurhat- II block the amount of ascorbic acid contents in Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf were of lower amount in comparison to those of control area (Table 35) and decrement was maximum in onion leaf (PBC = 58.56) and minimum in radish leaf (PBC = 25.0). But in Papaya (*Carica papaya*) fruit (PBC = -6.05), Kundri (*Coccinia grandis*) fruit (PBC = -29.05), Brinjal (*Solanum melongena*) fruit (PBC = -12.3), Seem (*Dolichos lablob*) fruit (PBC = -4.33) and Korola (*Momordica charantia*) fruit (PBC = -11.11) increment in ascorbic acid were found.

The vegetable samples namely, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf and Squash (*Cucurbita maxima*) fruit collected from Khoyrasol block showed a decreased level of ascorbic acid content (Table 36) and decrement was highest in potato leaf (PBC = 43.88) and lowest in Squash (PBC = 2.42). The ascorbic acid contents in Brinjal (*Solanum melongena*) fruit (PBC = -16.27), Seem (*Dolichos*

lablob) fruit (PBC = -6.9) and Korola (*Momordica charantia*) fruit (PBC = -9.68) were in higher amount collected from this block in comparison to that of the control area.

Ascorbic acid content of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit and Seem (*Dolichos lablob*) fruit samples collected from Mahammad Bazar block reduced with respect to the samples collected from control area (Table 37). The highest reduction was observed in potato leaf (PBC = 43.15) and the lowest in seem (PBC = 6.11). A reverse trend was noticed in case of Squash (*Cucurbita maxima*) fruit (PBC = -2.75) and Brinjal (*Solanum melongena*) fruit (PBC = -14.98), and Korola (*Momordica charantia*) fruit (PBC = -8.2).

The summarized vision made it to be observed that the ascorbic acid content in most of the vegetable leaves and fruits of different blocks decreased due to inhibition of ascorbic acid synthesis under fluoride stress (Yang and Miller, 1963). In few vegetables like, Brinjal, Seem and Korola, the ascorbic acid content of the affected area showed an increasing trend over the controlled area, which may be attributed to binding of fluoride with ascorbic acid oxidase enzyme thereby inhibiting the breakdown of ascorbic acid in the plant system (Gupta et al., 2009).

5.2.1.4 Protein

From the Table 34 it can be designated explicitly, that the protein contents of Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Nalhati-I block decreased with respect to the control area and the reduction was found to be maximum in Cabbage leaf (PBC = 6.32) and minimum in Spinach leaf (PBC = 2.2). But in Cauliflower (*Brassica oleracea* var. *botrytis*) leaf (PBC = -1.02) and Papaya (*Carica papaya*) fruit (PBC = -1.13), increment in protein content were noticed.

In Rampurhat-II block, the protein contents in most of the vegetable samples namely, Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach

(*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit, Korola (*Momordica charantia*) fruit decreased consistently with respect to the control area (Table 35). The maximum reduction was found in onion leaf (PBC = 7.38) and minimum in spinach leaf (PBC = 1.12). But in Papaya (*Carica papaya*) fruit (PBC = -0.11) and Kundri (*Coccinia grandis*) fruit (PBC = -24.82) a reversed trend was noticed.

In all the vegetable samples namely, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf and Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit except in Potato (*Solanum tuberosum*) leaf, (PBC = -1.41) collected from Khoyrasol block showed a decreased level of protein content in comparison to those of the control area (Table 36). The decrement was found to be the highest in seem fruit (PBC = 4.96) and the lowest in Cauliflower leaf (PBC = 0.95).

Protein content in Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Squash (*Cucurbita maxima*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit collected from Mahammad Bazar block showed a steady decrease in comparison to the control area (Table 37). The maximum reduction was found in seem fruit (PBC = 4.71) and minimum in spinach fruit (PBC = 0.95). A little increment in sugar content was noticed only in Papaya (*Carica papaya*) fruit (PBC = -1.3).

An overview of the study regarding protein content of different vegetables collected from the fluoride affected study areas, explicitly inferred that in most of the vegetables had a relatively lower amount of protein with respect to the protein content of the vegetables collected from the control area. This fact can be elucidated according to Chang (1970). He stated that fluoride decreases the number of ribosomes and destroys the structure of ribosomal proteins, which negatively affects the entire protein synthesis and thereby a decrease in protein content is noticed. Protein content in the vegetables of

different species under fluoride stress might also appear due to reduced rate of amino acid synthesis under fluoride stress (Yang and Miller, 1963).

5.2.1.5 Amino acid

The assessed amino acid content of the vegetables namely, Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit and Korola (*Momordica charantia*) fruit showed a decreasing tendency in Nalhathi-I with respect to those of Control area (Table 34). The highest decrement was found in spinach leaf (PBC = 110.71) and lowest in papaya fruit (PBC = 1.13). Brinjal (*Solanum melongena*) fruit (PBC = -8.25) and Seem (*Dolichos lablob*) fruit (PBC = -15.93) showed a reversed trend.

In Rampurhat- II block the amount of amino acid contents in Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf and Korola (*Momordica charantia*) were of relatively lower amount in comparison to those of control area (Table 35) and decrement was maximum in spinach leaf (PBC = 322.36) and minimum in cabbage leaf (PBC = 8.27). But in Papaya (*Carica papaya*) fruit (PBC = -8.81), Kundri (*Coccinia grandis*) fruit (PBC = -13.69), Brinjal (*Solanum melongena*) fruit (PBC = -8.68) and Seem (*Dolichos lablob*) fruit (PBC = -18.87) relative increment in amino acid contents were found.

The vegetable samples namely, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea* var. *botrytis*) leaf, Brinjal (*Solanum melongena*) fruit and Korola (*Momordica charantia*) fruit collected from Khoyrasol block had comparatively lower level of amino acid with respect to that of the vegetables collected from the control area (Table 36). The decrement was highest in Spinach leaf (PBC = 102.99) and lowest in Brinjal (PBC = 7.67). Oppositely, the amino acid contents in Squash (*Cucurbita maxima*) fruit (PBC =

-2.67) and Seem (*Dolichos lablob*) fruit (PBC = -14.88) collected from this block were in higher amount in comparison to those of the control area.

Amino acid content of Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf and Brinjal (*Solanum melongena*) fruit samples collected from Mahammad Bazar block reduced with respect to the samples collected from control area (Table 37). The highest reduction was observed in potato leaf (PBC = 63.85) and the lowest in Brinjal (PBC = 9.83). A reverse trend was noticed in case of Papaya (*Carica papaya*) fruit (PBC = -0.93), Squash (*Cucurbita maxima*) fruit (PBC = -0.74), Seem (*Dolichos lablob*) fruit (PBC = -17.13), and Korola (*Momordica charantia*) fruit (PBC = -3.25).

The total free amino acid content in some of the different vegetables of the polluted site showed a decreasing trend with respect to the control site. This may be due to less degradation of storage protein, amino acid synthesis and amino acid utilization for protein synthesis and for respiration under fluoride stress (Kundu and Mondal, 2010). The increased amino acid content in few of the vegetables in the affected area in comparison to control area may be attributed to increased rates of dark CO₂ fixation under fluoride stress (Yang and Miller, 1963).

The magnitude of percent biochemical changes with respect to control in different vegetables collected from different blocks with average fluoride levels in water are plotted (Fig. 45-56) to get an overview of the changes in biochemical parameters with respect to the average fluoride level in water in different blocks. The average fluoride levels in water of different blocks were calculated averaging the mean values of fluoride concentrations in water collected during PRM and POM and was found to be the highest in Rampurhat- II block (3.77 mg/L). PBC of most of the biochemical parameters of almost all vegetables namely, Cabbage (*Brassica oleracea*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Papaya (*Carica papaya*) fruit, Squash (*Cucurbita maxima*) fruit, Seem (*Dolichos lablob*) fruit and Korola (*Momordica charantia*) fruit were higher in amount in Rampurhat – II block where the mean value of water is comparatively higher than the other blocks. This phenomenon can be easily speculated

from the higher peaks of Rampurhat- II block on the graphical representations of different vegetables (Fig.45-56). This study clearly indicates the hazardous effect of biochemical changes due to higher level of fluoride in irrigational water which in turn may affect the food value of different vegetables in the fluoride affected area.

5.2.2 Fluoride concentration and Bio concentration Factor (BCF)

To understand the transfer of fluoride from soil to foliage, fluoride concentration in different vegetables and nearby field soils were measured and the Bio Concentration Factors (BCF) of fluoride were computed using the average values. Because of its simple application, BCF is widely used as an indicator of affinity for the accumulation of F in plants (Tome et al., 2003; Alonso et al., 2003).

The maximum average fluoride concentration in the vegetable samples collected from Nalhati – I block was found in Papaya (*Carica papaya*) fruit (1.19 ± 0.05) and minimum in Korola (*Momordica charantia*) fruit (0.4 ± 0.02) (Table 38). But the mean BCF was highest in Potato (*Solanum tuberosum*) leaf (1.3) and lowest in Seem (*Dolichos lablob*) fruit (0.45) (Table 38).

In Rampurhat –II block, the highest and lowest levels of fluoride were observed in Radish (*Raphanus sativus*) leaf (3.21 ± 0.04) and Korola (*Momordica charantia*) fruit (0.4 ± 0.03) respectively amongst the vegetable samples collected (Table 39). The highest mean BCF in Radish (*Raphanus sativus*) leaf (1.4) complied with the fluoride concentration. But the lowest Mean BCF in Kundri (*Coccinia grandis*) fruit (0.36) was not compatible with the fluoride concentration.

Among the vegetables collected in Khoyrasol block Radish (*Raphanus sativus*) leaf had the highest fluoride concentration (2.94 ± 0.10) and highest mean BCF (1.26) (Table 40). The lowest concentration of fluoride was observed in Brinjal (*Solanum melongena*) fruit (0.61 ± 0.03) and lowest mean BCF was noticed in Seem (*Dolichos lablob*) fruit (0.47).

Spinach (*Spinacia oleracea*) leaf had the maximum fluoride concentration (1.25 ± 0.09) and Mean BCF (1.06) among the vegetables collected from Mahammad Bazar block (Table 41). The lowest level of fluoride and mean BCF observed was in Brinjal

(*Solanum melongena*) fruit (0.61 ± 0.03) and Squash (*Cucurbita maxima*) fruit (0.48) respectively.

Although no exclusive conclusion can be portrayed from the above results but it can be conjectured that the leafy vegetables like potato, radish, spinach shows higher value of BCF. Earlier investigations found increased fluoride translocation in plants where metabolism is higher (Ribang et al., 1975). Leafy vegetables like radish, potato, papaya, spinach, cabbage and cauliflower leaves had BCF values of F greater than 1.0 collected from all these four blocks, which indicates a higher rate of photosynthesis in leafy vegetables associated with higher intake of water resulting in a higher BCF value of F. However, Swartjes et al., (2007) reported that BCF values are not always constant in specific vegetables and are largely affected by soil properties like soil pH, clay content, organic matter and fluoride concentration in soil and plant factors like the type of plant and growth rate.

The graphical representations (Fig. 57-60) were framed to illustrate the comprehensive study of understanding the relation between fluoride in soil and BCF of different vegetables fetched from different blocks.

From Fig. 57, it can be indicated explicitly that higher level of mean fluoride concentrations near Potato (1.3 mg/L) and Papaya (1.22 mg/L) field in Nalhati – I block resulted in higher BCF in them (0.89 and 1.19 respectively). In Rampurhat- II block also, high BCF were found in Radish (1.4) and Spinach (1.31) in consequence of high mean fluoride concentration (3.2 and 4.5 mg/L respectively) in soil of the respective fields (Fig. 58). Potato and Radish had high BCF values (1.3 and 1.26 respectively) with the high mean fluoride concentrations (2.22 and 2.33 mg/L respectively) in their nearby field soils collected from Khoyrasol block (Fig. 59). Spinach showed the highest BCF value (1.06) in Mahammad Bazar block, where in the field soil fluoride concentration was also high (1.18 mg/L) (Fig. 60).

From the summarized view it can be speculated that higher fluoride in soil resulted in higher BCF of fluoride. This fact might have been arisen from the higher transition of fluoride from soil to foliage during water absorption depending on the rate of photosynthesis.

TABLES AND FIGURES

Table 1 Average rainfall, population and exact location of study area

Block	Average Rain fall	Villages	Population	G.P.S. reading
Nalhati-I	1420 mm	Nasipur	800	N 24°06'0.15" E 087°46'53.5"
		Deshnabagram	600	N 24°17'32.1" E 087°45'14.2"
		Vabanandapur	1500	N 24°17'34.1" E 087°45'13.9"
Rampurhat-II	1430.5 mm	Kamdebpur	200	N 24°06'30.4" E 087°47'24.0"
		Chak Atla	150	N 24°06'30.3" E 087°47'23.9"
		Nowapara	150	N 24°06'20.7" E 087°47'03.1"
		Junidpur	350	N 24°06'01.4" E 087°46'53.5"
Mahammad Bazar	1435 mm	Loha Bazar	1120	N 23°59'35" E 087°34'08"
		Kaijuli	350	N 23°59'30" E 087°33'45.4"
		Chak Sehara	450	N 24°00'24" E 087°34'43"
		Seharakuri	1250	N 23°57'44" E 087°31'43"
		Sankarpur	1340	N 23°57'44" E 087°31'38"
Khoyrasol	1405 mm	Gostho Dungal	350	N 23°47'20" E 87°15'46"
		Sarsa	750	N 23°47'22" E 87°15'9"
		Tithikapur	250	N 23°47'46" E 87°15'7"
		Lauberia	825	N 23°47'33" E 87°14'32"
		Tarapur	430	N 23°47'53" E 87°14'43"
		Nowpara	410	N 23°47'51" E 87°14'02"
		Bhadulia	460	N 23°48'22" E 87°13'21"
		Paschim Sibpur	380	N 23°48'11" E 87°13'33"
		Rasa	650	N 23°47'18" E 87°13'12"
		Hazratpur	780	N 23°46'56" E 47°14'09"
Nalhati (Control area)	1420 mm	Jagdhari	240	N 24°16'44" E 087°50'12"

Table 2 Physico-chemical parameters of groundwater samples of Nalhati -I block in PRM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
N _{pr} 1	Nasipur	7.11	7.21	2.81	944.1	171	445.5	98.8	40.2	102.6	186.0	0.41	0.17	1376	95.8	69.4	45.9
N _{pr} 2		6.84	7.52	0.42	128.0	171	39.7	97.9	36.6	9.1	11.8	0.12	0.09	268	31.9	0.2	27
N _{pr} 3		2.15	7.63	2.70	592.2	252	357.3	87.8	44.0	115.7	255.6	0.25	0.11	1009	142.2	138.8	18.6
N _{pr} 4		2.21	8.81	2.51	428.2	324	122.0	175.7	36.4	81.1	180.1	0.09	0.43	1275	127.7	148.5	32.8
N _{pr} 5		2.89	8.34	3.30	954.0	113	120.1	82.4	16.8	209.4	280.2	0.37	0.00	1811	133.5	59.5	62.5
N _{pr} 6		5.37	8.30	0.70	136.0	207	15.1	142.7	36.4	11.6	33.9	0.43	0.34	469	78.4	34.6	40.1
N _{pr} 7		5.42	7.52	0.62	108.0	95	27.0	60.4	32.8	16.7	18.4	0.11	0.24	402	84.6	33.8	42.5
N _{pr} 8		2.30	7.81	2.30	302.1	308	127.2	42.7	42.0	47.3	55.9	0.21	0.21	941	32.5	64.5	33.2
N _{pr} 9		4.81	8.11	0.90	171.0	195	140.3	15.5	32.8	21.8	132.2	0.11	0.33	603	37.8	21.2	43.7
N _{pr} 10		4.50	8.05	1.41	143.1	232	137.2	146.7	38.4	11.6	145.7	0.17	0.11	938	102.3	0.4	42.9
N _{pr} 11	Vabandapur	1.41	8.14	0.31	73.3	99	19.9	54.9	20.1	5.6	14.8	0.42	0.72	201	49.4	29.7	42.3
N _{pr} 12		3.22	8.36	2.22	413.5	144	198.5	87.8	128.	22.6	148.5	0.28	0.50	874	107.4	0.8	44.3
N _{pr} 13		4.01	8.05	2.04	677.7	216	150.7	175.7	124.	28.3	121.8	0.03	0.48	1108	107.4	1.2	35.1
N _{pr} 14		2.80	8.09	0.30	200.1	198	38.1	109.8	40.4	24.0	18.4	0.12	0.48	201	31.9	11.2	37.7
N _{pr} 15		2.71	7.91	2.10	538.8	216	146.2	98.5	52.0	98.3	42.8	0.12	0.40	967	65.8	6.8	37.9
N _{pr} 16		3.80	7.96	1.81	282.5	198	133.7	103.8	40.0	43.8	78.3	0.24	0.80	906	34.9	22.4	47.7
N _{pr} 17		3.50	8.32	0.82	136.3	187	155.2	125.7	44.6	6.9	14.7	0.12	0.54	536	26.9	1.6	28.0
N _{pr} 18		3.62	8.10	1.53	157.0	216	162.1	90.1	42.4	13.7	120.4	0.09	0.48	805	45.8	10.6	19.3
N _{pr} 19		2.81	7.80	3.20	733.1	178	135.1	62.8	56.4	142.3	17.3	0.16	0.67	944	98.7	42.3	34.0
N _{pr} 20		1.96	7.91	0.65	256.3	236	97.6	41.3	64.0	23.1	132.2	0.09	0.65	402	33.5	32.5	65.0
N _{pr} 21	Deshnabagram	2.16	8.36	0.10	20.4	45	54.6	32.9	36.0	12.5	13.9	0.97	0.80	67	8.70	0.6	41.6
N _{pr} 22		1.83	8.18	0.30	36.8	81	148.9	32.9	12.2	11.6	16.9	3.26	0.28	201	46.6	4.8	44.2
N _{pr} 23		1.92	8.38	0.60	167.5	126	44.5	65.9	44.1	13.8	17.8	0.10	0.40	402	61.0	6.9	34.5
N _{pr} 24		1.27	8.47	0.41	134.7	216	33.4	175.7	20.1	20.3	12.1	0.28	0.51	268	34.8	0.8	45.4
N _{pr} 25		3.5	8.12	0.52	167.5	270	93.2	153.7	16.1	30.6	11.8	0.51	0.58	335	34.8	0.4	44.5
N _{pr} 26		1.41	8.20	0.80	184.2	252	98.4	75.7	38.6	21.4	17.6	0.20	0.34	536	40.6	19.8	43.9
N _{pr} 27		2.55	8.15	0.73	102.4	268	10.5	142.3	22.4	12.4	13.9	0.15	0.62	469	28.9	20.8	46
N _{pr} 28		1.65	7.95	0.63	109.3	172	120.2	87.6	34.3	6.6	14.8	0.15	0.54	402	30.7	1.2	36.4
N _{pr} 29		2.32	8.31	0.51	107.0	270	110.7	136.5	26.3	10.2	16.4	0.10	0.51	335	46.2	3.5	39.1
N _{pr} 30		2.45	8.50	0.45	191.6	290	13.1	147.6	22.4	32.9	13.9	0.12	0.74	268	42.2	4.8	39.4

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 3 Physico-chemical parameters of groundwater samples of Nalhati -I block in POM

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
N _{po1}	Nasipur	6.58	7.64	2.95	981.9	176	454.4	94.8	41.8	103.6	193.4	0.37	0.18	1445	91.0	65.2	44.1
N _{po2}		6.43	7.97	0.44	133.1	176	40.5	94	38.1	9.2	12.3	0.11	0.1	281	30.3	0.2	25.9
N _{po3}		1.98	8.09	2.84	615.9	260	364.4	84.3	45.8	116.9	265.8	0.23	0.12	1059	135.1	130.5	21.9
N _{po4}		2.08	9.34	2.64	445.3	334	124.4	168.7	37.9	81.9	187.3	0.08	0.46	1339	121.3	139.6	31.5
N _{po5}		2.93	8.84	3.47	992.2	116	122.5	79.1	17.5	211.5	291.4	0.33	0	1902	126.8	55.9	70.2
N _{po6}		5.05	8.8	0.74	141.4	213	15.4	137	37.9	11.7	35.3	0.39	0.36	492	74.5	32.5	38.5
N _{po7}		4.98	7.97	0.65	112.3	98	27.5	58	34.1	16.9	19.1	0.1	0.25	422	80.4	31.8	40.8
N _{po8}		2.16	8.28	2.42	314.2	317	129.7	41	43.7	47.8	58.1	0.19	0.22	988	30.9	60.6	31.9
N _{po9}		4.52	8.6	0.95	177.8	201	143.1	14.9	34.1	22	137.5	0.1	0.35	633	35.9	19.9	42
N _{po10}		4.13	8.53	1.48	148.8	239	139.9	140.8	39.9	11.7	151.5	0.15	0.12	985	97.2	0.4	41.2
N _{po11}	Vabanaandapur	1.33	8.47	0.33	74.8	97	20.7	56	20.5	5.7	15.4	0.38	0.76	211	46.9	27.9	40.6
N _{po12}		3.03	8.69	2.35	421.8	141	206.4	89.6	131.	23.1	154.4	0.25	0.53	918	102	0.8	42.5
N _{po13}		3.6	8.37	2.16	691.3	212	156.7	179.2	126.	28.9	126.7	0.03	0.51	1163	102	1.1	37.7
N _{po14}		2.69	8.41	0.32	204.1	194	39.6	112	41.2	24.5	19.1	0.11	0.51	211	30.3	10.9	36.2
N _{po15}		2.81	8.23	2.23	549.6	212	152	100.5	53	100.3	44.5	0.13	0.42	1015	62.5	6.6	36.4
N _{po16}		3.56	8.28	1.92	288.2	194	139	105.9	40.8	44.7	81.4	0.24	0.85	951	33.2	21.7	45.8
N _{po17}		3.6	8.65	0.87	139	183	161.4	128.2	45.5	7	15.2	0.12	0.57	563	25.6	1.6	26.9
N _{po18}		3.48	8.42	1.62	160.1	212	168.6	91.9	43.2	14	124.3	0.09	0.51	837	43.5	10.3	18.5
N _{po19}		2.66	8.11	3.39	747.8	174	140.5	64.1	57.5	145.1	17.9	0.16	0.7	982	93.8	41	36.6
N _{po20}		1.88	8.23	0.69	261.4	231	101.5	42.1	65.3	23.6	136.4	0.09	0.68	418	31.8	31.5	70.4
N _{po21}	Deshnabagram	2.07	8.78	0.1	20.2	44	56.2	32.2	37.2	12.4	14.3	0.98	0.84	70	8.3	0.6	39.9
N _{po22}		1.76	8.59	0.31	36.4	79	153.4	32.2	12.6	11.5	17.4	3.29	0.29	209	43	4.7	42.4
N _{po23}		1.84	8.8	0.62	165.8	122	45.8	64.6	45.6	13.7	18.4	0.1	0.42	418	57	6.7	33.1
N _{po24}		1.19	8.89	0.42	133.4	210	34.4	172.2	20.8	20.2	12.5	0.28	0.54	279	32	0.8	43.6
N _{po25}		3.55	8.53	0.54	165.8	262	96	150.6	16.6	30.4	12.2	0.52	0.61	348	32	0.4	42.7
N _{po26}		1.33	8.61	0.82	182.4	244	101.4	74.2	39.9	21.3	18.2	0.2	0.36	557	38	19.2	42.1
N _{po27}		2.36	8.56	0.75	101.4	260	10.8	139.5	23.2	12.3	14.3	0.15	0.65	488	27	20.2	44.2
N _{po28}		1.55	8.35	0.65	108.2	167	123.8	85.8	35.5	6.6	15.3	0.15	0.57	418	29	1.2	34.9
N _{po29}		2.1	8.73	0.53	105.9	262	114	133.8	27.2	10.1	16.9	0.1	0.54	348	43	3.4	37.5
N _{po30}		2.3	8.93	0.46	189.7	281	13.5	144.6	23.2	32.7	14.3	0.12	0.78	279	39	4.7	38.8

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 4 Physico-chemical parameters of groundwater samples of Rampurhat -II block in PRM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
R _{pr} 1	Kamdebpur	1.87	8.29	0.31	53.0	126	43.8	65.9	16.2	3.1	13.3	0.48	0.67	201	37.7	39.6	44.6
R _{pr} 2		2.11	8.36	0.27	28.7	189	27.6	164.7	8.2	2.1	19.0	0.51	0.55	134	65.2	58.2	26.2
R _{pr} 3		3.47	8.36	0.22	65.2	144	8.3	143.9	24.0	1.3	6.9	0.60	0.6	134	136.5	36.5	18.1
R _{pr} 4		4.4	8.41	0.30	70.4	251	133.2	177.3	8.0	12.1	16.2	0.12	0.72	201	174.3	95.3	31.8
R _{pr} 5		4.01	8.33	0.52	45.4	226	141.4	160.2	8.0	6.1	11.5	0.54	0.55	335	170.3	65.2	60.7
R _{pr} 6		3.77	8.28	0.61	40.0	249	97.2	138.9	12.3	2.4	13.6	0.33	0.45	402	126.3	36.2	38.9
R _{pr} 7		1.82	7.96	0.42	109.2	85	37.4	44.6	28.3	9.4	15.4	0.09	0.77	268	67.9	66.4	41.3
R _{pr} 8		2.32	8.48	0.53	46.3	201	46.3	92.1	16.0	1.5	13.9	0.17	0.65	335	78.9	56.2	32.2
R _{pr} 9		1.78	8.35	0.25	65.4	170	58.4	83.6	20.1	3.7	11.6	0.28	0.51	134	38.6	15.4	42.4
R _{pr} 10		2.23	8.01	0.21	86.3	195	124.1	90.2	28.2	3.9	20.2	0.32	0.4	206	45.2	43.5	41.6
R _{pr} 11	Chalk Alta	2.7	8.21	0.52	87.8	334	352.5	109.8	28.2	4.3	16.6	0.58	0.68	355	61.0	69.4	41
R _{pr} 12		2.01	8.18	0.63	187.8	360	235.8	87.8	44.0	18.7	18.4	0.90	0.50	402	72.2	62.3	43
R _{pr} 13		2.64	8.52	0.61	94.7	326	272.8	101.6	27.5	6.5	13.9	0.69	0.54	402	95.3	42.2	34.1
R _{pr} 14		4.16	8.31	0.48	73.3	402	130.1	175.8	8.5	12.8	16.2	0.57	0.74	268	122.2	19.7	36.6
R _{pr} 15		3.76	8.16	0.82	130.4	305	128.0	145.6	11.3	24.7	17.6	0.74	0.41	536	132.8	32.0	36.8
R _{pr} 16		4.11	8.10	0.75	53.8	350	106.0	180.2	9.8	7.5	12.9	0.65	0.65	469	111.7	54.0	49.6
R _{pr} 17		1.90	8.19	0.59	145.9	175	117.0	76.2	34.3	14.6	19.2	0.63	0.65	335	61.2	43.5	29.1
R _{pr} 18		1.77	8.31	0.62	217.1	132	33.2	56.5	46.0	24.5	12.8	0.31	0.53	402	37.5	25.2	20.1
R _{pr} 19		2.51	8.20	0.91	170.4	221	42.5	98.7	32.0	21.7	16.5	0.98	0.47	603	148.3	49.3	35.4
R _{pr} 20		1.85	8.26	0.28	161.5	136	46.7	67.4	47.0	10.6	16.9	0.55	0.68	134	78.9	16.2	67.6
R _{pr} 21	Nowapara	9.98	7.80	0.32	48.7	436	45.2	205.0	16.4	1.9	432.8	0.15	0.68	201	119.0	19.8	43.3
R _{pr} 22		6.6	7.60	0.71	14.5	242	44.2	142.2	2.2	2.1	212.5	0.22	0.23	469	66.8	0	45.9
R _{pr} 23		6.57	7.91	0.63	30.8	218	50.1	146.0	2.0	6.2	516.0	0.14	0.31	402	49.3	19.8	35.8
R _{pr} 24		2.32	8.01	0.48	34.7	86	36.6	60.1	4.2	5.8	126.7	0.21	0.13	268	81.3	32.5	47.2
R _{pr} 25		9.82	7.80	0.90	245.8	235	49.1	204.9	6.3	55.8	78.3	0.63	0.00	603	112.0	44.5	46.3
R _{pr} 26		6.76	7.90	0.54	50.4	162	33.4	138.3	1.5	11.2	122.3	0.51	0.03	335	202.5	52.9	45.6
R _{pr} 27		3.36	8.11	0.42	58.6	239	138.0	78.5	1.6	13.1	459.9	0.20	0.16	268	96.3	22.2	47.8
R _{pr} 28		3.41	8.31	0.80	169.8	235	120.1	154.9	14.4	32.1	48.9	0.18	0.04	536	102.5	23.5	37.9
R _{pr} 29		4.71	7.80	0.35	39.3	228	101.3	136.3	2.7	7.8	216.3	0.31	0.18	201	132.2	56.3	40.7
R _{pr} 30		6.23	7.7	0.36	87.6	252	136.0	144.3	14.2	12.5	122.7	0.40	0.24	201	234.7	106.	40.9

Table 4 continued

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TD S	Na	K	SiO ₂
R _{pr} 31	Junitpur	1.70	7.2	0.41	61.5	59	44.2	27.6	2.1	13.5	423.7	0.25	0.06	268	34.8	11.2	46.3
R _{pr} 32		7.21	7.3	0.80	53.2	140	95.1	77.1	1.1	12.1	358.5	0.71	0.04	536	131.9	36.2	27.2
R _{pr} 33		9.10	6.2	0.91	160.0	144	46.0	72.3	10.2	32.3	221.7	0.69	0.02	603	240.6	86.5	18.8
R _{pr} 34		7.12	7.2	0.72	98.7	162	84.0	88.4	8.8	18.4	122.6	0.64	0.04	469	145.3	32.9	33.1
R _{pr} 35		6.60	7.5	0.62	156.3	72	39.2	42.6	10.5	31.2	105.6	0.31	0.17	402	133.4	33.7	63.1
R _{pr} 36		2.51	7.1	0.47	127.8	46	44.2	28.5	33.1	10.8	302.8	0.26	0.30	268	62.9	21.1	40.4
R _{pr} 37		3.10	7.8	0.52	164.0	75	33.9	34.7	14.6	30.6	508.7	0.46	0.18	335	78.2	36.5	42.9
R _{pr} 38		1.81	7.9	0.54	67.3	25	51.3	11.1	1.6	15.2	324.4	0.18	0.40	335	42.6	11.0	33.5
R _{pr} 39		2.30	8.1	0.62	91.2	51	101.0	22.7	6.8	17.8	207.5	0.25	0.21	402	52.8	17.3	44.1
R _{pr} 40		2.11	7.5	0.73	116.0	57	37.2	28.1	7.2	23.5	98.3	0.21	0.13	469	50.3	16.5	43.2

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 5 Physico- chemical parameters of groundwater samples of Rampurhat -II block in POM

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
R _{po} 1	Kamdebpur	1.68	8.79	0.33	55.1	130	44.7	63.3	16.8	3.1	13.8	0.43	0.71	211	35.8	37.3	46.8
R _{po} 2		1.9	8.86	0.28	29.8	195	28.2	158.1	8.5	2.1	19.8	0.46	0.58	141	61.9	54.7	27.3
R _{po} 3		3.12	8.86	0.23	67.8	148	8.5	138.1	25	1.3	7.2	0.54	0.64	141	129.7	34.3	18.7
R _{po} 4		3.96	8.91	0.32	73.2	259	135.9	170.2	8.3	12.2	16.8	0.11	0.76	211	165.6	89.6	27.9
R _{po} 5		3.61	8.83	0.55	47.2	233	144.2	153.8	8.3	6.2	12	0.49	0.58	352	161.8	61.3	53.9
R _{po} 6		3.39	8.78	0.64	41.6	256	99.1	133.3	12.8	2.4	14.1	0.3	0.48	422	120	34.0	40.7
R _{po} 7		1.64	8.44	0.44	113.6	88	38.1	42.8	29.4	9.5	16	0.08	0.82	281	64.5	62.4	52.1
R _{po} 8		2.09	8.99	0.56	48.2	207	47.2	88.4	16.6	1.5	14.5	0.15	0.69	352	75	52.8	33.6
R _{po} 9		1.6	8.85	0.26	68	175	59.6	80.3	20.9	3.7	12.1	0.25	0.54	141	36.7	14.5	44.4
R _{po} 10		2.01	8.49	0.22	89.8	201	126.6	86.6	29.3	3.9	21	0.29	0.42	216	42.9	40.9	43.6

Table 5 continued

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
R _{po} 11	Chalk Atta	1.33	8.54	0.55	89.6	327	366.6	112	28.8	4.4	17.3	0.52	0.72	373	58	65.2	33.8
R _{po} 12		3.03	8.51	0.67	191.6	353	245.2	89.6	44.9	19.1	19.1	0.81	0.53	422	68.6	58.6	45.1
R _{po} 13		3.6	8.86	0.65	96.6	319	283.7	103.6	28.1	6.6	14.5	0.62	0.57	422	90.5	39.7	30.2
R _{po} 14		2.69	8.64	0.51	74.8	394	135.3	179.3	8.7	13.1	16.8	0.51	0.78	281	116.1	19.1	32.5
R _{po} 15		2.81	8.49	0.87	133	299	133.1	148.5	11.5	25.2	18.3	0.78	0.43	563	126.2	31.0	38.5
R _{po} 16		3.56	8.42	0.8	54.9	343	110.2	183.8	10	7.7	13.4	0.66	0.69	492	106.1	52.4	50.1
R _{po} 17		3.6	8.52	0.63	148.8	172	121.7	77.7	35	14.9	19.8	0.64	0.69	352	58.1	42.2	20.3
R _{po} 18		3.48	8.64	0.66	221.4	129	34.5	57.6	46.9	25	13.2	0.31	0.56	418	35.6	24.4	11.8
R _{po} 19	Nowapara	2.66	8.53	0.96	173.8	217	44.2	100.7	32.6	22.1	17	0.99	0.49	627	140.9	47.8	37.3
R _{po} 20		1.88	8.59	0.3	164.7	133	48.6	68.7	47.9	10.8	17.4	0.56	0.71	139	75	15.7	71.2
R _{po} 21		7.98	8.19	0.32	48.2	423	46.6	200.9	17	1.9	446.6	0.15	0.71	209	113.1	19.2	45.4
R _{po} 22		5.28	7.98	0.28	14.4	235	45.5	139.4	2.3	2.1	219.3	0.22	0.24	488	62	0.8	48.2
R _{po} 23		5.26	8.31	0.23	30.5	211	51.6	143.1	2.1	6.2	532.5	0.14	0.33	418	46	19.2	37.4
R _{po} 24		1.86	8.41	0.31	34.4	83	37.7	58.9	4.3	5.8	130.8	0.21	0.14	279	76	31.5	49.5
R _{po} 25		7.86	8.19	0.54	243.3	228	50.6	200.8	6.5	55.5	80.8	0.64	0	627	104	43.2	38.6
R _{po} 26		5.41	8.3	0.63	49.9	157	34.4	135.5	1.6	11.1	126.2	0.52	0.03	348	188	51.3	47.8
R _{po} 27	Junitpur	2.69	8.52	0.43	58	232	142.1	76.9	1.7	13	474.6	0.20	0.17	279	90	21.5	50.2
R _{po} 28		2.73	8.73	0.55	168.1	228	123.7	151.8	14.9	31.9	50.5	0.18	0.04	557	95	22.8	39.7
R _{po} 29		3.77	8.19	0.26	38.9	221	104.3	133.6	2.8	7.8	223.2	0.31	0.19	209	123	54.6	42.6
R _{po} 30		4.98	8.09	0.22	86.7	244	140.1	141.4	14.7	12.4	126.6	0.4	0.25	209	218	103.1	42.9
R _{po} 31		1.62	7.56	0.54	60.9	57	45.5	27	2.2	13.4	437.3	0.25	0.05	279	32	10.9	48.6
R _{po} 32		6.84	7.67	0.65	52.7	136	98	75.6	1.1	12	370	0.72	0.04	557	123	35.1	28.3
R _{po} 33		8.65	6.51	0.63	158.4	140	47.4	70.9	10.5	32.1	228.8	0.70	0.04	627	224	83.9	19.4
R _{po} 34		6.75	7.56	0.49	97.7	157	86.5	86.6	9.1	18.3	126.5	0.65	0.04	488	135	31.9	34.6
R _{po} 35	Junitpur	6.27	7.88	0.77	154.7	70	40.4	41.7	10.9	31	109	0.31	0.12	418	124	32.7	56.4
R _{po} 36		2.38	7.46	0.71	126.5	45	45.5	27.9	34.2	10.7	312.5	0.26	0.3	279	58	20.5	42.3
R _{po} 37		2.95	8.19	0.55	162.4	73	34.9	34	15.1	30.4	525	0.46	0.1	348	73	35.4	45.0
R _{po} 38		1.71	8.3	0.58	66.6	24	52.8	10.9	1.7	15.1	334.8	0.18	0.14	348	40	10.7	35.0
R _{po} 39		2.19	8.51	0.86	90.3	49	104	22.2	7	17.7	214.1	0.25	0.22	418	49	16.8	46.2
R _{po} 40		2.00	7.88	0.26	114.8	55	38.3	27.5	7.4	23.4	101.4	0.21	0.13	488	47	16	45.3

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 6 Physico- chemical parameters of groundwater samples of Khoyrasol block in PRM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{pr} 1	Gostho Dangal	0.98	8.11	0.66	164.1	44	115.6	19.7	52.2	9.6	129.7	0.45	0.43	46	58.1	9.9	56.2
K _{pr} 2		0.2	8.49	0.28	92.6	43	15	19.7	20.1	12.1	142.2	0.38	0.12	20	34.8	10.1	32.5
K _{pr} 3		1.28	8.27	0.3	85.5	39	10	24.6	24.1	7.2	166.4	0.21	0.14	21	37.7	9.8	22
K _{pr} 4		2.15	8.5	0.45	44.4	59	20	39.6	6.0	8.4	180.6	0.17	0.12	31	75.5	1	39.7
K _{pr} 5		1.32	7.9	0.42	85.5	29	60.1	14.8	24.1	7.2	117.2	0.35	0.89	30	37.7	9.5	76.9
K _{pr} 6		3.28	7.87	3.44	349.5	53	305.8	29.5	72.3	48.2	199.3	0.46	0.13	240	98.7	9.9	48.8
K _{pr} 7		1.56	7.67	1.66	366.8	58	250.6	29.5	74.2	51.8	215.6	0.65	0.12	119	130.6	8.9	51.9
K _{pr} 8		2.14	7.64	1.96	497	63	375.9	38.6	104.3	67.5	120.8	1.21	0.12	135	119	8.9	40.3
K _{pr} 9		1.8	8	0.45	107.8	126	40.1	98	16.1	19.3	157.4	0.31	0.11	32	63.9	9.9	53.4
K _{pr} 10		1.8	7.84	1.92	493	34	350.9	19.7	94.3	73.5	134.2	0.25	0.14	135	130.6	9.8	52.3
K _{pr} 11	Sarsa	1.2	7.54	2.69	457	34	446.1	19.3	88.3	67.5	163.5	0.36	0.12	190	148	19.8	51.6
K _{pr} 12		2.8	7.75	2.23	539.7	43	441.1	24.3	126.4	63.9	213	0.34	0.13	157	127.7	9.7	54.1
K _{pr} 13		1.7	7.66	2.27	400.3	39	355.9	24.5	94.3	47	201.2	0.84	0.14	160	156.7	79.3	42.6
K _{pr} 14		0.9	7.77	1.89	387.5	58	386	34.3	104.3	36.2	134.8	0.26	0.12	133	153.9	59.5	45.8
K _{pr} 15		1.42	7.53	4.99	543.6	39	461.2	24.5	136.5	57.8	194.5	0.34	0.12	355	133.5	10.3	46.1
K _{pr} 16		2.88	7.61	3.53	224.9	43	254.9	24.5	72.3	12.6	134.9	0.48	0.12	250	60.4	10.5	58.4
K _{pr} 17		3.55	8.39	1.05	110.4	48	81.1	34.3	32.1	8.6	147.9	0.92	0.32	74	36.2	10.2	33.8
K _{pr} 18		2.82	7.47	0.96	204.7	67	113.7	43.8	36.1	32.7	173.1	0.61	0.27	82	39.2	1	22.9
K _{pr} 19		2.84	8.39	1.25	269.9	58	84.3	29.1	84.3	16.9	187.8	0.56	0.12	89	78.5	9.9	41.3
K _{pr} 20		4.8	8.31	3.16	315.2	48	313.3	24.3	94.3	22.7	121.9	0.30	0.13	223	39.2	10.3	80
K _{pr} 21	Tithikapur	2.38	7.85	1.23	153.7	58	105.5	29.2	44.1	12.4	207.3	1.23	0.12	116	102.6	9.3	50.8
K _{pr} 22		2.5	7.99	1.49	216.1	39	42.9	24.3	32.1	38.8	224.2	0.54	0.53	105	135.8	9.2	54
K _{pr} 23		2.13	7.81	2.25	183.9	38	63	24.3	10.0	45.4	125.6	0.78	0.14	17	123.8	10.3	41.9
K _{pr} 24		1.68	8.15	0.78	236.4	43	133.9	24.5	72.3	15.9	163.7	0.92	0.37	55	66.4	10.2	55.5
K _{pr} 25		2.12	8.14	0.65	212.2	43	205.8	29.4	24.1	43.4	139.6	0.36	0.45	46	135.8	20.6	54.4
K _{pr} 26		1.01	8.43	0.3	170.8	45	120.3	20.5	54.3	10	170	0.46	0.12	48	154	10.1	53.7
K _{pr} 27		0.2	8.83	0.31	96.4	45	15.6	20.4	20.9	12.6	221.5	0.56	0.15	21	132.8	82.5	56.3
K _{pr} 28		1.32	8.6	0.47	89	40	10.4	25.6	25.1	7.5	209.2	0.82	0.12	22	163	61.8	44.3
K _{pr} 29		2.23	8.84	0.44	46	61	20.8	41.1	6.2	8.7	140.2	0.64	0.93	32	160	10.9	47.7
K _{pr} 30		1.36	8.22	3.61	89	30	62.6	15.3	25.1	7.5	202.3	0.70	0.14	31	138.9	10.6	48

Table 6 continued

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{pr} 31	Lauberia	3.4	8.18	1.74	363.4	55	318	30.7	75.2	50.1	275.7	0.09	0.12	249	56.3	1	54.5
K _{pr} 32		1.61	7.98	2.06	381.7	60	260.6	30.7	77.2	53.9	87.7	0.34	0.12	123	33.8	10.3	31.5
K _{pr} 33		2.22	7.95	0.47	517	65	391	40.1	108.5	70.2	123	0.25	0.11	140	36.6	10.7	21.4
K _{pr} 34		4.02	8.32	2.01	112.1	131	41.7	101.9	16.7	20.1	91.2	0.61	0.15	33	73.2	9.7	38.5
K _{pr} 35		1.86	8.15	2.83	512.7	36	364.9	20.5	98.1	76.4	338.9	0.32	0.12	140	36.6	9.6	74.6
K _{pr} 36		1.24	7.84	2.34	475.2	35	464	20	91.8	70.2	114.1	0.19	0.14	197	95.7	10.7	47.4
K _{pr} 37		2.9	8.06	2.38	561.5	45	458.7	25.3	131.5	66.5	46.4	0.16	0.15	163	126.7	10.6	50.3
K _{pr} 38		1.76	7.97	1.99	416.4	50	370.1	25.5	98.1	48.9	68.2	0.58	0.12	167	115.4	21.4	39.1
K _{pr} 39		5.36	8.68	5.24	403.2	170	401.4	135.7	108.5	37.7	144.8	0.31	0.18	138	141.9	10.5	51.8
K _{pr} 40		1.47	7.83	3.71	565.4	60	479.6	25.5	142	60.1	222.6	0.38	0.12	369	126.7	85.8	50.8
K _{pr} 41	Tarapur	2.98	7.91	1.1	233.9	50	265.1	25.5	75.2	13.1	31.8	0.56	0.33	260	143.6	64.3	50.1
K _{pr} 42		4.72	8.73	1.01	114.7	60	84.3	35.6	33.4	8.9	125.8	0.42	0.28	77	123.9	10.7	52.5
K _{pr} 43		2.92	7.77	1.31	212.8	46	118.3	40.1	37.5	34	137.9	0.49	0.42	86	152	10.2	41.3
K _{pr} 44		3.98	8.73	3.32	280.9	40	87.7	30.3	87.7	17.6	161.4	0.85	0.12	92	149.2	9.9	44.5
K _{pr} 45		4.98	8.64	1.29	327.9	45	325.8	25.3	98.1	23.6	175.2	0.35	0.14	232	129.5	1	44.8
K _{pr} 46		4.54	8.16	1.57	159.9	45	109.8	30.4	45.9	12.9	113.7	0.61	0.12	120	60.4	9.6	60.8
K _{pr} 47		2.59	8.31	2.36	224.9	47	44.6	25.3	33.4	40.4	193.3	0.31	0.86	109	36.2	10	35.1
K _{pr} 48		4.28	8.12	0.82	191.2	47	65.5	25.3	10.4	47.2	209.1	0.35	0.13	18	39.2	9	23.8
K _{pr} 49		1.74	8.48	0.69	245.8	42	139.3	25.5	75.2	16.5	117.2	0.36	0.12	57	78.5	9	43
K _{pr} 50		2.19	8.47	0.29	220.6	63	214.1	30.6	25.1	45.1	152.7	0.95	0.12	48	39.2	10	83.2
K _{pr} 51	Nowpara	0.94	7.87	0.3	159.1	31	112.2	19.1	50.6	9.3	130.2	0.65	0.11	45	102.6	9.9	52.8
K _{pr} 52		0.18	8.24	0.45	89.7	57	14.6	19.1	19.5	11.7	158.6	0.34	0.14	19	135.8	20	56.1
K _{pr} 53		1.23	8.02	0.43	83	62	9.7	23.8	23.4	7	206.6	0.16	0.12	21	123.8	9.8	43.5
K _{pr} 54		2.08	8.25	3.5	43.2	68	19.4	38.4	5.8	8.2	195.2	0.8	0.13	30	66.4	80	57.8
K _{pr} 55		1.27	7.66	1.69	83	136	58.3	14.3	23.4	7	130.8	0.16	0.14	29	135.8	60	56.6
K _{pr} 56		2.17	7.63	2	339.1	37	296.6	28.6	70.1	46.8	188.7	0.18	0.12	233	154	10	55.8
K _{pr} 57		1.5	7.44	0.45	356.1	37	243.1	28.6	72	50.3	257.2	0.34	0.12	115	132.8	11.2	58.5
K _{pr} 58		2.07	7.41	1.95	482.3	42	364.7	37.4	101.2	65.5	81.8	0.52	0.12	131	163	10.6	46.1
K _{pr} 59		2.62	7.76	2.74	104.5	95	38.9	46.8	15.6	18.7	114.7	0.26	0.31	31	160	10.3	49.6
K _{pr} 60		1.74	7.6	2.27	478.3	65	340.3	19.1	91.5	71.3	85.1	0.22	0.26	131	138.9	1	49.9

Table 6 continued

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{pr} 61	Bhadulia	1.15	7.31	2.31	443.5	56	432.7	18.7	85.7	65.5	316	0.34	0.47	184	62.8	10	32.8
K _{pr} 62		2.71	7.52	1.93	523.5	47	427.9	23.6	122.6	62	106.5	0.12	0.12	152	37.7	10.4	22.2
K _{pr} 63		1.64	7.43	5.08	388.4	56	345.2	23.8	91.5	45.6	43.3	0.19	0.16	155	40.8	9.4	40.1
K _{pr} 64		0.86	7.54	3.6	375.9	37	374.4	33.3	101.2	35.1	63.6	0.36	0.12	129	81.6	9.3	77.6
K _{pr} 65		1.37	7.3	1.07	527.4	37	447.3	23.8	132.4	56.1	135.1	0.38	0.97	344	40.8	10.4	49.3
K _{pr} 66		2.78	7.38	0.98	218	42	247.3	23.8	70.1	12.2	207.6	0.42	0.15	243	106.8	10.3	52.4
K _{pr} 67		3.4	8.14	1.27	106.8	42	78.7	33.2	31.1	8.3	29.7	0.43	0.12	72	141.3	20.8	40.6
K _{pr} 68		2.73	7.25	3.22	198.5	44	110.3	42.5	35	31.7	176.8	0.56	0.12	80	128.7	10.2	53.9
K _{pr} 69		4.42	8.41	1.26	261.9	44	81.8	28.3	81.8	16.4	230.4	0.61	0.11	86	69.1	83.2	52.8
K _{pr} 70		2.75	8.28	1.52	305.8	39	303.9	23.6	91.5	22	217.6	0.68	0.16	216	141.3	62.4	52.1
K _{pr} 71	Paschim Sibpur	1.05	8.47	2.29	177.6	59	125.1	30.6	56.47	10.4	145.8	0.35	0.12	50	160.1	10.4	54.6
K _{pr} 72		0.21	8.77	0.79	100.2	29	16.2	21.3	21.74	13.1	210.4	0.71	0.15	21	138.1	10.4	43
K _{pr} 73		1.37	9.18	0.67	92.6	53	10.8	21.3	26.1	7.8	286.7	0.20	0.16	23	169.5	11.6	46.2
K _{pr} 74		2.32	8.94	0.7	47.8	58	21.7	26.6	6.45	9.05	91.2	0.32	0.12	34	166.4	11	46.6
K _{pr} 75		1.41	9.19	0.3	92.6	63	65.1	42.8	26.1	7.8	127.9	0.54	0.12	33	144.4	10.7	56.7
K _{pr} 76		2.54	8.55	0.32	377.9	127	330.7	16	78.21	52.1	94.8	0.52	0.12	259	58.6	1.1	32.8
K _{pr} 77		1.67	8.51	0.48	396.9	34	271.1	31.9	80.29	56.06	352.5	0.51	0.34	128	35.1	10.4	22.2
K _{pr} 78		2.31	8.3	0.45	537.6	34	406.6	31.9	112.84	73.01	118.7	0.46	0.29	146	38.1	10.8	40.1
K _{pr} 79		3.26	8.27	3.68	116.6	42	43.4	38.5	17.37	20.9	48.3	0.48	0.44	35	76.1	9.7	77.6
K _{pr} 80		1.93	8.65	1.77	533.2	106	379.5	43.4	102.02	79.46	70.9	0.92	0.12	146	38.1	9.7	49.3
K _{pr} 81	Kasa	1.29	8.48	2.1	494.2	43	482.5	21.3	95.47	73.01	150.6	0.38	0.15	205	99.6	10.8	52.4
K _{pr} 82		3.02	8.15	0.48	584	46	477.1	20.8	136.76	69.16	231.5	0.39	0.12	170	131.8	10.7	40.6
K _{pr} 83		1.83	8.38	2.05	433.1	45	384.9	26.3	102.02	50.86	33.1	0.25	0.89	173	120.1	21.6	53.9
K _{pr} 84		0.97	8.29	2.88	419.3	41	417.5	26.5	112.84	39.21	130.8	0.28	0.14	144	64.4	10.6	52.8
K _{pr} 85		1.53	8.4	2.39	588	61	498.8	37.1	147.68	62.5	143.4	0.72	0.12	384	131.8	86.5	52.1
K _{pr} 86		3.1	8.14	2.43	243.2	30	275.7	26.5	78.21	13.62	167.9	0.27	0.12	271	149.3	64.9	54.6
K _{pr} 87		4.91	8.23	2.02	119.3	55	87.7	26.5	34.74	9.26	182.2	0.2	0.11	80	128.9	10.8	43
K _{pr} 88		3.04	9.08	5.34	221.3	61	123	37.1	39	35.36	118.2	0.37	0.15	89	158.1	9.7	46.2
K _{pr} 89		4.14	8.08	3.78	292.1	66	91.2	47.3	91.21	18.3	201	0.48	0.12	96	155.2	10.8	46.6
K _{pr} 90		5.08	9.08	1.12	340.9	132	338.9	31.5	102.02	24.54	217.5	0.06	0.14	241	134.7	10.3	52.9
K _{pr} 91	Hazratpur	3.72	8.99	1.03	166.3	36	114.1	26.3	47.74	13.42	121.9	0.16	0.15	125	56.3	10	30.6
K _{pr} 92		2.69	8.49	1.34	233.9	35	46.4	31.6	34.74	42.02	158.8	0.37	0.12	113	33.8	1	20.7
K _{pr} 93		3.45	8.64	3.38	198.9	36	68.2	26.3	10.82	49.09	135.4	0.38	0.12	19	36.6	9.7	37.4
K _{pr} 94		1.81	8.44	1.32	255.6	40	144.8	26.3	78.21	17.16	164.9	0.52	0.12	60	73.2	10.1	72.4
K _{pr} 95		2.28	8.82	1.6	229.4	41	222.6	26.5	26.1	46.9	214.9	0.32	0.32	50	36.6	9.1	46
K _{pr} 96		0.98	8.81	2.41	190.8	43	31.8	31.8	31.8	31.8	164.9	0.26	0.27	46	95.7	9	48.8
K _{pr} 97		0.19	7.9	0.83	165.6	42	116.7	28.5	52.67	9.7	214.9	0.61	0.44	20	126.7	10.1	37.9
K _{pr} 98		1.28	8.18	0.7	93.4	38	15.2	19.9	20.27	12.22	202.9	0.32	0.12	22	115.4	10	50.3
K _{pr} 99		2.16	8.57	0.29	86.4	57	10.1	19.8	24.35	7.28	136	0.24	0.15	31	61.9	20.2	49.2
K _{pr} 100		1.32	8.34	0.3	44.6	28	20.2	24.8	6.01	8.44	196.2	0.36	0.12	30	126.7	9.9	32.8

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 7 Physico- chemical parameters of groundwater samples of Khoyrasol block in POM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{po} 1	Gosho Dargal	0.88	7.7	0.68	151	45	116.8	20.1	50.1	10	136	0.39	0.4	39	52.3	9.5	58.4
K _{po} 2		0.18	8.07	0.29	85.2	45	15.2	20	19.3	12.6	149	0.33	0.11	17	31.4	9.7	33.8
K _{po} 3		1.15	7.86	0.31	78.6	40	10.1	25.1	23.1	7.5	175	0.18	0.13	18	34	9.4	22.9
K _{po} 4		1.94	8.08	0.46	40.9	61	20.2	40.3	5.8	8.7	190	0.15	0.11	26	67.9	0.9	41.3
K _{po} 5		1.19	7.51	0.43	78.6	30	60.7	15	23.1	7.5	123	0.3	0.84	26	34	9.1	80
K _{po} 6		2.95	7.48	3.54	321.5	55	308.8	30.1	69.4	50.1	209	0.4	0.12	204	88.8	9.5	50.8
K _{po} 7		1.4	7.29	1.71	337.5	60	253.1	30.1	71.2	53.9	226	0.56	0.11	101	117.6	8.6	54
K _{po} 8		1.93	7.26	2.02	457.2	65	379.7	39.4	100.1	70.2	127	1.04	0.11	115	107.1	8.5	41.9
K _{po} 9		1.62	7.6	0.46	99.2	131	40.5	100	15.5	20.1	165	0.27	0.1	27	57.5	9.5	55.5
K _{po} 10		1.62	7.45	1.98	453.6	36	354.4	20.1	90.5	76.4	141	0.22	0.13	115	117.6	9.5	54.4
K _{po} 11	Sarsa	1.08	7.16	2.64	420.4	34	455	20	90.1	68.9	172	0.35	0.11	161	133.2	19	53.7
K _{po} 12		2.52	7.36	2.19	496.5	44	449.9	25.3	128.9	65.2	224	0.15	0.12	133	115	8.9	56.3
K _{po} 13		1.63	7.28	2.22	360.2	39	363	25.5	96.2	47.9	211	0.22	0.13	136	141.1	84.1	44.3
K _{po} 14		0.86	7.38	1.85	348.7	59	393.7	35.7	106.4	36.9	142	0.08	0.12	113	138.5	63	47.7
K _{po} 15		1.36	7.15	4.89	489.2	40	470.4	25.5	139.2	59	204	0.32	0.12	301	140.2	10.9	48
K _{po} 16		2.76	7.76	3.46	202.4	44	260	25.5	73.7	12.9	142	0.37	0.12	213	61	11.1	60.7
K _{po} 17		3.41	8.89	1.03	99.3	49	82.7	35.6	32.7	8.8	155	0.09	0.31	63	36.6	10.8	34.8
K _{po} 18		2.71	7.92	0.94	184.2	69	116	45.5	36.8	33.4	180	0.18	0.26	70	39.6	1.1	23.6
K _{po} 19		2.73	8.89	1.23	242.9	59	86	30.3	86	17.2	195	0.09	0.12	67	79.3	10.5	42.6
K _{po} 20		4.51	8.81	3.1	283.7	49	319.6	25.3	96.2	23.2	127	0.15	0.13	167	39.6	10.9	82.6
K _{po} 21	Tithikapur	2.24	8.35	1.19	138.3	57	105	30.1	43.2	12.8	216	0.36	0.12	87	103.7	9.8	52.4
K _{po} 22		2.35	8.74	1.45	194.5	38	42.7	25	31.5	40.1	233	0.24	0.51	79	137.2	9.8	55.7
K _{po} 23		2	8.52	2.18	165.5	36	62.7	25.1	9.8	46.9	131	0.03	0.14	13	125	10.9	43.2
K _{po} 24		1.58	8.76	0.76	212.8	40	133.2	25.2	70.9	16.4	170	0.1	0.36	41	67.1	10.8	57.3
K _{po} 25		1.99	8.14	0.63	190.9	40	204.8	30.3	23.6	44.9	145	0.1	0.44	35	137.2	21.9	56.2
K _{po} 26		0.95	8.11	0.29	153.7	42	119.7	21.1	53.2	10.3	177	0.21	0.12	36	155.5	10.7	55.4
K _{po} 27		0.19	7.9	0.3	86.7	42	15.5	21.1	20.5	13	230	0.1	0.15	15	134.2	87.4	58.1
K _{po} 28		1.24	7.87	0.46	80.1	38	10.4	26.3	24.6	7.8	218	0.08	0.12	17	164.6	65.6	45.7
K _{po} 29		2.1	8.24	0.43	41.4	57	20.7	42.4	6.1	9	146	0.14	0.9	24	161.6	11	49.2
K _{po} 30		1.28	8.08	3.5	80.1	28	62.2	15.8	24.6	7.8	210	0.08	0.14	23	140.3	10.7	49.5

Table 7 continued

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{po} 31	Lauberia	3.2	7.77	1.69	327	51	316.4	31.6	73.7	51.8	287	0.83	0.12	187	56.9	1.1	56.2
K _{po} 32		1.51	7.98	2	343.5	56	259.3	31.6	75.7	55.7	91	0.80	0.12	93	34.1	10.4	32.5
K _{po} 33		2.09	7.89	0.46	465.3	61	389	41.3	106.3	72.6	128	0.09	0.11	105	37	10.8	22
K _{po} 34		3.78	8	1.95	100.9	121	41.5	105	16.4	20.8	95	0.24	0.15	25	73.9	9.8	39.8
K _{po} 35		1.75	7.08	2.75	461.4	33	363.1	21.1	96.1	79	352	0.44	0.12	105	37	9.7	77
K _{po} 36		1.17	7.15	2.27	427.7	33	461.6	20.6	90	72.6	119	0.17	0.14	148	96.7	10.8	48.9
K _{po} 37		2.73	7.89	2.31	505.4	45	456.4	26	128.9	68.8	48	0.13	0.15	122	128	10.8	52
K _{po} 38		1.65	7.02	1.93	374.8	50	368.3	26.3	96.1	50.6	71	0.13	0.12	158	116.6	21.6	40.3
K _{po} 39		4.93	7.89	5.08	362.9	168	399.4	139.8	106.3	39	151	0.09	0.17	131	143.4	10.6	53.5
K _{po} 40		1.35	8.14	3.6	542.7	66	508.4	23	156.2	63.7	236	0.1	0.11	350	116.6	81.5	53.8
K _{po} 41	Tarapur	2.74	7.69	0.99	224.5	55	281	22.9	82.7	13.9	34	0.31	0.3	247	132.1	61.1	53.1
K _{po} 42		4.34	7.83	0.91	110.1	66	89.4	32.1	36.7	9.4	133	0.29	0.26	73	114	10.2	55.7
K _{po} 43		2.69	7.65	1.18	204.2	50	125.4	36.1	41.3	36	146	0.72	0.39	81	139.9	9.7	43.8
K _{po} 44		3.66	7.99	2.99	269.6	43	93	27.3	96.5	18.7	171	0.22	0.11	88	137.3	9.4	47.1
K _{po} 45		4.58	7.98	1.16	314.7	49	345.4	22.8	107.9	25	186	0.29	0.13	220	119.2	0.9	47.4
K _{po} 46		4.18	8.26	1.41	153.5	49	116.3	27.3	50.5	13.7	121	0.41	0.11	114	55.5	9.1	64.4
K _{po} 47		2.38	8.65	2.12	215.9	51	47.3	22.8	36.7	42.8	205	0.79	0.79	103	33.3	9.5	37.2
K _{po} 48		3.94	8.43	0.74	183.6	51	69.5	22.8	11.4	50	222	0.52	0.12	17	36.1	8.6	25.2
K _{po} 49		1.65	8.66	0.62	235.9	38	147.6	22.9	82.7	17.5	124	0.48	0.12	55	72.2	8.5	45.5
K _{po} 50		2.08	8.06	0.26	211.8	57	226.9	27.5	27.6	47.8	162	0.26	0.12	46	36.1	9.5	88.2
K _{po} 51	Nowpara	0.89	8.02	0.27	155.9	28	118.9	17.2	55.7	9.9	138	1.06	0.11	42	94.4	9.4	56
K _{po} 52		0.17	7.82	0.41	87.9	52	15.4	17.2	21.5	12.4	168	0.46	0.14	17	125	19	59.5
K _{po} 53		1.05	7.79	0.39	81.3	56	10.3	21.4	25.7	7.4	219	0.67	0.12	19	116.3	9.3	46.2
K _{po} 54		1.77	7.65	3.15	42.3	61	20.6	34.5	6.4	8.7	207	0.79	0.13	27	62.4	76	61.2
K _{po} 55		1.08	7.5	1.52	81.3	122	61.8	12.9	25.7	7.4	139	0.31	0.14	26	127.7	57	60
K _{po} 56		1.84	7.21	1.8	332.3	33	314.4	25.7	74.3	49.6	200	0.4	0.12	209	144.7	9.5	59.2
K _{po} 57		1.28	7.42	0.41	348.9	33	257.7	24.3	76.3	53.3	273	0.48	0.12	104	124.9	10.6	62
K _{po} 58		1.76	7.33	1.76	472.6	38	386.5	31.8	107.3	69.4	87	0.71	0.12	118	153.2	9.9	48.8
K _{po} 59		2.44	7.99	2.47	102.4	86	42.8	39.7	16.5	19.8	122	0.55	0.32	28	150.4	9.6	52.6
K _{po} 60		1.62	7.2	2.04	440	59	374.4	16.3	97	75.6	94	0.6	0.27	118	130.5	0.9	52.9

Table 7 continued

Sample No.	Loc atio	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
K _{ps} 61	Bhadulia	1.07	7.28	2.08	408	51	476	15.9	90.8	69.4	348	0.18	0.48	165	59	9.3	60.1
K _{ps} 62		2.52	8.03	1.74	481.6	42	470.6	20	130	65.7	117	0.29	0.11	137	35.4	9.7	34.7
K _{ps} 63		1.54	7.15	4.57	357.3	51	379.7	20.2	97	48.3	48	0.22	0.15	140	38.4	8.7	23.5
K _{ps} 64		0.81	8.03	3.24	345.8	36	411.8	28.3	107.3	37.2	70	0.52	0.11	116	74.3	8.7	42.5
K _{ps} 65		1.29	7.95	0.96	485.2	36	492.1	20.2	140.3	59.5	149	0.28	0.9	310	37.1	9.7	82.2
K _{ps} 66		2.61	7.51	0.88	200.5	40	272	20.2	74.3	12.9	228	0.16	0.14	219	97.1	9.6	52.2
K _{ps} 67		3.2	7.65	1.14	98.3	40	86.5	28.3	33	8.8	33	0.14	0.11	65	128.6	19.3	55.5
K _{ps} 68		2.57	7.47	2.9	182.6	42	121.3	36.1	37.1	33.6	194	0.5	0.11	72	117.1	9.5	43
K _{ps} 69		4.15	7.8	1.13	241	42	90	24	86.7	17.4	253	0.27	0.1	77	62.9	80.7	57.1
K _{ps} 70		2.59	7.79	1.37	281.3	38	334.3	20.1	97	23.3	239	0.33	0.15	195	128.6	60.5	58.6
K _{ps} 71	Paschim Sibirpur	0.99	7.24	1.95	163.4	57	137.6	26	59.9	11	160	0.48	0.11	45	145.7	10.1	57.8
K _{ps} 72		0.2	7.58	0.67	92.2	28	17.9	18.1	23.5	13.9	231	0.36	0.14	19	131.2	10.1	60.6
K _{ps} 73		1.29	7.38	0.57	85.2	51	11.9	18.1	28.2	8.3	315	0.42	0.15	21	161.1	11.3	47.7
K _{ps} 74		2.18	7.43	0.6	44	56	23.8	22.6	7	9.6	100	0.73	0.11	30	158.1	10.7	51.3
K _{ps} 75		1.33	6.89	0.26	85.2	61	71.6	40.6	28.2	8.3	141	0.3	0.13	29	137.2	10.4	51.7
K _{ps} 76		2.39	6.87	0.27	347.7	117	363.8	15.2	84.5	55.2	104	0.52	0.13	233	55.6	1	62.9
K _{ps} 77		1.57	6.7	0.41	365.2	32	276.5	30.3	86.7	59.4	388	0.27	0.36	116	33.4	10.1	36.4
K _{ps} 78		2.17	6.67	0.38	494.6	31	414.8	30.3	121.9	77.4	131	0.3	0.31	131	36.2	10.5	24.7
K _{ps} 79		3.06	6.98	3.13	107.3	38	44.2	36.6	18.8	22.2	53	0.31	0.47	31	72.3	9.4	44.5
K _{ps} 80		1.81	6.84	1.5	490.5	98	387.1	41.2	110.2	84.2	72	0.82	0.13	131	36.2	9.4	86.1
K _{ps} 81	Rasa	1.21	6.58	1.79	454.7	40	492.2	20.3	103.1	77.4	154	0.56	0.16	170	94.6	10.5	54.7
K _{ps} 82		2.84	6.77	0.41	537.2	42	486.6	19.8	147.7	73.3	236	0.29	0.13	141	122.6	10.4	58.1
K _{ps} 83		1.65	6.69	1.74	402.8	42	392.6	25	110.2	53.9	34	0.14	0.94	144	111.7	21	42.6
K _{ps} 84		0.87	6.79	2.45	390	37	425.8	25.2	121.9	41.6	133	0.69	0.15	119	59.9	10.3	56.6
K _{ps} 85		1.38	6.57	2.03	546.8	56	508.8	35.3	159.5	66.3	146	0.14	0.13	318	122.6	79.6	55.4
K _{ps} 86		2.79	6.64	2.07	226.2	28	281.2	25.2	80.6	14.4	171	0.15	0.13	225	138.9	59.7	54.7
K _{ps} 87		4.42	7.33	1.72	110.9	51	89.5	25.2	35.8	9.8	186	0.29	0.12	67	119.8	10	57.3
K _{ps} 88		2.74	6.53	4.54	205.8	56	125.4	35.2	40.2	36.1	121	0.45	0.16	74	147.1	8.9	45.1
K _{ps} 89		3.73	7.57	3.21	271.6	61	93	45	93.9	18.7	205	0.22	0.13	80	144.4	10	48.6
K _{ps} 90		4.06	7.45	0.95	317.1	121	345.6	29.9	105.1	25	222	0.19	0.15	200	125.3	9.5	48.9
K _{ps} 91	Hazratpur	2.98	7.62	0.96	154.7	33	116.4	25	49.2	13.7	124	0.29	0.16	104	52.4	9.2	55.5
K _{ps} 92		2.15	7.89	1.25	217.6	33	47.3	30	35.8	42.9	154	0.1	0.13	94	31.4	0.9	32.1
K _{ps} 93		2.76	9.27	3.14	200.9	33	69.5	25	11.1	50.1	131	0.16	0.13	16	34	8.9	21.8
K _{ps} 94		1.45	9.03	1.23	258.1	38	150.6	24.2	80.6	17.5	160	0.31	0.13	50	68.1	9.3	39.2
K _{ps} 95		2.05	9.28	1.49	231.7	39	231.5	24.4	26.9	47.8	208	0.36	0.29	42	34	8.4	76
K _{ps} 96		0.88	8.64	2.24	192.7	40	33.1	29.3	32.8	32.4	160	0.36	0.34	38	89	8.3	48.2
K _{ps} 97		0.17	8.6	0.77	167.3	40	121.3	26.2	54.3	9.9	208	0.37	0.48	17	117.8	9.3	51.3
K _{ps} 98		1.15	8.38	0.65	94.4	36	15.8	18.3	20.9	12.5	197	0.48	0.13	18	107.4	9.2	39.8
K _{ps} 99		1.94	8.35	0.27	87.2	54	10.5	18.2	25.1	7.4	132	0.52	0.17	26	57.6	18.6	52.8
K _{ps} 100		1.19	8.74	0.28	45	27	21	22.8	6.2	8.6	190	0.58	0.13	25	117.8	9.1	51.7

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 8 Physico- chemical parameters of groundwater samples of Mahammad Bazar block in PRM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
M _{pr} 1	Chak Sechara	1.3	7.57	0.46	86.6	52	60.7	39.9	24.4	7.3	267.4	0.3	0.9	242	143.6	80.7	48.6
M _{pr} 2		1.56	7.97	0.43	352.4	56	308.4	14.9	72.9	48.6	85.1	0.61	0.14	120	123.9	60.5	50.9
M _{pr} 3		1.15	7.13	3.53	370.3	62	252.8	29.7	74.9	52.3	119.3	0.17	0.12	136	152	10.4	40.1
M _{pr} 4		0.84	6.74	1.7	501.6	123	379.3	29.8	105.3	68.1	88.5	0.28	0.12	32	149.2	1	43.1
M _{pr} 5		1.8	7.71	2.02	108.8	39	40.4	33.4	16.2	19.5	328.7	0.46	0.11	136	129.5	10.1	43.4
M _{pr} 6		1.2	7.07	0.46	497.4	99	354	33	95.2	74.1	110.7	0.45	0.15	191	58.6	10.5	58.9
M _{pr} 7		0.81	7.01	1.97	461.1	39	450	19.9	89.1	68.1	45	0.44	0.12	158	35.1	9.4	34.1
M _{pr} 8		1.71	7.6	2.76	544.8	60	445	19.4	127.6	64.5	66.2	0.4	0.14	162	38.1	9.4	23.1
M _{pr} 9		0.9	6.82	1.29	403.9	29	359	24.5	95.2	47.4	140.5	0.41	0.15	134	76.1	10.5	41.7
M _{pr} 10		1.33	7.73	1.33	391.4	54	389.4	24.8	105.3	36.6	215.9	0.79	0.12	358	38.1	10.4	80.7
M _{pr} 11	Kaiyuli	0.89	6.84	1.94	548.3	59	465.2	34.6	137.7	58.3	30.8	0.33	0.12	253	99.6	21	51.2
M _{pr} 12		1.38	7.6	5.12	226.7	64	257.2	24.8	72.9	12.7	122	0.34	0.12	75	131.8	10.3	54.5
M _{pr} 13		0.83	6.87	3.63	111.1	128	81.8	24.7	32.4	8.6	133.8	0.22	0.32	83	120.1	83.9	42.2
M _{pr} 14		0.86	7.47	1.08	206.5	35	114.7	34.6	36.4	33	156.6	0.24	0.27	90	64.4	62.9	56
M _{pr} 15		0.83	7.54	0.98	272.6	44	85.1	34.4	85.1	17.1	169.9	0.62	0.41	225	131.8	9.7	63.2
M _{pr} 16		0.4	6.67	1.28	318.2	37	316.1	29.4	95.2	22.9	110.3	0.23	0.12	117	149.3	1	36.5
M _{pr} 17		0.51	6.38	3.24	155	55	106.5	24.6	44.5	12.5	187.5	0.17	0.14	106	128.9	9.4	24.8
M _{pr} 18		1.15	7.62	1.27	218.2	29	43.3	27.5	32.4	39.2	202.8	0.32	0.12	18	158.1	9.8	44.7
M _{pr} 19		1.39	8.06	1.53	185.6	50	63.6	24.5	10.1	45.8	113.7	0.41	0.83	56	155.2	8.8	86.5
M _{pr} 20		1.12	7.18	1.31	238.3	55	135.1	24.6	72.9	16	148.1	0.05	0.13	47	134.7	8.8	54.9
M _{pr} 21	Lohabazar	0.83	7.2	0.51	157.2	42	107.5	18.9	48.6	10.2	146.9	0.14	0.38	242	48.1	8.9	61.9
M _{pr} 22		0.17	6.6	0.22	91.9	42	14	18.8	18.7	12.9	160.9	0.32	0.1	72	28.8	9.1	35.8
M _{pr} 23		1.08	7.4	0.23	83	37	9.3	23.6	22.4	7.7	189	0.33	0.1	80	31.2	8.9	24.3
M _{pr} 24		1.02	7.6	0.34	45.2	57	18.6	37.9	5.6	8.9	205.2	0.45	0.1	86	62.5	0.9	43.8
M _{pr} 25		1.12	7.1	0.32	83	28	55.8	14.1	22.4	7.7	132.8	0.28	0.77	216	31.2	8.6	84.8
M _{pr} 26		0.77	7	1.66	347.1	51	284.1	28.3	67.3	51.1	225.7	0.22	0.1	112	81.7	9	53.8
M _{pr} 27		1.32	6.9	1.28	365.3	56	232.9	28.3	69.1	55	244.1	0.52	0.1	101	108.2	8.1	57.2
M _{pr} 28		0.81	6.8	1.52	493.4	61	349.3	37	97.1	71.6	137.2	0.28	0.1	17	98.5	8	44.4
M _{pr} 29		0.52	7.1	0.34	109.3	121	37.3	94	15	20.5	178.2	0.21	0.1	54	52.9	8.9	58.8
M _{pr} 30		0.56	7	1.48	492.2	33	326	18.9	87.8	77.9	152.3	0.31	0.1	45	108.2	8.9	57.7

Table 8 continued

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TD S	Na	K	SiO ₂
M _{pr} 31	Seharakuri	1.02	6.7	1.98	464.6	32	418.6	18.8	87.4	70.3	185.8	0.14	0.1	233	122.6	17.9	56.9
M _{pr} 32		1.37	6.9	1.64	545.3	41	413.9	23.8	125	66.5	241.9	0.69	0.1	69	105.8	8.4	59.7
M _{pr} 33		1.13	6.8	1.67	404.4	37	334	24	93.3	48.9	227.9	0.14	0.1	77	129.8	79	47
M _{pr} 34		0.81	6.9	1.39	389.6	55	362.2	33.6	103.2	37.6	153.4	0.15	0.1	83	127.4	59.3	50.6
M _{pr} 35		1.28	6.7	1.67	548.2	37	432.8	24	135	60.2	220.3	0.29	0.1	212	129	10.3	50.9
M _{pr} 36		0.59	7.3	2.59	225	41	239.2	24	71.5	13.2	153.4	0.45	0.1	110	56.1	10.5	64.3
M _{pr} 37		1.01	7.4	0.77	110.8	46	76.1	33.5	31.7	9	167.4	0.22	0.29	99	33.7	10.2	36.9
M _{pr} 38		0.55	7.4	0.7	208.6	64	106.7	42.8	35.7	34.1	194.4	0.19	0.29	17	36.5	1	25
M _{pr} 39		0.57	7.4	0.92	269.8	55	79.1	28.5	83.4	17.5	210.6	0.29	0.1	52	72.9	9.8	45.2
M _{pr} 40		1.24	7.3	1.32	316.2	46	294	23.8	93.3	23.7	137.2	0.1	0.1	44	36.5	10.3	87.6
M _{pr} 41	Sankarpur	1.11	7.8	0.9	150.6	53	96.6	28.3	41.9	13.1	233.3	0.16	0.1	228	95.4	9.3	55.5
M _{pr} 42		1.21	7.2	1.09	219.7	36	39.3	23.5	30.6	40.9	251.6	0.31	0.48	68	126.2	9.2	59
M _{pr} 43		0.88	7	0.64	191.1	33	57.7	23.6	9.5	47.8	141.5	0.33	0.1	75	115	10.3	45.8
M _{pr} 44		0.49	7.2	0.57	230.5	37	122.5	23.7	68.8	16.7	183.6	0.36	0.38	81	61.7	10.2	60.7
M _{pr} 45		0.87	6.7	0.48	217.6	37	188.4	28.5	22.9	45.8	156.6	0.37	0.38	207	126.2	20.5	59.6
M _{pr} 46		0.89	6.6	0.22	165.8	39	110.1	19.8	51.6	10.5	191.2	0.48	0.1	108	143.1	10	58.7
M _{pr} 47		0.18	6.4	0.23	96.3	39	14.3	19.8	19.9	13.3	248.4	0.52	0.1	97	123.4	82.2	61.6
M _{pr} 48		1.17	7.4	0.34	87.8	35	9.6	24.7	23.9	8	235.4	0.58	0.1	16	151.5	61.6	48.4
M _{pr} 49		0.97	7.2	0.32	47	53	19	39.9	5.9	9.2	157.7	0.3	0.86	51	148.7	10.4	52.2
M _{pr} 50		1.2	7.6	1.63	87.8	26	57.2	14.9	23.9	8	226.8	0.14	0.1	43	129	10.1	52.5

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 9 Physico-chemical parameters of groundwater samples of Mahammad Bazar block in POM

Sample No.	Loca tion	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
M _{po} 1	Chak Sehara	1.17	7.19	0.47	79.5	54	61.3	40.7	23.4	7.6	280.8	0.36	0.85	218	129.2	77.5	50.5
M _{po} 2		1.4	7.57	0.44	324.3	59	311.5	15.2	70	50.5	89.4	0.22	0.13	108	111.5	58.1	53
M _{po} 3		1.04	6.77	3.64	340.6	64	255.3	30.3	71.9	54.4	125.3	0.15	0.11	123	136.8	10	41.7
M _{po} 4		0.76	6.4	1.75	461.3	12	383	30.4	101	70.8	92.9	0.25	0.11	29	134.3	1	44.9
M _{po} 5		1.62	7.32	2.08	100.1	41	40.8	34.1	15.6	20.3	345.1	0.41	0.1	123	116.6	9.7	45.2
M _{po} 6		1.08	6.72	0.47	457.5	10	357.5	33.7	91.4	77.1	116.2	0.41	0.14	172	52.7	10.1	61.3
M _{po} 7		0.73	6.66	2.03	424.1	41	454.5	20.3	85.5	70.8	47.3	0.4	0.11	142	31.6	9.1	35.4
M _{po} 8		1.54	7.22	2.84	501.1	62	449.4	19.8	122	67.1	69.5	0.27	0.13	145	34.3	9	24
M _{po} 9		0.81	6.48	1.33	371.6	31	362.6	25	91.4	49.3	147.5	0.37	0.14	120	68.5	10.1	43.3
M _{po} 10		1.2	7.34	1.37	359.8	56	393.2	25.2	101	38	226.7	0.71	0.11	322	34.3	10	83.9
M _{po} 11	Kaijuli	0.8	6.5	2	504.5	60	474.5	36	140	59.5	32.3	0.3	0.11	227	89.6	20.1	53.3
M _{po} 12		1.24	7.22	5.27	208.7	65	262.3	25.7	74.4	13	128.1	0.31	0.11	68	118.6	9.4	56.6
M _{po} 13		0.8	6.53	3.74	100.1	13	83.4	25.7	33	8.8	140.5	0.2	0.3	75	108.1	89	43.9
M _{po} 14		0.83	7.1	1.11	185.7	35	117	36	37.1	33.6	164.4	0.55	0.26	81	58	66.7	58.3
M _{po} 15		0.8	7.16	1.01	245.2	45	86.8	35.7	86.8	17.4	178.4	0.56	0.4	203	138.4	10.3	65.7
M _{po} 16		0.38	6.8	1.32	286.2	38	322.4	30.6	97.1	23.3	115.8	0.21	0.12	112	150.8	1	38
M _{po} 17		0.49	6.76	3.34	139.6	57	108.6	25.5	45.4	12.8	196.9	0.15	0.14	101	130.1	9.9	25.6
M _{po} 18		1.1	8.08	1.31	196.4	30	44.2	28.6	33	40	210.9	0.29	0.12	17	159.7	10.4	46.1
M _{po} 19		1.33	8.54	1.58	166.9	51	64.8	25.5	10.3	46.7	118.2	0.37	0.81	53	156.8	9.3	89.3
M _{po} 20		1.05	7.61	1.35	214.6	56	137.8	25.5	74.4	16.3	154	0.06	0.13	45	136	9.3	56.7
M _{po} 21	Lohabazar	0.78	7.8	0.53	130.4	42	107	19.5	47.6	10.5	152.8	0.16	0.37	233	48.6	9.5	63.9
M _{po} 22		0.16	8.21	0.23	73.6	42	13.9	19.4	18.3	13.3	167.3	0.37	0.1	69	29.1	9.7	36.9
M _{po} 23		1.02	7.34	0.24	67.9	35	9.3	24.3	22	8	196.6	0.38	0.1	77	31.6	9.4	25.1
M _{po} 24		0.96	6.94	0.35	35.3	53	18.5	39	5.5	9.2	213.4	0.52	0.1	83	63.1	0.9	45.2
M _{po} 25		1.05	7.94	0.33	67.9	26	55.5	14.5	22	8	138.1	0.32	0.75	207	31.6	9.1	87.5
M _{po} 26		0.72	7.28	1.71	277.8	48	282.7	29.1	66	52.8	234.7	0.25	0.1	108	82.5	9.5	55.5
M _{po} 27		1.24	7.22	1.32	291.6	52	231.7	29.1	67.7	56.9	253.9	0.6	0.1	97	109.2	8.5	59
M _{po} 28		0.76	7.83	1.57	395.1	57	347.6	38.1	95.2	74	142.7	0.32	0.1	16	99.5	8.5	45.8
M _{po} 29		0.49	7.02	0.35	85.7	11	37.1	96.8	14.7	21.2	185.3	0.24	0.1	51	53.4	9	60.7
M _{po} 30		0.53	7.96	1.52	391.9	31	324.4	19.5	86	80.5	158.4	0.36	0.1	43	109.2	9	59.5

Table 9 continued

Sample No.	Location	F ⁻	pH	EC	TH	TA	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na	K	SiO ₂
M _{po} 31	Seharakuri	0.96	7.0	2.04	363.3	30	416.5	19.4	85.7	72.7	193.2	0.16	0.1	223	123.8	18.1	58.7
M _{po} 32		1.29	7.8	1.69	429	38	411.8	24.5	122.	68.8	251.6	0.79	0.1	66	106.8	8.5	61.6
M _{po} 33		1.06	7.0	1.72	311.2	34	332.3	24.7	91.4	50.6	237	0.16	0.1	71	131.1	79.8	48.5
M _{po} 34		0.76	7.6	1.43	301.3	51	360.4	34.6	101.	38.9	159.5	0.17	0.1	77	128.7	59.8	52.2
M _{po} 35		1.2	7.0	1.72	422.7	34	430.6	24.7	132.	62.2	229.1	0.33	0.1	197	130.3	10.4	52.5
M _{po} 36		0.55	6.2	2.67	174.9	38	238	24.7	70.1	13.6	159.5	0.52	0.1	102	56.7	10.6	66.4
M _{po} 37		0.95	6	0.79	85.8	45	75.7	34.5	31.1	9.3	174.1	0.25	0.28	92	34	10.3	38.1
M _{po} 38		0.52	7.1	0.72	159.2	63	106.2	44.1	35	35.3	202.2	0.22	0.28	15	36.8	1	25.8
M _{po} 39		0.52	7.5	0.95	209.9	55	78.7	29.4	81.7	18.1	219	0.33	0.1	49	73.7	9.9	46.6
M _{po} 40		1.14	7.0	1.36	261.4	50	311.6	21.4	102.	25.1	145.4	0.12	0.09	41	33.5	9.8	92.9
M _{po} 41	Sankarpur	1.02	7.0	0.93	127.5	58	102.4	25.5	46.1	13.9	247.3	0.18	0.09	212	87.8	8.8	58.8
M _{po} 42		1.11	6.4	1.12	179.2	39	41.7	21.2	33.7	43.4	266.7	0.36	0.44	63	116.1	8.7	62.5
M _{po} 43		0.81	7.2	0.66	152.5	36	61.2	21.2	10.5	50.7	150	0.38	0.09	70	105.8	9.8	48.5
M _{po} 44		0.45	7.4	0.59	196.1	41	129.9	21.3	75.7	17.7	194.6	0.41	0.35	75	56.8	9.7	64.3
M _{po} 45		0.8	6.9	0.49	176	41	199.7	25.7	25.2	48.5	166	0.43	0.35	193	116.1	19.5	63.2
M _{po} 46		0.82	6.8	0.23	141.6	43	116.7	17.8	56.8	11.1	202.7	0.55	0.09	100	131.6	9.5	62.2
M _{po} 47		0.17	6.7	0.24	79.9	43	15.2	17.8	21.9	14.1	263.3	0.6	0.09	91	113.6	78.1	65.3
M _{po} 48		1.08	6.6	0.35	73.8	38	10.2	22.2	26.3	8.5	249.5	0.67	0.09	15	139.4	58.5	51.3
M _{po} 49		0.92	6.9	0.33	38.1	47	20.1	35.9	6.5	9.8	167.2	0.35	0.88	48	136.8	9.9	55.3
M _{po} 50		1.14	6.8	1.68	73.8	23	60.6	13.4	26.3	8.5	240.4	0.16	0.1	40	118.7	9.6	55.7

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 10 Statistical summary of various physico-chemical parameters for groundwater samples of Nalhati-I block

Water Parameters	PRM						POM					
	Min	Max	Mean	SE Mean	SD	Median	Min	Max	Mean	SE Mean	SD	Median
F ⁻	1.27	7.11	3.15	0.28	1.53	2.76	1.19	6.58	2.98	0.26	2.68	1.42
pH	7.21	8.81	8.09	0.06	0.33	8.12	7.64	9.34	8.49	0.06	8.53	0.35
EC	0.1	3.3	1.26	0.18	0.98	0.77	0.1	3.47	1.32	0.19	0.79	1.03
TH	20.4	954	286.6	47.1	258.1	169.3	20.2	992.2	293.7	48.9	171.8	267.8
TA	45	324	198	13	69	203	44	334	197	13	206	69
Cl	10.5	445.5	116.5	17.3	94.7	120.2	10.8	454.4	119.9	17.7	123.2	96.9
HCO ₃ ⁻	15.5	175.7	98.4	8.4	45.7	94	14.9	179.2	97.1	8.2	93	44.9
Ca	12.2	128.6	41.4	4.7	26	37.5	12.6	131.2	42.6	4.8	39	26.4
Mg	5.6	209.4	40.3	8.8	48.2	21.6	5.7	211.5	40.7	8.9	21.7	48.8
SO ₄ ²⁻	11.8	280.2	71.9	14.4	78.6	18.4	12.2	291.4	74.7	14.9	19.1	81.7
Fe	0.03	3.26	0.33	0.11	0.59	0.16	0.03	3.29	0.32	0.11	0.15	0.59
PO ₄ ³⁻	0	0.8	0.44	0.04	0.22	0.48	0	0.85	0.46	0.04	0.51	0.23
TDS	67	1811	644	76	416	503	70	1902	674	80	525	437
Na ⁺	8.7	142.2	61.4	6.7	36.7	46	8.3	135.1	58.1	6.4	43	35
K ⁺	0.2	148.5	26.5	6.9	37.6	10.9	0.2	139.6	25.1	6.5	10.6	35.4
SiO ₂	18.6	65	39.9	1.8	9.8	40.9	18.5	70.4	39.3	2	39.4	10.8

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 11 Statistical summary of various physico-chemical parameters for groundwater samples of Rampurhat II block

Water Parameters	PRM					POM						
	Min	Max	Mean	SE Mean	SD	Median	Min	Max	Mean	SE Mean	SD	Median
F-	1.7	9.98	3.96	0.38	2.38	3.23	1.33	8.65	3.57	0.31	1.96	2.99
pH	6.2	8.52	7.95	0.07	0.47	8.1	6.51	8.99	8.35	0.08	0.5	8.49
EC	0.21	0.91	0.54	0.03	0.2	0.54	0.22	0.96	0.51	0.03	0.2	0.55
TH	14.5	245.8	95.2	9	56.7	79.8	14.4	243.3	96	9	56.8	80.8
TA	25	436	194	16	102	192	24	423	191	16	100	198
Cl	8.3	352.5	87.8	11.2	70.5	50.7	8.5	366.6	90.6	11.6	73.3	52.2
HCO ₃ ⁻	11.1	205	102.6	8.5	54	91.2	10.9	200.9	101.1	8.4	53.1	89
Ca	1.1	47	15.5	2.1	13	10.9	1.1	47.9	15.9	2.1	13.3	11.2
Mg	1.3	55.8	13.6	1.8	11.4	11.7	1.3	55.5	13.7	1.8	11.4	11.6
SO ₄ ²⁻	6.9	516	132.8	25.4	160.3	34.5	7.2	532.5	137.1	26.2	165.4	35.8
Fe	0.09	0.98	0.42	0.04	0.23	0.37	0.08	0.99	0.41	0.04	0.23	0.36
PO ₄ ³⁻	0	0.77	0.38	0.04	0.25	0.41	0	0.82	0.39	0.04	0.27	0.43
TDS	134	603	346	22	137	335	139	627	361	23	142	352
Na ⁺	34.8	240.6	100.8	8.4	53.2	88.3	32	224	94.7	7.9	49.7	83
K ⁺	0	106.3	40.2	3.7	23.7	36.4	0.8	103.1	38.5	3.6	22.5	34.7
SiO ₂	18.1	67.6	39.9	1.7	10.5	41	11.8	71.2	40.1	1.8	11.5	42.5

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 12 Statistical summary of various physico-chemical parameters for groundwater samples of Khoyrasol block

Water Parameters	PRM					POM				
	Min	Max	Mean	SE Mean	SD	Median	Min	Max	Mean	SE Mean
F ⁻	5.36	0.18	2.26	0.12	1.19	2.13	0.17	4.93	2.06	0.11
pH	9.19	7.25	8.17	0.05	0.46	8.17	6.53	9.28	7.74	0.06
EC	5.34	0.28	1.73	0.12	1.23	1.55	0.26	5.08	1.6	0.11
TH	588	43.2	272	16.1	160.5	231.7	40.9	546.8	252.2	14.7
TA	170	28	53	3	25	45	27	168	51	2
Cl	498.8	9.7	202.5	15.9	159	129.5	10.1	508.8	209.8	16.5
HCO ₃ ⁻	135.7	14.3	30.4	1.6	16.4	26.3	12.9	139.8	29.1	1.7
Ca	147.7	5.8	62.6	3.9	38.8	70.1	5.8	159.5	64.9	4.1
Mg	79.5	7	33	2.3	22.8	28.1	7.4	84.2	34.5	2.4
SO ₄ ²⁻	352.5	29.7	158.8	6.2	62.3	155.1	33	388	166.4	6.6
Fe	1.23	0.06	0.45	0.02	0.23	0.38	0.03	1.06	0.35	0.02
PO ₄ ³⁻	0.97	0.11	0.21	0.02	0.19	0.13	0.1	0.94	0.21	0.02
TDS	384	17	115	9	88	101	13	350	99	8
Na ⁺	169.5	33.8	100.9	4.5	44.7	117.2	31.4	164.6	95.5	4.2
K ⁺	86.5	1	17.7	2.1	21	10.3	0.9	87.4	17.3	2.1
SiO ₂	83.2	20.7	47.9	1.3	12.5	49.3	21.8	88.2	50.8	1.3

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 13 Statistical summary of various physico-chemical parameters for groundwater samples of Mahammad Bazar block

Water Parameters	PRM					POM						
	Min	Max	Mean	SE Mean	SD	Median	Min	Max	Mean	SE Mean	SD	Median
F-	0.17	1.8	0.97	0.05	0.35	0.99	0.16	1.62	0.9	0.05	0.32	0.94
pH	6.38	8.06	7.16	0.06	0.4	7.16	6	8.54	7.15	0.07	0.53	7.1
EC	0.22	5.12	1.33	0.14	1.01	1.28	0.23	5.27	1.37	0.15	1.04	1.32
TH	45.2	548.3	268.9	22.2	157	225.8	35.3	504.5	228.8	19.2	136	196.3
TA	26	128	51	3	23	45	23	130	51	3	23	45
Cl	9.3	465.2	192.3	21.3	150.9	118.6	9.3	474.5	194.4	21.4	151.4	123.5
HCO ₃ ⁻	14.1	94	27.9	1.7	11.7	24.7	13.4	96.8	28.1	1.7	12.2	25.5
Ca	5.6	137.7	60.8	5.3	37.7	68.1	5.5	140.5	60.7	5.2	36.9	66.9
Mg	7.3	77.9	33.4	3.2	22.9	28.4	7.6	80.5	34.7	3.4	23.7	29.4
SO ₄ ²⁻	30.8	328.7	170.7	8.4	59	164.2	32.3	345.1	178.8	8.8	62	170.7
Fe	0.05	0.79	0.33	0.02	0.16	0.31	0.06	0.79	0.34	0.02	0.16	0.33
PO ₄ ³⁻	0.1	0.9	0.21	0.03	0.21	0.12	0.09	0.88	0.21	0.03	0.21	0.11
TDS	16	358	115	11	76	94	15	322	106	10	70	87
Na ⁺	28.8	158.1	98.8	6	42.4	111.6	29.1	159.7	94.6	5.8	40.6	108.7
K ⁺	0.9	83.9	19.4	3.3	23.5	10.1	0.9	89	19.3	3.3	23.5	9.8
SiO ₂	23.1	87.6	51.6	2.1	14.5	51.7	24	92.9	53.7	2.2	15.2	54.3

Units of all water parameters are expressed in mg/L except pH and EC (mS/cm)

Table 14 Correlation matrix of different physico-chemical parameters in the ground water of Nalhathi-I in PRM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	-.552**														
EC	.150	-.235													
TH	.212	-.303	.891**												
TA	-.104	.134	.173	.049											
Cl ⁻	.263	-.470**	.645**	.636**	.061										
HCO ₃ ⁻	.091	.331	.033	.068	.546**	-.091									
Ca	.121	-.070	.359	.348	-.001	.274	.063								
Mg	.017	-.172	.829**	.873**	.020	.445*	-.049	-.018							
SO ₄ ²⁻	.178	-.107	.720**	.681**	.101	.645**	.000	.256	.618**						
Fe	-.162	.074	-.208	-.185	-.442*	.066	-.315	-.268	-.085	-.134					
PO ₄ ³⁻	-.418*	.369*	-.348	-.335	.013	-.371*	.075	.080	-.341	-.488**	-.072				
TDS	.228	-.153	.938**	.861**	.182	.604**	.132	.291	.779**	.806**	-.233	-.454*			
Na	.180	-.078	.754**	.717**	.032	.485**	.203	.340	.649**	.741**	-.111	-.498**	.754**		
K	-.028	-.111	.602**	.489**	.304	.445*	-.001	-.082	.577**	.621**	-.108	-.335	.556**	.614**	
SiO ₂	-.083	.109	-.070	.108	-.192	-.181	-.140	-.098	.139	.118	.151	.103	.054	-.061	-.163

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 15 Correlation matrix of different physico-chemical parameters in the ground water of Nalhathi-I in POM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	-.480**														
EC	.153	-.219													
TH	.221	-.295	.891**												
TA	-.073	.148	.205	.069											
Cl ⁻	.257	-.454*	.645**	.639**	.087										
HCO ₃ ⁻	.078	.325	.032	.067	.521**	-.091									
Ca	.109	-.154	.365*	.343	-.001	.285	.094								
Mg	.036	-.138	.829**	.875**	.044	.444*	-.058	-.014							
SO ₄ ²⁻	.174	-.049	.719**	.689**	.146	.643**	-.011	.260	.617**						
Fe	-.166	.086	-.218	-.192	-.436*	.058	-.318	-.270	-.094	-.147					
PO ₄ ³⁻	-.413*	.244	-.344	-.344	-.038	-.363*	.113	.076	-.341	-.485**	-.066				
TDS	.234	-.114	.937**	.864**	.218	.604**	.128	.294	.779**	.808**	-.243	-.452*			
Na	.170	-.027	.756**	.722**	.073	.485**	.187	.348	.649**	.744**	-.129	-.496**	.758**		
K	-.041	-.024	.600**	.497**	.357	.439*	-.028	-.076	.578**	.620**	-.119	-.330	.556**	.615**	
SiO ₂	-.099	.082	.042	.233	-.193	-.126	-.158	-.050	.270	.237	.106	.046	.157	.046	-.074

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 16 Correlation matrix of different physico-chemical parameters in the ground water of Rampurhat – II in PRM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	-.509**														
EC	.346*	-.338*													
TH	.006	-.121	.438**												
TA	.296	.359*	.058	-.105											
Cl ⁻	-.134	.287	.055	.021	.573**										
HCO ₃ ⁻	.504**	.310	.010	-.202	.779**	.173									
Ca	-.436**	.288	-.150	.546**	.080	.210	-.208								
Mg	.306	-.338*	.626**	.819**	-.174	-.116	-.093	-.033							
SO ₄ ²⁻	.321*	-.510**	.025	-.191	-.224	-.243	-.229	-.439**	.069						
Fe	.090	.000	.399*	.362*	.318*	.312	.169	.300	.229	-.341*					
PO ₄ ³⁻	-.410*	.643*	-.441	-.138	.387*	.208	.209	.519*	-.516**	-.0483*	.056				
TDS	.358*	-.338*	.987**	.437**	.066	.087	.015	-.150	.625**	.026	.382*	-.452**			
Na	.614**	-.277	.220	.014	.272	.043	.445**	-.252	.188	-.091	.334*	-.220	.210		
K	.156	.002	-.049	.058	.243	.328*	.290	.086	.011	-.348*	.273	.175	-.035	.611**	
SiO ₂ **	-.021	.071	-.131	-.023	-.016	.045	-.053	-.059	.013	.035	-.143	-.052	-.140	-.087	-.186

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 17 Correlation matrix of different physico-chemical parameters in the ground water of Rampurhat – II in POM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	-.546**														
EC	.062	-.121													
TH	.129	-.153	.418**												
TA	.202	.341*	-.003	-.109											
Cl ⁻	-.140	.237	.177	.032	.572**										
HCO ₃ ⁻	.373*	.307	-.167	-.183	.803**	.192									
Ca	-.287	.246	.134	.565**	.083	.210	-.193								
Mg	.365*	-.365**	.412**	.809**	-.188	-.110	-.081	-.027							
SO ₄ ²⁻	.277	-.504**	-.091	-.212	-.248	-.243	-.236	-.440**	.061						
Fe	.231	-.119	.489**	.395*	.275	.261	.182	.264	.291	-.299					
PO ₄ ³⁻	-.371*	-.630**	-.097	-.110	.463**	.248	.276	.536**	-.517**	-.526**	.028				
TDS	.424**	-.376*	.638**	.425**	.054	.095	.036	-.152	.624**	.019	.437**	-.428**			
Na	.592**	-.258	.127	.004	.281	.046	.449**	-.245	.179	-.102	.366*	-.160	.205		
K	.192	.001	-.001	.072	.253	.317*	.283	.080	.027	-.338*	.263	-.197	-.021	.627**	
SiO ₂ **	-.192	.012	-.102	-.131	-.098	-.080	-.128	-.094	-.091	.123	-.208	-.094	-.193	-.111	-.215

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 18 Correlation matrix of different physico-chemical parameters in the ground water of Khoyrasol in PRM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	.179														
EC	.230*	-.217*													
TH	.011	-.370**	.338**												
TA	.279**	.142	.099	-.022											
Cl ⁻	.009	-.385**	.338**	.940**	.012										
HCO ₃ ⁻	.356**	.104	.220*	-.046	.655**	-.045									
Ca	.063	-.324**	.330**	.926**	-.013	.904**	-.048								
Mg	-.055	-.350**	.278**	.888**	-.028	.792**	-.034	.647**							
SO ₄ ²⁻	-.073	.047	-.139	-.026	-.145	-.079	-.133	-.042	-.001						
Fe	-.036	.003	-.070	-.094	-.051	-.140	.070	-.080	-.092	.025					
PO ₄ ³⁻	-.085	-.049	-.120	-.059	-.113	-.057	-.048	-.091	-.008	-.084	-.015				
TDS	.181	-.319**	.347**	.728**	.001	.798**	-.092	.783**	.513**	.006	-.117	-.012			
Na	-.062	.012	.107	-.069	.036	-.020	.024	.017	-.160	.022	.035	-.122	.017		
K	-.113	-.004	.062	.027	.005	.076	-.076	.127	-.100	.086	.191	-.103	.208*	.259**	
SiO ₂ **	-.030	.014	-.034	.041	.071	.138	-.090	.083	-.019	.119	.102	.131	.177	.088	.114

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 19 Correlation matrix of different physico-chemical parameters in the ground water of Khoyrasol in POM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	.106														
EC	.226*	-.153													
TH	.013	-.411**	.347**												
TA	.304**	-.079	.107	-.030											
Cl ⁻	.012	-.466**	.349**	.934**	.008										
HCO ₃ ⁻	.351**	.006	.223*	-.042	.688**	-.044									
Ca	.071	-.401**	.326**	.918**	-.013	.900**	-.055								
Mg	-.054	-.378**	.287**	.889**	-.038	.788**	-.024	.640**							
SO ₄ ²⁻	-.077	.037	-.123	-.015	-.137	-.066	-.123	-.031	.003						
Fe	-.155	-.126	-.043	.002	.011	-.039	-.113	-.071	.084	-.033					
PO ₄ ³⁻	-.084	.080	-.129	-.052	-.109	-.045	-.048	-.080	.005	-.080	-.080				
TDS	.184	-.387**	.351**	.715**	.030	.794**	-.082	.783**	.499**	.012	-.081	-.008			
Na	-.064	-.225*	.106	-.074	.039	-.032	.021	.007	-.163	.028	-.074	-.110	.017		
K	-.120	-.128	.050	.023	-.001	.071	-.077	.133	-.099	.100	-.204*	-.108	.203*	.256*	
SiO ₂ **	-.027	-.095	-.045	.046	.062	.144	-.107	.090	-.010	.115	.113	.116	.174	.090	.106

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 20 Correlation matrix of different physico-chemical parameters in the ground water of Mahammad Bazar in PRM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	.566**														
EC	.214	-.026													
TH	.168	-.259	.315*												
TA	-.056	-.053	.226	.095											
Cl ⁻	.181	-.264	.392**	.937**	.089										
HCO ₃ ⁻	-.173	.053	-.159	-.148	.523**	-.173									
Ca	.122	-.237	.363**	.916**	.081	.907**	-.178								
Mg	.184	-.229	.191	.882**	.090	.770**	-.082	.619**							
SO ₄ ²⁻	.112	.083	-.234	-.386**	-.279*	-.445**	.081	-.362**	-.330*						
Fe	.234	.196	-.160	.124	-.098	.094	-.129	.101	.125	.110					
PO ₄ ³⁻	.118	.255	-.229	-.379**	-.050	-.377*	.058	-.408**	-.264	-.003	-.028				
TDS	.209	.040	-.009	.200	-.101	.305*	-.123	.267	.078	-.055	.233	.156			
Na	.176	-.103	.223	.013	-.016	-.050	-.074	-.037	.070	.175	-.015	.110	-.173		
K	-.001	-.056	-.029	-.145	.073	-.087	-.052	-.118	-.146	.149	.023	.121	.009	.264	
SiO ₂	.159	.181	-.172	-.021	-.112	-.005	-.074	-.001	-.039	.071	.193	.319*	.243	.014	.006

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 21 Correlation matrix of different physico-chemical parameters in the ground water of Mahammad Bazar in POM

	F	pH	EC	TH	TA	Cl	HCO ₃	Ca	Mg	SO ₄	Fe	PO ₄	TDS	Na	K
pH	.111														
EC	.207	-.171													
TH	.173	-.031	.335*												
TA	-.058	-.252	.229	.146											
Cl ⁻	.161	-.107	.391**	.934**	.089										
HCO ₃ ⁻	-.168	-.111	-.117	-.110	.475**	-.138									
Ca	.094	-.070	.358*	.896**	.072	.894**	-.145								
Mg	.176	.082	.187	.864**	.088	.764**	-.057	.590**							
SO ₄ ²⁻	.126	.054	-.236	-.461**	-.297*	-.458**	.049	-.363**	-.334*						
Fe	-.058	-.252	.229	.146	1.000**	.089	.475**	.072	.088	-.297*					
PO ₄ ³⁻	.127	.185	-.232	-.366**	-.057	-.377**	.040	-.410**	-.266	-.003	-.057				
TDS	.179	-.090	-.019	.218	-.087	.296*	-.118	.246	.069	-.045	-.087	.147			
Na	.161	.048	.212	.023	-.036	-.041	-.078	-.002	.082	.191	-.036	.102	-.185	.220	
K	-.005	-.100	-.012	-.151	.101	-.090	-.049	-.119	-.145	.144	.101	.109	-.009	.026	
SiO ₂	.168	.241	-.180	-.049	-.109	-.009	-.107	.015	-.048	.080	-.109	.314*	.245	.006	.005

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

Table 22 Percent sample exceeding the BIS (2009) permissible of water parameters limit in the four blocks during PRM and POM

Parameters	BIS (2009) permissible limit	% Sample exceeding the BIS (2009) upper limit							
		Nalhati		Rampurhat		Khoyrasol		Mahammad Bazar	
		PRM	POM	PRM	POM	PRM	POM	PRM	POM
pH	6.5-8.5	3.33	53.33	5	47.5	21	14	4	12
EC	0.3	90	96.67	85	75.0	92	91	92	92
TDS	2	0	0	0	0	0	0	0	0
TH	600	13.33	16.67	0	0	0	0	0	0
TA	600	0	0	0	0	0	0	0	0
Ca	200	0	0	0	0	0	0	0	0
Mg	30	33.33	16.67	12.5	12.5	50	50	50	50
Na	200	0	0	7.5	5	0	0	0	0
K	10	53.33	53.33	97.5	97.5	58	46	50	36
Cl ⁻	1000	0	0	0	0	0	0	0	0
SO ₄ ²⁻	400	0	0	12.5	12.5	0	0	0	0
Fe	0.3	23.33	3.33	62.5	57.5	75	48	52	58
PO ₄ ³⁻	0.3	73.33	73.33	57.5	55.0	18	18	20	18

Each chemical parameter in BIS (2009) permissible limit are expressed in mg/L except for conductivity (mS/cm) and pH

Table 23 The weight and relative weight of each of the physico-chemical parameters used for WQI determination

Parameters	BIS desirable limit	Weight	Relative weight
pH	6.5-8.5	3	0.075
EC	2	3	0.075
TDS	0.5	5	0.125
TA	200	2	0.05
TH	200	3	0.075
Ca	75	2	0.05
Mg	30	2	0.05
Na	100	3	0.075
K	10	2	0.05
Fe	0.3	2	0.05
Cl ⁻	250	3	0.075
F ⁻	1.0	5	0.125
PO ₄ ³⁻	0.3	2	0.05
SO ₄ ²⁻	200	3	0.075
		Σw _i = 40	ΣW _i = 1

Each chemical parameter in BIS (2009) desirable limit are expressed in mg/L except for conductivity (mS/cm) and pH

Table 24 Computed values of %Na, SAR, PI, MH and WQI in Nalhati- I Block

Sample No.	PRM					Sample No.	POM				
	%Na	SAR	PI	MH	WQI		%Na	SAR	PI	MH	WQI
N _{pr} 1	25.41	1.82	37.2	80.77	242.52	N _{po} 1	24.36	1.72	35.7	80.31	236.59
N _{pr} 2	34.93	1.22	66.92	29.04	116.12	N _{po} 2	33.06	1.14	64.3	28.44	111.92
N _{pr} 3	28.82	2.55	41.23	81.23	206.04	N _{po} 3	27.81	2.41	39.64	80.77	202.33
N _{pr} 4	31.11	2.69	51.61	78.58	198.4	N _{po} 4	30.17	2.54	49.87	78.06	195.19
N _{pr} 5	22.85	1.93	29.17	95.35	201.23	N _{po} 5	21.86	1.82	27.95	95.21	202.9
N _{pr} 6	48.22	2.89	79.86	34.41	133.61	N _{po} 6	46.75	2.71	77.71	33.69	129.27
N _{pr} 7	48.67	3	69.83	45.6	122.36	N _{po} 7	47.21	2.81	67.83	44.93	116.65
N _{pr} 8	15.6	0.82	30.38	64.96	129.56	N _{po} 8	14.91	0.77	28.99	64.29	127.91
N _{pr} 9	29.24	1.25	42.29	52.25	123.1	N _{po} 9	27.94	1.18	40.48	51.5	120.56
N _{pr} 10	60.66	3.71	81.92	33.21	116.36	N _{po} 10	58.74	3.48	79.97	32.55	113.19
N _{pr} 11	49.11	2.51	85.69	31.44	73.77	N _{po} 11	48.02	2.36	84.83	31.4	72.25
N _{pr} 12	35.97	2.29	45.29	22.44	126.13	N _{po} 12	34.33	2.16	43.79	22.47	125.53
N _{pr} 13	35.3	2.26	48.24	27.31	140.3	N _{po} 13	33.68	2.13	46.8	27.33	137.51
N _{pr} 14	24.47	0.98	50.7	49.44	82.25	N _{po} 14	23.22	0.92	49.55	49.47	81.63
N _{pr} 15	20.84	1.24	30.49	75.68	122.53	N _{po} 15	19.7	1.16	29.37	75.7	126.11
N _{pr} 16	19.72	0.91	39.62	64.32	132.71	N _{po} 16	18.7	0.85	38.55	64.33	131.85
N _{pr} 17	29.18	0.99	65.66	20.3	92.10	N _{po} 17	27.79	0.93	64.65	20.21	94.81
N _{pr} 18	36.14	1.56	61.21	34.72	110.25	N _{po} 18	34.59	1.47	59.93	34.79	110.11
N _{pr} 19	21.56	1.59	28.19	80.59	163.15	N _{po} 19	20.45	1.5	27.01	80.6	163.21
N _{pr} 20	19.71	0.91	34.76	37.27	98.35	N _{po} 20	18.69	0.86	33.59	37.3	98.3
N _{pr} 21	11.74	0.32	34.69	36.37	74.32	N _{po} 21	11.08	0.3	33.55	35.43	74.5
N _{pr} 22	54.56	2.29	76.88	61.02	109.42	N _{po} 22	52.42	2.11	75.34	60.04	109.49
N _{pr} 23	42.99	2.05	61.6	34	69.61	N _{po} 23	40.91	1.9	59.59	33.09	69.19
N _{pr} 24	35.95	1.31	76.64	62.44	59.36	N _{po} 24	33.82	1.2	75.03	61.52	59.09
N _{pr} 25	31.22	1.17	64.1	75.78	98.38	N _{po} 25	29.39	1.08	62.72	75.09	99.92
N _{pr} 26	29.6	1.3	52.77	47.72	77.16	N _{po} 26	28.04	1.21	51.02	46.77	76.64
N _{pr} 27	31.98	1.21	81.95	47.68	86.72	N _{po} 27	30.39	1.13	80.27	46.6	84.92
N _{pr} 28	36.83	1.26	70.5	24.05	64.01	N _{po} 28	34.93	1.17	68.37	23.43	63.81
N _{pr} 29	47.23	1.94	84.18	38.97	74.63	N _{po} 29	45.07	1.79	82.51	37.94	72.63
N _{pr} 30	31.71	1.33	59.87	70.74	82.99	N _{po} 30	29.92	1.22	58.32	69.88	81.82

Table 25 Computed values of %Na, SAR, PI, MH and WQI in Rampurhat-II Block

Sample No.	PRM					Sample No.	POM				
	%Na	SAR	PI	MH	WQI		%Na	SAR	PI	MH	WQI
R _{pr} 1	44.1	2.25	99.05	23.95	84.04	R _{po} 1	43.17	2.1	97.12	23.3	81.09
R _{pr} 2	57.78	5.25	131.0	29.65	95.98	R _{po} 2	57.41	4.92	130.7	28.91	91.83
R _{pr} 3	72.59	7.34	103.1	8.19	109.2	R _{po} 3	71.62	6.85	102.1	7.88	103.7
R _{pr} 4	66.41	9.07	103.4	71.34	155.9	R _{po} 4	65.99	8.55	102.9	70.76	148.5
R _{pr} 5	74.24	11.03	108.6	55.66	140.1	R _{po} 5	73.83	10.34	108.3	55.15	133.3
R _{pr} 6	75.96	8.62	111.0	24.31	114.1	R _{po} 6	75.35	8.06	110.5	23.58	108.9
R _{pr} 7	43.17	2.82	74.06	35.35	97.33	R _{po} 7	42.16	2.64	72.03	34.72	94.47
R _{pr} 8	59.23	5.05	107.0	13.37	99.75	R _{po} 8	58.6	4.72	105.9	12.95	96.28
R _{pr} 9	49.63	2.07	95.35	23.25	66.02	R _{po} 9	48.12	1.94	93.14	22.57	64.04
R _{pr} 10	40.87	2.11	86.07	18.54	89.49	R _{po} 10	39.71	1.97	83.72	17.97	86.1
R _{pr} 11	42.84	2.82	90.44	20.06	132	R _{po} 11	42.09	2.66	89.66	20.09	113.2
R _{pr} 12	37.05	2.3	63.08	41.16	127.1	R _{po} 12	35.94	2.16	61.69	41.18	137.8
R _{pr} 13	58.09	4.24	89.77	28.01	118.7	R _{po} 13	57.04	3.99	89.04	27.88	129.4
R _{pr} 14	72.83	6.18	103.2	71.25	124.4	R _{po} 14	71.61	5.8	103.0	71.25	105.6
R _{pr} 15	62.83	5.07	87.42	78.25	129.3	R _{po} 15	61.45	4.77	86.62	78.29	118.4
R _{pr} 16	66.12	6.53	110.2	55.75	139.9	R _{po} 16	65.09	6.13	110.4	55.9	133.4
R _{pr} 17	39.77	2.2	67.75	41.2	102.0	R _{po} 17	38.38	2.07	66.42	41.2	124.1
R _{pr} 18	24.74	1.11	43.6	46.72	83.57	R _{po} 18	23.54	1.04	42.34	46.74	105.7
R _{pr} 19	58.12	4.96	78.5	52.75	126.9	R _{po} 19	56.74	4.67	77.4	52.74	128.9
R _{pr} 20	48.54	2.7	67.36	27.07	82.03	R _{po} 20	46.94	2.54	66.04	27.07	83.13
R _{pr} 21	77.72	7.4	113.9	16.02	199.1	R _{po} 21	76.66	6.93	113.6	15.54	174.5
R _{pr} 22	91.13	7.72	139.0	61.11	126.4	R _{po} 22	90.35	7.11	141.0	60.05	108.8
R _{pr} 23	65.74	3.88	134.0	83.61	145.8	R _{po} 23	64.38	3.61	135.0	82.93	128.7
R _{pr} 24	69.95	6.03	107.2	69.45	79.35	R _{po} 24	68.81	5.62	107.2	68.95	72.83
R _{pr} 25	44.61	3.11	68.55	93.58	207.8	R _{po} 25	42.98	2.89	67.3	93.36	181.4
R _{pr} 26	78.93	12.47	105.1	92.48	161.1	R _{po} 26	78	11.6	105.4	91.95	143.4
R _{pr} 27	70.81	5.5	99.56	93.09	109.5	R _{po} 27	69.65	5.15	99.37	92.64	101.5
R _{pr} 28	52.93	3.44	77.38	78.58	104.6	R _{po} 28	51.09	3.18	76.1	77.9	94.86
R _{pr} 29	72.17	9.22	111	82.62	135.1	R _{po} 29	71.06	8.55	111.3	82.1	122.2
R _{pr} 30	69.6	10.94	98.32	59.17	190.1	R _{po} 30	68.33	10.12	97.93	58.13	171.8
R _{pr} 31	50.17	1.94	80.09	91.37	68.48	R _{po} 31	48.26	1.79	78.97	90.93	68.54
R _{pr} 32	74.37	7.91	101.0	94.77	169.8	R _{po} 32	73.38	7.41	101.1	94.73	164.7
R _{pr} 33	66.03	8.31	84.74	83.9	226.6	R _{po} 33	64.7	7.74	83.81	83.42	218.6
R _{pr} 34	69.32	6.39	90.93	77.49	160.9	R _{po} 34	67.88	5.93	90.17	76.8	155.4
R _{pr} 35	59.46	4.66	74.62	83.03	145.9	R _{po} 35	57.82	4.33	73.26	82.4	141.7
R _{pr} 36	47	2.42	64.76	34.94	86.09	R _{po} 36	44.74	2.22	62.55	33.99	85.85
R _{pr} 37	44.84	2.67	62.48	77.53	120.6	R _{po} 37	43.26	2.49	60.96	76.82	119.3
R _{pr} 38	53.46	2.27	71.59	93.99	69.03	R _{po} 38	52.06	2.13	70.49	93.6	68.77
R _{pr} 39	50.53	2.42	70.86	81.16	84.48	R _{po} 39	48.79	2.24	69.43	80.63	84.62
R _{pr} 40	44.6	2.04	63.95	84.31	74.01	R _{po} 40	43.03	1.91	62.56	83.88	71.31

Table 26 Computed values of %Na, SAR, PI, MH and WQI in Khoyrasol block

Sample No.	PRM					Sample No.	POM				
	%Na	SAR	PI	MH	WQI		%Na	SAR	PI	MH	WQI
K _{pr} 1	40.88	1.94	52.22	23.24	65.04	K _{po} 1	38.9	1.76	50.84	24.73	61.18
K _{pr} 2	40.11	1.51	59.23	49.77	39.81	K _{po} 2	37.76	1.36	57.55	51.8	37.89
K _{pr} 3	44.45	1.73	66.17	32.97	50.7	K _{po} 3	42.35	1.57	65.21	34.83	47.73
K _{pr} 4	76.35	4.66	95.66	69.74	59.2	K _{po} 4	74.15	4.16	95.12	71.17	55.42
K _{pr} 5	44.55	1.73	62.03	32.97	65.53	K _{po} 5	42.44	1.57	60.73	34.83	61.48
K _{pr} 6	35.39	2.2	42	52.32	125.59	K _{po} 6	33.01	1.98	39.84	54.3	118.87
K _{pr} 7	40.91	2.84	46.69	53.47	100.86	K _{po} 7	38.36	2.56	44.36	55.48	95.63
K _{pr} 8	31.99	2.23	37.44	51.58	126.08	K _{po} 8	29.74	2.01	35.37	53.58	118.57
K _{pr} 9	51.21	2.54	78.23	66.37	65.63	K _{po} 9	48.33	2.27	76.69	68.1	61.79
K _{pr} 10	34.02	2.45	37.99	56.2	106.77	K _{po} 10	31.62	2.2	35.71	58.15	102.02
K _{pr} 11	38.05	2.88	42.65	55.72	112.04	K _{po} 11	35.2	2.57	39.86	55.73	107.84
K _{pr} 12	31.95	2.31	36.09	45.42	129.29	K _{po} 12	29.34	2.06	33.57	45.43	120.31
K _{pr} 13	39.1	3.29	48.37	45.07	149.58	K _{po} 13	36.01	2.93	45.55	45.04	138.47
K _{pr} 14	40.78	3.31	49.99	36.36	115.24	K _{po} 14	37.66	2.95	47.2	36.34	111.4
K _{pr} 15	32.89	2.41	37.03	41.07	124.8	K _{po} 15	33.51	2.51	37.64	41.1	122.81
K _{pr} 16	34.8	1.72	44.79	22.29	105.18	K _{po} 16	34.52	1.72	44.58	22.37	101.62
K _{pr} 17	37.95	1.46	59.79	30.6	100.63	K _{po} 17	37.65	1.47	59.62	30.7	85.58
K _{pr} 18	27.37	1.14	41.15	59.86	89.12	K _{po} 18	27.16	1.14	40.97	59.9	80.7
K _{pr} 19	36.81	2.04	45.5	24.81	97.08	K _{po} 19	36.55	2.04	45.32	24.77	88.16
K _{pr} 20	19.93	0.94	28.18	28.38	130.35	K _{po} 20	19.74	0.94	28.03	28.42	123.9
K _{pr} 21	56.29	3.51	67.04	31.64	98.82	K _{po} 21	56.55	3.56	67.48	32.78	82.74
K _{pr} 22	53.98	3.81	61.06	66.55	102.5	K _{po} 22	53.78	3.82	60.93	67.7	95.82
K _{pr} 23	54.47	3.7	62.52	88.2	92.32	K _{po} 23	54	3.69	62.1	88.74	78.81
K _{pr} 24	35.77	1.84	45.08	26.58	87.99	K _{po} 24	36.07	1.86	45.57	27.58	73.09
K _{pr} 25	52.68	3.82	61.78	74.78	97.31	K _{po} 25	52.32	3.82	61.53	75.8	91.51
K _{pr} 26	63.82	5.03	71.09	23.26	68.72	K _{po} 26	64.13	5.11	71.57	24.17	63.47
K _{pr} 27	57.94	5.66	80.86	49.81	90.56	K _{po} 27	57.4	5.7	81	51.07	84.43
K _{pr} 28	67.24	7.32	86.33	32.97	99.22	K _{po} 28	66.84	7.4	86.54	34.29	87.24
K _{pr} 29	84.21	9.71	97.43	69.79	91.76	K _{po} 29	84.11	9.72	97.37	70.83	80.85
K _{pr} 30	73.81	6.24	82.66	32.97	83.26	K _{po} 30	73.98	6.31	82.9	34.29	71.46
K _{pr} 31	23.63	1.23	30.56	52.31	111.28	K _{po} 31	23.67	1.24	30.64	53.64	119.43
K _{pr} 32	14.65	0.72	22.31	53.47	88.06	K _{po} 32	14.65	0.72	22.35	54.78	93.18
K _{pr} 33	12.18	0.67	18.78	51.57	102.2	K _{po} 33	12.21	0.68	18.85	52.92	96.45
K _{pr} 34	53.76	2.85	78.9	66.46	103.76	K _{po} 34	53.59	2.86	78.76	67.61	93.79
K _{pr} 35	12.21	0.67	16.98	56.18	114.33	K _{po} 35	12.22	0.68	17.01	57.5	112.73
K _{pr} 36	28.11	1.83	32.58	55.73	100.46	K _{po} 36	28.11	1.84	32.6	57.04	97.04
K _{pr} 37	30.9	2.24	35.04	45.43	124.81	K _{po} 37	31.01	2.26	35.18	46.77	120.25
K _{pr} 38	34.62	2.37	40.61	45.07	109.61	K _{po} 38	34.74	2.39	40.79	46.43	98.91
K _{pr} 39	41.22	2.99	52.13	36.39	165.41	K _{po} 39	41.48	3.02	52.5	37.65	154.17
K _{pr} 40	27.89	2.24	35.06	41.06	162.4	K _{po} 40	25.09	1.98	31.36	40.17	155.28
K _{pr} 41	49.06	4.01	62.18	22.28	132.8	K _{po} 41	45.64	3.54	57.67	21.67	122.98
K _{pr} 42	66.81	4.92	78.96	30.49	113.09	K _{po} 42	63.33	4.34	75.11	29.66	104.39
K _{pr} 43	57.25	4.32	65.76	59.88	104.37	K _{po} 43	53.55	3.84	61.67	58.93	104
K _{pr} 44	51.59	3.8	58.37	24.83	128.85	K _{po} 44	47.48	3.35	53.82	24.18	112.18
K _{pr} 45	45.03	3.04	50.28	28.37	132.13	K _{po} 45	40.94	2.68	45.86	27.61	125.57
K _{pr} 46	42.16	2.03	55.69	31.63	110.72	K _{po} 46	38.31	1.79	50.81	30.87	102.37
K _{pr} 47	23.06	1	33.76	66.57	101.48	K _{po} 47	20.54	0.88	30.26	65.75	105.56
K _{pr} 48	26.89	1.15	38.44	88.19	103.73	K _{po} 48	24.24	1.03	34.87	87.83	102.72
K _{pr} 49	38.96	2.13	47.59	26.53	74.45	K _{po} 49	35.15	1.88	43.05	25.83	75.3
K _{pr} 50	24.6	1.08	36.16	74.73	90.74	K _{po} 50	22.02	0.96	32.56	74.03	77.86

Table 26 continued

Sample						Sample					
No.	%Na	SAR	PI	MH	WQI	No.	%Na	SAR	PI	MH	WQI
K _{pr} 51	55.69	3.48	64.73	23.23	63.62	K _{po} 51	51.66	3.06	60.17	22.63	69.72
K _{pr} 52	70.68	6	82.42	49.69	52.93	K _{po} 52	67.8	5.31	79.22	48.7	53.41
K _{pr} 53	72.94	5.76	84.27	32.99	57.57	K _{po} 53	70.34	5.2	81.27	32.16	63.14
K _{pr} 54	48.95	4.16	95.55	69.94	119.6	K _{po} 54	47.66	3.77	92.42	69.11	111.88
K _{pr} 55	64.28	6.32	83.5	32.99	89.37	K _{po} 55	62.36	5.71	80.74	32.16	86.82
K _{pr} 56	46.8	3.49	52.52	52.36	103.6	K _{po} 56	43.9	3.19	49.26	52.36	102.28
K _{pr} 57	41.84	2.94	47.79	53.49	91.62	K _{po} 57	39.06	2.68	44.47	53.49	91.54
K _{pr} 58	39.79	3.1	44.87	51.58	114.3	K _{po} 58	37.02	2.83	41.62	51.57	113.16
K _{pr} 59	72.93	6.46	84.44	66.37	91.52	K _{po} 59	70.78	5.9	81.68	66.39	92.71
K _{pr} 60	36.58	2.64	40.03	56.19	102.4	K _{po} 60	33.84	2.41	36.97	56.2	106.76
K _{pr} 61	21.56	1.24	26.47	55.71	108.9	K _{po} 61	19.65	1.13	24	55.72	106.16
K _{pr} 62	12.48	0.69	17.57	45.43	111.2	K _{po} 62	11.24	0.63	15.7	45.41	112.21
K _{pr} 63	17.15	0.87	23.74	45.07	98.43	K _{po} 63	15.58	0.79	21.39	45.04	95.76
K _{pr} 64	30.23	1.78	37.29	36.34	87.82	K _{po} 64	27.19	1.57	33.56	36.33	89.11
K _{pr} 65	13.36	0.75	18.43	41.09	113.4	K _{po} 65	11.71	0.66	16.18	41.11	110.56
K _{pr} 66	49.31	3.09	57.56	22.27	99.04	K _{po} 66	45.67	2.73	53.31	22.23	92.2
K _{pr} 67	68.92	5.81	82.1	30.52	96.16	K _{po} 67	66.1	5.13	78.74	30.51	86.26
K _{pr} 68	54.78	3.79	64.6	59.85	103.3	K _{po} 68	51.14	3.35	60.35	59.85	98.79
K _{pr} 69	28.42	1.82	43.65	24.81	154.1	K _{po} 69	25.88	1.61	39.54	24.83	143.13
K _{pr} 70	43.49	3.44	54	28.36	141.5	K _{po} 70	40.21	3.04	49.89	28.34	132.04
K _{pr} 71	63.82	5.13	72.08	23.26	75.49	K _{po} 71	60.37	4.54	68.27	23.21	73.91
K _{pr} 72	71.18	5.77	80.73	49.8	58.72	K _{po} 72	68.88	5.3	77.89	49.33	51.25
K _{pr} 73	76.66	7.47	85.44	32.97	70.29	K _{po} 73	74.62	6.85	82.98	32.64	71.11
K _{pr} 74	84.29	9.9	95.1	69.79	73.91	K _{po} 74	82.94	9.1	93.37	69.3	76.67
K _{pr} 75	73.87	6.36	86.51	32.97	68.13	K _{po} 75	71.66	5.83	84.15	32.64	61.05
K _{pr} 76	23.65	1.26	28.47	52.3	99.34	K _{po} 76	21.56	1.15	26.07	51.81	96.63
K _{pr} 77	14.64	0.73	22.15	53.47	100.6	K _{po} 77	13.28	0.68	20.2	53	95.03
K _{pr} 78	12.19	0.69	17.88	51.58	111.1	K _{po} 78	11	0.63	16.23	51.1	105.73
K _{pr} 79	53.84	2.91	69.58	66.45	99.89	K _{po} 79	51.1	2.67	66.29	66.03	91.56
K _{pr} 80	12.23	0.69	18.8	56.18	115.3	K _{po} 80	11.04	0.63	17.1	55.71	109.58
K _{pr} 81	28.14	1.87	32.56	55.73	107.8	K _{po} 81	25.86	1.71	29.99	55.27	106.8
K _{pr} 82	30.92	2.29	34.58	45.43	131.9	K _{po} 82	28.03	2.06	31.47	44.96	126.16
K _{pr} 83	34.67	2.42	40.52	45.07	118.9	K _{po} 83	31.66	2.18	37.13	44.6	112.23
K _{pr} 84	23.45	1.33	29.64	36.39	92.16	K _{po} 84	21.03	1.19	26.78	35.97	94.68
K _{pr} 85	27.99	2.29	35.66	41.06	164.2	K _{po} 85	25.63	2.06	32.46	40.63	145.62
K _{pr} 86	49.24	4.09	62.05	22.28	137.4	K _{po} 86	47.25	3.74	59.37	22.73	125.22
K _{pr} 87	66.88	5.01	77.29	30.5	115.1	K _{po} 87	64.62	4.57	74.97	31.06	107.55
K _{pr} 88	57.37	4.41	65.23	59.88	116.2	K _{po} 88	55.11	4.05	62.89	59.65	107.15
K _{pr} 89	51.55	3.87	59.53	24.83	129.6	K _{po} 89	49.17	3.56	57.04	24.69	116.17
K _{pr} 90	44.23	3.1	50.67	28.36	138.3	K _{po} 90	41.9	2.85	48.18	28.14	124.02
K _{pr} 91	39.51	1.85	52.27	31.63	92.72	K _{po} 91	37.34	1.7	49.75	31.43	83.3
K _{pr} 92	21.96	0.91	32.85	66.57	82.14	K _{po} 92	20.35	0.84	30.91	66.36	69.33
K _{pr} 93	24.78	1.05	36.42	88.19	101.4	K _{po} 93	23.15	0.97	34.41	88.14	88.42
K _{pr} 94	36.32	1.95	45.14	26.53	82.97	K _{po} 94	34.15	1.79	42.59	26.33	74.63
K _{pr} 95	22.77	0.99	33.31	74.73	91.92	K _{po} 95	21.2	0.91	31.24	74.52	89.11
K _{pr} 96	48.39	2.87	58.35	62.21	70.55	K _{po} 96	46.13	2.64	55.8	61.92	69.55
K _{pr} 97	59.88	4.21	69.26	23.26	66.64	K _{po} 97	57.62	3.86	66.78	23.08	62.36
K _{pr} 98	68.8	4.99	79.42	49.81	61.84	K _{po} 98	66.91	4.59	77.37	49.61	61.85
K _{pr} 99	53.56	2.82	72.34	32.98	69.1	K _{po} 99	51.7	2.59	69.83	32.67	69.78
K _{pr} 100	81.53	7.81	94.5	69.8	59.4	K _{po} 100	80.38	7.18	93.38	69.54	60.57

Table 27 Computed values of %Na, SAR, PI, MH and WQI in Mahammad Bazar block

Sample No.	PRM					Sample No.	POM				
	%Na	SAR	PI	MH	WQI		%Na	SAR	PI	MH	WQI
M _{pr} 1	61.64	6.54	87.45	33	116.96	M _{po} 1	59.79	5.93	86.8	34.84	112.6
M _{pr} 2	36.95	2.76	45.13	52.32	117.3	M _{po} 2	34.65	2.48	42.76	54.29	105.79
M _{pr} 3	44.28	3.29	49.85	53.48	93.61	M _{po} 3	41.66	2.96	47.45	55.47	90.09
M _{pr} 4	37.32	2.78	41.4	51.56	90.26	M _{po} 4	34.88	2.5	39.15	53.57	86.88
M _{pr} 5	67.81	5.12	79.18	66.46	84.4	M _{po} 5	65.26	4.58	77.35	68.17	80.26
M _{pr} 6	18.63	1.09	24.49	56.16	93.37	M _{po} 6	17.02	0.98	22.98	58.13	89.55
M _{pr} 7	12.9	0.68	18.1	55.72	87.32	M _{po} 7	11.73	0.61	17	57.68	84.35
M _{pr} 8	12.19	0.69	16.64	45.42	107.22	M _{po} 8	11.15	0.62	15.69	47.41	101.34
M _{pr} 9	27.04	1.59	32.94	45.04	85.18	M _{po} 9	25.1	1.43	31.18	47.03	81.8
M _{pr} 10	16.24	0.81	23.09	36.39	100.17	M _{po} 10	15.03	0.74	22.07	38.25	95.64
M _{pr} 11	26.16	1.79	31.74	41.07	102.26	M _{po} 11	23.85	1.6	29.49	41.08	98.52
M _{pr} 12	53.64	3.74	61.11	22.29	93.33	M _{po} 12	50.62	3.33	58.37	22.34	89.72
M _{pr} 13	53.86	4.84	77.59	30.41	108.09	M _{po} 13	50.26	4.31	75.61	30.51	108.86
M _{pr} 14	31.3	1.86	48.43	59.88	90.57	M _{po} 14	28.5	1.66	46.06	59.85	96.28
M _{pr} 15	49.23	3.41	56.89	24.86	80.78	M _{po} 15	49.92	3.54	57.53	24.81	79.41
M _{pr} 16	49.32	3.56	54.7	28.36	67.34	M _{po} 16	49.09	3.56	54.5	28.32	66.89
M _{pr} 17	61.6	4.39	70.44	31.62	65.54	M _{po} 17	61.26	4.39	70.19	31.7	66.13
M _{pr} 18	57.42	4.42	64.38	66.57	73.95	M _{po} 18	57.14	4.42	64.18	66.61	73.78
M _{pr} 19	59.99	4.62	66.97	88.19	88	M _{po} 19	59.73	4.62	66.79	88.18	87.12
M _{pr} 20	53.03	3.72	60	26.54	67.8	M _{po} 20	52.74	3.72	59.77	26.5	67.83
M _{pr} 21	37.42	1.64	49.39	25.68	57.04	M _{po} 21	37.73	1.66	50	26.64	56.93
M _{pr} 22	35.97	1.25	55.63	53.17	36.58	M _{po} 22	35.91	1.26	55.85	54.47	38.85
M _{pr} 23	40.64	1.45	63.61	36.14	48.99	M _{po} 23	40.74	1.47	64.01	37.44	49.18
M _{pr} 24	72.41	3.82	93.99	72.35	48.77	M _{po} 24	72.22	3.82	93.84	73.36	48.65
M _{pr} 25	40.73	1.45	59.07	36.14	60.51	M _{po} 25	40.83	1.47	59.43	37.44	60.7
M _{pr} 26	31.29	1.83	38.06	55.55	79.33	M _{po} 26	31.26	1.83	38.08	56.84	78.58
M _{pr} 27	36.49	2.35	42.45	56.71	91.6	M _{po} 27	36.43	2.36	42.44	58.04	91.2
M _{pr} 28	28.11	1.85	33.67	54.83	87.65	M _{po} 28	28.1	1.86	33.71	56.13	86.97
M _{pr} 29	46.33	2.08	74.76	69.23	46.27	M _{po} 29	46.14	2.09	74.59	70.36	45.98
M _{pr} 30	29.9	2.02	33.93	59.36	86.15	M _{po} 30	29.85	2.03	33.9	60.64	85.64
M _{pr} 31	33.43	2.37	38	56.97	100.63	M _{po} 31	33.4	2.38	37.99	58.27	98.73
M _{pr} 32	27.81	1.9	32.01	46.69	111.09	M _{po} 32	27.89	1.91	32.12	48.04	110.39
M _{pr} 33	34.51	2.71	43.75	46.32	124.56	M _{po} 33	34.6	2.73	43.9	47.68	122.91
M _{pr} 34	36.18	2.73	45.54	37.49	106.72	M _{po} 34	36.38	2.75	45.83	38.78	105.49
M _{pr} 35	31.91	2.32	36.02	42.33	107.06	M _{po} 35	32.07	2.34	36.22	43.63	104.42
M _{pr} 36	33.1	1.6	43.19	23.31	70.07	M _{po} 36	33.49	1.62	43.75	24.21	68.96
M _{pr} 37	36.16	1.36	58.2	31.85	55.5	M _{po} 37	36.39	1.37	58.71	32.99	53.51
M _{pr} 38	25.58	1.05	39.24	61.12	52.85	M _{po} 38	25.47	1.05	39.17	62.41	51.84
M _{pr} 39	35.1	1.89	43.89	25.67	61.49	M _{po} 39	35.48	1.92	44.41	26.72	60.67
M _{pr} 40	18.75	0.87	26.96	29.49	71.85	M _{po} 40	16.36	0.77	23.68	28.71	70.6
M _{pr} 41	54.87	3.29	65.96	33.98	64.83	M _{po} 41	50.96	2.91	61.43	33.17	62.98
M _{pr} 42	51.67	3.51	58.82	68.75	79.51	M _{po} 42	47.95	3.11	54.71	67.95	77.15
M _{pr} 43	51.69	3.37	59.75	89.23	62.7	M _{po} 43	48.18	3	55.81	88.82	61.86
M _{pr} 44	34.58	1.73	44.1	28.55	62.31	M _{po} 44	31.03	1.53	39.69	27.79	62.24
M _{pr} 45	50.22	3.5	59.32	76.7	80.44	M _{po} 45	46.75	3.12	55.31	76.01	79.25
M _{pr} 46	62.71	4.74	70.26	25.09	65.31	M _{po} 46	58.88	4.18	66.09	24.34	65.06
M _{pr} 47	56.14	5.25	79.61	52.38	87.33	M _{po} 47	53.73	4.65	76.16	51.45	86.41
M _{pr} 48	65.77	6.84	85.58	35.53	91.24	M _{po} 48	63.32	6.04	82.52	34.73	88.88
M _{pr} 49	83.06	8.91	96.76	71.96	66.91	M _{po} 49	81.11	7.91	94.85	71.28	66.26
M _{pr} 50	72.65	5.83	81.79	35.53	63.07	M _{po} 50	69.54	5.14	78.46	34.73	61.56

Table 28 Percent sample with different water category according to WQI in the four blocks during PRM and POM

WQI Value	Water Quality	Nalhati-I		Rampurhat-II		Khoyrasol		Mahammad Bazar	
		PRM	POM	PRM	POM	PRM	POM	PRM	POM
<50	Excellent	0	0	0	0	1	2	8	0
50-100	Good	43.33	43.33	35	35	46	55	70	56
100-200	Poor	46.67	46.67	60	62.5	53	43	22	38
200-300	Very poor	10	10	5	2.5	0	0	0	6
>300	Unsuitable for drinking	0	0	0	0	0	0	0	0

Values are expressed in percentage (%)

Table 29 Biochemical constituents in different vegetable plants collected from Nalhati-I block

Name of vegetables	Sugar	Chlorophyll		Ascorbic acid	Protein	Amino acid
		Chl a	Chl b			
Cabbage (<i>Brassica oleracea</i>) leaf	534.65±2.35	0.095±0.020	0.279±0.003	0.513±0.014	0.245±0.011	546.17±3.62
Onion (<i>Allium cepa</i>) leaf	712.53±4.32	0.049±0.009	0.285±0.005	0.422±0.016	0.226±0.012	193.90±1.52
Spinach (<i>Spinacia oleracea</i>) leaf	745.27±1.28	0.186±0.030	0.551±0.017	0.845±0.021	0.16±0.010	891.02±6.12
Radish (<i>Raphanus sativus</i>) leaf	552.62±4.12	0.239±0.008	0.156±0.007	0.832±0.024	0.06±0.005	490.25±1.25
Potato (<i>Solanum tuberosum</i>) leaf	868.80±7.97	0.136±0.011	0.241±0.008	0.393±0.011	0.191±0.008	409.89±3.46
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	577.16±5.22	0.215±0.006	0.298±0.010	0.575±0.019	0.172±0.006	760.69±5.62
Papaya (<i>Carica papaya</i>) fruit	151.15±1.62	0.100±0.002	0.25±0.009	0.428±0.011	0.950±0.026	770.99±3.92
Squash (<i>Cucurbita maxima</i>) fruit	862.65±2.15	0.082±0.008	0.13±0.005	0.3±0.010	0.206±0.012	401.49±2.76
Brinjal (<i>Solanum melongena</i>) fruit	162.59±1.52	0.184±0.006	0.549±0.012	0.903±0.045	0.336±0.016	297.11±1.87
Seem (<i>Dolichos lablob</i>) fruit	552.09±3.54	0.230±0.010	0.156±0.011	0.555±0.023	0.262±0.008	305.40±2.35
Korola (<i>Momordica charantia</i>) fruit	98.57±1.82	0.135±0.005	0.238±0.010	0.354±0.018	0.063±0.006	488.30±2.27

All the biochemical constituents are represented as mean ± standard deviation (n=3) and measured in terms of mg/100g of vegetable sample

Table 30 Biochemical constituents in different vegetable plants collected from Rampurhat-II block

Name of vegetables	Sugar	Chlorophyll		Ascorbic acid	Protein	Amino acid
		Chl a	Chl b			
Cabbage (<i>Brassica oleracea</i>) leaf	566.38±4.07	0.101±0.02	0.245±0.001	0.357±0.013	0.241±0.01	555.41±3.51
Onion (<i>Allium cepa</i>) leaf	703.61±3.36	0.048±0.003	0.280±0.007	0.531±0.03	0.222±0.014	188.67±3.83
Spinach (<i>Spinacia oleracea</i>) leaf	751.84±3.61	0.182±0.009	0.542±0.008	0.888±0.014	0.172±0.008	892.48±7.54
Radish (<i>Raphanus sativus</i>) leaf	554.19±13.85	0.234±0.007	0.154±0.008	0.573±0.007	0.064±0.08	491.82±5.89
Potato (<i>Solanum tuberosum</i>) leaf	883.29±7.25	0.133±0.005	0.235±0.007	0.379±0.003	0.191±0.01	411.26±4.06
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	951.40±19.2	0.210±0.014	0.292±0.018	0.598±0.006	0.158±0.007	739.85±4.9
Papaya (<i>Carica papaya</i>) fruit	148.48±5.24	0.101±0.02	0.245±0.001	0.357±0.013	1.108±0.102	763.17±7.06
Kundri (<i>Coccinia grandis</i>) fruit	307.36±7.89	0.048±0.003	0.280±0.007	0.531±0.03	0.444±0.041	572.37±8.01
Brinjal (<i>Solanum melongena</i>) fruit	152.26±5.70	0.182±0.009	0.542±0.008	0.888±0.014	0.317±0.012	296.79±6.57
Seem (<i>Dolichos lablob</i>) fruit	549.45±7.97	0.234±0.007	0.154±0.008	0.573±0.007	0.254±0.017	301.58±6.83
Korola (<i>Momordica charantia</i>) fruit	96.8±6.78 ^{NS}	0.133±0.005	0.235±0.007	0.379±0.003	0.063±0.007	487.57±7.86

All the biochemical constituents are represented as mean ± standard deviation (n=3) and measured in terms of mg/100g of vegetable sample

Table 31 Biochemical constituents in different vegetable plants collected from Khoyrasol block

Name of vegetables	Sugar	Chlorophyll		Ascorbic acid	Protein	Amino acid
		Chl a	Chl b			
Spinach (<i>Spinacia oleracea</i>) leaf	747.04±7.34	0.190±0.027	0.555±0.014	0.859±0.028	0.163±0.008	891.82±5.32
Radish (<i>Raphanus sativus</i>) leaf	553.68±2.67	0.245±0.022	0.156±0.008	0.844±0.34	0.061±0.005	491.10±1.45
Potato (<i>Solanum tuberosum</i>) leaf	870.69±6.43	0.140±0.009	0.232±0.012	0.403±0.019	0.196±0.010	426.50±2.13
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	976.12±8.25	0.221±0.011	0.315±0.021	0.587±0.022	0.176±0.009	745.80±3.56
Squash (<i>Cucurbita maxima</i>) fruit	864.52±4.36	0.082±0.006	0.131±0.009	0.301±0.016	0.207±0.007	402.30±1.32
Brinjal (<i>Solanum melongena</i>) fruit	162.3±1.28	0.176±0.006	0.551±0.035	0.862±0.043	0.332±0.005	297.54±2.11
Seem (<i>Dolichos lablob</i>) fruit	552.93±3.37	0.231±0.012	0.157±0.009	0.557±0.031	0.261±0.005	306.50±2.51
Korola (<i>Momordica charantia</i>) fruit	98.86±1.85	0.136±0.013	0.239±0.019	0.356±0.027	0.062±0.002	489.28±2.25

All the biochemical constituents are represented as mean ± standard deviation (n=3) and measured in terms of mg/100g of vegetable sample

Table 32 Biochemical constituents in different vegetable plants collected from Mahammad Bazar block

Name of vegetables	Sugar	Chlorophyll			Ascorbic acid	Protein	Amino acid
		Chl <i>a</i>	Chl <i>b</i>	Total Chl			
Spinach (<i>Spinacia oleracea</i>) leaf	756.43±3.56	0.199±0.008	0.574±0.013	0.894±0.035	0.164±0.008	894.03±7.23	0.833±0.029
Radish (<i>Raphanus sativus</i>) leaf	560.37±2.85	0.256±0.012	0.161±0.008	0.878±0.042	0.061±0.004	492.3±2.61	2.840±0.048
Potato (<i>Solanum tuberosum</i>) leaf	881.44±7.21	0.146±0.007	0.26±0.021	0.422±0.018	0.197±0.010	411.62±2.17	1.599±0.011
Papaya (<i>Carica papaya</i>) fruit	154.42±3.27	0.106±0.005	0.264±0.015	0.451±0.029	0.955±0.021	772.32±2.12	6.248±0.033
Squash (<i>Cucurbita maxima</i>) fruit	875.2±6.52	0.086±0.005	0.13±0.009	0.300±0.037	0.218±0.005	403.28±1.57	1.360±0.012
Brinjal (<i>Solanum melongena</i>) fruit	163.64±2.12	0.194±0.011	0.567±0.013	0.934±0.041	0.327±0.013	298.27±1.61	29.408±0.154
Seem (<i>Dolichos lablob</i>) fruit	559.37±1.96	0.243±0.023	0.162±0.007	0.577±0.021	0.229±0.008	307.22±3.19	28.334±0.186
Korola (<i>Momordica charantia</i>) fruit	100.15±1.24	0.143±0.012	0.246±0.011	0.369±0.015	0.061±0.006	490.47±2.54	15.762±0.098

All the biochemical constituents are represented as mean ± standard deviation (n=3) and measured in terms of mg/100g of vegetable sample

Table 33 Biochemical constituents in different vegetable plants collected from control area (Jagdhari)

Name of vegetables	Sugar	Chlorophyll			Ascorbic acid	Protein	Amino acid
		Chl <i>a</i>	Chl <i>b</i>	Total Chl			
Cabbage (<i>Brassica oleracea</i>) leaf	580.2±5.34	0.12±0.006	0.482±0.015	0.810±0.047	0.361±0.005	580.70±4.21	6.53±0.03
Onion (<i>Allium cepa</i>) leaf	728.7±6.28	0.072±0.003	0.33±0.011	0.561±0.025	0.352±0.006	202.60±1.65	4.68±0.02
Spinach (<i>Spinacia oleracea</i>) leaf	771.5±4.63	0.261±0.009	0.63±0.031	1.100±0.011	0.208±0.010	902.50±4.18	1.36±0.01
Radish (<i>Raphanus sativus</i>) leaf	568.2±3.37	0.342±0.012	0.162±0.010	1.040±0.008	0.08±0.005	502.60±2.19	4.35±0.01
Potato (<i>Solanum tuberosum</i>) leaf	896.6±6.51	0.211±0.011	0.381±0.009	0.625±0.033	0.282±0.012	420.50±3.02	2.62±0.01
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>)	962.5±6.95	0.340±0.021	0.39±0.014	0.823±0.048	0.223±0.018	752.90±5.19	2.35±0.02
Papaya (<i>Carica papaya</i>) fruit	164.3±2.13	0.112±0.005	0.325±0.009	0.542±0.012	1.041±0.083	762.30±2.38	6.19±0.03
Kundri (<i>Coccinia grandis</i>) fruit	318.92±2.25	0.05±0.006	0.35±0.012	0.586±0.024	0.315±0.021	430.32±1.26	19.42±0.14
Brinjal (<i>Solanum melongena</i>) fruit	158.53±1.32	0.192±0.013	0.583±0.023	0.921±0.038	0.278±0.015	303.40±1.68	32.3±0.22
Seem (<i>Dolichos lablob</i>) fruit	564.24±2.62	0.248±0.020	0.172±0.008	0.590±0.009	0.243±0.012	321.70±1.29	23.48±0.18
Korola (<i>Momordica charantia</i>) fruit	102.81±1.13	0.153±0.010	0.256±0.005	0.392±0.010	0.056±0.004	502.68±2.51	15.25±0.11
Squash (<i>Cucurbita maxima</i>) fruit	890.25±6.52	0.083±0.009	0.132±0.006	0.305±0.007	0.212±0.010	413.28±2.06	1.35±0.01

All the biochemical constituents are represented as mean ± standard deviation (n=3) and measured in terms of mg/100g of vegetable sample

Table 34 Percent biochemical change with respect to control in different vegetable plants collected from Nalhathi -I block

Name of vegetables	Sugar	Chlorophyll			Ascorbic acid	Protein	Amino acid
		Chl a	Chl b	Total			
Cabbage (<i>Brassica oleracea</i>) leaf	8.52	26.87	72.89	58.05	47.3	6.32	17.86
Onion (<i>Allium cepa</i>) leaf	2.27	46.5	15.97	32.87	55.63	4.49	37.2
Spinach (<i>Spinacia oleracea</i>) leaf	3.52	40.24	14.43	30.18	29.88	1.29	110.71
Radish (<i>Raphanus sativus</i>) leaf	2.82	42.84	3.93	24.93	33.75	2.52	58.1
Potato (<i>Solanum tuberosum</i>) leaf	3.20	54.72	58.02	59.16	47.55	2.59	69.29
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	-1.50	57.81	30.88	43.25	29.43	-1.02	25.09
Papaya (<i>Carica papaya</i>) fruit	8.70	12.35	30.02	26.73	9.56	-1.13	1.13
Squash (<i>Cucurbita maxima</i>) fruit	3.20	1.35	1.21	1.59	2.76	2.94	2.90
Brinjal (<i>Solanum melongena</i>) fruit	-2.50	4.22	6.18	2.03	-17.38	2.12	-8.25
Seem (<i>Dolichos lablob</i>) fruit	2.20	7.68	10.11	6.32	-7.41	5.34	-15.93
Korola (<i>Momordica charantia</i>) fruit	4.30	13.29	7.49	10.76	-10.55	2.95	5.53

All the values are expressed in percentage (%)

Table 35 Percent biochemical change with respect to control in different vegetable plants collected from Rampurhat-II block

Name of vegetables	Sugar	Chlorophyll			Ascorbic acid	Protein	Amino acid
		Chl a	Chl b	Total Chl			
Cabbage (<i>Brassica oleracea</i>) leaf	2.44	18.81	96.73	126.89	49.79	4.55	8.27
Onion (<i>Allium cepa</i>) leaf	3.57	50.00	17.86	5.65	58.56	7.38	32.35
Spinach (<i>Spinacia oleracea</i>) leaf	2.61	43.41	16.24	23.87	20.93	1.12	322.36
Radish (<i>Raphanus sativus</i>) leaf	2.53	46.15	5.19	81.50	25.00	2.19	50.52
Potato (<i>Solanum tuberosum</i>) leaf	1.51	58.65	62.13	64.91	47.64	2.25	103.73
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	1.17	61.9	33.56	37.63	41.14	1.76	21.82
Papaya (<i>Carica papaya</i>) fruit	10.65	10.89	32.65	51.82	-6.05	-0.11	-8.81
Kundri (<i>Coccinia grandis</i>) fruit	3.76	4.17	25.00	10.36	-29.05	-24.82	-13.69
Brinjal (<i>Solanum melongena</i>) fruit	4.12	5.49	7.56	3.72	-12.3	2.23	-8.68
Seem (<i>Dolichos lablob</i>) fruit	2.69	5.98	11.69	2.97	-4.33	6.67	-18.87
Korola (<i>Momordica charantia</i>) fruit	6.21	15.04	8.94	3.43	-11.11	3.10	6.87

All the values are expressed in percentage (%)

Name of vegetables	Chlorophyll				Total	Ascorbic acid	Protein	Amino acid
	Sugar	Chl <i>a</i>	Chl <i>b</i>	Chl				
Spinach (<i>Spinacia oleracea</i>) leaf	3.27	37.37	13.51	28.06	27.61	1.20	102.99	
Radish (<i>Raphanus sativus</i>) leaf	2.62	39.59	3.85	23.22	31.15	2.34	54.04	
Potato (<i>Solanum tuberosum</i>) leaf	2.98	50.71	64.22	55.09	43.88	-1.41	64.47	
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	-1.4	53.85	23.81	40.20	26.70	0.95	23.36	
Squash (<i>Cucurbita maxima</i>) fruit	2.98	1.22	0.76	1.33	2.42	2.73	-2.67	
Brinjal (<i>Solanum melongena</i>) fruit	-2.32	9.09	5.81	6.84	-16.27	1.97	7.67	
Seem (<i>Dolichos lablob</i>) fruit	2.05	7.36	9.55	5.92	-6.90	4.96	-14.81	
Korola (<i>Momordica charantia</i>) fruit	4.00	12.50	7.11	10.11	-9.68	2.74	5.14	

All the values are expressed in percentage (%)

Name of vegetables	Sugar	Chlorophyll		Total Chl	Ascorbic acid	Protein	Amino acid
		Chl <i>a</i>	Chl <i>b</i>				
Spinach (<i>Spinacia oleracea</i>) leaf	1.99	31.16	9.76	23.04	26.83	0.95	63.27
Radish (<i>Raphanus sativus</i>) leaf	1.40	33.59	0.62	18.45	31.15	2.09	53.17
Potato (<i>Solanum tuberosum</i>) leaf	1.72	44.52	46.54	48.10	43.15	2.16	63.85
Papaya (<i>Carica papaya</i>) fruit	6.40	5.66	23.11	20.18	9.01	-1.30	-0.93
Squash (<i>Cucurbita maxima</i>) fruit	1.72	-3.49	1.54	1.67	-2.75	2.48	-0.74
Brinjal (<i>Solanum melongena</i>) fruit	-3.12	-1.03	2.82	-1.39	-14.98	1.72	9.83
Seem (<i>Dolichos lablob</i>) fruit	0.87	2.06	6.17	2.25	6.11	4.71	-17.13
Korola (<i>Momordica charantia</i>) fruit	2.66	6.99	4.07	6.23	-8.20	2.49	-3.25

All the values are expressed in percentage (%)

Table 38 Fluoride concentration levels of different types of vegetable samples and BCF in Nalhati-I block

Vegetable	F ⁻ (mg.Kg ⁻¹)	Mean BCF
Radish (<i>Raphanus sativus</i>) leaf	0.96 ± 0.04	0.86
Potato (<i>Solanum tuberosum</i>) leaf	0.89±0.07	1.3
Spinach (<i>Spinacia oleracea</i>) leaf	1.06±0.09	0.94
Papaya (<i>Carica papaya</i>) leaf	1.19±0.05	1.22
Squash (<i>Cucurbita maxima</i>) fruit	0.79±0.03	0.76
Brinjal (<i>Solanum melongena</i>) fruit	0.61±0.03	0.76
Seem (<i>Dolichos lablob</i>) fruit	0.73±0.03	0.45
Korola (<i>Momordica charantia</i>) fruit	0.4±0.02	0.47

Fluoride concentrations in vegetable samples are represented as mean ± standard deviation (n=3)

Table 39 Fluoride concentration levels of different types of vegetable samples and BCF in Rampurhat-II block

Vegetable	F ⁻ (mg.Kg ⁻¹)	Mean BCF
Cabbage (<i>Brassica oleracea</i>) leaf	1.25± 0.07	1.22
Onion (<i>Allium cepa</i>) leaf	3.19± 0.07	0.92
Radish (<i>Raphanus sativus</i>) leaf	3.21± 0.04	1.4
Potato (<i>Solanum tuberosum</i>) leaf	0.65±0.07	0.23
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	1.11±0.12	1.01
Spinach (<i>Spinacia oleracea</i>) leaf	2.56±0.09	1.31
Papaya (<i>Carica papaya</i>) fruit	0.68±0.05	0.82
Kundri (<i>Coccinia grandis</i>) fruit	0.80±0.03	0.36
Brinjal (<i>Solanum melongena</i>) fruit	1.35±0.03	0.51
Seem (<i>Dolichos lablob</i>) fruit	0.65±0.03	0.62
Korola (<i>Momordica charantia</i>) fruit	0.40±0.03	0.51

Fluoride concentrations in vegetable samples are represented as mean ± standard deviation (n=3)

Table 40 Fluoride concentration levels of different types of vegetable samples and BCF in Khoyrasol block

Vegetable	F ⁻ (mg.Kg ⁻¹)	Mean BCF
Cabbage (<i>Brassica oleracea</i>) leaf	1.22± 0.07	1.13
Radish (<i>Raphanus sativus</i>) leaf	2.94± 0.1	1.26
Potato (<i>Solanum tuberosum</i>) leaf	2.89±0.06	1.3
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) leaf	0.62±0.02	0.85
Spinach (<i>Spinacia oleracea</i>) leaf	1.36±0.09	0.94
Papaya (<i>Carica papaya</i>) fruit	2.39±0.05	1.22
Squash (<i>Cucurbita maxima</i>) fruit	0.79±0.03	0.76
Brinjal (<i>Solanum melongena</i>) fruit	0.61±0.03	0.76
Seem (<i>Dolichos lablob</i>) fruit	0.84±0.03	0.47

Fluoride concentrations in vegetable samples are represented as mean ± standard deviation (n=3)

Table 41 Fluoride concentration levels of different types of vegetable samples and BCF in Mahammad Bazar block

Vegetable	F ⁻ (mg.Kg ⁻¹)	Mean BCF
Radish (<i>Raphanus sativus</i>) leaf	0.94± 0.035	0.96
Potato (<i>Solanum tuberosum</i>) leaf	0.69±0.067	0.89
Spinach (<i>Spinacia oleracea</i>) leaf	1.25±0.090	1.06
Papaya (<i>Carica papaya</i>) fruit	1.19±0.05	0.68
Squash (<i>Cucurbita maxima</i>) fruit	0.76±0.03	0.48
Brinjal (<i>Solanum melongena</i>) fruit	0.61±0.03	0.72
Seem (<i>Dolichos lablob</i>) fruit	0.62±0.01	0.56

Fluoride concentrations in vegetable samples are represented as mean ± standard deviation (n=3)

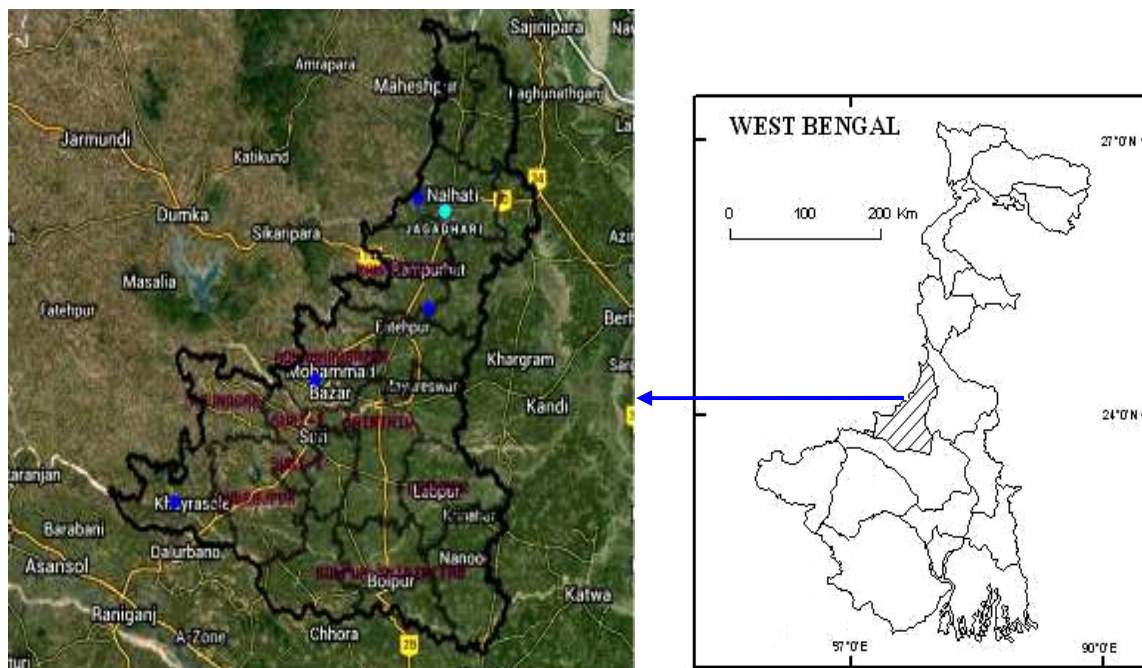
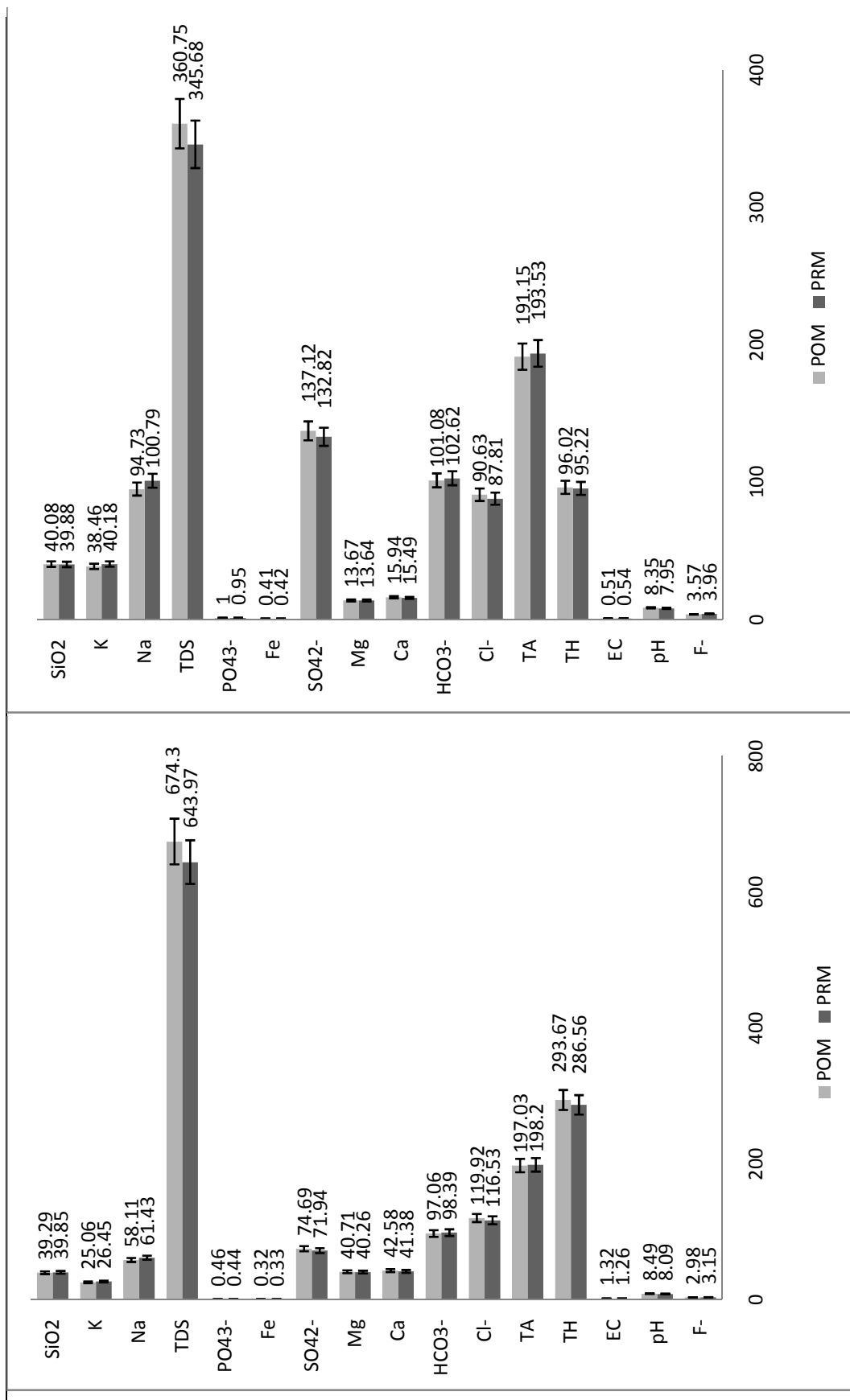


Fig. 1 Birbhum District in West Bengal



Fig. 2 Study locations in Nalhati-I block





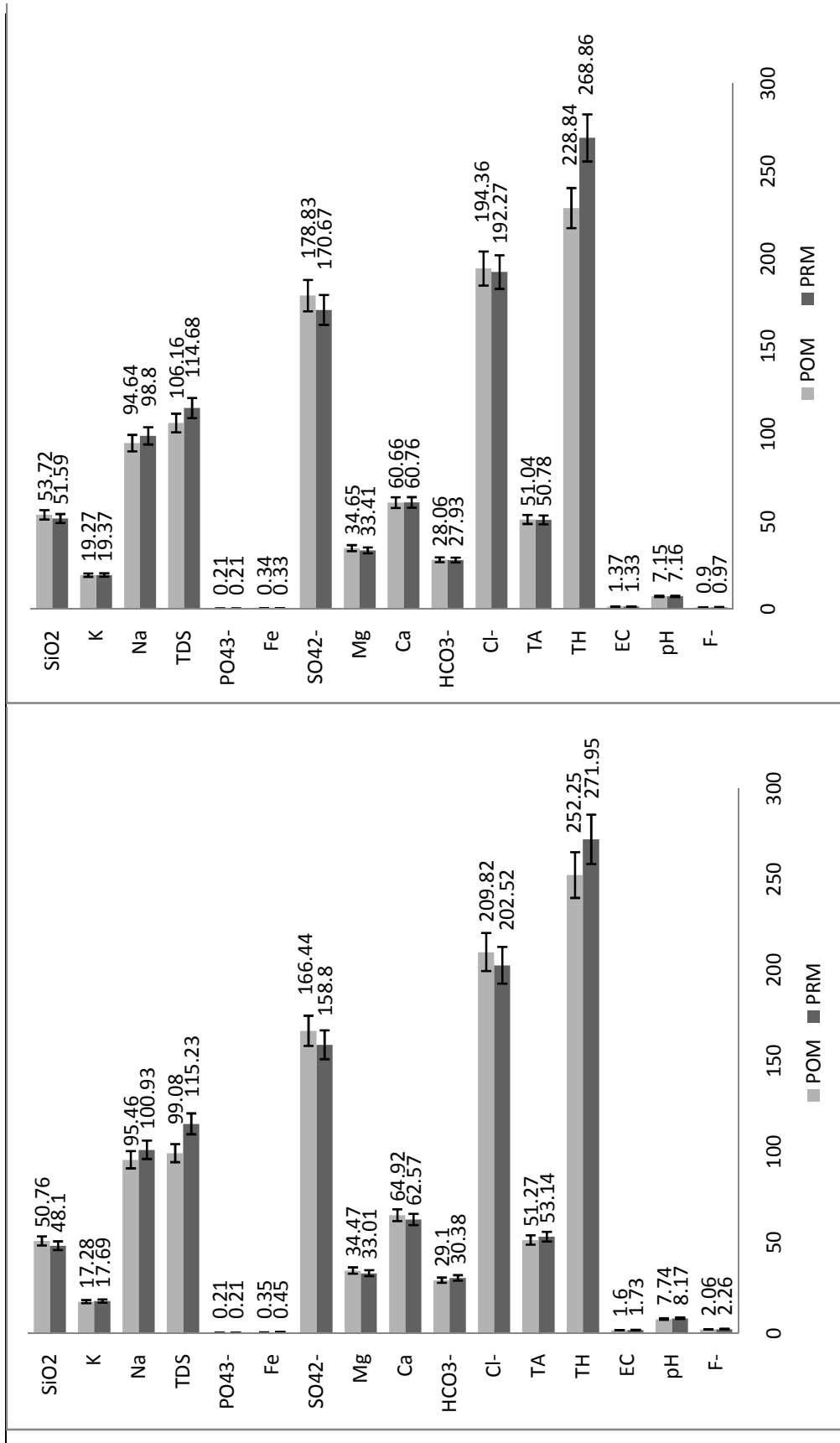


Fig.9 Comparison of water parameters values of Khoyrasol Block in PRM and POM

Fig. 10 Comparison of water parameters values of Bazar Block in PRM and POM

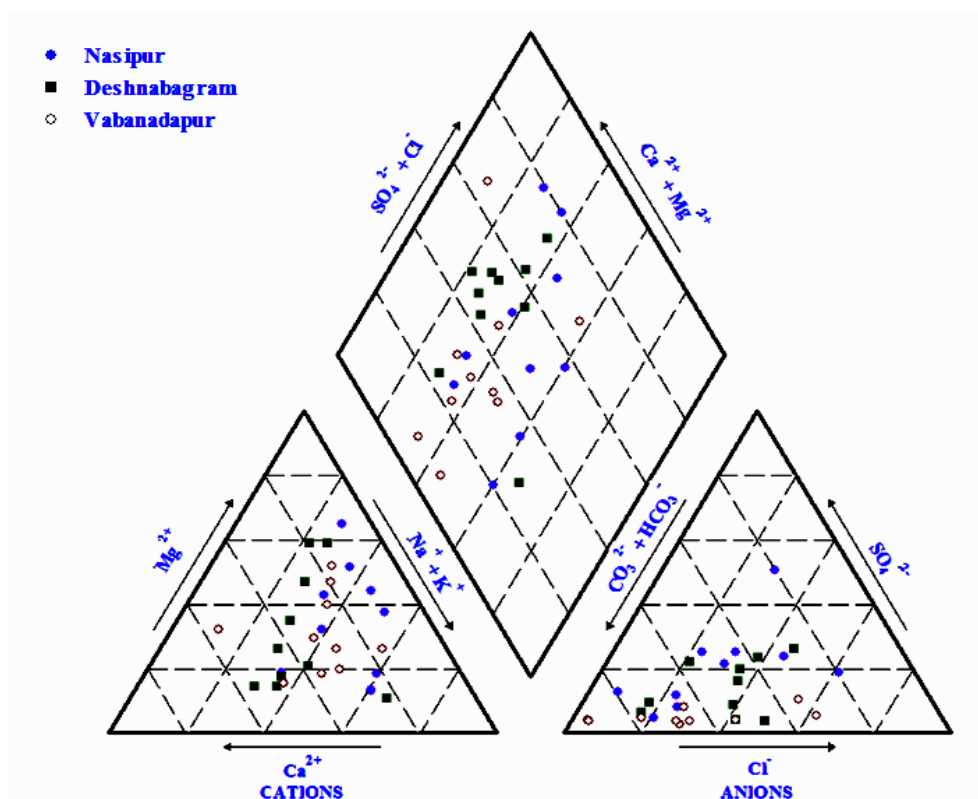


Fig.11 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Nalhati-I in PRM

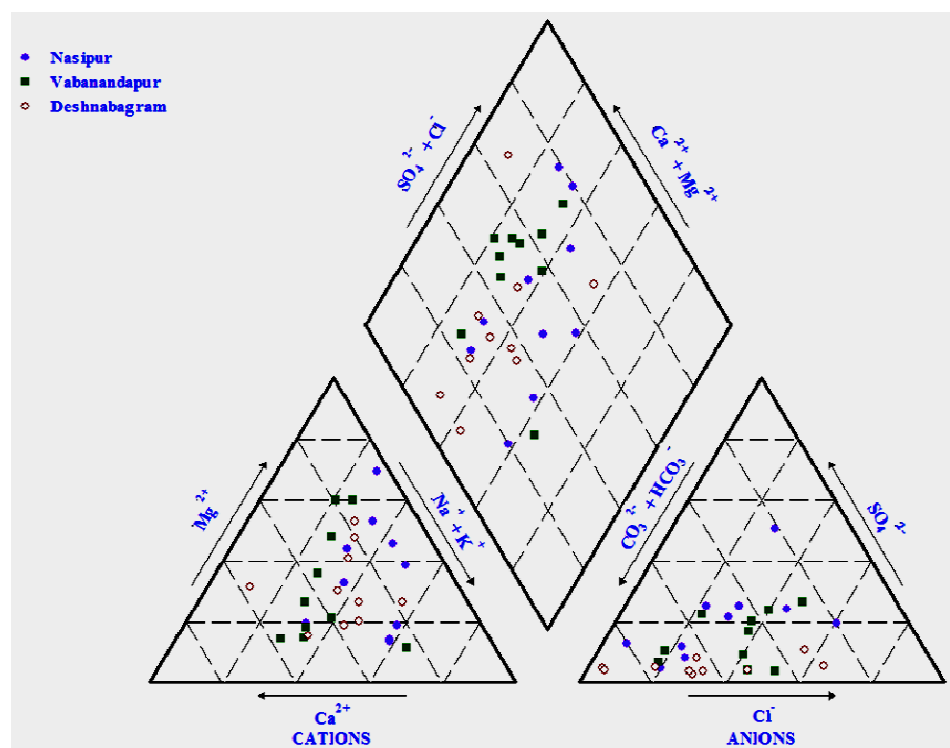


Fig. 12 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Nalhati-I in POM

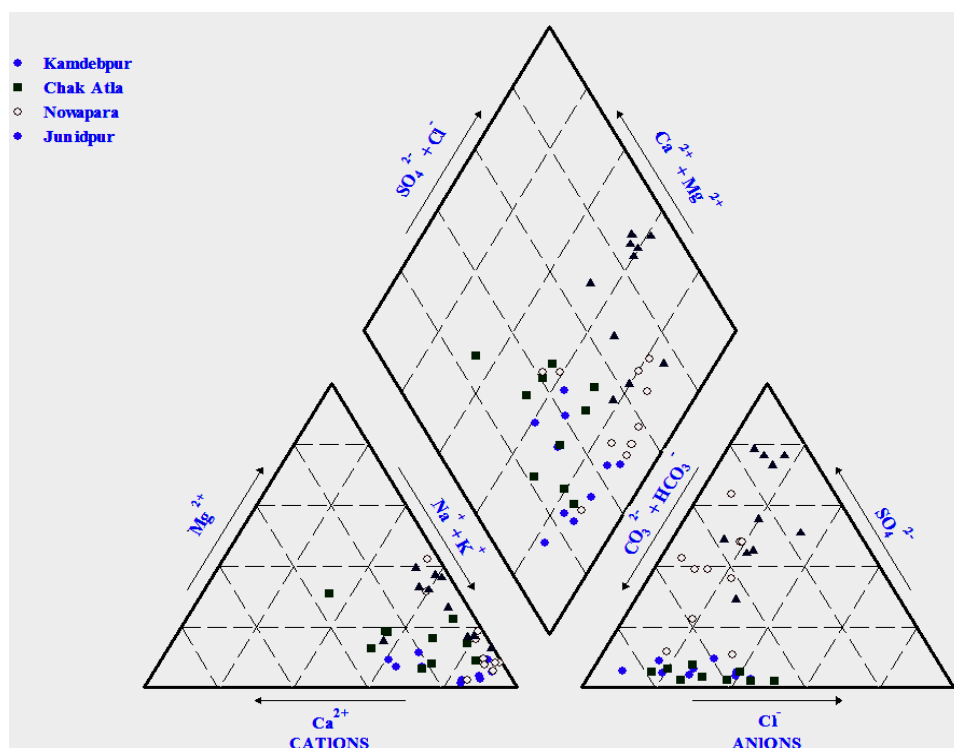


Fig. 13 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Rampurhat-II in PRM

Figures

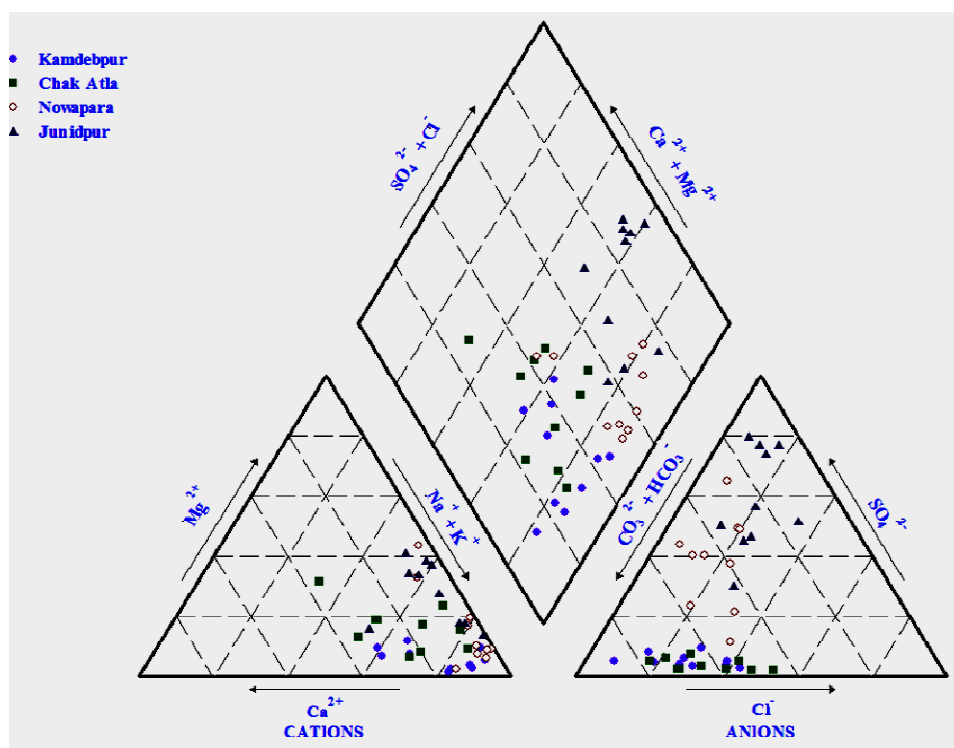


Fig. 14 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Rampurhat-II in POM

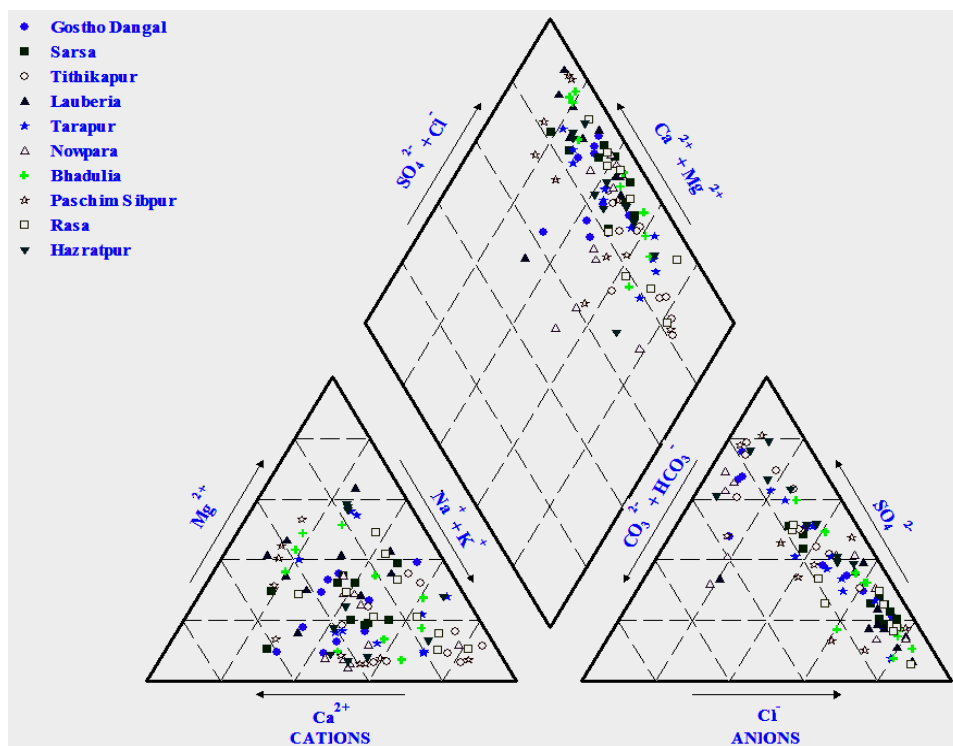


Fig. 15 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Khoyrasol in PRM

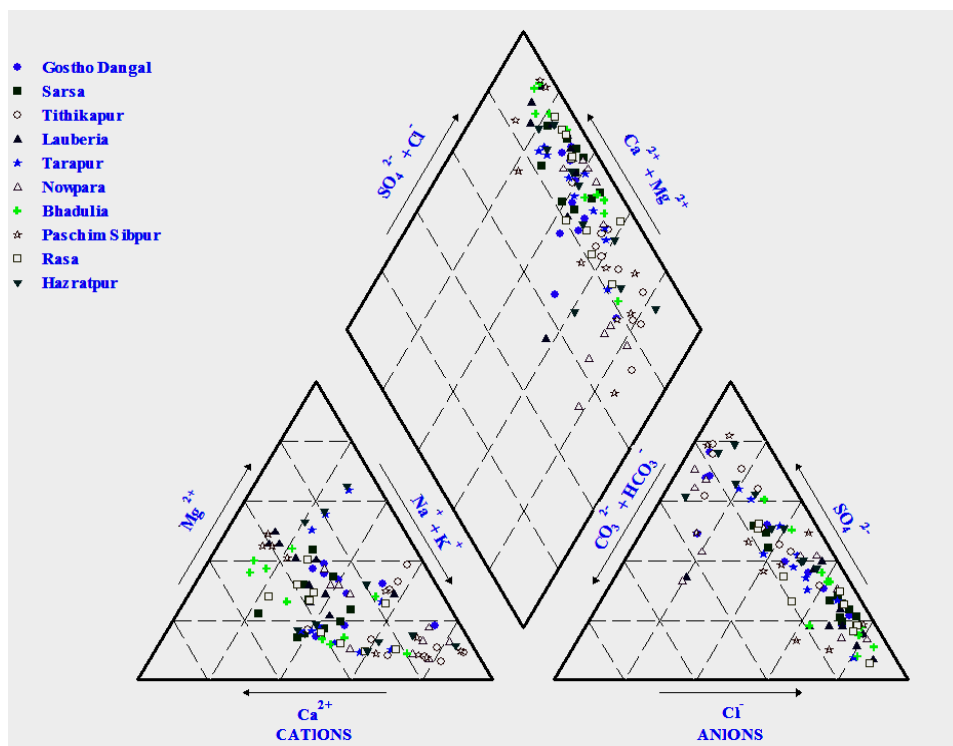


Fig. 16 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Khoyrasol in POM

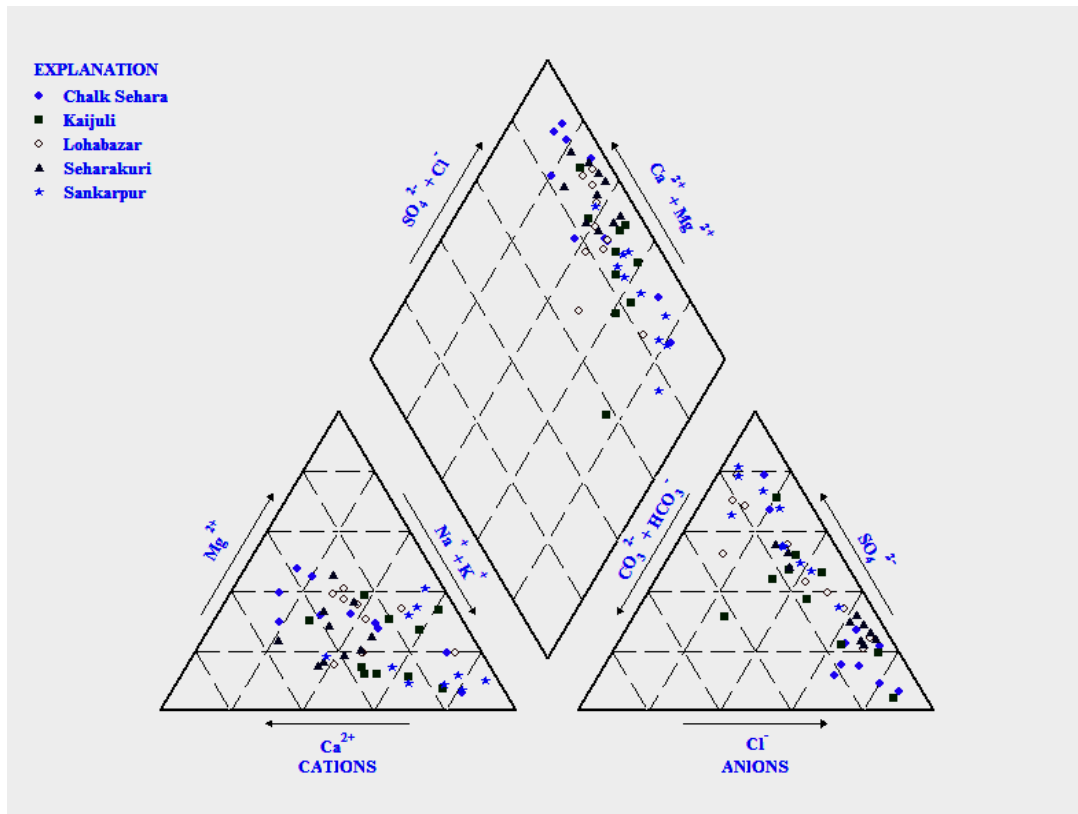


Fig. 17 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Mohammad Bazar in PRM

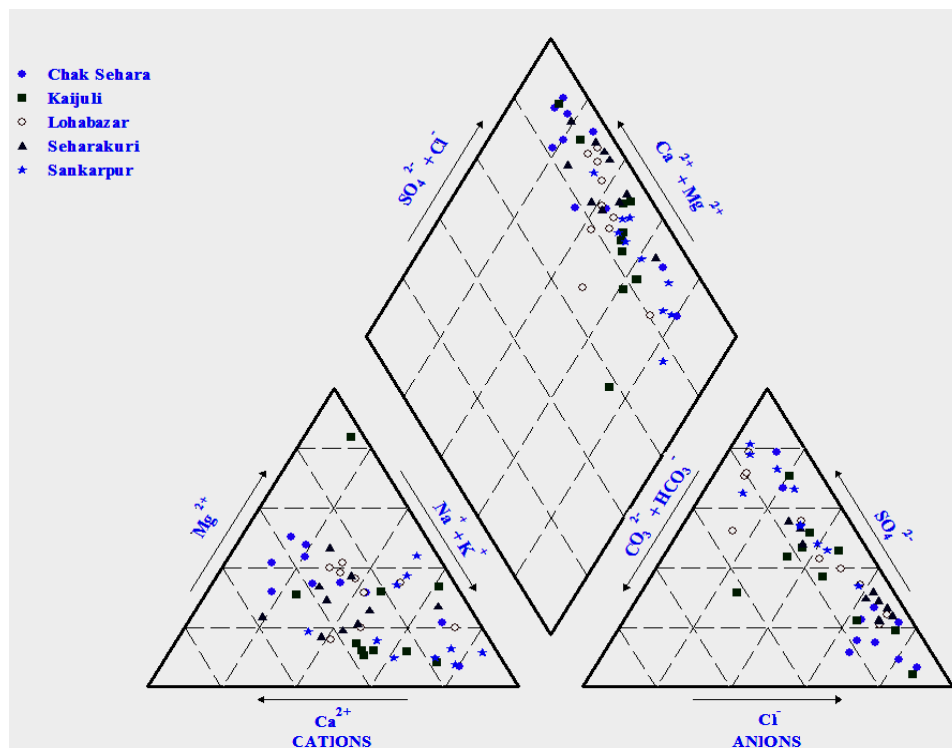


Fig.18 Piper trilinear diagram showing hydrogeochemical facies for groundwater of Mohammad Bazar in POM

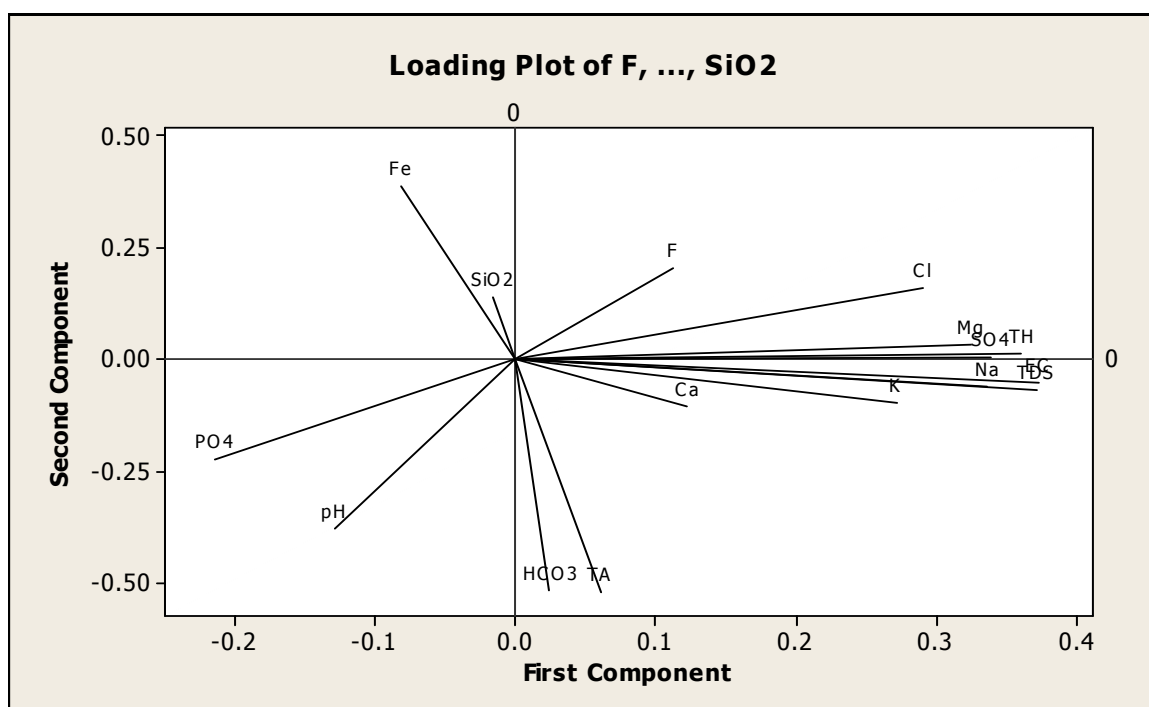


Fig. 19 PCA loading plot of the water parameters in PRM season of Nalhati –I block

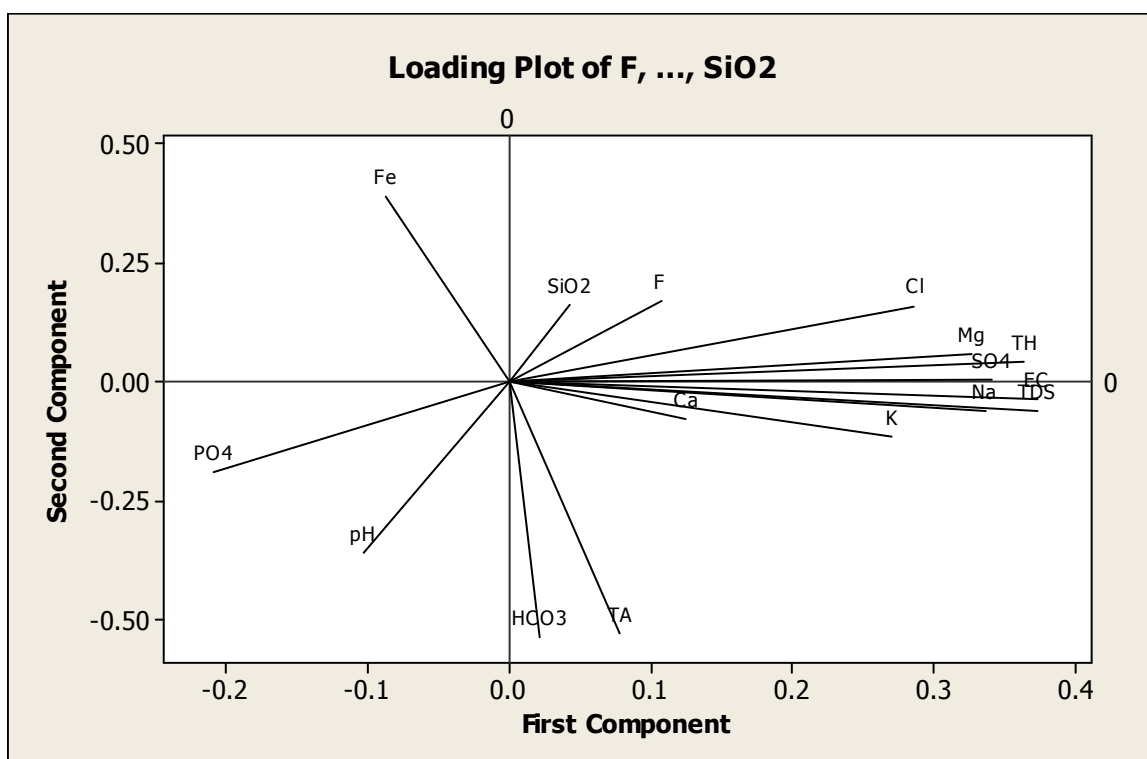


Fig. 20 PCA loading plot of the water parameters in POM season of Nalhati –I block

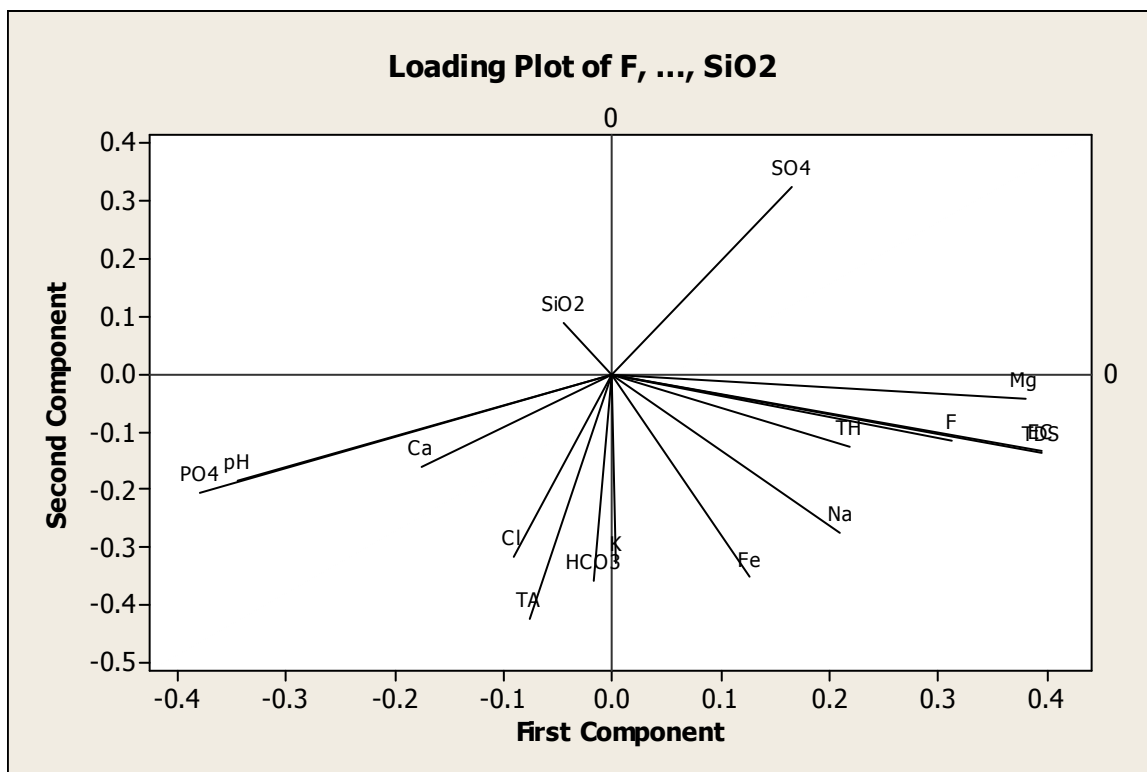


Fig.21 PCA loading plot of the water parameters in PRM season of Rampurhat -II block

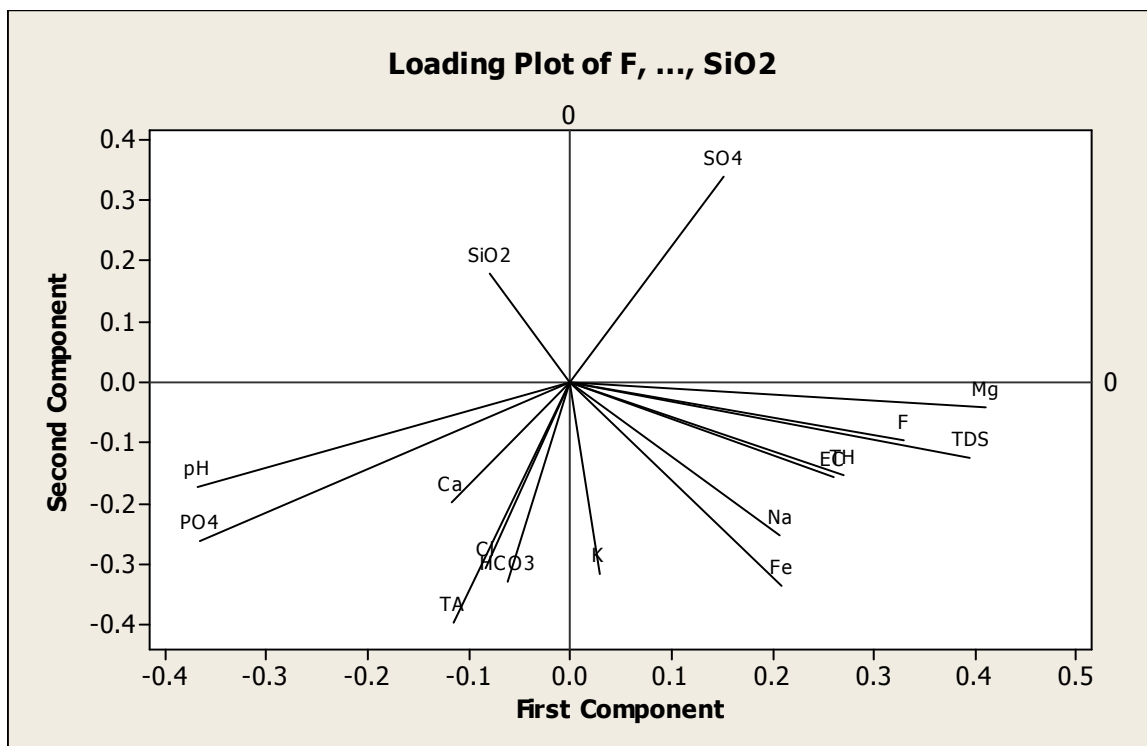


Fig. 22 PCA loading plot of the water parameters in POM season of Rampurhat -II block

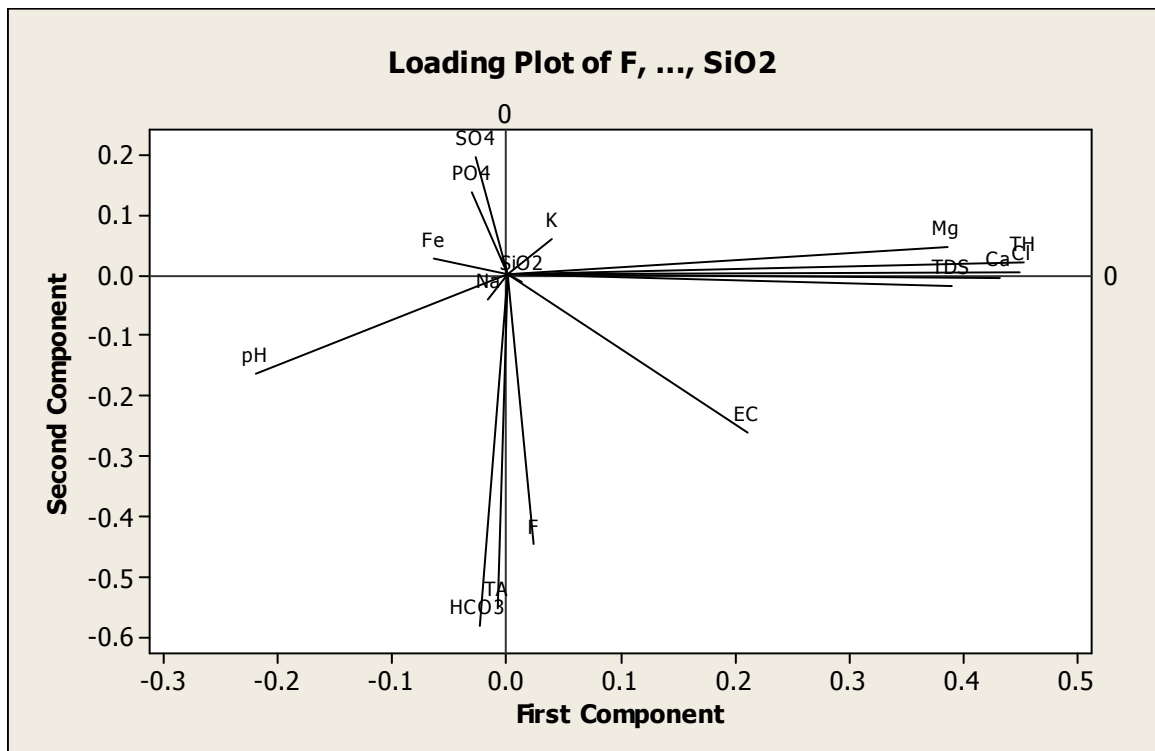


Fig. 23 PCA loading plot of the water parameters in PRM season of Khoyrasol block

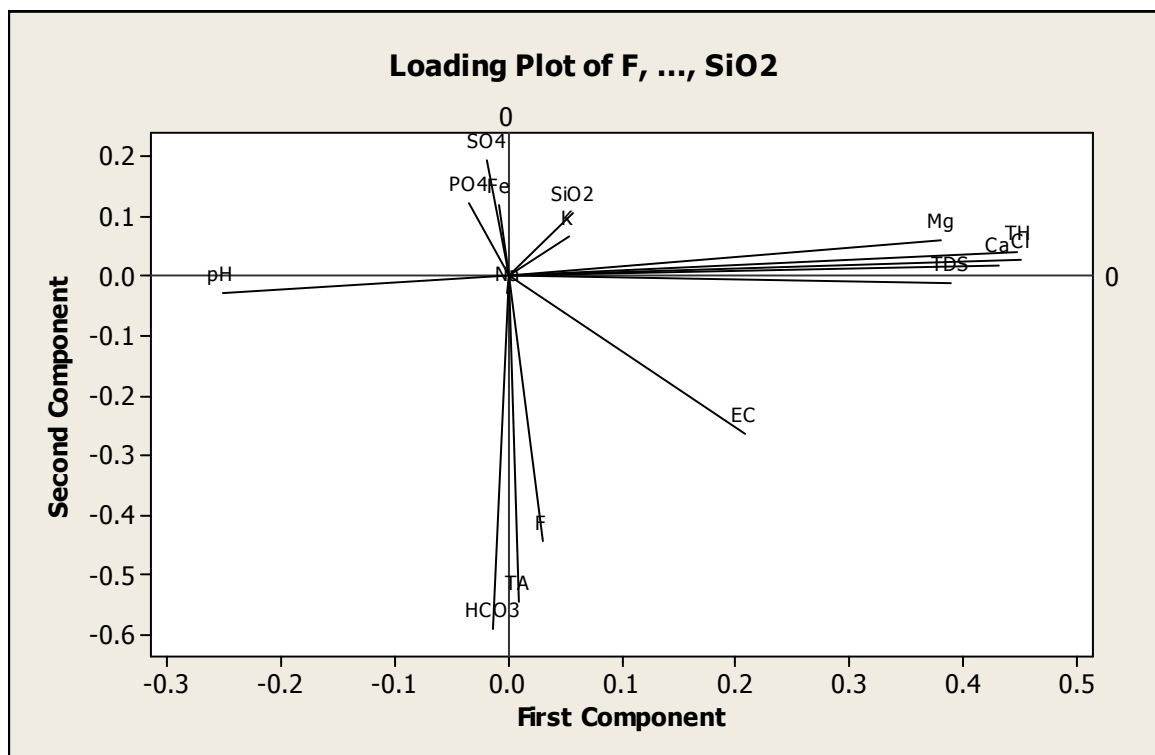


Fig. 24 PCA loading plot of the water parameters in POM season of Khoyrasol block

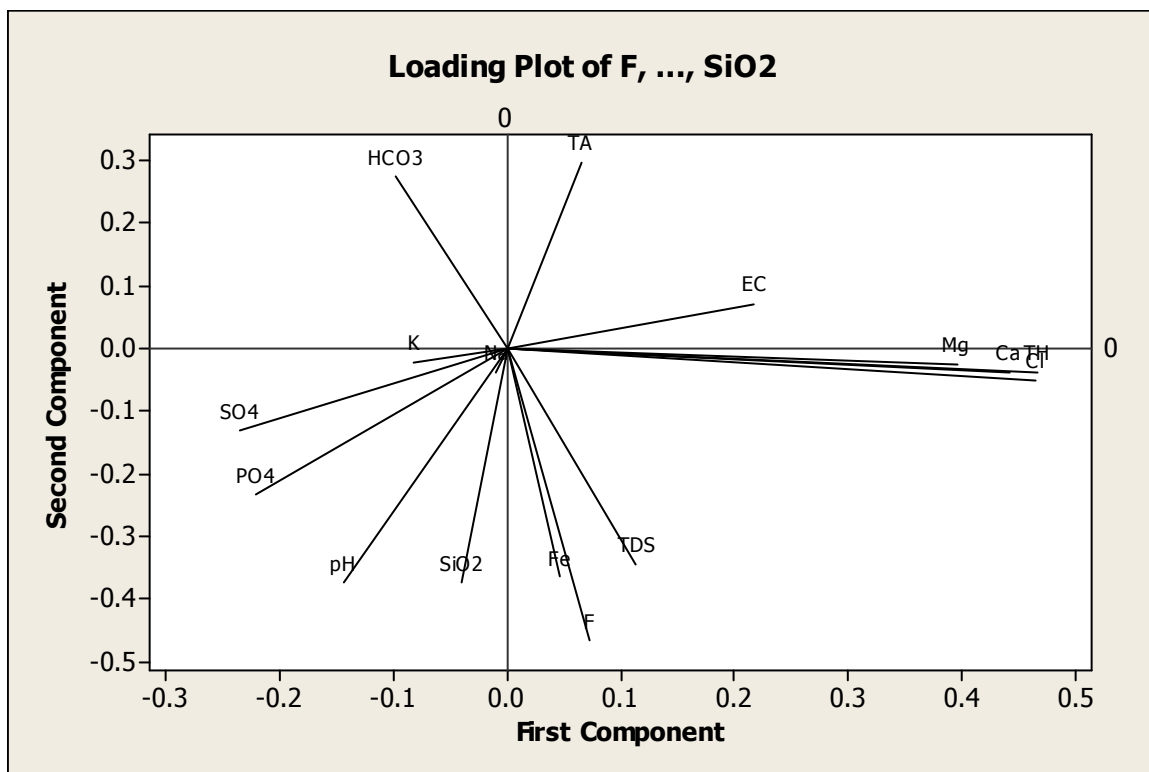


Fig. 25 PCA loading plot of the water parameters in PRM season of Mohammad Bazar block

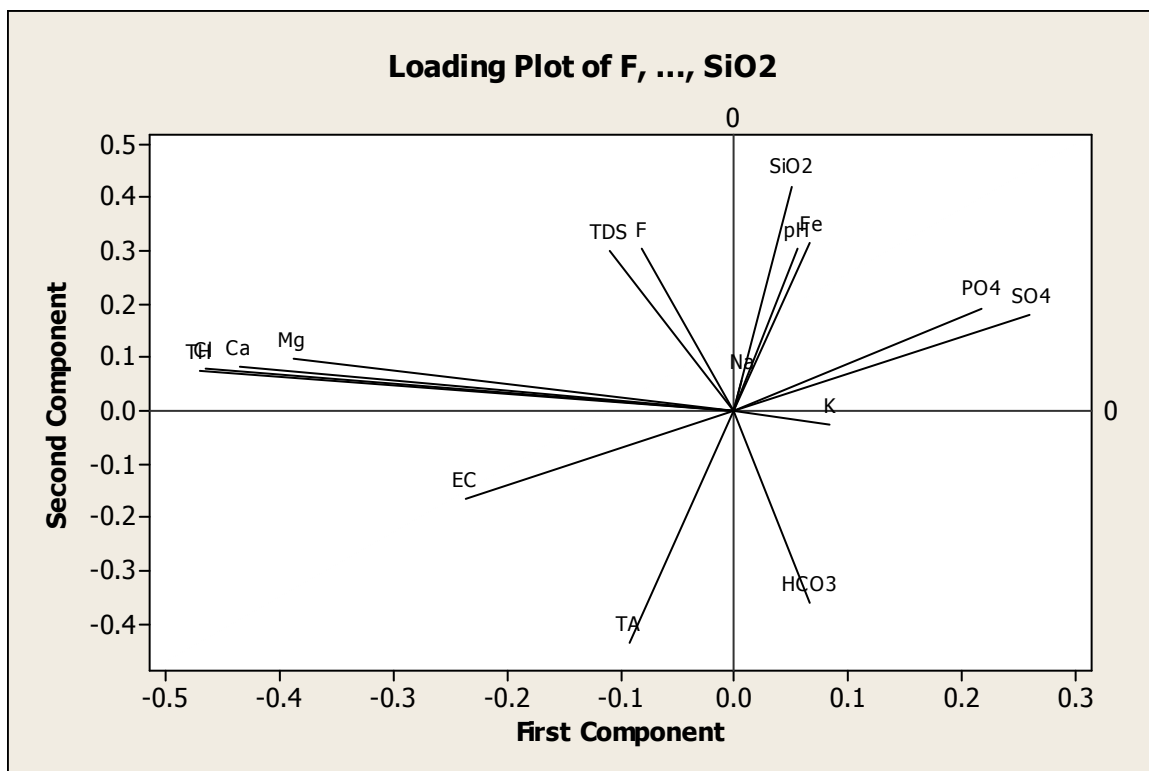


Fig. 26 PCA loading plot of the water parameters in POM season of Mohammad Bazar block

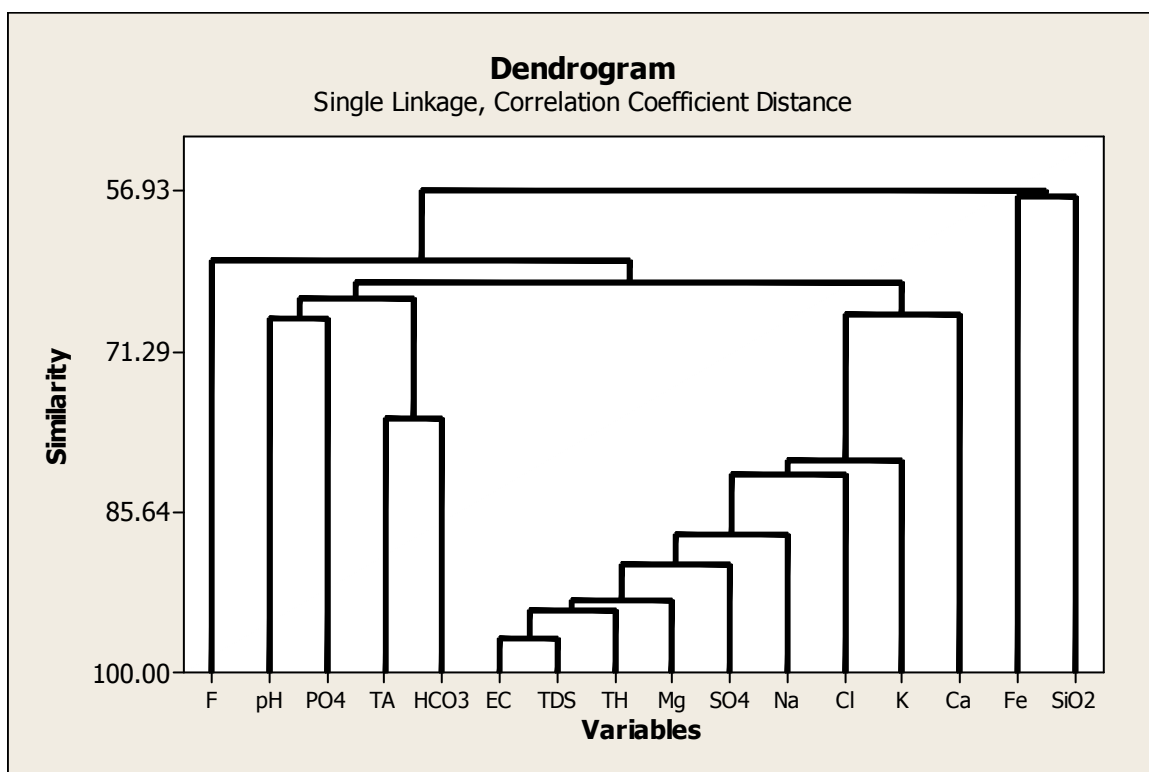


Fig. 27 Cluster Analysis Dendrogram of the water parameters in PRM season of Nalhati-I Block

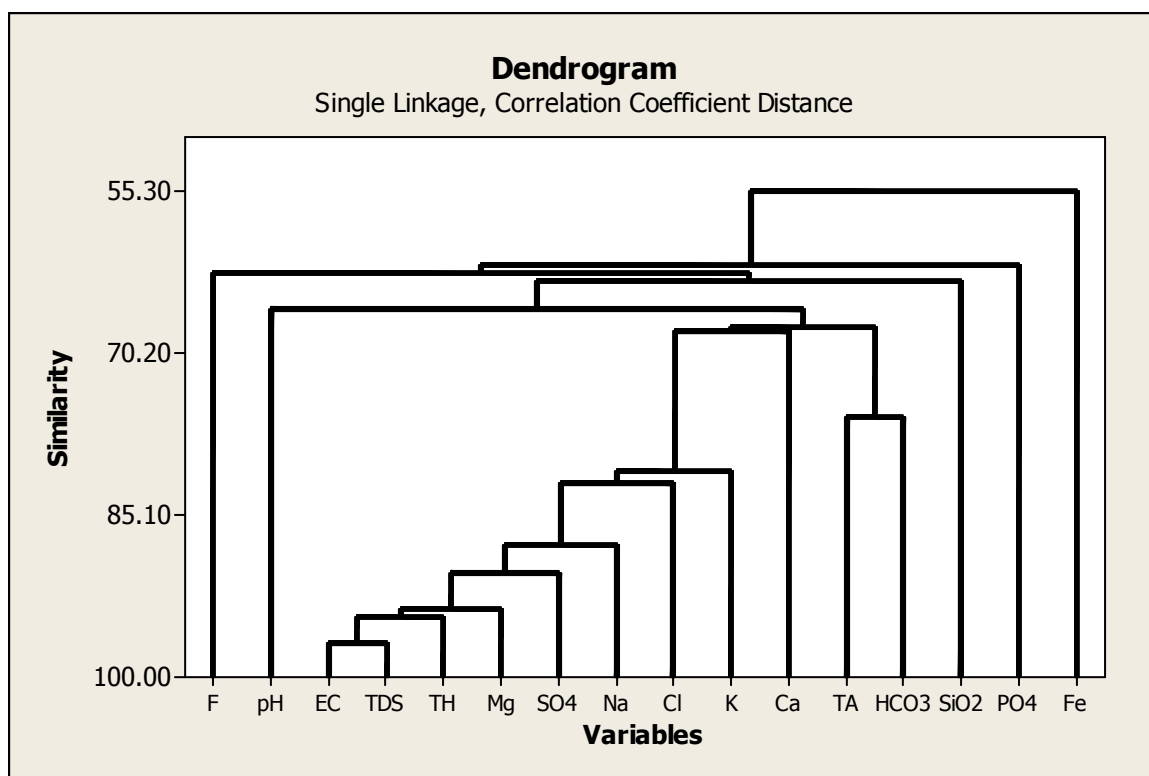


Fig. 28 Cluster Analysis Dendrogram of the water parameters in POM season of Nalhati-I Block

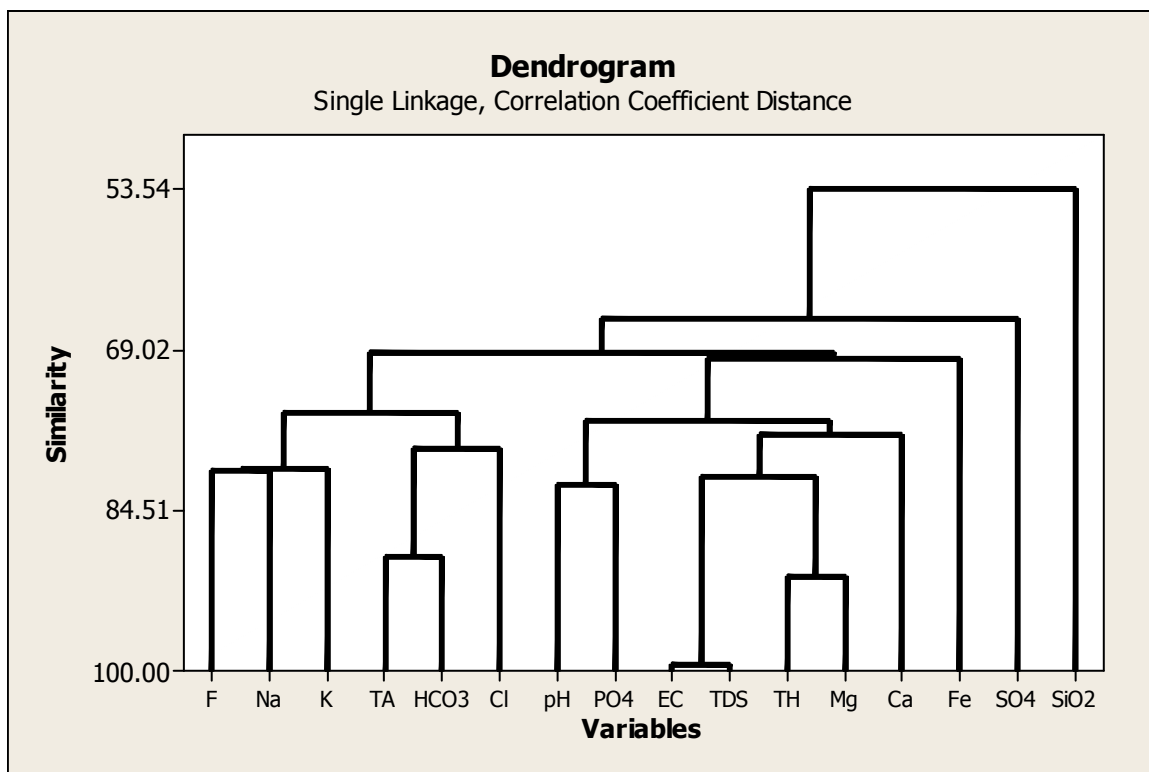


Fig. 29 Cluster Analysis Dendrogram of the water parameters in PRM season of Rampurhat-II Block

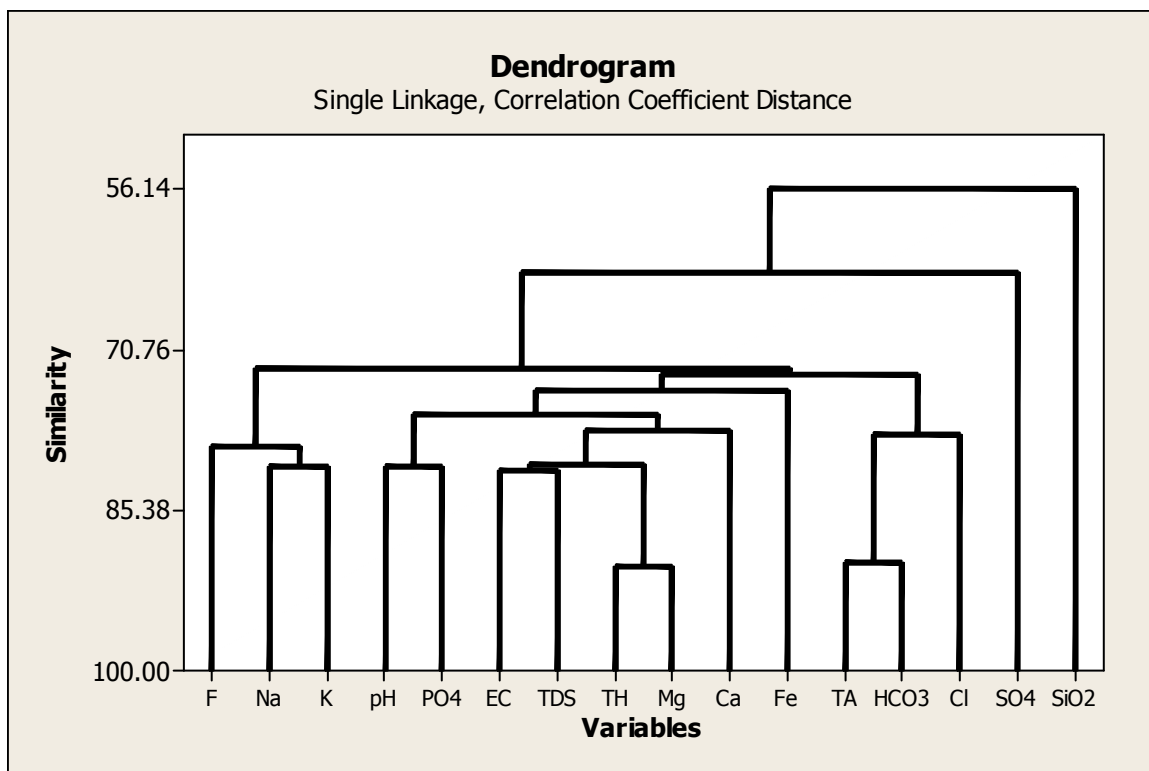


Fig. 30 Cluster Analysis Dendrogram of the water parameters in POM season of Rampurhat-II Block

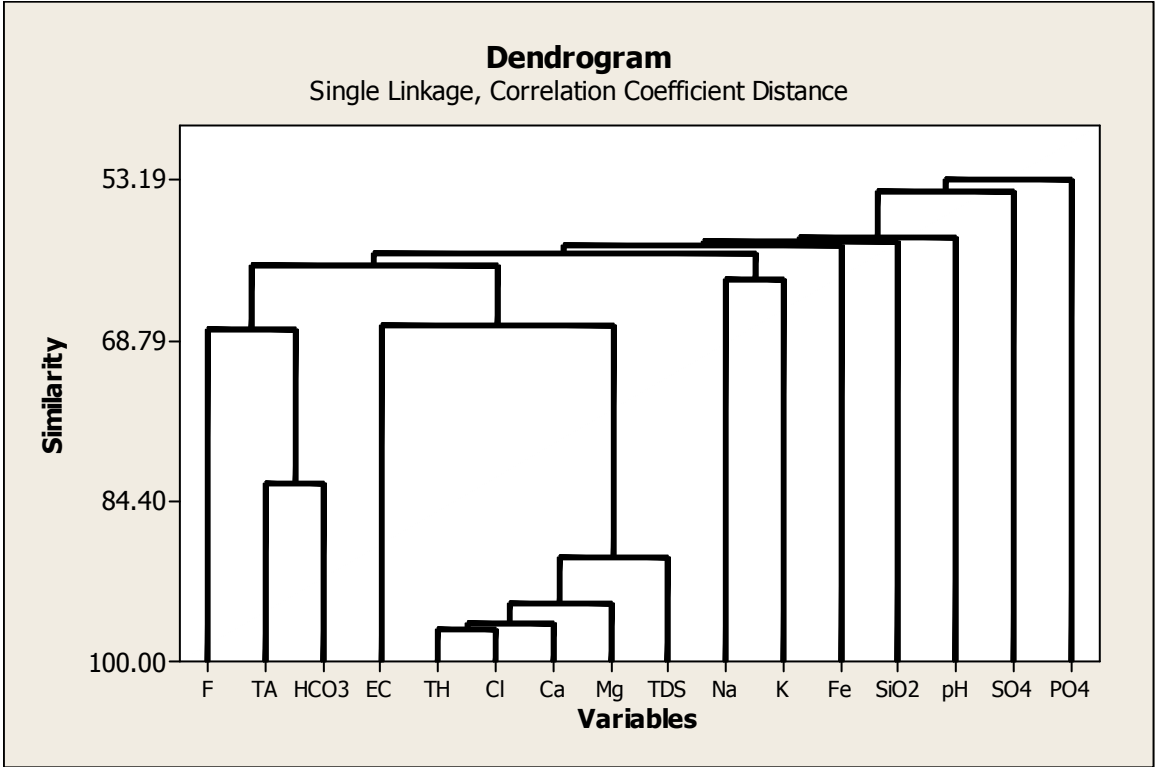


Fig. 31 Cluster Analysis Dendrogram of the water parameters in PRM season of Khoyrasol Block

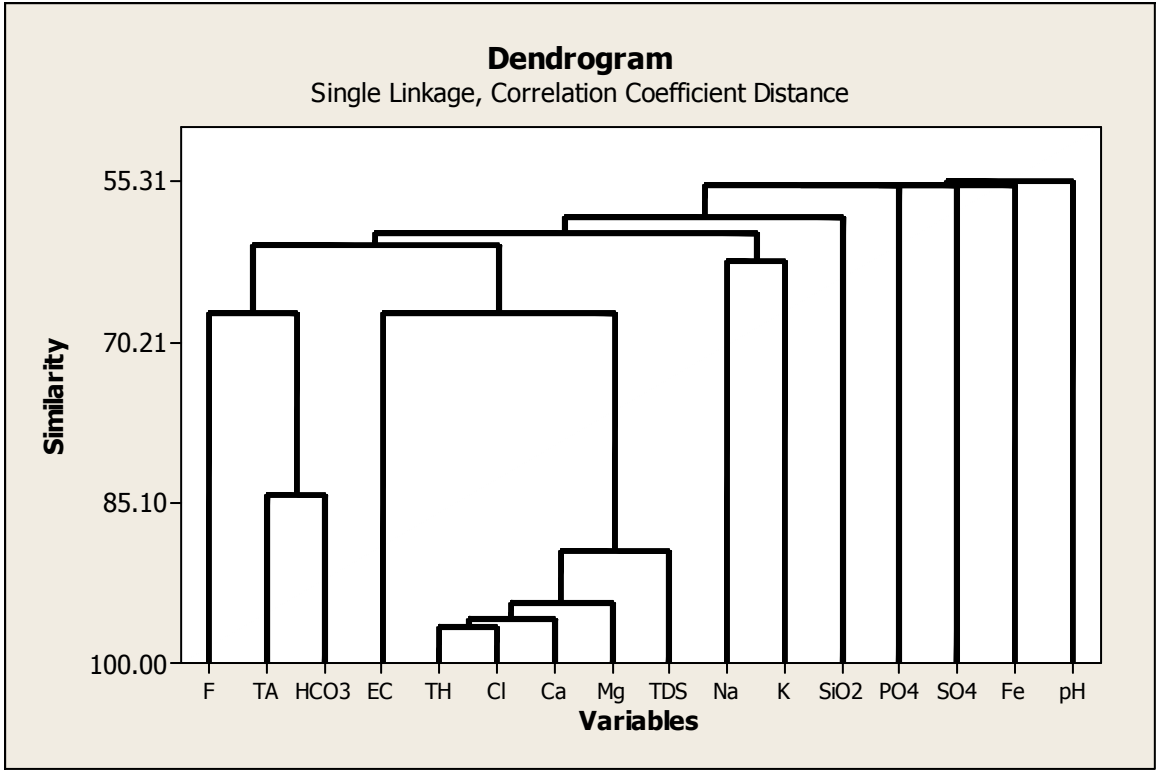


Fig. 32 Cluster Analysis Dendrogram of the water parameters in POM season of Khoyrasol Block

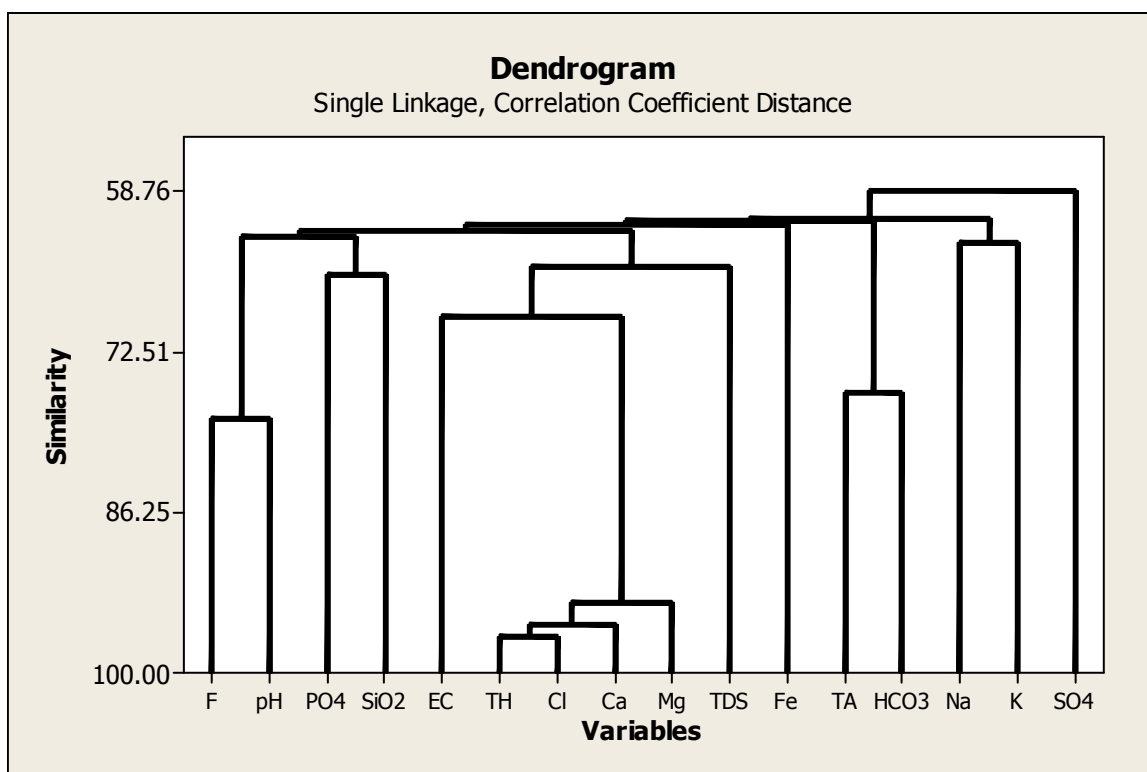


Fig. 33 Cluster Analysis Dendrogram of water parameters in PRM season of Mahammad Bazar Block

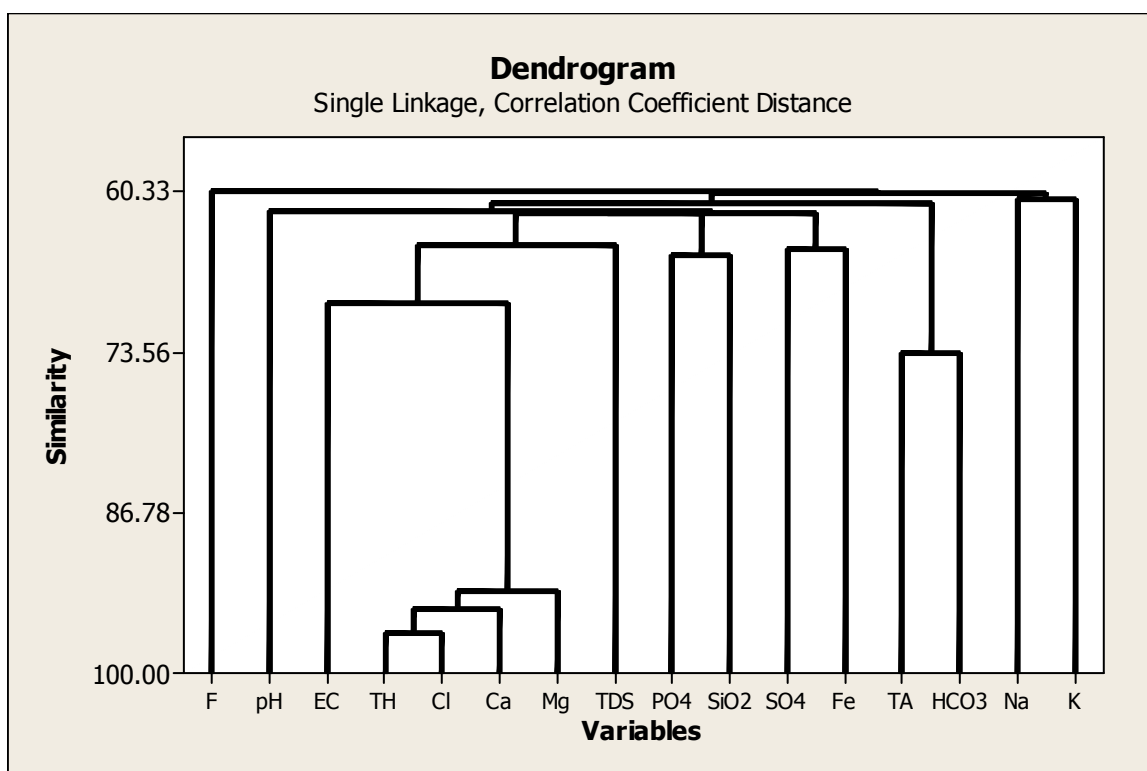


Fig. 34 Cluster Analysis Dendrogram of water parameters in POM season of Mahammad Bazar Block

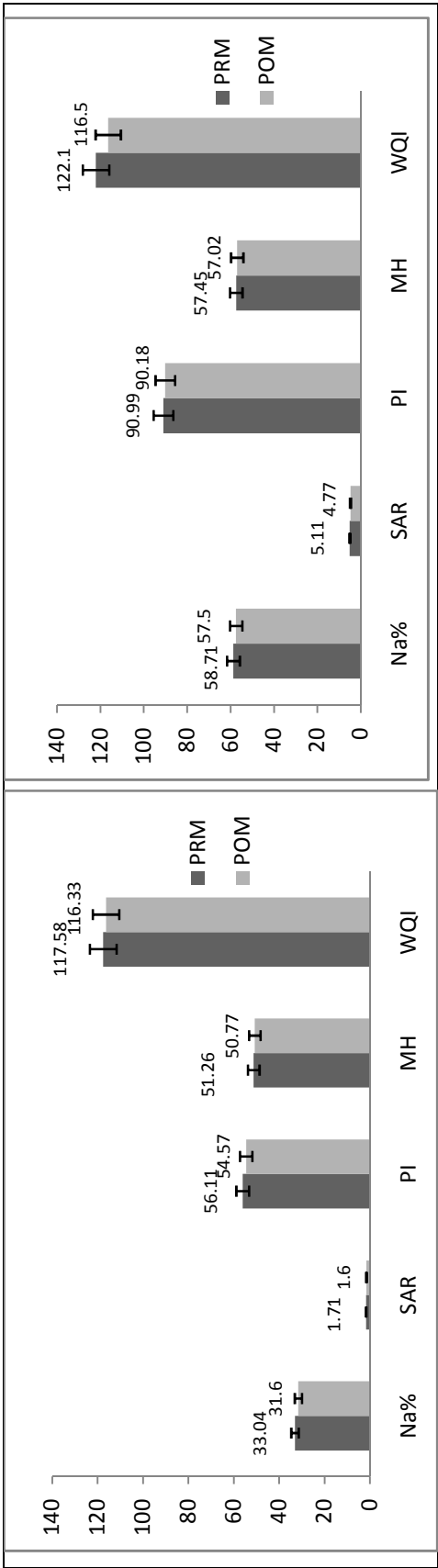


Fig. 35 Comparison of average of %Na, SAR, PI , MH and WQI values in Nalhati I Block during PRM and POM

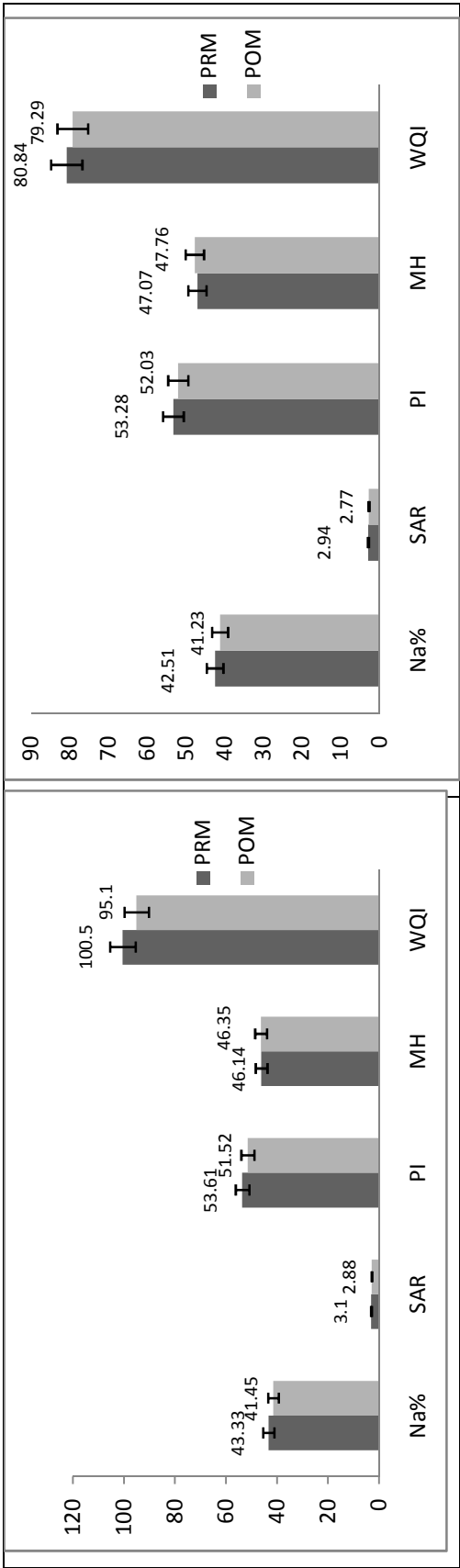


Fig. 37 Comparison of average of %Na, SAR, PI , MH and WQI values in Khowrasol Block during PRM and POM

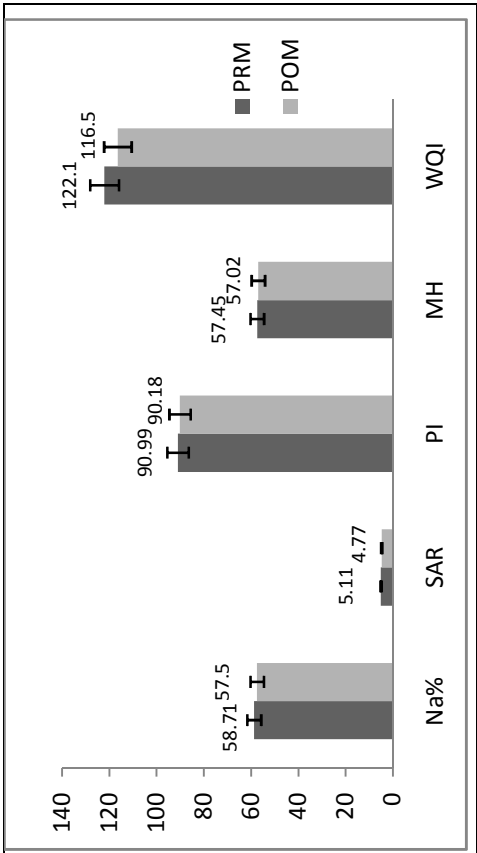


Fig. 36 Comparison of average of %Na, SAR, PI , MH and WQI values in Rampurhat-II Block during PRM and POM

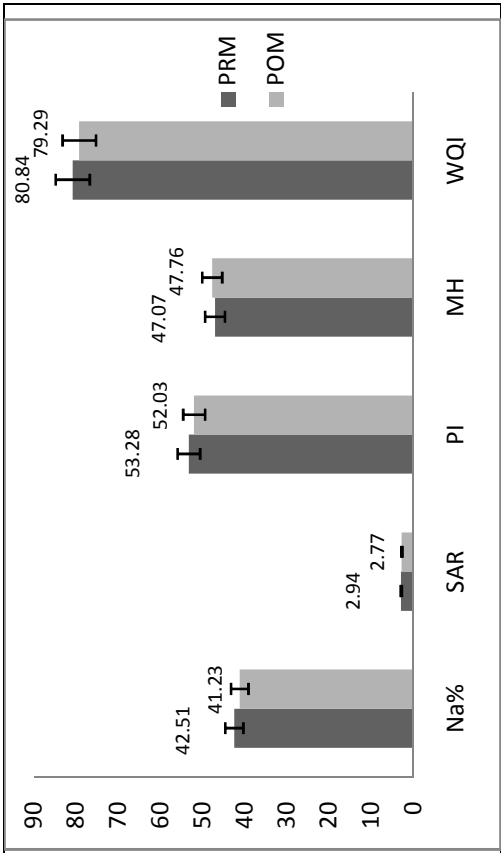
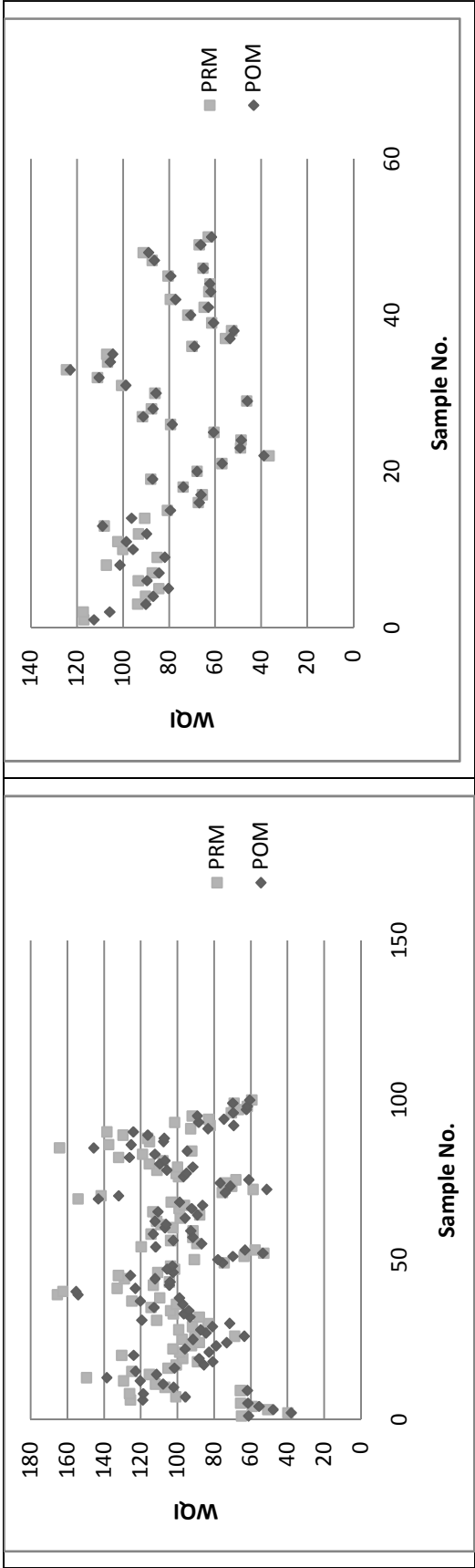
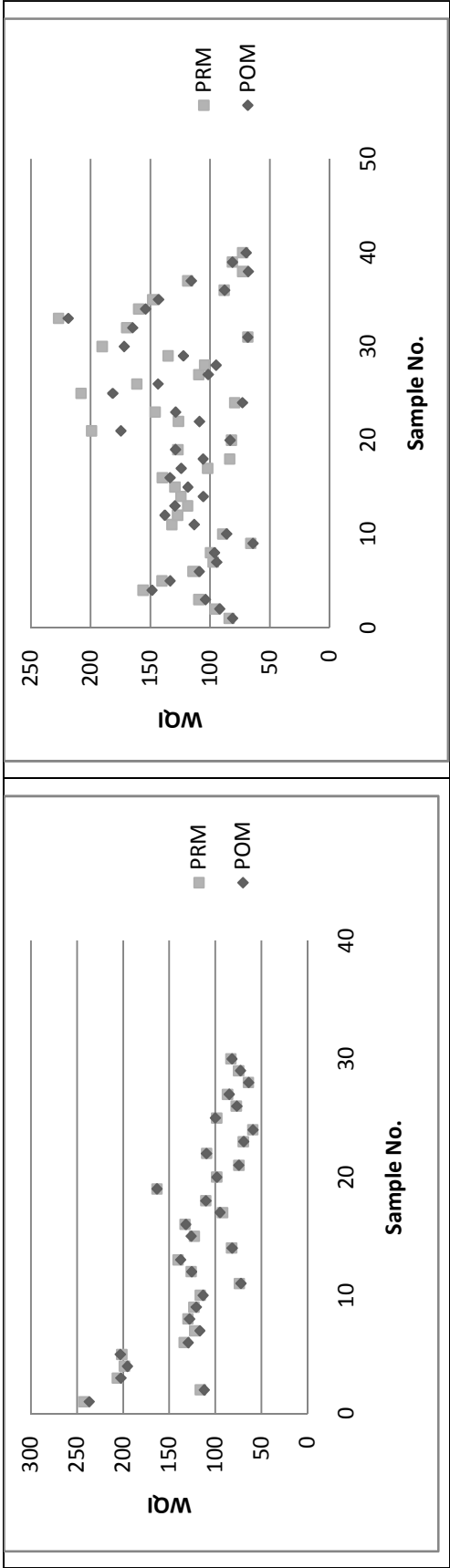


Fig. 38 Comparison of average of %Na, SAR, PI , MH and WQI values in Mohammad Bazar Block during PRM and POM



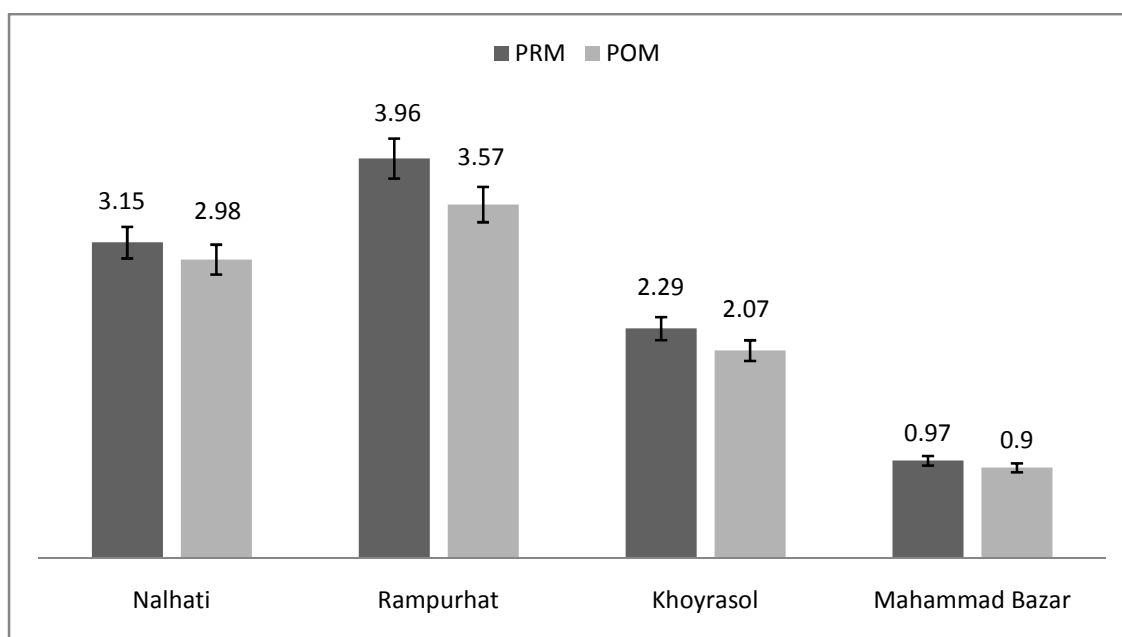


Fig. 43 Average Fluoride level in different four blocks during PRM and POM in Birbhum district

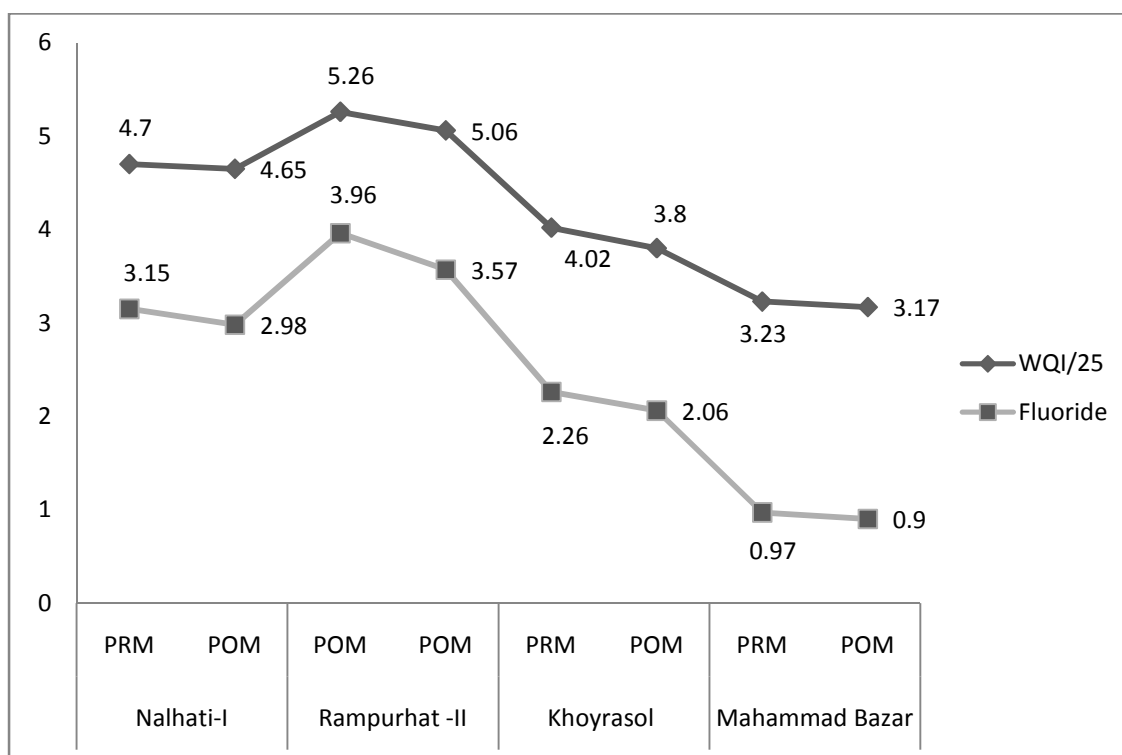


Fig. 44 Comparison between average Fluoride level and average WQI/25 in different four blocks of Birbhum district during PRM and POM

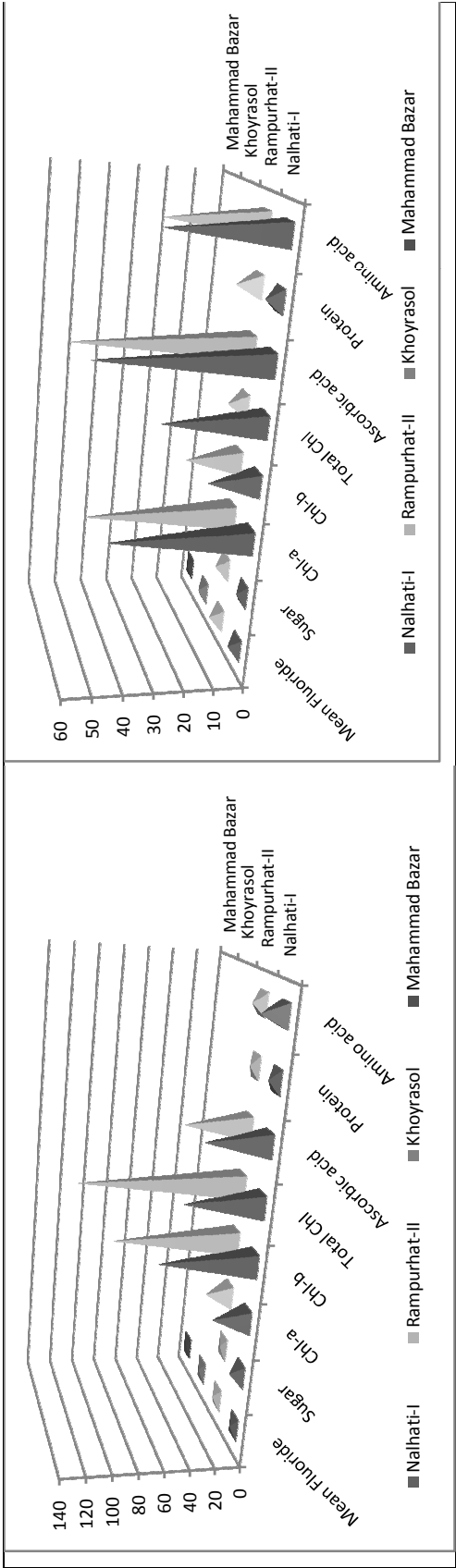


Fig. 45 Percent biochemical change with respect to control in Cabbage collected from different blocks

Fig. 46 Percent biochemical change with respect to control in Onion collected from different blocks

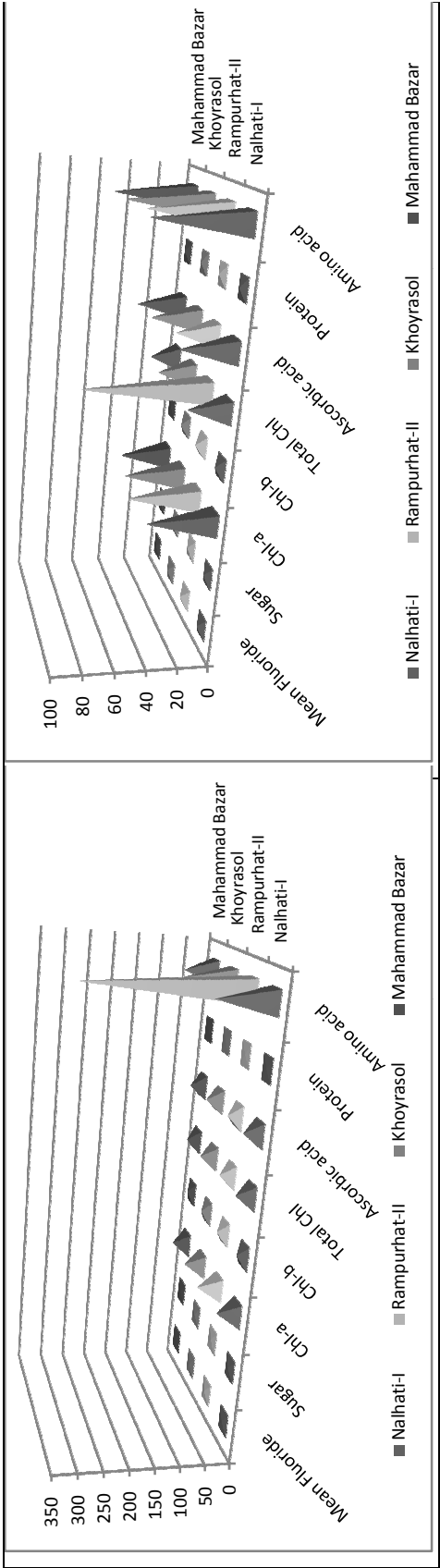


Fig. 47 Percent biochemical change with respect to control in Spinach collected from different blocks

Fig. 48 Percent biochemical change with respect to control in Radish collected from different blocks

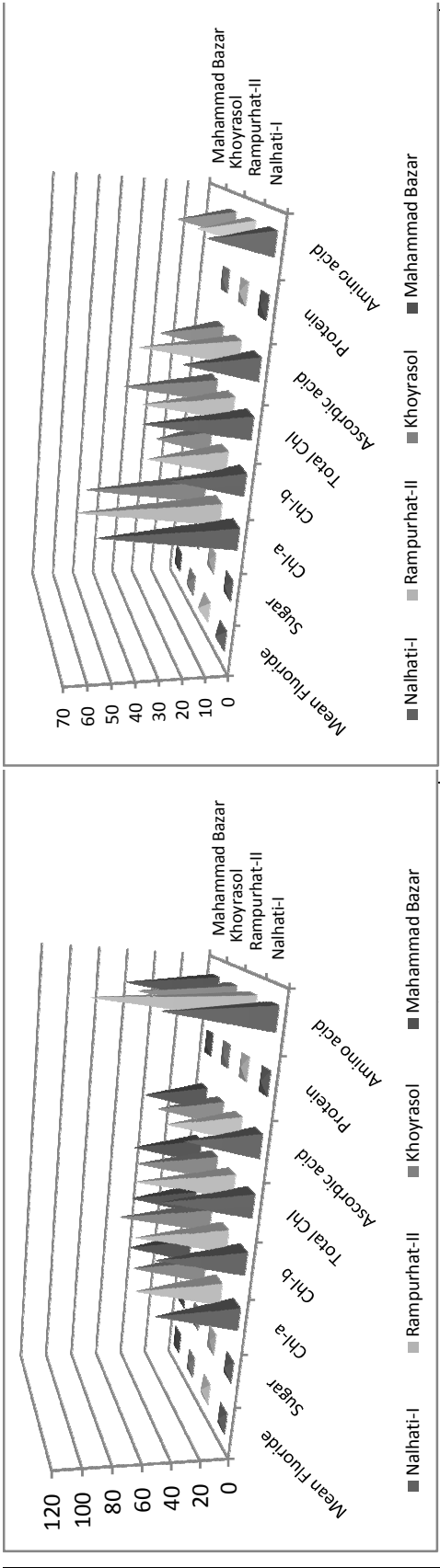


Fig. 49 Percent biochemical change with respect to control in Potato collected from different blocks

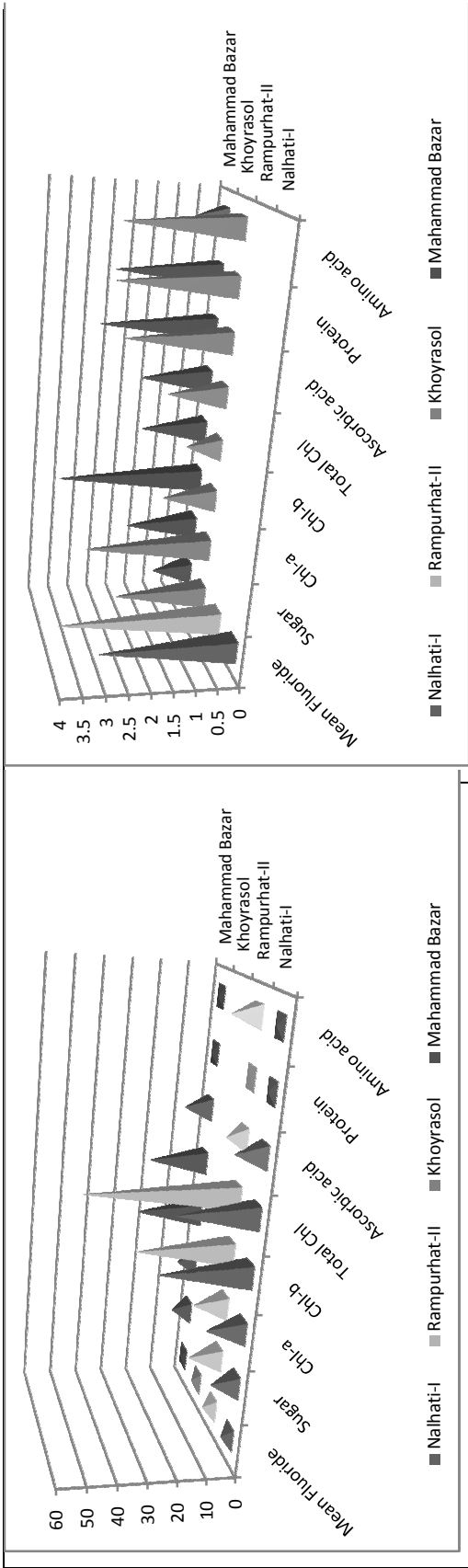


Fig. 51 Percent biochemical change with respect to control in Papaya collected from different blocks

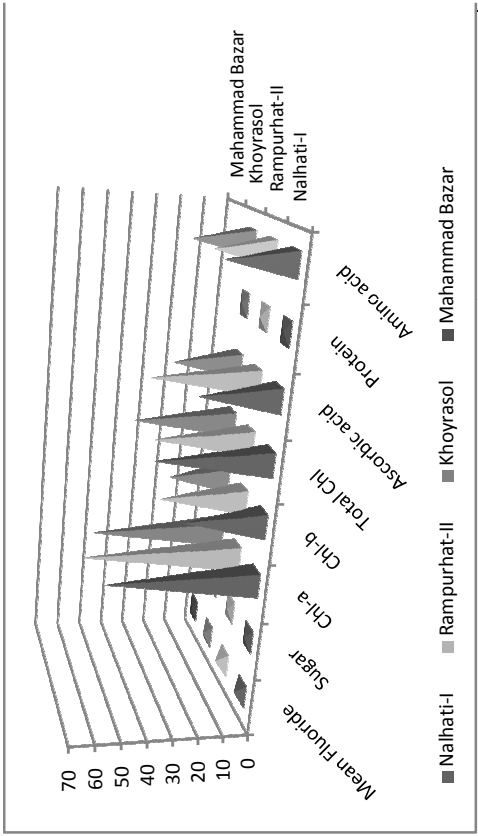


Fig. 50 Percent biochemical change with respect to control in Cauliflower collected from different blocks

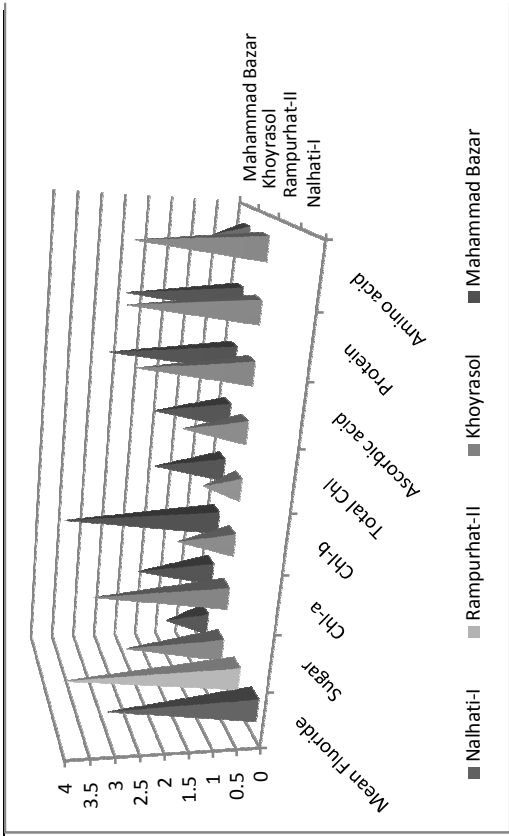


Fig. 52 Percent biochemical change with respect to control in Squash collected from different blocks

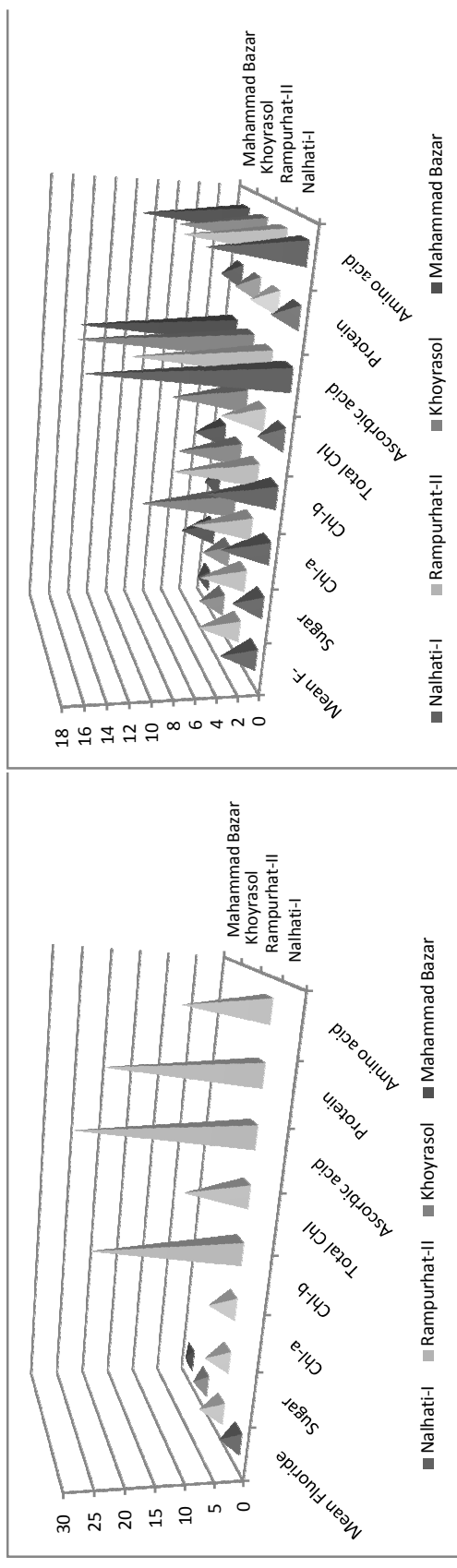


Fig. 53 Percent biochemical change with respect to control in Kundri collected from different blocks

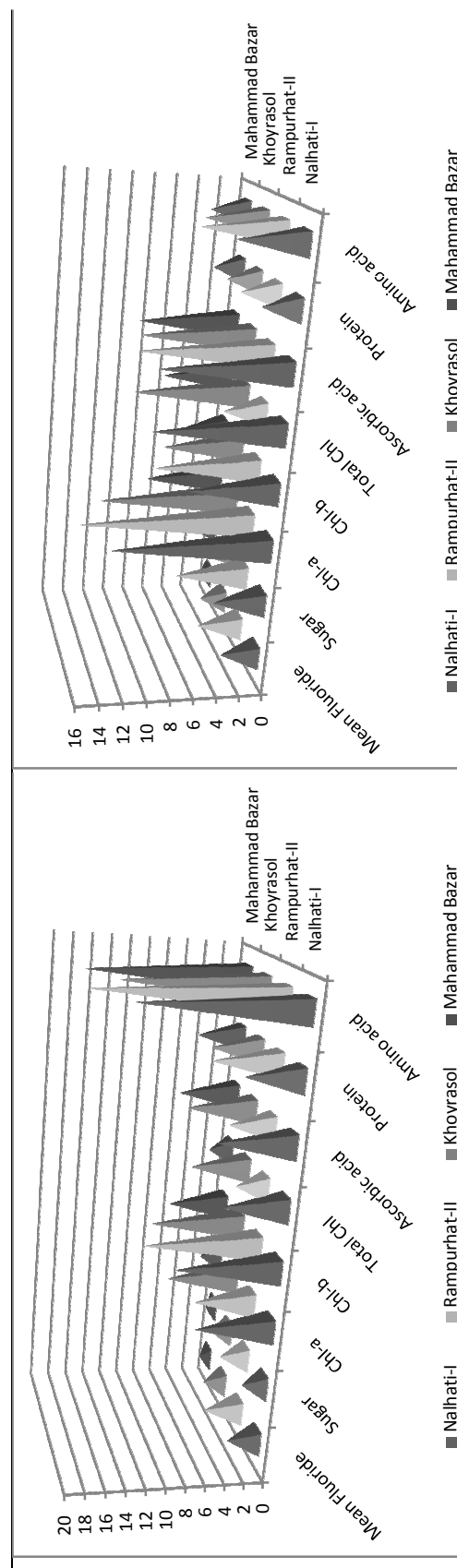


Fig. 54 Percent biochemical change with respect to control in Brinjal collected from different blocks

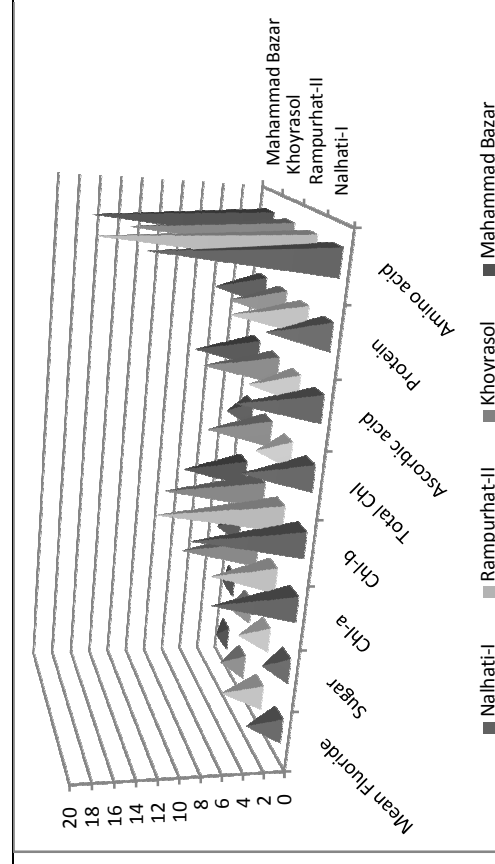


Fig. 55 Percent biochemical change with respect to control in Seem collected from different blocks

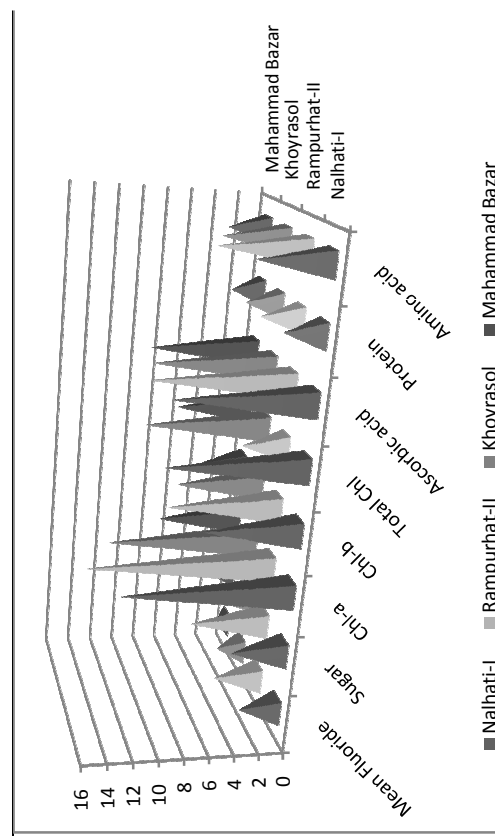


Fig. 56 Percent biochemical change with respect to control in Korola collected from different blocks

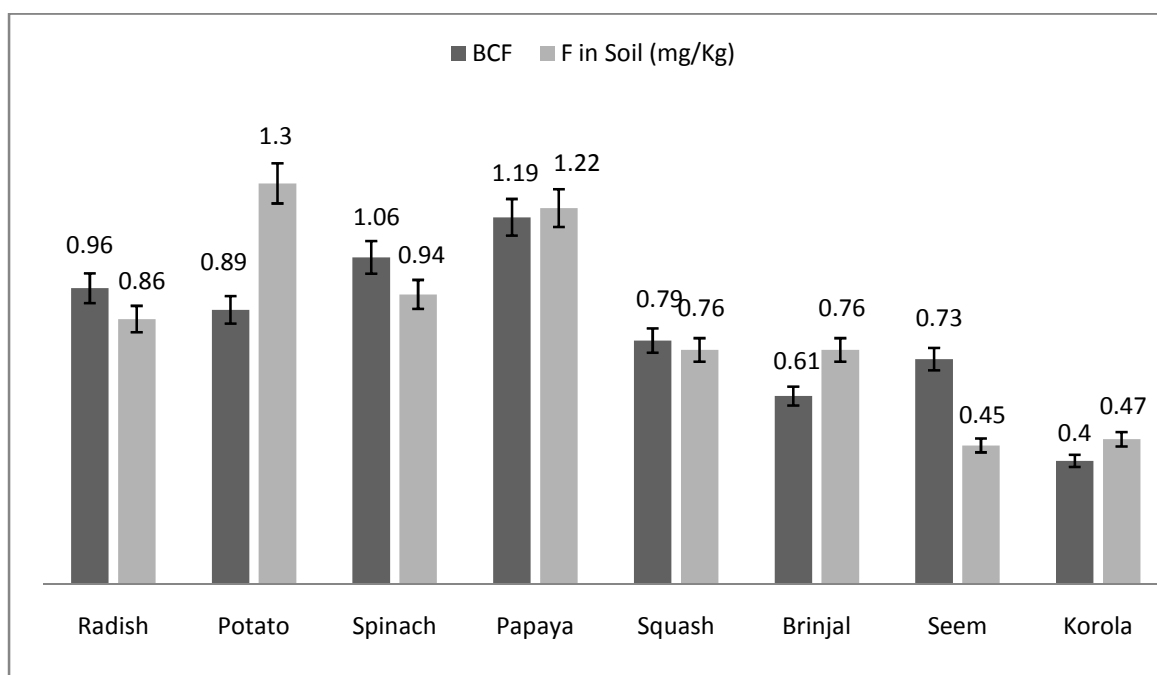


Fig. 57 BCF of different vegetables and Fluoride in soil in Nalhati-I block

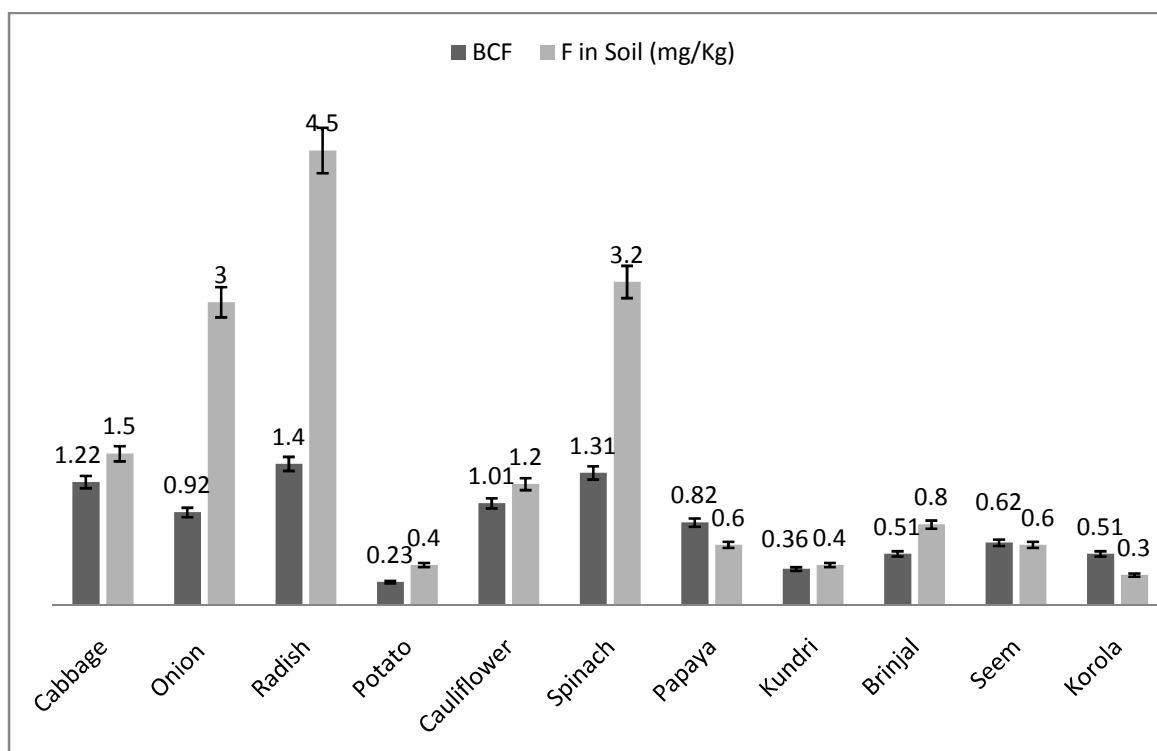


Fig. 58 BCF of different vegetables and Fluoride in soil in Rampurhat-II block

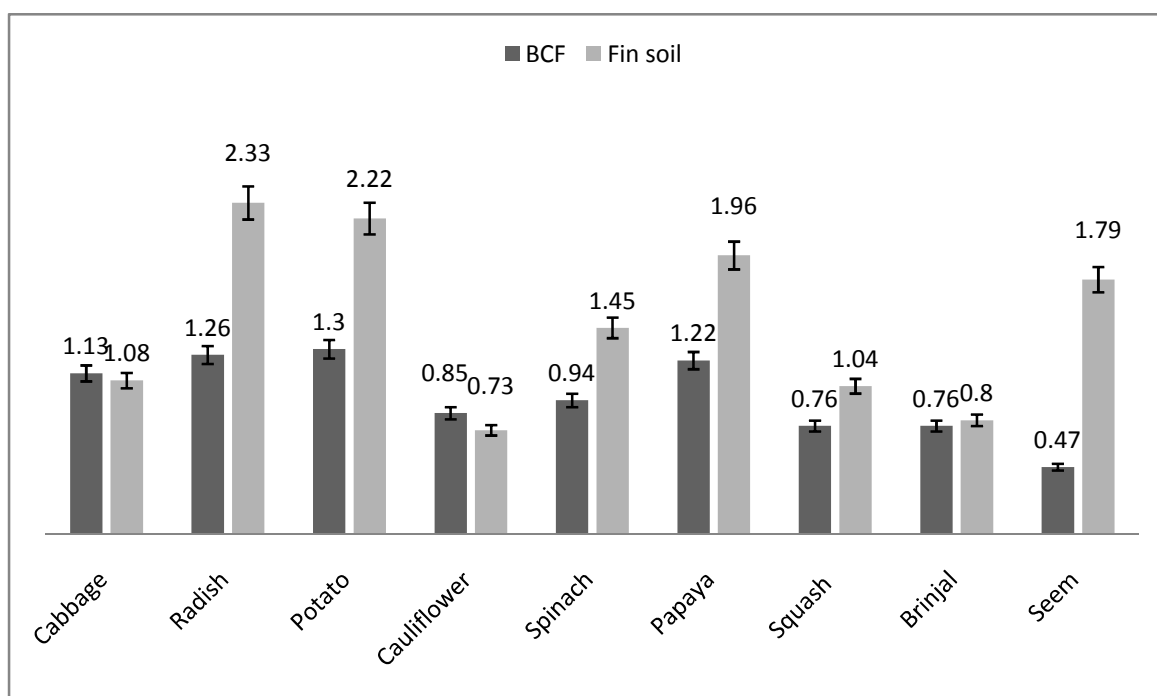


Fig. 59 BCF of different vegetables and Fluoride in soil in Khoyrasol block

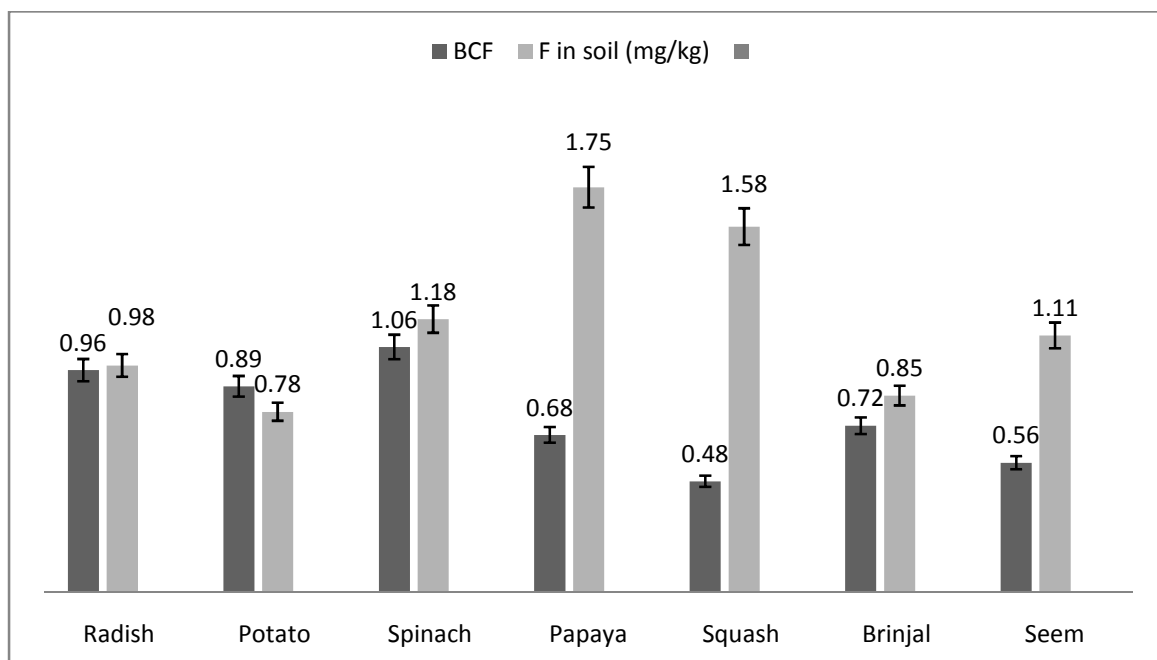


Fig. 60 BCF of different vegetables and Fluoride in soil in Mahammad Bazar block

CHAPTER - 6

CONCLUSION

The villages of Birbhum district of West Bengal, India, is showing endemic fluorosis caused by ground water as the main source of drinking water as well as the irrigational water. Throughout the study, fluoride and other water parameters were estimated in 220 sites of 22 villages from 4 blocks, namely, Nalhati-I, Rampurhat-II, Khoyrasole and Mahammad Bazar in Birbhum district during pre monsoon (PRM) and post monsoon (POM) seasons along with fluoride accumulation and biochemical changes of locally grown vegetables. On the basis of mean fluoride level in ground water during both PRM and POM these four blocks can be arranged as: Rampurhat-II > Nalhati-I > Khoyrasole > Mahammad Bazar. There is a potential threat of endemic fluorosis in these three blocks namely, Nalhati-I, Rampurhat-II and Khoyrasole among these four blocks. Fluoride incidence in groundwater is of greater inconvenience in Khoyrasole block as the people residing in this area are not well aware about it. The average fluoride level in all four blocks decreased slightly during POM season in comparison to PRM season. This fact might have been originated from the dilution effect due to ground water recharge during monsoon season.

Other physico-chemical parameters of water rendered the relations between fluoride and the parameters, accounted for the hydrogeochemical facies of ground water, assessed the water quality for drinking acceptability computing WQI and analyzed the irrigational quality of the water samples.

Thorough analysis of the water parameters did not reveal any consistent correlation between fluoride and other water parameters in all the four blocks. But the positive correlation of calcium and magnesium with fluoride found in almost all cases indicates the presence of limestone in those areas which on leaching raises the fluoride level. A positive correlation was found between fluoride and bicarbonate in the fluoride prone blocks namely Nalhati-I, Rampurhat-II and Khoyrasole during both PRM and POM complying with the favorable dissolution of fluorite minerals at higher bicarbonate concentration.

Principle component analysis (PCA) loading plots portrayed different associations with fluoride corroborating correlation among the water parameters in different blocks during different seasons. The cluster analysis of the water parameters in all the four blocks during PRM and POM, graphically represented in the dendograms according to Ward's linkage was adopted for the revelation of the similarity between the parameters. From all the dendograms obtained, remarkable and closest similarity was observed with fluoride, total alkalinity and bicarbonate in Khoyrasol block during PRM settling high concentration of bicarbonate and alkalinity to be favorable condition for the dissolution of fluoride bearing minerals.

Piper diagrams used to discriminate the hydrogeochemical facies depicted separate type of water in terms of major constituent cations (Na, K, Ca, and Mg) and anions (Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-}) in each different block. The difference may be attributed to the difference in regional lithology and different leaching pattern in correlation with fluoride abundance.

Different irrigational quality parameters namely, percentage of sodium, sodium adsorption ratio, permeability index, magnesium hazard were computed to judge the reliability of the water used for irrigation from different speculative aspects. In view of average percent sodium value the water collected from Rampurhat-II, Khoyrasol, Mahammad Bazar block during both PRM and POM were categorized as class II ($30 < \% \text{Na} < 75$) rendering the water samples permissible to doubtful for irrigation. But in Nalhati-I block the water collected during both PRM and POM were of class I ($\% \text{Na} < 30$) category indicating its goodness to use for irrigation. From the point of mean SAR values, all the water samples collected (except a few in Rampurhat-II block) from Nalhati-I, Khoyrasol, Mahammad Bazar block during both PRM and POM were of excellent category ($\text{SAR} < 10$) to use in irrigation. On the basis of permeability index Rampurhat-II block during both PRM and POM had the highest percentage of class 1 ($\text{PI} > 75$) category samples according to WHO classification. Because, the water samples of Rampurhat-II had high fluoride levels and in

correlation had high Na and HCO_3^- level which resulted in higher permeability index. Magnesium hazard ratio depicted the highest percentage (60 %) of unsuitable water for irrigation ($\text{MH} > 50$) in Rampurhat- II block during both PRM and POM indicating the ability to cause adverse effects on agricultural yield. The origin of this fact is the elevated level of fluoride and its significant positive correlation with magnesium.

The study of biochemical parameters (chlorophyll, amino acids, proteins, soluble sugars, ascorbic acid) in edible part of different vegetable plants namely, Cabbage (*Brassica oleracea* var. *botrytis*) leaf, Onion (*Allium cepa*) leaf, Spinach (*Spinacia oleracea*) leaf, Radish (*Raphanus sativus*) leaf, Potato (*Solanum tuberosum*) leaf, Cauliflower (*Brassica oleracea*) leaf, Papaya (*Carica papaya*) fruit, Kundri (*Coccinia grandis*) fruit, Brinjal (*Solanum melongena*) fruit, Seem (*Dolichos lablob*) fruit, Korola (*Momordica charantia*) fruit, Squash (*Cucurbita maxima*) fruit) collected from Nalhati-I, Rampurhat-II, Khoyrasol, Mahammad Bazar block and control area was conducted to understand the effect of fluoride along with the accumulation. For the conjecture of stress effect of fluoride, the new parameter PBC (percent biochemical change) was introduced to calculate the biochemical changes with respect to control.

The study revealed that the reducing sugar in most of the vegetable leaves and fruits collected from fluoride-affected area decreased considerably ($\text{PBC} > 0$) in comparison to the control area. This may be due to decreased photosynthesis resulting in lower accumulation of photo assimilate in leaves and fruits under fluoride stress, decreasing the sensitivity of different crop plants. Since formation of reducing sugars such as glucose, fructose, and mannose in leaves presumably inhibited by F, the tendency of plants exposed to F decrease the concentrations of such sugars indicating the possible conversion of these sugars to non-reducing sugars, such as sucrose and raffinose or sugar alcohols. Increased levels of non-reducing sugars in some cases might have been arisen from a mechanism adopted by plants to reduce F toxicity.

The PBC in chlorophyll content (Chl *a*, Chl *b*, total Chl) rendered that about in all vegetables collected from all four blocks there were lesser amount of chlorophyll in the fluoride affected areas with respect to control area. The highest reduction in chlorophyll content (Chl *a*, Chl *b*, total Chl) were found mainly the leafy vegetables namely, cauliflower, potato and cabbage. Reduction in the Chl *a*, Chl *b* and total chl content may be due to the breakdown of chlorophyll under stress or due to inhibition of chlorophyll biosynthesis. Decrease in chlorophyll content may also be due to the disruption of chloroplast membranes as described by earlier researchers. The higher PBC in leafy vegetables occurred presumably due to the higher stress of fluoride as a consequence of higher fluoride adsorption during photo assimilation.

The ascorbic acid content in most of the vegetable leaves and fruits of different blocks decreased in comparison to control probably due to inhibition of ascorbic acid synthesis under fluoride stress. However, In few vegetables like, Brinjal, Seem and Korola, the ascorbic acid content collected from the fluoride affected area showed the opposite trend, which may be explained on the basis of previous thoughts of binding of fluoride with ascorbic acid oxidase enzyme inhibiting the breakdown of ascorbic acid in the plant.

Protein content in most of the vegetables collected from the fluoride affected sites had a relatively lower amount of protein with respect to the protein content of the vegetables collected from the control area. As the fluoride decreases the number of ribosomes and destroys the structure of ribosomal proteins which negatively affects the entire protein synthesis, a decrease in protein content is therefore observed. Reduced rate of amino acid synthesis under fluoride stress may also be a probable reason of lower protein content in the vegetables collected from fluoride affected area. The total free amino acid content in some of the different vegetables collected from polluted areas was in lower amount with respect to the control area and in few the reversed trend was noticed. This may be due to less degradation of storage protein, amino acid synthesis and amino acid utilization for protein synthesis and for respiration under fluoride stress. Increased rates of dark CO₂

fixation under fluoride stress may be the reason of increased amino acid content in few of the vegetables in the affected area in comparison to control area.

In this district, substantial amounts of different vegetables are cultivated with fluoride contaminated groundwater. As a result, fluoride accumulation in different parts of vegetables grown there is likely leading to fluoride contamination in the food chain. The changes in biochemical parameters with respect to the average fluoride level in water in different blocks portrayed higher biochemical changes due to higher level of fluoride in irrigational water. Fluoride accumulation and the cumulative change in biochemical parameters due to fluoride stress may affect the food value of different vegetables in the fluoride affected area.

The transport of fluoride from soil to vegetation was measured by calculating the bioconcentration factor (BCF) and the effect of fluoride on biochemical constituents of leaves and fruits of the fluoride affected area in comparison to the control area. The high value of BCF were found in the leafy vegetables due to higher rate of metabolism and consequent absorption of water soluble fluoride from soil. Furthermore, it was observed that higher fluoride in soil resulted in higher BCF of fluoride. This fact might have been arisen from the higher transition of fluoride from soil to foliage during water absorption depending on the rate of photosynthesis.

Along with the water quality both for drinking and irrigation in the four blocks studied, it is presumable that stress effect fluoride on plant metabolism can produce disturbances in natural biosynthetic turnover. Therefore, future mitigation attempts should consider alternative fluoride-free water sources for drinking and irrigation purposes in these fluoride affected areas of Birbhum district.

CHAPTER - 7

REFERENCES

-
- Abdallah, F. B., Elloumi, N., Mezghani, I., Garrec, J. P., & Boukhris, M. (2006). Industrial fluoride pollution of Jerbi grape leaves and the distribution of F, Ca, Mg, and P in them. *Fluoride*, 39: 43-48.
- Abdelgawad, A. M., Watanabe, K., Takeuchi, S., & Mizuno, T. (2009). The origin of fluoride-rich groundwater in Mizunami area, Japan - Mineralogy and geochemistry implications. *Engineering Geology*, 108: 76-85.
- Abdulrahman, I., Alabdulaaly, Abdullah, I., Al-Zarah, & Mujahid, A. K. (2013). Occurrence of fluoride in ground waters of Saudi Arabia. *Applied Water Science*, 3: 589–595.
- Agarwal, V., Vaish, A. K., & Vaish, P. (1997). Ground water quality: Focus on fluoride and fluorosis in Rajasthan. *Current Science*, 73(9): 743–746.
- Alagumuthu, G., & Rajan, M. (2010). Chemometric studies of water quality parameters of Sankarankovil block of Tirunelveli, Tamilnadu. *Journal of Environmental Biology*, 31: 581-586.
- Alonso, J., Garcí'a, M. A., Pe´rez-Lo´pez, M., & Melgar, M. J. (2003). The concentrations and bio-concentration factors of copper and zinc in edible mushrooms. *Archives of Environmental Contamination and Toxicology*, 44: 180-188.
- Amadi, A. N, Olasehinde, P. I., Yisa, J., Okosun, E. A., Nwankwoala, H. O., & Alkali Y. B. (2012). Geostatistical Assessment of Groundwater Quality from Coastal Aquifers of Eastern Niger Delta, Nigeria. *Geosciences*, 2(3): 51-59.
- Anderson, B. G., & Stevenson, P. H. (1930). The occurrence of mottled enamel among the Chinese. *Journal of Dental Research*, 10: 233-238.
- Aoba, T. (1997). The effect of fluoride on apatite structure and growth. *Critical Reviews in Oral Biology & Medicine*, 8: 136–153.

-
- Aoba, T., & Fejerskov, O. (2002). Dental fluorosis: chemistry and biology. *Critical Reviews in Oral Biology & Medicine*, 13(2): 155–170.
- Apambire, W. M., Boyle, D. R., & Michel, F. A. (1997). Geochemistry, genesis, and health implications of fluoriferous groundwater in the upper regions of Ghana. *Environmental Geology*, 35(1): 13-24.
- APHA (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, Washington DC.
- Areas, J. O., Villa, A., & Mondadori, G. (1980). Air pollutant uptake by xerophytic vegetation: Fluoride. *Environmental and Experimental Botany*, 20: 259-269.
- Arnon, D. I. (1949). Copper enzymes in isolated chloroplast and polyphenol oxidase in *Beta vulgaris*. *Plant Physiology*, 24: 1-15.
- Arveti, Nagaraju , Sarma, M. R. S., Aitkenhead-Peterson, J. A., & Sunil, K. (2011). Fluoride incidence in groundwater: a case study from Talupula, Andhra Pradesh, India. *Environmental Monitoring and Assessment*, 172:427–443.
- Asthir, B., Basra, A. S., & Batta, S. K. (1998). Fluoride-induced alteration of carbon and nitrogen metabolism in developing wheat grains. *Biologia Plantarum*, 41: 287-292.
- Avishek, K., Pathak, G., Nathawa, M. S., Jha, U., & Kumari, N. (2010). Water quality assessment of Majhiaon block of Garwa district in Jharkhand with special focus on fluoride analysis. *Environmental Monitoring and Assessment*, 167: 617–623.
- Ayoko, G. A., Singh, K., Balarea, S., & Kokot, S. (2007). Exploratory multivariate modeling and prediction of the physico-chemical properties of surface water and groundwater. *Journal of Hydrology*, 336: 115– 124.
- Banks, D., Frengstad, B., Midtgard, A., Krog, J. R., & Strand, T. (1998). The chemistry of Norwegian groundwaters:I. The distribution of radon, major and minor elements in

- 1604 crystalline bedrock groundwaters. *The Science of the Total Environment*, 222: 71-91.
- Bell, M., Largent, E., Ludwig, T., Muhler, J., & Stookey, G. (1970). *Fluorides and Human Health*. Monograph Series No. 59, World Health Organization, Geneva.
- Bhardwaj, V., & Singh, D. S. (2010). Surface and groundwater quality characterization of Deoria District, Ganga Plain, India. *Environmental Earth Science*. doi:10.1007/s12665-010-0709x
- Bhargava, D., & Bhardwaj, N. (2010). Effect of sodium fluoride on seed germination and Seedling growth of *Triticum aestivum* var. Raj. 4083. *Journal of Phytology*, 2(4): 41–43.
- BIS (Bureau of Indian Standards) (2009). *Indian Standard Specifications for Drinking Water*, Second Revision of IS: 10500.
- Bishnoi, M., & Arora, S. (2007). Potable groundwater quality in some villages of Haryana, India: Focus on fluoride. *Journal of Environmental Biology*, 28(2): 291-294.
- Bo, Z., Mei, H., Yongsheng, Z., Xueyu, L., Xuelin, Z., & Jun, D. (2003). Distribution and risk assessment of fluoride in drinking water in the west plain region of Jilin province, China. *Environmental Geochemistry & Health*, 25: 421-431.
- Borah, J. (2011). Monitoring the fluoride concentration in the Ground water of tea gardens and brick Industry areas of Dibrugarh district, Assam, India. *International Journal of Chemical Sciences*, 9(4): 1613-1618.
- Borah, J. (2013). Estimation of fluoride in the drinking water of Tengakhat circle of the Dibrugarh district, Assam. *Archives of Applied Science Research*, 5 (1): 238-240.

-
- Borah, J., & Saikia, D. (2011). Estimation of the concentration of Fluoride in the Groundwater of Tinsukia Town Master Plan area of the Tinsukia district, Assam, India. *Archives of Applied Science Research*, 3(3): 202-206.
- Boulton, I. C., Cooke, J. A., & Johnson, M. S. (1999). Lesion scoring in field vole teeth: application to the biological monitoring of environmental fluoride contamination. *Environmental Monitoring & Assessment*, 55: 409-422.
- Boyle, D. R., & Chagnon, M. (1995). An incidence of skeletal fluorosis associated with groundwaters of the Maritime Carboniferous Basin, Gaspé Region, Quebec. *Can. Environmental Geochemistry & Health*, 17: 5-12.
- Brahman, K. D., Kazi, T. G., Afridi, H. I., Naseem, H., Arain, S. S., Wadhwa, S. K., & Shah, F. (2013). Simultaneously evaluate the toxic levels of fluoride and arsenic species in underground water of Tharparkar and possible contaminant sources: A multivariate study. *Ecotoxicology and Environmental Safety*, 89: 95-107.
- Brandt, C. S., & Heck, W. W. (1968). Effect of Air Pollution on Vegetation, In Stern, A.C. *Air Pollution*, Vol 1. Academic Press, New York, pp. 401-443.
- Brindha, K., Rajesh, R., Murugan, R., & Elango, L. (2011). Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. *Environmental Monitoring and Assessment*, 172 (1-4): 481-92.
- Buzalaf, M. A. R., & Whitford, G. M. (2011). Fluoride metabolism. In: Buzalaf, M. A. R. (Ed). *Fluoride and the oral environment. Monographs in oral science. vol. 22.* Basel: Karger; pp. 20-36.
- Carpenter, R. (1969). Factors controlling the marine geochemistry of fluoride. *Geochimica et cosmochimica Acta*, 33: 1153-1167.

-
- Carvalho, J. C., Declerck, D., & Vinckier, F. (1998). Oral health status in Belgian 3- to 5-year-old children. *Clinical Oral Investigations*, 2: 26–30.
- Chae, G. T., Yun, S. T., Kwon, M. J., Kim, Y. S., & Mayer, B. (2006). Batch dissolution of granite and biotite in water: Implication for fluorine geochemistry in groundwater. *Geochemical Journal*, 40: 95-102.
- Chakrabarti, S., & Patra, P. K. (2013). Effect of fluoride on superoxide dismutase activity in four common crop plants. *Fluoride*, 46(2):59–62.
- Chakrabarti, S., Patra, P. K., & Mondal, B. (2013). Uptake of fluoride by two paddy (*Oryza sativa* L.) varieties treated with fluoride-contaminated water. *Paddy Water Environment*, 11:619–623.
- Chang, C. C. (1968). Effect of Fluoride on Nucleotides and RNA in Germinating Corn Seedling Roots. *Plant Physiology*, 43: 669-678.
- Chatterjee, A., Roy, R. K., Ghosh, U. C., Pramanik, T., Kabi, S. P., & Biswas, K. (2008). Fluoride in water in parts of Raniganj Coalfield, West Bengal. *Current Science*, 94: 309-311.
- Chebotarev, I. I. (1955). Metamorphism of natural water in the crust of weathering, *Geochimica et Cosmochimica Acta*, 8: 22-48, 137-170, 198-212.
- Chen, H., Yan, M., Yang, X., Chen, Z., Wang, G., Schmidt-Vogt, D., Xu, Y., & Xu, J. (2012). Spatial distribution and temporal variation of high fluoride contents in groundwater and prevalence of fluorosis in humans in Yuanmou County, Southwest China. *Journal of Hazardous Materials*, 235–236: 201– 209.
- Chinoy, N. J., & Narayana, M. V. (1994). In vitro fluoride toxicity in human spermatozoa. *Reproductive Toxicology*, 8(2): 155–159.

-
- Choubisa, S. L. (1999). Some observations on endemic fluorosis in domestic animals in Southern Rajasthan (India). *Veterinary Research Communication*, 23: 457-65.
- Choubisa, S. L. (2007). Fluoridated ground water and its toxic effects on domesticated animals residing in rural tribal areas of Rajasthan (India). *International Journal of Environmental Study*, 64: 151-159.
- Choubisa, S. L. (2008). Dental fluorosis in domestic animals. *Current Science*, 95: 1674-1675.
- Choubisa, S. L. (2010a). Fluorosis in dromedary camels in Rajasthan, India. *Fluoride*, 43: 19-49.
- Choubisa, S. L. (2010b). Natural amelioration of fluoride toxicity (fluorosis) in goats and sheep. *Current Science*, 99: 1331-1332.
- Choubisa, S. L. (2010c). Osteo-dental fluorosis in domestic horses and donkeys in Rajasthan, India. *Fluoride*, 43: 5-12.
- Choubisa, S. L., Mishra, G. V., Sheikh, Z., Bhardwaj, B., Mali, P., & Jaroli, V. J. (2011). Food, fluoride, and fluorosis in domestic ruminants in the Dungarpur District of Rajasthan, India. *Fluoride*, 44(2): 70-76.
- Choubisa, S. L., Sompura, K., & Choubisa, D. K. (1995). Fluoride content in domestic water sources of Dungarpur district of Rajasthan. *Indian Journal of Environmental Health*, 37: 154-60.
- Christian, G. D. (1986). *Analytical Chemistry* (4th Ed.). John Wiley & Sons, New York, pp. 590-592.
- Chunlei, Li, Dejiang, Ni, & Wuhan. (2009). Effect of fluoride on chemical constituents of tea leaves. *Fluoride*, 42(3): 237-243.

-
- Churchill, H. V., Rowley, R. J., & Martin, L. N. (1948). Fluorine content of certain vegetation in Western Pennsylvania area. *Analytical Chemistry*, 20(1): 69-71.
- Clarkson, J. J., & McLoughlin, J. (2000). Role of fluoride in oral health promotion. *International Dental Journal*, 50: 119–128.
- Cooke, J. A., Johnson, M. S., & Davison, A. W. (1978). Uptake and translocation of fluoride in *Helianthus annuus* L. grown in sand culture. *Fluoride*, 11: 76-78.
- Cooke, J., Johnson, M., Davison, A., & Bradshaw, A. (1976). Fluoride in plants colonizing fluorspar mine waste in the Peak District and Weardale. *Environmental Pollution*, 11: 9-23.
- Cordeiro, S., Coutinho, R., & Cruz, J. V. (2012). Fluoride content in drinking water supply in São Miguel volcanic island (Azores, Portugal). *Science of the Total Environment*, 432: 23-36.
- Cronin, S. J., Manaharan, V., Hedley, M. J., & Loganathan, P. (2000). Fluoride: a review of its fate, bio availability and risks of fluorosis in grazed-pasture systems in New Zealand. *New Zealand journal of Agricultural Research*, 43: 295-321.
- Czarnowski, W., Wrześniowska, K., & Krechniak, J. (1996). Fluoride in drinking water and human urine in northern and central Poland. *Science of the Total Environment*, 191(1-2): 177-84.
- D'Alessandro, W. (2006). Human fluorosis related to volcanic activity: a review. *Environmental Toxicology Transaction: Biomedicine and Health*, 10: 21-30.
- da Cunha, L. F., & Tomita, N. E. (2006). Dental fluorosis in Brazil: a systematic review from 1993 to 2004. *Cad Saude Publica*, 22(9): 1809–1816.

-
- Dabkowska, E., Machoy-Mokrzyńska, A., Straszko, J., Machoy, Z., & Samujło, D. (1995). Temporal changes in the fluoride levels of jaws of European deer in industrial regions of Western Pomerania, Poland. *Environmental Geochemistry and Health*, 17: 155–158.
- Darral, N. M. (1989). The effect of air pollutants on physiological processes in plants. *Plant, Cell Environ.*, 12: 1-30.
- Dasarathy, S., Das, T. K., Gupta, I. P., Susheela, A. K., & Tandon, R. K. (1996). Gastroduodenal manifestations in patients with skeletal fluorosis. *Journal of Gastroenterology*, 31(3): 333–337.
- Datta, P. S., & Tyagi, S. K. (1996). Major ion chemistry of groundwater in Delhi area: Chemical weathering processes and groundwater flow regime. *Journal of the Geological Society of India*, 47: 179–188.
- Datta, P. S., Deb, D. L., & Tyagi, S. K. (1996). Stable isotope (^{18}O) investigations on the processes controlling fluoride contamination of groundwater. *Journal of Contaminant Hydrology*, 24: 85-96.
- Dave, R. S., Acharya, D. G., VEDIYA, S. D., & Machhar, M. T. (2010). Status of fluoride in ground water of several villages of Modasa Taluka, North Gujarat for drinking purpose. *Der Pharma Chemica*, 2(2): 237-240.
- Davison, A.W. (1982). The effects of fluorides on plant growth and forage quality. In: Unsworth, M.H. and Ormrod, D.P. (eds). *Effects of Gaseous Air Pollution in Agriculture and Horticulture*. Butterworths, London, pp 267-292.
- Davison, A.W. (1983). Uptake, translocation and accumulation of soil and airborne fluorides by vegetation. In: Shupe, J.L., Peterson, H.B., Leone N.C.(eds) *Fluorides*:

-
- Effects on vegetation, Animals and Humans. Paragon Press, Salt Lake City, Utah, pp. 62-82.
- Day, T. K., & Powell-Jackson, P. R. (1972). Fluoride, water hardness, and endemic goitre. *Lancet*, 1(7761): 1135–1138.
- Dean, H. T. (1933). Distribution of mottled enamel in the United States. *Public Health Reports*, 48(25): 703-734.
- Deer, W. A., Howie, R. A., & Zussman, J. Z. (1983) *An Introduction to Rock Forming Minerals*, 528. The English Language Book Society and Longman.
- Den Besten, P. K. (1994). Dental fluorosis: its use as a biomarker. *Advances in Dental Research*, 8: 105–110.
- Desai, V. K., Solanki, D. M., & Bansalm, R. K. (1993). Epidemiological study on goitre in endemic fluorosis district of Gujarat. *Fluoride*, 26(3): 187–190
- Dey, R. K., Swain, S. K., Mishra, S., Sharma, P., Patnaik, T., Singh, V. K., Dehury, B. N., Jha, U., & Patel, R. K. (2012). Hydrogeochemical processes controlling the high fluoride concentration in groundwater: a case study at the Boden blocks area, Orissa, India. *Environmental Monitoring and Assessment*, 184: 3279– 3291.
- Dhar, V., & Bhatnagar, (2009) M. Physiology and toxicity of fluoride. *Indian Journal of Dental Research*, 20(3):
- Dharmagunawardhane, H. A., & Dissanayake, C. B. (1993). Fluoride problems in Sri Lanka. *Environmental Management and Health*, 4(2): 9-16.
- Dissanayake, C. B. (1991). The fluoride problem in the ground water of Sri Lanka - environmental management and health. *International Journal of Environmental Studies*, 38(2): 137-155.

-
- Domenico, P. A. (1972). Concepts and Models in Ground water Hydrology, McGraw-Hill, Inc, p. 405.
- Doneen, L. D. (1964). Notes on water quality in agriculture. Water Science and Engineering, University of California, Davis.
- Doull, J., Boekelheide, K., Farishian, B. G., Isaacson, R. L., Klotz, J. B., Kumar, J. V. et al. (2006). Fluoride in drinking water: a scientific review of EPA's standards, Committee on Fluoride in Drinking Water, Board on Environmental Studies and Toxicology, Division on Earth and Life Sciences, National Research Council of the National Academies. National Academies Press, Washington, DC, p 530. (<http://www.nap.edu>)
- Dutta, J., Nath, M., Chetia, M., & Misra, A. K. (2010). Monitoring of Fluoride Concentration In Ground Water of Small Tea Gardens in Sonitpur District, Assam, India: Correlation with physico-chemical Parameters. International Journal of ChemTech Research, 2(2): 1199-1208.
- Edmunds, W. M., & Smedley, P. L. (2005). Fluoride in natural waters. In: Selinus O (ed) Essentials of medical geology. Elsevier Academic Press, Burlington, MA, pp. 301–329.
- Ekstrand, J. (1996). Fluoride metabolism. In: Fejerskov, O., Ekstrand, J., Burt, B. A. (Eds.), Fluoride in dentistry. Second ed. Copenhagen: Munksgaard, pp. 55 –68.
- Elloumi, N., Abdallah, F. B., Mezghani, I., Rhouma, A., & Boukhris, M. (2005). Effect of fluoride on almond seedlings in culture solution. Fluoride, 38: 193-198.
- Elrashidi, M.A. & Lindsay, W.L. (1985). Solubility Relationships of Fluorine Minerals in Soils. Soil Science Society of America Journal, 4: 1133-1136.

-
- Farooqi, A., Masuda, H., Kusakabe, M., Naseem, M., & Firdous, N. (2007). Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. *Geochemical Journal*, 41: 213-234.
- Fawell, J., Bailey K., Chilton J., Dahi, E., Fewtrell. L., & Magara, Y. (2006). Fluoride in drinking water, WHO, IWA publishing, 1-144.
- Florence, P. L., Raj, A. P., & Ramachandramoorthy, T. (2013). Ground water quality assessment of Gangavalli Taluk, Salem District, Tamil Nadu, India using multivariate statistical techniques. *IRACST – Engineering Science and Technology: An International Journal (ESTIJ)*, 3(1): 2250-3498.
- Fordyce, F. M., Vrana, K., Zhovinsky, E., Povoroznuk, V., Toth, G., & Hope, B. C. (2007). A health risk assessment for fluoride in Central Europe. *Environ. Geochem. Health*, 29(2): 83– 102.
- Freni, S. C. (1994). Exposure to high fluoride concentrations in drinking water is associated with decreased birth rates. *Journal of Toxicology and Environmental Health*, 42(1): 109–121.
- Fridriksson, S. (1983). Fluoride problems following volcanic eruption, In: Shupe, J.L., Peterson, H.B., & Leone, N.C., (Eds.) *Fluorides, - Effect on vegetation, animals and humans*, Pearagon Press, UT, 339-344.
- FRRDF. (1999). State of art report on the extent of fluoride in drinking water and the resulting endemicity in India. *Fluorosis Research and Rural Development Foundation*, New Delhi.
- Fung K. F., Zhang, Z. Q., Wong, J. W. C., & Wong, M. H. (1999). Fluoride Contents in Tea and Soil from Tea Plantations and the Release of Fluoride into Tea Liquor during Infusions. *Environmental Pollution*, 104: 197-205.

-
- Gaciri, S. J., & Davies, T. C. (1993). The occurrence and geochemistry of fluoride in some natural waters of Kenya. *Journal of Hydrology*, 143: 395-412.
- Garber, K. (1967). Über den Fluorgehalt der Pflanzen. *Qual. Plant. Mater. Veg.*, 15: 29-35.
- Garg, V. K., Suthar, S., Singh, S., Sheoran, A., Garima, M., & Jain, S. (2009). Drinking water quality in villages of southwestern Haryana, India: assessing human health risks associated with hydrochemistry. *Environmental Geology*, 58(6): 1329–1340
- Garrels, R. M., & Christ, C. L. (1965). *Solutions minerals and equilibria* (p. 450). New York: Harper and Row.
- Gaumat, M. M., Rastogi, R., & Misra, M. M. (1992). Fluoride level in shallow groundwater in central part of Uttar Pradesh. *Bhu-Jal News*, 7(2 & 3): 17-19.
- Gautam, R., & Bhardwaj, N. (2010). Bioaccumulation of fluoride in different plant parts of *Hordeum vulgare* (barley) var. rd-2683 from irrigation water. *Fluoride*, 43(1):57–60.
- Gautam, R., & Bhardwaj, N. (2010). Groundwater quality assessment of Nawa Tehsil in Nagaur district (Rajasthan) with special reference to Fluoride. *Environmentalist*, 30: 219–227.
- Gautam, R., Bhardwaj, N., & Saini, Y. (2010). Fluoride accumulation by vegetables & crops grown in nawa tehsil of Nagaur district (Rajasthan, India). *Journal of Phytology*, 2(2): 80-85.
- Gautam, R., Bhardwaj, N., & Saini, Y. (2011). Study of fluoride content in groundwater of Nawa Tehsil in Nagaur, Rajasthan. *Journal of Environmental Biology*, 32 (1) 85-89.
- Gazzano, E., Bergandi, L., Riganti, C., Aldieri, E., Doublier, S., Costamagna, C., Bosia, A., & Ghigo, D. (2010). Fluoride Effects: The two faces of Janus. *Current Medicinal Chemistry*, 17: 2431-2441.

-
- Ge, Y., Niu, R., Zhang, J., & Wang, J. (2010). Proteomic analysis of brain proteins of rats exposed to high fluoride and low iodine. *Archives of Toxicology*, doi:10.1007/s00204-010-0537-5
- Geeson, N. A., Abrahams, P. W., Murphy, M. P. & Thronton, I. (1998). Fluorine and metal enrichment of soil and pasture herbage in the old mining areas of Derbyshire, UK. *Agriculture, Ecosystems and Environment*, 68: 217-231.
- Gessner, B. D., Beller, M., Middaugh, J. P., & Whitford, G. M. (1994). Acute fluoride poisoning from a public water system. *New England Journal of Medicine*, 330(2): 95–99. doi:10.1056/NEJM199401133300203
- Ghosh, S., Chakraborty, S., Roy, B., Banerjee, P., & Bagchi, A. (2010). Assessment of health risks associated with fluoride contaminated ground water in Birbhum district of West Bengal, India. *Journal of Environmental Protection Science*, 4: 13-21.
- Gillespie, R. J., Humphries, D. A., Baird, N. C., & Robinson, E. A. (1989). *Chemistry*. Second ed. Allyn and Bacon, Boston.
- Grandjean, P., & Olsen, J. H. (2004). Extended follow-up of cancer incidence in fluoride-exposed workers. *Journal of the National Cancer Institute*, 96(10): 802–203.
- Grandjean, P., Horder, M., & Thomassen, Y. (1990). Fluoride, aluminum, and phosphate kinetics in cryolite workers. *Journal of Occupational Medicine*, 32(1): 58–63. doi:10.1097/00043764-199001000-00015
- Grandjean, P., Olsen, J. H., Jensen, O. M., & Juel, K. (1992). Cancer incidence and mortality in workers exposed to fluoride. *Journal of the National Cancer Institute*, 84(24):1903–1909. doi:10.1093/jnci/84.24.1903
- Greenwood, N. N., & Earnshaw, A. (1984). *Chemistry of the Elements*. Pergamon Press, Toronto.

-
- Guan, Z. Z., Wang, Y. N., Xiao, K. Q., Dai, D. Y., Chen, Y. H., Liu, J. L., Sindelar, P., & Dallner, G. (1999). Influence of chronic fluorosis on membrane lipids in rat brain. *Neurotoxicology and Teratology*, 20: 537–542.
- Guo, Q., Wang, Y., Ma, T., & Ma, R. (2007). Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. *Journal of Geochemical Exploration*, 93: 1-12.
- Guo, Z., Tan, H., Zhu, Z., Lu, S., & Zhou, B. (2005). Effect of intermediates on ascorbic acid and oxalate biosynthesis of rice and inrelation to its stress resistance. *Plant Physiology and Biochemistry*, 43: 955-962.
- Gupta, I. P., Das, T. K., Susheela, A. K., Dasarathy, S., & Tandon, R. K. (1992). Fluoride as a possible aetiological factor in non-ulcer dyspepsia. *Journal of Gastroenterology and Hepatology*, 7(4): 355–359.doi:10.1111/j.1440-1746.1992.tb00996.x
- Gupta, S. K., Gupta, R. C., Seth, & A. K. (1994). Increased incidence of Spina Bifida Occulta in fluorosis prone areas. *Indian Pediatr*, 31(11): 1431–1432.
- Gupta, S. K., Gupta, R. C., Seth, A. K., & Chaturvedi, C. S. (1995). Increased incidence of Spina Bifida Occulta in fluorosis prone areas. *Acta Paediatrica Japonica*, 37(4): 503–506.
- Gupta, S., & Banerjee, S. (2009). Fluoride accumulation in paddy (*Oryza sativa*) irrigated with fluoride-contaminated groundwater in an endemic area of the Birbhum District, West Bengal. *Fluoride*, 42(3): 224-227.
- Gupta, S., & Banerjee, S. (2011). Fluoride Accumulation in Crops and Vegetables and Dietary Intake in a Fluoride-Endemic Area of West Bengal. *Fluoride*, 44(3):153–157.

-
- Gupta, S., Banerjee, S., & Mondal, S. (2009). Phytotoxicity of fluoride in the germination of paddy (*Oryza sativa*) and its effect on the physiology and the biochemistry of germinated seedlings. *Fluoride*, 42(2):142-146.
- Gupta, S., Banerjee, S., Saha, R., Datta, J. K., & Mondal, N. (2006). Fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum District, West Bengal, India. *Fluoride*, 39(4): 318-320.
- Gupta, S., Maheto, A., Roy, P., Datta, J. K., & Saha, R. N. (2008). Geochemistry of groundwater Burdwan district, West Bengal India. *Environmental Geology*, 53:1271–1282. doi:10.1007/s00254-007-0725-7
- Gupta, S., Mondal, D., & Bardhan, A. (2012). Geochemical provenance and spatial distribution of fluoride in Groundwater in parts of Raniganj coal field, West Bengal, India. *Archives of Applied Science Research*, 4 (1): 292-306.
- Gutowska, I., Machoy, Z., Machaliński, B., & Chlubek, D. (2004). Living conditions of deer in the provinces of Western Pomerania and Lubuskie as revealed by mandibular content of fluoride, calcium, and magnesium. 1. Inter-relations between fluoride, calcium, and magnesium content in mandible. *Ann. Acad. Med. Stet.* (suppl), 50: 42-46, in Polish, English summary.
- Haidouti, C. (1991). Fluoride distribution in soils in the vicinity of a point emission source in Greece. *Geoderma*, 49: 129-138.
- Handa, B. K. (1975). Geochemistry and genesis of fluoride containing groundwater in India. *Ground Water*, 3:275–281
- Handa, B. K. (1988). Fluoride occurrence in natural waters in India and its significance. *Bhu-Jal News*, 3(2): 31-37.

-
- Harilal, C. C., Hashim, A., Arun, P. R., & Baji, S. (2004). Hydro geochemistry of two rivers of Kerala with special reference to drinking water quality. *Ecology Environment and Conservation*, 10(2):187–192.
- Hayes, A. W. (2001). *Principles and methods of toxicology*, 4th Edition, Taylor and Francis, London, England.
- Helgeson, H. C. (1969). Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science*, 267: 279-804.
- Hem, J. (1989). Study and interpretation of the chemical characteristics of natural water(3rd edn). U.S. Geological Survey Water- Supply Paper 2254. 263p.
- Hem, J. D. (1985). Study and interpretation of chemical characteristics of natural water. US Geological Survey, Water Supply Paper 2254.
- Hileman, B. (1988). Fluoridation of water: questions about health risks and benefits remain after more than 40 years. *Chemical & Engineering News*, 1: 26–42.
- Hitchcock, A. E., McCune, D. C., Weinstein, L. H., MacLean, D. C., Jacobson, J. S., & Mandl, R. H. (1971). Effects of hydrogen fluoride fumigation on alfalfa and Orchard Grass: A summary of experiments from 1952 through 1965. Contribution from the Boyce Thompson Institute, 24: 363-386.
- Hitchcock, A. E., Zimmerman, P. W., & Coe, R. R. (1962). Results of Ten Years of Work (1951-1960) on the Effect of Fluoride on Gladiolus. Con- trib. Boyce Thompson Inst., 21: 303-344.
- Hodge H. C., & Smith F. A. (1977). Occupational fluoride exposure. *Journal of Occupational Medicine*, 19: 12-39.

-
- Horowitz, H. S. (1986). Indexes for measuring dental fluorosis. *Journal of Public Health Dentistry*, 46(4): 179–183.
- Horvath, I., Klasova, A., & Navara, J. (1978). Some physiological and ultra-structural changes of *Vicia faba* L after fumigation with hydrogen fluoride. *Fluoride*, 11: 89–99.
- Hrudey, S. E., Soskolne, C. L., Berkel, J., & Fincham, S. (1990). Drinking water fluoridation and osteosarcoma. *Canadian Journal of Public Health*, 81(6): 415–416.
- Huang, P. M., & Jackson, M. L. (1965). Mechanism of reaction of neutral fluoride solution with layer silicates and oxides of soils. *Soil Science Society Proceedings*, 29: 661–665.
- Hudak, P. F., & Sanmanee, S. (2003). Spatial patterns of nitrate, chloride, sulfate, and fluoride concentrations in the woodbine aquifer of north-central Texas. *Environmental Monitoring and Assessment*, 82: 311–320.
- Indermitte, E., Saava, A., & Karro, E. (2009). Exposure to high fluoride drinking water and risk of dental fluorosis in Estonia. *International Journal of Environmental Research and Public Health*, 6: 710–721.
- IPCS (2002). Fluorides. *Environmental Health Criteria* 227. World Health Organization, Geneva.
- Jacks, G. (1973). Geochemistry of fluoride in ground water. *Swedish Dental Journal*, 66:211–215.
- Jacks, G., Bhattacharya, P., Chaudhary, V., & Singh, K. P. (2005). Controls on the genesis of some high-fluoride groundwaters in India. *Applied Geochemistry*, 20: 221–228.
- Jelenko, I., & Pokorny, B. (2010). Historical biomonitoring of fluoride pollution by determining fluoride contents in roe deer (*Capreolus capreolus* L.) antlers and

-
- mandibles in the vicinity of the largest Slovene thermal power plant. *Science of the Total Environment* 409: 430-438. doi:10.1016/j.scitotenv.2010.10.012
- Jha, S. K., Nayak, A. K., & Sharma, Y. K. (2011). Site specific toxicological risk from fluoride exposure through ingestion of vegetables and cereal crops in Unnao district, Uttar Pradesh, India. *Ecotoxicology and Environmental Safety*, 74: 940–946.
- Jha, S. K., Nayak, A. K., Sharma, Y. K. (2009). Potential fluoride contamination in the drinking water of Marks Nagar, Unnao district, Uttar Pradesh. *Environmental Geochemistry and Health*, 32(3): 217-226.
- Jha, S. K., Nayak, A. K., Sharma, Y. K., Mishra, V. K., & Sharma, D. K. (2008). Fluoride Accumulation in Soil and Vegetation in the Vicinity of Brick Fields. *Bulletin of Environmental contamination and Toxicology*, 80: 369-373.
- Jolly, S. S., Singh, L. D., Prasad, S., Sharma, R., Singh, B. M., & Mathur, O. C. (1969). An epidemiological study of endemic fluorosis in Punjab. *Indian Journal of Medical Research*, 57:1333–1346.
- Jones, L., & Atkins, P., (1999). *Chemistry Molecules Matter and Change*. W.H. Freeman and Company. 998 p.
- Jooste, P. L., Weight, M. J., Kriek, J. A., & Louw, A. J. (1999). Endemic goitre in the absence of iodine deficiency in schoolchildren of the northern cape province of South Africa. *European Journal of Clinical Nutrition*., 53(1): 8–12. doi:10.1038/sj.ejcn.1600671
- Joseph, S., & Gadhia, P. K. (2000). Sister chromatid exchange frequency and chromosome aberrations in residents of fluoride endemic regions of South Gujarat. *Fluoride*, 33: 154-158.

-
- Juncos, L. I., & Donadio, J. V. Jr. (1972). Renal failure and fluorosis. *Journal of the American Medical Association*, 222(7):783-785. doi:10.1001/jama.222.7.783
- Kadu, A. S., Nampalliwar, A. R., & Gothecha, V. K. (2012). Skeletal Fluorosis Due To Chronic Fluoride Intoxication- An Over Review. *International Journal of Ayurvedic and Herbal Medicine*, 2(3): 561-568.
- Kamaluddin, M., & Zwiazek, J. J. (2003). Fluoride inhibits root water transport and affects leaf expansion and gas exchange in aspen (*Populus tremuloides*) seedlings. *Physiologia Plantarum*, 117: 368-375.
- Kaminsky, L. S., Mahoney, M. C., Leach, J., Melius, J., & Miller, J. M. (1990). Fluoride: benefits and risks of exposure. *Critical Reviews in Oral Biology & Medicine*, 1: 261–281.
- Karthikeyan, G., & Shunmugasundarraaj, A. (2000). Isopleth mapping and in-situ fluoride Dependence on water quality in the Krishnagiri block of Tamil Nadu in South India. *Fluoride*, 33: 121-127.
- Kierdorf, H., Kierdorf, U., Richards, A., & Sedlacek, F. (2000). Disturbed enamel formation in wild boars (*Sus scrofa* L.) from fluoride polluted areas in Central Europe. *Anatomical Record*, 259: 12–24. doi:10.1002/(SICI)1097-0185(20000501)259:1<12::AID-AR2>3.0.CO;2-6
- Kierdorf, U., Kierdorf, H., Sedlacek, F., & Fejerskov, O. (1996). Structural changes in fluorosed dental enamel of reed deer (*Cervus elaphus* L.) from a region serve environmental pollution by fluorides. *Journal of Anatomy*, 188:183 –195.
- Kim, C. G., Power, S. A., & Bell, J. N. B. (2003). Effects of cadmium and soil type on mineral and Carbon partitioning in seedlings of *Pinus sylvestris*. *Water, Air, & Soil Pollution*, 145: 253-66.

-
- Kim, K., & Jeong, G. Y. (2005). Factors influencing natural occurrence of fluoride rich ground waters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere*, 58 (10): 1399-1408.
- Kim, Y., Kim, J. Y., & Kim, K. (2010). Geochemical characteristics of fluoride in groundwater of Gimcheon, Korea: Lithogenic and agricultural origins. *Environmental Earth Sciences*, doi:10.1007/s12665-010-0789-7
- Koritnig, S. (1978). Fluorine. In: Wedepohl, K.H. (Ed.), *Handbook of Geochemistry*, vol. II/1. Springer-Verlag, Berlin, 9C1-B9O3.
- Krauskopf, K. B., & Bird, D. K. (1995). *An introduction to geochemistry*. McGraw-Hill Int., Singapore, 647.
- Kumar, K. A., & Rao, A. V. B. (2008). Physiological Responses to Fluoride in Two Cultivars of Mulberry. *World Journal of Agricultural Sciences*, 4 (4): 463-466.
- Kumar, K. A., Varaprasad, P., & Rao, A. V. B. (2009). Effect of Fluoride on Catalase, Guaiacol Peroxidase and Ascorbate Oxidase Activities in Two Varieties of Mulberry Leaves (*Morus alba* L.). *Research Journal of Earth Sciences*, 1(2): 69-73.
- Kundu, M. C., & Mandal, B. (2009). Assessment of potential hazards of fluoride contamination in drinking groundwater of an intensively cultivated district in West Bengal, India. *Environmental Monitoring and Assessment*, 152: 97-103.
- Kundu, M. C., Mandal, B., & Hazra, G. C. (2009). Nitrate and fluoride contamination in groundwater of an intensively managed agroecosystem: a functional relationship. *Science of the Total Environment*, 407: 2771--2782.
- Kundu, M. C., & Mondal, B. (2010). Fluoride concentration in ground water in the North 24 Parganas District of West Bengal, India. *Fluoride*, 43(2): 116-210.

-
- Kundu, N., Panigrahi, M. K., Tripathy, S., Munsu, S., Powell, M. A., & Hast, B. R. (2001). Geochemical appraisal of fluoride contamination of ground water in the Nayagarh district of Orissa, India. *Env. Geol.*, 41: 451-60.
- Lakshmanan, E., Kannan, K., & Senthil Kumar, M. (2003). Major ion chemistry and identification of hydrogeochemical process of groundwater in part of Kancheepuram district, Tamilnadu, India. *Journal of Environmental Geosciences* 10(4): 157–166.
- Lal, B., & Ambasht, R. S. (1981). Impairment of chlorophyll content in leaves of *Diospyros melanoxylon* by fluoride pollution. *Water, Air, & Soil Pollution*, 16: 361-365.
- Lee, C. J., Miller, G. W., & Welkie, G. W. (1965). The Effects of Hydrogen Fluoride and Wounding on Respiratory Enzyme5 in Soybean Leaves. *International Journal of Air and Water Pollution*, 10:169-181.
- Li, L. (2003). The biochemistry and physiology of metallic fluoride: action, mechanism and implication. *Critical Reviews in Oral Biology & Medicine*, 14(2): 100-114.
- Li, X. S., Zhi, J. L., & Gao, R. O. (1995). Effect of fluoride exposure on intelligence in children. *Fluoride*, 28(4): 189–192.
- Li, Y., Dunipace, A. J., & Stookey, G. K. (1988). Genotoxic effects of fluoride: a controversial issue. *Mutation Research*, 195: 127-136.
- Lori, J. A. (1987). Determination of some essential Minerals in the Source Soil and two cultivars of white yam (*Discrorea rotundata*). M.Sc thesis, Ahmadu Bello University, Zaria, Nigeria.
- Lovelace, J., Miller, G.W. & Welkie, G.W. (1968) The Accumulation of Fluorocitrate in Forage Crops Collected Near a Phosphate Plant. *Atmospheric Environment*, 2: 187-190.

-
- Lowry, O. H., Rose Brough, N. J., Fan, A. L., & Randal, R. J. (1951). Protein measurement with the Folin phenol reagent. *Journal of Biological Chemistry*, 193: 265-275.
- Lu, Y., Sun, Z. R., Wu, L. N., Wang, X., Lu, W., & Liu, S. S. (2000). Effect of high-fluoride water on intelligence in children. *Fluoride*, 33(2): 75–78.
- Macicek, P., & Krook, L. P. (2008). Fluorosis in horses drinking artificially fluoridated water. *Fluoride*, 41:177 – 183.
- MacLean, D. C., McCune, D. C., Weinstein, L. H., Mandl, R. H., & Woodruff, G. N. (1968). Effects of Acute Hydrogen Fluoride and Nitrogen Di- oxide Exposures on Citrus and Ornamental Plants of Central Florida. *Environmental Science and Technology*, 2: 444-449.
- Madhnure, P., Sirsikar, D. Y., Tiwari, N., Ranjan, B., & Malpe, D. B. (2007). Occurrence of fluoride in the groundwaters of Pandharkawada area, Yavatmal district, Maharashtra, India. *Current Science*, 92(5): 675-679.
- Mahapatra, M. K. (2007). Health impacts of fluoride. In Padhi, T. K., Sahu, S. (Eds.), *Fluoride Menace in Orissa*. RCDC Centre for Water for Life 424, Sahid Nagar, Bhubaneswar: Perfect Print & Graphics Pvt. Ltd.
- Mahapatra, M. K. , Mishra, A., & Das, B. P. (2005). Fluorosis 1st reported in Nuapada district of Orissa, India. *India. Ecology, Environment and Conservation*, 11(2): 277-80.
- Mahoney, M. C., Nasca, P. C., Burnett, W. S., & Melius, J. M. (1991). Bone cancer incidence rates in New York State: Time trends and fluoridated drinking water. *American Journal of Public Health*, 81(4): 475-479.

-
- Mamatha, P., Rao, S.M. (2010). Geochemistry of fluoride rich groundwater in Kolar and Tumkur Districts of Karnataka. *Environmental Earth Sciences*, 61:131–142.
- Mangukiya, R., Bhattacharya, T., & Chakraborty, S. Quality Characterization of Groundwater using Water Quality Index in Surat city, Gujarat, India. *International Research Journal of Environment Sciences*, 1(4): 14-23.
- Marschner, H. (1995). Mineral nutrition of plants, 2nd edn. Academic Press, London, 889 pp.
- Matthess, G. (1982). *The Properties of Groundwater*, 498. Wiley & Sons, New York.
- Matvælastofnun (MAST-Icelandic Food and Veterinary Authority) (2010). Guidelines for livestock owners in areas where there is downfall of volcanic ash. Available from: <http://www.mast.is/Uploads/document/leidbeiningar/Enska/downfalofashguidelines.pdf>
- Mazhar Nazeeb Khan, S. M., & Ravikumar, A. (2013). Role of Alkalinity for the Release of Fluoride in the Groundwater of Tiruchengode Taluk, Namakkal District, Tamilnadu, India. *Chemical Science Transactions*. DOI:10.7598/cst2013.037
- McCready, R. M., Guggolz, J., Silviera, V. & Owens, H. S. (1950). Determination of starch and amylase in vegetables. *Analytical Chemistry*, 22: 1156-1158.
- McCune, D. C., & Hitchcock, A. E. (1971). Fluoride in forage: Factors determining its accumulation from the atmosphere and concentration in the plant. In: *Proceedings of the 2nd International Clean Air Congress*. Academic Press, New York, pp 289-292.
- McCune, D. C., Hitchcock, A. E., Jacobson, J. S., & Weinstein, L. H. (1965). Fluoride accumulation and growth of plants exposed to particulate cryolite in the atmosphere. *Contributions from the Boyce Thompson Institute*, 23: 1-12.

-
- McCune, D. C., Silberman, D. H., & Weinstein, L. H. (1977). Effects of relative humidity and free water on the phytotoxicity of hydrogen fluoride and cryolite. In: Proceedings, 4th International Clean Air Congress. Japanese Union of Pollution Prevention Association, Tokiyo, pp 116-1199.
- McLaughlin, M. J., Tiller, K. G. Naidu, R. & Stevens, D. P. (1996). Review: the behavior and environmental impact of contaminants in fertilizers. *Australian Journal of Soil Research*, 34: 1-54.
- McNulty, I. B., & Newman, D. W. (1961). Mechanism(s) of fluoride induced chlorosis. *Plant Physiology*, 36: 385-358.
- McQuaker NR, & Gurney M. (1977). Determination of total fluoride in soil and vegetation using an alkali fusion-selective ion electrode technique. *Analytical Chemistry*, 49: 53-56.
- Meenakshi, & Maheshwari R. C. (2006). Fluoride in drinking water and its removal. *Journal of Hazardous Materials*, B137: 456–463.
- Messaïfa, A. (2008). Fluoride contents in groundwaters and the main consumed foods (dates and tea) in Southern Algeria region. From the issue entitled "Special Issue: Groundwater Flow - selected papers from XXXIII IAH Congress, Zacatecas, Mexico (233-320)". *Environmental Geology*, 55(2): 377-383.
- Miller, G. W., Shupe, J. L., & Vedina, O. T. (1999). Accumulation of fluoride in plants exposed to geothermal and industrial water. *Fluoride*, 32: 74-83.
- Mirlean, N., & Roisenberg, A. (2007). Fluoride distribution in the environment along the gradient of a phosphate-fertiliser production emission (southern Brazil). *Environmental Geochemistry and Health*, 29(3): 179-87.

-
- Mitra, S., & Kumar, S. (2013). Fluoride and other inorganic parameters in drinking water of tube well, ring well and PHE of Hojai sub-division of Nagaon district, Assam, India. *International Journal of Chemical Sciences*, 11(1): 186-196.
- Moghaddam, A. A., & Fijani, E. (2008). Distribution of fluoride in groundwater of Maku area, northwest of Iran. *Environmental Geology*, 56: 281–287.
- Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management*, 91: 67–77.
- Mondal, N. C., Prasad, R. K., Saxena V. K., Singh Y., & Singh V. S. (2009). Appraisal of highly fluoride zones in groundwater of Kurmapalli watershed, Nalgonda district, Andhra Pradesh (India). *Environmental Earth Sciences*, 59: 63-73.
- Mondal, N. K., Pal, K. C., & Kabi, S. (2012). Prevalence and severity of dental fluorosis in relation to fluoride in ground water in the villages of Birbhum District, West Bengal, India. *Environmentalist*, 3: 70-84.
- Moore, S., & Stein, W. H. (1948). In *Methods in Enzymol* (Eds. Colwick SP and Kaplan ND). New York: Academic Press.
- Motalane, M. P., & Strydom, C. A. (2004). Potential groundwater contamination by fluoride from two South African phosphogypsums. *Water SA*, 30 (4): 465-468.
- Müller, K. (2005). *Fluorid im Grundwasser: Mögliche Ursachen und Aufbereitungstechnik en in Entwicklungsländern*. Diplomarbeit ETH Zürich.
- Murray, J. J. (1986). *Appropriate use of fluorides for human health*. World Health Organization (WHO), Geneva, Switzerland.

-
- Nanyaro, J. T., Aswathanarayana, U., Mungure, J. S., & Laiiermo P. W. (1984). A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. *Journal of African Earth Sciences*, 2(2): 129-140.
- Narasayya, B. L. (1970). Mineralogy of chromite, magnetite and apatite deposits of parts of eastern ghats, Andhra Pradesh, India. PhD Thesis, Andhra University, Andhra Pradesh, India.
- NAS (1971). Biologic Effects of Air Pollutants: Fluorides. National Academy of Sciences, Washington, DC.
- Naseem, S., Rafique, T., Bashir, E., Bhangar, M. I., Laghari, A., & Usmani, T. H. (2010). Lithological influences on occurrence of high-fluoride groundwater in Nagar Parkar area, Thar Desert, Pakistan. *Chemosphere*, 78: 1313–1321.
- NHMRC (1999). Review of Water Fluoridation and Fluoride Intake from Discretionary Fluoride Supplements, National Health and Medical Research Council, Melbourne.
- Nogami, K., Iguchi, M., Ishihara, K., Hirabayashi, J., & Miki, D. (2006). Behavior of fluorine and chlorine in volcanic ash of Sakurajima volcano, Japan in the sequence of its eruptive activity. *Earth Planets Space*, 58: 595-600.
- Obel. A. O. (1982). Goitre and fluorosis in Kenya. *East African Medical Journal*, 59(6): 363–365.
- Oelschläger, W., Wöhlbier, W., & Menke, K. H. (1967). Über Fluorgehalte pflanzlicher, tierischer und anderer Stoffe aus Gebieten ohne und mit Fluoremissions. *Z. Landwirt, Forsch.*, 20: 1-285.
- Okibe, F. G., Ekanem, E. J., Paul, E. D., Shallangwa, G. A., Ekwumemgbo, P. A., Sallau, M. S., & Abanka, O. C. (2010). Fluoride Content of Soil and Vegetables from

-
- Irrigation Farms on the Bank of River Galma, Zaria, Nigeria. *Australian Journal of Basic and Applied Sciences*, 4(5): 779-784.
- Ortiz-Perez, D., Rodriguez-Martinez, M., Martinez, F., Borja-Aburto, V. H., Castelo, J., & Grimaldo, J. I. (2003). Fluoride-induced disruption of reproductive hormones in men. *Environmental Research*, 93(1): 20–30. doi:10.1016/S0013-9351(03) 00059-8
- Oruc, N. (2008). Occurrence and problems of high fluoride waters in Turkey: An overview. From the issue entitled "Medical Geology in Developing Countries, Part 2. *Environmental Geochemistry and Health*, 30(4): 315-323.
- Ozsvath, D. L. (2009). Fluoride and environmental health: a review. *Reviews in Environmental Science and Biotechnology*, 8: 59–79.
- Paliwal, K.V. (1972). Irrigation with saline water [Z]. Monogram No. 2(new series). IARI, New Delhi, p 198.
- Pandey, J., & Pandey, U. (2011). Fluoride contamination and fluorosis in rural community in the vicinity of a phosphate fertilizer factory in India. *Bull. Environmental Contamination and Toxicology*, 87: 245–249. doi:10.1007/s00128-011-0344-6.
- Pant, S., Pant, P., & Bhiravamurthy, P. V. (2008). Effects of fluoride on early root and shoot growth of typical crop plants of India. *Fluoride*, 41: 57-60.
- Parikh, P., & Parikh, R. (2013). Current status of fluoride contamination in ground water of Kheralu block of Mehasana district, Gujarat. *International Journal of Environmental Sciences*, 3(6): 2199-2207.
- Patra, P.K., Mandal, B. & Chakraborty S. (2010). Hydrogeochemistry of fluoride rich groundwater in Birbhum district of West Bengal, India. *The Ecosan*, 4(2&3): 209-211.

-
- Paul, E. D., Gimba, C. E., Kagbu, J. A., Ndukwe, G. I., & Okibe, F. G. (2011). Spectrometric Determination of Fluoride in Water, Soil and Vegetables from the Precinct of River Basawa, Zaria, Nigeria. *Journal of Basic and Applied Chemistry*, 1(6): 33-38.
- Paya, P., & Bhatt, S. A. (2010). Fluoride Contamination in Groundwater of Patan District, Gujarat, India. *International Journal of Engineering Studies*. 2(2):171-177.
- Penman, A. D., Brackin, B. T., & Embrey, R. (1997). Outbreak of acute fluoride poisoning caused by a fluoride overfeed, Missis-sippi, 1993. *Public Health Reports*, 112(5): 403–409.
- PHED report, 2009; http://www.wbphed.gov.in/Static_pages/fluoride.html
- Pickering, W. F. (1985). The mobility of soluble fluoride in soils. *Environmental Pollution Series B*, 9: 281–308.
- Piekos, R., & Paslawska, S. (1998). Leaching characteristics of fluoride from coal fly ash. *Fluoride*, 31(4): 188-192.
- Pierre, D., Glynn, L., & Plummer, N. (2005). Geochem-istry and the understanding of ground-water systems. *Hydrogeology Journal*, 13: 263–287.
- Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water analyses. *American Geophysical Union Transactions*, 25: 914 – 923.
- Piper, A. M. (1953). A graphic procedure I the geo-chemical interpretation of water analysis. *USGS Groundwater Note no. 12*.
- Pizzo, G., Piscopo, M. R., Pizzo, I., & Giuliana, G. (2007). Community water fluoridation and caries prevention: a critical review. *Clinical Oral Investigations*, 11: 189–193.

-
- Prasad, B., & Mondal, K. K. (2006). Leaching Characteristics of Fluoride from Coal Ash. *Asian Journal of Water, Environment and Pollution*, 4(2): 17-21.
- Purandara, B. K., Varadarajan, N., & Jayashree, K. (2003). Impact of sewage on ground water: a case study. *Pollution Research*, 22(2):189–197.
- Raja Reddy, D., Lahiri, K., Ram Mohan Rao, N. V., Vedanayakam, H. S., Ebenezer, L. N., & Suguna R. M. (1985). Trial of magnesium compounds in the prevention of skeletal fluorosis—an experimental study. *Fluoride*, 18(3): 135–140.
- Raju, K.C.C, Karemuddin, Md. & Prabhakara Rao, P. (1979). Operation Anantapur. Geological Survey of India, Miscellaneous Publication No. 47,57.
- Raju, N. J., Dey, S., & Das, K. (2009). Fluoride contamination in groundwaters of Sonbhadra District, Uttar Pradesh, India. *Current Science*, 96(7):979-984.
- Ramakrishnaiah, C. R., Sadashivaiah, C., & Ranganna, G. (2009). Assessment of water quality index for the groundwater in Tumkur Taluk, Karnataka State, India. *E-Journal of Chemistry*, 6: 523-530.
- Ramamohana Rao, N. V., Suryaprakasa Rao, K., & Schuiling, R. D. (1993). Fluorine distribution in waters of Nalgonda District, Andhra Pradesh, India. *Environmental Geology*, 21: 84–89.
- Ramanaiah, S. V., Venkata Mohan, S., Rajkumar, B., & Sarma, P. N. (2006). Monitoring of Fluoride Concentration in Ground Water of Prakasham District in India: Correlation with Physico-chemical Parameters. *Journal of Environmental Science & Engineering*, 48(2): 129-134.
- Ramesam, V. & Rajagopalan, K. (1985). Fluoride ingestion into the natural waters of hard-rock areas, Peninsular India. *Journal of the Geological Society of India*, 26: 125-132.

-
- Rango, T., Kravchenko, J., Atlaw, B., McCornick, P. G., Jeuland, M., Merola, B., & Vengosh, A. (2012). Groundwater quality and its health impact: An assessment of dental fluorosis in rural inhabitants of the Main Ethiopian Rift. *Environment International*, 43: 37–47.
- Rao, N. C. R. (2003). Fluoride and environment—a review. In: Bunch, M. J. V., Suresh, M., Kumaran, T. V. (Eds.) *Proceedings of third international conference on environment and health*. York University, Chennai, India.
- Rao, N. V. R., Rao, N., Rao, K. S. P. & Schuiling, R. D. (1993) Fluorine distribution in waters of Nalgonda District, AP, India. *Environmental Geology*, 21, 89.
- Ravichandran, B., Roychowdhury, A., Mukherjee, A. K., Gangopadhyay, P. K., & Saiyed, H. N. (2007). Estimation of fluoride content in the edible vegetables of an industrial area in Orissa. *Asian Journal of Water, Environment and Pollution*, 5: 93-95.
- Ravikumar, P. Mehmood, M. A., & Somashekar, R. K. (2013). Water quality index to determine the surface water quality of Sankey tank and Mallathahalli lake, Bangalore urban district, Karnataka, India. *Applied Water Science*. DOI 10.1007/s13201-013-0077-2
- Rayner-Canham, G., & Overton, T. (2003). *Descriptive Inorganic Chemistry*. 3d edition. Ch 12 The Group 12 Elements. W. H. Freeman and Company. New York. pp 523-533.
- Reddy, N. B., & Prasad, K. S. S. (2003). Pyroclastic fluoride in groundwaters in some parts of Tadipatri Taluk, Anantapur District, Andhra Pradesh. *Indian Journal of Environmental Health*, 45: 285–288.

-
- RGNDWM. Prevention & Control of fluorosis in India. Water Quality and Defluoridation Techniques, Volume II, Published by Rajiv Gandhi National Drinking Water Mission, Ministry of Rural Development, New Delhi, 1993.
- Ribang, L., Jianan, T., Lizhen, W., Daxian, Z., & Wuyi, W. (1975). The fluoride content in cultivated soil under different geographical conditions in China and its relation to endemic fluorosis. *Geographical Research*, 1975, 4: 30.
- Robinson, C., Kirkham, J., & Weatherell, J. A. (1996). Fluoride in teeth and bone. In: Fejerskov O, Ekstrand J, Burt BA, editors. *Fluoride in dentistry*. Second ed. Copenhagen: Munksgaard, pp. 69–87.
- Roholam, K. (1937). *Fluorine intoxication. A Clinical- Hygienic Study, With a Review of the Literature and Some Experimental Investigations*. H.K. Lewis, London.
- Routroy, S., Harichandan, R., Mohanty, J. K., & Panda, C. R. (2013). A Statistical appraisal to hydrogeochemistry of fluoride contaminated ground water in Nayagarh district, Odisha. *Journal of the Geological Society of India*, 81(3): 350-360.
- Roy, P., Mondal, N. K., Das, B., & Das, K. (2012). Arsenic Contamination in Groundwater: A Statistical Modeling . *Journal of Urban and Environmental Engineering*, 7 (1): 24-29.
- Rukah, Y. A., & Alsokhny, K. (2004). Geochemical assessment of groundwater contamination with special emphasis on fluoride concentration, North Jordan. *Chemie der Erde - Geochemistry*, 64(2): 171-181.
- Sadasivam, S., & Manickam, A. (1996). *Biochemical methods* (2nd Ed). New Delhi: New Age International (P) Limited.

-
- Saini, P., Khan, S., Baunthiyal, M., & Sharma, V. (2013). Mapping of fluoride endemic area and assessment of F^- accumulation in soil and vegetation. *Environmental Monitoring and Assessment*, 185(2): 2001-2008.
- Sajil Kumar, P. J., & James, E. J. (2013). Physicochemical parameters and their sources in groundwater in the Thirupathur region, Tamil Nadu, South India. *Applied Water Science*, 3: 219–228.
- Salve, P. R., Maurya, A., Kumbhare, P. S., Ramteke, D. S., & Wate, S. R. (2008). Assessment of Groundwater Quality with Respect to Fluoride. *Bulletin of Environmental Contamination and Toxicology*, 81:289–293.
- Sanchez Martos, F., Pulido Bosch, A., & Calaforra, J. M. (1999). Hydrogeo-chemical processes in an arid region of Europe (Almeria, SE Spain). *Applied Geochemistry*, 14:735–745.
- Sankararamakrishnan, N., Sharma, A. K., & Iyengar, L. (2008). Contamination of nitrate and fluoride in ground water along the Ganges Alluvial Plain of Kanpur district, Uttar Pradesh, India. *Environmental Monitoring and Assessment*, 146: 375 –382.
- Sarath Prasanth, S. V., Magesh, N. S., Jitheshlal, K. V., Chandrasekar, N., & Gangadhar, K. (2012). Evaluation of groundwater quality and its suitability for drinking and agricultural use in the coastal stretch of Alappuzha District, Kerala, India. *Applied Water Science*, 2:165–175.
- Saxena, V. & Ahmed, S., (2001) Dissolution of Fluoride in Groundwater: a Water – Rock Interaction Study. *Environmental Geology*, 40(9): 1084-1087.
- Saxena, V. K. (2004). *Geothermal resources of India* (pp. 48–70). Chennai: Allied Publishers Pvt Ltd.

-
- Saxena, V.K., & Ahmed, S. (2003). Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environmental Geology*, 43:731–736.
- Schlichting I., & Reinstein, J. (1999). pH influences fluoride coordination number of the $AlFx$, phosphoryl transfer transition state analog. *Nature Structural Biology*, 6: 721-723.
- Schwartz, M. O., & Friedrich, G.H. (1973). Secondary dispersion patterns of fluoride in the Osor area, Province of Gerona, Spain. *Journal of Geochemical Exploration*, 2: 103-114.
- Sharma, B. S., Agrawal, J., & Gupta, A. K. (2011). Emerging Challenge: Fluoride Contamination in Groundwater in Agra District, Uttar Pradesh. *Asian Journal of Experimental Biological Sciences*, 2(1): 131-134.
- Sharma, Y. D. (1982a). Effect of Sodium Fluoride on Collagen Cross-Link Precursors. *Toxicological Letters*, 10: 97-100.
- Sharma, Y. D. (1982b). Variations in the Metabolism and Maturation of Collagen after Fluoride Ingestion, *Biochemica et Biophysica Acta*, 715: 137-141.
- Sheth, F. J., Multani, A. S., & Chinoy, N. J. (1994). Sister chromatid exchanges: A study in fluorotic individuals of North Gujarat. *Fluoride*, 27(4): 215-219.
- Shortt, H. E., Pandit, C. G., & Raghvachari, T. N. S. (1937). Endemic fuorosis in Nellore district of South India. *Indian Medical Gazettiar*, 72: 396-400.
- Shyam, R., & Kalwania, G. S. (2012). Health risk assessment of fluoride with other parameters in ground water of Sikar city (India). *Environmental Earth Sciences*, 65:1275–1282.
- Sidhu, K. S., & Kimmer, R. O. (2002). Fluoride overfeed at a well site near an elementary school in Michigan. *Journal of Environmental Health*, 65(3): 16–21, 38.

-
- Singh, C. K., Rina, K., Singh, R. P., Shashtri, S., Kamal, V., & Mukherjee, S. (2011). Geochemical modeling of high fluoride concentration in groundwater of Pokhran area of Rajasthan, India. *Bulletin of Environmental Contamination and Toxicology*, 86:152–158.
- Sinha, R. K. (1986). *Industrial Minerals* (2nd edn), 379. Oxford & IBH, New Delhi.
- Smith, F. A., & Hodge, H. C. (1979). Air borne fluorides and man. Part-I. Critical reviews in environmental control, 8: 293-371.
- South Carolina Ambient Groundwater Quality Report, (2003). Summary: Pee Dee Basin
Compiled by: Childress, J. M., Bureau of Water, South Carolina Department of Health and Environmental Control, 1-102.
- Sreedevi, P. D., Ahmed, S., Made, B., Ladous, E., & Gandolfi, J. M. (2006). Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. *Environmental Geology*, 50: 1-11.
- Srinivasa Rao, N. (1997). The occurrence and behaviour of fluoride in the groundwater of the Lower Vamsadhara River basin, India. *Hydrological Sciences*, 42(6): 877-892.
- Srinivasamoorthy, K., Chidambaram, M., Prasanna, M. V., Vasanthavigar, M., John Peter, A., & Anandhan, P. (2008). Identification of major sources controlling Groundwater Chemistry from a hard rock terrain— A case study from Mettur taluk, Salem district, Tamilnadu, India. *Journal of Earth System Sciences*, 117(1): 49–58.
- Steingrímsson, J. (1998). *Fires of the Earth. The Laki eruption 1783–84*. University of Iceland Press, Reykjavík, 95.
- Steyn, D. G. (1948). Fluorine and endemic goitre. *South African Medical Journal*, 22(16): 525–526.

-
- Strunecka, A., Strunecky, O and Patocka, J. (2002). Fluoride plus aluminium: Useful tools in the laboratory investigations, but messengers of false information. *Physiological Research*, 51: 557-564.
- Subba Rao, N., Prakasa Rao, J., John Devadas, D., Srinivasa Rao, K. V., Krishna, C., & Nagamalleswara Rao, (2002). Hydrogeochemistry and groundwater quality in a developing urban environment of a semi-arid region, Guntur, Andhra Pradesh. *Journal of the Geological Society of India*, 59: 159–166.
- Susheela A. K., & Mukerjee, D. (1981). Fluoride poisoning and the Effect of Collagen Biosynthesis of Osseous and Nonosseous Tissue. *Toxicological European Research*, 3(2): 99-104.
- Susheela, A. K. (2003). Treatise on fluorosis, 2nd edn. Fluorosis Research & Rural Development Foundation, Delhi, India, 137 pp.
- Susheela, A. K. (2005). Fluorosis: easily preventable diseases through practice of interventions. Delhi: Fluorosis research and rural development foundation.
- Susheela, A. K., & Jethanandani, P. (1996). Circulating testosterone levels in skeletal fluorosis patients. *Journal of Clinical Toxicology*, 34(2): 183–189.
- Susheela, A. K., & Jha, M. (1981). Effects of Fluoride on Cortical and Cancellous Bone Composition. *IRCS Medical Sciences: Library Compendium*, 9(11): 1021-1022.
- Susheela, A. K., Kumar, A., Bhatnagar, M., & Bahadur, R. (1993). Prevalence of endemic fluorosis with gastrointestinal manifestations in people living in some North-Indian villages. *Fluoride*, 26(2): 97–104.
- Suttie, J.S., Dickie, R., Clay, A.B., Nielsen, P., Mahan, W.E., Baumann, D.P., & Hamilton, R. J. (1987). Effects of fluoride emissions from modern primary aluminium smelter

- on a local population of white-tailed deer (*Odocoileus virginianus*). Journal of Wildlife Diseases, 23: 135 –143.
- Swartjes, F. A., Dirven-Van Breemen, E. M., Otte, P. F., Van Beelen, P., Rikken, M. G. J., Uinstra, J., Spijker, J., & Lijzen, J. P. A. (2007). Human health risks due to consumption of vegetables from contaminated sites: towards a protocol for site-specific assessment. RIVM Report 711701040, Bilthoven, the Netherlands.
- Szokolay, A., Rippel, A. and Grunt, J. (1960). Influence of Atmospheric Contaminant from Aluminum Works on the Content of Fluorine in Fruit, Vegetables, and Cereals. Pol'nohospodarstvo, 7: 497-504.
- Taher, M., & Ahmed, P. (2001). Geography of North-East India (2nd Ed). Guwahati: Mani Manik Prakash, pp. 12-40.
- Takahashi, K. (1998). Fluoride-linked down syndrome births and their estimated occurrence due to water fluoridation. Fluoride, 31(2): 61–73.
- Takahashi, K., Akiniwa, K., & Narita, K. (2001). Regression analysis of cancer incidence rates and water fluoride in the U.S.A. based on IACR/IARC (WHO) data (1978–1992). Journal of Epidemiology, 11(4): 170–179.
- Tataruch, F., & Kierdorf, H. (2004). Mammals as biomornitors. In: Markert, A. A., Breure, A. M., & Zechmeister, H. G. (Eds.) Bioindicators and biomonitors. Elsevier, Amsterdam, pp. 737– 772.
- Tebutt, T. H. Y. (1983). Relationship between natural water quality and health. United Nations Educational, Scientific and Cultural Organization, Paris.
- Telesiński, A., & Śnioszek, M. (2009). Bioindicators of environmental pollution with fluorine. Bromatol Chem Toksykol, 42:1148– 1154, in Polish, English summary.

-
- Teotia, S. P. S., & Teotia, M. (1988). Endemic skeletal fluorosis: clinical and radiological variants. *Fluoride*, 21: 39–44.
- Teotia, S. P. S., & Teotia, M. (1991). Endemic fluoride: bones and teeth—update. *Indian Journal of Environment and Toxicology*, 1: 1–16.
- Teotia, S. P. S., Teotia, M., & Singh, K. P. (2003). 4th International Workshop on Fluorosis Prevention and Defluoridation of Water. *Fluoride*, 36(2): 107–125.
- Teotia, S. P., & Teotia, M. (1994). Endemic fluorosis in India: A challenging national health problem. *Journal of Association of Physicians of India*, 32: 347–352.
- Thomas, M. D., & Alther, E. W. (1966). The Effects of Fluoride on Plants. In Smith, F. A.: *Handbook of Exp. Pharmacology*, Vol. 20, Part 1. Springer-Verlag, Inc., New York, 1: 231–306.
- Todd, D. K. (1980). *Groundwater hydrology* (2nd Ed.), New York: Wiley. p.535.
- Tohyama, E. (1996). Relationship between fluoride concentration in drinking water and mortality rate from uterine cancer in Okinawa Prefecture, Japan. *Journal of Epidemiology*, 23(4): 104–107.
- Tokalioglu, Ş., Kartal, Ş., Şahin, U. (2004). Determination of Fluoride in Various Samples and Some Infusions Using a Fluoride Selective Electrode. *Turkish Journal of Chemistry*, 28: 203–211.
- Tome, F. V., Rodriquez, M. P. B., & Lozano, J. C. (2003). Soil-to-plant transfer factors for natural radionuclides and stable elements in a Mediterranean area. *Journal of Environmental Radioactivity*, 65: 161–175.
- Tripathi, N., Bajpai, S., & Tripathi, M. (2009). Genotoxic alterations induced by fluoride in Asian catfish, *Clarias batrachus* (Linn.). *Fluoride*, 42(4): 292–296.

-
- Trivedi, M. H., Verna, R. J., Chinoy, N. J., Patel, R. S., & Sathawara, N. G. (2007). Effect of high fluoride water on intelligence of school children in India. *Fluoride*, 40(3): 178–183.
- United states Department of Health and Human Services (USDHHS). (1991). Review of Fluoride: Benefits and Risks. Report of the Ad Hoc Committee on Fluorides, Committee to Coordinate Environmental Health and Related Programs. Department of Health and Human Services, USA.
- USNRC (1993). Health Effects of Ingested Fluoride. US National Research Council, National Academy Press, Washington, D.C.
- Vasanthavigar, M., Srinivasamoorthy, K., Vijayaragavan, K., Rajiv Ganthi, R., Chidambaram, S., Anandhan, P. et al. (2010). Application of water quality index for groundwater quality assessment: Thirumanimuttar sub-basin, Tamilnadu, India. *Environmental Monitoring and Assessment*, 171:595–609.
- Veeraputhira, V., & Alagumuthu, G. (2010). A report on fluoride distribution in drinking water. *International Journal of Environmental Sciences*, 1(4): 558-566.
- Verma S, & Dubey RS. (2001). Effect of cadmium on soluble sugars and enzymes of their metabolism in rice. *Biologia Plantarum*, 44: 117-23.
- Vinod, K., Singh & Devendra Singh Bikundia & Ankur Sarswat & Dinesh Mohan (2011). Groundwater quality assessment in the village of Lutfullapur Nawada, Loni, District Ghaziabad, Uttar Pradesh, India. *Environmental Monitoring and Assessment*. DOI 10.1007/s10661-011-2279-0
- Viswanathan, G., Jaswanth, A., Gopalakrishnan, S., Sivailango, S., & Aditya, G. (2009). Determining the optimal fluoride concentration in drinking water for fluoride

- endemic regions in South India. *Science of the Total Environment*, 407: 5298-5307.
- Wallis, W. J., Miller, G. W., Psenak, M., & Shieh, J. (1974). Fluoride effects on chlorophyll biosynthesis. *Fluoride*, 7: 69-77.
- Walton, K. C. (1988). Environmental fluoride and fluorosis in mammals. *Mammal Review*, 18:77–90. doi:10.1111/j.1365-2907.1988.tb00077.x
- Wang, S. X., Wang, Z. H., Cheng, X. T., Li, J., Sang, Z. P., & Zhang, X. D. (2007). Arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin county, Shanxi province, China. *Environmental Health Perspectives*, 115(4): 643–647.
- Wedepohl, K. H. (Ed) (1969). *Handbook of geochemistry*. Vol. II-I. Berlin: Springer-Verlag.
- Wei, L., & Miller, G.W. (1972). Effect of HF on the Fine Structure of Mesophyll Cells from Glycine max, Merr. *Fluoride*, 2: 67-73.
- Weinstein, L. H., & Davison, A. (2004). *Fluorides in the environment: effects on plants and animals*. CABI Publishing, Wallingford, UK
- Weinstein, L.H. (1977). Fluoride and plant life. *Journal of Occupational Medicine*, 19: 49-78.
- Whelton, H. P., Ketley, C. E., McSweeney, F., & O'Mullane, D. M. (2004). A review of fluorosis in the European Union; prevalence, risk factors and aesthetic issues. *Community Dentistry and Oral Epidemiology*, 32(1): 9-18.
- Whitford, G. (1996). *The metabolism and toxicity of fluoride*. Second edition. Monographs in oral science, Vol. 16. Basel: Karger, pp.156.

-
- Whitford, G. M. (1990). The Physiological and Toxicological Characteristics of Fluoride. *Journal of Dental Research*, 69: 539-549.
- Whitford, G. M. (1994). Intake & metabolism of fluoride. *Advances in Dental Research*, 8: 5-14.
- Whiting, P., MacDonagh, M., & Kleijnen, J. (2001). Association of Down's syndrome and water fluoride level: a systematic review of the evidence. *BMC Public Health* 1(1): 6. doi: 10.1186/1471-2458-1-6
- WHO (1997). Guidelines for drinking water quality: Surveillance and control of community supplies (2nd ed) Vol.3. Geneva: World Health Organisation, pp. 113. http://www.who.int/water_sanitation_health/dwq/gdwqvol32ed.Pdf
- WHO (1999). Guidelines for drinking-water quality, vol 2, 2nd edn. World Health Organization, Geneva.
- WHO, (2002) Fluorides, Environmental Health Criteria 227. World Health Organisation, Geneva, pp. 268.
- WHO. (1984). Guidelines for Drinking Water Equality, World Health Organisation, Geneva, 2: 249.
- WHO. (1986). Guideline for Drinking Water Quality. Second edition. Health Criteria and other Supporting Information, Vol.2. Geneva.
- Wilcox, L. V. (1955). Classification and use of irrigation water. Washington DC: US Dept. of Agriculture, Circular 969.
- Wilcox, L. V. (1995). Classification and use of irrigation waters. US Department of Agriculture, Washington DC.

-
- World Health Organization (WHO) (2011). Guidelines for drinking water quality, 4th edn. Chapter 10: Acceptability aspects: taste, odour and appearance. WHO, Geneva, Switzerland, p 227. Available online at: http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/
- World Health Organization (WHO). (1970). Fluorides and human health. World Health Organization Publ., Monogr. Ser. 59, WHO, Geneva.
- World Health Organization (WHO). (1991). Fluoride and fluoride. Environmental health criteria, vol 36. WHO, Geneva, Switzerland, p 274.
- World Health Organization (WHO). (1997). Guidelines for drinking-water quality, 2nd edn. Volume 3: Surveillance and control of community supplies. WHO, Geneva, Switzerland, p 113.
- Xiang, Q., Liang, Y., Chen, L., Wang, C., Chen, B., Chen, X. et al. (2003). Effect of fluoride in drinking water on children's intelligence. *Fluoride*, 36(2): 84–94.
- Yadav, J. P., Lata, S., Kataria, S. K., & Kumar, S. (2009). Fluoride distribution in groundwater and survey of dental fluorosis among school children in the villages of the Jhajjar District of Haryana, India. *Environ. Geochemistry and Health*, 31: 431–438.
- Yadav, S., Khan, T. I., Gupta, S., Gupta, A. B., & Yadava, R. N. (1999). Fluorosis in India with special reference to Rajasthan. In: *Proceedings of the International Conference on Water, Environment, Ecology, Socioeconomics and Health Engineering (WEESHE)*, Seoul National University, 18–21st October, 3–10.
- Yang, C. Y., Cheng, M. F., Tsai, S. S., & Hung, C. F. (2000). Fluoride in drinking water and cancer mortality in Taiwan. *Environmental research, section A*, 82:189-193.

-
- Yang, L., Peterson P.J., Williams W.P., Wang W., Li, R., & Tan, J. (2003). Developing Environmental Health Indicators as Policy Tools for Endemic Fluorosis Management in the People's Republic of China. *Environmental Geochemistry and Health*, 25(3): 281-295. doi:10.1023/A:1024543819240
- Yang, S.F. and Miller, G.W. (1963). Biochemical Studies on the Effect of Fluoride on Higher Plants. *Biochemical Journal*, 88: 505-509.
- Yidana, S. M., Banoeng-Yakubo, B., & Akabzaa, T. M. (2010). Analysis of groundwater quality using multivariate and spatial analyses in the Keta basin, Ghana. *Journal of African Earth Sciences*, 58: 220–234.
- Young, S. M., Pitawala, A., & Ishiga, H. (2010). Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. *Environmental Earth Sciences*, doi:10.1007/s12665-010-0804-z
- Zakrzewska, H. (1996). Evaluation of some biochemical parameters in blood serum and bones of sheep Western Pomerania regions of various contamination degree. *Ann. Acad. Med. Stet.*, 10: 105-125.
- Zakrzewska, H., Machoy-Mokrzyńska, A., Materny, M., Gutowska, I., & Machoy, Z. (2005). Estimation of fluoride distribution in the mandible and teeth of the red deer (*Cervus elaphus* L.) from industrially polluted areas in Poland. *Archives of Oral Biology*, 50: 309-316. doi:10.1016/j.archoralbio.2004.08.012
- Zhao, L. B., Liang, G. H., Zhang, D. N., & Wu, X. R. (1996). Effect of a high fluoride water supply on children's intelligence. *Fluoride*, 29(4): 190–192.

CHAPTER - 8

PUBLICATIONS



INCORPORATION OF FLUORIDE IN VEGETATION AND ASSOCIATED BIOCHEMICAL CHANGES DUE TO FLUORIDE CONTAMINATION IN WATER AND SOIL: A COMPARATIVE FIELD STUDY

Kartick C. Pal, Naba K. Mondal*, Ria Bhaumik, Arnab Banerjee, Jayanta K. Datta

Department of Environmental Science, The University of Burdwan, Burdwan, West Bengal, India.

Received July 24, 2012; in final form November 24, 2012, accepted December 3, 2012.

ABSTRACT

High fluoride concentrations in natural groundwater of Nowapara and Junidpur villages of the Birbhum District in India has recently been highlighted as a serious environmental concern. A study has been conducted to estimate fluoride concentrations and water quality along with the translocation of fluoride into vegetables through soil and the stress effect of fluoride on some biochemical parameters in this area. The result has been compared with a non-contaminated area of Burdwan University farm of the Burdwan District as a control zone by collecting equal numbers and types of samples. The results showed a positive correlation of fluoride concentration with depth, indicating higher concentrations of fluoride in drinking water drawn from deep tubewells in this semi-arid region. A high bioconcentration factor (BCF) of fluoride in vegetables imposes a high health risk due to fluoride intake both from water and vegetation. Probable exposure to the inhabitants of these villages is speculated due to changed biochemical parameters like chlorophyll, sugar, amino acid, ascorbic acid and protein in the vegetables as a result of fluoride stress. In the future, ground water monitoring to supply safe drinking water may be an effective way against the negative impact of fluoride on the inhabitants.

* Corresponding author: Tel.: +919434545694 Email : nkmenvbu@gmail.com

Keywords: Fluoride; birbhum district; vegetables; chlorophyll; ascorbic acid; amino acid

1. INTRODUCTION

Water-related problems have become a modern day challenge and a worldwide health problem is caused by the consumption of drinking water containing high fluoride [1]. There is a risk of endemic fluorosis where the fluoride level is more than 1.0 mg L^{-1} in drinking water [2]. Fluorosis is endemic in 20 states of India, affecting more than 65 million people, including 6 million children [3]. The villages of the Birbhum District of West Bengal, India, are under threat of fluorosis [4]. Harmful effects of fluoride are more relevant in the context of India compared to most Western countries where fluoridation of water is recommended to help prevent dental caries [5]. In nature, fluoride mainly occurs in ground water [6]. Enhanced fluoride intake through drinking water coupled with dietary intake could significantly substantiate total fluoride accumulation in body tissue [7].

Lithology and soil are the main factors that control the quality of water [8]. The amount of fluoride occurring naturally in groundwater is governed principally by climate, composition of the host rock and hydrogeology. Some anthropogenic activities such as use of phosphate fertilizers, pesticides, sewage and sludges for agriculture, depletion of groundwater, etc., are also implicated as causes of increased fluoride concentration in groundwater [9,10]. These activities may take decades to increase the fluoride level in water by exceeding the adsorption capacity of soil [11]. Weathering of rocks and leaching of fluoride-bearing minerals are the major reasons of elevated concentrations of fluoride in groundwater [12,13]. Evaporation is another important phenomenon that concentrates the fluoride in arid regions [14]. When groundwater is used in irrigation, the vegetables grown also incorporate fluoride. Fluoride is absorbed by plant roots [15,16] and then transported via xylematic flow to the transpiratory organs, mainly leaves, where it can be accumulated with adverse effects. Certain physiological processes are known to be markedly affected by fluoride, including decreased plant growth, chlorosis, leaf tip burn and leaf necrosis [17-19]. This fluoride may affect the biochemical ratio of the plant body [20]. The toxic effect of fluoride on pigments like chlorophyll and some secondary metabolites like sugar, ascorbic acid, amino acids and proteins are well documented [18-24]. Fluoride causes

reduction in photosynthetic pigment concentration [25], inhibition of photosynthesis [26] and changes in carbohydrate metabolism [27].

An inventory of fluoride concentration in drinking groundwater and its effect on plant physiology is thus an important step toward curbing the spread of fluorosis. The ability of plants to uptake and accumulate the non-essential element fluorine makes a potential threat to human health through its entrance into the food chain.

In the present study, we concentrate on the semi-arid zone of Birbhum District. Its groundwater is known to have elevated level of fluoride as reported by the School of Environment Studies, Jadavpur University, Kolkata. In this district, substantial amounts of different vegetables are cultivated with fluoride contaminated groundwater. As a result, fluoride accumulation in different parts of vegetables grown there is likely leading to fluoride contamination in the food chain. Therefore, in continuation of the authors' previous study by sampling the water, soil and vegetable, an attempt was made to assess the water quality, the transport of fluoride from soil to vegetation by examining the bioconcentration factor (BCF) and the effect of fluoride on biochemical constituents of leaves and fruits of the fluoride-contaminated area in comparison with the control area.

2. MATERIALS AND METHODS

2.1. Study Area

Two areas are chosen for the present study: one is a highly endemic fluoride region and the other is the control region where fluoride pollution is not reported so far. The polluted regions Nowapara (24°6'20.7"N and 77°47'3.1"E) and Junidpur (24°6'1.4"N and 77°46'53.5"E) are located in the Birbhum District of West Bengal, India (Fig. 1). The most interesting part of the geology of this area stems from the gradient of red soil. A kind of sandy hard red soil of the alfisol type and laterite soil of this area give rise to potential aquifers at depth. Bore wells and open wells are the main source of water for domestic and agricultural purposes in this arid region. The Burdwan University seed multiplication farm and the nearby locality (23°15'12"N and 77°50'51"E) of the Burdwan District were chosen as the control area for the study (Fig. 1). Different types of soil are encountered in different topographical, biological and hydrological sites as well as geological conditions within the

Burdwan District. In the study area, alluvial soil attains an enormous thickness. This alluvial soil is formed of alluvium brought down by the Damodar and numerous other rivers. These soils are sandy, well drained and slightly acidic in nature. Here also bore wells is the main source of drinking water; water of shallow pumps and river water is used for irrigation purposes.

2.2. Sampling

Water from ponds (S4, S9); tube wells (S1, S2, S3, S5, S6, S7, S8, S10, S11) having depths of 10 ft, 12 ft, 100 ft, 65 ft, 65 ft, 97 ft, 67 ft, 60 ft, 60 ft, 75 ft, 90 ft, respectively, and shallow (S12, S13) (which is used for irrigation) having depths of 75 ft and 70 ft, respectively, were collected from the polluted zone during the winter season and stored in pre-cleaned and sterilized polythene bottles of one-liter capacity following standard protocols. The water samples were immediately refrigerated after collection. Vegetable samples were also collected from the polluted area, refrigerated immediately after collection and analysis was done as quickly as possible. Thirty-three soil samples were collected from the vegetable fields near the plants (three samples near each plant) in the polluted area and stored in zippered polythene packets. Pond water (C1, C2); tube well water (C3, C4, C5, C6, C7, C8, C9, C10, C11) and shallow water (C12, C13) having depths of 11 ft, 12 ft, 110 ft, 60 ft, 45 ft, 110 ft, 60 ft, 60 ft, 60 ft, 90 ft, 116 ft, 70 ft and 60 ft, respectively, along with vegetables and fruits similar to the polluted zone were collected from the control area.

2.3. Analysis of Water Quality Parameters

Some of water quality parameters such as pH, bicarbonate (HCO_3^-), calcium (Ca), magnesium (Mg), iron (Fe), nitrate (NO_3^-), phosphate (PO_4^{3-}), chloride (Cl^-), electrical conductivity (EC), sodium (Na), potassium (K), sulfate (SO_4^{2-}) values of the water samples were measured quantitatively using Standard methods of examination of water and waste water [28].

2.4. Analysis of Fluoride in Water and Soil

After adding 25 mL TISAB (4g 1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid (CDTA) + 57 g NaCl and 57 g glacial CH_3COOH in 1 L of distilled water adjusted to pH 5-5.5 with 6 N NaOH) to 25 mL of a water sample, fluoride concentration was measured

with a fluoride ion selective electrode using an ORION 5 star ion analyzer. For the determination of water soluble fluoride in soil [29], an extract was made (1:1) using distilled water. Then the same procedure was followed as used for the water samples using 25 mL of the extract in the place of 25mL water sample. The limit of detection (LOD) of the method was 0.02 mg/L. All of the water parameters were analyzed following standard methods [28]. Biochemical parameters such as sugar [30], chlorophyll [31], ascorbic acid [32], protein [33] and amino acid [34] were studied from leaves and fruits of different vegetables.

2.5. Analysis of Fluoride in Vegetable Samples

Fluoride concentrations in vegetables and leaves were measured by the following method. After thorough washing with water, the fresh vegetables/leaves harvested from the contaminated and control area

were dried at 105°C and crushed into powder so as to pass through a 40 mesh sieve. About 0.5 g each of the powdered samples was transferred into a 150-mL nickel crucible and moistened with a small amount of de-ionized water. Six mL of 16.8 N NaOH was added and the crucible was placed in an oven (150°C) for 1.5-2.0 hr until NaOH was solidified. The crucible was placed in a muffle furnace set at 300°C, then raised to 600°C and kept at 600°C for 30 min in order to fuse the sample in the crucible. The crucible was placed in a hood and allowed to cool, and 10 mL distilled water was added. Then, 37% HCl solution (about 7 mL) was added slowly to adjust the pH to 7-9. The sample solution was transferred to a 100 mL plastic volumetric flask, made up to volume with distilled water and filtered through a Whatman No. 40 filter paper [35]. The filtrate was used for analysis of fluoride with the same procedure and the same ion selective electrode used for water analysis.

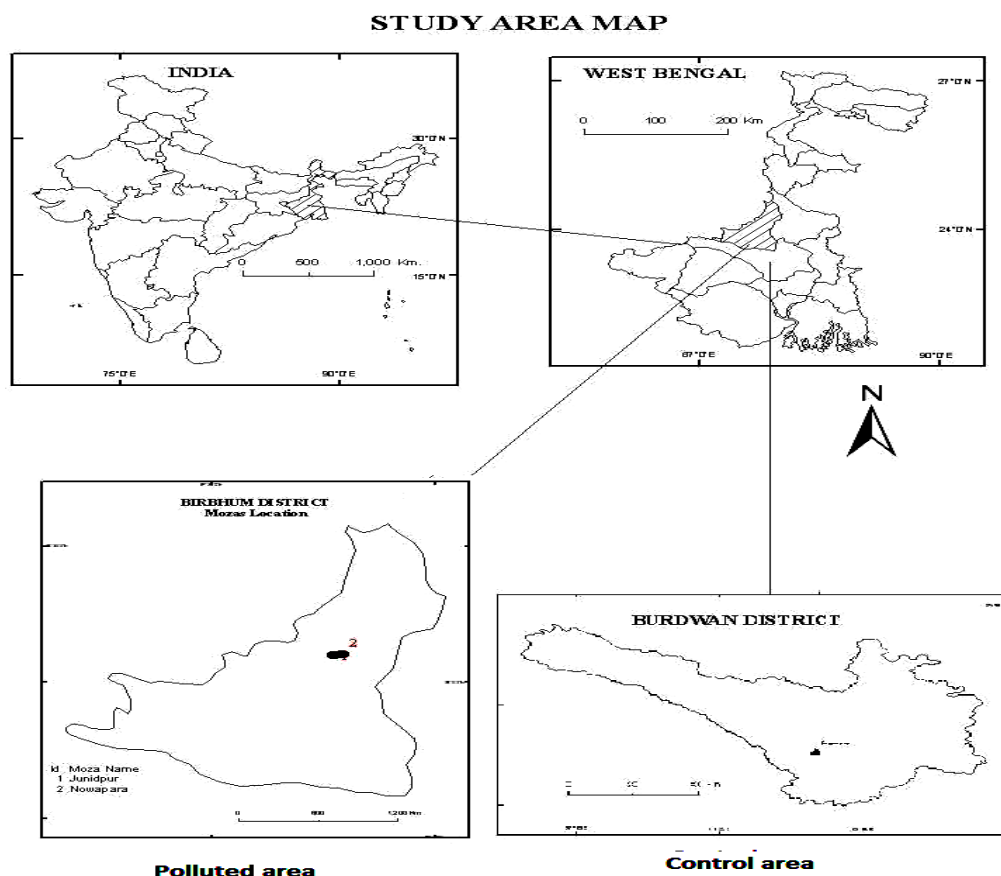


Figure 1 Study area

2.6. Bioconcentration Factor (BCF)

For estimating fluoride concentrations in vegetables the common parameter is the Bioconcentration Factor (BCF). BCF is the ratio of F concentration in the vegetable and F concentration in soil, i.e.,

$$BCF = \frac{\text{F concentration in vegetable (mg /kg of vegetable)}}{\text{F concentration in soil (mg/Kg soil)}}$$

2.7. Statistical Analysis

The data were expressed as mean \pm standard deviation. A correlation study between the water fluoride level and the other water quality parameters was performed with SPSS statistical version 16.0.

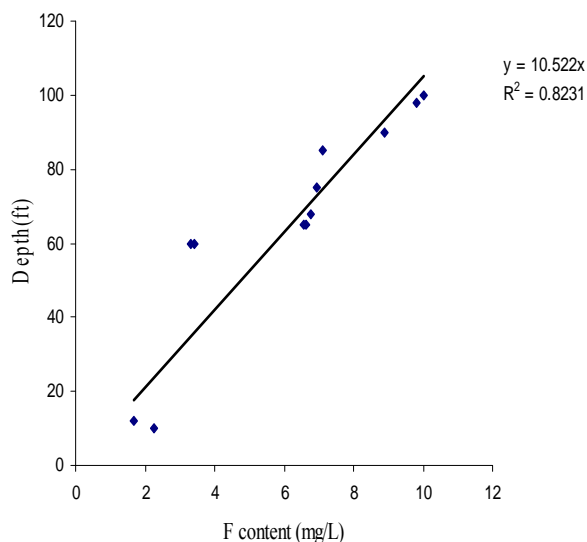


Figure 2 Correlation of depth of source with fluoride concentration in selected ground water samples in the polluted zone

3. RESULTS

3.1. Water Quality Parameters

The pond and shallow water samples were acidic (pH <7.0) and the water samples from the tube-wells were alkaline with pH values ranging from 7.1 to 8.7 in the polluted area. All the samples from different sources (pond, tube-well, shallow) were non-saline (EC <1.0 mS/cm) and soft in nature as the values of Ca and Mg were below the permissible limit of 75 mg/L and 150 mg/L, respectively [36]. Nitrate, chloride and iron

contents of all the water samples from different sources (pond, tube-well, shallow) were below the permissible limit of 45 mg/L, 500mg/L and 1 mg/L, respectively [36]. The phosphate content of 23.07% water sources was above the limit of 0.1mg/L permitted by USPH [37]. The phosphate content of shallow water samples were well below the permissible limit.

The concentration of fluoride in the water from different source types ranged from 3.05 mg/L to 10.2 mg/L for tube wells, 1.54 to 2.30 mg/L for ponds and 0.560 to 0.612 mg/L for shallow samples (Table 1). All the water samples from tube wells had fluoride concentration above the permissible limit of 1.5 mg/L [36]. The water samples from the control zone were non-fluorinated (F^- <1.5mg/L), slightly alkaline (pH >7), non-saline (EC <1mS/cm). The Cl^- , total iron, Ca and Mg contents, of this water was well below the permissible limit [36] (Table 2).

3.2. Depth Variation of Fluoride

The approximate depths of sources of the samples showed a positive correlation with the fluoride concentration in the polluted area (Fig. 2). But this correlation is not so significant (Fig. 3) in the control area as the control area contains low level of fluoride. The highest mean values of fluoride were found to be 10.0 mg/L in groundwater having the highest depth (100 ft) in the fluoride-contaminated area. The amounts of fluoride in surface water were lower in comparison to groundwater (Table 1).

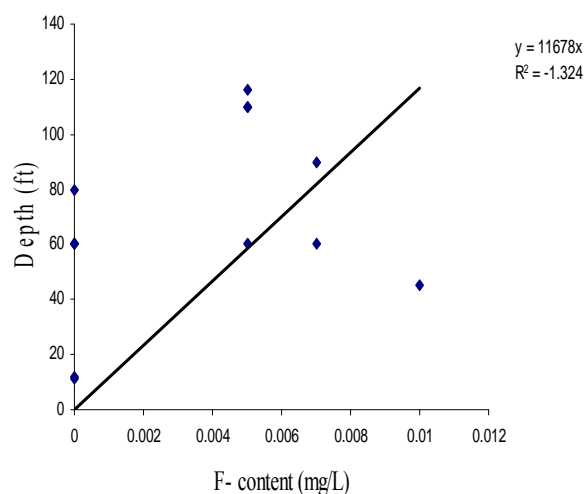


Figure 3 Correlation of depth of source with fluoride concentration in selected ground water samples in the control zone.

Table 1 Analytical data of selected water samples of Nowapara and Junidpur in the Birbhum District

ample (with depth)	F ⁻ (mg/L)	pH	HCO ₃ ⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	Cl ⁻ (mg/L)	EC (mS/cm)	Na (mg/L)	K (mg/L)	SO ₄ ²⁻ (mg/L)
S1(100ft)	10.00±0.27	8.4±0.2	200.60±4.69	40.0±5.3	4.7±1.2	0.153±0.013	1.093±0.092	0.048±0.005	31.48±0.81	0.3±0.0	116.30±2.92	19.93±0.23	426.13±6.12
S2(65ft)	6.56±0.35	7.7±0.1	144.17±1.90	2.7±1.2	3.3±1.2	0.218±0.004	0.759±0.035	0.152±0.003	44.07±0.40	0.6±0.1	68.57±2.64	32.97±0.57	216.43±4.06
S3(65ft)	6.62±0.29	8.1±0.2	71.5±1.9	4.7±1.2	8.0±2.0	0.135±0.003	2.151±0.069	0.219±0.013	195.17±0.38	0.5±0.1	80.23±1.22	45.13±0.57	129.93±2.89
S4(10ft)	2.24±0.10	6.9±0.4	81.67±3.13	4.7±1.2	24.0±3.5	0.200±0.007	1.622±2.105	0.084±0.006	56.66±0.63	0.4±0.1	51.67±1.26	53.10±0.44	173.27±8.28
S5(98ft)	9.80±0.18	7.9±0.2	32.8±2.6	2.0±2.0	230.0±7.2	0.620±0.036	14.145±0.403	0.000±0.00	119.62±0.52	0.8±0.1	135.00±2.55	23.30±1.01	309.27±6.50
S6(68ft)	6.78±0.17	7.8±0.3	28.13±0.47	2.7±1.2	44.0±5.3	0.480±0.015	2.668±0.161	0.010±0.009	44.07±0.25	0.4±0.0	98.23±2.61	56.40±0.66	103.87±7.83
S7(60ft)	3.31±0.23	7.3±0.3	59.50±2.36	3.3±1.2	64.0±6.9	0.190±0.020	1.380±0.322	0.114±0.008	37.78±0.70	0.5±0.0	234.1±1.3	107.33±0.9	144.53±4.87
S8(60ft)	3.42±0.92	8.5±0.3	135.77±2.16	36.0±5.3	132.0±5.3	0.174±0.005	2.001±0.127	0.030±0.014	188.87±0.61	0.7±0.1	147.93±2.47	31.26±1.03	329.70±7.13
S9(12ft)	1.67±0.11	6.7±0.2	19.33±1.85	4.0±2.0	56.0±5.3	0.246±0.219	1.909±0.053	0.012±0.002	62.96±0.06	0.4±0.0	199.07±3.09	33.40±0.70	227.63±5.48
S10(85ft)	7.10±0.13	8.5±0.1	110.33±2.15	2.0±2.0	50.0±6.0	0.709±0.004	1.714±0.127	0.015±0.003	44.07±0.14	0.8±0.1	64.30±1.45	87.17±0.83	213.77±3.96
S11(90ft)	8.88±0.23	8.2±0.2	70.80±6.12	24.0±4.0	132.0±10.6	0.700±0.006	0.667±0.064	0.010±0.002	62.96±0.29	0.9±0.0	135.33±2.01	61.67±0.71	401.10±8.78
S12(75ft)	6.94±0.12	6.6±0.2	50.03±1.99	36.0±3.5	76.0±5.3	0.632±0.008	1.576±0.058	0.029±0.004	94.44±0.43	0.7±0.0	90.30±1.45	71.40±0.46	214.90±8.69
S13(70ft)	0.58±0.03	6.2±0.1	64.83±1.40	28.0±4.0	128.0±10.6	0.290±0.004	0.334±0.040	0.031±0.005	44.07±0.03	0.4±0.0	76.80±1.45	92.57±0.71	137.63±7.07

Table 2 Analytical data of selected water samples of control area of the Burdwan District

Sample (with depth)	F ⁻ (mg/L)	pH	HCO ₃ ⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	Cl ⁻ (mg/L)	EC (mS/cm)	Na (mg/L)	K (mg/L)	SO ₄ ²⁻ (mg/L)
C1(11ft)	0.00± 0.00	8.6± 0.1	16.27± 0.50	34.1± 2.2	14.1± 2.2	0.053± 0.013	0.22± 0.03	0.082± 0.004	63.01± 0.06	0.8±0.1	35.53± 0.70	11.47± 0.57	130.04±2.39
C2(12ft)	0.00± 0.00	8.5± 0.2	40.37± 0.07	14.0± 2.2	36.2± 4.2	0.061± 0.004	0.25± 0.07	0.066± 0.011	44.11± 0.41	0.6±0.0	24.30± 0.75	8.93± 0.25	144.87±3.55
C3(110ft)	0.00± 0.06	7.8± 0.2	34.70± 0.92	22.2± 2.0	44.0± 5.3	0.124± 0.003	0.10± 0.02	0.121± 0.010	63.10± 0.29	0.7±0.0	43.47± 0.03	15.57± 0.38	92.80±2.51
C4(60ft)	0.01± 0.06	8.2± 0.1	46.73± 0.50	36.0± 4.2	18.1± 2.0	0.082± 0.007	0.334± 0.08	0.154± 0.004	37.81± 0.71	0.4±0.0	52.47± 0.76	21.33± 0.87	47.03±3.85
C5(45ft)	0.01± 0.11	8.1± 0.1	51.67± 0.63	10.3± 2.0	20.9± 2.1	0.061± 0.004	0.121± 0.01	0.100± 0.015	47.12± 2.01	0.5±0.0	49.37± 0.70	12.43± 0.21	198.83±5.40
C6(110ft)	0.01± 0.06	7.8± 0.2	36.27± 0.41	56.2± 5.3	24.2± 4.0	0.174± 0.005	1.33± 0.11	0.265± 0.004	44.07± 0.25	0.7±0.1	60.13± 1.20	13.47± 0.61	173.2±2.82
C7(60ft)	0.00± 0.00	8.0± 0.2	27.77± 0.38	50.4± 6.0	22.1± 2.0	0.290± 0.004	1.02± 0.21	0.351± 0.016	45.80± 0.71	0.4±0.0	21.90± 0.36	16.67± 0.45	221.27±3.33
C8(60ft)	0.00± 0.00	7.9± 0.1	23.43± 0.70	18.1± 2.0	36.1± 4.2	0.120± 0.008	0.226± 0.01	0.045± 0.002	56.66± 0.63	0.4±0.1	14.47± 0.94	10.20± 0.56	83.30±2.69
C9(60ft)	0.00± 0.00	7.8± 0.1	13.83± 0.35	21.0± 2.1	22.3± 2.0	0.051± 0.011	0.76± 0.04	0.115± 0.009	52.92± 0.78	0.8±0.1	12.40± 0.66	8.93± 0.25	152.73±3.23
C10(90ft)	0.01± 0.06	7.7± 0.1	43.87± 0.31	36.0± 4.2	10.0± 2.0	0.075± 0.010	0.25± 0.08	0.282± 0.075	44.07± 0.14	0.3±0.0	17.87± 0.65	17.30± 0.44	232.1±3.72
C11(116ft)	0.01± 0.06	8.1± 0.1	17.73± 0.50	24.2± 3.5	36.0± 5.3	0.133± 0.012	0.12± 0.01	0.131± 0.007	75.52± 1.15	0.6±0.1	15.93± 0.35	25.93± 0.25	187.13±5.04
C12(80ft)	0.00± 0.00	7.7± 0.1	25.40± 0.78	56.1± 4.2	40.2± 2.0	0.095± 0.012	0.67± 0.07	0.057± 0.005	30.22± 3.20	0.5±0.1	24.77± 0.55	32.37± 0.42	78.10±4.03
C13(60ft)	0.01± 0.06	8.0± 0.2	54.57± 1.81	40.1± 5.3	10.3± 2.0	0.046± 0.008	0.10± 0.02	0.081± 0.004	44.07± 0.03	0.4±0.0	31.83± 1.23	20.03± 0.40	210.33±2.15

Table 3 Correlation matrix of different parameters in ground water of a fluoride polluted area of Birbhum

	F ⁻	pH	HCO ₃ ⁻	Ca	Mg	Fe	NO ₃ ⁻	PO ₄ ³⁻	Cl ⁻	EC	Na	K
pH	0.756**											
HCO ₃ ⁻	0.271	0.494*										
Ca	0.088	0.169	0.446									
Mg	0.081	-0.017	-0.38	0.145								
Fe	0.482*	0.264	-0.357	-0.039	0.475							
NO ₃ ⁻	0.391	0.140	-0.335	-0.301	0.665**	0.326						
PO ₄ ³⁻	-0.076	0.011	0.221	-0.289	-0.571*	-0.604*	-0.255					
Cl ⁻	0.043	0.353	-0.057	0.128	0.265	-0.159	0.290	0.287				
EC	0.429	0.501*	-0.088	0.01	0.565*	0.727**	0.330	-0.260	0.288			
Na	-0.164	-0.074	-0.247	-0.045	0.270	-0.175	0.125	-0.157	-0.002	-0.019		
K	-0.388	-0.319	-0.295	-0.075	0.009	0.230	-0.377	-0.015	-0.335	0.081	0.059	
SO ₄ ²⁻	0.536*	0.527*	0.513*	0.549*	0.303	0.175	0.156	-0.379	0.054	0.369	0.189	-0.511*

* Correlation is significant at the 0.05 level ** Correlation is significant at the 0.01 level

Table 4 Correlation matrix of different parameters in ground water of the control area of Burdwan

	F ⁻	pH	HCO ₃ ⁻	Ca	Mg	Fe	NO ₃ ⁻	PO ₄ ³⁻	Cl ⁻	EC	Na	K
pH	-0.156											
HCO ₃ ⁻	-0.279	0.509*										
Ca	-0.149	-0.333	-0.351									
Mg	-0.309	-0.152	0.265	-0.214								
Fe	-0.184	-0.241	-0.198	0.454	0.212							
NO ₃ ⁻	-0.301	-0.348	-0.134	0.664**	-0.039	0.598*						
PO ₄ ³⁻	0.192	-0.299	-0.236	0.499*	-0.361	0.700**	0.586*					
Cl ⁻	-0.033	0.235	-0.15	-0.481*	0.229	0.044	-0.378	-0.146				
EC	-0.303	0.247	0.090	-0.160	0.244	-0.160	0.182	-0.254	0.456			
Na	0.558*	0.126	-0.123	0.199	-0.143	0.005	0.156	0.112	-0.235	0.152		
K	0.147	-0.309	-0.326	0.528*	0.176	0.116	-0.023	0.006	-0.224	-0.343	-0.036	
SO ₄ ²⁻	0.256	-0.081	-0.023	0.06	-0.501*	0.2	0.117	0.533	0.09	-0.178	-0.187	0.256

* Correlation is significant at the 0.05 level ** Correlation is significant at the 0.01 level

Table 5 Variation of biochemical constituents in leaves of different vegetable plants

Name of vegetables	Sugar		Chlorophyll						Ascorbic acid		Protein		Amino acid	
			Chl-a		Chl-b		Total Chl							
	Control	Polluted	Control	Polluted	Control	Polluted	Control	Polluted	Control	Polluted	Control	Polluted	Control	Polluted
Cabbage (<i>Brassica oleracea</i>)	578.9± 8.3	566± 4.07**	0.11± 0.01	0.10± 0.02 ^a	0.42± 0.01	0.25± 0.001*	0.41± 0.02	0.36± 0.01*	0.30± 0.01	0.241 ±0.01*	560.1 ±3.2	555.41 ±3.51 ^a	6.13± 0.14	6.03± 0.08 ^a
Onion (<i>Allium cepa</i>)	718.1± 5.3	703.6± 3.4*	0.08± 0.001	0.05± 0.003*	0.43± 0.008	0.28± 0.01*	0.66± 0.01	0.53± 0.03*	0.24± 0.01	0.22± 0.01 ^a	192.4 ±3.3	188.6± 3.8 ^a	4.18± 0.04	3.54± 0.09*
Spinach (<i>Spinacia oleracea</i>)	762.45 ±3.1	751.84 ±3.61*	0.20± 0.006	0.18± 0.01**	0.59± 0.016	0.54± 0.01*	1.00± 0.003	0.89± 0.01*	0.18± 0.03	0.17± 0.01 ^a	895.5 ±4.6	892.48 ±7.54 ^a	1.28± 0.04	0.32± 0.01*
Radish (<i>Raphanus sativus</i>)	559.2± 8.1	554.2± 13.9 ^a	0.34± 0.004	0.23± 0.01*	0.66± 0.01	0.15± 0.01*	1.02± 0.15	0.57± 0.01*	0.08± 0.01	0.06± 0.08 ^a	492.8 ±3.5	491.8± 5.9 ^a	4.18± 0.16	2.89± 0.07*
Potato (<i>Solanum tuberosum</i>)	891.4± 12.5	883.3± 7.3 ^a	0.96± 0.047	0.13± 0.01*	1.48± 0.04	0.24± 0.01*	1.02± 0.05	0.38± 0.003*	0.25± 0.01	0.19± 0.01*	418± 1.9	411± 4.1**	2.25± 0.11	1.29± 0.03*
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>)	952.4± 3.4	951.4± 19.2 ^a	0.33± 0.006	0.21± 0.01*	0.37± 0.008	0.29± 0.02*	0.73± 0.02	0.60± 0.01*	0.21± 0.02	0.16± 0.01*	742.9 ±6.4	739.9± 4.9 ^a	2.25± 0.02	1.93± 0.13*

* Change is significant at 1% level, ** Change is significant at 5% level, ^a Change is not significant. All the biochemical constituents are measured in terms of mg/100g leaf

Table 6 Variation of biochemical constituents in different vegetables

Name of the sample	Sugar		Ascorbic acid		Protein		Amino acid	
	Control	Polluted	Control	Polluted	Control	Polluted	Control	Polluted
Papaya (<i>Carica papaya</i>)	154.68±4.30	148.48±5.24 ^a	1.012±0.019	1.12±0.10 ^a	766.22±6.11	763.17±7.06 ^a	5.99±0.19	6.79±0.91 ^a
Kundri (<i>Coccinia grandis</i>)	107.92±7.80	107.81±2.49 ^a	0.290±0.100	0.38±0.04 ^a	425.33±4.46	423.98±6.14 ^a	18.12±2.75	19.3±3.01 ^a
Radish (<i>Raphanus sativus</i>)	290.49±8.66	287.49±6.89 ^a	0.480±0.119	0.57±0.06 ^a	806.44±8.92	805.56±5.00 ^a	15.44±3.03	16.08±2.83 ^a
Potato plant (<i>Solanum tuberosum</i>)	307.46±8.81	307.36±7.89 ^a	0.364±0.061	0.44±0.04 ^a	580.42±5.03	572.37±8.01 ^a	21.75±3.51	22.5±3.06 ^a
Brinjal (<i>Solanum melongena</i>)	153.33±2.94	152.26±5.70 ^a	0.278±0.022	0.32±0.01 ^{**}	300.11±8.10	296.79±6.57 ^a	33.21±3.75	35.37±3.72 ^a
Seem (<i>Dolichos lablob</i>)	554.41±8.43	549.45±7.97 ^a	0.243±0.002	0.25±0.02 ^a	311.68±9.56	301.58±6.83 ^a	21.49±4.00	28.94±1.49 ^{**}
Korola (<i>Momordica charantia</i>)	98.11±8.03	96.80±6.78 ^a	0.052±0.012	0.06±0.01 ^a	496.66±4.49	487.57±7.86 ^a	14.00±1.15	14.27±2.53 ^a

* Change is significant at 1% level, ** Change is significant at 5% level, ^a Change is not significant. All the biochemical constituents are measured in terms of mg/100g vegetable

3.3. Correlation between Water Parameters

An attempt was made to correlate the fluoride with various parameters for both the polluted and control zones, as indicated in Tables 3 and 4, respectively. All the parameters showed positive correlation with fluoride except phosphate, sodium and potassium in the polluted area. The positive correlation between bicarbonate and fluoride along with the significant positive correlation between pH and fluoride was found in the fluoride-contaminated area.

Calcium and magnesium showed positive correlation with fluoride as found by Alagumuthu and Rajan [38]. However, the correlations between fluoride and other water parameters are not as significant as the fluoride level is very low in the control area (Table 4).

3.4. Piper Diagrams

Figures 4 and 5 show Piper diagrams taking the mean values of the parameters of the water samples collected from the study and polluted areas to illustrate the chemical analyses. On the basis of Walton's classification [39], in 92% of the water samples of the polluted area, the non-carbonate hardness (secondary salinity) exceeds 50%, i.e., by alkaline earths and weak acid. 15.4% of the water samples showed an excess of alkalis with respect to alkaline earths and 7.7% showed an excess of weak acid with respect to strong acid in the polluted area.

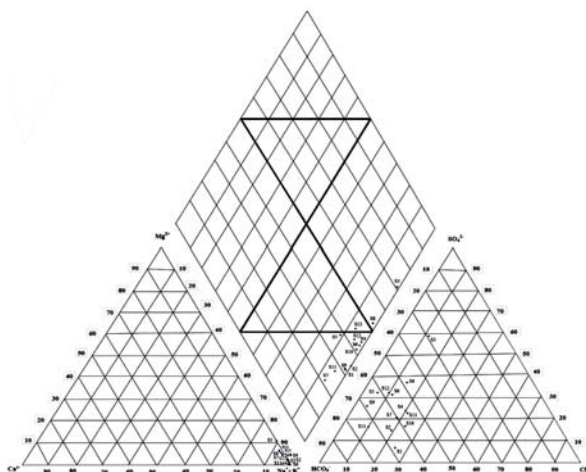


Figure 4 Piper diagram of water parameters of Nowpara and Junidpur

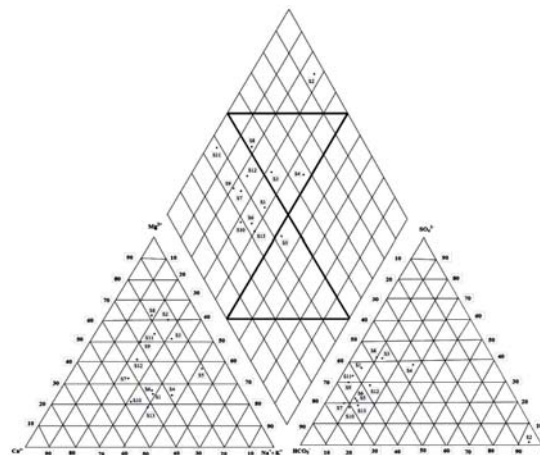


Figure 5 Piper diagram of water parameters of the control area

In the control area 69.2% of the water samples showed an excess of alkaline earths with respect to alkalis, 7.7% showed an excess of weak acid with respect to strong acid and 23.1% showed an excess of strong acid with respect to weak acid.

3.5. Fluoride in Soil

Fluoride concentrations in the soil samples were measured to access the translocation of fluoride from soil to plant body by calculating the BCF. The fluoride content was found to be highest (4.5 mg/kg soil) in the soil of a radish field (Fig. 6). High fluoride concentrations in soil are indicated by high mean concentrations of fluoride in radish (4.21 mg/kg vegetables) and its leaves (3.21 mg/kg vegetables).

3.6. Biochemical Parameters

Along with the water study, biochemical parameter such as chlorophyll, amino acids, proteins, soluble sugars, ascorbic acid in some vegetables and vegetable leaves were studied and are listed in Tables 5 and 6. In Table 5, we see that the reducing sugar contents of the leaves decreased monotonically with respect to the control area and the reduction was maximum in case of cabbage (2.15%) and minimum in case of cauliflower (0.11%). The chl. a, chl. b and total chlorophyll of leaves in the fluoride-affected area were reduced considerably comprised to the control area. For potatoes, maximum reduction of 86.1%, 84.1%, 62.7% of chl a, chl b and total chl content, respectively were obtained, indicating the susceptibility, of potato plants to fluoride.

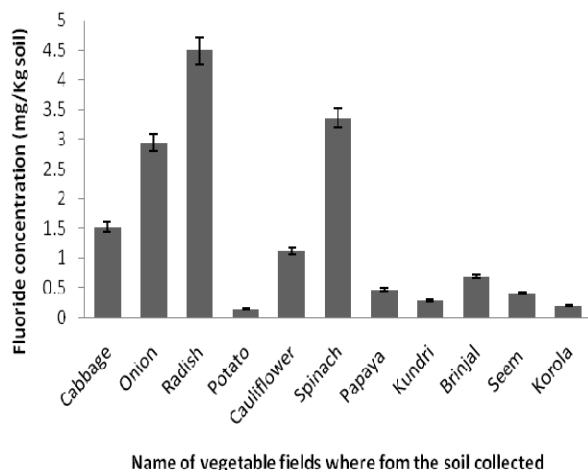


Figure 6 Fluoride concentration in soil where vegetables are cultivated. Values are means \pm SE N(3) from two independent experiments.

Lesser amounts of ascorbic acid were found in leaves of different vegetables in the fluoride-affected area than in the control area. Reduction caused by fluoride was found to be highest in cauliflower (26.2%) and lowest in spinach (6.5%). The change of total protein content in leaves of different vegetables of the polluted site due to the stress of fluoride was not as significant but showed a decreasing trend with respect to the control site. The highest reduction was found in onion (1.9%) and lowest in radish (0.2%).

The free amino acid contents in the leaves and vegetables of different species under fluoride stress showed significant reduction in comparison to the

control area. For spinach the maximum reduction was 78.8% of ascorbic acid was found and minimum reduction was found in cabbage (1.5%).

For vegetables, sugar and protein levels showed a decreasing tendency, whereas ascorbic acid and amino acid showed increasing tendency due to the fluoride stress in the affected area in comparison to the control area. The highest and lowest reductions of sugar were found in papaya (4.0%) and potato (0.03%) respectively. The reduction of protein was highest in seem (3.2%) and lowest in radish (0.10%). Ascorbic acid and amino acid contents in the vegetables were significantly higher in the fluoride affected area with respect to the control area. Enhancement of ascorbic acid content due to fluoride stress was found to be the highest in kundri (31.0%) and lowest in seem (4.5%). Seem showed the highest degree of augmentation of amino acid (34.7%) and korola showed the lowest (1.9%).

3.7. Bioconcentration Factor

Fluoride concentration along with mean BCF values of F in vegetable leaves and vegetables are presented in Tables 7 and 8. The fluoride concentration and mean BCF value of F was found to be highest in leaves and vegetable of *Raphanus sativus* (radish). Higher concentrations of fluoride in soil where the vegetable is cultivated may be the reason for higher BCF. Other than radish, leafy vegetables like spinach, cabbage and cauliflower leaves had BCF values of F greater than 1.

Table 7 Mean fluoride concentration levels of different types of vegetable leaf samples and BCF

Sl.No.	vegetable	Polluted zone (F ⁻ mg.kg ⁻¹)	control zone (F ⁻ mg.kg ⁻¹)	Mean BCF in polluted zone
1.	Cabbage (<i>Brassica oleracea</i>) (N = 3)	1.25 \pm 0.07	ND	1.22
2.	Onion (<i>Allium cepa</i>) (N = 3)	3.19 \pm 0.07	ND	0.92
3.	Radish (<i>Raphanus sativus</i>) (N = 3)	3.21 \pm 0.04	0.009 \pm 0.001	1.40
4.	Potato (<i>Solanum tuberosum</i>) (N = 3)	0.65 \pm 0.07	0.004 \pm 0.001	0.23
5.	Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i>) (N = 3)	1.11 \pm 0.12	ND	1.01
6.	Spinach (<i>Spinacia oleracea</i>) (N = 3)	2.56 \pm 0.09	0.010 \pm .001	1.31

ND: Not Detectable

Table 8 Mean fluoride concentration levels of different types of vegetable samples and BCF

Sl.No.	vegetable	Polluted zone (F ⁻ mg.kg ⁻¹)	control zone (F ⁻ mg.kg ⁻¹)	Mean BCF in polluted zone
1.	Papaya (<i>Carica papaya</i>) (N = 3)	0.58±0.05	ND	0.82
2.	Kundri (<i>Coccinia grandis</i>) (N = 3)	0.80±0.03	ND	0.36
3.	Radish (<i>Raphanus sativus</i>) (N = 3)	4.21±0.02	0.006±0.001	1.06
4.	Potato (<i>Solanum tuberosum</i>) (N = 3)	1.47±0.03	0.005±0.001	1.1
5.	Brinjal (<i>Solanum melongena</i>) (N = 3)	1.35±0.03	ND	0.51
6.	Seem (<i>Dolichos lablob</i>) (N = 3)	0.65±0.03	ND	0.62
7.	Korola (<i>Momordica charantia</i>) (N = 3)	0.40±0.03	ND	0.51

ND: Not Detectable

4. DISCUSSION

4.1. Variation of Fluoride with Depth

A positive correlation between fluoride concentration and depth of sampling indicates that fluoride is present in the form of fluorite minerals in the Precambrian granite or granitic-gneiss of the underground basement [40,41]. The process of weathering of rock releases fluoride in soil and groundwater. With <1.0 µg/L of F in drinking water as the optimum level for warmer climates as suggested by WHO [42], people living in the villages Nowapara and Junidpur in the Birbhum District are under threat from potential F toxicity from groundwater as well as contamination from surface water sources. Depth-wise variation in F concentration may be attributed to the lithological homogeneity of the area. Trace amounts of F found in surface water and shallow water may be attributed to long time application of phosphate fertilizers and subsequent leaching as agricultural runoff into the surface water-body sources [24].

4.2. Correlation of F with other Water Parameters

Water quality parameters such as alkalinity, pH and hardness have high impact on water fluoride levels due to the release of fluoride from fluoride-containing minerals by carbonates and dissolved solids [43]. The positive correlation between bicarbonate and fluoride indicates that high alkalinity water promotes leaching of fluoride and thus affects the concentration of

fluoride in groundwater [44]. The ionic radius of fluoride (0.136 nm) is the same as that of hydroxyl ion, which can be easily substituted from water at high pH [45,46]. Alkaline pH where bicarbonate activity is high, promotes the fluoride dissolution represented as: $\text{CaF}_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + 2\text{Na}^+ + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2$ [44]. Calcium and magnesium showed positive correlation with fluoride [38]. The positive correlation with calcium observed may be attributed to the presence of limestone in those areas [40]. There was a positive correlation between chloride and fluoride [47,48]. Iron and sulfate had a significant positive correlation with fluoride [49]. However, the correlation between fluoride and other water parameters are not so significant as the fluoride level is very low in the control area.

4.3. Biochemical Parameters

Chlorophyll. It is reported that tuberous vegetables such as potato appear to accumulate relatively higher to levels of fluoride [50] and a high stress effect is observed. Reduction in the chl a, chl b and total chl content may be due to the breakdown of chlorophyll under stress or due to inhibition of chlorophyll biosynthesis [51]. Magnesium is a central component of chlorophyll; it traps fluoride as MgF_2 in a detoxification mechanism [52] and this may be cause decrease in the chlorophyll content in the plant body. Decrease in chlorophyll content may also be due to the disruption of chloroplast membranes as described by Horvath et al. [21]. Earlier studies confirm that fluoride causes a reduction in the chlorophyll content

of foliage [19]. The biochemical basis of this effect may be a consequence of inhibition by fluoride of incorporation of γ -aminolevulinic acid into chlorophyll synthetic pathway [53].

Sugar. The sugar levels in plants are directly related to stress factors [22]. The reducing sugar of both leaves and vegetables of the fluoride-affected area were significantly decreased considerably in comparison to the control area. This may be due to a lower level of photosynthesis leading to lower accumulation of photo assimilate in leaves and fruits under fluoride stress, decreasing the sensitivity of different crop plants [18]. Since formation of reducing sugars such as glucose, fructose, and mannose in leaves is thought to be inhibited by F, the tendency of plants exposed to F to decrease the concentrations of such sugars in their leaves indicates the possible conversion of these sugars to non-reducing sugars, such as sucrose and raffinose or sugar alcohols. Under these conditions, increased levels of non-reducing sugars in tissues might be a mechanism adopted by plants to reduce F toxicity [23]

Ascorbic acid. Ascorbic acid as an antioxidant plays an important role in protection against physiological stress [54]. Ascorbic acid content in leaves of different vegetables of the fluoride-affected area decreased due to inhibition of ascorbic acid synthesis under fluoride stress [20]. In vegetables, the ascorbic acid content of the affected area showed an increasing trend over the controlled area, which may be attributed to binding of fluoride with ascorbic acid oxidase enzyme thereby inhibiting the breakdown of ascorbic acid in the plant system [51].

Protein. Chang [55] stated that fluoride decreased the number of ribosomes and destroyed the structure of ribosomal proteins, which negatively affected the entire protein synthesis. We can reach the same inference with our results. Protein content in the leaves and vegetables of different species under fluoride stress showed significant reduction in comparison to the control area due to the reduced rate of amino acid synthesis under fluoride stress [20].

Amino acid. The total free amino acid content in leaves of different vegetables of the polluted site showed a decreasing trend with respect to the control site. This may be due to less degradation of storage protein, amino acid synthesis and amino acid utilization for protein synthesis and for respiration under fluoride stress [24]. The increased amino acid

the content in vegetables in the affected area in comparison to control area may be attributed to increased rates of dark CO₂ fixation under fluoride stress [20].

4.4. BCF of Fluoride

BCF has been used as an indicator of affinity for the accumulation of F in plants and because of its simple application, it is widely used [56,57]. Earlier investigations found increased fluoride translocation in plants where metabolism is higher [58]. Leafy vegetables like radish, spinach, cabbage and cauliflower leaves had BCF values of F greater than 1, which indicates a higher rate of photosynthesis in leafy vegetables associated with higher intake of water resulting in a higher BCF value of F. However, Swartjes et al. [59] reported that BCF values are not always constant in specific vegetables and are largely affected by soil properties like soil pH, clay content, organic matter and fluoride concentration in soil and plant factors like the type of plant and growth rate.

5. CONCLUSION

Keeping in view the ground water quality that is the source of drinking water, the residents of this locality of the Birbhum District are in an alarming position. A positive correlation was found with the depth of water sample, which imposes a greater risk in these fluoride-affected villages. Because the drinking water level got down deep due to dryness in this area, the fluoride levels were higher in the drinking water. Vegetable plants are also under stressed conditions. It is presumable that this kind of stress effect on plant metabolism could produce disturbances in natural biosynthetic turnover. Working on cell tissue culture, Diesendorf and Sutton [60] reported that in the presence of fluoride, DNA molecules may be damaged and genetic malformations may be induced. Genetic malformation can produce any type of physiological or biochemical change in a plant body, imposing harmful effect on plant species and the agricultural system. Beside this fact, by estimating the BCF it may be speculated that the people in this area are in chronic toxic exposure to organo-fluorine compounds which can be synthesized by crops and vegetable plants after transportation of fluoride from water and soil. Future mitigation attempts should consider alternative fluoride-free water sources for drinking and irrigation purposes.

6. ACKNOWLEDGEMENTS

The authors are grateful to Dr. N. Jana, Associated Professor in Geography, Department of Geography, The University of Burdwan, Burdwan for technical support and valuable suggestion for preparation of this manuscript.

7. REFERENCES

- [1] Susheela AK, Kumar A, Bhatnagar M, Bahadur R. Prevalence of endemic fluorosis with gastrointestinal manifestation in people living in some north-indian villages. *Fluoride*, 1993, 26: 97-104.
- [2] Bo Z, Mei H, Yongsheng Z, Xueyu L, Xuelin Z, Jun D. Distribution and risk assessment of fluoride in drinking water in the west plain region of Jilin province, China. *Environ. Geochem. Health*, 2003, 25: 421-431.
- [3] Susheela AK. *State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India*. New Delhi: UNICEF and Fluorosis and Rural Development Foundation, 1999.
- [4] Mondal NK, Pal KC, Kabi S. Prevalence and severity of dental fluorosis in relation to fluoride in ground water in the villages of Birbhum District, West Bengal, India. *Environmentalist*, 2012, 3: 70-84.
- [5] Teotia SPS, Teotia M. Endemic fluoride: Bone and teeth-update. *Indian J. Environ. Toxicol.*, 1991, 1: 1-16.
- [6] Bhagavan SVBK, Raghu V. Utility of check dams in dilution of fluoride concentration in ground water and the resultant analysis of blood serum and urine of villagers, Anantapur District, Andhra Pradesh, India. *Environ. Geochem. Health*, 2005, 27: 97-107.
- [7] Pandey J, Pandey U. Fluoride contamination and fluorosis in rural community in the vicinity of a phosphate fertilizer factory in India. *Bull. Environ. Contam. Toxicol.*, 2011, 87: 245-249.
- [8] Arveti N, Sarma MRS, Aitkenhead-Peterson JA, Sunil K. Fluoride incidence in groundwater: a case study from Talupula, Andhra Pradesh, India. *Environ. Monit. Assess.*, 2011, 172: 427-443.
- [9] Environmental Health Hazard Assessment. *Public health goal for fluoride in drinking water*. Sacramento, CA: Pesticide and Environmental Toxicology Selection Section, Office of Environmental Health Hazard Assessment, 1997.
- [10] Ramanaiah SV, Venkatamohan S, Rajkumar B, Sarma PN. Monitoring of fluoride concentration in ground water of Prakasham district in India: correlation with physico-chemical parameters. *J. Environ. Sci. Eng.*, 2006, 48: 129-134.
- [11] Skjelkvale B. Water chemistry in areas with high deposition of fluoride. *Sci. Total Environ.*, 1994, 152: 105-112.
- [12] Brindha K, Rajesh R, Murugan R, Elango L. Fluoride contamination in ground water in parts of Nalgonda District, Andhra Pradesh, India. *Environ. Monit. Assess.*, 2011, 172: 481-492.
- [13] Gautam R, Bhardwaj N. Groundwater quality assessment of Nawa Tehsil in Nagaur district (Rajasthan) with special reference to fluoride. *Environmentalist*, 2010, 30: 219-227.
- [14] Weinstein LH, Davison A. *Fluorides in the Environment*. UK: CABI Publishing, 2004.
- [15] Kamaluddin M, Zwiazek JJ. Fluoride inhibits root water transport and affects leaf expansion and gas exchange in aspen (*Populus tremuloides*) seedlings. *Physiol. Plantarum*, 2003, 117: 368-375.
- [16] Pant S, Pant P, Bhiravamurthy PV. Effects of fluoride on early root and shoot growth of typical crop plants of India. *Fluoride*, 2008, 41: 57-60.
- [17] Miller GW, Shupe JL, Vedina OT. Accumulation of fluoride in plants exposed to geothermal and industrial water. *Fluoride*, 1999, 32: 74-83.
- [18] Elloumi N, Abdallah FB, Mezghani I, Rhouma A, Boukhris M. Effect of fluoride on almond seedlings in culture solution. *Fluoride*, 2005, 38: 193-198.
- [19] McNulty IB, Newman DW. Mechanism(s) of fluoride induced chlorosis. *Plant Physiol.*, 1961, 36: 385-358.
- [20] Yang SF, Miller GW. Biochemical studies on the effect of fluoride on higher plants. *Biochem. J.*, 1963, 88: 505-509.
- [21] Horvath I, Klasova A, Navara J. Some physiological and ultra-structural changes of *Vicia faba L* after fumigation with hydrogen fluoride. *Fluoride*, 1978, 11: 89-99.
- [22] Verma S, Dubey RS. Effect of cadmium on soluble sugars and enzymes of their metabolism in rice. *Biol. Plantarum*, 2001, 44: 117-23.
- [23] Kim CG, Power SA, Bell JNB. Effects of cadmium and soil type on mineral and Carbon

- partitioning in seedlings of *Pinus sylvestris*. *Water Air Soil Poll.*, 2003, 145: 253-66.
- [24] Kundu NC, Mondal B. Fluoride concentration in ground water in the North 24 Parganas District of West Bengal, India. *Fluoride*, 2010, 43: 116-210.
- [25] Lal B, Ambasht RS. Impairment of chlorophyll content in leaves of *Diospyros melanoxylon* by fluoride pollution. *Water Air Soil Poll.*, 1981, 16: 361-365.
- [26] Darral NM. The effect of air pollutants on physiological processes in plants. *Plant, Cell Environ.*, 1989, 12: 1-30.
- [27] Asthir B, Basra AS, Batta SK. Fluoride-induced alteration of carbon and nitrogen metabolism in developing wheat grains. *Biol. Plantarum*, 1998, 41: 287-292.
- [28] APHA. *Standard methods for the examination of water and wastewater* (21st ed.), Washington DC: American Public Health Association (APHA), 2005.
- [29] Brewer RF. *Fluorine*. In: Black, C.A. (ed.), *Methods of Soil Analysis: Agronomy Monograph, (Part 2)*. Madison, WI, USA: ASA and SSSA, 1965.
- [30] Sadashivam S, Manikam A. *Biochemical methods* (2nd ed). New Delhi: New Age International (P) Ltd., 1996.
- [31] Arnon DI. Copper enzymes in isolated chloroplast and polyphenol oxidase in *Beta vulgaris*. *Plant Physiol.*, 1949, 24: 1-15.
- [32] Mukherjee SP, Choudhury MA. Implications of water stress induced changes in the levels of endogenous ascorbic acid and hydrogen peroxide in *Vigna* seedlings. *Physiol. Plantarum*, 1983, 58: 166-170.
- [33] Lowry OH, Rose Brough NJ, Fan AL, Randal RJ. Protein measurement with the Folin phenol reagent. *J. Biol. Chem.*, 1951, 193: 265-275.
- [34] Moore S, Stein WH. In *Methods in Enzymol* (Eds. Colwick SP and Kaplan ND). New York: Academic Press, 1948.
- [35] McQuaker NR, Gurney M. Determination of total fluoride in soil and vegetation using an alkali fusion-selective ion electrode technique. *Anal. Chem.*, 1977, 49, 53-56.
- [36] WHO. *Guidelines for drinking water quality: Surveillance and control of community supplies* (2nd ed) Vol.3. Geneva: World Health Organisation, 1997, pp. 113. http://www.who.int/water_sanitation_health/dwq/gdwqvol32ed.Pdf
- [37] USPH. United States Public Health Service Drinking Water Standards, *Journal of American WaterWorks Association*, 1961, 53: 935-945.
- [38] Alagumuthu G, Rajan M. Chemometric studies of water quality parameters of Sankarankovil block of Tirunelveli, Tamilnadu. *J. Environ. Biol.*, 2010, 31: 581-586.
- [39] Walton WC. Ground water resources evolution. New York: McGraw Hill, 1970.
- [40] Taher M, Ahmed P. *Geography of North-East India* (2nd Ed). Guwahati: Mani Manik Prakash, 2001, pp. 12-40.
- [41] Handa BK. Geochemistry and genesis of fluoride-containing groundwater in India. *Ground Water*, 1975, 3: 275-281.
- [42] WHO. *Guidelines for Drinking-water Quality (Vol. 2): Health Criteria and Other Supporting Information*. Geneva: World Health Organization, 1984.
- [43] Viswanathan G, Jaswanth A, Gopalakrishnan S, Sivailango S, Aditya G. Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India. *Sci. Total Environ.*, 2009, 407: 5298-5307.
- [44] Salve PR, Maurya A, Kumbhare PS, Ramteke DS, Wate SR. Assessment of ground water quality with respect to Fluoride. *Bull. Environ. Contam. Toxicol.*, 2008, 81: 289-293.
- [45] Sreedevi PD, Ahmed S, Made B, Ladous E, Gandolfi JM. Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. *Environ. Geol.*, 2006, 50: 1-11.
- [46] Gupta S, Banerjee S, Saha R, Datta JK, Mondal N. Fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum District, West Bengal, India. *Fluoride*, 2006, 39: 318-320.
- [47] Dutta J, Nath M, Chetia M, Misra AK. Monitoring of Fluoride Concentration in Ground Water of Small Tea Gardens in Sonitpur District, Assam, India: Correlation with physico-chemical Parameters. *Int. J. Chem. Tech. Res.*, 2010, 2: 1199-1208.
- [48] Karthikeyan G, Shunmugasundarraaj A. Isopleth mapping and in-situ fluoride Dependence on water quality in the Krishnagiri block of Tamil Nadu in South India. *Fluoride*, 2000, 33: 121-127.
- [49] Ramakrishnaiah CR, Sadashivaiah C, Ranganna G. Assessment of water quality index for the groundwater in Tumkur Taluk, Karnataka State, India. *E-J. Chem.*, 2009, 6: 523-530.

- [50] Ravichandran B, Roychowdhury A, Mukherjee AK, Gangopadhyay PK, Saiyed HN. Estimation of fluoride content in the edible vegetables of an industrial area in Orissa. *Asian J. Water Environ. Poll.*, 2007, 5: 93-95.
- [51] Gupta S, Banerjee S, Mondal S. Phytotoxicity of fluoride in the germination of paddy (*Oryza sativa*) and its effect on the physiology and the biochemistry of germinated seedlings. *Fluoride*, 2009, 42: 142-146.
- [52] Abdallah FB, Elloumi N, Mezghani I, Garrec JP, Boukhris M. Industrial fluoride pollution of Jerbi grape leaves and the distribution of F, Ca, Mg, and P in them. *Fluoride*, 2006, 39: 43-48.
- [53] Wallis WJ, Miller GW, Psenak M, Shieh J. Fluoride effects on chlorophyll biosynthesis. *Fluoride*, 1974, 7: 69-77.
- [54] Guo Z, Tan H, Zhu Z, Lu S, Zhou B. Effect of intermediates on ascorbic acid and oxalate biosynthesis of rice and inrelation to its stress resistance. *Plant Physiol. Biochem.*, 2005, 43: 955-962.
- [55] Chang CW. Effect of fluoride on ribosomes from corn roots. Changes with growth retardation. *Plant Physiol.*, 1970, 23: 536-543.
- [56] Tome FV, Rodriquez MPB, Lozano JC. Soil-to-plant transfer factors for natural radionuclides and stable elements in a Mediterranean area. *J. Environ. Radioact.*, 2003, 65: 161-175.
- [57] Alonso J, Garcí'a MA, Pe'rez-Lo'pez M, Melgar MJ. The concentrations and bio-concentration factors of copper and zinc in edible mushrooms. *Arch. Environ. Contam. Toxicol.*, 2003, 44: 180-188.
- [58] Ribang L, Jianan T, Lizhen W, Daxian Z Wuyi W. The fluoride content in cultivated soil under different geographical conditions in China and its relation to endemic fluorosis. *Geogr. Res.*, 1975, 4: 30.
- [59] Swartjes FA, Dirven-Van Breemen EM, Otte PF, Van Beelen P, Rikken MGJ, Uinstra J, Spijker J, Lijzen JPA. *Human health risks due to consumption of vegetables from contaminated sites: towards a protocol for site-specific assessment*. RIVM Report 711701040, Bilthoven, the Netherlands, 2007.
- [60] Diesendorf M, Sutton PRN. Fluoride: New grounds for concern. *The Ecologist*, 1986, 16: 237-242.

AES 120724

© Northeastern University, 2012

Prevalence and severity of dental fluorosis in relation to fluoride in ground water in the villages of Birbhum district, West Bengal, India

Naba Kumar Mondal · Kartick Chandra Pal ·
Sahadeb Kabi

Published online: 8 January 2012
© Springer Science+Business Media, LLC 2012

Abstract In relation to fluoride in ground water, dental fluorosis is studied in seven villages, viz., Nasipur, Vabandapur, and Deshnabagram under Nalhati I block and Kamdebpur, Chalk Atla, Nowapara, and Junitpur under Rampurhat II block, of Birbhum district, West Bengal, India. Water samples ($N = 70$) were collected from the tube wells of the mentioned villages in the months of December 2010 to February 2011 and analyzed for fluoride and other water parameters. The study result revealed that the fluoride levels of almost all the water samples (95.7%) were higher than 1.5 mg/L, with mean values of 3.15 and 3.83 mg/L in Nalhati I block and Rampurhat II block, respectively. Dental fluorosis of 490 respondents was visually determined by a competent dentist using Dean's index (DI) and the tooth surface index of fluorosis (TSIF). According to the DI, the percentage of severely affected respondents was lowest in Chalk Atla (0%) and highest in Deshnabagram (50%). The percentage of severely affected respondents was lowest in Kamdebpur and Chalk Atla (0%) and highest in Nowapara (20%) according to the TSIF score. The age group 10–20 years showed the highest percentage of severe DI (40.8%) and the age group 21–30 years showed the highest percentage of severe TSIF (22.51%) compared to the other age groups in the study. The positive relationship between the fluoride level in water and the severity of dental fluorosis has been proved

statistically. The high mean score of dental fluorosis indicates that dental fluorosis is endemic throughout the study area.

Keywords Ground water · Fluoride · Dental fluorosis · Dean's index · Tooth surface index of fluorosis

1 Introduction

Chronic fluoride intoxication (fluorosis) is a worldwide health problem which originated mainly due to the consumption of drinking water containing high fluoride concentration (Susheela et al. 1993). The quality of ground water, which is the main source of drinking water, depends mainly on the lithology and soil of the contaminated area (Arveti et al. 2011). The amount of fluoride has increased in the subsoil water with the lowering of the water level (Gautam and Bhardwaj 2010). The problem of high fluoride concentration in ground water sources is one of the most important toxicological and geo-environmental issues in India. The weathering of rocks and leaching of fluoride-bearing minerals are the major reasons for elevated concentrations of fluoride in ground water (Brindha et al. 2011). Evaporation is another important phenomenon that concentrates fluoride in arid regions (Weinstein and Davison 2004). Besides the climate, the composition of the host rock, and hydrogeology, some anthropogenic activities such as the use of phosphatic fertilizers, pesticides, sewage, and sludges for agriculture, depletion of ground water, etc. are also implicated as causes of increased fluoride concentration in ground water (Office of Environmental Health Hazard Assessment [OEHHA] 1997; Ramanaiah et al. 2006). Handa examined the geochemistry and genesis of fluoride-containing ground water from different parts of

N. K. Mondal (✉) · K. C. Pal · S. Kabi
Department of Environmental Science, The University
of Burdwan, Burdwan 713104, West Bengal, India
e-mail: nabakumar_mondal@indiatimes.com

K. C. Pal
e-mail: pal_kartick@rediffmail.com

S. Kabi
e-mail: nababandana_jico@yahoo.co.in

India and observed that there is an inverse relation between fluoride and soluble calcium content in ground water (Handa 1975; Kundu et al. 2001). Evapo-transpiration, which precipitates calcite in ground water and increases the sodium-to-calcium ion ratio, may be contributing to the increase in the fluoride ion concentration (Jacks et al. 2005; Mamatha and Rao 2010). Studies have also shown that fluoride and bicarbonate ions in ground water are positively correlated and bicarbonate accelerates the dissolution of calcium fluorite to release fluoride into the water.

Fluoride intake and its harmful effects are more relevant in the context of India compared to Western countries, where the fluoridation of water is, instead, recommended to help prevent dental caries (Teotia and Teotia 1991). In areas with warm climate, the fluoride concentration in drinking water should remain below 1.0 mg/L, whereas in cooler climates, the recommended limit may increase up to 1.2 mg/L (World Health Organization [WHO] 1991). This is due to higher water consumption in warmer climates as a result of higher perspiration (Yadav et al. 2009). Enhanced fluoride intake through drinking water coupled with dietary intake could significantly substantiate the total fluoride accumulation in body tissue (Pandey and Pandey 2011). Drinking water is typically the largest single contributor to daily fluoride intake (Murray 1986). For a given individual, fluoride exposure (mg/kg of body weight per day) via drinking water is determined by the fluoride level in the water and the daily water consumption (liters per day).

Fluoride has been used for many years in carries prevention, mainly as community water fluoridation, whereby 1 ppm of fluoride in drinking water leads to a reduction in dental caries, with minor side effects such as dental fluorosis (Clarkson and McLoughlin 2000; da Cunha and Tomita 2006; Pizzo et al. 2007). Approximately 50% of the fluoride absorbed is deposited in the bones and teeth, and the remainder is excreted in urine, storing about 99% of the fluoride retained in the mineralized bones and teeth due to its affinity for calcium phosphate (Teotia et al. 2003). Dental fluorosis, a hypoplasia or hypomineralization of tooth enamel or dentin, produced the chronic ingestion of excessive amounts fluoride during a period when teeth are developing in a range of intensity from barely noticeable whitish striations to confluent pitting and staining (Horowitz 1986). The severity of dental fluorosis depends on when and for how long the overexposure of fluoride occurs (Den Besten 1994). The duration of exposure of fluoride may be indicated by the age of male and unmarried respondents, but for married females (belonging to the age group over 21 years old), it is indicated by the duration of married life. Radiographically detectable mineralization of the primary incisors occurs by 24 months of age and prior to 6 years of age for the second molars and premolars. Therefore, dental fluorosis does not occur when exposure

occurs in children <6–7 years of age (Ishii and Suckling 1986).

Keeping in mind the above facts, the present study was conducted in a semi-arid zone of Birbhum district in order to determine the fluoride levels in ground water which is used for drinking purposes and the dental fluorosis status of the target locations.

2 Materials and methods

2.1 Study area

The study area is in the Birbhum district, which is located between 23°32'30" and 24°35'0"N and 87°05'25" and 87°01'40"E (Fig. 1), having an area of 4,545 km². Geographically, this district lies at the north eastern end of Chota Nagpur Plateau, as it slopes down and merges with alluvial plains of the Ganges. The climate on the western side is dry and extreme, but it is relatively milder on the eastern side. During the summer, the temperature can shoot to well above 40°C and, in the winter, it can drop to around 10°C, with an annual average rainfall of 1,405 mm.

The present cross sectional study was conducted among seven villages, viz., Nasipur (24°17'33.7"N and 87°45'13.6"E), Vabanandapur (24°17'34.1"N and 87°45'13.9"E), Deshnabagram (24°17'32.1"N and 87°45'14.2"E) under Nalhati I block and Kamdebpur (24°6'30.4"N and 87°47'24"E), Chalk Atla (24°6'30.3"N and 87°47'23.9"E), Nowapara (24°6'20.7"N and 87°47'3.1"E), Junitpur (24°6'1.4"N and 87°46,53.5"E) under Rampurhat II block of Birbhum district, West Bengal, India. The most interesting part of the geology of this area stems from the gradient of red soil. A kind of sandy hard red soil of the alfisil type and laterite soil of this area give rise to potential aquifers at depth. Open wells and bore wells are the main source of water supply for domestic and agricultural purposes in this arid region.

2.2 Analytical methods

Ground water samples ($N = 70$) were collected from each of the mentioned villages of the two blocks during the winter season and stored in precleaned and sterilized polythene bottles of 1-L capacity following standard protocol. The water samples were immediately refrigerated after collection. The pH and EC values of the water samples were measured in situ immediately after collection. Water samples were analyzed for fluoride with an ion-selective electrode (model: Thermo Scientific Orion 4-Star) and the rest of the water parameters were analyzed following standard methods (American Public Health Association [APHA] 2005).

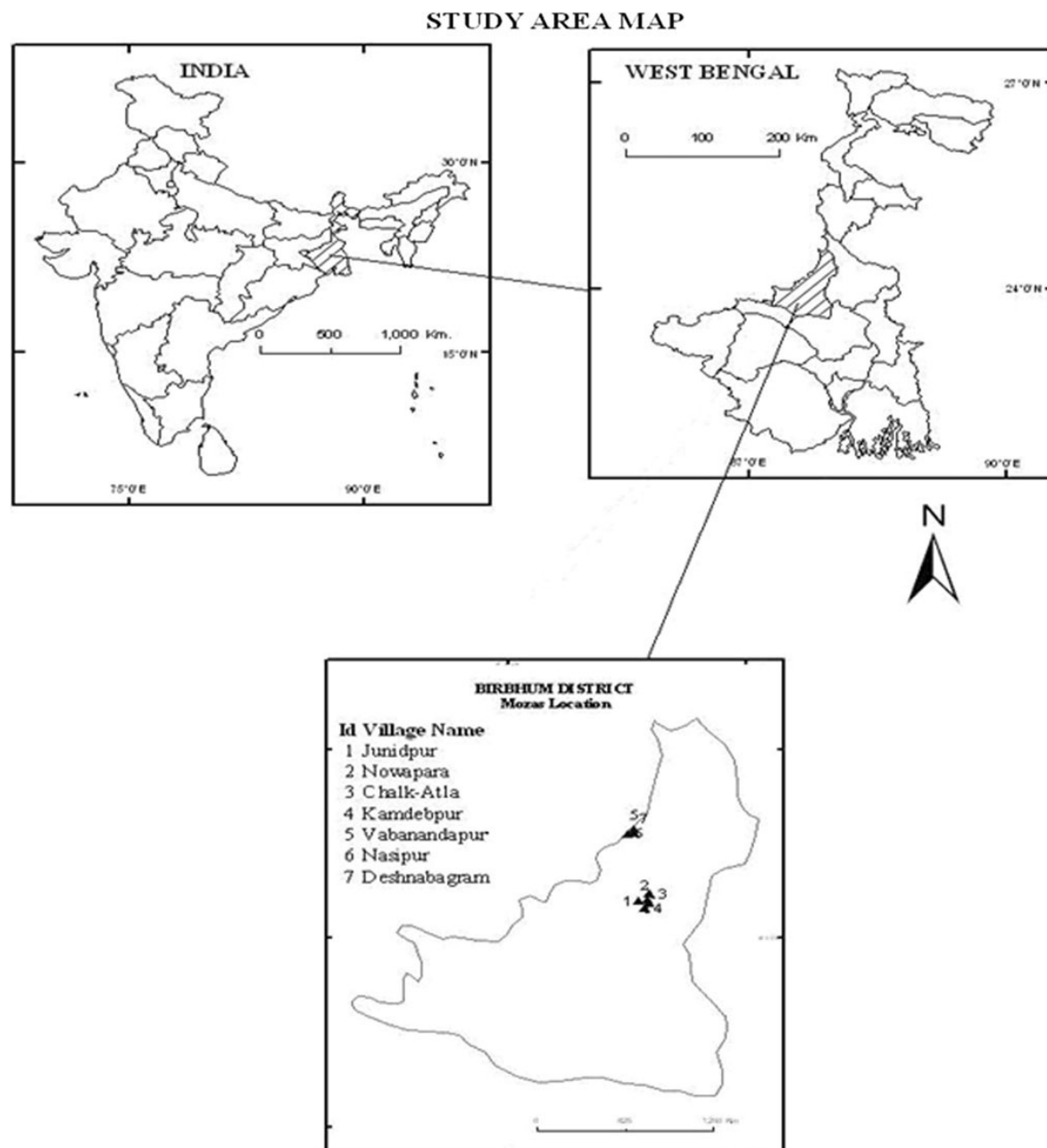


Fig. 1 Study area

For the dental study, the recruitment of respondents was performed at seven primary schools in the study area with pupils in the age range of 4–10 years and the rest of the age group samples were collected from the respective villages, confirming their permanent residency in these villages from birth. Written permission was given from school teachers and parents. Dental fluorosis was visually

determined by a competent dentist using the Dean's index (DI) and the tooth surface index of fluorosis (TSIF), improvised by Horowitz et al. (1984). The DI identified six gradations of clinical symptoms, denoting them as none, questionable, very mild, mild, moderate, and severe, and assigned them the respective numeric values 0, 0.5, 1, 2, 3, and 4 (Table 1). This diagnosis process requires the

inspection of dry and clear dental surfaces under a good light source. But in the TSIF, there was no need to dry the tooth prior to the determination of the score of fluorosis. In the TSIF, the minimum score is 0 and the maximum score

is 7 (Table 2). All the children and other respondents were instructed to brush their teeth before the examination by a trained dental hygienist. The dental fluorosis examinations were carried out with artificial light, using a plane dental

Table 1 Dean's index (DI)

Classification	Description
Normal	The enamel represents the usual translucent semivitre form type of structure. The surface is smooth, glossy, and usually of a pale creamy white color
Questionable	The enamel discloses slight aberrations from the translucency of normal enamel, ranging from a few white flecks to occasional white spots. This classification is utilized in those instances where a definite diagnosis of the mildest form of fluorosis is not warranted and a classification of "normal" not justified
Very mild	Small, opaque, paper-white area scattered irregularly over the tooth but not involving as much as approximately 25% of the tooth surface. Frequently included in this classification are teeth showing no more than about 1–2 mm of white opacity at the tip of the summit of the cusps of the bicuspid or second molars
Mild	The white opaque areas in the enamel of the teeth are more extensive but do not involve as much as 50% of the tooth
Moderate	All enamel surfaces of the teeth are affected, and surfaces subject to attrition show marked wear. Brown stain is frequently a disfiguring feature
Severe	Includes teeth formerly classified as "moderately severe" and "severe." All enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be altered. The major diagnostic sign of this classification is the discrete or confluent pitting. Brown stains are widespread and teeth often present a corroded appearance

Table 2 Tooth surface index of fluorosis (TSIF) (Horowitz et al. 1984)

Score	Description
0	Enamel shows no evidence of fluorosis
1	Enamel shows definite evidence of fluorosis, namely, areas with parchment-white color that total less than one-third of the visible enamel surface. This category includes fluorosis confined only to incisal edges of anterior teeth and cusp tips of posterior teeth (snow capping)
2	Parchment-white fluorosis totals at least one-third of the visible surface, but less than two-thirds
3	Parchment-white fluorosis totals at least two-thirds of the visible surface
4	Enamel shows staining in conjunction with any of the preceding levels of fluorosis. Staining is defined as an area of definite discoloration that may range from light to very dark brown
5	Discrete pitting of the enamel exists, unaccompanied by evidence of staining of intact enamel. A pit is defined as definite physical defect in the enamel surface with a rough floor that is surrounded by a wall of intact enamel. The pitted area is usually stained or differs in color from the surrounding enamel
6	Both discrete pitting and staining of the intact enamel exist
7	Confluent pitting of the enamel surface exists. A large area of the enamel may be missing and the anatomy of the tooth may be altered. Dark brown stain is usually present

Table 3 Population, demography, soil type, and average rainfall of the different villages under study

Block	Villages	Population	Demography	Soil type	Average rainfall (mm)
Nalhati I	Nasipur	800	Flat horizon	Old alluvial and red lateritic (pH 5–6.5)	1,420
	Deshnabagram	600	Flat horizon	Old alluvial and red lateritic (pH 5–6.5)	1,420
	Vabanandapur	1,500	Flat horizon	Old alluvial and red lateritic (pH 5–6.5)	1,420
Rampurhat II	Kamdebpur	200	Very near to the 'Dwarka' river	Old alluvial and red lateritic (pH 5–6.5)	1,430.5
	Chalk Atla	150	Very near to the 'Dwarka' river	Old alluvial and red lateritic (pH 5–6.5)	1,430.5
	Nowapara	150	Very near to the 'Dwarka' river	Old alluvial and red lateritic (pH 5–6.5)	1,430.5
	Juntpur	350	Very near to the 'Dwarka' river	Old alluvial and red lateritic (pH 5–6.5)	1,430.5

Table 4 Major cations, anions, and fluoride concentrations of the ground water samples of Nalhati I block

Sample no.	Location	pH	EC (mS/cm)	TH (mg/L)	TA (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	SO ₄ ²⁻ (mg/L)	Fe (mg/L)	PO ₄ ³⁻ (mg/L)	TDS (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)
1	Nasipur	7.21	2.81	944.1	171	7.11	445.5	98.8	40.2	102.6	186.0	0.41	0.17	1,376	95.8	69.4
2		7.52	0.42	128.0	171	6.84	39.7	97.9	36.6	9.1	11.8	0.12	0.09	268	31.9	0.2
3		7.63	2.70	592.2	92	2.15	357.3	87.8	44.0	115.7	255.6	0.25	0.11	1,009	142.2	138.8
4		8.81	2.51	428.2	124	2.21	122.0	175.7	36.4	81.1	180.1	0.09	0.43	1,275	127.7	148.5
5		8.34	3.30	954.0	113	2.89	120.1	82.4	16.8	209.4	280.2	0.37	0.00	1,811	133.5	59.5
6		8.30	0.70	136.0	207	5.37	15.1	142.7	36.4	11.6	33.9	0.43	0.34	469	78.4	34.6
7		7.52	0.62	108.0	195	5.42	27.0	60.4	32.8	16.7	18.4	0.11	0.24	402	84.6	33.8
8		7.81	2.30	302.1	108	2.30	127.2	42.7	42.0	47.3	55.9	0.21	0.21	941	32.5	64.5
9		8.11	0.90	171.0	195	4.81	140.3	15.5	32.8	21.8	132.2	0.11	0.33	603	37.8	21.2
10		8.05	1.41	143.1	132	4.50	137.2	146.7	38.4	11.6	145.7	0.17	0.11	938	102.3	0.4
11	Vabanandapur	8.14	0.31	73.3	99	1.41	19.9	54.9	20.1	5.6	14.8	0.42	0.72	201	49.4	29.7
12		8.36	2.22	413.5	144	3.22	198.5	87.8	128.6	22.6	148.5	0.28	0.50	874	107.4	0.8
13		8.05	2.04	677.7	216	4.01	150.7	175.7	124.0	28.3	121.8	0.03	0.48	1,108	107.4	1.2
14		8.09	0.30	200.1	198	2.80	38.1	109.8	40.4	24.0	18.4	0.12	0.48	201	31.9	11.2
15		7.91	2.10	538.8	216	2.71	146.2	98.5	52.0	98.3	42.8	0.12	0.40	967	65.8	6.8
16		7.96	1.81	282.5	198	3.80	133.7	103.8	40.0	43.8	78.3	0.24	0.80	906	34.9	22.4
17		8.32	0.82	136.3	187	3.50	155.2	125.7	44.6	6.9	14.7	0.12	0.54	536	26.9	1.6
18		8.10	1.53	157.0	216	3.62	162.1	90.1	42.4	13.7	120.4	0.09	0.48	805	45.8	10.6
19		7.80	3.20	733.1	178	2.81	135.1	62.8	56.4	142.3	17.3	0.16	0.67	944	98.7	42.3
20		7.91	0.65	256.3	236	1.96	97.6	41.3	64.0	23.1	132.2	0.09	0.65	402	33.5	32.5
21	Deshnabagram	8.36	0.10	20.4	45	2.16	54.6	32.9	36.0	12.5	13.9	0.97	0.80	67	8.7	0.6
22		8.18	0.30	36.8	81	1.83	148.9	32.9	12.2	11.6	16.9	0.36	0.28	201	46.6	4.8
23		8.38	0.60	167.5	126	1.92	44.5	65.9	44.1	13.8	17.8	0.10	0.40	402	61.0	6.9
24		8.47	0.41	134.7	216	1.27	33.4	175.7	20.1	20.3	12.1	0.28	0.51	268	34.8	0.8
25		8.12	0.52	167.5	270	3.5	93.2	153.7	16.1	30.6	11.8	0.51	0.58	335	34.8	0.4
26		8.20	0.80	184.2	252	1.41	98.4	75.7	38.6	21.4	17.6	0.20	0.34	536	40.6	19.8
27		8.15	0.73	102.4	268	2.55	10.5	142.3	22.4	12.4	13.9	0.15	0.62	469	28.9	20.8
28		7.95	0.63	109.3	172	1.65	120.2	87.6	34.3	6.6	14.8	0.15	0.54	402	30.7	1.2
29		8.31	0.51	107.0	270	2.32	110.7	136.5	26.3	10.2	16.4	0.1	0.51	335	46.2	3.5
30		8.50	0.45	191.6	290	2.45	13.1	147.6	22.4	32.9	13.9	0.12	0.74	268	42.2	4.8

Table 5 Major cations, anions, and fluoride concentrations of the ground water samples of Rampurhat II block

Sample no.	Location	pH	EC (mS/cm)	TH (mg/L)	TA (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	SO ₄ ²⁻ (mg/L)	Fe (mg/L)	PO ₄ ³⁻ (mg/L)	TDS (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)
1	Kamdebpur	8.29	0.31	53.0	126	1.87	43.8	65.9	16.2	3.1	13.3	0.48	0.67	201	37.7	39.64
2		8.36	0.27	28.7	189	2.11	27.6	164.7	8.2	2.1	19.0	0.51	0.55	134	65.2	58.2
3		8.36	0.22	65.2	144	3.47	8.3	143.9	24.0	1.3	6.9	0.60	0.60	134	136.5	36.5
4		8.41	0.30	70.4	251	4.4	133.2	177.3	8.0	12.1	16.2	0.12	0.72	201	174.3	95.3
5	Chalk Atla	8.33	0.52	45.4	226	4.01	141.4	160.2	8.0	6.1	11.5	0.54	0.55	335	170.3	65.2
6		8.28	0.61	40.0	249	3.77	97.2	138.9	12.3	2.4	13.6	0.33	0.45	402	126.3	36.2
7		7.96	0.42	109.2	85	1.82	37.4	44.6	28.3	9.4	15.4	0.09	0.77	268	67.9	66.4
8		8.48	0.53	46.3	201	2.32	46.3	92.1	16.0	1.5	13.9	0.17	0.65	335	78.9	56.2
9		8.35	0.25	65.4	170	1.78	58.4	83.6	20.1	3.7	11.6	0.28	0.51	134	38.6	15.4
10		8.01	0.21	86.3	195	2.23	124.1	90.2	28.2	3.9	20.2	0.32	0.40	206	45.2	43.5
11		8.21	0.52	87.8	334	2.7	352.5	109.8	28.2	4.3	16.6	0.58	0.68	355	61.0	69.38
12		8.18	0.63	187.8	360	2.01	235.8	87.8	44.0	18.7	18.4	0.90	0.50	402	72.2	62.3
13		8.52	0.61	94.7	326	2.64	272.8	101.6	27.5	6.5	13.9	0.69	0.54	402	95.3	42.2
14		8.31	0.48	73.3	402	4.16	130.1	175.8	8.5	12.8	16.2	0.57	0.74	268	122.2	19.7
15		8.16	0.82	130.4	305	3.76	128.0	145.6	11.3	24.7	17.6	0.74	0.41	536	132.8	32.0
16		8.10	0.75	53.8	350	4.11	106.0	180.2	9.8	7.5	12.9	0.65	0.65	469	111.7	54.0
17		8.19	0.59	145.9	175	1.90	117.0	76.2	34.3	14.6	19.2	0.63	0.65	335	61.2	43.5
18		8.31	0.62	217.1	132	1.77	33.2	56.5	46.0	24.5	12.8	0.31	0.53	402	37.5	25.2
19		8.20	0.91	170.4	221	2.51	42.5	98.7	32.0	21.7	16.5	0.98	0.47	603	148.3	49.3
20		8.26	0.28	161.5	136	1.85	46.7	67.4	47.0	10.6	16.9	0.55	0.68	134	78.9	16.2
21	Nowapara	7.80	0.32	48.7	436	9.98	45.2	205.0	16.4	1.9	432.8	0.15	0.68	201	119.0	19.82
22		7.60	0.71	14.5	242	6.6	44.2	142.2	2.2	2.1	212.5	0.22	0.23	469	66.8	0
23		7.91	0.63	30.8	218	6.57	50.1	146.0	2.0	6.2	516.0	0.14	0.31	402	49.3	19.82
24		8.01	0.48	34.7	86	2.32	36.6	60.1	4.2	5.8	126.7	0.21	0.13	268	81.3	32.5
25		7.80	0.90	245.8	135	9.82	49.1	204.9	6.3	55.8	78.3	0.63	0.00	603	112.0	44.5
26		7.90	0.54	50.4	62	6.76	33.4	138.3	1.5	11.2	122.3	0.51	0.03	335	202.5	52.9
27		8.11	0.42	58.6	239	3.36	138.0	78.5	1.6	13.1	459.9	0.20	0.16	268	96.3	22.2
28		8.31	0.80	169.8	235	3.41	120.1	154.9	14.4	32.1	48.9	0.18	0.04	536	102.5	23.5
29		7.80	0.35	39.3	228	4.71	101.3	136.3	2.7	7.8	216.3	0.31	0.18	201	132.2	56.3
30		7.7	0.36	87.6	252	6.23	136.0	144.3	14.2	12.5	122.7	0.40	0.24	201	234.7	106.3

Table 5 continued

Sample no.	Location	pH	EC (mS/cm)	TH (mg/L)	TA (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	SO ₄ ²⁻ (mg/L)	Fe (mg/L)	PO ₄ ³⁻ (mg/L)	TDS (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)
31	Junipur	7.2	0.41	61.5	59	1.7	44.2	27.6	2.1	13.5	423.7	0.25	0.05	268	34.8	11.2
32		7.3	0.80	53.2	140	7.2	95.1	77.1	1.1	12.1	358.5	0.71	0.04	536	131.9	36.2
33		6.2	0.91	160.0	144	9.1	46.0	72.3	10.2	32.3	221.7	0.69	0.02	603	240.6	86.5
34		7.2	0.72	98.7	162	7.1	84.0	88.4	8.8	18.4	122.6	0.64	0.04	469	145.3	32.9
35		7.5	0.62	156.3	72	6.6	39.2	42.6	10.5	31.2	105.6	0.31	0.17	402	133.4	33.7
36		7.1	0.47	127.8	46	2.5	44.2	28.5	33.1	10.8	302.8	0.26	0.30	268	62.9	21.1
37		7.8	0.52	164.0	75	3.1	33.9	34.7	14.6	30.6	508.7	0.46	0.18	335	78.2	36.5
38		7.9	0.54	67.3	25	1.8	51.3	11.1	1.6	15.2	324.4	0.18	0.40	335	42.6	11.0
39		8.1	0.62	91.2	51	2.3	101.0	22.7	6.8	17.8	207.5	0.25	0.21	402	52.8	17.3
40		7.5	0.73	116.0	57	2.1	37.2	28.1	7.2	23.5	98.3	0.21	0.13	469	50.3	16.5

mirror. Prior to the examination, the teeth were dried with an air syringe for 1 min. The survey team was composed of an examiner, a recorder, and a logistical human resource. The first phase of the examination using the DI and the second examination phase using the TSIF with a 5-day interval between the two was performed. The interval between the examinations using the two processes was to minimize the habits (possible memorization) of clinical examinations.

3 Results and discussion

Both the areas of Birbhum district are prone to being highly dry and the average rainfall lies in the range of 1,420–1,430.5 mm. The soil type, demography, average rainfall, and population of all these seven villages are given in Table 3. The minimum values of fluoride concentrations in ground water are 1.27 and 1.7 mg/L (Tables 4, 5) with average values of 3.15 and 3.83 mg/L in Nalhati I block and Rampurhat II block, respectively. The average fluoride concentration was minimum in the village of Deshnabagram (2.11 mg/L). One hundred percent of the water samples of Rampurhat II block and 90% of the samples of Nalhati I block had a fluoride concentration level of more than 1.5 mg/L (Table 6).

When this fluorinated water was consumed by the dwellers of these villages in these two blocks, they take in more than 3.15 mg/day of fluoride in Nalhati I block and more than 4.21 mg/day in Rampurhat II block, irrespective of their age and sex (Tables 7, 8). From several studies, a rough estimate of the total daily fluoride exposure in a temperate climate would be approximately 0.6 mg per adult per day in an area in which no fluoride is added to the drinking water and 2 mg per adult per day in a fluoridated area (WHO 1984). Therefore, the inhabitants of these two blocks are in endemic fluoride pollution.

Water sample analysis (Tables 3, 4) shows that almost all the water samples of both blocks were alkaline (pH > 7.0) in nature. 97.14% of the water samples from the two blocks were soft in nature, as the values of Ca and Mg were below the permissible limits of 75 and 150 mg/L, respectively, by the WHO (1997). The chloride and iron content of all the water samples were below the permissible limits of 500 and 1 mg/L, respectively, as prescribed by the WHO (1997). The phosphate content of 93.3 and 82.5% of water sources of Nalhati I block and Rampurhat II block, respectively, were found to be above the permissible limit of 0.1 mg/L permitted by the United States Public Health Service (USPHS 1961). 80 and 93.3% water samples of Nalhati I block and Rampurhat II block, respectively, were below the secondary maximum SO₄²⁻ contaminant level (SMCL) of 250 mg/L, based on esthetic effects, i.e., taste and odor (WHO 2011).

Table 6 Sampling location and percentage of samples having different fluoride levels

Area	Sampling location	No. of samples	Percentage of samples with different fluoride levels		
			<1.50 mg/L	1.50–4.00 mg/L	>4.00 mg/L
Nalhati I block	Nasipur	10	0	40	60
	Vabanandapur	10	10	80	10
	Deshnabagram	10	20	80	0
Rampurhat II block	Kamdebpur	10	0	80	20
	Chalk Atla	10	0	80	20
	Nowapara	10	0	30	70
	Junitpur	10	0	60	40

Table 7 Average fluoride intake in Nalhati I block

Age (years)	Sex	Average daily water intake (L)	Average daily intake of fluoride (mg)
<10	M	1.3	4.10
	F	1.0	3.15
10–20	M	2.4	7.56
	F	1.8	5.67
21–30	M	2.8	8.82
	F	2.1	6.62
>50	M	2.0	6.30
	F	1.6	5.04

Table 8 Average fluoride intake in Rampurhat II block

Age (years)	Sex	Average daily water intake (L)	Average daily intake of fluoride (mg)
<10	M	1.4	5.36
	F	1.1	4.21
10–20	M	2.3	8.81
	F	1.8	6.89
21–30	M	3.0	11.49
	F	2.0	7.66
>50	M	1.9	7.28
	F	1.6	6.13

An attempt was made to correlate the fluoride with various parameters of both the blocks, as indicated in Tables 9 and 10, respectively.

All the parameters showed positive correlation with fluoride except pH, iron (Fe), phosphate (PO_4^{3-}), and potassium (K^+) in Nalhati I block, but in Rampurhat II block, all the parameters showed positive correlation with fluoride except pH, chloride (Cl^-), calcium (Ca^{2+}), and phosphate (PO_4^{3-}). Calcium and magnesium showed positive correlation with fluoride in Nalhati I block. A similar observation was reported by Alagumuthu and Rajan (2010). The positive correlation with calcium observed may be attributed to the presence of limestone in those areas (Taher and Ahmed 2001). But the negative

correlation of fluoride with Ca^{2+} indicates that it has higher affinity for sodium than calcium, and this may be due to the dominance of ion exchange between Na^+ and Ca^{2+} ions (Singh et al. 2011). Amongst all the villages of the two blocks, Nowapara had the highest average sodium-to-calcium ion ratio (36.72). The highest average fluoride concentration in this village (5.96 mg/L) indicates that an elevated sodium-to-calcium ion ratio increases the fluoride level in water (Jacks et al. 2005; Mamatha and Rao 2010). A positive correlation was found between chloride and fluoride in Nalhati I block (Dutta et al. 2010; Karthikeyan and Shunmugasundarraj 2000). In both blocks, the HCO_3^- concentration shows a positive correlation with fluoride. The plot of fluoride concentration versus bicarbonate concentration also justifies the correlation (Figs. 2, 3). According to Saxena and Ahmed (2003), high concentration of HCO_3^- and alkaline pH are the favorable conditions for the dissolution of fluorite (CaF_2) minerals. The chemical process of fluoride dissolution can be represented as: $\text{CaF}_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + 2\text{Na}^+ + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2$ (Salve et al. 2008). The interpretation of the results of the chemical analyses of water samples was done using Piper diagrams to discriminate the type of waters in terms of the major constituent cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and anions (Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-}). Figures 4 and 5 show Piper diagrams for the illustration of the chemical analyses of the water samples taken from the two blocks of the study area. On the basis of Walton's classification (Walton 1970), 90% of the water samples of Rampurhat II block and 30% of the water samples of Nalhati I block showed an excess of alkaline earth with respect to alkalis at the three drawing points and 40% showed an excess of strong acid with respect to weak acid in Nalhati I block. In water samples of Nalhati I block, the carbonate hardness (secondary alkalinity) exceeds 50%, i.e., by alkaline earths and weak acid.

The dental fluorosis status using the DI and TSIF scores of all the villages of the two blocks is presented in Figs. 6 and 7. From the graphical representations, it is clear that the village Nowapara is highly affected by severe dental fluorosis, which is indicated both by the DI (50%) and the

Table 9 Correlation matrix of different parameters in the ground water of Nalhati I block

	pH	EC	TH	TA	F ⁻	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na ⁺
EC	-0.235													
TH	-0.303	0.891**												
TA	0.031	-0.243	-0.125											
F ⁻	-0.552**	0.150	0.212	0.106										
Cl ⁻	-0.470**	0.645**	0.636**	-0.240	0.263									
HCO ₃ ⁻	0.331*	0.033	0.068	0.465**	0.091	-0.091								
Ca	-0.070	0.359*	0.348*	-0.004	0.121	0.274	0.063							
Mg	-0.172	0.829**	0.873**	-0.220	0.017	0.445**	-0.049	-0.018						
SO ₄ ²⁻	-0.107	0.720**	0.681**	-0.314*	0.178	0.645**	0.000	0.256	0.618**					
Fe	0.080	-0.127	-0.059	-0.449**	-0.044	0.022	-0.218	-0.235	0.052	-0.045				
PO ₄ ³⁻	0.369*	-0.348*	-0.335*	0.297	-0.418*	-0.371*	0.075	0.080	-0.341*	-0.488**	0.157			
TDS	-0.153	0.938**	0.861**	-0.195	0.228	0.604**	0.132	0.291	0.779**	0.806**	-0.158	-0.454**		
Na ⁺	-0.078	0.754**	0.717**	-0.297	0.180	0.485**	0.203	0.340*	0.649**	0.741**	-0.129	-0.498**	0.754**	
K ⁺	-0.111	0.602**	0.489**	-0.350*	-0.028	0.445**	-0.001	-0.082	0.577**	0.621**	-0.030	-0.335**	0.556**	0.614**

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Bold data indicate significance correlation among the variables

Table 10 Correlation matrix of different parameters in the ground water of Rampurhat II block

	pH	EC	TH	TA	F ⁻	Cl ⁻	HCO ₃ ⁻	Ca	Mg	SO ₄ ²⁻	Fe	PO ₄ ³⁻	TDS	Na ⁺
EC	-0.338*													
TH	-0.121	0.438**												
TA	0.362*	0.012	-0.149											
F ⁻	-0.509**	0.346*	0.006	0.200										
Cl ⁻	0.287*	0.055	0.021	0.594**	-0.134									
HCO ₃ ⁻	0.310*	0.010	-0.202	0.700**	0.504**	0.173								
Ca	0.288*	-0.150	0.546**	0.122	-0.436**	0.210	-0.208							
Mg	-0.338*	0.626**	0.819**	-0.256	0.306*	-0.116	-0.093	-0.033						
SO ₄ ²⁻	-0.510**	0.025	-0.191	-0.210	0.321*	-0.243	-0.229	-0.439**	0.069					
Fe	-0.000	0.399*	0.362*	0.280*	0.090	0.312*	0.169	0.300*	0.229	-0.341				
PO ₄ ³⁻	-0.644**	-0.440**	-0.137	0.452**	-0.409**	0.229	0.210	0.519**	-0.516**	-0.484**	0.057			
TDS	-0.338*	0.987**	0.437**	0.021	0.358*	0.087	0.015	-0.150	0.625**	0.026	0.382**	-0.450**		
Na ⁺	-0.277*	0.220	0.014	0.214	0.614**	0.043	0.445**	-0.252	0.188	-0.091	0.334*	-0.218	0.210	
K ⁺	0.002	-0.049	0.058	0.220	0.156	0.328*	0.290*	0.086	0.011	-0.348*	0.273*	0.176	-0.035	0.611**

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Bold data indicate significance correlation among the variables

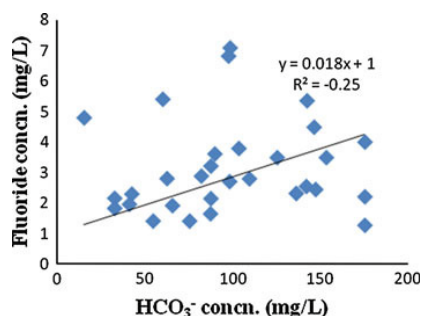


Fig. 2 Fluoride concentration versus HCO_3^- concentration plot of water samples in Nalhathi I block

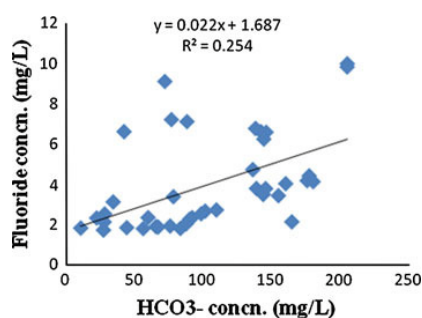
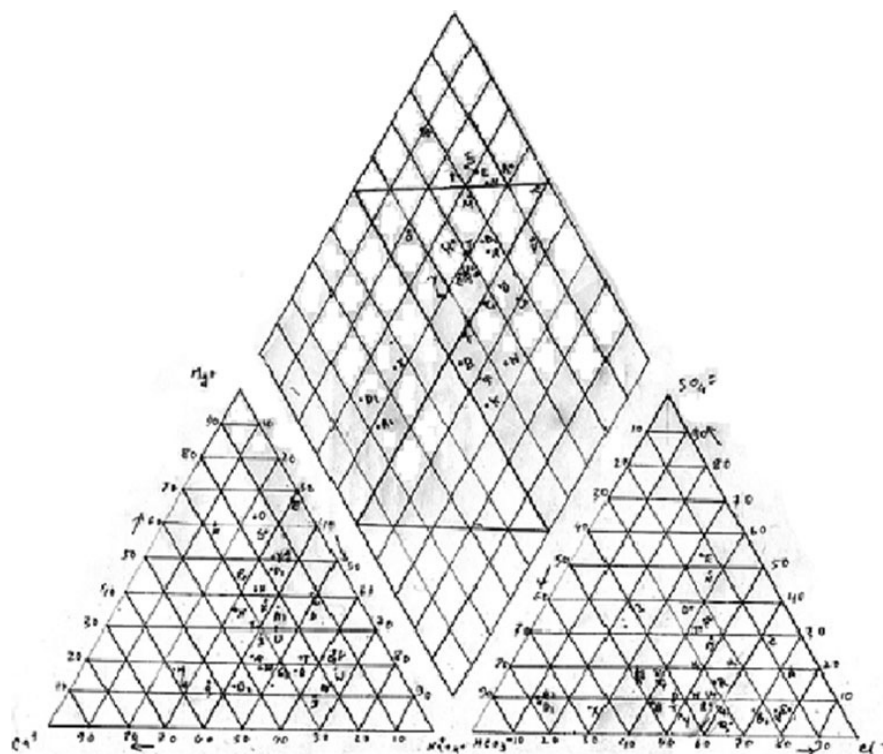


Fig. 3 Fluoride concentration versus HCO_3^- concentration plot of water samples in Rampurhat II block

Fig. 4 Piper diagram for representing the analyses of the ground water quality in Nalhathi I block



TSIF (20%). The relative comparison between fluoride levels in drinking water revealed that the highest severity in Nowapara is predicted by the highest average fluoride concentration in this village (5.96 mg/L).

In the age group 21–30 years, a greater percentage of male respondents are affected severely compared to the female respondents in both the blocks, irrespective of the DI or TSIF score (Tables 11, 12, 13, 14). This may be due to the fact that, in this age range, virtually all the female residents are married who were not inhabitants of these villages before marriage and are not in prolonged fluoride contamination as among the male respondents. The different pattern of fluorosis in the two blocks suggests that the prevalence of dental fluorosis can vary widely between different geographical locations having almost the same average fluoride concentration in drinking water.

The study results revealed that all the villages are highly fluoride affected. The dental fluorosis status indicates that the age groups 10–20 years and 31–50 years are very vulnerable according to the DI in both the Nalhathi I and Rampurhat II blocks, although only the age group 31–50 years showed the highest dental fluorosis percentage in Rampurhat II block. Again, the highest percentage of the DI was recorded in Nowapara and the minimum in Chalk Atla (Fig. 4). The intermediate percentages of the DI of 4 were recorded in Vabanandapur, Kamdebpur, Nasipur, and

Fig. 5 Piper diagram for representing the analyses of the ground water quality in Rampurhat II block

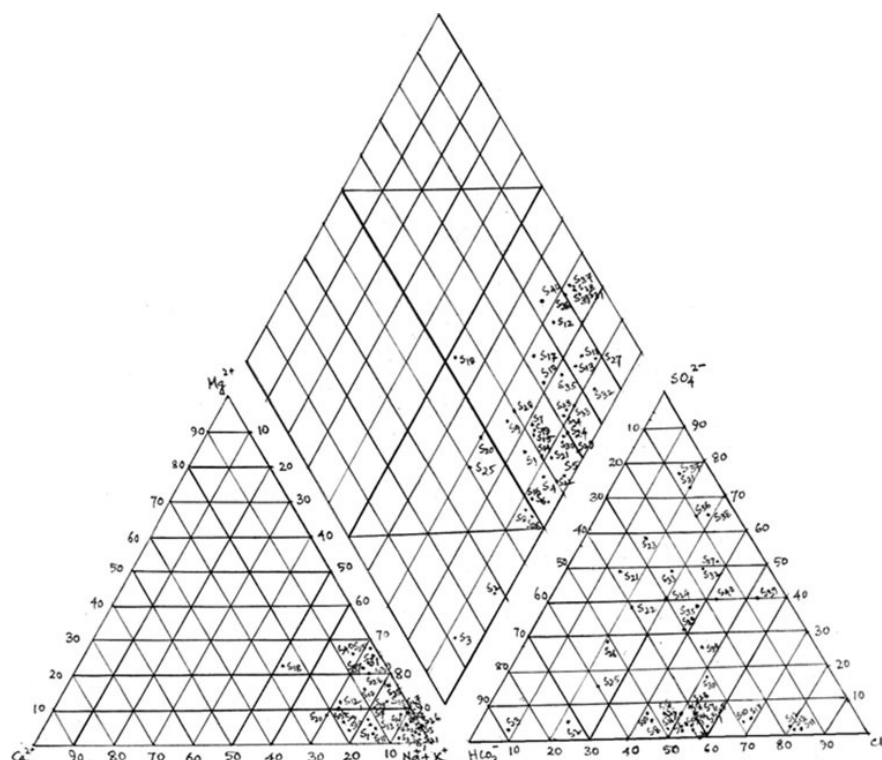
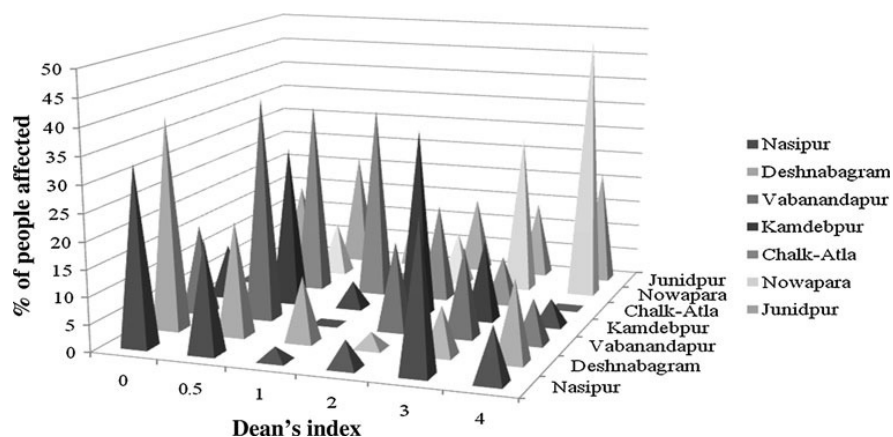


Fig. 6 Graphical presentation of the percentage of people affected in the villages of the two blocks with respect to the Dean's index (DI)



Junidpur. The percentage of the TSIF values of the different villages were recorded and highest was found to be in Nowapara and the minimum in Kamdebpur and Chalk Atla. It was found that dental fluorosis was more prevalent with increasing age. This was due to the fact that dental fluorosis occurs at an early age, especially at the time of eruption of secondary teeth (Gautam et al. 2011). The dental fluorosis status of the affected areas can be observed in Figs. 8 and 9 (in the age group <10 years);

Fig. 10 (in the age group 10–20 years); Fig. 11 (in the age group 21–30 years); Figs. 12 and 13 (in the age group 31–50 years); and Figs. 14 and 15 (in the age group >50 years).

The data from this study indicate that the prevalence of dental fluorosis increases with the fluoride concentration in drinking water (Choubisa 1997; Choubisa et al. 2001; Gopal 2000; Dhar et al. 2007). Fluorosis is a result of the destruction of metabolic calcium and phosphorus, leading

Fig. 7 Graphical presentation of the percentage of people affected in the villages of two the blocks with respect to the tooth surface index of fluorosis (TSIF) scores

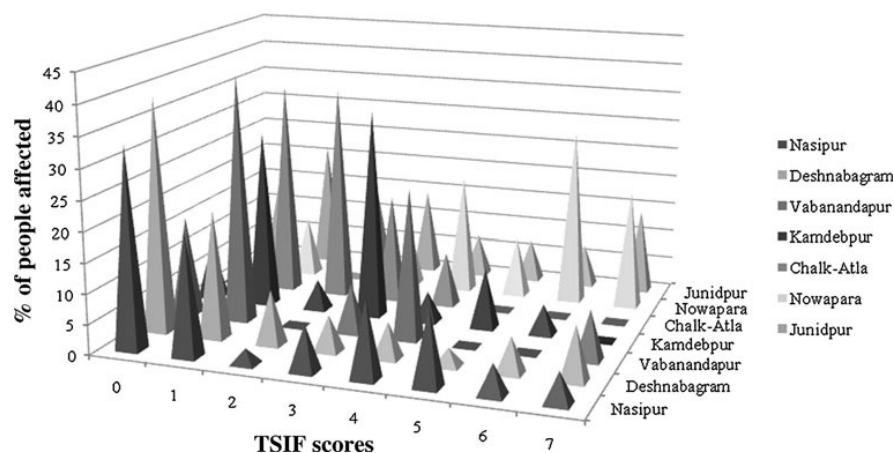


Table 11 Frequency distribution of the dental fluorosis classification (DI) of inhabitants of Nalhati I block

Age (years)	Sex	Number of respondents	DI classification					
			0, no. (%)	0.5, no. (%)	1, no. (%)	2, no. (%)	3, no. (%)	4, no. (%)
<10	M	21	6 (28.57)	6 (28.57)	0 (0)	3 (14.29)	2 (9.52)	4 (19.05)
	F	21	7 (33.33)	4 (19.05)	0 (0)	2 (9.52)	4 (19.05)	4 (19.05)
10–20	M	21	5 (23.81)	4 (19.05)	2 (9.52)	4 (19.05)	3 (14.29)	3 (14.29)
	F	21	7 (33.33)	6 (28.57)	2 (9.52)	1 (4.76)	3 (14.29)	2 (9.52)
21–30	M	21	4 (19.05)	9 (42.86)	1 (4.76)	2 (9.52)	3 (14.29)	2 (9.52)
	F	21	9 (42.86)	6 (28.57)	1 (4.76)	1 (4.76)	3 (14.29)	1 (4.76)
31–50	M	21	4 (19.05)	7 (33.33)	1 (4.76)	1 (4.76)	5 (23.81)	3 (14.29)
	F	21	9 (42.86)	5 (23.81)	0 (0%)	2 (9.52)	5 (23.81)	0 (0%)
>50	M	21	5 (23.81)	6 (28.57)	2 (9.52)	1 (4.76)	3 (14.29)	4 (19.05)
	F	21	7 (33.33)	5 (23.81)	1 (4.76)	1 (4.76)	6 (14.29)	1 (4.76)

Table 12 Frequency distribution of the dental fluorosis classification (DI) of inhabitants of Rampurhat II block

Age (years)	Sex	Number of respondents	DI classification					
			0, no. (%)	0.5, no. (%)	1, no. (%)	2, no. (%)	3, no. (%)	4, no. (%)
<10	M	28	3 (10.71)	8 (28.57)	3 (10.71)	5 (17.86)	3 (10.71)	6 (21.43)
	F	28	3 (10.71)	7 (25)	4 (14.29)	5 (17.86)	3 (10.71)	6 (21.43)
10–20	M	28	0 (0)	6 (21.43)	4 (14.29)	6 (21.43)	3 (10.71)	9 (32.14)
	F	28	2 (7.14)	9 (32.14)	3 (10.71)	5 (17.86)	3 (10.71)	6 (21.43)
21–30	M	28	1 (3.57)	8 (28.57)	3 (10.71)	5 (17.86)	5 (17.86)	6 (21.43)
	F	28	3 (10.71)	5 (17.86)	6 (21.43)	7 (25)	4 (14.29)	3 (10.71)
31–50	M	28	1 (3.57)	6 (21.43)	5 (17.86)	4 (14.29)	6 (21.43)	6 (21.43)
	F	28	4 (14.29)	7 (25)	4 (14.29)	5 (17.86)	5 (17.86)	3 (10.71)
>50	M	28	0 (0)	6 (21.43)	4 (14.29)	6 (21.43)	8 (28.57)	4 (14.29)
	F	28	1 (3.57)	6 (21.43)	3 (10.71)	6 (21.43)	7 (25)	5 (17.86)

to the inhibition of active enzymatic processes in the human body, which interrupts the function of the endocrine system, leading to fluorosis (Xiang et al. 2004). Therefore,

a more comprehensive study is necessary in order to explore other endemic fluoride-contaminated areas and make villagers aware of such irreversible damages.

Table 13 Frequency distribution of the dental fluorosis classification (TSIF) of inhabitants of Nalhati I block

Age (years)	Sex	Number of respondents	TSIF score							
			0, no. (%)	1, no. (%)	2, no. (%)	3, no. (%)	4, no. (%)	5, no. (%)	6, no. (%)	7, no. (%)
<10	M	21	8 (38.1)	8 (38.1)	0 (0)	0 (0)	4 (19.05)	1 (4.76)	0 (0)	0 (0)
	F	21	10 (47.62)	5 (23.81)	1 (4.76)	1 (4.76)	3 (14.29)	1 (4.76)	0 (0)	0 (0)
10–20	M	21	8 (38.1)	5 (23.81)	1 (4.76)	2 (9.52)	2 (9.52)	0 (0)	1 (4.76)	2 (9.52)
	F	21	6 (28.57)	7 (33.33)	2 (9.52)	2 (9.52)	2 (9.52)	1 (4.76)	0 (0)	1 (4.76)
21–30	M	21	5 (23.81)	7 (33.33)	0 (0)	0 (0)	2 (9.52)	2 (9.52)	2 (9.52)	3 (14.29)
	F	21	7 (33.33)	3 (14.29)	2 (9.52)	3 (14.29)	2 (9.52)	2 (9.52)	0 (0)	1 (4.76)
31–50	M	21	4 (19.05)	5 (23.81)	0 (0)	3 (14.29)	2 (9.52)	0 (0)	2 (9.52)	5 (23.81)
	F	21	7 (33.33)	7 (33.33)	2 (9.52)	2 (9.52)	3 (14.29)	0 (0)	0 (0)	0 (0)
>50	M	21	3 (14.29)	6 (28.57)	0 (0)	1 (4.76)	3 (14.29)	1 (4.76)	3 (14.29)	4 (19.05)
	F	21	5 (23.81)	5 (23.81)	1 (4.76)	2 (9.52)	5 (23.81)	2 (9.52)	0 (0)	1 (4.76)

Table 14 Frequency distribution of the dental fluorosis classification (TSIF) of inhabitants of Rampurhat II block

Age (years)	Sex	Number of respondents	TSIF score							
			0, no. (%)	1, no. (%)	2, no. (%)	3, no. (%)	4, no. (%)	5, no. (%)	6, no. (%)	7, no. (%)
<10	M	28	2 (9.52)	9 (32.14)	3 (10.71)	6 (21.43)	1 (3.57)	2 (9.52)	3 (10.71)	2 (9.52)
	F	28	2 (9.52)	7 (25)	4 (14.29)	5 (17.86)	3 (10.71)	3 (10.71)	2 (9.52)	2 (9.52)
10–20	M	28	0 (0)	5 (17.86)	4 (14.29)	6 (21.43)	3 (10.71)	1 (3.57)	5 (17.86)	4 (14.29)
	F	28	1 (3.57)	8 (28.57)	5 (17.86)	3 (10.71)	4 (14.29)	1 (3.57)	3 (10.71)	3 (10.71)
21–30	M	28	2 (9.52)	6 (21.43)	3 (10.71)	7 (25)	3 (10.71)	1 (3.57)	2 (9.52)	4 (14.29)
	F	28	3 (10.71)	9 (32.14)	4 (14.29)	3 (10.71)	3 (10.71)	1 (3.57)	4 (14.29)	1 (3.57)
31–50	M	28	1 (3.57)	5 (17.86)	5 (17.86)	6 (21.43)	3 (10.71)	3 (10.71)	3 (10.71)	2 (9.52)
	F	28	2 (9.52)	9 (32.14)	5 (17.86)	6 (21.43)	2 (9.52)	2 (9.52)	0 (0)	2 (9.52)
>50	M	28	1 (3.57)	4 (14.29)	2 (9.52)	6 (21.43)	5 (17.86)	4 (14.29)	3 (10.71)	3 (10.71)
	F	28	3 (10.71)	6 (21.43)	4 (14.29)	6 (21.43)	3 (10.71)	1 (3.57)	4 (14.29)	1 (3.57)

**Fig. 8** Dental fluorosis status of the age group <10 years**Fig. 9** Dental fluorosis status of the age group <10 years

4 Conclusion

The villages of Birbhum district of West Bengal, India, is showing endemic fluorosis caused by drinking water where ground water is the main source of drinking water. From

this study, it is concluded that the fluoride level in all the drinking water sources should be tested and that the water sources should be highlighted as to which are in a safe condition for the use of drinking. This study gives an overview of the existing caries in the people of Nalhati I



Fig. 10 Dental fluorosis status of the age group 10–20 years

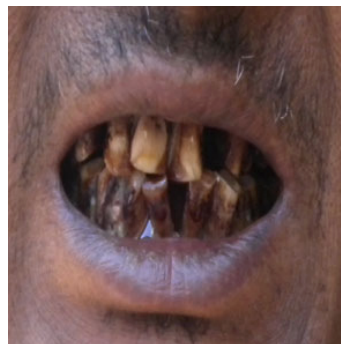


Fig. 13 Dental fluorosis status of the age group 31–50 years



Fig. 11 Dental fluorosis status of the age group 21–30 years

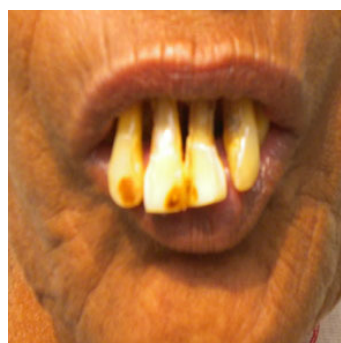


Fig. 14 Dental fluorosis status of the age group >50 years



Fig. 12 Dental fluorosis status of the age group 31–50 years



Fig. 15 Dental fluorosis status of the age group >50 years

block and Rampurhat II block of Birbhum district and helps in the implementation of programs to achieve optimal health. Apart from this study, other health hazards like skeletal fluorosis and gastrointestinal problems are also observed in this area. Therefore, it is of immense importance that any government or non-governmental organizations should help in the identification of the fluoride level and to arrange for fluoride-free drinking water supplies to help the poorer section of society.

Acknowledgments The authors gratefully acknowledge all the villagers who supported the completion of this exhaustive work. The authors also express their gratitude to all the staff members of the

Department of Environmental Science, The University of Burdwan, for their cooperation.

References

- Alagumuthu G, Rajan M (2010) Chemometric studies of water quality parameters of Sankarankovil block of Tirunelveli, Tamilnadu. *J Environ Biol* 31(5):581–586
- American Public Health Association (APHA) (2005) Standard methods for the examination of water and wastewater, 21st edn. APHA, Washington DC
- Arveti N, Sarma MRS, Aitkenhead-Peterson JA, Sunil K (2011) Fluoride incidence in groundwater: a case study from Talupula, Andhra Pradesh, India. *Environ Monit Assess* 172:427–443

- Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. *Environ Monit Assess* 172:481–492
- Choubisa SL (1997) Fluoride distribution and fluorosis in some villages of Banswara district of Rajasthan. *Indian J Environ Health* 39:281–288
- Choubisa SL, Choubisa L, Choubisa DK (2001) Endemic fluorosis in Rajasthan. *Indian J Environ Health* 43:177–189
- Clarkson JJ, McLoughlin J (2000) Role of fluoride in oral health promotion. *Int Dent J* 50:119–128
- da Cunha LF, Tomita NE (2006) Dental fluorosis in Brazil: a systematic review from 1993 to 2004. *Cad Saude Publica* 22(9):1809–1816
- Den Besten PK (1994) Dental fluorosis: its use as a biomarker. *Adv Dent Res* 8:105–110
- Dhar V, Jain A, Van Dyke TE, Kohli A (2007) Prevalence of dental caries and treatment needs in the school-going children of rural areas in Udaipur district. *J Indian Soc Pedod Prev Dent* 25(3):119–121
- Dutta J, Nath M, Chetia M, Misra AK (2010) Monitoring of fluoride concentration in ground water of small tea gardens in Sonitpur district, Assam, India: correlation with physico-chemical parameters. *Int J ChemTech Res* 2(2):1199–1208
- Gautam R, Bhardwaj N (2010) Groundwater quality assessment of Nawa Tehsil in Nagaur district (Rajasthan) with special reference to fluoride. *Environ* 30:219–227
- Gautam R, Bhardwaj N, Saini Y (2011) Dental fluorosis—a case study from Nawa tehsil in Nagaur district, Rajasthan (India). *Environ* 31:401–406
- Gopal KS (2000) Prevalence of fluorosis in 20 villages of Manur block, Tirunelveli Kattabomman district. *Indian J Environ Prot* 20:663–667
- Handa BK (1975) Geochemistry and genesis of fluoride containing groundwater in India. *Ground Water* 3:275–281
- Horowitz HS (1986) Indexes for measuring dental fluorosis. *J Public Health Dent* 46(4):179–183
- Horowitz HS, Driscoll WS, Meyers RJ, Heifetz SB, Kingman A (1984) A new method for assessing the prevalence of dental fluorosis—the Tooth Surface Index of Fluorosis. *J Am Dent Assoc* 109:37–41
- Ishii T, Suckling G (1986) The appearance of tooth enamel in children ingesting water with a high fluoride content for a limited period during early tooth development. *J Dent Res* 65:974–977
- Jacks G, Bhattacharya P, Chaudhary V, Singh KP (2005) Controls on the genesis of some high-fluoride groundwaters in India. *Appl Geochem* 20(2):221–228
- Karthikeyan G, Shunmugasundarraj A (2000) Isoleth mapping and in-situ fluoride dependence on water quality in the Krishnagiri block of Tamil Nadu in South India. *Fluoride* 33(3):121–127
- Kundu N, Panigrahi M, Tripathy S, Munshi S, Powell MA, Hart BR (2001) Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh District of Orissa, India. *Environ Geol* 41:451–460
- Mamatha P, Rao SM (2010) Geochemistry of fluoride rich groundwater in Kolar and Tumkur districts of Karnataka. *Environ Earth Sci* 61:131–142
- Murray JJ (1986) Appropriate use of fluorides for human health. World Health Organization (WHO), Geneva, Switzerland
- Office of Environmental Health Hazard Assessment (OEHHHA) (1997) Public health goal for fluoride in drinking water. Pesticide and Environmental Toxicology Section, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. OEHHHA, Sacramento, CA. Available online at: http://oehha.ca.gov/water/phg/pdf/fluor_c.pdf
- Pandey J, Pandey U (2011) Fluoride contamination and fluorosis in rural community in the vicinity of a phosphate fertilizer factory in India. *Bull Environ Contam Toxicol* 87:245–249. doi: 10.1007/s00128-011-0344-6
- Pizzo G, Piscopo MR, Pizzo I, Giuliana G (2007) Community water fluoridation and caries prevention: a critical review. *Clin Oral Invest* 11:189–193
- Ramanaiah SV, Venkata Mohan S, Rajkumar B, Sarma PN (2006) Monitoring of fluoride concentration in ground water of Prakasham district in India: correlation with physico-chemical parameters. *J Environ Sci Eng* 48:129–134
- Salve PR, Maurya A, Kumbhare PS, Ramteke DS, Wate SR (2008) Assessment of groundwater quality with respect to fluoride. *Bull Environ Contam Toxicol* 81:289–293
- Saxena VK, Ahmed S (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environ Geol* 43:731–736
- Singh CK, Rina K, Singh RP, Shashtri S, Kamal V, Mukherjee S (2011) Geochemical modeling of high fluoride concentration in groundwater of Pokhran area of Rajasthan, India. *Bull Environ Contam Toxicol* 86:152–158
- Susheela AK, Kumar A, Bhatnagar M, Bahadur R (1993) Prevalence of endemic fluorosis with gastrointestinal manifestations in people living in some north-Indian villages. *Fluoride* 26:97–104
- Taher M, Ahmed P (2001) Geography of North-East India, 2nd edn. Mani Manik Prakash, Guwahati, India, pp 12–40
- Teotia SPS, Teotia M (1991) Endemic fluoride: bones and teeth—update. *Indian J Environ Toxicol* 1:1–16
- Teotia SPS, Teotia M, Singh KP (2003) 4th International Workshop on Fluorosis Prevention and Defluoridation of Water. *Fluoride* 36(2):107–125
- United States Public Health Service (USPHS) (1961) Drinking water standards. *J Am Water Works Assoc* 53:935–945
- Walton WC (1970) Ground water resources evolution. McGraw Hill, New York, p 300
- Weinstein LH, Davison A (2004) Fluorides in the environment: effects on plants and animals. CABI Publishing, Wallingford, UK
- World Health Organization (WHO) (1984) Fluorine and fluorides. Environmental health criteria, vol 36. WHO, Geneva, Switzerland
- World Health Organization (WHO) (1991) Fluoride and fluoride. Environmental health criteria, vol 36. WHO, Geneva, Switzerland, p 274
- World Health Organization (WHO) (1997) Guidelines for drinking-water quality, 2nd edn. Volume 3: Surveillance and control of community supplies. WHO, Geneva, Switzerland, p 113. Available online at: http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en/index2.html
- World Health Organization (WHO) (2011) Guidelines for drinking water quality, 4th edn. Chapter 10: Acceptability aspects: taste, odour and appearance. WHO, Geneva, Switzerland, p 227. Available online at: http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/
- Xiang QY, Liang YX, Chen BH, Wang CS, Zhen SQ, Chen XD, Chen LS (2004) Serum fluoride and dental fluorosis in two villages in China. *Fluoride* 37(1):28–37
- Yadav JP, Lata S, Kataria SK, Kumar S (2009) Fluoride distribution in groundwater and survey of dental fluorosis among school children in the villages of the Jhajjar District of Haryana, India. *Environ Geochem Health* 31:431–438