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Fluoride and nitrate in groundwater of south-western Punjab, India—occurrence, distribution and statistical analysis

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ABSTRACT

Prevalence of fluoride and nitrate in groundwater has become major concern due to their potential environmental related health impacts. High fluoride and nitrate concentrations have been reported from many parts of rural southwestern Punjab causing serious health threats to the inhabitants. The present study is focussed on evaluating the recent status of fluoride and nitrate contamination of drinking water sources from Ferozepur, Faridkot, and Bathinda districts of Punjab. The sampling sites were selected after comprehensive surveying and preliminary analysis of the data collected through questionnaire. Other physico-chemical parameters analyzed were the pH, TDS, electrical conductivity, phosphate concentration along with depth, and age of source. Findings showed that 59 and 95% groundwater samples were found to have fluoride and nitrate content, respectively, beyond permissible limits (WHO). High fluoride concentration up to 10.6 mg/L and nitrate concentration up to 90 mg/L in drinking water is observed from Faridkot and Bathinda districts. Mean fluoride and nitrate concentration was found to be 3.0302 and 25.14 with standard deviation 1.317 and 10.32, respectively. Statistical analysis was also done to study the correlation/association between various studied parameters viz. nitrate, fluoride, pH, EC, and depth, and it was found that fluoride showed positive correlation with pH ($R^2 = 0.82$) and negative correlation with depth and EC ($R^2 = 0.4118$ and 0.9169, respectively). Similarly, nitrate showed negative trend with depth, EC, and pH ($R^2 = 0.95$, 0.9199, and 0.395, respectively). Phosphate concentration was also analyzed but none was found conclusive as all the samples were found within permissible range. Geospatial variation with fluoride was also observed at certain locations.

Keywords: Fluoride, Nitrate; Global positioning system; Statistical analysis

1. Introduction

Chemical composition of natural ground water is predominantly influenced by type, depth of soils, and a subsurface geological formation through which it percolates and picks up a large amount of dissolved constituents and reaches the aquifer system and contaminates the ground water. Generally, higher proportions of dissolved constituents are found in groundwater because of greater interaction with

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various materials in geological strata. Groundwater quality is also influenced by contribution from the atmosphere and surface water bodies.

The quality of groundwater is of great importance in determining its suitability for domestic, irrigation and industrial purposes. There is a growing concern about the deterioration of groundwater quality due to geogenic and anthropogenic activities. Rapid urbanization, industrialization, and overexploitation of natural resources have resulted in many incidents of groundwater contamination, e.g. excessive use of fertilizers and pesticides in agriculture and improper disposal of urban/industrial waste have caused contamination of groundwater resources.

Fluoride and nitrate are reported contaminants in drinking water/groundwater from many parts of the world. The states with high prevalence rate of fluoride in India are Andhra Pradesh, Bihar, Assam, Gujarat, Haryana, Jammu & Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Manipur, Orissa, Rajasthan, Tamil Nadu, West Bengal, Jharkhand, Chhattisgarh, and Uttar Pradesh [1,2]. The same has also been reported in high concentration from various districts of Punjab.

Fluoride occurs naturally as minor constituent of groundwater in all categories of hydro-geological strata as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluorapatite [$3Ca_3(PO_4)_2$ $Ca(F,Cl_2)$]. Fluoride is found in sedimentary rocks and igneous rocks in the form of fluorspar and cryolite, respectively. These fluoride minerals are nearly insoluble in water. Hence, fluorides will be present in groundwater only when conditions favor their dissolution or high fluoride-containing effluents are discharged to the water bodies from industries [3].

Various factors such as type of rock, nature of geological strata, contact time between rock and circulating groundwater, and climatic conditions directly affect the amount of fluoride in groundwater. It has been reported that arid and semi-arid areas are more prone to high fluoride content in their groundwater due to evaporation as compared to humid areas which have low incidences of high fluoride content due to high rainfall inputs and the subsequent diluting effect [4]. The groundwater flow in these areas is usually slow that further enriches fluoride content in water. The presence of certain ions, particularly bicarbonate and calcium, also affect the concentration of fluoride in groundwater [5].

The occurrence of fluoride in higher concentration in groundwater is a complex phenomenon which results from interplay of multiple complex interdependent hydro-geochemical processes. These processes directly affect the quality of groundwater. The major cations and anions present in the groundwater are Na^+, Ca^{2+}, K^+, Mg^{2+}, and HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-. The major weathering processes occurring in the water are carbonate, gypsum, and silicate weathering [6]. The abundance of Ca^{2+} and Mg^{2+} is attributed to carbonate and gypsum weathering [6–8]. Sodium and potassium ions to the groundwater mainly results from dissolution of silicates and soda feldspar (albite) and potash feldspars (orthoclase and microcline). Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks.

Anthropogenic activities such as use of phosphatic fertilizers, clays used in brick and ceramic industries, and coal burning also contribute to high fluoride in shallow and surface waters [9].

Maximum permissible limit for fluoride in drinking water is 1.5 mg/L (WHO water quality standards). The desirable fluoride concentration in drinking water is 0.6–1.2 mg/L and at this level it prevents dental caries and promotes bone development; however, if consumed in higher doses for longer may lead to dental and skeletal fluorosis, a disease that can cause mottling of the teeth, calcification of ligaments, crippling bone deformities, and many other physiological disorders that can ultimately, lead to death [10]. It has also been linked with cancer, decreased cognitive ability, lower intelligence quotient (IQ), and developmental issues in children [11–13]. Recently, it has also been known to have adverse effects on male fertility and reproductive system by disrupting the reproductive hormones [14,15].

High nitrate concentration in drinking water is another significant global water quality issue. It has been reported from many countries, including the United States, the Netherlands, Nigeria, South Africa, Palestine, Chile, Nepal, and India [16,17]. The intensive farming belt of Western UP, Haryana, Punjab, and parts of Rajasthan, Delhi, and West Bengal have been reported to contain high nitrate in their groundwater [18,19].

Nitrate may be naturally present in significant quantities in soil containing nitrogen-fixing bacteria, decaying plants, and animal manure, where most of nitrate is absorbed by the plants to synthesize organic nitrogenous compounds. Because of its high solubility in water, the nitrate may reach the groundwater by leaching through soil with rain or irrigation water.

The extent of leaching further depends on percentage of cropland in a given region. The environmental characteristics such as temperature and precipitation are important cofactors, affecting nitrate concentration in groundwater. Higher average temperatures usually result in lower nitrate contamination of groundwater, possibly due to increased evapotranspiration. Higher average precipitation dilutes nitrates in the soil, further reducing groundwater nitrate concentration [20]. Soil types and composition are important determinants of nitrate concentration in groundwater [21]. Soil texture, drainage, climate, vegetation, and long-term land use lead to a gradual build up of soil organic carbon [22,23].

Nitrate leaching to ground water predominantly occurs in sandy, well-drained soils with shallow water tables. Leaching is also a problem in areas that receive high rainfall or intensive irrigation, and have frequent use of fertilizers, manures, or other sources of nitrogen. Aerobic conditions in the shallow aquifers commonly allow high nitrate (NO_3^-) concentrations to persist for longer periods of time

Anthropogenic activities viz. the increasing use of artificial fertilizers, disposal of wastes, and change in land use, also contribute to nitrate levels especially in Indian groundwater [19,24]. High nitrate concentration in surface and groundwater is direct indicator of nitrate discharges from non-point sources such as use of nitrogenous fertilizers or pollution by organic compounds resulting from microbial oxidation of organic nitrogen compounds and ammonia [25]. Nitrate is a major component of human and animal wastes, and the occurrence of abnormally high concentrations of nitrate suggests possible pollution of water resources. Furthermore, the higher concentration of nitrate may also be a result of the presence *of E. coli*, *Staphylococcus aureus*, *Proteus vulgaris*, *Salmonella typhi*, and *Pseudomonas aeruginosa* in the fecal matter [26].

Usually the ammonia within nitrogen fertilizers is transformed into nitrate by the process of biological nitrification, and the possible reaction responsible is shown as:

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O \quad (1)$$

The deleterious health effects attributed to nitrate include infantile methemoglobinemia also known as blue-baby syndrome. Due to the nature of the infant digestive system, nitrate is reduced to nitrite which can render hemoglobin unable to carry oxygen [27]. Long term consumption of elevated levels of nitrate can affect the health of adults causing cancer risks due to formation of nitrosamines or nitrosamides [28]. It has also been known to cause spontaneous abortions, birth defects, respiratory tract infections, and changes in immune system [29–33]. Similarly, it has adverse effect on livestock especially, the young animals. The ruminants (cattle, sheep) are also susceptible or at risk to nitrate poisoning as bacteria present in the rumen convert nitrate to nitrite.

The study area undertaken in the present study has already reported with high arsenic concentration in the groundwater [34]. Simultaneous occurrence of high nitrate and fluoride has also been reported from Rajasthan and Agra region in India and rift valley in Ethiopia [35–37]. Studies have shown a strong correlation between coexistence of nitrate and fluoride in groundwater. Coexistence of nitrate and arsenic has also been observed at many places, including Nepal and West Bengal in India [17,38].

The present study is focussed on evaluating the recent status of fluoride and nitrate in drinking water/groundwater sample obtained from south-western Punjab, India. The study is also focussed on finding correlation between the various contaminants in the region. The phosphate levels are also analyzed to get insights into the anthropogenic source of these contaminants in groundwater. The relationship between cooccurrences of nitrate and fluoride will also be checked.

2. Materials and methods

2.1. Study area

The present study area is located in the southwestern Punjab (India), commonly known as Malwa region. More than 95% rural population of this area rely on groundwater to meet their requirements for drinking, domestic, and irrigation purposes. The geographical coordinates of the surveyed area have been determined with the help of global positioning system (Garmin GPS 60, Sr No. 1DG048032). The entire study area lies between latitudes of 30˚ 25.113 and 30˚ 44.928 north, and longitudes of 74.32230 and 74.86022 east (Table 1).

2.2. Topography

The geological formations of area under study are unconsolidated alluvial-type deposits of quaternary age and mainly comprised of sand, silt, and clay such as polyhalites, anhydrites (gypsum), limestone, dolomite, shale, quartzite, etc. that contain fluoride [39,40]. Fine- to medium-grained sand horizon forms the potential aquifer in the area. The major source of groundwater recharge are inflow of groundwater from north-eastern and northern parts, rainfall, seepage from canals and return seepage through irrigation, and percolation from surface water bodies. The groundwater is mainly abstracted through hand pumps (up to 25 m) and shallow and medium depth tube wells (up to 175 m).

Table 1
Physico-chemical characteristics of groundwater/drinking water

S. No.	Village ID	Sample ID	Latitude	Longitude	pH	TDS (mg/L)	EC (μS/cm)	Depth (in feet)	Fluoride conc. (mg/L)	Nitrate conc. (mg/L)
1	S1	S1A	30˚ 25.397N	74˚ 50.601E	7.12	577	887	50	6.38	10
2		S1B	30˚ 25.446N	74˚ 50.339E	6.81	2,210	3,397	50	2.9	37
3		S1C	30˚ 25.313N	74˚ 50.29E	7.33	1,480	2,275	90	6.45	32
4		S1D	30˚ 25.113N	74˚ 50.379E	7.22	945	1,452	50	9.92	25
5		S1E	30˚ 25.305N	74˚ 50.532E	6.74	2062	3,169	45	0.99	19
6		S1F	30˚ 25.436N	74˚ 50.51E	7.52	105	161	0	3.467	15
7	S2	S2A	30˚ 27.407N	74˚ 56.857E	6.40	730	1,120	105	0.9999	20
8		S2B	30˚ 27.38N	74˚ 56.870E	6.69	580	891	130	3.225	17
9		S2C	30˚ 27.351N	74˚ 56.700E	6.67	2,370	3,643	125	2.17	36
10		S2D	30˚ 27.517N	74˚ 56.759E	6.71	604	928	125	1.29	25
11		S2E	30˚ 27´ 22.0˝N	74˚ 56´ 50.8˝E	6.89	1,354	2081	90	2.016	20
12	S3	S3A	30˚ 34.079N	74˚ 57.868E	6.81	1,020	1,568	100	5.08	14
13		S3B	30˚ 34.109 N	74˚ 57.898E	6.88	975	1,499	95	5.16	14
14		S3C	30˚ 34´ 18.3˝N	74˚ 51´ 59.0˝E	7.12	889	1,366	90	4.62	23
15		S3D	30˚ 34´ 4.63˝N	74˚ 52´ 2.5˝E	6.89	1,240	1906	90	3.98	25
16		S3E	30˚ 31.528N	74˚ 56.639E	7.68	567	871	135	5.23	16
17	S4	S4A	30˚ 44´ 2˝N	74˚ 44´ 0˝E	6.44	5,120	7,869	25	1.278	30
18		S4B	30˚ 42′ 37˝N	74˚ 43´ 56˝E	7.68	2,180	3,351	40	1.129	38
19		S4C	30˚ 44´ 54˝N	74˚ 42´ 50˝E	6.55	3,680	5,656	30	2.213	20
20		S4D	30˚ 44.30N	74˚ 43´ 48E	6.24	6,590	10,129	25	1.94	28
21		S4E	30˚ 44.60N	74˚ 43´ 58E	6.91	610	938	50	2.59	12
22	S5	S5A	30˚ 44.893N	74˚ 41.249E	7.59	381	586	90	3.78	25
23		S5B	30˚ 44.902N	74˚ 41.327E	7.44	242	372	90	2.98	13
24		S5C	30˚ 44.928N	74˚ 41.445E	7.38	399	613	90	4.87	14
25		S5D	30˚ 44.650N	74˚ 41.936E	7.42	125	192	85	5.08	50
26		S5E	30˚ 44.453N	74˚ 41.201E	7.58	489	752	40	3.49	18
27	S6	S6A	30˚ 41.544N	74˚ 47.742E	7.88	341	524	25	2.65	12
28		S6B	30˚ 41.491N	74˚ 47.918E	7.89	789	1,213	45	2.86	16
29		S6C	30˚ 44.392N	74˚ 47.420E	8.12	768	1,180	60	3.14	18
30		S6D	30˚ 44.118N	74˚ 47.730E	8.67	869	1,336	100	4.26	10
31		S6E	30˚ 44.382N	74˚ 47.426E	7.90	381	586	50	4.64	10
32	S7	S7A	30˚ 27.413N	74˚ 53.405E	8.57	1,050	1,614	75	5.48	16
33		S7B	30˚ 27.809N	74˚ 53.743E	8.41	1,630	2,505	45	4.74	25
34		S7C	30˚ 27.304N	74˚ 53.357E	8.03	3,070	4,719	70	3.64	12
35		S7D	30˚ 27.744N	74˚ 53.961E	8.33	909	1,397	75	3.88	10
36		S7E	30˚ 27.753N	74˚ 53.726E	8.37	2,580	3,965	45	2.84	25
37	S8	S8A	30˚ 16´ 41.76˝ N	74˚ 56´ 21.00˝E	6.80	790	1,090	80	0.41	12
38		S8B	30˚ 16´ 43.86˝N	74˚ 56´ 20.76˝E	7.81	2,373	3,650	80	1.06	4
39		S8C	30˚ 16´ 40.23˝N	74˚ 56´ 19.45˝E	7.69	30	45	0	4.35	80
40		S8D	30˚ 16´ 38.92˝N	74˚ 56´ 22.35˝E	7.30	733	1,127	70	3.65	75
41		S8E	30˚ 16´ 40.86˝N	74˚ 56´ 23.55˝E	6.67	1,048	1,613	70	0.27	20
42		S8F	30˚ 16´ 41.16˝N	74˚ 56´ 21.31˝E	6.85	807	1,242	70	0.46	15
43	S9	S9A	30˚ 15´ 49.79˝N	74˚ 54´ 1.12˝E	6.80	731	1,124	220	0.57	6
44		S9B	30˚ 15´ 47.25˝N	74˚ 53´ 57.49˝E	6.98	1,091	1,678	220	0.78	12
45		S9C	30˚ 15´ 36.91˝N	74˚ 53´ 53.78˝E	8.10	3,218	4,950	180	5.8	20
46		S9D	30˚ 15´ 30.71˝N	74˚ 53´ 58.65˝E	7.20	7,976	12,270	40	7.4	90
47		S9E	30˚ 15´ 33.98˝N	74˚ 54´ 8.77˝E	7.86	3,562	5,480	70	8.8	18
48		S9F	30˚ 15´ 39.85˝N	74˚ 54´ 12.86˝E	6.84	4,414	6,790	35	1.27	60
49	S10	S10A	30˚ 54´ 1.78˝N	74˚ 38´ 12.54˝E	7.68	674	1,037	40	2.25	45
50		S10B	30˚ 53´ 57.83˝N	74˚ 38´ 6.44˝E	8.26	148	227	60	1.25	60

(*Continued*)

Table 1 (*Continued*)

S. No.	Village ID	Sample ID	Latitude	Longitude	pH	TDS (mg/L)	EC (μS/cm)	Depth (in feet)	Fluoride conc. (mg/L)	Nitrate conc. (mg/L)
51		S10C	30° 53′ 53.49″N	74° 38′ 8.40″E	8.34	230	380	75	1.05	26
52		S10D	30° 53′ 56.04″N	74° 38′ 15.36″E	6.74	4,641	7,140	70	1.07	30
53		S10E	30° 53′ 58.83″N	74° 38′ 13.66″E	7.02	4,050	6,230	220	1.4	60
54		S10F	30° 53′ 57.00″ N	74° 38′ 11.07″E	6.98	3,640	5,600	50	1.26	20
55	S11	S11A	30° 51′ 27.97″N	74° 40′ 15.15″E	8.07	1,320	2,030	35	10.6	6
56		S11B	30° 51′ 25.71″N	74° 39′ 52.44″E	7.47	1,651	2,540	35	4.8	8
57		S11C	30° 51′ 10.99″N	74° 39′ 59.70″E	7.55	453	697	180	0.65	55
58		S11D	30° 50′ 52.82″ N	74° 40′ 9.43″E	7.88	432	664	240	1.31	15
59		S11E	30° 51′ 22.27″N	74° 40′ 10.98″E	7.78	610	939	300	0.86	14
60		S11F	30° 51′ 16.83″N	74° 40′ 3.72″E	7.40	112	173	50	1.25	50
61	S12	S12A	30° 54′ 4.96″N	74° 40′ 1.26″E	7.33	787	1,210	115	0.42	10
62		S12B	30° 54′ 0.72″N	74° 39′ 59.49″E	7.06	698	1,074	120	0.46	18
63		S12C	30° 53′ 58.46″ N	74° 39′ 59.95″E	7.09	867	1,334	80	0.42	26
64		S12D	30° 53′ 55.25″N	74° 40′ 6.87″E	6.99	1,007	1,549	200	0.56	20
65		S12E	30° 54′ 0.35″N	74° 40′ 3.85″E	7.26	954	1,593	180	0.98	28
66		S12F	30° 54′ 0.09″N	74° 40′ 1.38″E	7.18	807	1,331	150	1.2	35

2.3. Sampling

The primary data regarding extent of fluoride and nitrate contamination was collected in the form of questionnaire drafted in the local language containing questions related to water source (type, age, and bore depth), use of water (drinking/domestic/irrigation), Number of persons depending on source water and medical history related to fluoride and nitrate contamination. The data were analyzed thoroughly to determine the sample size and the sampling sites. Field visits were carried out in this regard to collect drinking water samples of surface and underground water sources (Hand-pumps/submersible pumps/public and private Tube wells) from the selected sites. All the samples were collected in duplicates and stored in PET bottles (500-mL capacity).

2.4. Instrumentation and analysis

The samples were analyzed for physico-chemical parameters such as pH, TDS, EC, phosphate, fluoride, and nitrate concentration by standard methods [41]. All parameters including fluoride and nitrate concentrations were determined onsite using portable handy pH meter, TDS meter, and fluoride and nitrate field test kits of Merck (catalogue product no.). The samples were also tested in the laboratory, and the results were cross-analyzed by colorimetric determination of fluoride by SPADNS method, nitrate by cadmium reduction method, and phosphate by ascorbic acid method, respectively [42].

3. Research and discussion

Most of the drinking water samples analyzed were found to have high TDS, electrical conductivity along with high fluoride and nitrate concentrations when compared with WHO standards for drinking water (Table 1). The pH of water samples was slightly alkaline and varied from 6.24 to 8.67 with mean pH 7.36. The minimum pH of 6.24 was observed in the sample ID S2A, while the maximum pH 8.67 was observed from sample ID S6D. High pH is mainly due to presence of high carbonate and bicarbonate ions in the groundwater that result from carbonate weathering.

The EC values analyzed for all the samples ranged from 173 to 12,270 μS/cm with mean value 2,326 μS/cm. Eighteen samples (26.15%) and 52 samples (80%) were found to have values beyond BIS (3,000 μS/cm) and WHO (750 μS/cm) standards, respectively, and were found unfit for human consumption. The higher EC values (10,129 and 12,270 μS/cm) were noticed in the samples taken from coordinates 30˚44.30N & 74˚43′48E (Peepli) and 30˚15′30.71″N & 74˚53′58.65″E (Sivian). High TDS values were also observed at many locations. The higher TDS and EC values are likely due to extensive agricultural practices, and over extraction of groundwater resulted in high concentrations of dissolved materials. The major ions contributing to high TDS and EC are Na^{2+}, Ca^{2+}, K^{+}, Mg^{2+}, and HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-. Summary of water quality parameters of surveyed area is given in Table 2.

Table 2
Summary of water quality parameters of studied area

Name of village	No. of samples	pH	Total dissolved solids (mg/L)	EC (μS/cm)	Fluoride conc. (mg/L)	Nitrate conc. (mg/L)
S1	6	6.74–7.52	577–2,210	887–3,397	0.99–9.92	10.0–37.0
S2	5	6.40–6.89	580–2,370	891–3,643	0.9999–3.225	17.0–36.0
S3	5	6.81–7.68	567–1,240	871–1,906	3.98–5.23	14.0–16.0
S4	5	6.24–7.68	610–6,590	3,351–10,129	1.129–2.59	12.0–38.0
S5	5	7.38–7.59	125–489	192–752	2.98–5.08	13.0–5.0
S6	5	7.88–8.67	381–869	524–1,336	2.65–4.64	10.0–18.0
S7	5	8.03–8.57	909–3,070	1,397–4,719	2.84–4.48	10.0–25.0
S8	6	6.67–7.81	709–2,373	1,090–3,650	0.06–1.06	0–20.0
S9	6	6.80–8.30	731–7,976	1,124–12,270	0.20–8.80	4.0–90.0
S10	6	6.74–8.34	674–4,641	1,037–7,140	0.03–1.40	0–60.0
S11	6	6.98–8.07	432–3,640	664–5,600	0.65–10.60	0–20.0
S12	6	6.99–7.33	112–1,007	173–1,549	0.20–0.98	0–20.0
Total	66	6.20–8.67	381–7,976	173–12,270	0.03–10.60	0.00–90
Mean		7.361515	1511.59	2326.03	3.0302	25.143

3.1. Statistical analysis

3.1.1. Fluoride analysis

The fluoride concentration in the groundwater samples varied from 0.27 to 10.6 mg/L with mean value 3.0302 mg/L and SD 1.317. The data revealed that 59% of total samples exceeded the permissible limit (Table 3). The maximum fluoride concentration (10.6 mg/L) was observed in sample with sample ID S11A obtained from village Kasu Begu (S11). Five of six samples (S1A, S1B, S1C, S1D, and S1F) from village Chena were found to have fluoride concentration more than permissible limit (1.5 mg/L) at all depths. Fluoride concentration (3.467 mg/L) in the sample taken from municipal water supply was also more than the permissible limit. The similar trend has also been observed at many locations from Faridkot district including the villages; Dhilwan (S3), Peepli (S4), Arianwala (S5), and Jaito (S6), where all the samples collected exceeded the WHO permissible limit. As majority of the population residing in these areas extract groundwater to meet their daily requirements, the inhabitants of these villages are at most risk of fluoride poisoning.

12.3% of total samples with fluoride concentration were below 0.6 mg/L which is the minimum concentration required to prevent dental caries and to promote bone development and considered unfit for drinking. Village Bazidpur (S12, District Firozepur) was the only location from where all the samples were found within the permissible limit. The frequency distribution of fluoride with respect to sampling area is given in Table 3 and Fig. 1.

The major cause of fluoride occurrence in this area is the release of fluoride from fluoride-bearing minerals such as fluorite, fluorapatite, topaz, quartz, and mica, in the bed rock.

A higher value of pH favors the enrichment of F^- in groundwater as the OH^- in groundwater with high value of pH and same charge and radius can replace the exchangeable F^- of fluoride containing minerals (illite, chlorite, micas/muscovite, and amphiboles) thus, can increase the concentration of fluoride in groundwater [43,44].

The mechanism of replacement of F^- from muscovite by hydroxyl ion is as shown below:

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \xrightarrow{\text{Muscovite}} KAl_2[AlSi_3O_{10}][OH]_2 + 2F^- \quad (2)$$

It has been put forth that alkaline conditions with pH ranging between 7.6 and 8.6 are favorable for dissolution of fluorite mineral from the host rocks. Moreover, the hydrolysis of alumino-silicate minerals in the sandstone aquifers produces bicarbonate ion which can further enhance fluorite dissolution as depicted below:

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad (3)$$

The study showed that fluoride has a negative correlation with depth as most of the fluoride occurrence is observed in shallow surface waters which may be due to water logging and high saline conditions in the studied area which further leads to presence of most

Table 3
Frequency distribution of water quality parameters of studied area

S. No.	Name of village	No. of samples	Fluoride conc. (mg/L)			Nitrate conc. (mg/L)		
			<1.0 mg/L	1.0–1.5 mg/L	>1.5 mg/L	0–10 mg/L	10–45 mg/L	>45 mg/L
1	S1	6	1	Nil	5	Nil	6	Nil
2	S2	5	1	1	3	Nil	5	Nil
3	S3	5	Nil	Nil	5	Nil	5	Nil
4	S4	5	Nil	2	3	Nil	5	Nil
5	S5	5	Nil	Nil	5	Nil	4	1
6	S6	5	Nil	Nil	5	Nil	5	Nil
7	S7	5	Nil	Nil	5	Nil	5	Nil
8	S8	6	3	1	2	1	3	2
9	S9	6	2	1	3	1	3	2
10	S10	6	Nil	5	1	Nil	4	2
11	S11	6	2	2	2	2	2	2
12	S12	6	5	1	Nil	Nil	6	Nil

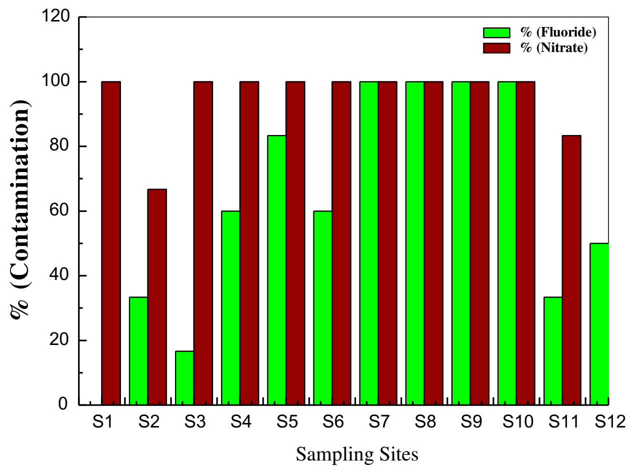

Fig. 1. Concentration of fluoride and nitrate (frequency wise) at various sampling sites.

of the salts on the surface layers. Although the possibility of fluoride contribution from agricultural activities including excessive use of phosphatic fertilizers and atmospheric deposition of fluoride cannot be ruled out. The similar findings have also been reported by other researchers [45,46]. Phosphate concentrations in the groundwater samples were also analyzed, but all the samples were found within the permissible limit with the exception of three samples which were of marginally higher concentration than the prescribed permissible limit. Again, the higher concentration was observed in the surface water samples, which further indicates the contribution of anthropogenic sources towards groundwater contamination.

Fluoride concentration in the groundwater has showed highly non-uniform trends of geospatial distribution, as samples taken from coordinates 30˚ 25.113N and 74˚ 50.379E (Sample ID S1D) and 30˚ 25.305N and 74˚ 50.532E (Sample ID S1E) from almost similar depth (45–50 ft) have shown large variations in fluoride concentration (9.92 and 0.99 mg/L, respectively). Similar trends have also been observed at other places with non-uniform geospatial distribution of the fluoride which further confirms the findings.

3.1.2. Nitrate analysis

Samples analyzed for nitrate concentration (nitrate–nitrogen) in the groundwater in the study area were found to vary from 0 to 90 mg/L with a mean value 25.14 and SD 10.32 which is 2.5 times more than the WHO prescribed limit for drinking water (Table 3). More than 95% samples exceeded the WHO permissible limit of 10 mg/L. The maximum nitrate concentration up to 90 mg/L was observed in the sample obtained from Village Sivian (S9D, District Bathinda), while the minimum nitrate concentration 4 mg/L was observed in the sample with Sample ID S8B taken from village Gill Patti (S8).

Most of the samples in shallow waters (up to depth of 100 ft) were found with nitrate concentration higher than permissible limit. The cause of occurrence of high nitrate in shallow water samples is likely due to anthropogenic activities as no geologic source of nitrate has been found from the previous studies carried out in the studied area. As compared to WHO permissible limit, an average concentration of 25.1.4 mg/L in groundwater samples clearly show an indication for the influence of fertilizer used in surrounding agricultural areas as well as microbial mineralization in the groundwater.

Table 4
Statistical analysis of water samples

S. No.	Name of village	No. of samples	Fluoride conc. (mg/L)	Range	Mean	SD	Nitrate conc. (mg/L)	Range	Mean	SD
1	S1	6	0.99–9.92	8.93	5.01	3.195	10.0–37.0	27	23	10.29
2	S2	5	0.9999–3.225	2.225	1.9408	0.8683589	17.0–36.0	19	23.6	7.5
3	S3	5	3.98–5.23	1.25	4.814	0.523622	14.0–25.0	11	18.4	5.22
4	S4	5	1.127–2.59	1.461	1.83	0.6189	12.0–38.0	26	25.6	9.9398
5	S5	5	2.98–5.08	2.1	4.04	0.9033549	13.0–50.0	37	24	15.28
6	S6	5	2.65–4.64	1.99	3.51	0.8857765	10.0–18.0	8	13.2	3.63318
7	S7	5	2.84–5.48	2.64	4.116	1.0198431	10.0–25.0	15	17.6	7.09225
8	S8	6	0.27–4.35	4.08	1.7	1.8155	4.0–80.0	76	34.33	33.87
9	S9	6	0.57–8.8	8.23	4.103333	3.67048	6.0–60.0	54	34.33	33.26
10	S10	6	1.05–2.25	1.2	1.38	0.4457	20.0–60.0	40	40.166	17.44
11	S11	6	0.65–10.6	9.95	3.245	3.9156	6.0–55.0	49	24.66	21.89
12	S12	6	0.42–1.20	0.78	0.6733	0.334106	10.0–35.0	25	22.83	8.7273

Moreover the study area is an intensive farming belt where farmers use much more fertilizers and pesticides for agricultural purposes and the excessive use of such agrochemicals and unmanaged irrigation have resulted in the nitrate contamination of shallow as well as groundwater. Poor sanitation, limited sewage management practices associated with water-logging conditions have also contributed to further increase in nitrate content in surface waters. The statistical analysis of fluoride and nitrate concentration is given in Table 4.

3.2. Correlation analysis

The fluoride and nitrate concentrations in groundwater have showed significant relationship with pH, electrical conductivity, and depth.

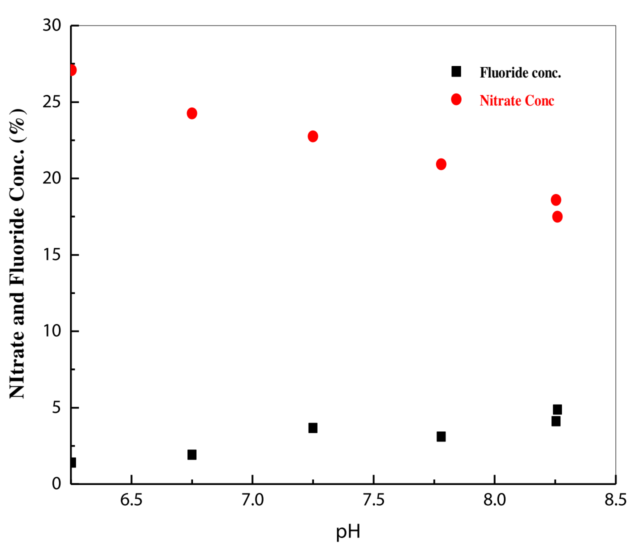

Fig. 2(a). Fluoride and nitrate relationship with pH.

3.2.1. Effect of pH on fluoride and nitrate

Fluoride concentration has showed a positive correlation with pH whereas nitrate showed slightly negative trend with pH ($R^2 = 0.8214$ and 0.395, respectively) (Figs. 2(a) and 2(b)).

The positive correlation between the pH and fluoride levels might be due to the release of hydroxyl and bicarbonate ions simultaneously during the leaching and dissolution process of fluoride-bearing minerals in the groundwater [Eqs. (4) and (5)].

$$CaF_2 + CO_3^{2-} \rightarrow CaCO_3 + 2F^- \quad (4)$$

$$CaF_2 + 2HCO_3^{2-} \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad (5)$$

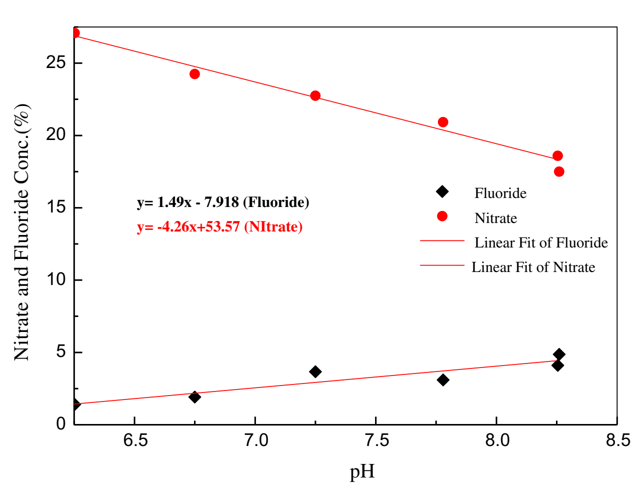

Fig. 2(b). linear fit showing fluoride and nitrate relationship with pH.

Table 5
ANOVA: showing effect of pH on nitrate and fluoride in groundwater

		DF	Sum of squares	Adjusted R^2	Mean square	F-Value	Prob. > F
Fluoride	Model	1	7.45907	0.8214	7.45907	23.99028	0.00806
Fluoride	Error	4	1.24368		0.31092		
Fluoride	Total	5	8.70275				
Nitrate	Model	1	60.70519	0.395	60.70519	4.26182	0.10791
Nitrate	Error	4	56.97581		14.24395		
Nitrate	Total	5	117.681				

Similarly, negative trend of nitrate with pH may be due to its reduction in the alkaline medium to nitrate resulting lowering down the pH of the water and increase in the concentration of nitrate.

This is in compliance with the findings of research studies carried out in many other areas where elevated groundwater fluoride levels have been observed [47]. The F^- solubility is lowest in the pH range of 5.00–5.60 due to its absorption on the surface of clay minerals present in subsurface rocks. Value of p (<01) shows that data fits well with the findings and is significant (Table 5).

3.2.2. Effect of EC on fluoride and nitrate

Electrical conductivity has shown variable results with various parameters, as in some studies, EC has shown positive trend with nitrate and fluoride concentration in drinking/underground water but in some cases it is vice versa. The trend is entirely based on the local geology of the area and nature of various anions and cations present in ground water. Present study has shown strong negative trend of EC with nitrate and fluoride (R^2 = 0.91695 and 0.91992, respectively) (Figs. 3(a) and 3(b)). Sample with the highest electrical conductivity correlates to the lowest concentrations of nitrates and phosphates and the sample with the lowest conductivity correlates to the highest concentrations of nitrates. It is likely due to occurrence of various anions and cations other than nitrate and fluoride in the underground water. Higher F-value shows that data is non-significant and fits well with the hypothesis (Table 6).

3.2.3. Effect of depth on fluoride and nitrate

Fluoride and nitrate have showed a noteworthy negative correlation with depth (R^2 = 0.95002 and 0.4351, respectively) (Figs. 4(a) and 4(b)). High fluoride and nitrate content has been observed in the shallow surface waters up to the depth of 100–150 ft. The maximum fluoride and nitrate contamination has been

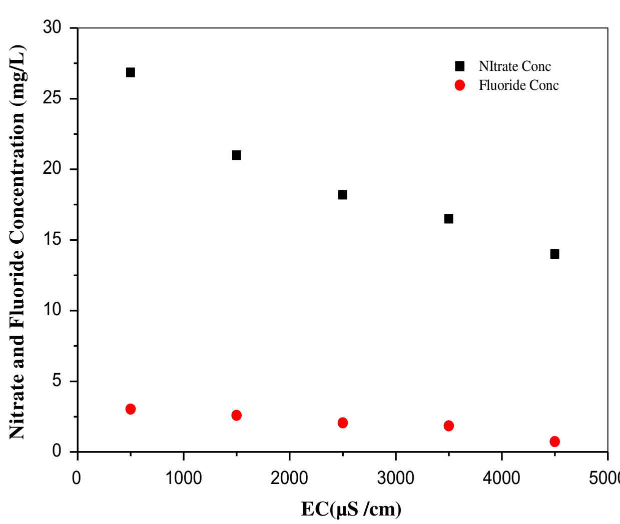

Fig. 3(a). Fluoride and nitrate relationship with electrical conductivity.

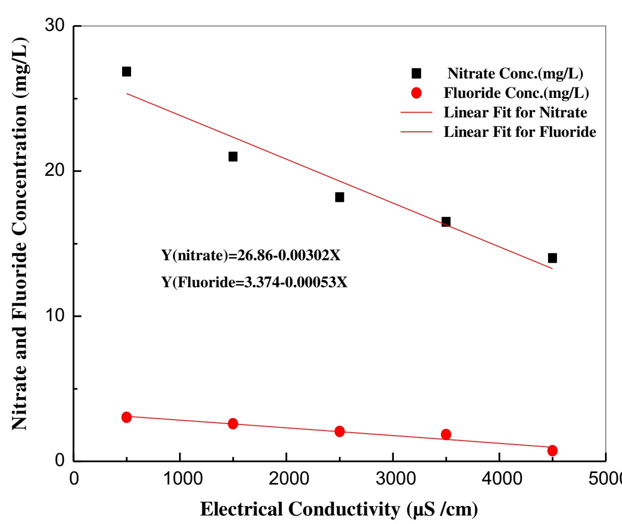

Fig. 3(b). Linear fit showing fluoride and nitrate relationship with electrical conductivity.

Table 6
ANOVA: showing effect of EC on nitrate and fluoride in groundwater

		DF	Sum of squares	Adjusted R^2	Mean square	F-value	Prob. > F
Nitrate	Model	1	91.204	0.91992	91.204	46.9478	0.00636
Nitrate	Error	3	5.828		1.94267		
Nitrate	Total	4	97.032				
Fluoride	Model	1	2.8371	0.91695	2.8371	45.1658	0.00672
Fluoride	Error	3	0.18845		0.06282		
Fluoride	Total	4	3.02555				

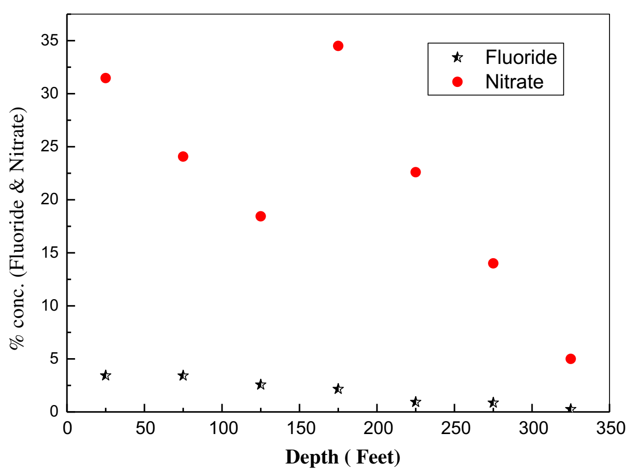

Fig. 4(a). Fluoride and nitrate relationship with depth.

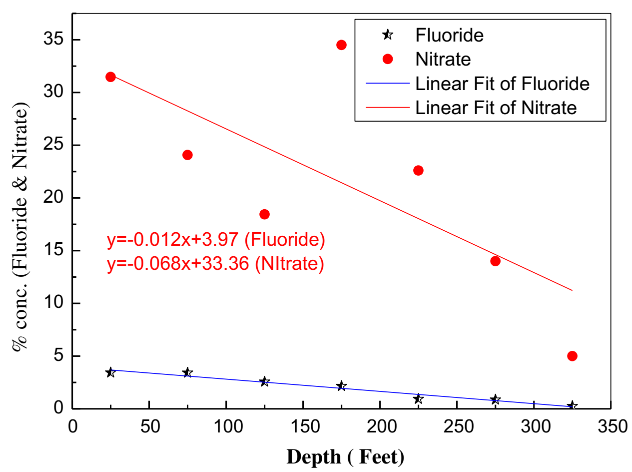

Fig. 4(b). Linear fit showing fluoride and nitrate relationship with electrical conductivity.

observed in the range of 0–50 ft, suggesting that the surface water is more vulnerable to contamination through anthropogenic inputs.

The findings indicated that in addition to geogenic sources, the anthropogenic sources have made significant contribution to fluoride and nitrate richness in the aquifers of the studied area (Table 7).

The negative relationship of nitrate concentration with depth is likely due to reduction of nitrate to dinitrogen by denitrifying organisms under reducing environment prevailing at depth. On the other hand, various sources of nitrogen can be transformed to nitrate by bacterial nitrification, by hydrolysis, and mineralization in oxygen-rich conditions of soil and water. Also, the problem of water logging in the south-western Punjab is highly prevalent and this is the another reason for the occurrence of ions, specially nitrate and fluoride in surface water.

No significant relationship was observed between nitrate and fluoride concentration. It may be due to

Table 7
ANOVA: showing effect of depth on nitrate and fluoride in groundwater

		DF	Sum of squares	Adjusted R^2	Mean square	F-value	Prob. > F
Fluoride	Model		9.47624	0.41184	9.47624	115.0483	0.0001
Fluoride	Error	15	0.41184		0.08237		
Fluoride	Total	6	9.88808				
Nitrate	Model	1	324.96648	0.95002	324.96648	5.62144	0.06388
Nitrate	Error	5	289.04198		57.8084		
Nitrate	Total	6	614.00845				

differential origin of their occurrences. Fluoride occurrence is due to geogenic as well as anthropogenic reasons but nitrate occurrence in shallow water is purely of anthropogenic existence.

4. Conclusions

The outcomes of study have revealed that some of the rural parts of south-western districts of Indian Punjab are suffering from both fluoride and nitrate pollution due to highly contaminated groundwater and surface water. The maximum fluoride and nitrate has been observed at shallow depths up to 50–60 ft with decreasing trend afterward suggesting that water below 250 ft is less contaminated and can be considered as safe water source.

The geogenic occurrence of fluoride along with excessive use of fertilizers and unmanaged irrigation as well as poor sanitation and limited sewage management have resulted in cocontamination with nitrate in these areas.

Another noteworthy feature observed regarding fluoride occurrence is the highly non-uniform geospatial distribution. This geospatial variability is of great concern as each and every village was found to have at least one water source with fluoride content within the permissible range, which can be used for drinking or domestic purposes.

References

[1] P. Mariappan, V. Yegnaraman, T. Vasudevan, Occurrence and removal possibilities of fluoride in ground waters of India, Pollut. Res. 19(2) (2000) 165–177.
[2] CGWB (Central Ground Water Board), Ground Water Quality in Shallow Aquifers of India, Ministry of water resources, Government of India, Faridabad, 2010.
[3] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh, Review of fluoride removal from drinking water, J. Environ. Manage. 91 (2009) 67–77.
[4] J.E. Frencken, Endemic Fluorosis in Developing Countries, Cause, Effects and Possible Solutions, Publication No. 91.082, NIPG-TNO, Leiden, The Netherlands, 1992.
[5] M. Pahwa, V.K. Garg, K. Yadava, R. Gupta, A. Malik, Groundwater quality in some villages of Haryana, India: Focus on fluoride and fluorosis, J. Hazard. Mater. 106(B) (2004) 85–97.
[6] K. Singh, H.S. Hundal, D. Singh, Geochemistry and assessment of hydrogeochemical processes in groundwater in the southern part of Bathinda district of Punjab, northwest India, Environ. Earth. Sci. 64 (2011) 1823–1833.
[7] B.D. Sharma, S.S. Mukhopadhyay, P.S. Sidhu, Microtopographic controls on soil formation in the Punjab region, India, Geoderma 81 (1998) 357–368.
[8] M. Kumar, K. Kumari, A.L. Ramanathan, R. Saxena, A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India, Environ. Geol. 53 (2007) 553–574.
[9] G. Jacks, P.V. Bhatacharya, K.P. Singh, Controls on genesis of some high fluoride groundwater in India, App. Geochem. 20(2) (2004) 221–228.
[10] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara, Fluoride in Drinking Water, IWA Publishing, London, 2006.
[11] J.A. Yiamouyiannis, Fluoridation and cancer. The Biology and epidemiology of bone and oral cancer related to fluoridation, Fluoride 26 (1993) 83–96.
[12] X.S. Li, J.L. Zhi, R.O. Gao, Effect of fluoride exposure on intelligence in children, Fluoride 28(4) (1994) 189–192.
[13] Q. Xiang, Y. Liang, L. Chen, C. Wang, B. Chen, X. Chen, M. Zhou, Effect of fluoride in drinking water on children's intelligence, Fluoride 36 (2003) 84–94.
[14] D. Ortiz-Perez, M. Rodriguez-Martinez, F. Martinez, V.H. Borja-Aburto, J. Castelo, J.I. Grimaldo, Fluoride-induced disruption of reproductive hormones in men, Environ. Res. 93 (2003) 20–30.
[15] R.S. Gupta, T.I. Khan, D. Agrawal, J.B.S. Kachhawa, The toxic effects of sodium fluoride on the reproductive system of male rats, Toxicol. Ind. Health 23 (2007) 507–513.
[16] P.F. Hudak, S. Sanmanee, Spatial patterns of nitrate, chloride, sulfate, and fluoride concentrations in the Woodbine Aquifer of north-central Texas, Environ. Monit. Assess. 82 (2003) 311–320.
[17] S. Guha, B.C. Raymahashay, A. Banerjee, S.K. Acharyya, A. Gupta, Collection of depth-specific groundwater samples from an arsenic contaminated aquifer in West Bengal, India, Environ. Eng. Sci. 22(6) (2005) 870–881.
[18] S.P. Malve, S.S. Dhage, Nitrate: An environmental pollutant, Everyman's Sci. 31(5) (1996) 158–163.
[19] A. Bhardwaj, S. Garg, S.K. Sondhi, D.S. Taneja, Nitrate contamination of Shallow aquifer groundwater in the central districts of Punjab, India, J. Environ. Sci. Eng. 54 (2012) 90–97.
[20] K. Wick, C. Heumesser, E. Schmid, Groundwater nitrate contamination: Factors and indicators, J. Environ. Manage. 111 (2012) 178–186.
[21] U. Buczko, R.O. Kuchenbuch, B. Lennartz, Assessment of the predictive quality of simple indicator approaches for nitrate leaching from agricultural fields, J. Environ. Manage. 91 (2010) 1305–1315.
[22] K. D'Haene, E. Moreels, S. de Neve, B.C. Daguilar, P. Boeckx, G. Hofman, O. Van Cleemput, Soil properties influencing the denitrification potential of Flemish agricultural soils, Biol. Fert. Soils 38(6) (2003) 358–366.
[23] F.J. de Ruijter, L.J.M. Boumans, A.L. Smit, M. van den Berg, Nitrate in upper groundwater on farms under tillage as affected by fertilizer use, soil type and groundwater table, Nutr. Cycling Agroecosyst. 77 (2007) 155–167.
[24] S. Behera, M.K. Jha, S. Kar, Dynamics of water flow and fertilizer solute leaching in lateritic soils of Kharagpur region, India, Agric. Water Manage. 63(2) (2003) 77–98. Available from: https://www.google.co.in/?gfe_rd=cr&ei=W55yVOqAMajV8gf204DACw&gws_rd=ssl#q=Dynamics+of+water+flow+and+fertilizer+solut

e+leaching+in+laterite+soils+of+Kharagpur+region,+India,+Agric.+Water+Manage.+63%282%29+%282003%29+77%E2%80%9398.&spell=1.

[25] N. Imtiaz, T. Aftab, Z. Iqbal, M. Rasi, A. Hussain, Nitrate burden in drinking water in northern Punjab, Pakistan: A challenge for public health, J. Chem. Soc. Pak. 26(4) (2004) 450–452.

[26] L.C. Saha, S. Kumar, Comparative quality of potable waters at Bhagalpur, India, Acta Hydroch. Hydrob. 18 (4) (2006) 459–467.

[27] A.M. Fan, V.E. Steinberg, Health implications of nitrate and nitrite in drinking water: An update on methemoglobinemia occurrence and reproductive and developmental toxicity, Regul. Toxicol. Pharm. 23 (1996) 35–43.

[28] A. El Midaoui, F. Elhannouni, M. Taky, L. Chay, M.A. Menkouchi Sahli, L. Echihabi, M. Hafsi, Optimization of nitrate removal operation from ground water by electrodialysis, Sep. Purif. Technol. 29(3) (2002) 235–244.

[29] N. Lohumi, S. Gosain, A. Jain, V.K. Gupta, K.K. Verma, Determination of nitrate in environmental water samples by conversion into nitrophenols and solid phase extraction−spectrophotometry, liquid chromatography or gas chromatography–mass spectrometry, Anal. Chim. Acta 505(2) (2004) 231–237.

[30] L. Fewtrell, Drinking-water nitrate, methemoglobinemia, and global burden of disease: A discussion, Environ. Health Perspect. 112(14) (2004) 1371–1374.

[31] F.R. Greer, M. Shannon, Infant methemoglobinemia: The role of dietary nitrate in food and water, Paediatrics 116(3) (2005) 784–786.

[32] M.H. Ward, T.M. deKok, P. Levallois, J. Brender, G. Gulis, B.T. Nolan, J. Van Derslice, Workgroup report: Drinking-water nitrate and health—Recent findings and research needs, Environ. Health Perspect. 113(11) (2005) 1607–1614.

[33] A. Rachid, M. Christophe, B. Marc, O. Laure, T. Sylvie, P. Paul, Methemoglobinemia by cerium nitrate poisoning, Burns 32(8) (2006) 1060–1061.

[34] C. Sharma, A. Mahajan, U.K. Garg, Assessment of arsenic in drinking water samples in south–western districts of Punjab, India, Desalin. Water Treat. 51 (2013) 1–9.

[35] S.S. Gupta, Management of high nitrate waters in Nagaur district, Rajasthan, J. Indian Water Works Assn. 24 (1992) 285–287.

[36] B. Pal, Potential hazards of nitrate and fluoride in underground waters, Water Res. 17(3) (1983) 353–354.

[37] R.P. Ashley, M.J. Burley, Control on occurrence of fluoride in groundwater in the rift valley of Ethiopia, Ground Water Qual. (1994) 45–54.

[38] N.R. Khatiwada, S. Takizawa, T.V.N. Tran, M. Inoue, Groundwater contamination assessment for sustainable water supply in Kathmandu Valley, Nepal, Water Sci. Technol. 46(9) (2002) 147–154.

[39] P.S. Sidhu, R.J. Gilkes, Mineralogy of soils developed on alluvium in the Indo-Gangetic plain (India), Soil Sci. Soc. Am. J. 41 (1977) 1194–1201.

[40] R. Kumar, B. Singh, H.S. Hundal, K. Singh, Y. Singh, Geospatial Quality of Underground Water of Punjab, Department of Soils, Punjab Agricultural University, Ludhiana, 2010, pp. 72.

[41] APHA, Standard Methods for the Examination of Water and Waste Waters, 20th ed., APHA, Washington, DC, 1999.

[42] J.D. Hem, Study and Interpretation of Chemical Characteristics of Natural Water, third ed., US Geological Survey, Washington, DC, Water Supply Paper, 1989, pp. 2254–2263.

[43] D.C. Adriano, Trace Elements in the Terrestrial Environment, Springer, New York, NY, 1986.

[44] S. Gupta, D. Mondal, A. Bardhan, Geochemical provenance and spatial distribution of fluoride in Groundwater in parts of Raniganj coal field, West Bengal, India, Arch. Appl. Sci. Res. 4(1) (2012) 292–306.

[45] S.P.S. Teotia, M. Teotia, D.P. Singh, R.S. Rathour, C.V. Singh, N.P.S. Tomar, Endemic fluorosis: Changes to deeper bore wells as a practical community acceptable approach to its eradication, Fluoride 17 (1984) 48–52.

[46] S. Shekhar, A.C. Pandey, M.S. Nathawat, Evaluation of fluoride contamination in groundwater sources in hard rock terrain in Garhwa district, Jharkhand, India, Int. J. Environ. Sci. 3(3) (2012) 1022–1030.

[47] V.K. Saxena, S. Ahmed, Dissolution of fluoride in groundwater: A water–rock interaction study, Environ. Geol. 40(9) (2001) 1084–1087.