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REVIEW ARTICLE

AN INVESTIGATION BASED ON ELEMENTS CORRELATION AND RISK LEVEL OF FLUORIDE IN GROUNDWATER IN INDIA. A REVIEW

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ABSTRACT

This paper reviews the concentration and distribution of fluoride in Indian groundwater with particular emphasis and similarities between different components. Groundwater is an essential and precious source of water for drinking. Fluoride is frequently found naturally in the groundwater. Through human activities, organic pollutants enter the groundwater are also a significant concern that can not be avoided. The data for this review paper was obtained from nineteen locations from 2007 to 2018. The data revealed that fluoride concentration ranged from 0.26 to 5.636 mg/L, with 37% of sites with a higher fluoride concentration level. Excessive fluoride ingestion contributes to fluorosis of the dentures and skeletons and bone deformities. It is observed that eight sites were found with higher concentrations (>180 mg/L) of hard water minerals out of nineteen sites. The correlation between the elements itself shows a strong positive correlation, which is $r = +1$ but the correlation of F^- , Ca^{2+} , Na^+ , K^+ , Mg^{2+} , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , Fe , Mn , PO_4^{3-} , CO_3^{2-} between each other is either strong, medium, or small positive and negative or shows no linear relationship between each other. It was noted that the level of health risk in the district of Dhandband and the state of Telangana was calculated to have a higher risk with greater probability and consequences.

KEYWORDS

Groundwater fluoride, Health effects, India, Pearson correlation, Risk level

1. INTRODUCTION

Groundwater is the primary source of drinking water, and almost half of the world's population depends on it for survival (Ayooob, 2006). Contamination of such a vital source with toxic metals is of great concern. Among the groundwater contaminants, Fluoride is one of the common, most electronegative, and reactive elements. It is highly reactive and typically bonded as inorganic Fluoride and is not found in its basic state (Fawell et al., 2006). Unfortunately, this Fluoride causes fluorosis disease; thus, over six million children suffer from fluorosis due to intake of F from groundwater in India (Susheela, 1999). Due to the higher reactive and typically bonded as inorganic Fluoride and is not found in its basic state of F^- , it is tough to be separated from the water.

India, the second-most populous country after China, had 1.353 billion of the population in 2018. Health researchers are gaining importance due to the rising of diseases in the country; however, providing universal health care would reduce and prevent the spreading of these diseases (Kalita et al., 2015). On the other hand, the prevalence of fluorosis is a public health problem in India's states. In case the Fluoride sources are identified, corrective mitigation measures can be used (Amalraj et al., 2013). Still, when these various sources through which Fluoride reaches human metabolism are unknown, specific methods can be used to determine these sources' roots. The first sign of an excessive amount of fluoride toxicity is dental fluorosis (Bronckers et al., 2009). The teeth' white spots show dental fluorosis characterized by the horizontal streaks on the teeth surface (Susheela et al., 2005). The change of colors (from yellow to brown, even black) of these spots shows moderate/ severe dental fluorosis (Subba et al., 2003). Besides, the excess amount of

Fluoride causes skeletal fluorosis in which the bone mass and its density are increased. Crippling deformities are the other severe form of skeletal fluorosis. When joints of the knee, shoulder bones, pelvic, and neck get deposited by Fluoride, it works as a barrier in the movement and walking (Shrivastava et al., 2009).

The fluoride removal treatment methods divided into two categories: membrane techniques (reverse osmosis, nanofiltration, dialysis, and electro dialysis) and adsorption technique that uses adsorbents (aluminum-based materials, clays, and soils, minerals based on calcium, synthetic compounds, and carbon-based materials) were used (Mohapatra et al., 2009). Also, two famous methods to remove Fluoride from municipal water supply are reverse osmosis filtration and activated alumina defluorination (Maheswari et al., 2006).

Geochemistry distribution of Fluoride India indicated that the fluoride content of groundwater varies significantly (Liu et al., 2009). The environment of the region and the presence of accessory minerals (fluorite and (or) apatite in the rock mineral arrangement through which groundwater circulates) are among the factors which control the fluoride concentration (Khan et al., 2017). Additionally, regional and tectonic factors play their part in affecting the concentration of the Fluoride. The rainwater falling on the ground is enriched by soil, air, and biochemical reactions of bacteria and organic matter during their downward migration in CO_2 . Secondary salts in soil (a mixture of $NaHCO_3$, $NaCl$, and Na_2SO_4 varying in content) are also leached out (Kumar et al., 2018). When phosphate fertilizers are added to the soil, the soil may contain fluoride-bearing compounds of varying proportions. For more detail, see the addition file. The excess Fluoride recorded in groundwater is essential due to the high soil sodium in the vicinity of the major South Indian irrigation

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schemes that induce fluorosis among the nearby populations (Datta et al., 2000; Singh, 2000; Umar et al., 2000).

Groundwater can be polluted from many sources, including water pollution from sewage and septic systems, river flow, and the use of fertilizers and agrochemicals. These substances make emerging organic contaminants (E.O.C.s) in groundwater (Foster, 2001; Vazquez-Sune et al., 2010). Those pose a danger to groundwater safety in aquifers; however, proper groundwater quality assessment requires such pollutants to be identified (Jurado et al., 2012). The E.O.C.s are of particular concern among the various organic pollutants for several reasons. Firstly, pharmaceuticals, abuse drugs, wetter substances, and personal care items were found in the Effluent of Water Treatment Plant (WWTP).

Consequently, WWTP effluents may be the primary source of groundwater contamination (Boleda et al., 2009; Bueno et al., 2012). Secondly, E.O.C.s are endocrine disruptor compounds (E.D.C.s) that can be found in several items, including plastic bottles, detergents, flame retardants, food, toys, cosmetics, and pesticides (Liu et al., 2009). These compounds are believed to be adverse to development and effects on both human and wildlife reproduction (Campbell, et al., 2006). Thirdly, E.O.C.s can be harmful and permanent, and even if they are detected at low concentrations, it can potentially cause harm to ecosystems and human health (Reungoat et al., 2010).

Despite the contribution of previous studies, a rigorous literature review was conducted and presented several gaps. However, this study aims to understand fluoride in groundwater and relationships amongst different elements of selected sites in India for 11 years (2007-2018) and Fluoride's risk level through a risk assessment chart based on previous data.

2. METHODOLOGY

2.1 Selected Sites

The Study area state of Haryana, situated between 27.37° N and 30.35° N latitude and 74.28° E and 77.36° E longitude (Bishnoi et al., 2007), Kolar District (lat. 13° 2'-13° 20' N and long. 77° 56'-78° 17' E) and Tumkur District (lat. 12° 45'-14° 20' N and long. 76° 20'-77° 31' E) (Mamatha et al., 2010), Boden block, Orissa, India, located between 20°6'-20°27'(N) and 82°24'-82°42'(E) (Dey et al., 2012), Ghaziabad 28°40' to 28°67'N (latitude) and 77°25' to 77°42'E (longitude) (Singh et al., 2012), In Ramanathapuram District, Rameswaram is located at 9° 28' North Latitudes and 79° 3' East Longitudes (Sivasankar et al., 2013), Jaisalmer and Pokharan, the area lies between 70.81-72.10°E longitudes and 26.29-27.54°W latitudes (Singh et al., 2015), Birbhum district lies between latitudes 24° 12' 28" N and 24° 17' 52" N and longitudes 87° 38' 16" E and 87° 04' 38" E (Batabyal, 2017), Dhanbad, district of Jharkand, area lies between the latitude 23° 39' 20" N to 23° 40' 00" N and longitude 86° 32' 40" to 86° 33' 30" E (Patolia et al., 2017), Raipur district, Chhattisgarh, India, it falls under longitude 81°35' to 81°40' and latitudes 21°10' to 21°20' (Khan et al., 2017), Sonapat, Haryana state, lies between 28° 48'15" to 29° 17'10"N latitude and 76° 28'40" to 77° 12'45" E longitude (Sheikh et al., 2017), another study area lies in between 80° 29'10"-80° 03'20" East and 15° 23'50"-15° 49'50" North (Rao et al., 2017), Hyderabad, E longitude 78.76942-78.90232 and N latitude 18.06768-18.24402 (Narsimha and Sudarshan et al., 2017), Dharmapuri District (Morappur) and Harur blocks of Harur Taluk and small portion of Dharmapuri block, Uthankarai and Mathur block of Krishnagiri has been taken up for this study. The study area falls in Survey of India toposheet no. 57L/8 falling in north latitudes 12° 00'00" and 12° 15'00" and longitude 78° 15'00" to 78° 30'00" covering an aerial extent of about 720 sq. km (Panneer et al., 2017), Parambikulam Aliyar, Coimbatore District, Tamil Nadu, India between the latitudes of 10° 10' 00"N to 10° 57' 20"N and the longitudes of 76° 43' 20"E to 77° 12' 30"E (Elangovan and Rani, 2017), Tirupati lies between 13° 37' and 13° 40' North latitude and 79° 21' and 79° 26' East longitude (Balaji et al., 2017), Alleppey district lies between latitude 9° 35'00"N and longitude 76° 10'00"E (Raj et al., 2017), The District of Dantewada covers an area of 9046.29 sq km. It comprises 608 villages, which are administratively divided into seven blocks of community development (Kumar et al., 2018) and Nalbari district, western part of the Assam and is situated between 26°8'30"N and 26°52'15"N latitude and 91°14'30"E and 91°38'10"E longitude (Swinscow, 1997) as shown in Fig. 1.

2.2 Research Strategy

Following the common strategy of finding the research papers from the google scholar of different locations focusing on India (now set to become a leading country in the field of research and development [39]. After going through all the articles, the review paper's design was constructed. The data was collected from 19 different articles/studies published between

the period 2007-2018 with various more references and text. At the end of this review paper, WHO (2011) guidelines and the Bureau of Indian Standards (BIS) for groundwater quality parameters have also been mentioned.

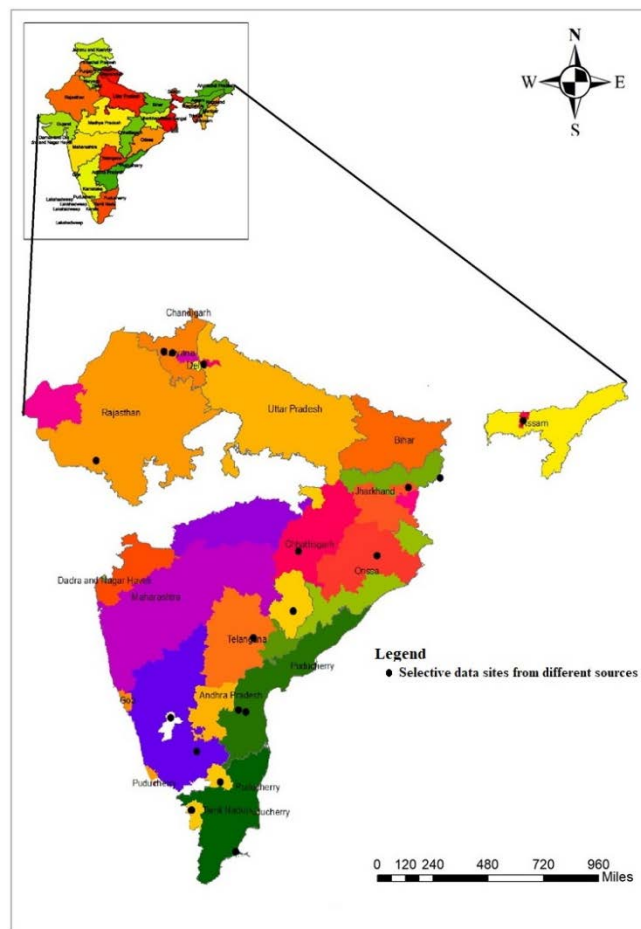


Figure 1: Shows selective data sites from different sources

2.3 Data Analysis

Pearson's correlation method shows the strength between the two variables, and statistical analysis was performed through Origin 2018 and Excel 2016. The coefficient of correlation of Pearson's product-moment is denoted as ρ for a population parameter and sr for a sample statistic. It is used when the distribution of both variables is usually under analysis. Extreme values influence this equation, which may exaggerate or dampen the relationship's strength and is thus unacceptable if one or both variables are not normally distributed. For a correlation between variables x and y , the formula for calculating the coefficient of correlation of the Pearson sample is given by (Swinscow, 1997).

$$\frac{\sum Zx * Zy}{n-1} = \frac{\sum \left(\frac{x-\bar{x}}{s_x}\right) \left(\frac{y-\bar{y}}{s_y}\right)}{n-1} \quad \text{eq (1)}$$

2.4 The Risk Level of Fluoride

The risk level of fluoride contamination has been estimated by knowing the number of populations in the high fluoridated areas at each site. The more the population is, the high risk it would be. The following formulae can calculate the risk level. The high the concentration of Fluoride but the low population, the more will be the consequences. The low the Fluoride concentration (above permissible limit) but the high population, the more chances of likelihood.

$$R = L * C$$

Where,

R= Risk level

L= Likelihood

C= Consequences

The likelihood shows the chances or how many times people can meet the Fluoride, and the consequences mean the result of the risk, i.e., illness. Risk has three levels low (green), medium (yellow), and high (red).

3. RESULTS AND DISCUSSION

It is clear from Fig.2 that 36.8 % of locations in India has a high concentration of Fluoride, which is higher than 1.5 mg/L (BIS standards 2012) (WHO 2011) in drinking water; in these areas, defluorination

techniques should be used for groundwater to make it suitable for drinking purpose. Dhanbad District, Telangana State, India, has high concentrations (5, 5.636 mg/L), whereas the areas with a low concentration of Fluoride less than 1.5 mg/L recommended fluoride concentration carries control.

Major ionic species have been investigated by Fig. 3. The peaks and troughs of the under-groundwater samples from different sites show that Cl⁻ is the most dominant while potassium is the less dominant among all.

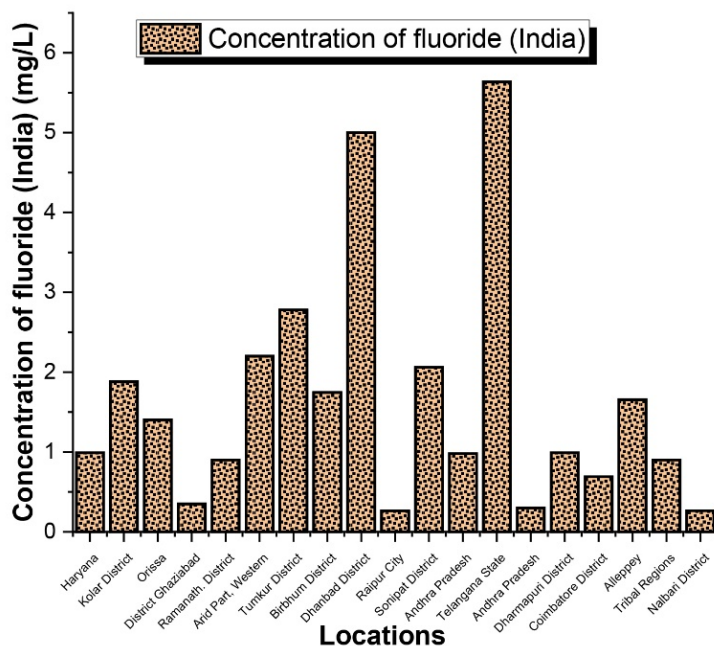


Figure 2: Concentration of Fluoride in different studies

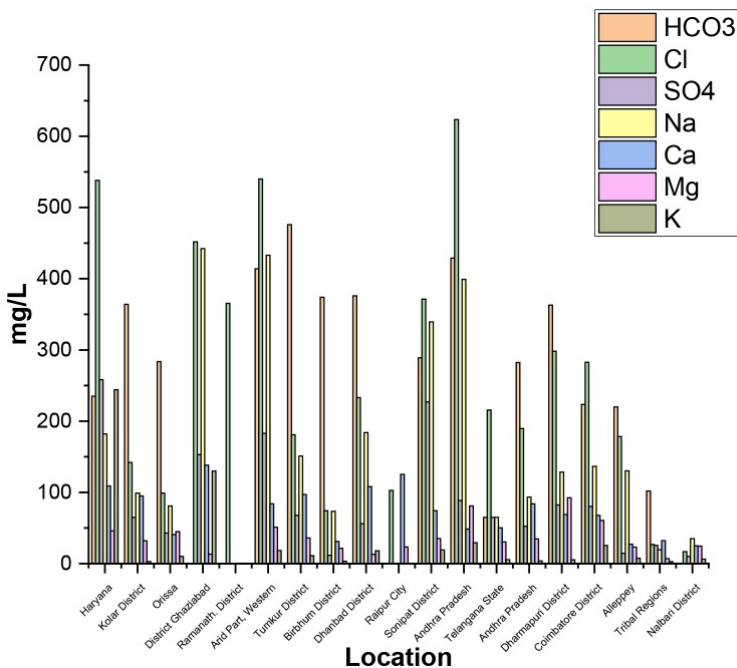


Figure 3: Major ionic species investigated

3.1 Drinking Suitability

The Physio-chemical characteristics of groundwater from 19 different studies have been submerged, as shown in Table. 1 to know about the suitability for drinking purposes.

The limit of pH value for drinking water is 6.5-8.5, E.C. is 1500 $\mu\text{S cm}^{-1}$, T.D.S. maximum desirable limit is 200 mg/L and maximum permissible limit is 2000 mg/L, for T.A. and T.H. maximum desirable limit is 200 while maximum permitted limit is 600, for Na⁺ the standard is 200 mg/L, for K⁺ is 12 mg/L, for Ca²⁺ 75 mg/L and its maximum desirable limit is 75 mg/L and maximum permissible limit is 200 mg/L, for Mg²⁺ is 50 mg/L while

maximum desirable limit is 30 mg/L and maximum permitted limit is 100 mg/L, for HCO₃⁻ the standard is 500 mg/L, for Cl⁻ and SO₄²⁻ the standard is same which is 250 mg/L while maximum desirable limit for Cl⁻ is 250 mg/L and maximum permissible limit is 1000 mg/L and for SO₄²⁻ maximum desirable limit is 200 mg/L and maximum permissible limit is 400 mg/L, for F⁻ standard and maximum permissible limit is same which is 1.5 mg/L and maximum desirable limit is 1 mg/L, for NO₃⁻ standard and maximum desirable limit is same which is 45 mg/L, for Fe is 0.3 mg/L while for Mn is 0.4 mg/L as per WHO 2011 and maximum desirable and permissible limits are as per Bureau of Indian standards (BIS) 2012 as shown in Table 2.

Table 1: Physio-chemical characteristics of groundwater in India

Location	pH	EC ($\mu\text{S cm}^{-1}$)	TDS mg/L	TA	TH	Na+ mg/L	K+ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	HCO ₃ ⁻ mg/L	Cl- mg/L	SO ₄ ²⁻ mg/L	F- mg/L	NO ₃ ⁻ mg/L	Fe mg/L	Mn mg/L	PO ₄ ³⁻ mg/L	CO ₃ ²⁻ mg/L	References
Haryana, India	7.8	2.9	1848	390	447	182	244	109	46	235	538	258.4	0.99	-	-	-	-	-	(Bishnoi and Arora 2007)
Kolar District, Karnataka, India	7.35	1045	670	300	370	99	3	95	32	364	142	65	1.88	-	-	-	-	-	(Mamatha and Rao 2010).
Orissa, India	7.79	917.6	364.3	234	288.8	80.9	10	40.8	45	283.6	99	43	1.4	15.5	-	-	-	-	(Dey, Swain et al. 2012).
District Ghaziabad, India	7.74	2167600	1434.33	-	-	442.2	129.99	138.27	13.19	-	451.77	152.94	0.35	2.94	1.46	0.398	0.002	-	(Singh, Bikundia et al. 2012).
Ramanathapuram District, India	7.66	2215.5	1174	257	435.5	-	-	-	-	-	365.5	-	0.9	-	-	-	-	-	(Sivasankar, Ramachandramoorthy et al. 2013).
Arid Part, Western India	7.9	2886	1790	-	-	433	18.5	84	51	414	540	183	2.2	149	-	-	-	-	(Singh, Mukherjee et al. 2015).
Tumkur District, Karnataka, India	7.09	1510	968	392	391	151	11	97	36	476	181	68	2.78	-	-	-	-	-	(Mamatha and Rao 2010).
Birbhum District, India (Pre-Monsoon)	8.41	365.29	260	150.97	120.23	34.45	1.16	30.04	10.84	187.34	36.34	3.17	1.83	3.59	0.38	0.19	0.15	22.74	(Batabyal, Gupta et al. 2017).
Birbhum District, India (Post-Monsoon)	8.63	391.48	276.4	153	124.19	39.05	2.13	32.04	10.78	186.66	37.96	8.57	1.66	1.96	2.06	0.23	0.25	-	(Batabyal, Gupta et al. 2017).
Dhanbad District, Jharkhand, India	8	-	1006	330	308	184	18	108	13	376	233	56	5	2	-	-	-	4	(Patolia and Sinha 2017).
Raipur City, Chhattisgarh	7.52122	-	-	-	-	-	-	125.223	23.3842	-	102.805	-	0.26235	34.7059	-	-	-	-	(Khan and Jhariya 2017).
Haryana, India	7.78	2011.23	1074.54	-	-	339.22	19.24	74.31	35.19	288.78	371.39	227.1	2.06	32.76	-	-	-	14.85	(Sheikh, Azad et al. 2017).
Andhra Pradesh, India	7.81	-	1745.8	-	-	399.12	29.34	48.6	80.9	429	623.3	88.4	0.98	51.84	-	-	-	-	(Rao, Rao et al. 2017).
Telangana State, India	7.5	1806.45	1156.13	-	192.67	64.835	5.46	50.3575	30.5325	64.955	215.68	64.9875	5.636	96.77	-	-	-	-	(Narsimha and Sudarshan 2017).
Andhra Pradesh, South India	7.8	-	-	-	-	93.4	3.7	84	34.7	282.2	189.6	52.4	0.3	-	-	-	-	4.4	(Balaji, Nagaraju et al. 2017).
Dharmapuri District, South India	7.88	1613.45	-	-	546.18	128.43	5.41	68.94	92.47	362.8	298.1	82.45	0.99	40.85	-	-	-	0.5	(Panneer, Sivakumar et al. 2017).
Coimbatore District, Tamil Nadu, India	8.42	1448.75	846.45	-	418.63	136.65	25.53	67.8	60.62	223.42	282.78	80.35	0.69	-	-	-	-	18.52	(Elangovan and Rani 2017).
Alleppey, Southern India	8.585	1025.4375	-	-	-	130.25	7.525	27.33	23.126	219.938	178.444	14.3993	1.65438	-	-	-	-	-	(Raj and Shaji 2017).
Tribal Regions, India	8.3	273.7	193.2	-	-	19.4	2.7	32.2	6.9	101.9	26.9	25.6	0.9	1.4	-	-	0.03	-	(Kumar, Chanda et al. 2018).
Nalbari District, Assam, India (Pre-monsoon 2016)	7.1	399	255	143	116	19	3.42	22	15	-	11	6.16	0.27	2.92	-	-	-	-	(Jain and Vaid 2018).
Nalbari District, Assam, India (Post-monsoon 2016)	7.4	367	235	136	108	16	2.96	28	9.58	-	5.82	3.87	0.26	1.61	-	-	-	-	(Jain and Vaid 2018).
Min	7.09	2.9	193.2	136	108	16	1.16	22	6.9	101.9	5.82	3.87	0.26	1.4	0.38	0.19	0.002	0.5	
Max	8.63	2167600	1848	390	546.18	442.2	244	138.27	92.47	288.78	451.77	258.4	5.636	149	1.46	0.398	0.25	22.74	
Mean	7.831725	128581.1051	899.822353	248.597	297.4	157.4687	28.58237	68.14553	33.51064	280.9745	234.7804	78.09457	1.571082	31.27471	1.148	0.272667	0.108	10.835	
Standard Deviation	0.415128	525443.7541	579.75992	101.4398	150.94	141.6484	59.56014	35.85709	23.8089	117.1542	187.3453	75.35807	1.440774	43.66697	0.851352	0.110369	0.114379	9.07576057	

Table 2: Comparison of groundwater quality with drinking water parameters

Chemical Parameter	Minimum	Maximum	Mean	± SD	WHO 2011	BIS 2012 Max. desirable limit (MDL)	Maximum permissible limit (M.P.L.)
pH	7.09	8.63	7.831725	0.41513	6.5-8.5	6.5-8.5	-
E.C.	2.9	2167600	128581.1	525443.8	1500	-	-
TDS	193.2	1848	899.8224	579.7599	1000	500	2000
TA	136	390	248.597	101.4398	-	200	600
TH	108	546.18	297.4	150.94	-	200	600
Na+	16	442.2	157.4687	141.6484	200	-	-
K+	1.16	244	28.58237	59.56014	12	-	-
Ca ²⁺	22	138.27	68.14553	35.85709	75	75	200
Mg ²⁺	6.9	92.47	33.51064	23.8089	50	30	100
HCO ₃ ⁻	101.9	288.78	280.9745	117.542	500	-	-
Cl ⁻	5.82	451.77	234.7804	187.3453	250	250	1000
SO ₄ ²⁻	3.87	258.4	78.09457	75.35807	250	200	400
F ⁻	0.26	5.636	1.571082	1.440774	1.5	1	1.5
NO ₃ ⁻	1.4	149	31.27471	43.66697	45	45	-
Fe	0.38	1.46	1.148	0.851352	0.3	-	-
Mn	0.19	0.398	0.272667	0.110369	0.4	-	-
PO ₄ ³⁻	0.002	0.25	0.108	0.114379	-	-	-
CO ₃ ²⁻	0.5	22.74	10.835	9.075761	-	-	-

*WHO 2011 (Khalid 2019), Bureau of Indian standards (BIS) 2012 (Jain and Vaid 2018).
All the values are in mg/L, except pH and E.C. Units of E.C. are $\mu\text{S cm}^{-1}$.

3.2 Total Hardness

Out of 19 locations, no site found to have soft water, which is 0-60 mg/L, 5.263% was found moderately hard, which is 61-120 mg/L, 10.56% means 2 sites were found to have hard water while 42.105% (8 locations) were found to have very hard water which is >180 mg/L as shown in the Table. 3.

Table 3: Classification of groundwater based on the total hardness

Sr. No.	Total hardness mg/L	Description	No. of Locations	Percentage
1	0-60	Soft	0	0
2	61-120	Moderately hard	1	5.263
3	121-180	Hard	2	10.526
4	>180	Very hard	8	42.105

3.3 Pearson Correlation Matrix

The correlation between EC and pH is -0.09, TDS and PH =-0.19, TDS and EC= +0.17, TA and pH= -0.10, TA and EC= -0.21, TA and TDS= 0, TH and pH= 0.10, TH and EC= -0.21, TH and TDS= -0.03, TH and TA= 0.01, F and pH = -0.12, F and EC= -0.11, F and TDS= 0.23, F and TA= 0.17, F and TH= -0.07, Ca and PH= -0.12, Ca and EC= 0.44, Ca and TDS= 0.08, Ca and TA= -0.10, Ca and TH= -0.07, Ca and F= 0.07, Na and PH -0.24, Na and EC= 0.48, Na and TDS= 0.35, Na and TA= 0.29, Na and TH= -0.35, Na and F= -0.08, Na and Ca= 0.41, K and pH = -0.41, K and EC= 0.41, K and TDS= 0.39, K and TA= -0.02, K and TH= 0.23, K and F= -0.12, K and Ca= 0.46, K and Na= 0.36, Mg and PH= -0.18, Mg and EC= -0.23, Mg and TDS= 0.21, Mg and TA= 0.27, Mg and TH= -0.30 Mg and F= 0.48, Mg and Ca= 0.08, Mg and Na= 0.34, Mg and K=0.07, HCO₃ and pH = -0.05, HCO₃ and EC= -0.35, HCO₃ and TDS= -0.04, HCO₃ and TA= 0.24, HCO₃ and TH= 0.10, HCO₃ and F= 0.15, HCO₃ and Ca= 0.13, HCO₃ and Na= 0.36, HCO₃ and K= -0.10, HCO₃ and Mg= 0.54, Cl and pH = -0.40, Cl and EC= 0.26, Cl and TDS= 0.47, Cl and TA= 0.35, Cl and TH= -0.11, Cl and F= 0.03, Cl and Ca= 0.27, Cl and Na= 0.78, Cl and K= 0.54, Cl and Mg= 0.43, Cl and HCO₃= 0.23, SO₄ and pH= -0.31, SO₄ and EC= 0.24, SO₄ and TDS= 0.66, SO₄ and TA= 0.19, SO₄ and TH= -0.05, SO₄ and F= -0.03, SO₄ and Ca= 0.49, SO₄ and Na= 0.71, SO₄ and K= 0.70, SO₄ and Mg= 0.33, SO₄ and HCO₃= 0.25, SO₄ and Cl= 0.72, NO₃ and pH= -0.17, NO₃ and EC= -0.12, NO₃ and TDS= 0.36, NO₃ and TA= 0.16, NO₃ and TH= -0.39, NO₃ and

F= 0.07, NO₃ and Ca= 0.04, NO₃ and Na= 0.42, NO₃ and K= -0.15, NO₃ and Mg= 0.36, NO₃ and HCO₃= 0.16, NO₃ and Cl= 0.40, NO₃ and SO₄= 0.30, Fe and pH = 0.65, Fe and EC= 0.48, Fe and TDS= -0.02, Fe and TA= -0.16, Fe and TH= 0.00, Fe and F= -0.16, Fe and Ca= 0.02, Fe and Na= 0.13, Fe and K= 0.13, Fe and Mg= -0.24, Fe and HCO₃= -0.01, Fe and Cl= -0.08, Fe and SO₄= -0.06, Fe and NO₃= -0.16, Mn and pH = 0.53, Mn and EC= 0.67, Mn and TDS= 0.03, Mn and TA= -0.19, Mn and TH= -0.05, Mn and F= -0.16, Mn and Ca= 0.13, Mn and Na= 0.24, Mn and K= 0.21, Mn and Mg= -0.26, Mn and HCO₃= -0.10, Mn and Cl= 0.00, Mn and SO₄= , Mn and NO₃= -0.17, Mn and Fe= 0.97, PO₄ and pH= -0.04, PO₄ and EC= 0.01, PO₄ and TDS= -0.21, PO₄ and TA= -0.13, PO₄ and TH= -0.22, PO₄ and F= -0.12, PO₄ and Ca= -0.20, PO₄ and Na= -0.20, PO₄ and K= -0.08, PO₄ and Mg= -0.31, PO₄ and HCO₃= -0.22, PO₄ and Cl= -0.30, PO₄ and SO₄= -0.15, PO₄ and NO₃= -0.14, PO₄ and Fe= -0.05, PO₄ and Mn= -0.04, CO₃ and pH = 0.51, CO₃ and EC= -0.12, CO₃ and TDS= 0.11, CO₃ and TA= 0.23, CO₃ and TH= -0.13, CO₃ and F= 0.20, CO₃ and Ca= -0.12, CO₃ and Na= 0.01, CO₃ and K= -0.12, CO₃ and Mg= 0.03, CO₃ and HCO₃= 0.22, CO₃ and Cl= -0.11, CO₃ and SO₄= 0.06, CO₃ and NO₃= , CO₃ and Fe= -0.17, CO₃ and Mn= 0.41, CO₃ and PO₄= -0.13 as shown in Table. 4 and Fig. 4.

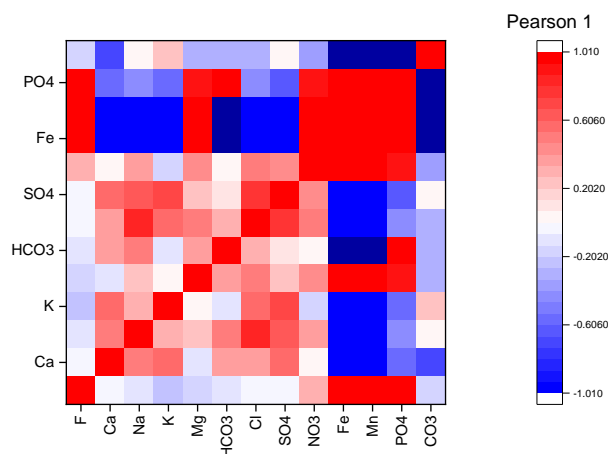


Figure 4: A clustered heatmap of Pearson correlation coefficients between the elements

Table 4: Pearson correlation matrix of various parameters of groundwater (India)

	pH	EC (μS cm-1)	TDS mg/L	TA	TH	F mg/L	Ca mg/L	Na mg/L	K mg/L	Mg mg/L	HCO ₃ mg/L	Cl mg/L	SO ₄ mg/L	NO ₃ mg/L	Fe mg/L	Mn mg/L	PO ₄ mg/L	CO ₃ mg/L
pH	1.00																	
EC (μS cm-1)	0.09	1.00																
TDS mg/L	0.19	0.17	1.00															
TA	0.10	-0.21	0.00	1.00														
TH	0.10	-0.21	-0.03	0.01	1.00													
F mg/L	0.12	-0.11	0.23	0.17	0.17	1.00												
Ca mg/L	0.41	0.44	0.08	0.10	0.07	0.07	1.00											
Na mg/L	0.24	0.48	0.35	0.29	0.35	-0.08	0.41	1.00										
K mg/L	0.14	0.41	0.39	0.02	0.23	-0.12	0.46	0.36	1.00									
Mg mg/L	0.18	-0.23	0.21	0.27	0.30	0.48	0.08	0.34	0.07	1.00								
HCO ₃ mg/L	0.05	-0.35	-0.04	0.24	0.10	0.15	0.13	0.36	-0.10	0.54	1.00							
Cl mg/L	0.40	0.26	0.47	0.35	0.11	0.03	0.27	0.78	0.54	0.43	0.23	1.00						
SO ₄ mg/L	0.31	0.24	0.66	0.19	0.05	-0.03	0.49	0.71	0.70	0.33	0.25	0.72	1.00					
NO ₃ mg/L	0.17	-0.12	0.36	0.16	0.39	0.07	0.04	0.42	-0.15	0.36	0.16	0.40	0.30	1.00				
Fe mg/L	0.65	0.48	-0.02	0.16	0.00	-0.16	0.02	0.13	0.13	-0.24	-0.01	-0.08	-0.06	-0.16	1.00			
Mn mg/L	0.53	0.67	0.03	0.19	0.05	-0.16	0.13	0.24	0.21	-0.26	-0.10	0.00	0.01	-0.17	0.97	1.00		
PO ₄ mg/L	0.04	0.01	-0.21	0.13	0.22	-0.12	-0.20	-0.20	-0.08	-0.31	-0.22	-0.30	-0.15	-0.14	-0.05	-0.04	1.00	
CO ₃ mg/L	0.51	-0.12	0.11	0.23	0.13	0.20	-0.12	0.01	-0.12	0.03	0.22	-0.11	0.06	-0.17	0.52	0.41	-0.13	1.00

3.4 The Risk Level of Fluoride

With the help of a risk assessment chart, the risk level has been carried out of different sites with a high concentration of Fluoride, i.e., <1.5 mg/L, compared with its population. Alleppey (Southern India), Kolar District, and Haryana were found to have a low level of risk while Tumkur district and Arid part, Western India were found to have medium risk level and Dhandband district and Telangana state were estimated to have a high-risk level with more likelihood and consequences as shown in Fig. 5.

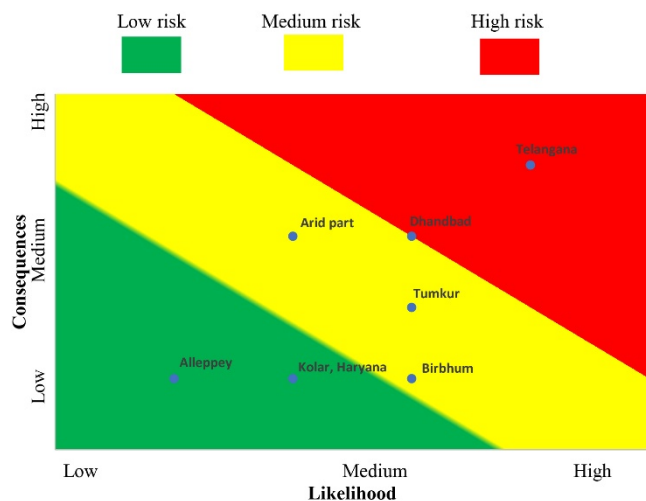


Figure 5: Risk assessment chart shows the risk level of different sites in India

4. CONCLUSION

Fluoride's concentration is fluctuated every year, even at times it is more than its permissible limit, which is 1.5 mg/L during the year 2007-2018. Fluoride's problem in India is now a big concern as it can lead to severe health effects as well. The water supply to the population living in the high fluoridated areas needs defluorination to make it suitable for drinking. The water that has less Fluoride needs to add Fluoride to avoid getting any side effects means to avoid dental caries. The correlation of F⁻ with other elements shows medium negative, small negative, medium positive, and strongly positive correlation. Organic contaminants can also pose a danger to groundwater because proper Assessment is required to remove such pollutants. Risk level with the help of a risk assessment chart shows Dhandband district and Telangana state were estimated to have a high-risk level with more likelihood and consequences.

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