An Analysis of Fluoride Contamination in Global Groundwater

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ABSTRACT

Fluoride is a mineral that can be found in seawater, oceans, and groundwater which is the main source of drinking water in many parts of the world and, therefore, is the main source of fluoride ingestion. Fluoride pollution in groundwater in the past few decades has gained significance, mainly because of its dual impact on living beings, i.e., the small intake of fluoride is necessary for teeth whereas the excess amount of it if consumed, may cause a very painful incurable disease called fluorosis that directly affects the teeth, bones, and muscles. The risk of fluorosis increases with increase in the concentration of fluoride beyond 1.5 ppm. Several environmental and natural factors contribute to high fluoride levels in the ground waters. Until now the problem of high fluoride concentration has not received enough attention. The aim of the present study was to assess the fluoride content and its contamination around the globe, and also methods of disposal and reuse of fluorides.

KEYWORDS:-Ingestion, contamination, groundwater, detection, measurement, fate, disposal, global fluoride data,fluorosis .

INTRODUCTION

Fluoride is a compound that is present is groundwater as well as other sources of water in varying concentration in different locations. Fluoride forms a crystalline-like structure around the enamel which acts as a protective layer. Excess intake of fluorine during the infancy stage causes Fluorosis. *(Committee on Nutrition, 1986)*.Fluoride is also used in toothpaste for the same reason of protection of enamel from dental caries, but intake of the excess amount can be harmful hence parents are advised to keep a check on their children.

Skeletal Fluorosis is a kind of bone disorder caused due to increase in fluorine intake. It doesn't happen for the concentration of fluorine below 1.4 ppm but chances of happening increases with the increase in concentration (Jolly *et al.*, 1968). Apart from that, a study conducted in some regions of America reveals that exposure of fluoride may also lead to harmful effects on fertility rates*(Freni, 1994)*.

Fluoride is given as a supplement to the children in the area where the concentration of fluoride is nil or low. It is to be prescribed by the medical authorities in the area generally where fluoride concentration is below 0.3mg fluoride per liter *(Riordan, 1989)*.Fluoride wastewater generated can be used to prepare synthetic calcium fluoride which can be further utilized for the production of Hydrofluoric acid and also can be used in the metallic or ceramic industry. *(Aldaco, Garea and Irabien, 2007)*.

Fluoride varnish can be used in the prevention of dental caries and also help in the prevention of hypersensitivity in teeth. The main ingredient of Fluoride varnish is 5% of sodium fluoride *(Chu and Lo, 2008)*.The Bone char sludge generated from *Nalgonda technique* can be partially used for construction purposes in place of the river sand or fine aggregate. The strength of the produced concrete doesn't degrade and this helps in reduction of sludge waste generated to the environment *(Rao et al., 2009)*.

Some countries have introduced fluoride salts to prevent dental problems. Fluorides are also used in mouth rinses (0.05 – 0.2 %) which are very famous among young children. Other uses of fluoride include gels, solutions, and floss which is used in dentistry. Other uses of fluoride contain gels. Hydrogen Fluoride (HF) is an important component which is widely used in industrial purposes. Some of the purposes of HF includes etching semiconductor devices, cleaning bricks, cleaning, and etching glass, etc*(Environmental Health Criteria 227)*.Fluoride ion (FÉ) is generated from Fluorine which is available in ample quantity in nature. The sources of fluoride in water *(Fig 1.)* includes natural fertilizers, ceramics, bricks, and ironworks etc.(Gill, Tiwari and Kumar, 2014). Fluoride is added to the local water supply because it helps in the prevention of tooth decay.

Filtration of fluoride from water leads to the generation of the huge amount of fluoride-rich wastewater which is ultimately dumped into the environment, that is very harmful to the environment and the ecosystem. Nanomembrane based hybrid treatment is done at 5-16 bars of operating pressure and it is tested on the water having fluoride concentration for 17 mg/l in West Bengal and the efficiency of these filters are found to be 99%. But the important outcome from this study is that the sludge generated can be taken care of by stabilization. *(Chakrabortty et al., 2016)*. Thyroid stimulating hormone (TSH) test is a blood test used to determine the working of thyroid hormones. TSH is found to be in high quantity in people consuming a huge amount of fluoride contaminated water even when the concentration of fluoride is as low as 0.5 mg/l (KheradPisheh *et al.*, 2018).

These methods ultimately help in the protection of the environment by reducing the harmful effects of fluoride wastewater, which instead has to be discharged into the environment.

METHODS USED TO DETERMINE FLUORIDE CONTENT

The method which is widely used to determine Fluoride concentration in the groundwater sample is named as " *Colorimetric SPADNS* (Sodium 2-(Parasulphophenyl Oazo)- 1,8 - dihydroxy -3,6 - naphthalene disulfonate)". Some other methods include *Complexone method* which is also extensively used method, methods using some sophisticated instruments like Ion Chromatograph in which Ion-selective electrodes are available to measure the concentration in the sample. This *Ion selective method* can be used in both Lab and Field.*(Brindha et al., 2011)*

SPADNS Spectrophotometric Method

The method is based on fluoride interaction with some zirconium dyes, that results in the formation of a colorless complex anion and a dye is formed. As the fluoride concentration in the water sample is increased, the complex formed during the interaction that is proportional to the fluoride content, bleaches the dye and makes it lighter.

There are also other compounds present in the water sample which is required to be removed; for e.g.distillation is preferred on the sample having concentration of dissolved solids higher than the amount which interacts with the result. Some other components also interfere with the water sample results; such as Iron, Sulphonates and Alumina have a negative impact whereas Phosphate and Chlorine show positive impacts.

During the reaction of fluoride ion and Zr-SPADNS (Sodium 2-(Parasulphophenyloazo)- 1,8 - dihydroxy -3,6 - naphthalene disulfonate), the complex compound which is obtained is a colored compound and is measured through a spectrophotometer of 570 nm. *(HP Hydrology Project, Training Module # WQ-36,2000)*.

Ion Selective Electrode (ISE) Method

This is a method based on a potentiometric analysis method. In Ion-Selective Potentiometry (ISP) method, the sample can not be used further.This kind of method is categorized as Non-

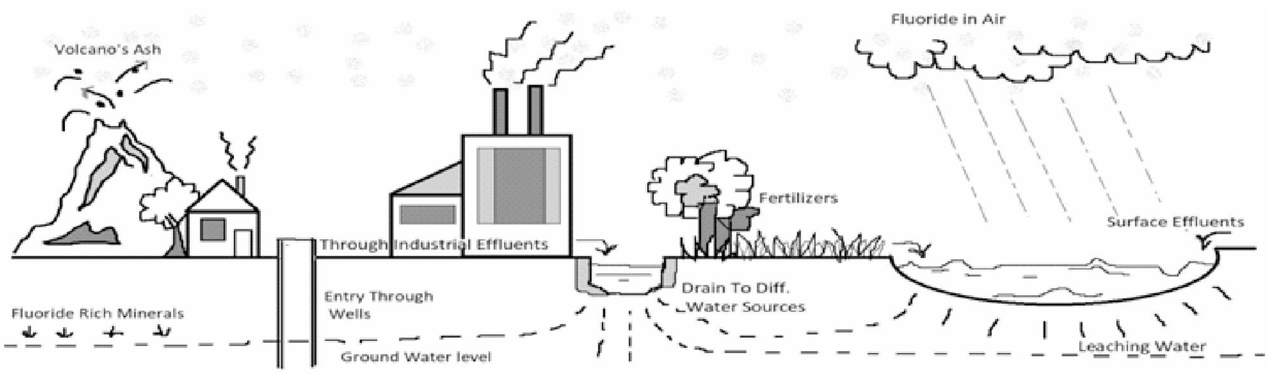

Fig 1. Different Sources for the introduction of Fluoride in Groundwater.

destructive method of evaluation. The electrical potential difference generated between a selective electrode and a reference electrode is calculated to determine the Fluoride content in water.

This method of Potentiometric determination using Fluoride electrode is most popular and this method is convenient because of its high sensitivity, low detection limit, and specificity. Moreover, this method is cheap, reliable and simple. This method is based on a physical characteristic, it does not involve the use of different chemicals and sample preparation after the test is also not required.*(Sunitha and Reddy, 2014).*

The electrode potential is determined by using the following formulae-

$$E=E^{O} - (RT/nF) \ln Q \quad (1)$$

Where,

E = Potential difference.

E^{O} =Standard Cell Potential.

Q = Ion Outside/ Ion Inside.

R,*F* = Constants.

T = Temperature.

n = Number of Electron.

Ion Chromatography

It is a method used to separate ions on the basis of their affinity to Ion Exchanger. For this purpose, the anion-exchange method is used to find Fluoride Ion concentration in the sample. The sea water sample is taken from Hokkaido, Japan. Fluoride Ion concentration can also be identified using the Ion Chromatography and the analytical condition including a column of Ionpac AS20, having mobile phase as Potassium hydroxide with a flow rate of 0.25 mL/min, with column temperature of $35^{O}C$ is kept for effective output . The Instrument is used for Conductivity detection, ICS-3000 (Dionex Co. Ltd). It was found out that this method can be used to identify high Fluoride content in samples. *(Miyake et al., 2007).*

FLUORIDE CONTAMINATION AROUND THE GLOBE

ASIA

Sri Lanka

491 nos. of water samples were collected from 14 districts of Sri Lanka and were tested using Ion Chromatography method. The outcome from most of the test shows that sample have Fluoride contamination more than the country's average. Anuradhapura, a district in Sri Lanka was found to be the most affected region having maximum concentration of Fluoride to be 7.03 mg/l whereas Polonnaruwa and Badulla were found out to be the second and third most affected respectively after Anuradhapura, having maximum fluoride contamination of 3 mg/l and 2 mg/l respectively.It was also found out that Chronic Kidney disease was maximum in people living in Anuradhapura i.e. 87% was mainly due to fluoride contamination in water. *(Weragoda and Kawakami, 2016).*

India

Groundwater is one of the important sources of drinking water in many parts of India. In Vijaypur (Bijapur) district of Karnataka, the water sample of 62 nos. of bores were tested and around 55% of the samples have fluoride content more than drinking permissible limit. *(Ugran et al., 2017).* Similarly out of samples tested from the other two districts namely Kolar and Tumkur is found out to have fluoride contamination of 76% *(Mamatha and Rao, 2010).* 16 nos. of samples were collected from Alleppey town which is situated in Kerala. In this region of the state, groundwater is the main source for water consumption and after doing the tests, it was found out that 50% of water samples have poor water quality *(Raj and Shaji, 2017).* Main concerned regions having a high concentration of Fluoride can be seen in (*Fig 2)*. Also during similar testing done in parts of central Rajasthan, samples from 44 habitations were examined. Around 32% of individuals of these habitats do a Fluoride intake of more than 4 mg/day. That's enough to cause Fluorosis of first and Second degree. *(Hussain, Arif, and Hussain, 2012).*

China

It was found out that many regions of China, regions of North China's groundwater sources were mainly affected by Fluoride contamination. A survey was done in those areas and the results were daunting as it was found that 26 million people were affected with Dental Fluorosis and around 1.7 million were affected by Skeletal Fluorosis and these numbers are likely to be increasing. Many of the sources identified across these regions

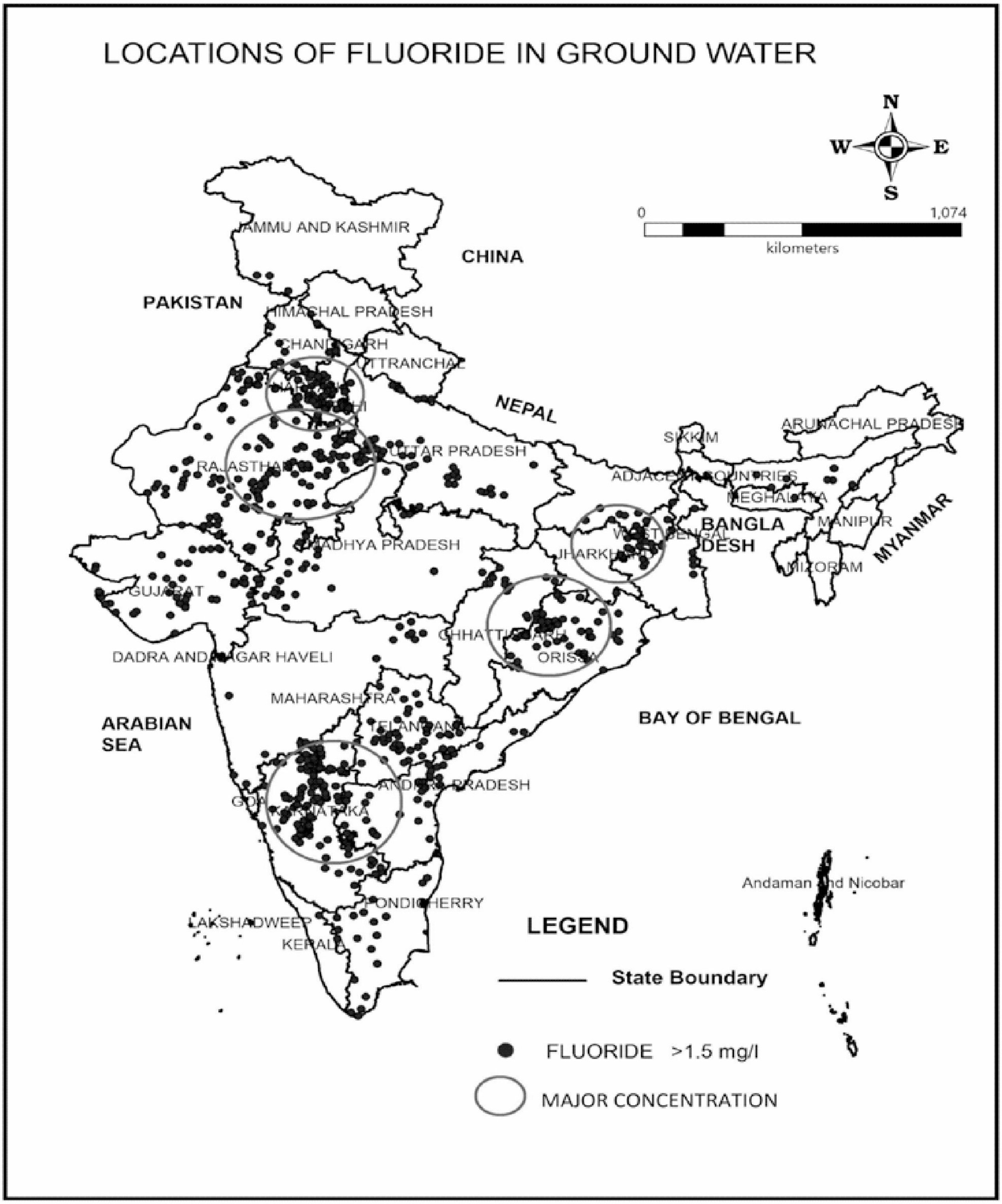

Fig 2: A Map of India showing a major concentration of Fluoride contamination in Groundwater. ***Website of Central Groundwater Board (Government of India), Fluoride map.***

NOTE: *Haryana, Rajasthan, West Bengal, Jharkhand, Chhattisgarh, Orissa, and Karnataka are the states having a high concentration of Fluoride contamination.*

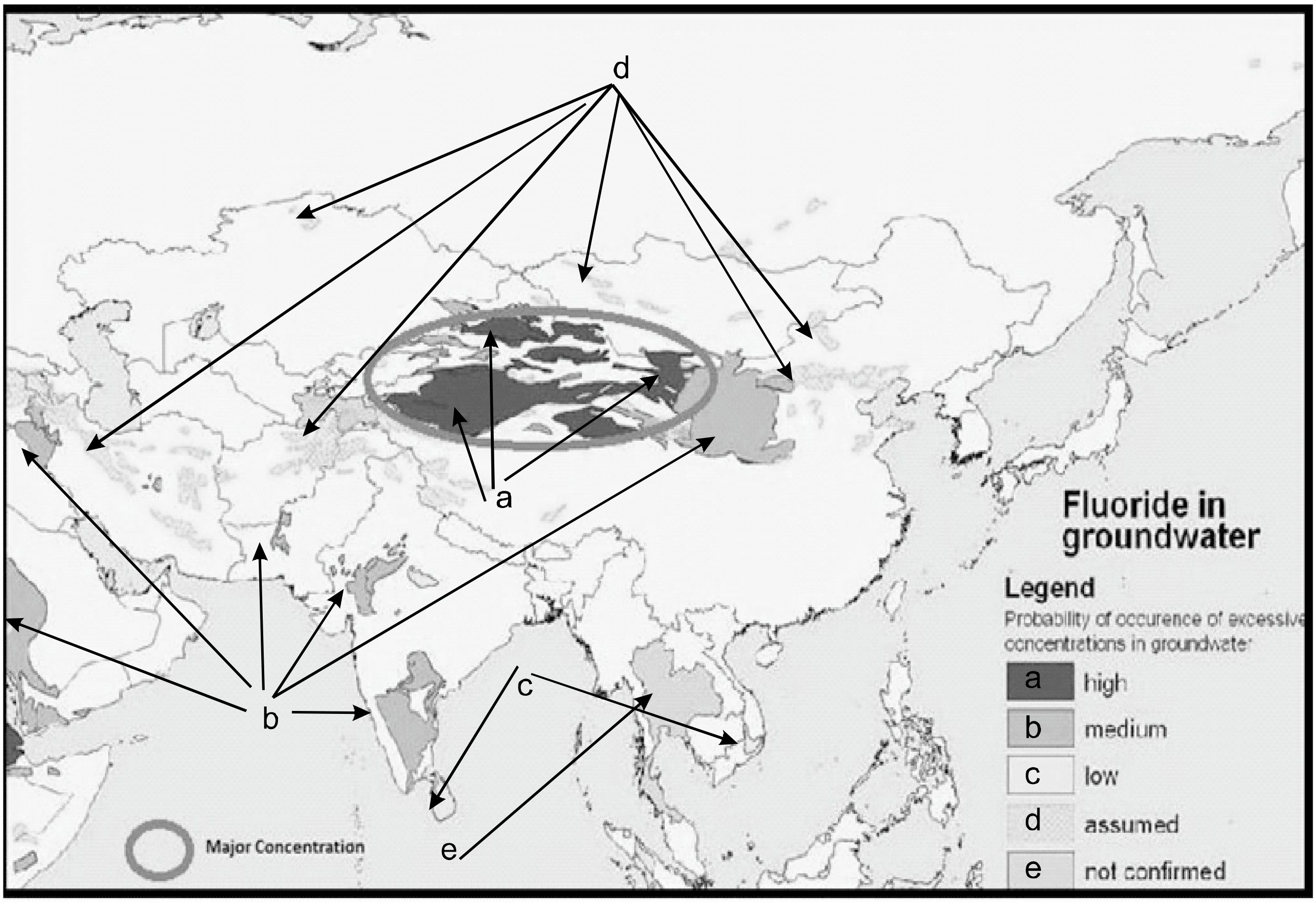

Fig 3: A Map of Asia showing a major concentration of Fluoride contamination in Groundwater. Website of International Groundwater Resources Assessment Centre - www.un-igrac.org

(Fig 3) were responsible for Fluoride contamination including Fluoride rich minerals leaching, Geothermal Fluoride fluids and Fluoride dissolution in groundwater having high HCO_3 concentration *(Eq 1)*. *(Wen et al., 2013).*

$$CaF_2 + 2HCO_3^- \; CaCO_3 + 2F^- + H_2O + CO_2 \qquad (2)$$

Iran

Due to many anthropogenic activities initially, the surface water was affected, but now groundwater is also not distinctive from that. Day-by-day the groundwater quality *(Fig 4)* is getting exacerbated. A total of 17nos. of the sample of groundwater was analyzed in Lars, South Iran and it was found out that the fluoride concentration was ranging from 0.59 mg/l to 3.92 mg/l. Eastern part of Lars has more regions where the concentration is found out to be around 1.50 mg/l. *(Rezaei, Nikbakht and Shakeri, 2017)*. 24 nos. of samples collected from Tabriz, Iran was also analyzed and fluoride concentration was found to be ranging from 0.7 to 111.1 mg/l. *(Vaezihir and Mohammadi, 2016).*

AFRICA

One of the continents in the world where the groundwater is the main source of drinking water like most part of Asian countries. Some portion of Africa mainly Eastern and westernmost region is highly affected by fluoride contamination as shown in *(Fig 5)*.

Kenya

From the area of Bondo- Rasida Area, Kenya a total of 23 numbers of water samples were collected from borewells of 6 divisions. The maximum concentration of Fluoride from water samples collected from borewell was found out to be 2.09 mg/l which is much higher than the permissible limit of WHO water sample i.e. 1.5 mg/l *(Wambu et al., 2014)*. A survey done in Kenya was found to have around 62% of samples have concentration more than 1 mg/l and around 20% of samples have concentration above 5mg/l. *(Menya et al., 2019).*

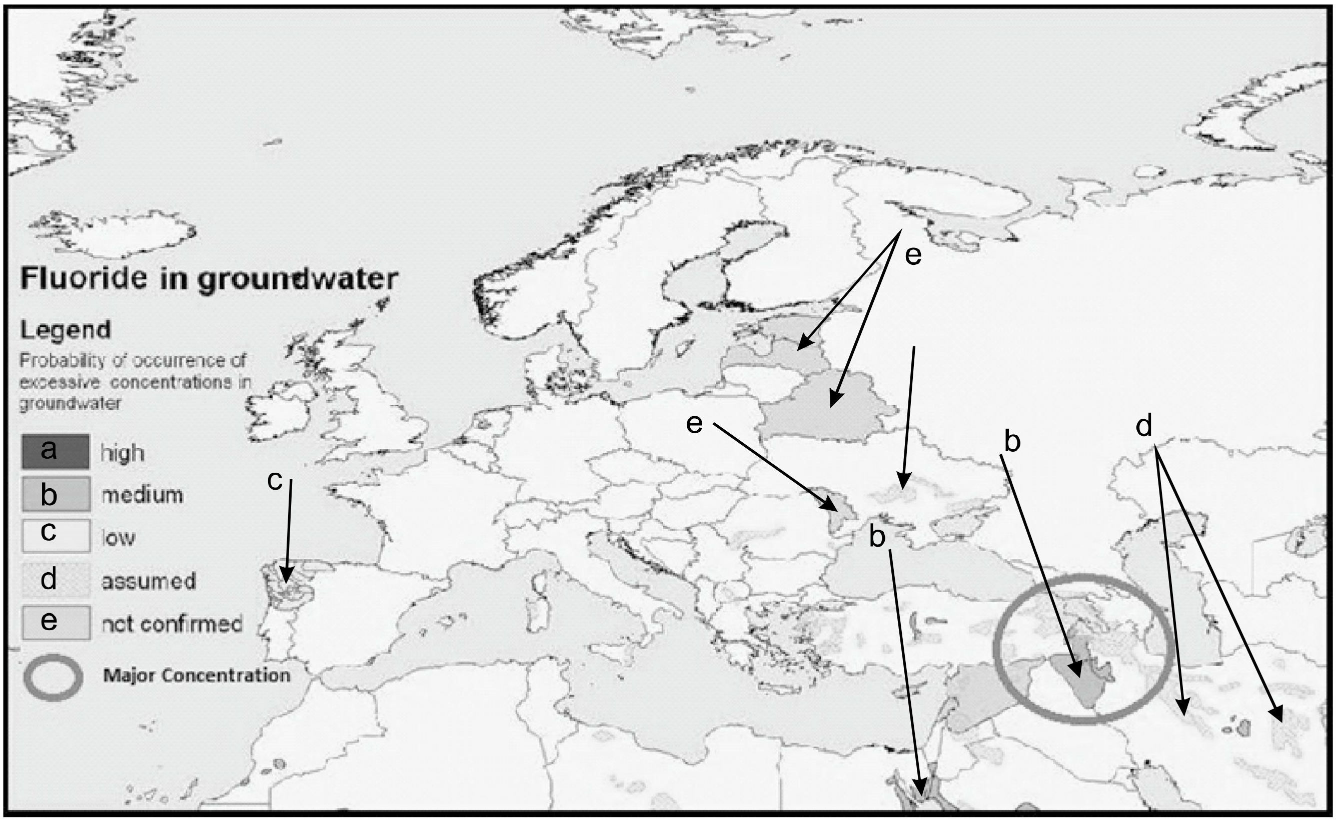

Fig 4: A Map of Western Asia showing a major concentration of Fluoride contamination in Groundwater. *Website of International Groundwater Resources Assessment Centre - www.un-igrac.org*

Algeria

Some study areas were chosen by the National Institute of Algerian Public Health on the basis of the population affected by dental fluorosis. It was observed that the three sources were responsible for fluorosis. The total intake of fluoride content was observed due to ingestion of Tea, Dates and drinking water (groundwater). After a thorough analysis of these three sources, it was found out that approximately 70% of the total fluoride consumption is from drinking water (groundwater) and it was in range from 0.4 mg/l to 2.3 mg/l which is also higher than the standard set by WHO (1.5 mg/l). *(Messaïtfa, 2008).*

AMERICA

America generally doesn't have any problems with drinking water quality, but in some parts of America, especially the rural and underdeveloped parts might have some water quality related issues. An overview map of North and South America can be seen in *(Fig 6 and Fig 7)***.**

USA

Wisconsin, a state in the USA received 88% of drinking water from surface water sources and the remaining 12% from groundwater. A study on 4000 water supplies from rural areas was examined for the test of Fluoride, Coliform bacteria, etc and the result was actually surprising, 47% of the tested water sources were found to have one or more than one health concerns and can be unfit for drinking. A fluoride concentration of 1.2 mg/l can prevent dental carries but a concentration more than that can cause dental fluorosis. Accordingly, 3 numbered districts were identified namely Cambrian and Ordovician confined aquifers, Shoreline along Lake Michigan and Marathon County having Fluoride concentration mean 1.32 mg/l, 2 mg/l - 4 mg/l and 0.07 mg/l - 7.6 mg/l respectively. These districts were found to have concentration more than 1.2 mg/l and the source for the contamination of groundwater were found out to be Fluorite and Fluorapatite. *(Luczaj and Masarik, 2015)***.**

Other Parts of America

A study for 2 years in Los Azufres, Michoacán identifies Fluoride content in groundwater ranges from 10 mg/l to 90 mg/l which is on the extreme higher side of the acceptable limit (1.5 mg/l). Araró,

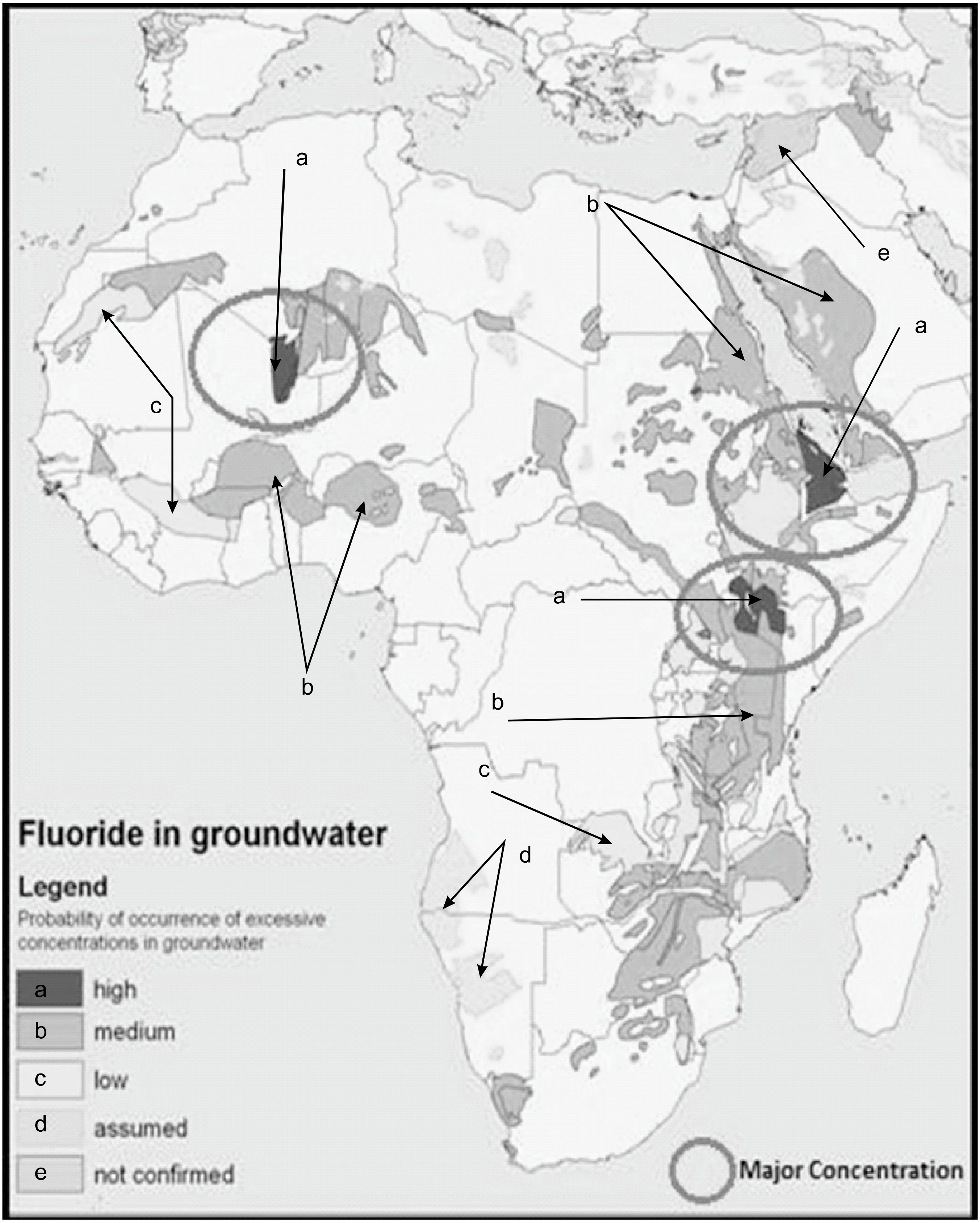

Fig 5: A Map of Africa showing a major concentration of Fluoride contamination in Groundwater. *Website of International Groundwater Resources Assessment Centre - www.un-igrac.org*

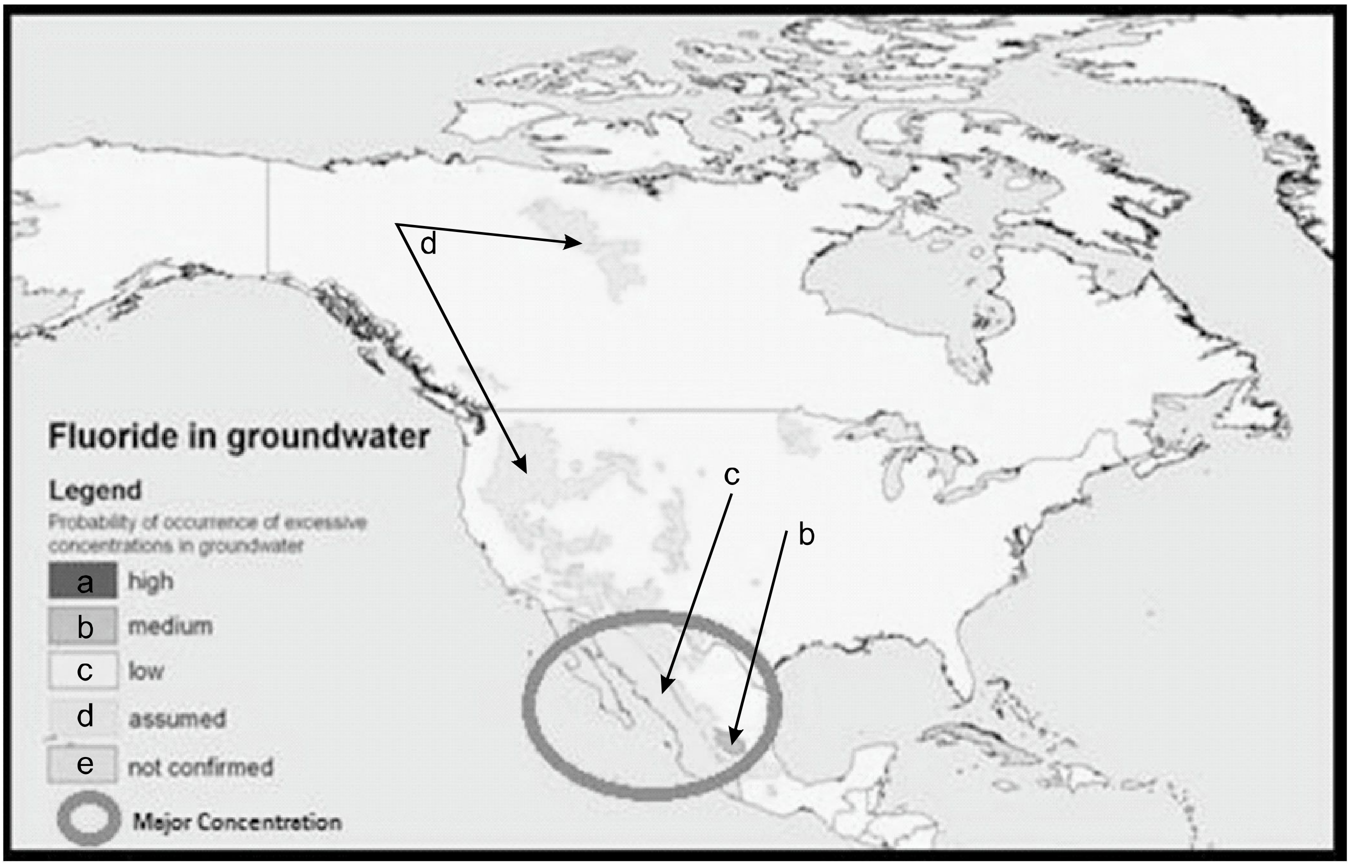

Fig 6: A Map of North America showing a major concentration of Fluoride contamination in Groundwater. *Website of International Groundwater Resources Assessment Centre - www.un-igrac.org*

Northern part of Michoacán shows the fluoride content around 0.7 mg/l to 4.2 mg/l, again high. Another study in Chaco-Pampean plain was organized to determine the different types of contaminants in groundwater and some areas which were mainly targeted including La Pampa, Northern Province (0.9 mg/l - 3.9 mg/l), Buenos Aires, Shallow wells (5 mg/l - 7mg/l), Córdoba, South Eastern Province (0.26 mg/l - 6.3 mg/l), Córdoba, Southern Province (1.4 mg/l - 6.8 mg/l), and Santiago del Estero, Rio Dulce Alluvial Cone (0.7 mg/l to 22 mg/l). After the study, it was prominent that the fluoride content in various parts of South America is also very high and is unfit for drinking.

The reason for high contamination deduced from these studies is the interaction between geomorphological, geology and local landform features. As a solution, the removal process used is alone or in combinations of different methods. The predominant methods used for removal of these fluoride contaminants in these parts of America includes Membrane technology, Coagulation/ Filtration process or adsorption by using activated Alumina. *(Alarcón-Herrera et al., 2013).*

OTHER PARTS OF THE GLOBE

Different studies were done in different parts of the world where the sign of any problem related to water contamination is detected. It was found out that major cause of Dental Fluorosis was because of high fluoride contamination in water sources used for drinking. An exhaustive list of Fluoride data across the globe is given in *Table 1*. Few areas which are pointed by British Geological Survey *(Fig 8)* which have more than 1.5 mg/l (WHO standard) fluoride contamination includes Region of North China, Southern Eastern Part of India, Eastern African region, Southern South American parts, and Some Parts along Western North America. There is moderate contamination of fluoride (up to 0.69 mg/l) groundwater in some parts of Australia. *(Petrides and Cartwright, 2006).* The map of contamination in Australia can be seen (*Fig, 9)*.

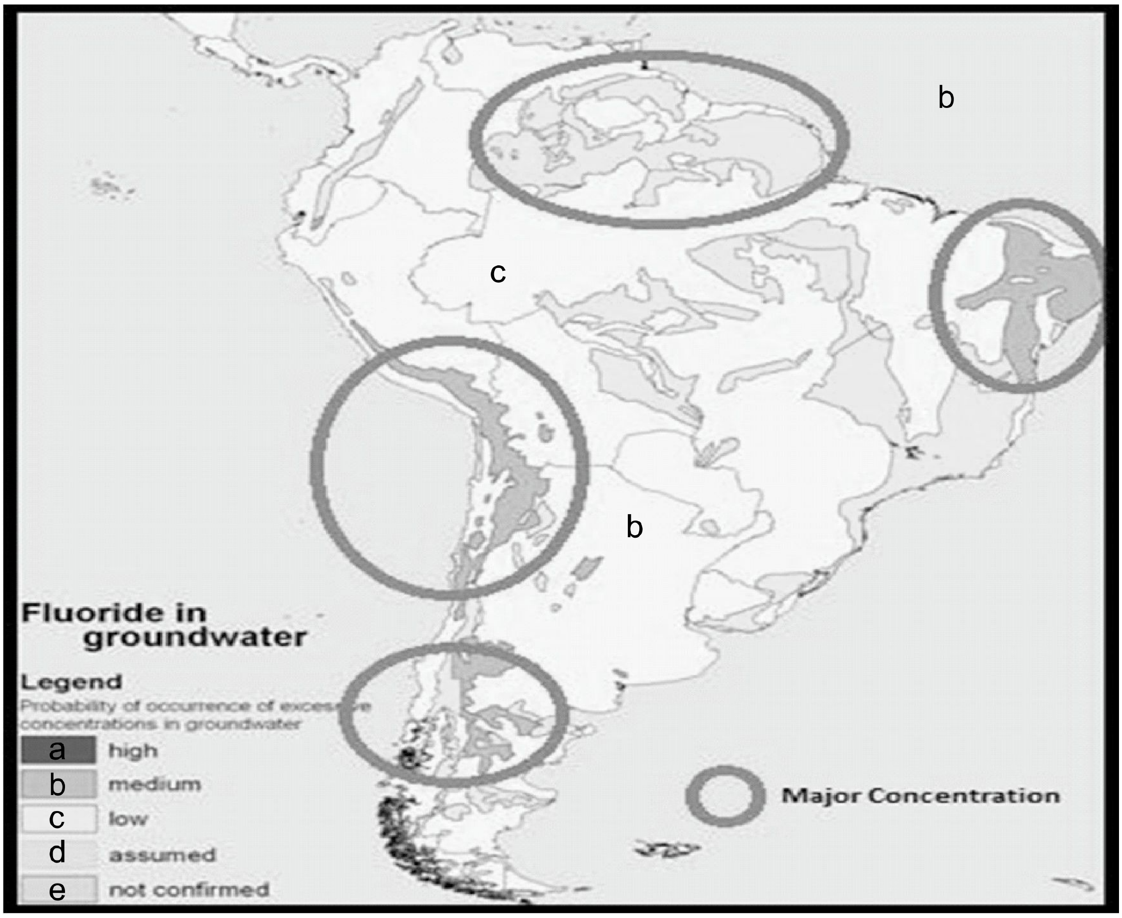

Fig 7: A Map of South America showing a major concentration of Fluoride contamination in Groundwater. *Website of International Groundwater Resources Assessment Centre - www.un-igrac.org*

Fig 8: A Map of the World showing a major concentration of Fluoride contamination in Groundwater. *Website of British Geological Survey - www.bgs.ac.uk.*

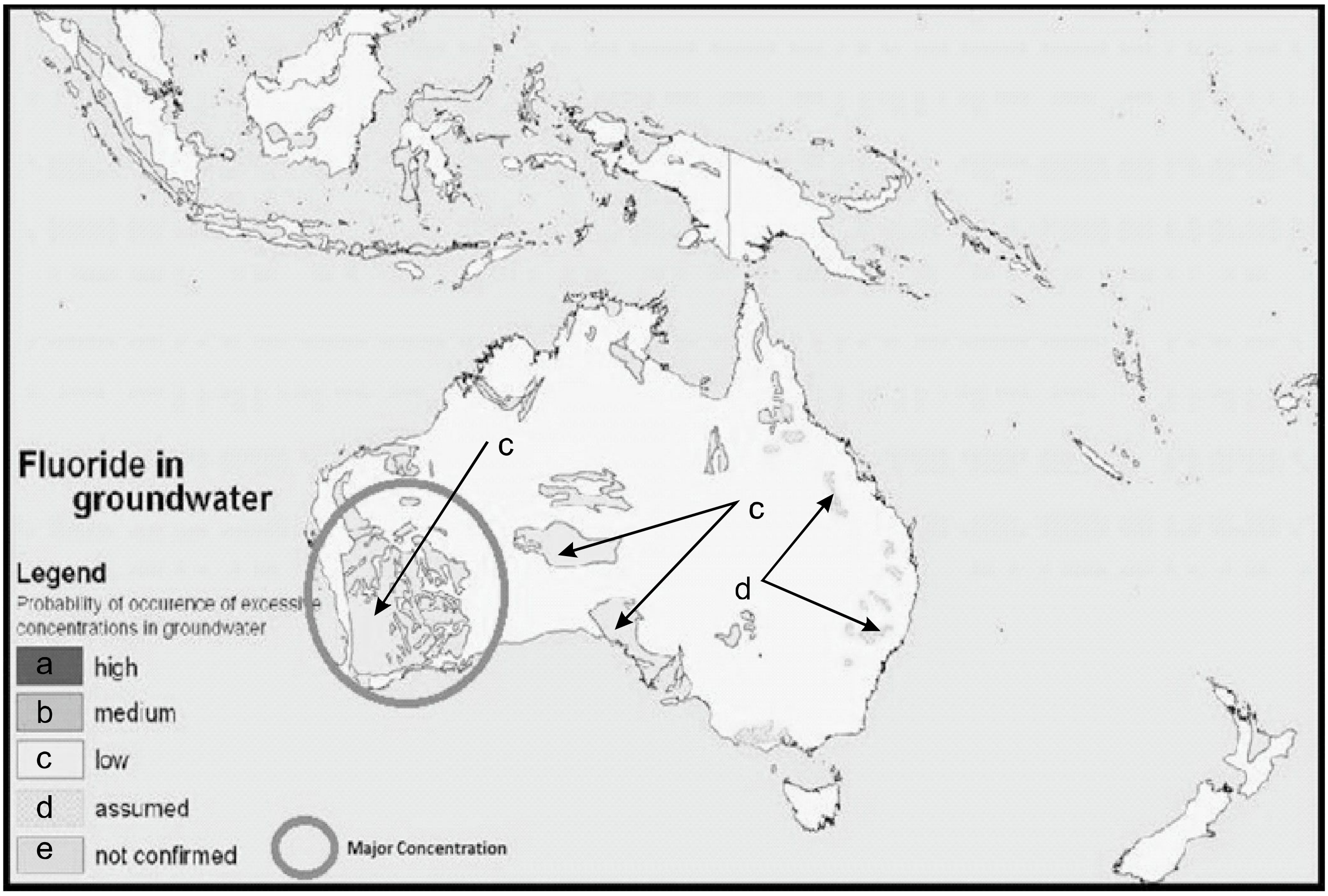

Fig 9: A Map of Australia showing a major concentration of Fluoride contamination in Groundwater. *Website of International Groundwater Resources Assessment Centre - www.un-igrac.org*

GLOBAL DATA OF FLUORIDE CONTAMINATION

Location	Range of Fluoride (mg/l)	Citations
Bogor, Java, Indonesia	3.0 mg/l	(Rugayah *et al.*, 2014)
Nakorn Patum, Thailand	3.5 mg/l	(Smittakorn *et al.*, 2010)
IRAN		
Chatrood village, Iran	0.20 – 1.99 mg/l	(Dehbandi *et al.*, 2017)
Yazd province, Iran	0.22 -2.35 mg/l	(Dehbandi *et al.*, 2018)
Bushehr province, Iran	1.52 – 3.94 mg/l	(Dobaradaran *et al.*, 2018)
Gonabad, Iran	0.44 – 1.62 mg/l	(Karimi *et al.*, 2018)
Wet Season, South of Iran	1.75 – 3.92 mg/l	(Rezaei *et al.*, 2017)
Dry Season, South of Iran	0.59 - 3.18 mg/l	(Rezaei *et al.*, 2017)
Tabriz, Iran	upto 9.0 mg/l	(Vaezihir *et al.*,2016)
Gonabad, Iran	0.46- 1.56 mg/l	(Karimi *et al.*, 2018)
Maku Area, Iran	0.3 – 5.96 mg/l	(Asghari M. *et al.*, 2008)
Areas of Iran	avg 1.86 mg/l	(Mesdaghinia *et al.*, 2010)
INDIA		
Vijaypura, Karnataka, India	0.26-3.53 mg/l	(Ugran V. *et al.*, 2017)
Sahibganj, Jharkhand, India	0.12- 29.0 mg/l	(Nayak *et al.*, 2009)

Alleppey town, Kerala, India	upto 2.88 mg/l	(Raj and Shaji, 2017)
Nayagarh, Orissa, India	0.16 - 10.1 mg/l	(Kundu N. *et al.*, 2001)
Central Rajasthan, India	5.91 mg/l	(Hussain *et al.*, 2012)
Kolar, Karnataka	0.36 – 3.34 mg/l	(Mamatha and Rao, 2010)
Tumkur, Karnataka	0.78 – 5.35 mg/l	(Mamatha and Rao, 2010)
Guntur District, Andhra Pradesh	0.3- 2.0 mg/l	(Subba Rao, 2006)
Mehsana, Gujrat	0.94 – 2.81 mg/l	(Salve *et al.*, 2008)
SRI LANKA		
Anuradhapura, Sri Lanka	max 7.0 mg/l	(Weragoda et al., 2017)
NuwaraEliya, Sri Lanka	max 0.1 mg/l	(Weragoda et al., 2017)
Puttalam, Sri Lanka	max 2.2 mg/l	(Weragoda et al., 2017)
Mannar, Sri Lanka	max 1.2 mg/l	(Weragoda et al., 2017)
Jaffna, Sri Lanka	max 1.3 mg/l	(Weragoda et al., 2017)
Incomalee, Sri Lanka	max 2.4 mg/l	(Weragoda et al., 2017)
Batticaloa, Sri Lanka	Max 0.7 mg/l	(Weragoda et al., 2017)
Hambantota, Sri Lanka	max 1.5 mg/l	(Weragoda et al., 2017)
Matale, Sri Lanka	max 0.8 mg/l	(Weragoda et al., 2017)
Kurunegala, Sri Lanka	max 5.0 mg/l	(Weragoda et al., 2017)
Polonnaruwa, Sri Lanka	max 1.8 mg/l	(Weragoda et al., 2017)
Vavuniya, Sri Lanka	max 3.1 mg/l	(Weragoda et al., 2017)
North Central Province, Sri Lanka	3.9 - 7.3 mg/l	(Dharmaratne, 2015)
Trincomalee, Sri Lanka	upto 2.4 mg/l	(Weragoda et al., 2017)
Mannar, Sri Lanka	upto 1.2 mg/l	(Weragoda et al., 2017)
Areas of Sri Lanka	max 10 mg/l	(Dissanayake, 1991)
PAKISTAN		
Nagar Parkar Area, Sindh	1.13 – 7.85 mg/l	(Rafique *et al.*, 2009)
East Punjab, Pakistan	max 22.8 mg/l	(FAROOQI *et al.*, 2007)
CHINA		
Guangdong, China	max 25.1 mg/l	(Wen et al., 2013)
Xinjiang, China	max 21.5 mg/l	(Wen et al., 2013)
Tibet, China	max 19.6 mg/l	(Wen et al., 2013)
Beijing, China	max 8.0 mg/l	(Wen et al., 2013)
Datong Basin, Northern China	0.1- 8.3 mg/l	(Su et al., 2013)
Taiyuan basin, northern China	6.20 mg/l	(Guo et al., 2007)
JAPAN		
Tono Area, Japan	max 12 mg/l	ABDELGAWAD *et al.,* 2008)
Mizunami Area, Japan	2 – 7 mg/l	(Abdelgawad *et al.*, 2009)
NORTH AMERICA		
Texas, USA	0.59 – 0.88 mg/l	(Chaudhuri and Ale, 2014)
Wisconsin, USA	0.01 – 7.6 mg/l	(Luczaj and Masarik, 2015)
San Luis Potosi basin, Mexico	3.7 mg/l	(Carrillo-Rivera *et* al., 2002)
Interlake, Manitoba, Canada	0.084 – 15.1 mg/l	(Leybourne *et al.*, 2008)
SOUTH AMERICA		
Buenos Aires, Atlantic region	0.9 – 3.9 mg/l	(Alarcón-Herrera *et al.*, 2013)
N. La Pampa	0.9-3.9 mg/l	(Alarcón-Herrera *et al.*, 2013)
S.E. Córdoba	0.26–6.3 mg/l	(Alarcón-Herrera *et al.*, 2013)
Santiago del Estero, Rio Dulce Alluvial Cone	0.7–22 mg/l	(Alarcón-Herrera *et al.*, 2013)

EUROPE		
South Eastern, Sweden	4.2 mg/l	(Berger *et al.*, 2012)
Laxemar, Sweden	1.2-7.4 mg/l	(Berger *et al.*, 2016)
Slovakiaya	0.05- 4 mg/l	(Fordyce *et al.*, 2007)
Bujanovac valley, Serbia	1-7 mg/l	(Krunice *et al.*, 2013)
SOUTH KOREA		
Jungwon area, South Korea.	6-10 mg/l	(CHAE *et al.*, 2007)
Spa Area, South Korea	4.4 mg/l	(CHAE *et al.*, 2007)
AFRICA		
Uyoma, Kenya	mean 1.39 mg/l	(Wambu *et al.*, 2014)
Nyang'oma, Kenya	mean 1.00 mg/l	(Wambu *et al.*, 2014)
Nakuru County, Kenya	8.0 mg/l	(Izuagie *et al.*, 2015)
Central Rift, Kenya	1.2- 36.0 mg/l	(Edmunds, W. M. 2012)
Asembo, Kenya	mean 0.92 mg/l	(Wambu *et al.*, 2014)
Eldoret, western Kenya.	1-5.0 mg/l	(Menya *et* al., 2019)
Siloam Village, South Africa	max 30 mg/l	(Odiyo and Makungo, 2012)
Florisbad, Karoo Basin, South Africa	0.9 -5.7 mg/l	(Harkness et al., 2018)
Siloam Village, South Africa	0-6.74 mg/l	(Odiyo and Makungo, 2018)
Upper Region, Ghana	0.11 – 4.60 mg/l	(Apambire et al., 1997)
Northern Region, Ghana	0.00 – 11.6 mg/l	(Salifu et al., 2012)
Chikhwawa, Malawi	0.2 – 4.8 mg/	(Grimason et al., 2013)
Ziway–Shala basin, Ethiopia	1.1 – 68 mg/l	(Rango et al., 2012)
Benguerir, Morocco	1.8- 20 mg/l	(Tahaikt et al., 2007)

Table 1: Table Showing data of Fluoride Contamination of the various regions across the Globe.

METHODS USED TO REMOVE FLUORIDE CONTAMINATION FROM GROUNDWATER

There are many methods used around the globe for the treatment of Fluoride contaminated water. Some of the principal used to remove fluoride from water sample includes Ion Exchange, Adsorption, Precipitation, Coagulation, Defluoridation using Electrolytic method, Electrodialysis and Membrane separation Process. There are different raw material used in these processes and further researches are going on to make these processes more economical and efficient. *(Nath and Dutta, 2010).*

Electrolytic Defluoridation

This method is based on the process of Electrocoagulation with electrodes of Bipolar Aluminium. In this process, it is to be ensured that there are no soluble salts present in the water which is supplied to be treated. The weight ratio of Aluminium to Fluoride is approx 17:1.

The optimum condition for this method is illustrated below-

pH range: 5- 7.6
Area/Volume ratio of Electrode: Order of 25
Temperature: 20 °C
Distance between electrodes: 2 cm
Current Density: 75 A
Type of Reactor: Batch Reactor.

This method is efficient in removing fluoride from 1l of water by just consuming approx 40kg of Aluminium. Some of the pros of this method can be that the operation of this process doesn't require a highly qualified or trained professional and it's easy to maintain*(Mameri et al., 2001).*

RO Membrane Separation

When the water has a high concentration of Fluoride are passed through a Reverse Osmosis Membrane it was found out that the removal of more than 97% of fluoride can be obtained from just passing the contaminated water from RO membrane. It was also observed that the retained concentration of fluoride by the membrane and water flux decrease with time, which indeed can be cleared by backwashing the membrane, making this process a technically difficult process but this process can be considered as one of the economic processes because in this process just a regular industrial RO membrane is used for the defluoridation process and that too with very good efficiency.*(Ndiaye et al., 2005)*.

Electrodialysis

Defluoridation is done using the applied varied potential difference (1.5 volts/cell to 2.5 volts/cell) for efficiency it was taken as 2.0 volts/cell. Other parameters are kept constant such as

Flow Rate: 8 Lph.

Feed Concentration : 1950 mg/l

Fluoride concentration : 9.5 mg/l (Initial).

Potential difference : 1.7 volts/cell.

In this test, it was also observed that desalination is observed along with defluoridation in the brackish water sample. TDS concentration (210 ppm), as well as Fluoride concentration (1.03 mg/l), reached approx to drinking water parameters. The process used is a Continuous reactor with the overall efficiency of the process is around 87%. Initially, the reaction is fast but the due course of time it reduces due to a decrease in ion concentration.*(Sharma et al., 2018)*.

Adsorption

For this method, a composite of Polymer/By-polymer is used as an adsorbent. In this particular process, the adsorbent used is Polyaniline/Chitosan and Polypyrrole/Chitosan. The mechanism used for this adsorption process is Dopant (Double) exchange mechanism. This doesn't change the crystalline nature of the polymer therefore not much change can be seen in X-Ray Powder Diffraction pattern for before and after the adsorption.

The following Initial conditions are adopted for this process-

Reactor: Batch Reactor.
The concentration of Fluoride: 2-10 mg/l.
Contact Time: 5- 30 minutes.
pH range: 3-9
Composite dosage: 25- 200 mg/ 50 ml.
Temperature: 30- 50 °C

It was observed that the L7ow pH and High temperature is favorable for this method and it was also inferred that the process is endothermic in nature. Further observations conclude that as the number of dosage increases the adsorption of Fluoride also increases, this is due to the fact that more dose equivalent to more ion for adsorption. Furthermore, Polypyrrole/Chitosan is more effective in this process of adsorption as compared to Polyaniline/Chitosan. *(Karthikeyan, 2011)*.

Coagulation/ Filtration

This method is widely used to filter suspended and dissolved solids from raw water before drinking. This method is also used to filter out fluoride from water ranging from 1.8 mg/l to 2.0 mg/l. The method involved in this process consists of particles becoming heavy through thorough agitating with a coagulant and then later it settles down. A single compound can be used as a coagulant or in some combinations. The generally used coagulants are Alum, Aluminium Polychloride,(PAC), Polymeric anionic flocculant (PAF), and Aluminium Sulphate alone or in combinations. The pH preferred for this method is around 6.9- 7.0. This process requires a constant check on the amount of contamination and its commensurated dosage. The combination of Alum and PAF can be used to treat water of 5.9 mg/l fluoride content with an approximate 77% efficiency and bring it to 1.5 mg/l. *(Alarcón-Herrera et al., 2013)*.

METHODS FOR EFFECTIVE DISCHARGE OF SLUDGE IN ENVIRONMENT

Defluoridation of water is sometimes necessary if the content of fluoride in water is more. After the process of defluoridation, a huge quantity of fluoride sludge is left out. This is one of the leading problems which needs to be addressed as far as the fluoride treatment is concerned. The fate of the sludge generated through the defluoridation process is generally disposed of off to the landfills which ultimately cause harmful effect on the environment and may also lead to the formation of leachates which ends up in the groundwater later. But, if looked at some of the erudite documents that can help in providing some ways by which this contamination can be decreased.

During the process of Electrocoagulation is used for the treatment of fluoride from water and wastewater, if the potential difference applied can be increased then a lapse in concentration of F(— can be seen and when the voltage is turned to high then this may lead to the formation of bubbles in the water which ultimately will help in the process of sludge separation process. *(Drouiche et al., 2011).*

Sludge produced during treatment using the processes of DCPD (Dicalcium Phosphate Dihydrate) method is due to the heterogeneous reaction of DCPD with fluoride. Settleability of the residual Fluoride is an important parameter for separating the sludge for its further treatment. It is always recommended that sludge should settle rapidly. So, in this process i.e. DCPD process, the sludge is rapidly settleable as compared to conventional Aluminium method in which it takes time to settle. The fluoride residue generated after this process is < 8 mg/l which is actually very less than the Environment standard for disposal of leachates. *(Tafu et al., 2016).* The aim for the successful fluoride treatment should also include efficient disposal of sludge also.

CONCLUSION

Global water scarcity, unavailability of fresh water and degradation in health plays an important role to think upon surface water pollution. There are various conceptual and empirical approaches that are being used for the study upon surface water pollution mainly caused due to fluoride. The present study has been done to cover almost all regions of the Globe and it was found out that almost every part of the Globe is affected by Fluoride Contamination. Even though many developed nations have figured their way to curb with these fluoride contamination problems but it is still predominant in developing countries and researchers are putting efforts to find a feasible and economical solution for the same.

Different possible methods for Fluoride Contamination detection which includes SPADNS Spectrophotometric Method, Ion Selective Electrode Method, and Ion Chromatography have been described along with few possible methods to remove the contamination. Electrolytic Defluoridation, RO membrane separation, Electrodialysis, Adsorption, and Coagulation and Filter process also have been discussed.

During the study, it was found out that there are not many ways available to dispose of the filtered fluoride from water. Some research can be done in the field of fate and disposal of filtered fluoride.

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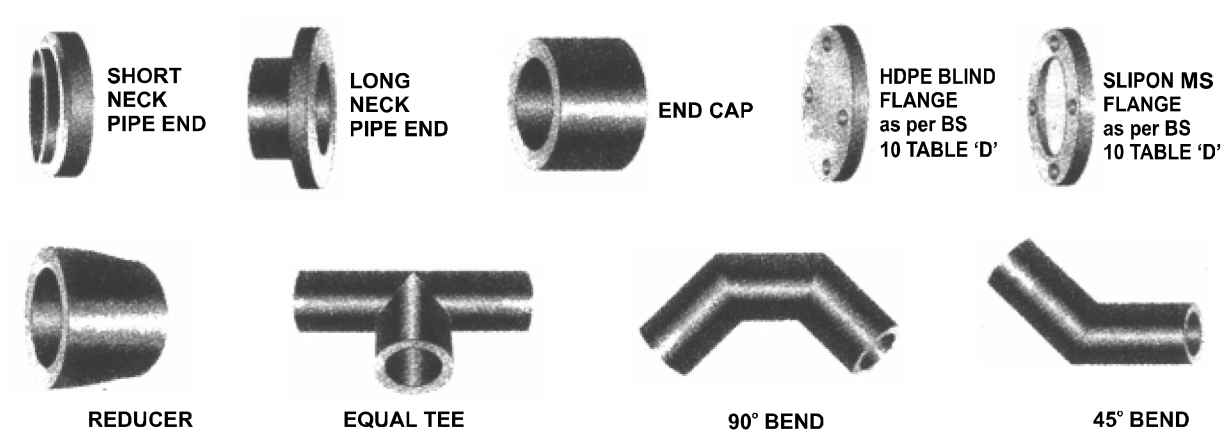

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