INTRODUCTION:

Water is an essential natural resources for sustaining life and environment that we have always thought to be available in abundance and free gift of nature. However, chemical composition of surface or subsurface is one of the prime factor on which the suitability of water for domestic, industrial and agricultural purpose depends. (Shahide, 2008)

In India ground water is the main source for both agricultural as well as for other household uses. Occurrence of fluorine in ground water has drawn worldwide attention due to its considerable impact on human physiology. Fluoride content in groundwater usually depends on rock type, interaction period with host rock, as well as the dissolution kinetics for fluorite, apatite or silicate minerals. There are no. of known fluoride minerals but the most common is fluorapatite. (Greenwood, 1997)

It is well known that trace elements are essential and beneficial to human health in minute concentrations, as they play an important role in many metabolic processes and act as cofactors. However, exceeding their permissible intake is known to be toxic and has adverse effects on general body metabolism. One such trace element, which is ubiquitously distributed in soil, earth and water, is fluoride. It is a fact that low amount of fluoride (<= 1.5 mg/l) in drinking water is helpful in the prevention of dental caries and in treatment of osteoporosis. However, high intake of fluoride (>1.5 mg/l) in drinking water for a prolonged period is known to cause damage to the teeth enamel and eventually leads to skeletal complications that result in fluorosis.

Fluoride is the common element in the earth's crust as component of the rocks and minerals. Fluoride is the reduced form of fluorine which is the member of halogen series. Fluorine, the first member of the halogens, is an element with unique physical and chemical properties. It has the highest electron affinity or the most non-metallic nature, and therefore, its compounds often display different properties from those of other halogens. It is highly reactive and not found in the elemental state in nature. It is only found in solid salts or fluoride ions in aqueous solution. Fluorine is capable of forming compounds with all the elements except helium and neon. Fluoride gives complex anions with silicon, aluminium and iron, forming SiF_6^{-2}, AlF_6^{-3} and FeF_6^{-3}, which are often found in natural waters besides fluoride (F^-) itself.

The geochemistry, biogeochemistry and biochemistry of fluoride are special and are of particular interest because of these fundamental special characteristics in both physics and chemistry. The analytical chemistry of fluorine is also unique in that it is one of the most difficult elements to handle in terms of both chemical and instrumental techniques used in its analysis.(Tsunoda H. And Ho Yu M., 1986)

Fluoride exists fairly abundantly in the earth's crust and can enter into groundwater by natural processes. Through weathering process of the primary minerals, fluoride is released into the soil and groundwater, i.e., leaching of fluoride containing minerals may yield fluoride in solution. Fluoride is common in semi-arid climate with crystalline igneous rocks and alkaline soils.(Handa 1975) Fluoride is considered as one of the minor constituents of natural waters, but it is an important parameter in ascertaining the suitability of water for potable purposes. Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulphate, pesticides other heavy metal etc. in underground water has become a major global problem.

Fluoride or fluorine deficiency is a disorder which may cause osteoporosis due to lack of fluoride in the diet. Dental fluorosis as a health condition caused by a child receiving too much fluoride during tooth development. The critical period of exposure is between 1 & 4 years old, children over age 8 are not at risk. (Alvarez, 2009) Nations which are suffering from fluorosis are Argentina, USA, Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran , Iraq, Tanzania, South Africa, China, Australia, Canada, India etc. (WHO, 2004) In India, high Fluoride concentrations in groundwater (> 1.5 mg/l) occur in 14 Indian states, namely, Andhra Pradesh, Bihar, Gujarat, Haryana, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal affecting a total of 69 districts, according to some estimates. Some other estimates find that 65 per cent of India’s villages are exposed to fluoride risk. Shortt *et al*. from the King’s Institute of Preventive Medicine at Chennai reported in 1937 endemic fluorosis for the first time in India in a cluster of villages around Podili and Darsi in Prakasam District, Andhra Pradesh.

STUDY AREA:

Mehsana district is situated in the northern part of Gujarat. Geographically this area is flat except Satlasana and Kheralu taluka. Geologically, 85% of the area comprises of alluvial formation in the form of alternate bands of sand and clay. Sandy formations act as groundwater bearing aquifers. Northern parts of the district consist of country rock as charnokites, calc-granites and calc-gneisses formation. Ground water occurs under confined and unconfined conditions. Therefore the sources of ground water in the area are deep and tube wells are of 150 m to 400 m depth and 150 mm to 300 mm in diameter.

Rajkot district is situated in saurashtra region of Gujarat. Geologically 85% of Rajkot district is composed of Basaltic Rocks. It is covered with inherent saline alluvium in Maliya taluka in the North. The area east and southeast of Morbi taluka and east and northeast of Wankaner taluka shows presence of sandstone , which is a good aquifer but highly exploited by farmers for abstraction of groundwater due to which the ground water level has gone down considerably. In sandstone area generally non potable aquifers occur below 150 mts depth. The deeper confined aquifers of basalt are generally non- potable (except few pockets such as Devki Galol, Jetalsar, and Dhank)

Amreli district is situated in saurashtra region of Gujarat. Physiographically the entire area of Amreli district is more or less plain except for a small hill ranges in areas of Babra, Khambha, Savarkundla and Rajula talukas. Geologically the area of Amreli district is covered by Deccan trap lava flows, supra trappeans, Gaj beds, Miliolite Limestone and recent unconsolidated deposits. Deccan trap lava flows cover greater part of the district. The Gaj beds consist of highly fossiliferous, pale yellow limestone, sand and silt along the coastal area of the district. Miliolitic limestone occurs along the coast. It is buff coloured, current bedded limestone in the form of coastal ridge and thinning out towards coastal plain. Ground water in the district occurs under unconfined to confined conditions in weathered, fractured and jointed basalt, vesicular basalt fractured dykes, sand and conglomerate's of supra trappeans, porous limestone of Gaj beds, silt and clay of alluvium. In the trap the aquifer ranges in depth from 15 m. to 150 m. below ground level.

OBJECTIVES:

1. Survey and selection of wells/ tube wells/ bore wells having Fluoride content from North Gujarat and Saurashtra regions.
2. Bioremoval of Fluoride in water samples collected from different localities/villages using various plant materials (Bioadsorbents).
3. Assessment of Fluoride accumulation in selected crop plants specific to the study area.
4. Biochemical changes caused due to Fluoride containing irrigated water in the selected crop plants.
5. E-DAX study pertaining to localization of Fluoride in different parts of test plants.

METHODOLOGY:

1. Survey and Selection of study sites.
    - Base data of ground water samples was collected from Gujarat Water Supply and Sewerage Board (2009-10) of Mehsana, Rajkot and Amreli districts.
    - Survey and selection of Villages for the study was done on the basis of available base data.
    - Fluoride content in the GW samples was estimated using Fluoride ion selective electrode (Orion ion meter-Model 920-A)
2. Bioremoval of Fluoride using bioadsorbents involved
    - Various Plant materials like *Moringa oleifera*. L. (bark), *Moringa oleifera* L. (seed), *Cocos nucifera* L. (shell), Cocos *nucifera* L. (fibre) and *Oryza sativa* L. (husk) were collected and were checked for defluoridation capacities in vitro and from the results obtained *M. oleifera*., L. (bark) and *M. oleifera* L.(seed) were selected for further

study. This was carried out following the methods of Veeraputhiran *et al.,* 2011.

- Experiments on Optimization study (Dose, Time and Volume) using *M. oleifera*., L. (bark) and *M. oleifera* L.(seed) was done by the methods of Suganandam *et al*.,2010.

- For in vivo bioremoval study, GW samples (wells/ tube wells /bore wells) were collected seasonally and were analyzed for potable parameters as well as Fluoride content which followed the methods described in APHA-AWWA-WPCB, 1998.

- Residual Fluoride after administration of standardized dose of *M. oleifera* L. (bark) and *M. oleifera* L.(seed) in the GW samples followed the methods of Harikumar *et al.*,2012.

3. For Bioaccumulation of Fluoride in crop plants
   Triticum aestivum L. and *Pennisetum glaucum* R.Br. were collected and preserved for further analysis. (Gautam *et al*., 2010) Fluoride accumulations in the root, stem, leaves and seeds of these plants yet to be analyzed.

4. Biochemical changes accompanied fluoride accumulation involved estimation of Chlorophyll (Arnon,1949) , Carbohydrate (Anthrone Method) Protein (Lowry's method) and Proline (Thimmaiah,1999), Lipid Peroxidase (Heath 1968), Peroxidase (Sadasivam and Manickam, 1996)

5. E-DAX study (Giere *et al*. 2012)

SUMMARY:

Base data for fluoride contamination in ground water was collected from Gujarat Water Supply and Sewerage Board of Mahesana, Rajkot and Amreli districts for the period of 2009-10. Villages were selected from each district on the basis of high fluoride concentration. Total 30 ground water samples were collected from each district for analysis of fluoride and physicochemical parameters. Fluoride concentration in rural ground water sample ranges from 0.2 mg/l to 7.0 mg/l, 0.2 mg/l to 6.0 mg/l and 0.4 mg/l to 6.5 mg/l from Mahesana, Rajkot and Amreli districts respectively. About 32 % rural ground water samples from Mahesana district, 54 % from Rajkot district and 41 % of Amreli district showed fluoride concentration within the permissible limit i.e. <=1.5 ppm, whereas 68 %, 46 % and 59 % of ground water samples revealed high contamination of fluoride in Mehsana, Rajkot and Amreli districts respectively could be due to high fluoride concentration in subsoil and due to fluoride bearing minerals in the rocks where these sites are located.

Various plant materials were selected to check their capabilities towards Fluoride removal invitro. They were selected on the basis of their adsorption property, cheapness, nontoxicity and their availability. Plant materials like *Moringa oleifera*., L. (bark), *Moringa oleifera* L.(seed), *Cocos nucifera* L. (shell), *Cocos nucifera* L. (fibre) and *Oryza sativa* L. (husk) were tested. Optimisation study using these bioadsorbents was carried out with lab generated NaF solution. The experiment was conducted in triplicate. Following parameters were taken into consideration: (1) Contact time (2, 4, 6, 8, 10 hrs.), (2) Dose of adsorbent (0.12, 0.25, 0.50, 0.75, 1.0 gm.), (3) Volume of initial fluoride solution (75, 150, 225, 300, 375 ml) and (4) Concentration of fluoride ions in the initial solution (1, 2, 3, 4, 5 ppm). The order of removal in the tested bioadsorbents was *Moringa oleifera*., L. (bark),> *Moringa oleifera* L.(seed), > *Cocos nucifera* L. (shell), > *Cocos nucifera* L. (fibre) > *Oryza sativa* L. (husk). This proved that *Moringa oleifera* L. (bark) and *Moringa oleifera* L. (seed) were efficient and effective bioadsorbents. Moreover, they showed maximum fluoride removal at 5 hours, 0.50 gm dose in 50 ml volume having initial fluoride concentration of 5 ppm.

Further, experiments were undertaken with Oven dried and Sundried *Moringa oleifera* L. (bark) powder. The adsorption capacity of sundried powder was found to be more

(37 %) than oven dried powder (26%) at 5 ppm initial concentration of Fluoride, with 0.50 gm adsorbent dose in 50 ml volume of fluoride solution.

Mehsana is one of the leading producer of crop plants like *Triticum aestivum* L., *Pennisetum glaucum* R.Br.,*Sorghum vulgare* L., *Cajanus cajan* L.and *Cuminum cyminum* L., *Triticum aestivum* L. being one of the major crop plant. Also, in this district, Fluoride concentration in GW samples ranged from 0.2 to 7 mg/l. i.e. 1 mg/l in Kesarpura, 3 mg/l in Mota kothada, 5 mg/l in Sheshpur and 7 mg/l in Nana Kothada. During field visits, it was frequently noticed that the fields were directly irrigated with Fluorinated groundwater. Hence, this district was selected for bioaccumulation of Fluoride in *Triticum aestivum* L. Samples of different plant parts like root, stem, leaves and seeds were collected from fields and were analysed for various biochemical parameters like Chlorophyll, Carbohydrate, Protein, Proline, Lipid Peroxidase and Peroxidase. Control plant samples were also processed from village Navavas-Rajpur as GW sample did not show even a negligible amount of Fluoride. No significant change in Chlorophyll, Carbohydrate and Protein contents was found in root stem and leaves of *Triticum aestivum* L. irrigated with fluorinated GW. Similarly in Fluoride treated plants, stress inducing parameters like Proline, Lipid Peroxidase and Peroxidase did not revealed enhancement/ decline than the control plants.

E-DAX Study on seeds is yet to be conducted and interpreted.

REFERENCES:

1. Alvarez *et al.*, 2009 ; Dental fluorosis exposure,prevention and management; *Med.Oral.Patol.Oral.Cir Bucul*.,**14** (2)
2. APHA-AWWA-WPCF; 1998 ; *In* :Standard methods for the examination of water and wastewater(20th Edn); American Public Health Association, Washington D.C.
3. Arnon, D.I., 1949; Copper enzymes in isolated chloroplast.Polyphenol oxidase in *Beta vulgaris*;*Plant physio.*,**24**: 65-71
4. Bell,M.C., and Ludwig T.G., 1970; The Supply of fluoride to man: ingestion from water,Fluorides & Human health, WHO Monograph series 59, world Health Organization,Geneve.
5. Cooke,J.A.,Johnson, M.S., and Davison, A.V., 1978;Uptake and translocation of Fluoride in *Helianthus annus* L. grown in sand culture; *Fluoride*,**11**:76-88
6. Gautam, R., and Bhardwaj, F., 2010; Bioaccumulation of fluoride in different plant Parts of *Hordeum vulgare* (barley) Var. RD-2683 from irrigation water; *Fluoride*, **43**(1): 57-60
7. Giere, R., Kaltenmeier, R. and Pourcelot, L., 2012; Uranium oxide and other Airborne particles deposited on cypress leaves close to a nuclear facility; *J. Environ. Monit*.,**14**: 1264-1274
8. Greenwood,N.N., and Eamshaw,A., 1997; Chemistry of the element(2nd ed.) oxford
9. Handa, B.K., 1975; Geochemistry and genesis of fluoride containing ground water; *Ground water*,**13**(3): 275-281
10. Harikumar, P.S.P., Jaseela, C., and Megha, T., 2012; Defluoridation of water using Biosorbents; *Nature Science*, **4** (4): 245-251
11. Heath, R.L., Packer, L., 1968; Photopetoxidation in isolated chloroplasts.Kinetics and stoichiometry of fatty acid peroxidation; *Arch. Biochem.Biophys*.,**125**:189-198
12. Rao,K.V.,Khandekar, A.K., and Vaidyanadhan D., 1973; Uptake of fluoride by water hyacinth,*Eicchornia crassipes*; *Ind. J. Exp. Biol*., **11**(1): 68-71
13. Sadasivam, S.and Manikam; 1996; In;Biochemical Methods (2nd Edn).New age International (P) Ltd.,New Delhi
14. Sahu, A., and Vaishnav M., 2006; Study of Fluoride in ground water around the Baleo,Korba area (India) ; *Journal of Environmental Science & Engineering*, **48** (1): 65-68

15.Shahide, M.,; 2008; Study on Fluoride content of ground water in Jind District, Haryana, India; *American Eurasian J. Agric. & Environ*. Sci.,**4** (6): 670- 676

16. Short H.E., Mc Robert J.R., Barnad, J.R., Manadi T.W., and Nayar A.S., 1937 ; Endemic flurosis in Madras presidency; *Indian Journal of Medical Research*, **25:**553-568

17. Sinha, S., Pandey, K., Mohan, D.,and Singh, K.,; 2003; Removal of fluoride from Aqueous solutions by *Eichhornia crassipes* biomass and its carbonized form; *Ind.Eng.Chem.Res*, **42**: 691-698

18. Suganandam, G., Paruthimalkalaigan, P., Neerja, P., and Pragathiswaran, C., 2010; Defluoridation of water using Bioadsorbents; *Pollution Research*, **29**(4) : 707-711

19.Thimmaiah, S.K.,1999; *In* :Standard Methods of Biochemical Analysis,Kalyani Publishers,New Delhi

20. Tsunoda, H., and Ho Yu, M., 1986; Fluoride Research 1985,Elsvier science Publishers, New York

21. Veeraputhiran, V., and Alagumuthu, G., 2011; Treatment of High fluoride drinking water using bioadsorbent; *Res. J. Chem. Sci.*,**1** (4): 49-54