CHAPTER 1

INTRODUCTION

1 INTRODUCTION

1.1 Research background

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, groundwater is the main source for both agricultural as well as for other household uses. Occurrence of Fluoride in groundwater 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.

In geochemistry, biogeochemistry and biochemistry of Fluoride are special and are of particular interest because 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 and Ho Yu, 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 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.

Distribution of Fluoride

The belts that are well known for Fluoride contamination are i) East African Rift from Eritrea to Malawi, ii) from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China, iii) America and Japan (Ayoob and Gupta, 2006). The other worst Fluoride affected areas include African countries like Ivory Coast, Senegal, North Algeria, Uganda, Northern Mexico and Central Argentina and the arid parts of northern China, Inner Mongolia (WHO, 2005). In India, most of the Fluoride containing aquifers have been reported from Rajasthan and Gujarat in north-western India, which is largely composed of alluvium aquifers, whereas, in southern India largely consisting of Karnataka, Andhra Pradesh and Tamilnadu, is composed of limestone, quartzite and shale containing aquifers (Fig. 1).

The major affected districts in India due to Fluoride in the ground water, are Kamrup, Karbi, Golaghat, Karimganj (eastern India), Naugaon, Gaya, Jamui, Kaimur, Munger, Bhatinda, Unnao, Sonbha- dra (northern India), Ajmer, Dholpur,

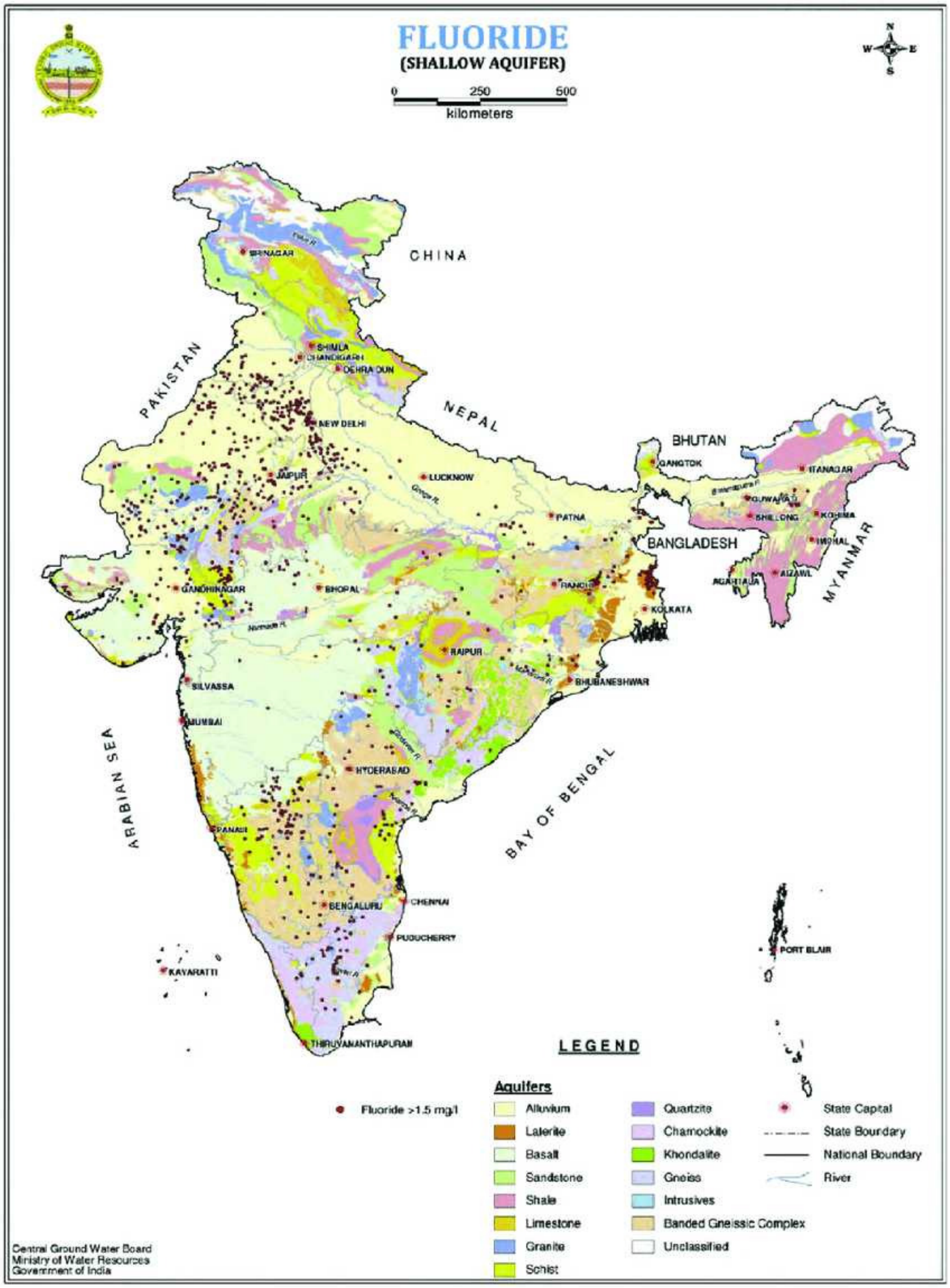

Figure 1: Distribution of Fluoride in aquifer systems of India

(CGWB, http://www.cgwb.gov.in/MAP/FLUORIDE.pdf)

Bundi, Chhitorgarh, Mehasana (western India) Salem and Nalgonda (southern India). According to a Indian ministry report, Rajasthan is on the top for Fluoride affectedarea having the highest number of 7670 habitations with 48, 84, 613 affected people followed by Telangana with 1,174 habitations consisting of 19, 22, 783 affected people and in Karnataka with 1122 habitations. In Uttar Pradesh, Unnao and its neighboring districts have been reported for the occurrence of fluorosis (Kumar et al., 2008).

The probability of occurrence of high Fluoride concentration (>1.5 mg/ L) in ground and surface water was detected in various countries which include India, China, Argentina, Mexico, Pakistan, Italy, Iran, Bangladesh, New-Zealand, Ethiopia and in several Afri- can countries and UK. India is one among 23 nations where fluorosis and other Fluoride associated health hazards occur due to consumption of groundwater (Pillai and Stanley, 2002; WHO,2006). More than 2/3rd of the rural population of India depends on ground-water for drinking (HT, 2017). According to Subarayan *et al*. (2012), 50% of the groundwater sources in India and in more than 90% of the villages use groundwater for drinking purposes have been contaminated with Fluoride. In India, excessive Fluoride was first reported in the groundwater from Andhra Pradesh in 1937. Total 19 states in India have been reported which are affected with high Fluoride in groundwater (CGWB, 2010). In total, 60 million of people are exposed to Fluoride contaminated water (Muralidharan *et al*., 2011).

Sources of Fluoride

Fluoride occurs naturally in varying concentrations in rocks, soil, water, air, plants and animals and anthropogenically in soil and water. The occurrence and movement of Fluoride in various environmental compartments have been schematically presented in Fig.2.

Natural source

Fluoride accounts for about 0.06 to 0.09% of the Earth's crust (Koritnig, 1951). Some of the common minerals containing Fluoride are fluorspar or fluorite (CaF_2), cryolite (Na_3AlF_6), fluorapatite ($Ca_5(PO_4)_3F$), villiaumite (NaF) and topaz ($Al_2(SiO_4)F_2$).

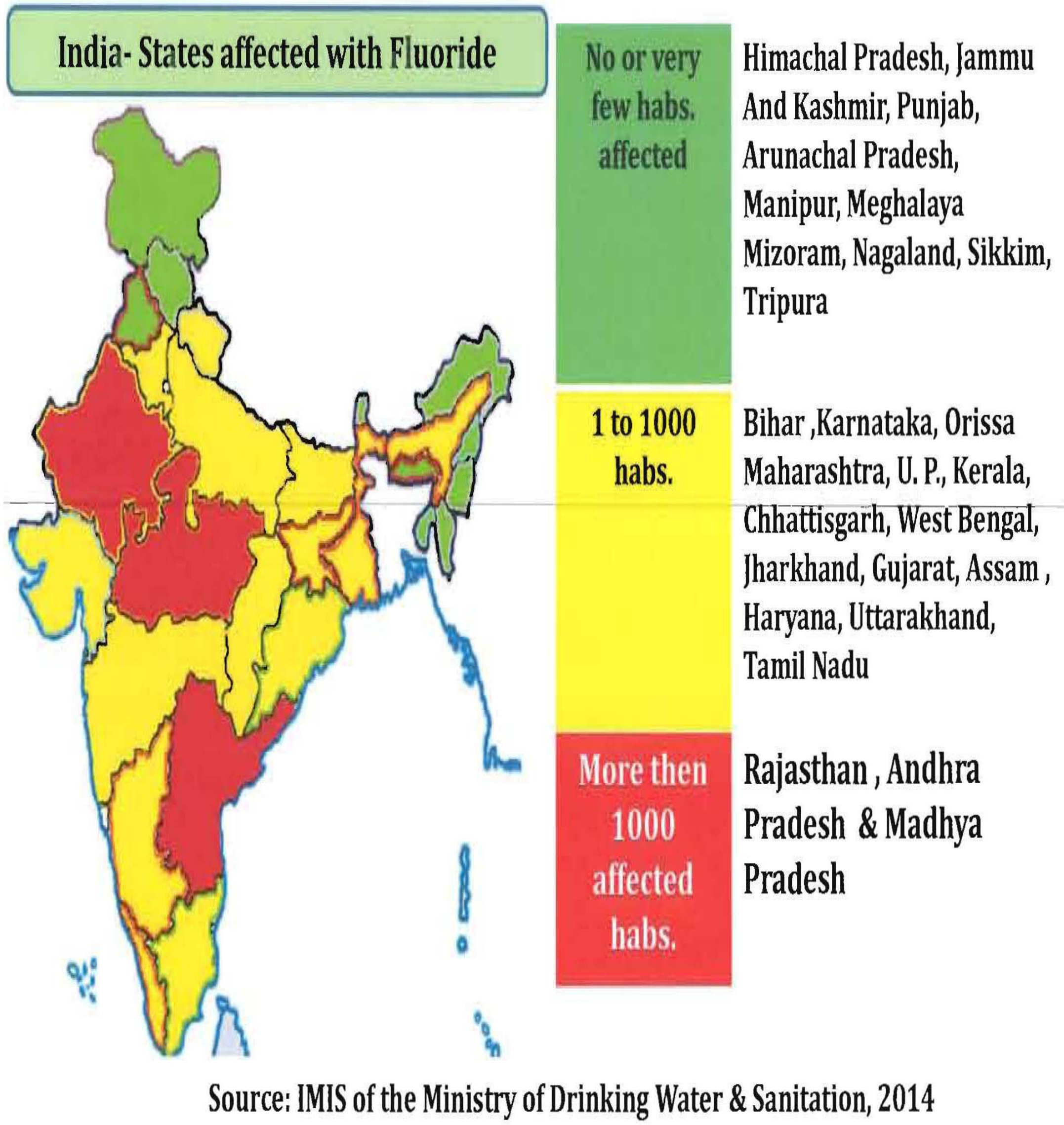

Figure 2 :Fluoride affected States in India

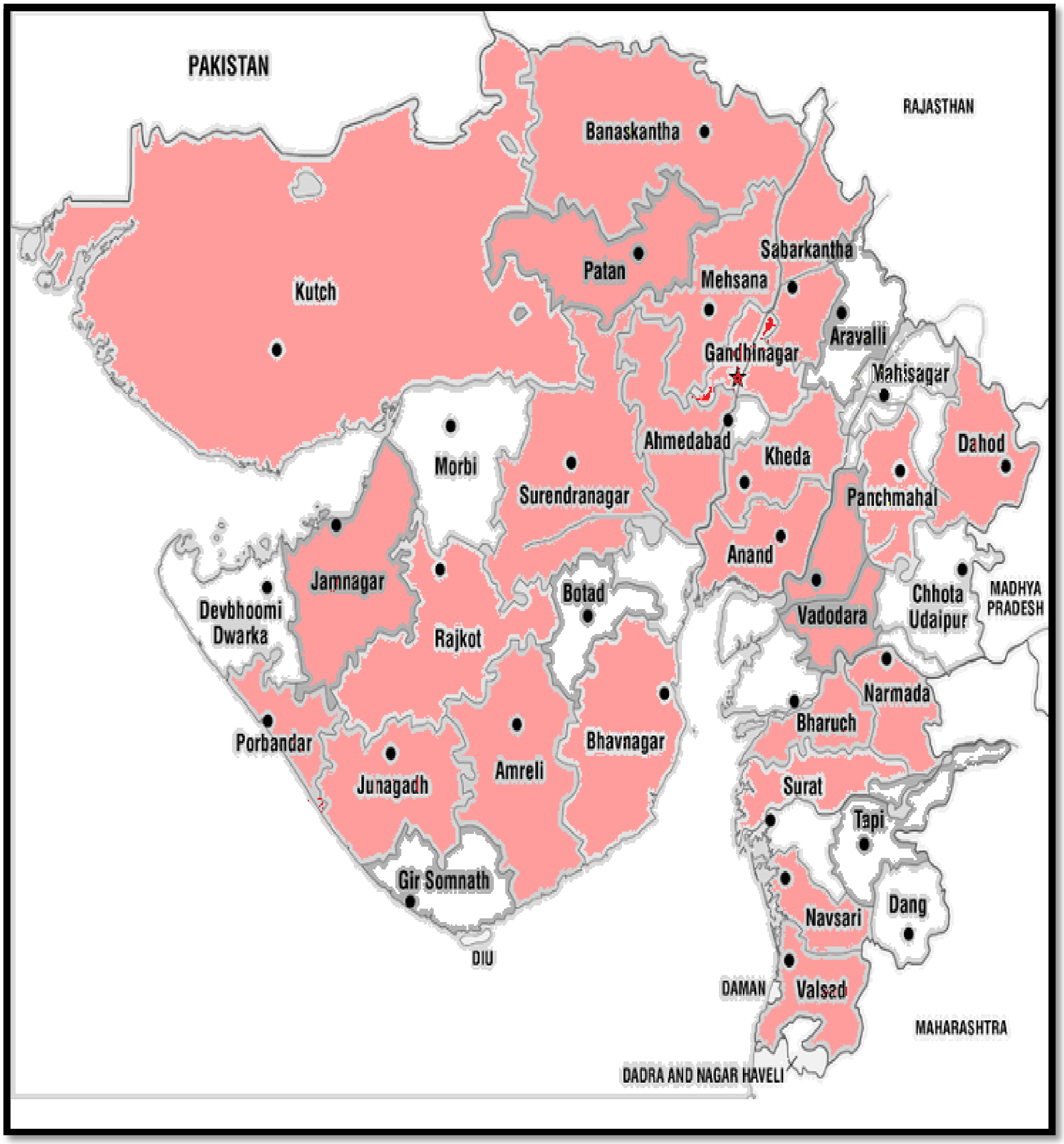

Figure 3 : Fluoride affected districts of Gujarat

Fluoride containing rocks are considered as the reservoir of Fluoride (WHO, 1984). Common rocks containing Fluoride are: Killas (1873 mg/ Kg) > schist (1703 mg /Kg) > gneiss (1563 mg/ Kg) > granite (1043mg/ Kg) > silexite (982 mg/Kg) > conglomerate (963 mg /Kg) > sandstone (903 mg /Kg) (He et al., 2013). The highest content of Fluoride was reported from volcanic rock (2000 mg/ Kg) (Anazawa, 2006) followed by alkaline igneous rock (1300 mg/kg) and in ultramafic rocks and limestone ~100 mg/ Kg(Hem,1985). The weathering of the primary minerals Fluorite, releases the Fluoride to the soil and groundwater. Volcanic activities and hydro-geothermal vents also release Fluoride into the environment which contaminates the soil; release of HF containing gases contaminates the air with Fluoride (CEPA, 1996; Vithanage and Bhattacharya, 2015). The third major natural source of Fluoride is from the marine aerosol, which contributes about 20,000 Kg globally of inorganic Fluoride annually (CEPA, 1996).

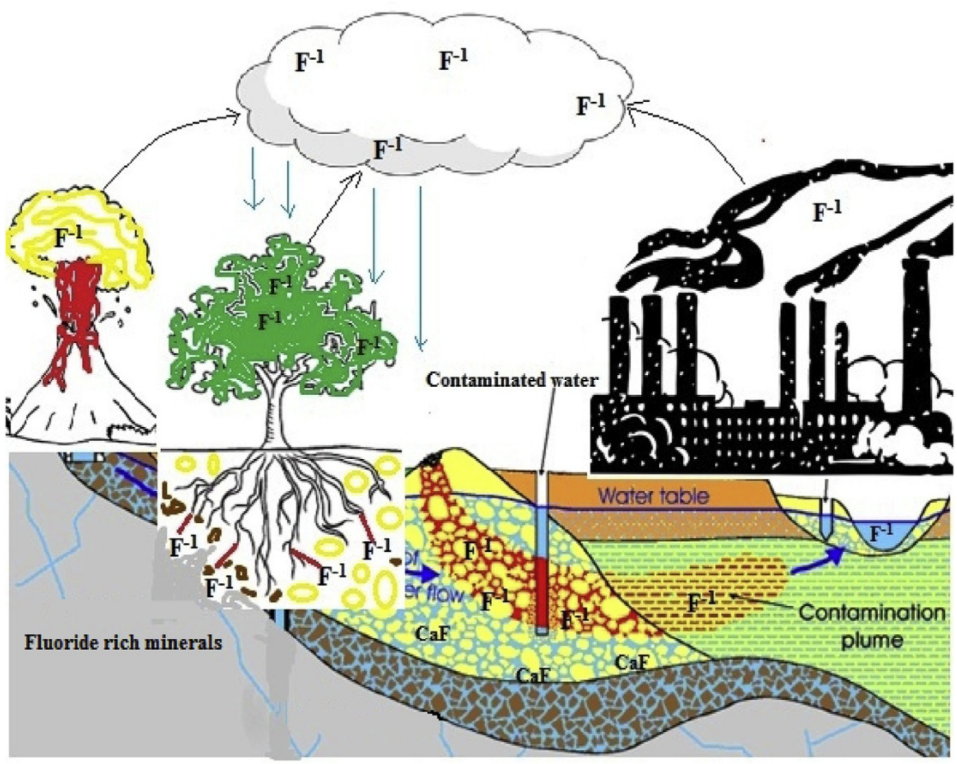

Figure 4 : Sources of Fluoride in the Environment

High Fluoride content in soil occurs in clay minerals (Robinson and Edington, 1946). Alternatively, during the hot, dry pre-monsoon season, high rate of evapo-transpiration causes precipitation of salts, including Fluoride salts, temporarily in the top layers of the soil which act as a semi-permanent reservoir of soluble Fluoride . During monsoon season, the precipitation infiltrates the soil, resulting in high TDS and addition of Fluoride to the soil and groundwater through the leachate from soils (Umar and Alam, 2012).

The enrichment of Fluoride in the aquifers depends largely on physical characteristics of soil such as porosity, depth of the wells and the acidity of the soils and rocks, temperature, ion exchange, presence of cations/ anions and other on-going chemical reactions (Annaduraia *et al*., 2014). Fluoride is found in groundwater upto 67 mg/l while in most surface water is <0.1mg/l, however, sea water has a relatively high Fluoride content of 1.2-1.4 mg/l (IPCS, 2002). This has been attributed to erosion and run off due to streams and rivers from mountains and highlands over the period of time.

Anthropogenic Sources

The use of Fluoride bearing fertilizers like aluminum phosphate fertilizer (Borah and Saikia, 2011), fumigants and pesticides containing barium fluorosilicate ($BaSiF_6$), sodium silico-fluoride (Na_2SiF_6), sulfuryl fluoride (SO_2F_2), trifluralin ($C_{13}H_{16}F_3N_3O_4$) at large-scale over the time, is attributed for the rise of Fluoride level in soil and groundwater. Industries related to glass, aluminum, steel etc. emit particulate Fluoride like AlF_3, $NaAlF_6$, CaF_2. Fluorinated compounds present in the atmosphere occurs as organic compounds like fluorocarbons, perfluoro-compounds, trifluoroacetic acid or inorganic gases i.e., HF, SF_6, SiF_4, F_2, $H_2Si\ F_4$ and minerals, i.e., CaF_2, NaF, Na_2SiF_6, $NaAlF_4$ (Ozsvath, 2009; Shoeib *et al*., 2004).

Fluorosis

Fluorine is often called as two-edged sword. Prolonged ingestion of fluoride through drinking water in excess of the daily requirement is associated with dental and skeletal Fluorosis. Similarly, inadequate intake of fluoride in drinking water is associated with dental caries.

Table 1: Criteria for Dean's Fluorosis Index

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

Defluorination

The major techniques currently available for defluorination involves : coagulation and precipitation, membrane processes, electrochemical treatments, ion-exchange and its modification and adsorption onto various adsorbents. Among all these techniques, adsorption methods have more advantages because it is comparatively cheaper, easily approachable and highly effective in removing Fluoride from water to the maximum extent.

1.2 Study Area

Mehsana District

Mehsana district is situated in the northern part of Gujarat. The district is encompassed by 23.02 and 24.09 North Latitude & 71.21 and 75.52 East Longitude. It has common boundaries with five other district of Gujarat State. 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 as as groundwater bearing aquifers. Northern parts of the district consist of country rock as charnikites, calc-granites and calc-gneisses formations. Ground water occurs under confined and unconfined conditions. Therefore the sources of groundwater in the area are deep and tube wells are of 150 m to 400 m depth and 150 mm to 330 mm in diameter.

Rajkot District

Rajkot district is situated in saurashtra region of Gujarat. There are total eight districts in Saurashtra Region of Gujarat State. Among them, Rajkot district constituted from the Central Region of Saurashtra. . Rajkot is located at 70.20 to 71.40 East longitudes. 20.582 – 23.089 North latitude. 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 groundwater 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

Amreli district is situated in north east corner of Saurashtra peninsula in Gujarat between 20.45° to 22.25° latitude and 70.30° to 71.75° longitude. 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. Groundwater 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 from15 m. to 150 m. below ground level.

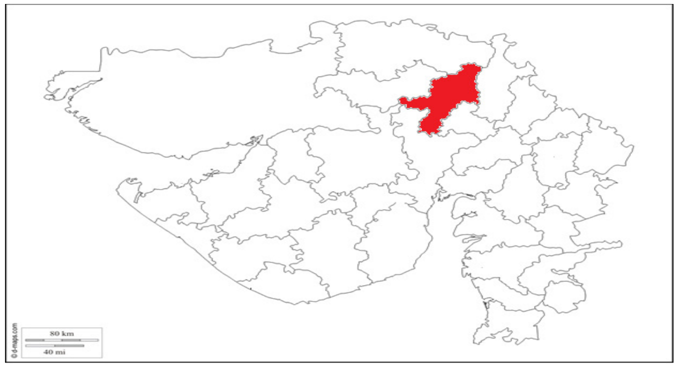

Figure 5 : The study area Satlasana

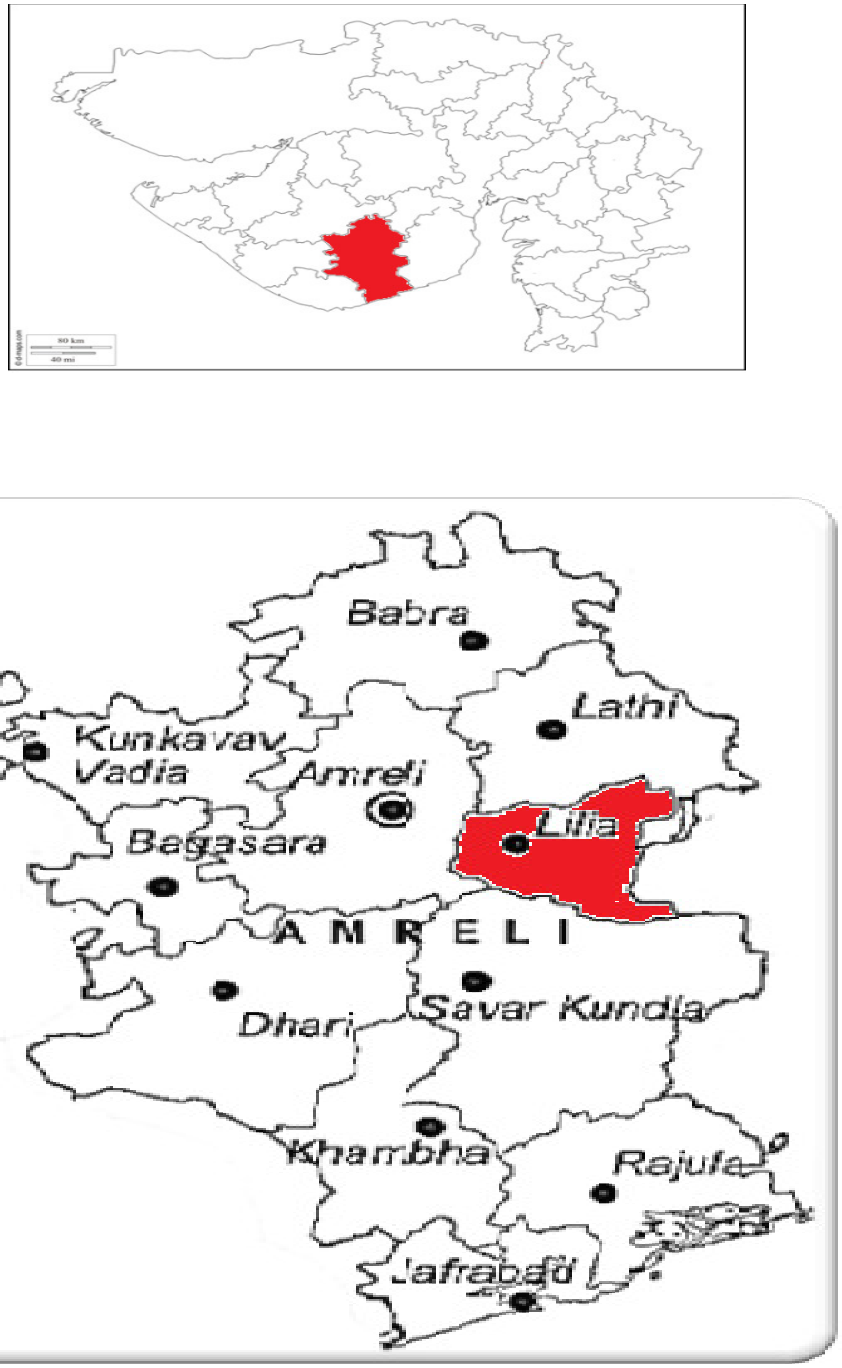

Figure 6 : The study area Lilia

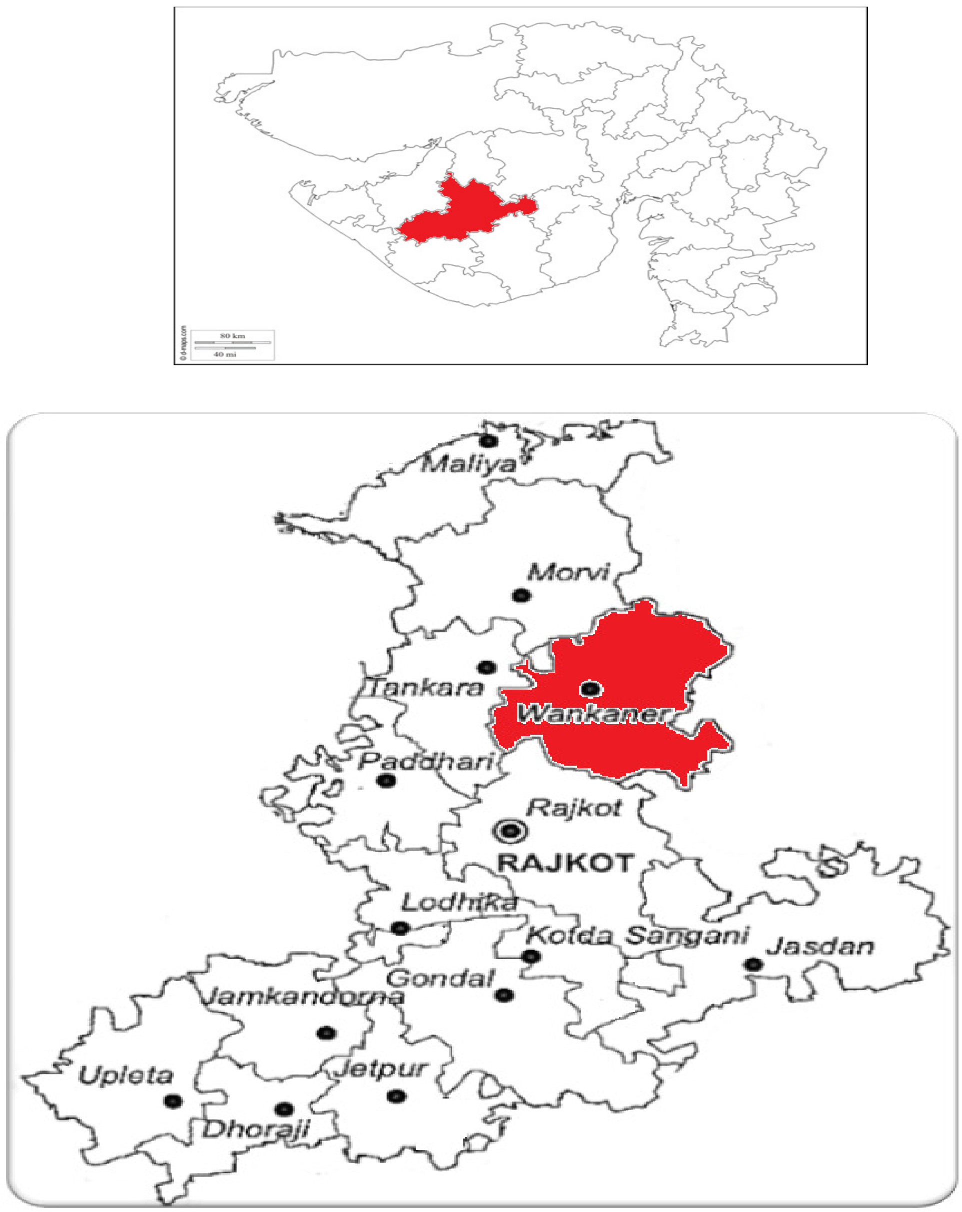

Figure 7 : The study area Wankaner

1.3 Objectives

1. Survey and Selection of wells/ tube wells/ bore wells having Flouride 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. EDX Study pertaining to localization of Fluoride in different Parts of test plants.