Chapter 2

LITERATURE REVIEW

2.1 GENERAL

Fluoride found in all natural waters at some concentration. Seawater typically contains about 1mg/L while rivers and lakes generally exhibit concentrations of less than 0.5 mg/L. In groundwater, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride bearing minerals. Concentrations in groundwater are limited by fluorite solubility, so that in the presence of 40 mg/L calcium it should be limited to 3.1mg/1 (Hem, 1989). In the absence of calcium in solution which allows higher concentrations to be stable (Edmunds and Smedley, 1996). High fluoride concentrations may therefore be expected in groundwater from calcium-poor aquifers and in areas where fluoride bearing minerals are common. Fluoride concentrations may also increase in groundwater in which cation exchange of sodium for calcium occurs (Edmunds and Smedley, 1996). Fluoride is an essential element for the human body. It is available in soils and water due to the weathering and erosion of fluoride bearing minerals. Fluoride rich groundwater has most often been reported from crystalline basement aquifers and from arid sedimentary basins (Edmunds and Smedley, 2005).

2.2 REMOTE SENSING AND GIS

Daniel and Karuppasamy (2012) evaluated the fluoride contamination in groundwater using GIS techniques in Virudhunagar District. The study find out the spatial distribution of fluoride in pre-monsoon and post-monsoon period using GIS. The fluoride concentration in groundwater varies from 0.2 mg/L to 1.6mg/L in pre-monsoon and 0.1mg/L to 1.9mg/L in post-monsoon. The overall distribution of fluoride concentration in the pre-monsoon and post-monsoon periods indicates slight dilution effect owing to fresh water recharge from precipitation.

Remote sensing and GIS based hydrogeological studies were carried out by in Panvel basin to generate groundwater potential and groundwater quality mapping Anbazhagan (2003).

Anbazhagan et al (2001) have carried out hydrological studies in Kinzig basin, Germany using ILWIS 2.1 GIS software. Water table depletion is the main issue in the basin. Aerial photographs and Landsat Thematic Mapper data were analyzed for interpreting the lineaments, land use / land cover and geomorphology. Hydrogeological data on water level, borehole lithology, specific yield, transmissivity, soil and their field capacity were generated for identification of artificial recharge favorable sites.

Remote sensing and GIS technique were adopted for groundwater development plan in drought prone areas in Tamil Nadu (Anbazhagan et al., 2006). The study had given an output of different groundwater potential zones. The aquifer type analysis provided good information for various developmental activities like groundwater development, type of agriculture practice and optimal aquifer management in the drought prone area.

Anbazhagan and Archana M. Nair (2003) have utilized GIS technique to pictorially represent groundwater quality zones in Panvel basin, Maharastra. Ghosh et al (2010) have reported that the groundwater quality of Nasipur and Noapara of Birbhum district of West Bengal and found to be highly polluted from excess fluoride contamination. The probable origin of such excess fluoride is due to volcanic eruption of basaltic composition.

Hydrogeochemical studies were carried out in hard rock aquifer system in parts of Hosur region, Tamil Nadu. The concentration of major cations and anions, TDS, hardness and fluoride were analyzed for drinking water and irrigation purposes and to integrate with the help of GIS (Anbazhagan et al, 2006). The results have shown that the TDS, hardness and fluoride are exceeding the desirable quality for drinking water and only 36% of study area to holding desirable groundwater quality and remaining area was undesirable. The high fluoride concentration (.>1.2ppm) in groundwater is observed at many locations. Singh et al (2010) assessed the quality of groundwater for each parameter and compared with the standard desirable limits prescribed by BIS standard.

Asadi et al (2007) studied to monitor the groundwater quality, relates it to the land use / land cover maps using remote sensing and GIS techniques for a part of Hyderabad metropolis. The concentration of fluoride was observed to be 3.15 mg/L at Yellareddyguda and the concentration above permissible limit was seen near Jubilee Hills, Sheikpet, Erragadda and Sanathnagar.

Avishek et al (2010) assessed of water quality with special reference to fluoride in Majhiaon block of Garwa district in Jharkhand. Results show that 402 samples have fluoride content above permissible limit. Fluoride present in almost 50% of water sources that were surveyed. It was also observed that more 50% samples collected from the schools had non-permissible limits of fluoride concentration. So, the remedial processes should be focused primarily for schools. Dental fluorosis is widely seen in the study area; however there are cases of skeletal fluorosis. The cases of skeletal fluorosis were mainly identified in families that are malnourished. It could be attributed to the lower intake of calcium-based products like milk. Cases of dental fluorosis have been observed in all age groups of population.

2.3 GROUNDWATER QUALITY ASSESSMENT

The quality of groundwater is important in evaluating its utility for agriculture, domestic public water supply and industrial purposes. To establish quality criteria, measures of chemical, physical and biological constituents must be specified, as well as standard methods for reporting results of water analysis. The chemical quality of groundwater depends on the environmental conditions in general and geological and pedological conditions encountered during the flow from the point of recharge to point of discharge.

Gowd (2005) assessed the groundwater quality for drinking and irrigation purposes in Peddavanka watershed, Anantapur District, Andhra Pradesh. Groundwater in this region is generally alkaline and shows marginal seasonal changes. The overall assessment has shown that the water quality was found to be useful for drinking and irrigation purposes, barring a few patches in the west and southwest.

Sharma et al (2003) have evaluated the groundwater quality with emphasis on fluoride concentration in Nalbari district, Assam, where groundwater is the main source of drinking water. Most of the groundwater samples have shown medium to high salinity and low sodium water, which can be used for irrigation almost in all types of soil with little problem of exchangeable sodium.

Chidambaram et al (2013) have studied the environmental hydrogeochemistry and genesis of fluoride in groundwaters of Dindigul district, Tamilnadu. The F- pollution in Dindigul groundwaters is mainly driven by two factors: (1) the geogenic weathering inputs, the geology of this area mainly comprises fluoride bearing minerals (e.g. hornblende biotite gneiss and charnockite); (2) the anthropogenic inputs (agri-fertilizers and tannery waste). Further, F- in the study area is mainly attributed to geogenic sources during pre and postmonsoons and anthropogenic sources in monsoon periods.

Ambade and Rao (2012) assessed the groundwater quality with a special emphasis on fluoride contamination in Rajnandgaon district of Chhattisgarh. Most of the places (about 23%) in the district are affected by high fluoride contamination with >1.5ppm concentration. It is also that the fluoride has poor and slightly positive correlations with calcium and sodium respectively.

Dey et al (2012) have studied the hydrogeochemical processes which control fluoride concentration in groundwater. A saturation index values evaluated for the groundwater of Boden block, Orissa indicated that it is oversaturated with respect to calcite, whereas the same is undersaturated with respect to fluoride content. The deficiency of calcium ion in the groundwater from calcite precipitation favors fluorite dissolution leading to excess of fluoride concentration. The risk index was calculated as a function of fluoride level in drinking water and mobility of fluorosis categorizes high risk for villages of in Boden block.

Singh et al (2002) have conducted hydrogeochemical study from samples of streams, springs, dug wells and tube wells of Upper Vindhyan aquifers of the Rewa region, Central India, indicates the study that groundwater from shallow aquifer zones are fresh and those from deep aquifer zones are slightly saline. It suggests that groundwater from shallow zones is suitable for drinking, livestock and selected industrial purposes. Although most of the water from deep zones from shale and limestone are not suitable for drinking and industrial purposes it can be profitably used after moderate treatments.

2.4 FLUORIDE IN GROUNDWATER

Fluoride is a global problem, which affects more than seventy million people in 25 countries. High fluoride concentration in groundwater have been reported from many parts of the world, particularly in arid and semi-arid areas of India, China, Sri Lanka, Spain, Mexico and many countries in Africa, western USA and south America (Edmunds and Smedley, 2005; Ayoob and Gupta, 2006). Fluorite (CaF_2) is the principal fluoride mineral, mostly present as an accessory mineral in granites. Dissolution of such minerals can constitute a major source of F in groundwater (Ramesham and Rajagopalan, 1985; Abu Rukah and Alsokhny, 2004; Edmunds and Smedley, 2005, Shaji et al., 2007).

The problem of excessive fluoride in groundwater in India was first reported in 1937 in the state of Andhra Pradesh (Short et al.1937). In India, about 6 million children suffer from fluorosis, because of consumption of water with high fluoride concentrations (Susheela 1999). Seventeen states in India have been identified as endemic for fluorosis, of which Tamil Nadu is one of the states. Groundwater is a major source of human intake of fluoride, including its subsequent incorporation into food items. Fluoride in groundwater evokes considerable interest due to its unique character as regards to its impact on physiological system of living beings. Due to excessive fluoride intake, enamel loses its luster. Dental fluorosis is characterized by discoloration in the form of spots or horizontal streaks on the tooth surface. Skeletal fluorosis occurs when fluoride deposits in the joint of neck, knee, and shoulder bones and makes it difficult to move or walk. Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fiber degeneration, low hemoglobin levels, excessive thirst, headache, skin rashes, nervousness, depression, etc., (Meenakshi, 2006). Mettur Taluk in Salem district is marked as one of the prevalent fluoride zones in Tamil Nadu, due to occurrence of diverse rock types which include higher fluoride-bearing minerals (RGNDWM, 1993).

Hoseinzadeh et al (2013) evaluated corrosion and scaling potential of water treated in Takab city, Western Iran, They calculated values of LSI index indicated slightly scale forming and corrosive, RI index showed heavy corrosion, AI index showed water is non-aggressive and based on PSI index results water is likely to dissolve scale.

Sreedevi et al (2006) have studied the temporal variations of fluoride concentration in a crystalline aquifer of Maheshwaram watershed in Andhra Pradesh. The fluoride concentration and pH values show inverse relationship during pre- and post-monsoon seasons. Fluoride content showed positive correlation with bicarbonate and negative correlation with calcium concentration. The analysis has shown that under saturation with respect to fluoride and almost super saturation with respect to calcite.

Kannan and Ramasubramanian (2011) have assessed the fluoride contamination in groundwater using GIS in Dharmapuri district. The study explore the possible relationship between fluoride and geological types and processes with respect to the suspected occurrence of endemic fluorosis.

High fluoride concentrations in groundwater also result from evapotranspiration which may trigger calcite precipitation and result in a reduction in the activity of 'Ca' (Jacks et al., 2005). Several studies have shown an increase in dissolved 'F' concentrations with increasing groundwater residence time (Apambire et al., 1997; Genxu and Guodong, 2001; Edmunds and Smedley, 2005). Relatively high 'F' concentrations have been found in some deeply circulating groundwaters along fault lines (Kim and Jeong, 2005, Kundu et al., 2001). The high contamination in groundwater in a granitic watershed located in Nalgonda district, about 70 km south of Hyderabad, India. Nalgonda district is one of the poorest and most drought-prone districts of Andhra Pradesh in southern India. The area has long been associated with high groundwater fluoride concentrations which have been reported up to 20mg/L (Rammohan Rao et al., 1993).

In Kenya, a detailed survey of fluoride in groundwater was undertaken. Overall 1,000 groundwater samples were taken nationally, 61% exceeded 1 mg/1, almost 20% exceeded 5 mg/1 and 12% exceeded 8 mg/1. The volcanic areas of the Nairobi, Rift Valley and Central Provinces had the highest concentrations, with maximum groundwater fluoride concentrations reaching 30–50 mg/1. Most of the sampled wells and boreholes were providing high fluoride in drinking water prevalence of dental fluorosis in the most affected areas (Manji and Kapila, 1986, Marleen Coetsiers et al, 2008).

In United Republic of Tanzania, about 30% of drinking water exceeds the 1.5mg/1 fluoride contamination (Latham and Gretch, 1967) and concentrations in the Rift Valley of up to 45mg/1.

High groundwater fluoride concentrations associated with igneous and metamorphic rocks such as granites and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa. In China, endemic fluorosis has been reported in more than 30 provinces, affecting 45 million populations (Ministry of Health PRC, 1997). Areas with endemic fluorosis in China have been divided into six types according to fluoride sources shallow groundwater with high fluoride >1.0 mg/L, deep groundwater with high fluoride, hot springs with high fluoride, abundant fluoride rock formations, high fluoride coal and high fluoride tea (Wang et al,2002). In these areas, enrichment of fluoride in groundwater occurs from fluoride rock formations as replenishment sources with relatively poor drainage and evaporation. In North China, aquifers have high fluoride groundwater in hornblende granite, granodiorites with hornblende with 'F' content 5-7%, muscovite, 2.1% 'F' and biotite 5.2% 'F' (Youg and Hua,1991). High fluoride groundwater in the fissured hard rocks, high HCO_3 concentration and alkaline condition favor dissolution of fluoride and ion exchange between OH in groundwater and exchangeable 'F' in some fluoride bearing minerals (Qinghai Guo et al, 2010). Li et al (2011) reports that high fluoride groundwater are strictly controlled by the host rock and geomorphic condition.

In Iran, fluoride concentration positively correlates with pH and HCO_3 indicated that alkaline, pH provides a suitable condition for leaching of fluoride from surrounding rocks. Fluoride in groundwater of Maku area, northwest of Iran, regional hydrogeochemical investigation indicates that rock water interaction is probably the main reason for their high concentration of ions in groundwater. The concentration of fluoride in groundwater is positively correlated with 'HCO_3' and 'Na' indicating that groundwater with high 'HCO_3' and 'Na' concentration help to dissolve some fluoride rich minerals (Maghaddam et al, 2008).

Gibbs (1970) elaborated the mechanism of controlling the world water chemistry. According to him atmospheric precipitation, rock water interaction and physical process such as evapotranspirtion are mainly control the concentration of ions in the groundwater. These mechanisms have been documented with examples from world river water chemistry and rainwater.

Varadarajan and Purandara (2008) observed high fluoride concentrations in Khanapur, Bailhongal and Saundi taluk, in Karnataka. The positive correlation of fluoride noticed with bicarbonates, alkalinity and pH during the pre monsoon, EC, TDS, carbonates, bicarbonates and potassium during the post monsoon Period.

Presence of dissolved fluoride in groundwater is possible only under favorable physicochemical conditions and with a sufficient residence time (Kullenberg and Sen, 1973; Handa, 1975). It has been observed that waters with relatively high pH have a tendency to displace fluoride ions from the mineral surface. It is evident that relatively high alkalinity has played an important role in the enrichment of fluoride in groundwater. The arid climate with low rainfall and high evapotranspiration and insignificant natural recharge cumulatively lead to salinization of groundwater and precipitation of calcite (Ramasesha et al. 2002). These conditions lower the activity of Ca and increase the Na/Ca ratios thus allowing fluoride to concentrate in the groundwater environment. Datta et al. (1999) have presented supporting evidence to explain a positive correlation between high evapotranspiration and F–concentration. Physiography, geology, hydrologyy, physico-chemical conditions and neo-tectonism seem to have significantly contributed to the fluoride accumulation in groundwater.

The fluorine content of near shore sediment is significantly lower than the off shore sediments. Fluorite, apatite, mica, illite and montmorillonite are the chiefly fluorine bearing minerals in sedimentary rocks. Wedepohl (1974) state that except for evaporates, fluorine is the most abundant halogen in the sedimentary rocks.

Handa (1977) states that there should be a positive correlation between ‘Ca’ and ‘F’ till the solubility product value for fluoride is reached and thereafter these ions should show a negative correlations. Further mentioned that a comparison of ions activity product for Ca^{+} and F^{-} with the solubility product of fluoride shows that groundwater is generally undersaturated in humid regions whereas in arid and semi-arid regions of India, ion activity product for Ca^{+} and F^{-} ions exceeds the solubility product value resulting in the supersaturation of groundwater with fluoride. The solubility product of CaF_2 is affected by the formation of ionic complexes in water (Srivastava et al, 1995). The solubility of fluorapatite (Ca_5F (PO_4) and fluorite (CaF_2) in natural water is very low (Handa 1977 and Appelo and Postma, 1993). In natural waters due to ionic strength of complex forming ions, the solubility in natural waters may cause CaF_2 precipitation (Handa, 1977, Perelman, 1977 and Deshmukh et al., 1995).

Under supergene environment, fluoride in natural waters gets precipitated as CaF_2, across calcium barrier (Perelman, 1977). Therefore, the distribution of Ca^+ and F^- in groundwater is antipathic (Handa, 1977; Deshmukh et al, 1995). Rajasooriyar et al (2003) have reported that fluoride in groundwater was found to be predominantly from a geological source mainly fluoride bearing silicate minerals such as biotite and hornblende. Specific hydrogeological conditions, mainly rock-water interaction, groundwater recharge and discharge patterns were found to determine the vulnerability of groundwater to fluoride. The groundwater vulnerability is higher in areas where there is limited recharge that promotes longer residence times and greater rock – water interaction. Mixing of waters from interconnected fractures may be one of the major factors controlling the higher concentration of fluoride.

Sajidu et al, (2007) have suggested that the main potential source of the fluoride groundwater pollution could be the gological setup of the aquifers. Fluoride solubility in groundwater is strongly influenced by the pH. At pH range of 6.0-6.5, fluoride solubility is low (Vieroet al., 2009). Fluoride occurs in almost all natural waters from trace concentrations to as high as 5,000 mg/L in mine water (Kraynovet al., 1969). The principal controls on fluoride concentration in natural water are the climate, host rock composition and the hydrogeology. The mount of fluoride from fluorite dissolution in waters of low ionic strength is about 8-10mg/L (Boyle, 1992; Apambireet al., 1997; Valenzuela-Vasquez et al. 2006). The concentrations of Ca_2^+, Na^+ and OH^- as well as certain ionic complexes such as Fe_3^+, Al_3^+, B_3^+, Si_4^+, Mg_2^+, and H^+ may modify fluoride concentrations (Valenzuela-Vasquez et al. 2006).

Many investigations highlighted the origin and hydrogeochemistry of high fluoride in groundwater from different parts of the world (Moghaddam and Fijani, 2008; Tirumalesh et al.2007; Sreedevi et al. 2006; Nanyaro et al. 1984; Kundu and Mandal, 2008; Farooqi et al.2007; Jacks et al.1993; Kumar and Syed, 1989; Srinivasamoorthy et al. 2007; Babulal et al.2003; Rao et al. 1996; Carrillo-Rivera et al. 2002; Abu Rukaha and Alsokhny, 2004; Karro etal.2006; Gizaw, 1996; Ozsvath, 2006 and Guo et al. 2007). In all these researches, groundwater samples were collected either from dug wells or bore wells and examined for fluoride concentration. The high fluoride content in groundwater originated from water rock interaction and anthropogenic sources like application of fertilizers, industrial effluents and household domestic effluents.

2.4.1 Fluoride in Indian Aquifers

Fluorosis remains a challenging and extensively studied national health problem in India, 13 out of India's 32 states and territories were reported to have high concentrations of fluoride in water (Mangla, 1991). This had risen to 17 during 1999 (UNICEF, 1999). The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh (Kumaran, et al., 1971; Teotia et al., 1984). About 65% to 85% populations in these states drink groundwater with fluoride content upto 16ppm. The highest concentration of 48 mg/L is noticed in Rewari district of Haryana (UNICEF, 1999). The high fluoride concentrations in groundwater are a result of dissolution of fluoride, apatite and topaz from the local bedrock. Handa (1975) noted the general negative correlation between fluoride and calcium concentrations in Indian groundwater.

Fluorosis in India is much more severe than arsenic poisoning in West Bengal. According to recent statistics, the number of people subjected to arsenic poisoning in India is 38 million and confined to West Bengal. About 150000 villages in India are endemic for fluorosis. Rajasthan, Gujarat and Andhra Pradesh are highly endemic fluorosis states in India, where 65% of population depends on groundwater with fluoride concentrations varying from 0.4 to >20ppm. Limestones, shale sandstones which form the sedimentary aquifers contain 200 to 940ppm of fluorine. The crystalline rocks of Rajasthan host a variety of fluorine bearing minerals and tourmaline bearing pegmatites are found extensively in Rajasthan.There is a severe fluoride problem in Nawa Tehsil of Nagaur district. Villagers are suffering from dental fluorosis and skeletal fluorosis. The maximum fluoride concentration is 14.62 mg/L. 86.92% had fluoride beyond permissable limit in this area (Radha Gautam et al, 2011).

Hydrogeochemical facies of the groundwater samples suggest that rock weathering and evaporation–crystallization control the groundwater composition in the study area. The saturation index values indicated that the groundwater in the study area is oversaturated with respect to calcite and under-saturated with respect to fluoride. The deficiency of calcium ion concentration in the groundwater from calcite precipitation favors fluorite dissolution leading to excess fluoride concentration. Kamineni and Bonardi (1982) pointed out the coexisting biotite and apatite in a granulitic charnockite from Eastern Ghats contains large amounts of chlorine and fluorine. Madhnure et al (2007) emphasized that aridity climate is one of the primary reasons for the origin of high ‘F’ in groundwater. Mica group of minerals like muscovite and biotite also contribute to groundwater fluoride content (Premsingh et al, 2010).

High degree of weathering, easy accessibility of circulating water to the weathered rocks due to intensive and long-term irrigation are responsible for the leaching of fluoride from their parent minerals in soils and rocks. Further concentration increased due to semi-arid climate of the region and long residence time of groundwater in the aquifer (Wodeyar and Sreenivasan, 1996).

Igneous suite of rocks contains fluorite, hornblende and biotite, which are the main source of fluoride (Ramamohan et al., 1993). Rao et al. (1993) concluded that the two main factors governing fluoride in groundwater from the Nalgonda District are the presence of acid-soluble ‘F’ minerals and low concentrations of ‘Ca’ and ‘Mg’ in rocks and soils, with high concentrations of HCO_3 in circulating groundwater.

2.4.2 Fluoride concentration in groundwater of Tamil Nadu

In Tamil Nadu, the high concentration of fluoride is found in Dharmapuri and Salem district closely followed by Coimbatore, Madurai, Trichy, Dindukal and Chidambaram districts. Fluoride concentrations are low in Tirunelvali, Ramanad, Pudukottai, Tindivanam and Vellore districts. Dharmapuri district has a high concentration of endemic fluoride as ranks the highest in the state. According to a recent survey conducted by Tamil Nadu Water supply and Drainage board (TWAD), out of 10451 water sample from hand pumps sources, 3161 were found high fluoride contamination and around 30% of the water in Dharmapuri and Krishnagiri districts are found contaminated when compared with the state average of 6.9%. Inadequate consecration of rainfall and excessive depletion of groundwater has lead to the high concentration of fluoride in the districts.

The hydrogeochemical study of groundwater in parts of Palar river basin show the abundance of certain chemical parameters responsible for the dissolution activity of fluoride (Dar et al, 2011). Alagumuthu and Rajan (2008) states that fluoride concentration ranges from 0.1-7.6ppm in Kadayam block of Tirunelveli district. Presence of large quantities of calcite indicates that the large input of HCO_3 due to prevailing weathering conditions, besides these rocks, granite powder resulting from the granitic industries are contributing high fluoride levels in groundwater system. High fluoride concentration in groundwater is identified in Palacode region of Dharmapuri district in Tamil Nadu, where it is the only source of drinking water. The fluoride concentration in this region varied from 1.4 to 2.4 mg/L, causing dental fluorosis and teeth molting among people in general and children in particular. The geology and over extraction of groundwater sources increases the level of fluoride in groundwater (Ramesh et al, 2012).

TWAD Board (2012) reports show that Nallampalli block in Dharmapuri district has high level of fluoride concentrations in groundwater. The analytical data of the water samples of the study area show that the fluoride concentration ranges from 1.0 mg/L to 8.0mg/L in groundwater. The highest fluoride concentration in groundwater noticed at Kombai and Palayampudur villages about 8.0 mg/L.

2.5 ROCK WATER INTERACTION

Young and Ishiga (2000) reports that the basement rocks including hornblende biotite gneiss, biotite gneiss and granitic gneiss seem to have contributed to the anomalous concentrations of fluoride in the groundwater. Longer residence time of aquifers within fractured crystalline bed rocks may enhance fluoride concentrations in the groundwater.

For example, in Central Norway the highest fluoride content was found in wells drilled in gneisses followed by rocks of unusual lithology and thirdly in rocks of amphibolites groups (Saether et al,1995). In Sri Lanka, Dissanayake (1991) found concentrations of 'F' upto 10mg/L in groundwater in the dry zone, associated with dental and possible skeletal fluorosis. In the west zone, the intensive rainfall and long-term leaching of fluoride and other minerals from the crystalline bedrock are probably responsible for the much lower concentrations.

The fluoride concentrations in groundwater are a result of dissolution of fluorite, apatite and topaz from the local bedrock. Fluoride-rich groundwater has most often been reported from crystalline basement aquifers and from arid sedimentary basins (Edmunds and Smedley, 2005). Dissolution rates of fluoride bearing minerals are generally slow (Gaus et al.2002), and hence, fluoride concentrations in water do not depend only on the solubility. Residence time in aquifers may also have an important influence on dissolved fluoride levels (Kim and Jeong, 2005; Saxena and Ahmed, 2003). The adsorption of fluoride in soils decreases from humid areas through to arid areas and from acidic soils to alkaline soils (Wang et al.2002). The adsorption-leaching process directly affects fluoride migration and exchange from soil to water. The action of evaporation and concentration is strengthened under arid climatic conditions, and thus, mutual action and exchange absorption reactions among ions are also strengthened. Fractured crystalline bed rock structures appear to correlate closely with the fluoride distribution in aquifers (Jacks et al. 2005; Rukah and Alsokhny, 2004; Rao, 2003). Felsic rocks contain significantly greater fluoride concentrations than mafic and meta sedimentary rocks. Granitic rocks and syenites release high concentrations of fluoride into groundwater (Ozsvath, 2006). Unstable minerals such as sepiolite and palygorskite may have a dominant control on fluoride distribution in groundwater (Wang et al.2002; Jacks et al. 2005). However, the dissolution of fluorspar, fluorapatite, amphiboles (e.g., hornblende and tremolite) and some mica also contributes fluoride to groundwater (Datta et al.1996).

Robinson (1946) had explained a detailed account of the fluoride content in soils where muscovite, biotite and hornblende are the common minerals contributing high fluoride to the soils. Fluorosis content of soils varies from 20ppm in fine sand to 7070ppm in murry silt loam. During weathering the fluorine in apatite is stable while in mica it is leached out rapidly (Robinson, 1946).

Carpenter (1969) suggested that fluorine in sedimentary rocks is due to the presence of fluorine bearing minerals like fluorite and apatite. The major exposure of the peninsular gneiss, charnockites and calc gneiss which have been marked for widespread fluoride-bearing minerals indicating their accessibility to water by weathering along with leaching process. Mica content is significantly noted in peninsular gneiss and apatite is noted in charnockites which are the sources of fluoride into the groundwater (Srinivasamoorthy et al. 2008).

Ramanaiah et al (2006) reported that the main source of fluoride in groundwater is the fluoride bearing rocks such as fluorspar, crysolite, fluorapatite and hydroxylapatite. The Central Groundwater Board, has indicated that the source of fluoride may be from weathered and fractured granite and pegmatite. The granitic rocks which contain fluoride bearing minerals release fluoride into groundwater.

Shekhar et al (2009) and Shaji et al (2007) explained that apatite and fluorite besides replacement of hydroxyl by fluoride ions in mica, hornblende and soil that mostly consist of clay minerals are major sources of fluoride in circulating water. The weathering activity characterized by alternate wet and dry conditions of the semi-arid climate is responsible for leaching of fluoride from the minerals present in the soils and rocks. It also reports that the intensive and long term irrigation is probably another factor that causes weathering and leaching fluoride. Raju et al, (1979) have reported that high concentration of fluoride (about 5.0mg/L) in groundwater present in the amphibole formation of the Anantapur district of Andhra Pradesh. Sodium carbonate waters are more effective in releasing fluoride from fluorite minerals, high concentrations of fluoride were observed in these waters (Srinivasarao, 1997).

Sumalatha et al, (1999) indicated the abnormal level of fluoride is common in fractured hard rock aquifer with pegmatite vein. The veins are composed of minerals like topaz, fluoroapatite, villuamite, and cryolite. Fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations.

Janardhanaraju et al, (2009) reported that fluoride concentration was found with granitic gneissic complexes than the other rock formation. The highest fluoride concentration corroborated with low calcium values and high sodium content in the groundwater. Weathering and leaching of fluorine in rock formations under alkaline environment lead to the enrichment of fluoride in the groundwater. Decomposition, dissociation and dissolution are the main chemical processes for the occurrence of fluoride in groundwater (Saxena and Ahmed, 2003).

Fluorspar occurs in structurally weak planes like shear fractures, joints and host rock–vein quartz interface. Chemical weathering (hydrolysis) of minerals results in formation of Ca^- and Mg^- carbonates which are serve as good sinks for fluoride ions (Jacks et al.1980). However, it is the leachable state of fluoride ions that determines the water fluoride levels which is mainly governed by pH of the draining solutions and dissolved carbon dioxide in the soil.

The high 'F' concentration may be attributed to the presence of either fluorine bearing minerals (or) due to leaching of F^- from weathered material like soil alluvium in Kadapa district. It is found that the fluoride concentration in groundwater increases along the groundwater flow direction and also increases with depth. Fluoride contamination is mainly a natural process leaching of fluorine bearing minerals (Sunitha etal, 2012). Subba Rao (2003) found a difference in fluoride concentration in pre and post monsoon water in India. High fluoride content in groundwater can be attributed to the continuous rock water interaction during the processes of percolation with fluorite bearing country rocks under arid, low precipitation and high evapotranspiration conditions (Reddy et al, 2010).

Sharma (2009) reported that during weathering and circulation of water in rocks and soils, fluoride is leached out and dissolved in groundwater. The high fluoride values in the waters may be due to leaching of fluoride from the hornblende gneiss and granulite (Mukhopadhayay, 1996). Presence of fluoride bearing minerals in the host rocks and their interaction with water is considered to be the main cause for fluoride in groundwater. Chemical weathering in arid and semi-arid condition with relatively high alkalinity favors high concentration of fluoride in groundwater (Dar et al, 2011).

The rock interaction with groundwater containing high concentration of HCO_3^- and Na^+ at a higher pH value of the medium could be one of the important reasons for the release of F^- from the aquatic matrix into groundwater (Dey et al, 2011).

Jacks et al (2005) reported that in Coimbatore district, Tamil Nadu, dark coloured minerals in rocks contain 180-2600 mg/L ‘F’ and the relative stability of fluoroapatite during the weathering process indicate that the main sources of fluoride in groundwater is from mica, hornblende and pyroxene. Srinivasamoorthy et al (2009) observed that high fluoride concentration in Salem district during pre monsoon is due to weathering and leaching of fluoride bearing minerals like apatite, biotite, muscovite, lepidote and hornblende. The correlation analysis shows that sulphate and fluoride, nitrate and fluoride, conductivity and chloride are having high correlation (Karunakaran et al, 2009).

Viswanathan et al (2009) repoted in Nilakkattai block of Dindukal district about 3.8% drinking water contain more than 3 mg/L of fluoride, around 74% of water have more than 1.5mg/L of fluoride and 21% of the water contain fluoride between 0.5 and1.5 mg/L.