Introduction
Water is one of the most basic of all needs - we cannot live for more than a few days without it. And yet, most people take water for granted. We waste water needlessly and don't realize that clean water is a very limited resource. More than 1 billion people.

- Robert Alan

Pure water is the world's first and foremost medicine.

- Slovakian Proverb

Water is critical for sustainable development, including environmental integrity and the alleviation of poverty and hunger, and is indispensable for human health and well-being.

- United Nations

Water is the one of the most precious resource in the earth. Today water pollution is heard from all corners of the world. Water pollution has become a distinct threat to the very existences of mankind on this earth. The unique physical and chemical properties of water have allowed life to evolve in it. Water is a colourless, tasteless and odourless liquid in its pure form, it’s a universal solvent as it dissolves nearly all natural compounds and it also transports the minerals and nutrients necessary for growth of plants. An essential natural resource for sustaining life and environment. Water is unfortunately deteriorating its fine quality due to it’s over exploitation so over the last few decades. Though we all know water is a life giving natural resources that sustains environment and through to be available in abundance, but we are helpless in maintaining it quantity. It essential parameter to be studied and its majorly taught around the world. The overall focus is sustainable development keeping mankind at focus point. Element that affect water quality are fluoride and other chemical composition of water. Chemical composition of Fresh water occurs as surface water and ground water. It is one of the prime factor on which the sustainability of water for any purpose like-domestic, industrial or agriculture depends. Ground water is the major source of drinking water in rural as well as in urban areas and over 94% of the drinking water demand is met by ground water. About the other chemical parameter fluoride influences quality of ground...
water mostly, it is necessary to know that excess intake of fluoride through drinking water causes fluorosis on human beings in many states of India. Ground water contributes only 0.6% of total water resources on earth. In rural and urban areas of India, it is major preferred source of drinking water flashing light on records, in India it is a major inorganic pollutants which naturally originates in ground water. An essential aspect of hydro geochemistry is fluoride concentration due to its impact on human health. Fluoride is the most electronegative chemical element and because of its high reactivity, never found naturally in elements form. Combined chemically in the form of fluorides, it ranks 7th in abundance of elements representing about 0.06-0.09% of the earth’s crust (WHO, 1994). Fluoride frequently occurs in igneous as well as in metamorphic rocks, especially ssdalkali rocks, granite, basalt, shale, clays and calcium phosphate rocks are the main source of fluoride. It is really shocking to know that Due to higher fluoride level in drinking water several case of dental and skeletal fluorosis have appeared at alarming rate in this region. Fluoride is essential for human body, imported for normal mineralization of bones and formation of dental enamel with presence in small quantity (Chouhan and Flora, 2010). But excess fluoride concentration in drinking water has deleterious effects and causes fluorosis, a dreadful disease. fluoride more than permissible limit i.e. 1.5mg/l (WHO 1994) become toxic and cause clinical and metabolic disturbance in animals and human being such as dental, skeletal and non-skeletal fluorosis (Hussain et al., 2012 and Singh et al., 2007).

Sources of Fluoride Occurrence in Environmental

Among the elements, Fluorine ranks 24th in universal abundance and 13th in terrestrial abundance in the Earth's crust. It rarely occurs as the element but normally is found as the fluoride ion or as a number of inorganic and organic fluorides. It occurs in varying concentrations in rocks, soil, water, air, plants and animals both naturally and as a consequence of human activity such as agricultural or industrial processes. Human exposure may be through any or all of these sources. This review is restricted to consideration of human exposure to fluoride through diet and the gastrointestinal tract (GIT), although exposure may also occur through inhalation of aerosols or dust particulates (e.g. cryolite, Na₃AlF₆) in the workplace or through volatile anesthetics (eg. Halothane, CH₃CHBrCl) used in certain types of surgery.
Geochemistry and Fluoride Distribution in Water

Water is an essential natural resource for sustaining life and is among nature’s most valuable gifts. Once viewed as an infinite and bountiful resource, today, water often defines the limits of human, social, and economic development for a region. The main source of freshwater for sustaining life on earth is groundwater. Unfortunately, groundwater is either being increasingly depleted for irrigation of crops, industrial, or other uses, or is becoming contaminated by various pollutants. The presence of fluoride as a contaminant of groundwater has become a worldwide problem, because it is commonly found in groundwater sources. The problem of high fluoride content in groundwater resources is important, because of both toxicological and geo-environmental concerns. The chief source of fluoride in groundwater is fluoride-bearing minerals that exist in rocks and soils. The weathering and aqueous leaching processes that occur in soils play an important role in determining the amounts of fluoride that reaches groundwater.

The various factors that govern the release of fluoride into water from fluoride-bearing minerals are (i) the chemical composition of the water, (ii) the presence and accessibility of fluoride minerals to water, and (iii) the contact time between the source mineral and water (Keller, 1979). Overall water quality (e.g., pH, hardness, and ionic strength) also plays an important role by influencing mineral solubility, complexation and sorption/exchange reactions (Apambire at el., 1997)

\[
\text{CaF}_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + 2\text{Na}^+ + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2
\]

The above equation clearly shows the processes that could control negative (between fluoride and calcium) and positive relationships (between fluoride and Bicarbonate) when both are in contact with each other. Water samples in which Fluoride levels exceed 5 mg/l are oversaturated with regard to fluorite. Once fluorite reaches equilibrium, calcite is removed by precipitation, which allows the fluoride concentration to increase (Kim and Jeong, 2005).

In groundwater, the natural concentration of fluoride depends on the geologic, chemical, and physical characteristics of the aquifers, porosity and the acidity of the soils and rocks, the temperature, the action of other chemical elements,
and the depth of the wells. In natural water, the fluoride forms strong complexes with Al, and therefore, fluorine chemistry is largely regulated by Al concentration and pH level. Below pH 5, fluoride is almost entirely complexes with Al, predominantly with the AlF$_2^+$ complex, and consequently the concentration of free fluoride is reduced to low levels. As the pH increases, the Al–OH complexes dominate over the Al–F complexes, and the free fluoride level increases. Fluoride occurs at some level in almost all groundwater, but the concentration found in most potable waters is less than 1 mg/L (Hem, 1985).

It has been postulated that fluoride-bearing minerals are normally only sparingly water soluble, with the exception of villiaumite, and these minerals release fluoride to water slowly. The rate of fluorite dissolution may be faster in sodium bicarbonate-containing waters, and the release of fluoride from clay minerals depends strongly on the pH level. The maximum concentration of fluoride in groundwater is usually controlled by the solubility of fluorite (Saxena and Ahmed, 2003). Once the solubility limit for fluorite (CaF$_2$) is reached; an inverse relationship will exist between fluoride and calcium concentrations. Earlier studies have revealed that there is a close association between high fluoride content and soft, alkaline (i.e., sodium bicarbonate) groundwater that is depleted of calcium (Chae at el., 2007). Igneous rocks that have been formed from highly evolved magmas are a rich source of fluorine bearing minerals. The plagioclase composition of igneous rocks is typically high in albite, the sodium-rich end-member (Hyandman, 1985). As a result, the groundwater in contact with these rocks is often soft and calcium deficient, which allows for higher fluoride concentrations when equilibrium with fluorite is attained (Ozsvath, 2006).

**Fluoride Distribution in Soil**

Whereas the fluorine content of most rocks ranges from 100 to 1,300 mg/kg soil concentrations typically vary between 20 and 500 mg/kg. However, much higher concentrations (1,000 g/kg) can occur in soils that are derived from rocks with high fluorine contents or in soils affected by anthropogenic inputs, such as phosphate fertilizers (Kabata Pendias and Pendias, 2001). Most of the fluorine found in soils occurs within minerals or is adsorbed to clays and oxy-hydroxides, with only
a few percent or less dissolved in the soil solution. Fluoride mobility in soil is highly dependent on the soil’s sorption capacity, which varies with pH, the types of sorbents present, and soil salinity (Cronin et al., 2000).

Although aluminum smelters, and therefore fluoride emissions, exist in the temperate regions, there is a lack of studies dealing with the effects of addition of fluoride on the chemistry of temperate soils. Moreover the published studies refer to forest soils, whereas the behavior of managed soils under this circumstance has not been investigated. However, in highly F-polluted soil, as the soil becomes more acidic or alkaline, the risk of zootoxic concentrations of F in shoots of plants would increase (Stevens et al., 2000). The San Ciprian Aluminium Smelter-Alumina Refinery Complex, located on the north coast of Galicia, NW Spain, since 1978, emits fluoride to the atmosphere, resulting in increased concentrations of fluorine in soils and vegetation in the immediate surroundings (Gago et al., 2001). Stated that the soils in the vicinity of the smelter have a high fluoride sorption capacity. The fluoride sorption may bring about changes in the soil composition. Understanding those changes is relevant for the management of the soils close to the smelter (Romar et al., 2002).

Fluoride Contamination in Worldwide

Fluoride is one of the most widespread groundwater pollutant. The concern is not limited to India but Over all 200 million people worldwide rely on water source contaminated with high fluoride. The probability of occurrence of high fluoride concentration in ground and surface water was detected in varies countries include India, China, Argentina, Mexico and in several African countries and Pakistan, Italy, Iran, Bangladesh, Newzeland, Ethiopia, UK were fluoride contaminated countries. The dental fluorosis and skeletal fluorosis are endemic in number of countries, they are U.S.A, Morocco, Algeria, Libya, Egypt, Jorden, Turkey, Franfraaq, kenya, Tanzania, South Africa, Australia, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Srilanka, Syria. The above said countries are most prominent fluorosis countries in worldwide (Amini et al., 2008). Fluorosis along with other disease produced by intake of fluoride rich water is a major health concern along the globe.
Introduction

Fluoride Contamination in India

In India, high fluoride in groundwater has been reported from many parts, fluorosis is known to occur for the past six decades and ranked highest among the major environmental health problems, particularly its impact on human health. The study shows that in India, 65 million peoples at risk in dental fluorosis and skeletal fluorosis. Many states in India are endemic fluorosis, Andhra Pradesh, Tamilnadu, Karnataka, Gujarat, Rajasthan, Punjab, Haryana, Bihar and Kerala (Susheela, 1999). These states are contributing dental fluorosis, which drinks above 1.5 mg/l of fluoride of drinking water. In Tamilnadu, Salem, Erode, Dharmapuri, Coimbatore, Thiruchirapalli, Vellore, Madurai, Viruthunagar and Krishnagiri are having fluoride contamination. According to WHO the permissible limit of fluoride concentration in drinking water is 1.5 mg/l. In India, most of the populations dependent on groundwater source for drinking water supply (Phansalkar at el., 2005).

Fluoride Contamination in Rajasthan

In Rajasthan, all the 33 districts are affected by high fluoride. Geological distribution of rocks here reveals that fluoride ores occupy large area of eastern and south east part, in constricted synclinal bands in the central region of Aravali Synchronium. Rajasthan is a rich source of mica and around those mines ground water is rich in fluorides (Chandra et al., 1983) Rajasthan have been declared as fluorosis prone area. Here fluorosis problem can be visualized at various intensity levels i.e. Dental fluorosis, skeletal fluorosis and non-skeletal fluorosis ect. It is quite common to have high fluoride in ground water at Tonk district, part of eastern Rajasthan (Yadav et al., 2009). Besides this polluting the sources of drinking water is frequent due to domestic water, earthen septic tanks, urban and rural garbage, agriculture discharges, soluble effluents, industrial effluents, seepage pits etc. As water has dissolved salts along with suspend bal particles and microorganisms it is not fit for drinking.

In Rajasthan many parts were contaminated by excess fluoride contamination in drinking water. The following areas are having high Fluoride contamination in drinking water, Fluoride range between 4.78 to 1.01 mg/L. Some parts of Rajasthan risk in endemic fluorosis, where as above 1.5 ppm of fluoride concentration in
Introduction

drinking water (Surindra at el., 2008). A study on distribution and health hazards by fluoride contaminate in groundwater was performed in bhilwara district were fluoride concentration varies from 0.2 to 13.0 mg/L (Hussain at el., 2010). Fluoride distribution was observed in groundwater and survey of dental fluorosis in villages of Didwana Tehsil of Nagaur district ranges from 1.1 to 8.5 mg/L (Hussain at el., 2011). The Ground water quality assessment of Nawa Tehsil area ground water having high fluoride contamination between 14.62 to 24ppm (Gautam and Bhardwaj, 2010).

SOURCES OF FLUORIDE

Sources of Fluoride in Environment:

Usually the ground water is contaminated with high fluoride where as surface water is not contaminated with high fluoride because the usual sources of fluoride is fluoride rich rocks. When water percolates through rocks it leaches out fluoride from these rocks. The rocks rich in fluoride are:

Table 1:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sellaite (MgF₂)</td>
<td>61%</td>
</tr>
<tr>
<td>Villianmite (NaF)</td>
<td>55%</td>
</tr>
<tr>
<td>Fluorite Fluorspar(Fluorspar)(CaF₂)</td>
<td>49%</td>
</tr>
<tr>
<td>Cryolite (Na₃AlF₆)</td>
<td>45%</td>
</tr>
<tr>
<td>Bastnaesite (Ce.La) (CO₃)F</td>
<td>9%</td>
</tr>
<tr>
<td>FluorapatiteCa₃(PO₄)₃F</td>
<td>3-4%</td>
</tr>
</tbody>
</table>

The geological survey of India has brought out considerable data which reveal that fluorite, Topaz, apatite, rocks phosphate, Phosphatic nodules and Phosphorites widespread in India and contain high Percentage of fluoride.

Sources of fluoride for human Exposure

1. **Drinking water:** Sixty percent of the total fluoride intake is through water as it is one of the most accessible source of Fluoride. In areas of the world in
which endemic fluorosis of teeth and skeleton is well-documented, levels of fluoride in drinking water sources ranges from 3 to more than 40mg/litre.

2. **Foods and beverages**: Food can make a significant contribution to the total fluoride intake as agricultural crops are heavily contaminated with fluoride as they are grown in the areas where the earth’s crust is loaded with fluoride bearing rocks. Fluoride content is highly variable in agriculture crop and other plants species which are mainly depends upon fluoride level in soil, atmosphere, use of fertilizer, pesticides and other sources of contamination. Beverages like tea, coffee, carbonated beverages, beers and juices are the chief sources of dietary fluoride. Among beverages tea has an exceptionally high fluoride content which varies in different brands from 122-260ppm or more. Each cup of tea may supply 0.3-0.5mg of fluoride. Bottled beverages which are increasingly being consumed around the world.

3. **Air**: In air Fluorides are emitted both gaseous and particulate forms. Particulate fluorides in the air around aluminium smelters vary in diameter from 0.1 µm to around 10 µm (Less,1975). Penetration of fluoride into the lungs is possible, with resulting health effects.

4. **Medicines**: In medicines such as anesthetics, antibiotics, anticancer and anti-inflammatory agents are used as Fluoride-Containing drugs. The replacement of a hydrogen atom and or hydroxyl group by a fluorine atom are common strategies in drug development (Alkorta *et al.*, 2000). In aluminium manufacturing industries, level of fluoride in the serum, urine and hair were high in workers who were suffering from osteoarthritis. Observation of industrial fluorosis led to the use of fluoride in medicine as a treatment to increase bone mass in osteoporosis patients (Franke, 1997).

5. **Tooth-Pastes and Mouth-Wash**: The positively significant association was found between tooth-pastes and fluoride ingestion. Dentifrice products for adults that is commercially available in many countries which generally contain fluoride at concentrations ranging from 1000 to 1500 µg/g.

6. **Industrial exposure**: Various types of industries involved in the manufacturing of phosphate fertilizers, aluminium extraction, fluorinated
hydrocarbons (refrigerants, aerosol propellants etc.), petroleum refining and hydrogen fluoride manufacturing units are mainly responsible for airborne fluoride. Fluoride dust and fumes pollutes the environments, inhaling dust and fumes is as dangerous as consuming fluoride containing food, water or drugs. Not only the industrial workers are affected but the people living in the vicinity of such industries may also get affected.

**Health Effect of Fluoride in Human Beings**

Fluorosis as an occupational disease in human beings was identified in 1930 and subsequently, occurrence of skeletal fluorosis in cryolite miners was reported in 1932 (Moller and Gudjonssson, 1932). In India, fluorosis was first detected by short et al. in 1937 in Andra Pradesh. In Rajasthan, the first case of skeletal fluorosis was reported from Jobner near Jaipur city (Kasliwal and Soloman, 1959).

Fluoride consumption is a double-edged sword regarded as often. When ingestion of fluoride in inadequate quantities (less than 0.5ppm), Fluoride causes health problems (e.g., dental caries, lack of formation of dental enamel, and deficiency of mineralization of bones), especially among children (WHO, 1996). In contrast, if fluoride is consumed or used in excess (more than 1.0 ppm), it can cause health problems in the young and old. The various forms of fluorosis that may arise from excessive intake of fluoride through drinking water. If fluoride is consumed in more than 4.0 ppm, it can promote the dental fluorosis in children. If fluoride is consumed in more than 10.0 ppm, it can promote dental fluorosis, skeletal fluorosis and crippling skeletal fluorosis, possibly cancer (Dissanayake, 1991). Fluorosis can be affected by a number of factors other than fluoride intake via ingestion, inhalation, imbibitions and dermal absorption. These include nutritional status, climate, individual susceptibility, biological exposure, duration of fluoride exposure and dissolved salts in drinking water (Choubisa, 2001).

1. **Dental Fluorosis**

Millions of people worldwide afflicts from Fluorosis. It is a preventable disease of teeth and bones, which was caused primarily by the prolonged ingestion of fluoride-rich drinking water, which is most often groundwater that has percolated
through and leached volcanic and sedimentary deposits ( Calderon, 2000; WHO, 2005; Ayenew, 2008). An accumulation of fluoride in teeth is known as dental fluorosis and is caused by ingestion of fluoride during the period of tooth development, i.e. prior to tooth eruption ( Pereira and Moreira, 1999; Aoba and Fejerskov, 2002). When fluoride becomes incorporated into the crystal lattice structure of the enamel it causes hypo-mineralization which increases the porosity of the enamel ( Fejerskov, 1994; Levy et al., 2002).

Excessive consumption of fluoride causes the enamel to lose its luster. In its mild form, dental fluorosis is characterized by the appearance of white, opaque areas on the tooth surface, and in severe form, it is manifested by the appearance of yellowish brown to black stains and severe pitting of the teeth. This discoloration may be in the form of spots or horizontal streaks. Normally, the degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8–10. It’s a fact fluoride stains only the developing teeth while they are being formed in the jawbones and are still under the gums. The effect of dental fluorosis may not be apparent if the teeth are already fully grown prior to excessive fluoride exposure. The amount of fluoride absorbed by the body depends on a number of complex factors to do with the health and condition of the individual ( Krishnamachari, 1986; Murry, 1986). In the mild forms of dental fluorosis are evidenced by the appearance of white horizontal striations on the teeth surface or opaque patches of chalky white discoloration ( Rao et al., 2003).

2. Skeletal Fluorosis

The main characteristic of Skeletal fluorosis was increased bone mass and density, accompanied by a range in skeletal and joint symptoms. In pre stages, the Symptoms include pain and stiffness in the backbone, hip region, and joints, accompanied by increased bone density ( osteosclerosis). The stiffness increases steadily until the entire spine becomes one continuous column of bone, a condition known as “poker back”. As the condition progresses, various ligaments of the spine can also become calcified and ossified. In advanced stages, fluorosis produces neurological defects, muscle wasting, paralysis, crippling deformities of the spine and major joints, and compression of the spinal cord. The threshold level of fluoride ingestion
needed to cause skeletal fluorosis varies depending on water intake, water quality, and other dietary factors (Reddy et al., 1985).

Both children and adults were affected by Skeletal fluorosis. It does not easily manifest itself until the disease attains an advanced stage. Fluoride is mainly deposited in the joints of the neck, knee, pelvic, and shoulder bones, and once it takes place, it makes movement or walking difficult. The symptoms of skeletal fluorosis are similar to those of spondylitis or arthritis. Early symptoms include sporadic pain, back stiffness, burning-like sensation, pricking and tingling in the limbs, muscle weakness, chronic fatigue, and abnormal calcium deposits in bones and ligaments. At an advanced stage, osteoporosis in long bones and bony outgrowths may occur. A rare bone cancer, osteosarcoma, may result, and finally, the spine, major joints, muscles, and the nervous system may sustain damage. The most advanced and severe form of skeletal fluorosis is known as Crippling skeletal fluorosis. Intake of high fluoride over the long period of time was accompanied by malnutrition, strenuous manual labor, and impaired renal function, leads to severe skeletal fluorosis (Reddy et al., 1985). In the Unites States some cases of skeletal fluorosis have been documented (Doull et al., 2006). The fluoride concentration in the bone also varies with age, sex, type, and specific part of bone, and it is believed to reflect an individual’s long-term exposure to fluoride. It was observed that approximately 99% of the fluoride in the body is found in bones and teeth. In teeth the amount of fluoride is very small as compared to bones (Kaminsky et al., 1990), with the remainder distributed in highly vascularized soft tissues and blood. Apart from skeletal and dental fluorosis, excessive consumption of fluoride may Lead to many other disease manifestations: neurological manifestations, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, muscle fiber degeneration, low hemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, reduced immunity, repeated abortions or still births, male sterility, reduced intelligence etc. Beyond this a significantly elevated risk of hip fractures in residents living in countries with fluoridated water (Jacobsen et al., 1992).

3. Renal Effects
The excess fluoride in the body’s is excreting through renal system and is exposed to higher concentrations of fluoride than are other organs (Whitford, 1996). It might be at higher risk of fluoride toxicity than most of the soft tissues as suggests. In the kidney chronic ingestion of fluoride can have non-carcinogenic effects and both pertain to the incidence of kidney stones (Doolat et al., 2006). People more than 18,700 were living in a region of India where fluoride Concentrations in the drinking water ranged from 3.5 to 4.9 mg/l and found that patients with clear signs of skeletal fluorosis were 4.6 times more likely to develop kidney stones.

4. Effect of Fluoride on Animals

Information about fluorosis in horses is almost nonexistent but the literature on fluorosis in cattle is extensive. In the year 1974, US National Academy of Science report on effect of fluoride in animals. In Justus Farm in Pagosa Springs, Colorado, Most of horses was affected by fluorosis due to consumption of artificially fluorinated water, concentration up to 1.3 to 3.4 ppm. Symptoms of horses affected by Fluorosis were dental fluorosis, crooked legs, hyperostosis and enostosis, hoof deformities and reduced bone resorption (krook and Justus, 2006). Dungarpur district in Rajasthan where natural occurrence of fluorosis was observed in a survey of domesticated dromedary camels. Among these eight camels were affected with mild to severe dental fluorosis (Choubisa at el., 2012). In Rajasthan Osteo- dental and non skeletal fluorosis was observed in domesticated cattles living in Chani village of Bikaner district. In drinking water concentration of fluoride varies between 1.5 and 2.5 ppm in this village (Choubisa at el., 2012). Herbivores animals were affected by dental and skeletal fluorosis due to excess of high fluoride concentration in water of Rajasthan (Choubisa, 2013). In invertebrates detritivores the highest fluoride concentration was found as compared to invertebrate Lebivores and carnivores (Andrews at el., 1989).