

Concept Note

On

GEOGENIC CONTAMINATION OF  
GROUND WATER IN INDIA

**With a special note on Nitrate**



Central Ground Water Board  
Ministry of Water Resources  
Govt. of India

Faridabad, February 2014





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## **Drafting Committee**

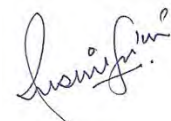
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# FOREWORD

Management of ground water resource is a challenging task and requires a structured approach starting from monitoring of water levels and quality to analysing hazards to groundwater regime, assessing the risk they may cause for a specific supply, setting priorities in addressing these and developing management strategies for their control. During recent years much of the emphasis in ground water has shifted from problem of ground water supply to considerations of ground water quality. Central Ground Water Board for the last nearly six decades has been carrying out hydrogeological investigations including water quality studies and has generated voluminous data. In addition, a lot of work has been done by State Govt. Departments, Academic Institutes, NGOs etc. on ground water quality. Many have even come up with indigenous techniques for remediation of ground water contamination and have also suggested long term policies to arrest the menace.

The report 'A Concept Note on Geogenic Contamination of Ground Water In India with a Special note on Nitrate' intends to serve as a national compilation of all relevant information on major geogenic contaminants reported in India. The report attempts to summarize various aspects of geogenic contamination of ground water with special emphasis on remediation and the way forward in respect of the following parameters viz. arsenic fluoride, salinity, iron and manganese, uranium, radon, strontium, selenium and chromium. A special note on nitrate has also been included due to its ubiquitous presence as a contaminant in ground water though not strictly due to geogenic causes. An attempt has been made in the report to correlate the contaminants with the Principal Aquifer Systems identified by CGWB. All efforts were made to incorporate exhaustive data related to aquifer contamination remediation techniques followed specially for arsenic and fluoride-the two main contaminants in India both in terms of the number of people affected and their areal extent.

I laud the efforts of the Committee Members, who have put their best to bring out the report. I am confident that the report would serve as an excellent source material for all the stakeholders in ground water including planners, researchers and even end users.



**(Sushil Gupta)**

Chairman

# PREFACE

Ground water is attracting special attention as it has become a critical resource for socio-economic development of our country. Though it is catering a major share of the demands from domestic, irrigation and industrial sector, its unplanned and accelerated development is creating concern among scientists, users and policy makers. The main concern is the depleting resources volumetrically, manifested by drying up of wells and lowering of water levels. Another significant concern is quality of ground water, as it is the back bone of drinking supply in rural areas as well as supplement supply in urban areas. The chemical quality of ground water varies significantly primarily depending upon the nature and extent of rock-water interaction and also influenced from inputs from various sources which are not related to nature. Diverse geological formations and varying climatic conditions influence the chemical character of ground water. During recent years ground water contamination from various chemical constituents is being reported from aquifers throughout the country and many a times it become non-potable as the constituent/constituents exceeds the limits prescribed by BIS.

Ground water quality deterioration can be caused by broadly two ways; (i) *anthropogenic* - those caused by manmade activities like, industries, urban sewage and waste landfills, mining etc. (ii) *geogenic* - those occurring due to natural causes mainly through rock-water interaction. This work primarily deals with geogenic contamination of ground water its distribution in different hydrogeologic terrains in India and remediation techniques available. This concept note also incorporates a special reference to nitrate contamination of ground water. Preparation of this detailed note is a desired output under Result Frame Work Document for studying aquifer contamination remediation.

This report is the compilation of the enormous data generated through various studies of CGWB. The members of the committee to prepare this report tried their best to include the researches carried out by various institutions and scholars. The committee acknowledges all, whose works are included in this report. Generous support received from all Regional Directors is also acknowledged. The committee extends thanks to Chairman for vesting the opportunity to deal with the subject and prepare this report.

It is expected that the report help in enhancing knowledge-base and prove useful in policy planning and implementation.



Dipankar Saha  
Regional Director,  
CGWB , MER, Patna  
&  
Chairman of the committee

# Acknowledgements

A committee was constituted by Chairman, CGWB in May,2013 to prepare a report on geogenic contamination in ground water in India and also to prepare a special note on nitrate pollution .The above report is a part of the commitment to the adhoc task force on Result Framework Document constituted by the Cabinet Secretariat.

First and foremost, the committee members are thankful to Sri Sushil Gupta, Chairman, CGWB for providing the opportunity to prepare the comprehensive report. This exercise provided the committee members to interact with a wide array of geoscientists and consult voluminous literature.

The committee members express their thanks to all the Regional Directors of CGWB for providing data and pertinent information from their respective Regions.

Thanks are extended to the distinguished academicians and researchers from JNU,New Delhi, BHU, Varanashi, ISM,Dhanbad, IIT,Kharagpur, NGRI, Hyderabad, CSMCRI, Bhavnagar who have contributed in enriching the document by sharing their publications with the committee.

Thanks are extended to the young scientists of CGWB, MER, Patna, in particular, Sh A.N. Chaudhury, Assistant Chemist and Suresh Kumar, STA (Chem) for providing valuable inputs in preparation of the report.

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# 1.0 INTRODUCTION

The water occurring below the earth's surface is divided into two components (i) *Ground water* – occurring in the zone of saturation, where all interconnected voids of the rocks are filled with water and (ii) *Vadose water* – occurring above the zone of saturation with water filling the voids of capillary dimension, or in the form of vapour occurring in the voids or in the process of filtration from surface.

Since pre-historic times, ground water is considered as dependable source of water for various uses and construed to be less vulnerable to quality (physical and bacteriological) deterioration because it is considered to be sealed in the envelop of vadose zone. However as the civilization grew, population density increased, urbanisation and industrialisation invaded and organised farming expanded rapidly, the quality of water started getting affected. Ground water quality is also getting deteriorated in different parts of the world in various climatic and hydrogeologic environments.

The possible pollutants in ground water are limitless; they may be physical, organic and inorganic chemical, biological and radiological. Complex and inter-related series of modifications of ground water quality is created by diverse human activities as well as due to altered rate and type of rock-water interaction.

Considerable differences of opinion exist over the distinction between the terms “*Pollution*” and “*Contamination*”. Todd 1980 has opined pollution as any degradation of natural quality while contamination is reserved for pollution that constitutes a hazard to human health. Freeze and Cherry (1979) expressed contaminants as solids introduced into hydrologic environment as a result of human activity regardless of whether or not, the concentrations reach levels that cause significant degradation of water quality, whereas the term pollution is reserved for situations where contaminant concentrations attain levels that are considered to be objectionable.

When the principal source and cause of ground water quality deterioration are related to human activities like municipal, industrial and agricultural; the pollution/contamination is referred as *anthropogenic*.

On the other hand the term “*geogenic pollution*” or more frequently used “*geogenic contamination*” refers to naturally occurring elevated concentration of certain elements in ground water having negative health effect. Geogenic contamination of ground water might emanate from geochemical characteristics of the aquifer material-high concentration of contaminant in rock matrix dissolved during rock-water interaction or occur due to environmental conditions, like array of climatic conditions, redox condition in aquifer, ground water flow congestion which facilitate the contaminant to enter in an aqueous phase. It is also possible that change in sub surface environmental condition is triggered by anthropogenic activities.

## 2.0 HYDROCHEMISTRY

The classical use of chemical characteristics in hydrology is to provide information about the distribution of water qualities. At the same time, hydrochemistry has a potential use for tracing the origin and path of water regimes, as well as can also be of immense help in yielding information about the environment through which water has circulated. Hydrochemistry involves study of atmospheric water (rainwater), surface water and ground water.

### 2.1 Chemistry of Rain water

A significant component of atmosphere is water vapor, beside dust particles and various gaseous components such as  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $SO_x$ ,  $NO_x$  etc. It is also said that pollutants in the atmosphere can be transported long distances by the wind and are mostly washed down to land surface and water bodies by rainfall, hail or snow and partly as dry fall out. The composition of rainwater is determined by the source of water vapors and by the ion, which are taken up during transport through the atmosphere. In general, chemical composition of rainwater shows EC generally  $< 50 \mu S/cm$ , chloride as generally  $< 5 \text{ mg/L}$ ,  $HCO_3^- < 10 \text{ mg/L}$ , while total cation content is generally  $< 15 \text{ mg/L}$  except in samples contaminated with dust. The concentration of  $SO_4$  and  $NO_3$  in rainwater may be high in areas near industrial hubs.

### 2.2 Chemistry of Surface water

Surface water is extremely variable in its chemical composition depending upon the interaction with the rocks on which it flows and in relative contribution of ground water and surface water run-off. The mineral content in river water usually bears an inverse relationship to discharge. The mineral content of river water tends to increase from source to mouth, although the increase may not be continuous or uniform. Other factors like discharge of wastewater from the cities located on the banks, industrial waste etc can also affect the nature and concentration of various chemical constituents in surface water.

Among anions,  $\text{HCO}_3^-$  is most important (>50% of the total anions in meq/L). In case of cations, the alkaline earth, viz, Ca predominates. With increasing salinity the hydrochemical facies tends to change from Ca- $\text{HCO}_3^-$  to mixed cation to Na- $\text{HCO}_3^-$  and finally to Na-Cl type.

### 2.3 Chemistry of Ground Water

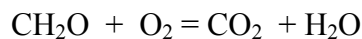
The quality of ground water is generally considered to be superior to surface water because of the purifying effects of the soil column and vadose zone during the process of percolation. The final composition of groundwater depends on the mineralogic composition of the aquifer framework and contact time or age of the water. According to Mathess (1982), the processes affecting the quality are dissolution, hydrolysis, precipitation, adsorption, ion-exchange, oxidation, reduction and bio-chemical mediated reactions. In general, the reactions that control the chemistry of ground water are:

1. Introduction of  $\text{CO}_2$  gas into the unsaturated zone.
2. Dissolution of calcite and dolomite and precipitation of calcite.
3. Cation-exchange.
4. Oxidation of pyrite and organic matter.
5. Reduction of oxygen, nitrate and sulphate with production of sulphide.
6. Reductive production of methane.
7. Dissolution of gypsum, anhydrite and halite.
8. Incongruent dissolution of primary silicates with formation of clays.

Ground water that is in perpetual motion, acquires various physical, chemical and biological characteristics as it flows from recharge area to the discharge area.

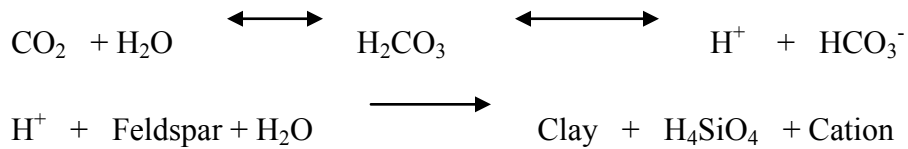
The factors that influence ground water quality are: local geology, land use, climatic conditions particularly pattern and frequency of rainfall and anthropogenic activities such as use of fertilizers and pesticides in agriculture, disposal of domestic sewage and industrial effluents and extent of exploitation of ground water resources.

The oxygen present in water is used for the oxidation of organic matter that subsequently generates  $\text{CO}_2$  to form  $\text{H}_2\text{CO}_3$ . This process goes on until oxygen is fully consumed.



Apart from these reactions, there are several other basic reactions involving microbiological mediated reactions, which tend to alter the chemical composition of the percolating waters.

Percolating water is charged with oxygen and carbon dioxide and is most aggressive in the first part. This water gradually loses its aggressiveness, as free CO<sub>2</sub> associated with the percolating water gets gradually exhausted through interaction of water with minerals.



Some rocks serve as sources of chloride and sulphate through direct solution. The circulation of sulphur, however, may be greatly influenced by biologically mediated oxidation and reduction reactions. Chloride circulation may be a significant factor influencing the anion content in many natural waters.

The list of the chemical constituents present in groundwater in varying proportions are given below(Todd, 1999, Table1)

**Table 1:** Major, minor and trace constituents of ground water

Constituent Classes	Constituents
Major Constituents(1.0 to 1000 mg/L)	Sodium,Calcium,Magnesium,Bicarbonate,Sulfate,Chloride,Silica
Secondary Constituents(0.01to10.0mg/L)	Iron,Strontium,Potassium,Carbonate,Nitrate,Fluoride,Boron
Minor Constituents(0.0001 to 0.1 mg/L)	Antimony,Aluminium,Arsenic,Barium,Bromide,Cadmium,Chromium,Cobalt,CopperGermanium,Iodide,Lead,Lithium,Manganese,Molybdenum,Nickel,Phosphate,Rubidium,Selenium,Titanium,Uranium,Vanadium,Zinc
Trace Constituents(generally less than 0.001 mg/L)	Beryllium,Bismuth,Cerium,Cesium,Gallium,Gold,Indium,Lanthanum,Niobium,Platinum,Radium,Ruthenium,Scandium,Silver,Thallium,Thorium,Tin,Tungsten,Ytterbium, Yttrium,Zirconium



## 3.0 AQUIFER SYSTEMS IN INDIA

The National Atlas on **Aquifer Systems of India** brought out by CGWB has adopted a two tier classification of aquifer systems of India. The aquifers are classified into 14 Principal aquifer systems, which in turn have been sub-divided into 42 major aquifer systems. In an earlier classification, the country was divided into eight broad ground water provinces depending upon broad rock types, geology and terrains (Taylor,1959). This classification of ground water provinces was subsequently endorsed by various authors like Karanth(2003). Subsequently, wide array of data generated on various facets of hydrogeology by Central Ground Water Board, State organizations and also by Research Institutions and Academia were compiled by CGWB to arrive at fourteen Principal Aquifer Systems in India(CGWB,2011).

The geological/ geochemical characteristics of aquifer systems is one of the major controls of ground water chemistry. Efforts have been made while compiling the data on geogenic contamination of ground water to understand whether a particular contaminant is confined to any of the Principal Aquifer System or not. Aquifer system wise distribution of contaminants are given in the respective chapter/sections.





## 4.0 GEOGENIC CONTAMINATION-A CONCERN IN INDIA

Commensurate with wide variety in rock types, ranging in age from some of the oldest proto-continentals in the world exceeding 2.6 billion years to Recent fluvio-lacustrine and delta deposits, there is a wide array of rock-water interaction giving rise to a variety of geogenic contamination in India. Besides, the various agro-climatic zones and physico-chemical conditions prevailing in aquifers also abets certain processes of leaching out of contaminants from aquifer framework to the aqueous phase.

The most widespread contamination in India is that of elevated levels of **fluoride**. It is widely prevalent in different parts of India, particularly in the state of Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat, and Rajasthan, where 50-100% of the districts have drinking water sources containing excess level of fluoride. As per an estimate (FRRDF 1999) about 66 million people in India are consuming water with fluoride level beyond the permissible limit. Considering the Principal Aquifer Systems, almost all are affected by fluoride contamination of different scales emanating from rock-water interaction (Table 2). The next important contamination is **arsenic** in terms of its carcinogenic nature and number of persons residing in the risk zone. Considering the Principal Aquifer Systems, arsenic is confined in alluvial aquifers except for a small patch in Chhattisgarh State where localized contamination is reported from gneissic aquifers. Geographically large areas affected by arsenic contamination are from West Bengal and Bihar, where the contamination has been reported from 146 blocks (89 blocks in West Bengal and 57 blocks in Bihar) distributed in 23 districts (8 districts of West Bengal and 15 districts of Bihar). Besides, arsenic affected alluvial aquifers are reported from Uttar Pradesh, and sporadically from Jharkhand, Haryana, Punjab, Manipur and Assam. If we consider the Principal Aquifer Systems the "Alluvium" is found to be affected by arsenic, however, if we go further in classification, elevated level of arsenic is confined only in Younger Alluvium which constitutes just one of the 42 Major Aquifer Systems.

**Salinity** does not cause serious health effects as compared to other geogenic contaminants. It is distributed mainly in western, north-western and southern part of India. The states largely affected by it are Rajasthan, Gujarat and Haryana. Salinity has been observed

almost in all major aquifer systems but primarily confined in Alluvium, Granite, Schist, Shale and also in Deccan Traps and Limestone. Inland salinity caused by high sulphate in ground water has also been reported from some parts of the country like Central part of Chhattisgarh in Durg, Bilaspur, Kawardha, Janjgir Champa, Raigarh and Raipur Districts(State Report,2006) .

Besides, salinity originated from saline-water intrusion in coastal areas due to over pumping of groundwater in various scales and has been reported in the states of Tamil Nadu, West Bengal, Orissa, Gujarat and Andhra Pradesh. Besides, percolation from spreaded sea water during high tide or storm event also contribute to groundwater salinity in low lying coastal areas.

**Iron** and **manganese** have got similar hydrogeochemistry. Both of them are found in widely distributed geographical areas. Elevated iron has been reported from almost all states, covering almost all Principal Aquifer Systems. Elevated levels of Mn are sporadic in nature in comparison to Fe. Elevated level of Mn has been reported mainly from West Bengal, Tamil Nadu, Orissa, UP and Bihar.

**Uranium, Radon and Strontium** contamination from geogenic source have been reported in last two decades with availability of better analytical facilities. The geographical distribution of elevated level of Uranium and Radon is limited in aerial extent and confined to the States of Andhra Pradesh, Himachal Pradesh, Chhattisgarh, Madhya Pradesh, Karnataka, Rajasthan and Punjab. Their elevated concentration has got affinity to Pre-Cambrian suite of rocks and also in alluvium as the ground water flows. Strontium has been reported from Ranga Reddy district of Andhra Pradesh.

**Chromium** has been reported from different parts of India; however, its origin has mostly been ascribed as anthropogenic. The geogenic source has been identified related to Chromite deposits in Sukinda area of Orissa.

**Selenium** in ground water is highly localized in distribution and has been reported as patches in Himachal Pradesh and Punjab, affecting the Alluvium and a variety of sedimentary and igneous rock types. The reported concentration from Himachal Pradesh remains within the limits of potable use but in Punjab it has been found exceeding the limit.

**Nitrate**, the end products of the biologic nitrification process, is the most ubiquitous chemical contaminant in the world's aquifers and the concentration levels are increasing. The distribution of  $\text{NO}_3$  in groundwater is controlled by a number of factors. They include source availability, thickness and composition of the vadose zone, precipitation, irrigation, ground water flow, aquifer heterogeneity, dissolved oxygen concentrations and electron donor availability and dispersion. Examples of nitrogen compounds found in naturally occurring waters include ammonia ( $\text{NH}_3$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), and the ammonium ion ( $\text{NH}_4^+$ ). Nitrogen is also found in many organic compounds such as proteins and protein derivatives including purines, pyrimidines, and urea. Generally, inorganic nitrogen salts are quite soluble in natural waters.

A state-wise list of the districts where ground water is affected by various contaminations reported by CGWB are given in Annexure I. Efforts have been made to include reportage of various geogenic and nitrate contamination from published literatures by researchers (**Annexure-I**). Uranium has also been recorded in ground water samples in remote areas by Atomic Mineral Division(AMD) which has also been included in **Annexure-I**.



## 5.0 DRINKING WATER QUALITY STANDARDS

Concern for water quality for drinking use is not new. By 1855 people were aware of the role of water in transmission of diseases such as typhoid, bacillary dysentery, cholera, amoebic dysentery and infectious hepatitis etc. In 1914, the U.S. Public Health Service established drinking water standards for public water supplies.

As on date several quality standards for drinking use are available. These recommendations/guidelines apply to all public, private, individual or small community water supplies which are used for drinking purpose. It must be cleared that the guideline values recommended are not mandatory limits worldwide. Such limits are based on socio-economic and environmental condition set by National/ Regional/international Authorities using a risk-benefit approach

### 5.1 Standards available at National level

The most widely used standard in India is Bureau of Indian Standard: IS 10500-2012. However, there are some other standards proposed and also in vogue in certain sectors of which an important one is that proposed by Indian Council of Medical Research, Report No.44 of 1975. For packaged drinking water and mineral water, the following two additional user-specification standards are available

1. *IS: 14543, specification for packed drinking water.*
2. *IS: 13428, specification for Mineral water.*

### 5.2 Standards available at International level

Most of the countries have their own standards. Besides many international organizations have formulated standards and advised guidelines. The international guidelines accepted widely are given below;

1. *World Health Organization (WHO) Guidelines 2011*

2. *European Economic Community (EEC) Norm*
3. *U S Environmental Protection Agency (USEPA) Norms*

### 5.3 Commonly adopted standards for contaminants under discussion

Two yardsticks are adopted while considering portability of water; “desirable” and “maximum permissible levels”. The limits described as ‘desirable’ apply to water which will be generally acceptable to the consumers. In case of absence of any other source the prescribed ‘maximum permissible level’ should be adhered to.

**Table2.** Commonly accepted Drinking Water Quality Guidelines

<i>Constituent</i>	<b>Drinking water standards recommended by BIS and WHO (in mg/l)</b>			<b>Undesirable effect when present beyond acceptable limit in drinking water</b>
	<b>BIS (2012)</b>		<b>WHO (2011)</b>	
	<b>Acceptable Limit</b>	<b>Permissible limit in the absence of alternate source</b>	<b>guideline values</b>	
<b>ARSENIC</b>	0.01	0.05	0.01	It is a cumulative poison, Carcinogenic
<b>TOTAL CHROMIUM</b>	0.05	No relaxation	0.05	Hexavalent Chromium is Toxic and causes Ulcers & Dermatitis
<b>STRONTIUM</b>				Can cause problems with bone growth. Radioactive strontium is more harmful, it may cause anemia and oxygen shortages, and at extremely high concentrations it is even known to cause cancer.
<b>DISSOLVED SOLIDS</b>	500	2000	1000	Causes Gastrointestinal irritation
<b>SILICA</b>				Silicon compounds cause silicosis leading to tuberculosis, bronchitis, and chronic obstructive pulmonary disease. Harmful in boiler scale and steam of high-pressure boilers to form deposits on turbine blades.
<b>MANGANESE</b>	0.1	0.3		Aesthetic taste / appearance are affected, has adverse effect on domestic uses and water supply

				structures.Total concentration of Manganese (as Mn) and Iron (as Fe) shall not exceed 0.3 mg/l
<b>FLUORIDE</b>	1.0	1.5	1.5	It is completely absorbed in the body, required for prevention of Dental Caries. High concentration causes Fluorosis
<b>IRON</b>	0.3	No relaxation		Aesthetic taste, essential for human health [Heamoglobin Synthesis] Excess stored in Spleen , Liver , Bone marrow & causes Haemochromatosis. Total concentration of Manganese (as Mn) and Iron (as Fe) shall not exceed 0.3 mg/l
<b>SELENIUM</b>	0.01	No relaxation	0.01	Very low selenium status in humans has been associated with juvenile, multifocal myocarditis called Keshan disease and chondrodystrophy called Kaschin-Beck disease. Symptoms in people with high urinary selenium levels include gastrointestinal disturbances, discoloration of the skin and decay of teeth .
<b>URANIUM</b>			0.015	Carcinogenic, liver damage or both. Long term chronic intakes of uranium isotopes in food, water, or air can lead to internal irradiation.
<b>NITRATE</b>	45	No relaxation	50	Beyond this methaemoglobinamia takes place/may be indicative of pollution
<b>RADON</b>				Radon is the primary cause of lung cancer





## 6.0 GEOGENIC CONTAMINANTS

### 6.1 Arsenic

Arsenic is classified chemically as non-metal or metalloid belonging to Group-15 of the periodic table. Its atomic number is 33 and atomic weight is 74.92. The most common oxidation states of arsenic are  $-3$  (arsenide, usually alloy like compound),  $+3$  (arsenite, As (III), organo arsenic compound),  $+5$  (arsenates, As (V), most stable inorganic arsenic oxi-compound). It can exist both in organic and inorganic forms. However, inorganic forms are more toxic than organic.

Arsenic is found in all natural environments in abundance in earth's crust and in small quantities in rock, soil, water and air. In continental crust, the average concentration is 1-2 mg/kg. Its mean concentration in igneous rock is 1.5-3.0 mg/kg whereas in sedimentary rock it ranges from 1.7-400 mg/kg.

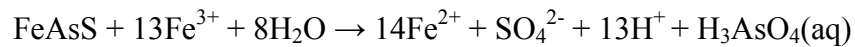
Transport and distribution of arsenic in environment is complex and there is continuous cycling of different forms of arsenic through air, soil and water. It is introduced in soil and ground water during weathering of rocks followed by leaching and run off. Of course, it can also be introduced from anthropogenic sources. In ground water inorganic arsenic is present commonly as arsenate (As V) and arsenite (As III), inter-conversion of which takes place by oxidation-reduction.

#### 6.1.1 Occurrence and Hydrogeochemistry

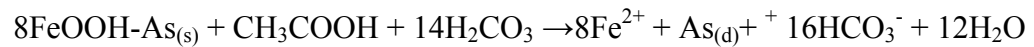
A range of arsenic compounds, both organic and inorganic, are introduced into the environment through geological (geogenic) and anthropogenic (human activities) sources. Small amounts of arsenic also enter the soil and water through various biological sources (biogenic) that are rich in arsenic.

Arsenic is widely distributed in all geological materials at varying concentrations. On the basis of the arsenic geochemistry, three probable mechanism of arsenic mobilisation in groundwater has been proposed.

- i. ***Mobilization of As due to the oxidation of As-bearing pyrite minerals.*** Insoluble As-bearing minerals such as arsenopyrite (FeAsS) are rapidly oxidized when exposed to atmosphere, releasing soluble arsenite [As(III)], sulfate (SO<sub>2</sub>), and ferrous iron [Fe(II)] (Mandal *et al.*, 1996). The dissolution of these As-containing minerals is highly dependent on the availability of oxygen and the rate of oxidation of sulfide (Loeppert, 1997). The released As(III) is partially oxidized to arsenate [As(V)] by microbially mediated reactions (Wilkie and Hering, 1998).



- ii. ***Dissolution of As-rich iron oxyhydroxides (FeOOH) due to onset of reducing conditions in the subsurface.*** Under oxidizing conditions, and in the presence of Fe, inorganic species of As are predominantly retained in the solid phase through interaction with FeOOH coatings on particles. The onset of reducing conditions in such environments can lead to the dissolution of FeOOH coatings. Fermentation of organic material like peat in the subsurface releases organic molecules (e.g., acetate) to drive reductive dissolution of FeOOH, resulting in the release of Fe(II), As(III), and As (V) present on such coatings (McArthur *et al.*, 2000; Nickson *et al.*, 2000; Saha *et al.*, 2009).



where As<sub>(s)</sub> is sorbed As and As<sub>(d)</sub> is dissolved As.

- iii. ***Release of As sorbed to aquifer minerals by competitive exchange with phosphate (H<sub>2</sub>PO<sup>-</sup>) ions that migrate into aquifers from the application of fertilizers to surface soil*** (Acharya *et al.*, 1999).

The second mechanism involving dissolution of FeOOH under reducing conditions is considered to be the most probable reason for excessive As accumulation in groundwater in large alluvial aquifers (Harvey *et al.*, 2002; Smedley and Kinniburgh, 2002).

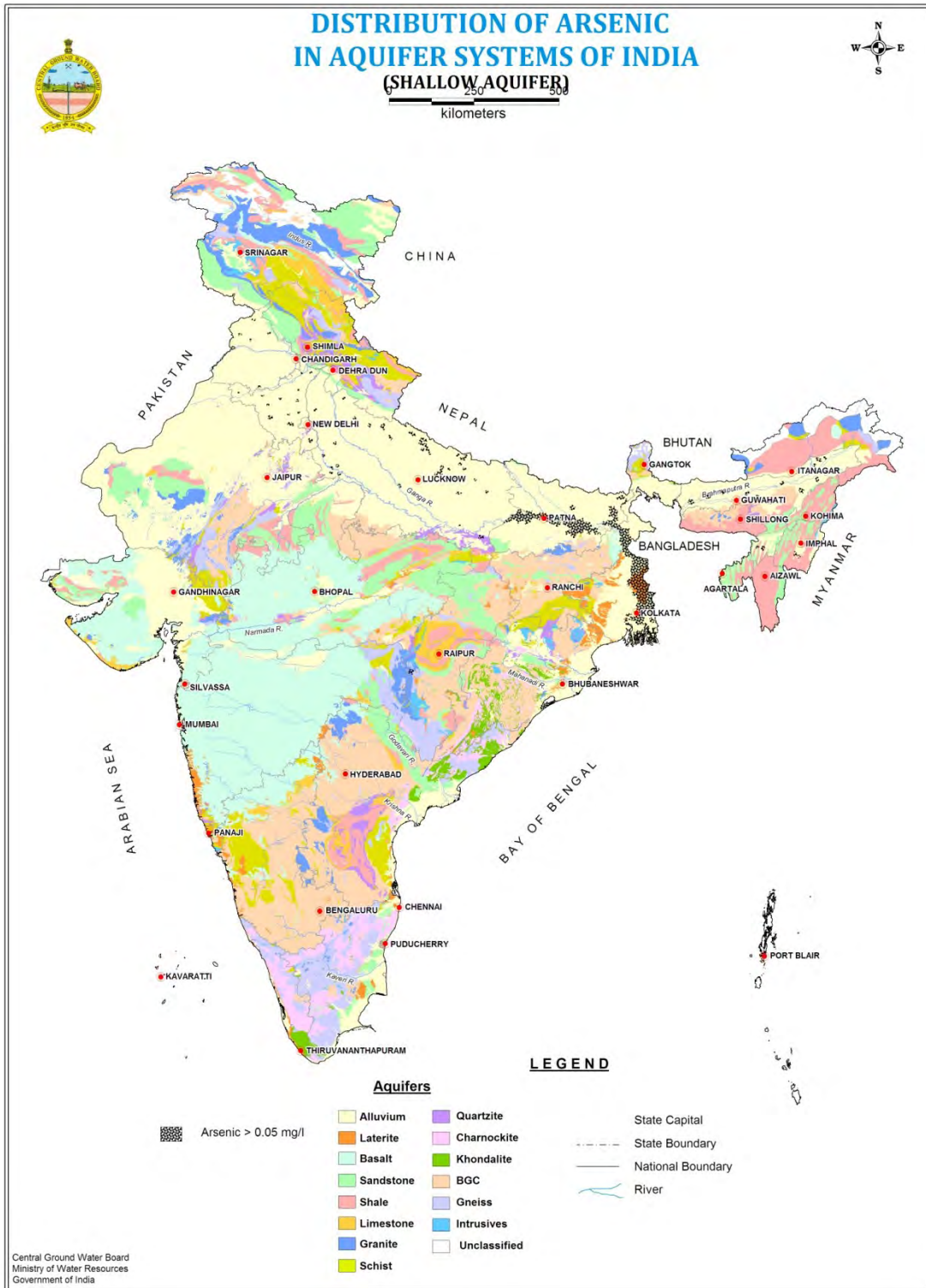
### ***Biogenic Redistribution***

Biological sources also contribute As into soil and water ecosystems, though in small amounts. Arsenic exhibits strong affinity for proteins, lipids, and other cellular components and as such accumulates readily in living tissues (Gavis and Ferguson 1972). Aquatic organisms are particularly known to accumulate As resulting in considerably higher concentrations than in the water in which they live (i.e., biomagnification). Upon disposal or consumption they subsequently become a source of environmental contamination. Arsenic could be transferred from soil to plants and then to animals and humans, involving terrestrial and aquatic food chains e.g poultry manure addition is considered to be one of the major sources of As input to soils. Thus plants along with micro- and macro-organisms affect the redistribution of As through bioaccumulation (e.g., biosorption), bio- transformation (e.g., biomethylation), and transfer (e.g., volatilization). However, in many situations the soil-plant transfer of As is low-scale (Smith *et al.*, 1998).

The distribution of Arsenic in the different Aquifer Systems of India is given in the **Figure 1**

#### **6.1.2 Health Hazard**

Human system is sensitive to arsenic. Animals are not as sensitive to arsenic as humans, owing to differences in gastrointestinal absorption. The excess arsenic may cause sufficient damage to human health and these may be respiratory distress due to irritation of mucous membranes, resulting into laryngitis, bronchitis or rhinitis, myocardial depolarization and cardiac arrhythmias that may lead to heart failure, gastrointestinal effects like burning lips, painful swallowing, thirst, nausea and abdominal colic. Anaemia and leucopenia are other common effects of arsenic poisoning. Ingestion of inorganic arsenic can also result in neural injury, having such symptoms like headache, lethargy, mental confusion, hallucinating, seizures and coma Skin disorders caused by long term arsenic ingestion have been commonly reported. It includes generalized hyperkeratosis, warts or corns on the palms and soles and areas of hyperpigmentation interspersed with small areas of hypopigmentation in the face, neck and back. Inorganic arsenic increases the risk of lung cancer when exposure occurs through inhalation. Ingestion of inorganic arsenic also increases the risk of skin cancer.



**Fig 1:** Distribution of Arsenic in Principal Aquifer Systems of India

### 6.1.3 Remedial Measures

Elevated Arsenic content in ground water is one of the most serious concerns as it affects large unconsolidated aquifers along many alluvial and deltaic plains of the world particularly in southern, south-eastern and eastern parts of Asia. The problem is compounded because the drinking water supply in these thickly populated parts is dependent on shallow aquifers which are found to be contaminated. In India approximately 40 million people are residing within the risk zone of arsenic contamination ( Acharyya 2005, Saha 2009).



**Fig 2 A typical arsenic affected village in the Gangetic Plains**



**Fig 3. An arsenic affected person**

Since the major source of arsenic in groundwater is of geogenic origin and is intricately linked to the aquifer geometry and ground water flow regime, its effective remediation warrants understanding of physicochemical processes in ground water and aquifer framework, lithology and groundwater flow regime of the area. The remedial measures includes variety of options, ranging from removing arsenic from ground water after it is extracted, searching alternative aquifers, reducing the level within the aquifer itself, dilution of the contaminants by artificial recharge, blending with potable water etc.

#### **6.1.3.1 Ex-situ arsenic treatment**

This method primarily targets to lower the concentration of As after the water is extracted from aquifers. A brief outline of the major processes in this group is given below;

- a) Precipitation processes-** includes coagulation/filtration, direct filtration, coagulation assisted microfiltration, enhanced coagulation, lime softening, and enhanced lime softening. Adsorption co-precipitation with hydrolysing metals such as  $Al^{3+}$  and  $Fe^{3+}$  is the most common treatment technique for removing arsenic from water. Sedimentation followed by rapid sand filtration or direct filtration or microfiltration is used to remove the precipitate. Coagulation with iron and aluminium salts and lime softening is the most effective treatment process. To improve efficiency of this method, a priory oxidation of As(III) to As(V) is advisable. Hypochlorite and permanganate are commonly used for the oxidation. Atmospheric oxygen can also be used, but the reaction is very slow. The major techniques based on this process include; Bucket treatment unit, Fill and draw treatment unit, Tubewell-attached arsenic treatment unit and Iron arsenic treatment unit.
- b) Adsorptive processes-** Adsorption onto activated alumina, activated carbon and iron/manganese oxide based or coated filter media. Adsorptive processes involve the passage of water through a contact bed where arsenic is removed by surface chemical reactions. The activated alumina-based sorptive media are being used in Bangladesh and India. No chemicals are added during treatment and the process relies mainly on the active surface of the media for adsorption. Granular ferric hydroxide is a highly effective adsorbent used for the adsorptive removal of arsenate, arsenite, and phosphorous from

natural water. In the Sono 3-Kolshi filter, used in Bangladesh and India zero valent iron fillings, sand, brick chips and wood coke are used as adsorbent to remove arsenic and other trace elements from groundwater

- c) **Ion-exchange processes**-This is similar to that of activated alumina, however, in this method the medium is synthetic resin of relatively well defined ion exchange capacity. In these processes, ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge dissolved in water. Usually, a synthetic anion exchange resin is used as a solid. Ion exchange removes only negatively charged As(V) species. If As(III) is present, it is necessary to oxidise it.
- d) **Membrane processes**- This includes nano-filtration, ultrafiltration, reverse osmosis and electrodialysis which uses synthetic membranes for removal of many contaminants including arsenic. They remove arsenic through filtration, electric repulsion, and adsorption of arsenic-bearing compounds.

A few emerging techniques based on the above processes are given below;

- (i) **Manganese Greensand**-Greensand is a granular material composed of the mineral glauconite, which has been coated with manganese oxide. It is a natural zeolite (microporous mineral), and has strong ion exchange properties, and has been found effective in removing iron, manganese, arsenic, sulphide, and many other anions (Water & Wastes, 2003). Greensand surface is strongly oxidizing, and is thus able to remove both arsenite and arsenate.
- (ii) **Coagulation assisted Microfiltration**-In this, microfiltration is used in a manner similar to a conventional gravity filter. The advantages of MF over conventional filtration are a more effective microorganism barrier, removal of smaller floc sizes and an increased plant capacity (EPA, 2000; Wachinski et al., 2006). The microfiltration membrane system works to remove arsenic from water by the addition of an iron-based coagulant, such as ferric chloride, to the water. The arsenic is adsorbed onto positively charged ferric hydroxide particles, which are then removed by microfiltration.
- (iii) **Enhanced coagulation (aka electrocoagulation, electroflotation)**In this technique soluble anodes made from iron or aluminum are used. Reported advantages are the in-situ oxidation of As(III) to As(V), and exhibits better



removal efficiencies than with classical coagulation. Organic arsenic, fluoride and dissolved metals are also removed by this method. An additional advantage of enhanced coagulation is the reported removal of natural organic matter (NOM).

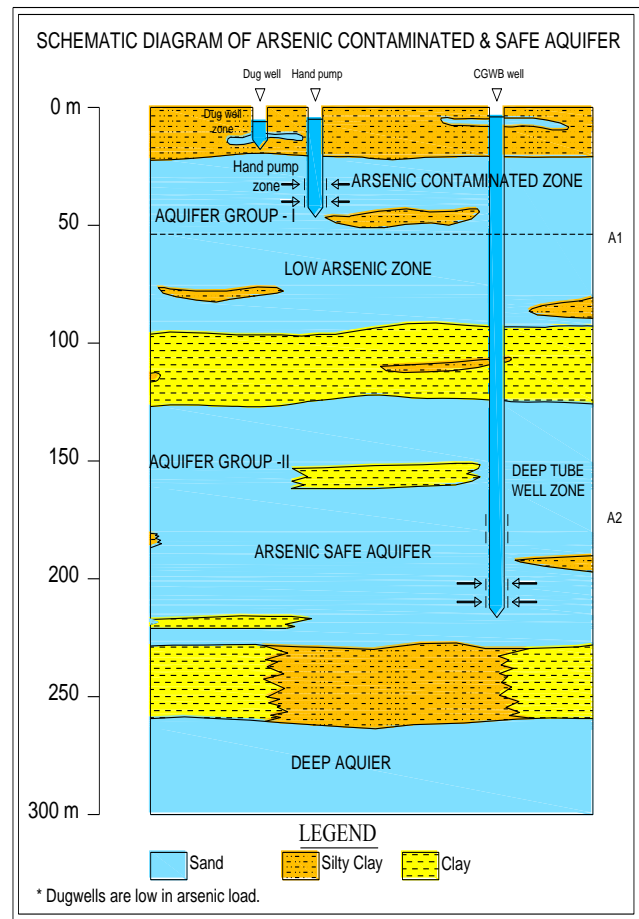
- (iv) **Solar Oxidation and Removal of Arsenic(SORAS)** is a simple method that uses irradiation of water with sunlight in PET or other UV transparent bottles to reduce arsenic level from drinking water (Wegelin et al., 2001). The method is based on photochemical oxidation of As (III) followed by precipitation or filtration of As (V) adsorbed on Fe (III) oxides. Field tests in Bangladesh show removal efficiency between 45-78% with an average of 67%.
- (v) **Iron oxide coated sand (IOCS)** UNESCO-IHE developed an arsenic removal method based on adsorption on iron oxide coated sand (IOCS). IOCS is a by-product from groundwater treatment plants and consequently very cheap. This technique is efficient for both As(III) and As(V). Different family scale removal filters were tested in Bangladesh (2004) and also a large scale centralized application was tested in Greece and Hungary (Petrusevski et al., 2007).

Majority of low cost methods rely on precipitation or adsorption. They are frequently capable of successfully treating a wide range of arsenic-contaminated influent concentrations to achieve or surpass drinking water standards

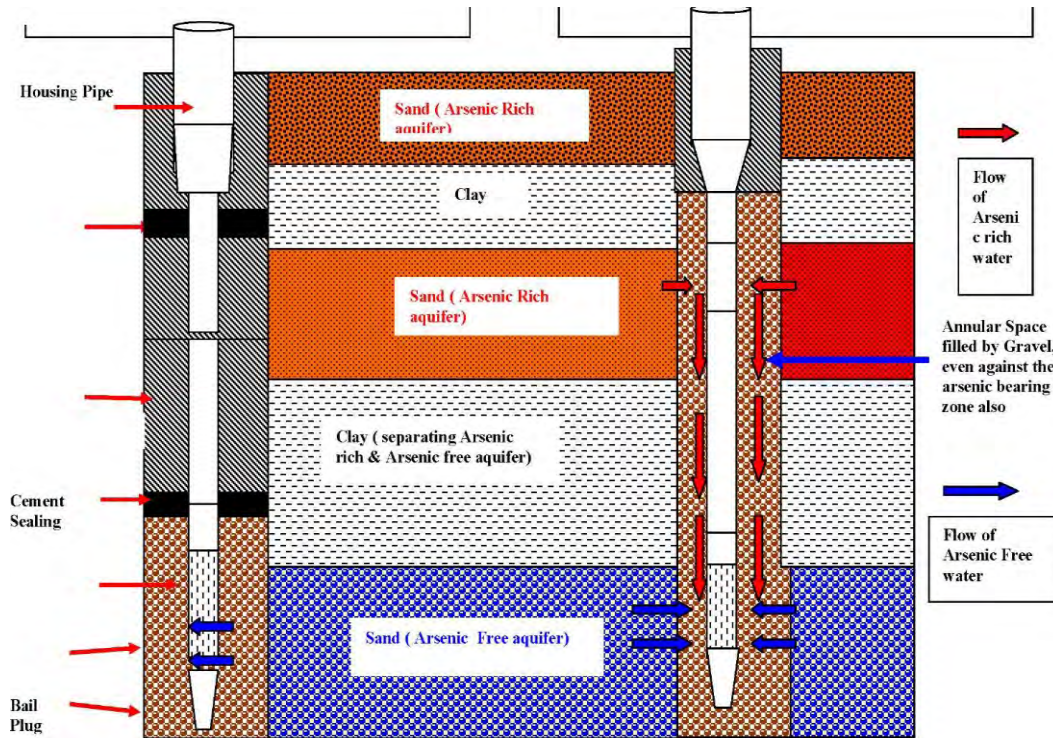
### **6.1.3.2 Arsenic safe alternate aquifers**

This technique advocates to tap safe alternate aquifers right within the affected areas. In India except at Rajnandgaon in Chhatisgarh state, the vast affected areas in the Gangetic Plains covering Bihar and Uttar Pradesh as well as Deltaic Plains in West Bengal is marked by multi-aquifer system (CGWB 1999, Acharyya 2005, Saha2009, Shah 2007). The sedimentary sequence is made up Quaternary deposits, where the aquifers made up of unconsolidated sands which are separated by clay/sandy clay, making the deeper aquifer/aquifers semi-confined to confined. The contamination is confined in the upper slice of the sediments, within 80 m and affecting the shallow aquifer system(CGWB, 1999, Saha et al 2009). At places, like Maldah district of West Bengal single aquifer exists till the bed rock is encountered at 70-120 m bgl.

Detailed CGWB exploration, isotope and hydrochemical modeling carried out by CGWB along with other agencies like BARC has indicated that the deep aquifers (>100 m bgl) underneath the contaminated shallow aquifer, have been normally found as arsenic free. Long duration pumping tests and isotopic studies in West Bengal and Bihar have indicated that there is limited hydraulic connection between the contaminated shallow and contamination free deep aquifers and the ground water belong to different age groups having different recharge mechanisms (CGWB 1999, Saha et al 2010, 2011, CGWB and BARC 2009). The deep aquifers in West Bengal, Bihar and Uttar Pradesh have the potential to be used for community-based water supply. However if a single aquifer system exists, as found in Malda district of West Bengal, this technique may not be useful. The generalized schematic diagram showing the distribution of arsenic in multi-layered alluvial aquifers and design of a deep-tube well tapping the deeper aquifer system (Talukdar and Ghosh 2009) is shown in **Fig 4a** and **4b** respectively.



**Fig 4a:** Schematic diagram showing distribution of arsenic in multi-layered alluvial aquifer and design of a deep-tube well tapping the deeper aquifer system (Talukdar and Ghosh 2009) is shown in **Fig 4a** and **4b** respectively.



**Fig 4b:** Tube-well design of a deep tube well tapping arsenic safe deeper aquifer (the well on the left shows a properly designed tube well tapping deeper aquifer while the one on the right shows an improperly designed well)



**Fig 5** Arsenic-free potential aquifer under development by pump in Middle Gangetic Plain



**Fig 6** Rotary drilling in arsenic affected village in Bhojpur district, Bihar

### 6.1.3.3 Will the deep aquifers remain arsenic free?

While advocating for supply from the deeper aquifers in the arsenic affected areas, the most pertinent question that needs answer is whether the deep aquifers will remain arsenic free or it may also get contaminated over time. Burgess et al (2010) through the results of a Basin-scale groundwater flow modelling in Bengal Basin have suggested that, over large regions, deep hand-pumped wells for domestic supply may be secure against As invasion for hundreds of years. However, deep irrigation pumping might effectively eliminate deep groundwater as an As-free resource within decades. The mechanism act as defence to As invasion is (i) flow pattern defence and (ii) geochemical defence. Groundwater flow paths to deep pumping wells provide an element of protection if As concentrations in recharge areas are low, or travel times to deep wells are long. The potential for sediments along induced flow paths to adsorb or otherwise trap As provides a 'geochemical defence'.

The *flow-pattern defence* would protect groundwater at depths greater than 150 m across more than 90% of the As-affected area indefinitely (modelled as more than 1,000 years) if deep groundwater abstraction was limited to domestic supply and distributed among hand-pumped wells. However, if there is large scale switch over to irrigation pumping from deep aquifers which is about ten times that of domestic pumping, simulations have shown that deep irrigation pumping would amplify downward flow, considerably shortening travel times to deep wells, to as little as 30 years. In contrast, shallow irrigation pumping does not compromise the flow-pattern defense of deep groundwater but rather provides extra protection by creating a hydraulic barrier against downward As migration.

*Geochemical defence* of the deeper aquifers is based on the reactivity of the sediments. The grey (shallow aquifer) and yellowish-brown sediments (deeper aquifers) have distinct chemical characteristics. The oxidised Pliocene sediments of the deeper aquifers containing ferric oxyhydroxides have a large capacity for adsorbing dissolved As. Oxidized sediments proximal to the Pleistocene inliers and boundary hills are likely to have high adsorption capacity because of sustained oxic recharge which has also been confirmed through laboratory experiments. The adsorption capacity is also enhanced by the oxidizing potential of in-situ manganese oxides. To maximize the security of deep As-free groundwater- domestic wells should

be screened as deep as possible within oxidized sediments and that deep aquifers in the arsenic contaminated areas should be largely used only for domestic supply.

#### **6.1.3.4 In-situ (sub-surface) arsenic treatment**

In-situ remediation refers to all such techniques that make arsenic immobilization possible within the aquifer itself. As arsenic is mobilized in groundwater under reducing conditions, it is also possible to immobilize the arsenic by creating oxidized conditions in the subsurface.

a) **Use of atmospheric O<sub>2</sub> for iron and arsenic rich water** In-situ treatment for the removal of arsenic, iron, manganese, or combination thereof, has been successfully applied to water wells. In the United States, in-situ remediation of other trace-elements, such as chromium, is gaining regulatory acceptance. In-situ remediation is generally thought to be less expensive than above-ground treatment.

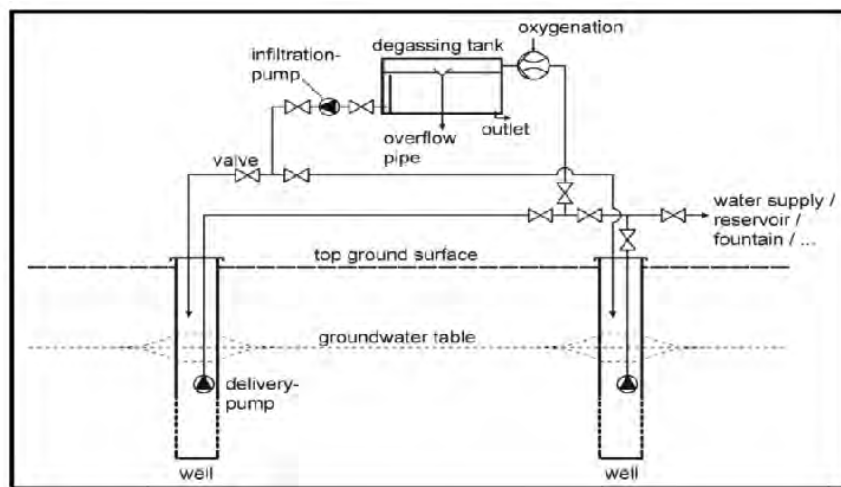
The concept of in-situ remediation of Fe (II) has been practiced in Europe for decades where concentrations are lowered through introduction of atmospheric O<sub>2</sub> to Fe (II)-rich water. The process is commonly cyclic, with a period of injection followed by a period of pumping. Beside Fe (II), Mn and As conc. have also been reduced. The efficiency of removal has been noted to increase after continued cycles. In addition, even after operation of such systems for decades, clogging of wells or aquifer materials has not been reported.

b) **Use of atmospheric O<sub>2</sub> and ferrous chloride for low Iron and Arsenic rich water** This removal technique has been demonstrated successfully from alkaline water (pH>8) with low iron load at Carson valley, USA. The low dissolved Fe content limits development of significant Fe oxide and the high pH limits As adsorption onto Fe oxide. In this case, dissolved O<sub>2</sub>, Fe (II), and HCl are added to water and injected into the aquifer to form Fe-oxide and lower the pH to remove As.

The SAR (**Sub-terranean Arsenic Removal**) Technology developed by a consortium of European & Indian scientists & demonstrated at a location near Kolkata during 2005-06 is a demonstration of in-situ technology. This technology was subsequently replicated successfully in

arsenic affected areas in West Bengal through World Bank Development Marketplace 2006 programme.

In this technique (**Fig 7**), the aerated water is stored in feed water tanks and released back into the aquifers through the tube well by opening a valve in a pipe connecting the water tank to the tube well pipe under the pump head. A number of different physical, chemical and biological processes are intensified in the surrounding area of the well screen section, the so called oxidation zone. Because of the input of oxygen, the redox potential of the water is increased. The dissolved oxygen in aerated water oxidizes arsenite to less-mobile arsenate, the ferrous iron to ferric iron and Manganese(II) to Manganese(III), followed by adsorption of arsenate on Fe(III) and manganese(III) resulting in a reduction of the arsenic content in tube well water.



**Fig 7:** Borehole and other equipment set up in the SAR technology for in-situ arsenic remediation

**Permeable Reactive Barriers (PRB) Technology** In this in-situ technique, walls containing reactive media are installed across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through the media which removes the components by precipitation, degradation, adsorption, or ion-exchange. This method is reported to have lower operation and maintenance costs than ex-situ (pump and treat) methods. PRBs are already commercially available and are being used to treat groundwater containing arsenic at a full scale at two sites in the USA, although arsenic is not the primary target (EPA, 2002). Four types of

materials have been used in the construction of permeable reactive barriers (PRB) used in the treatment of arsenic contaminated groundwater: zero valent iron (ZVI), furnace slag, sorbents and composite materials (organic + ZVI or a sorbent). It has been observed that iron Based Sorbents (IBS) can remove efficiently both the As (III), As (V) and their mixtures. As (V) is removed easier than As (III). Some of the Iron Based Sorbents (IBS) available in the market are; Adsorpas (Technical University of Berlin), ARM 300 (BASF), G2 (ADI International), SMI III (SMI), GEH 102 (GEH Wasserchemie GmbH & Co. KG) and Bayoxide E33 (Bayer AG). Iron oxide-bearing minerals (iron-oxide coated sand) have long been recognized as an effective reactive media for arsenic-contaminated groundwater remediation. Based on it, technique has been developed to facilitate in situ oxidative precipitation of  $Fe^{3+}$  in a soil (sand) media for generating a reactive barrier that could immobilize arsenic (As) and other dissolved metals in groundwater.

c) **Electrokinetic treatment** Electrokinetic treatment is an emerging insitu remediation method designed to remove heavy metal contaminants from soil and groundwater. The method is most applicable to soil with small particle sizes, such as clay. However, its applications for treating arsenic contaminated groundwater are not of practical interest as treatment is limited by the depth to which the electrodes can be placed.

Of the various in-situ remediation techniques, in India, only the SAR technology as described above has been demonstrated successfully in parts of West Bengal. Even though, in-situ immobilization has the great advantage of not producing any wastes that must be disposed of, however, experience is limited, and the technique should be considered with caution.

### ***Biological arsenic removal***

Arsenic in water can be removed by microbiological processes (Rahman and Ravenscroft, 2003). Two main types of metal-microbe interactions which can be potentially used for the removal of arsenic from ground water are, (a) microbial oxidation of arsenic (III) to arsenic (V) to facilitate its removal by conventional arsenic removal processes, and (b) bioaccumulation of arsenic by microbial biomass.

The Biological Activated Carbon (BAC) system: In this system a granular activated carbon (GAC) filter is used, which are continuously aerated to enhance the growth of biological activity within the filter media. This system has been used in rural Saskatchewan province of Canada on experimental basis for seven years with consistent arsenic removal exceeding 90% (Pokhrel et al., 2005).

In addition to the techniques mentioned above, researches have been conducted on *Phytoremediation*, which uses aquatic plants to accumulate arsenic and thus removing arsenic from groundwater. Azolla and Spirodella (duckweed) species have the highest efficiency. A study on duckweed was carried out in Bangladesh (Rahman and Ravenscroft, 2003) and found to be efficient. The results indicated that a complete cover of plant could accumulate about 175 g of arsenic from a pond of one hectare area per day.

## 6.2 Fluoride

Fluorine is the lightest member of halogen group of elements and most electronegative of all elements. In solution it forms fluoride ( $F^-$ ). Fluoride forms strong solute complexes with many cations. Concentration of fluoride in the continental crust is 611 mg/kg. Various rock types contain fluoride at different levels: basalt, 360  $\mu\text{g/g}$ ; granites, 810  $\mu\text{g/g}$ ; limestone, 220  $\mu\text{g/g}$ ; sandstone, 180  $\mu\text{g/gm}$ ; shale 800  $\mu\text{g/gm}$ ; oceanic sediments, 730  $\mu\text{g/gm}$  and soils, 285  $\mu\text{g/gm}$ . Fluoride is an essential constituent in minerals such as fluorite, apatite, cryolite and topaz. Minerals like biotite, muscovite and hornblende may contain considerable per cent of fluoride. Of the 85 million tons of fluoride deposits in the earth crust world-wide, 12 millions are found in India (Teotia and Teotia 1994). This amply indicates that the geogenic fluoride contamination of groundwater is widespread in India. Endemic fluorosis is prevalent in India since 1937 (Shrott et al., 1937). Beside rocks, it is commonly present in plants, soil, phosphatic fertilizers and rock minerals.

### 6.2.1 Occurrence and Hydrogeochemistry

Fluorite ( $\text{CaF}_2$ ) is a common fluoride mineral but has low solubility and occurs in sedimentary and igneous rocks. Apatite  $\text{Ca}_5(\text{Cl,F,OH})(\text{PO}_4)_3$  commonly contains fluoride. Amphibioles such as hornblende and some micas may contain fluoride which has replaced part



of hydroxide. At low pH the form “HF” could occur. Strong fluoride complexes could be formed with aluminium, beryllium and ferric ions and a series of mixed fluoride-hydroxide complexes is possible with Boron. In acid solution, fluoride could be associated with silica however their stability is seldom reached in natural water. There are several potential solubility controls that limit dissolved fluoride concentration in water. It appears that high fluoride concentration are more likely to occur in water that has low concentration of calcium. Ion exchange effects show amount of adsorption to be large for gibbsite, kaolinite and halloysite, especially for a fresh  $\text{Al}(\text{OH})_3$  precipitate. F-adsorption is dependent on pH.

The occurrence of the fluoride in groundwater is predominantly geogenic. Fluoride enrichment in groundwater takes place mainly through leaching and weathering of the Fluoride-bearing minerals present in the rocks and sediments which depends on several factors such as the origin of water, composition of water bearing medium, the length of time the water has been in contact with the medium, the temperature and pressure conditions, ion-exchange, rate of recharge and discharge etc. The important fluoride-bearing minerals are; fluorite (fluorspar), fluorapatite, cryolite, biotite, muscovite, lepidolite, tourmaline, hornblende series minerals, glucophane-riebeckite etc

Besides these, there are anthropogenic source of fluoride also, like phosphatic fertilizer, cow dung and urban waste etc

The distribution of Fluoride in different Principal Aquifer Systems of India is shown in **Fig 11**



**Fig 8** Typical Gneissic rocks, source of fluoride in ground water



**Fig 9** A typical fluoride affected village in Jharkhand state

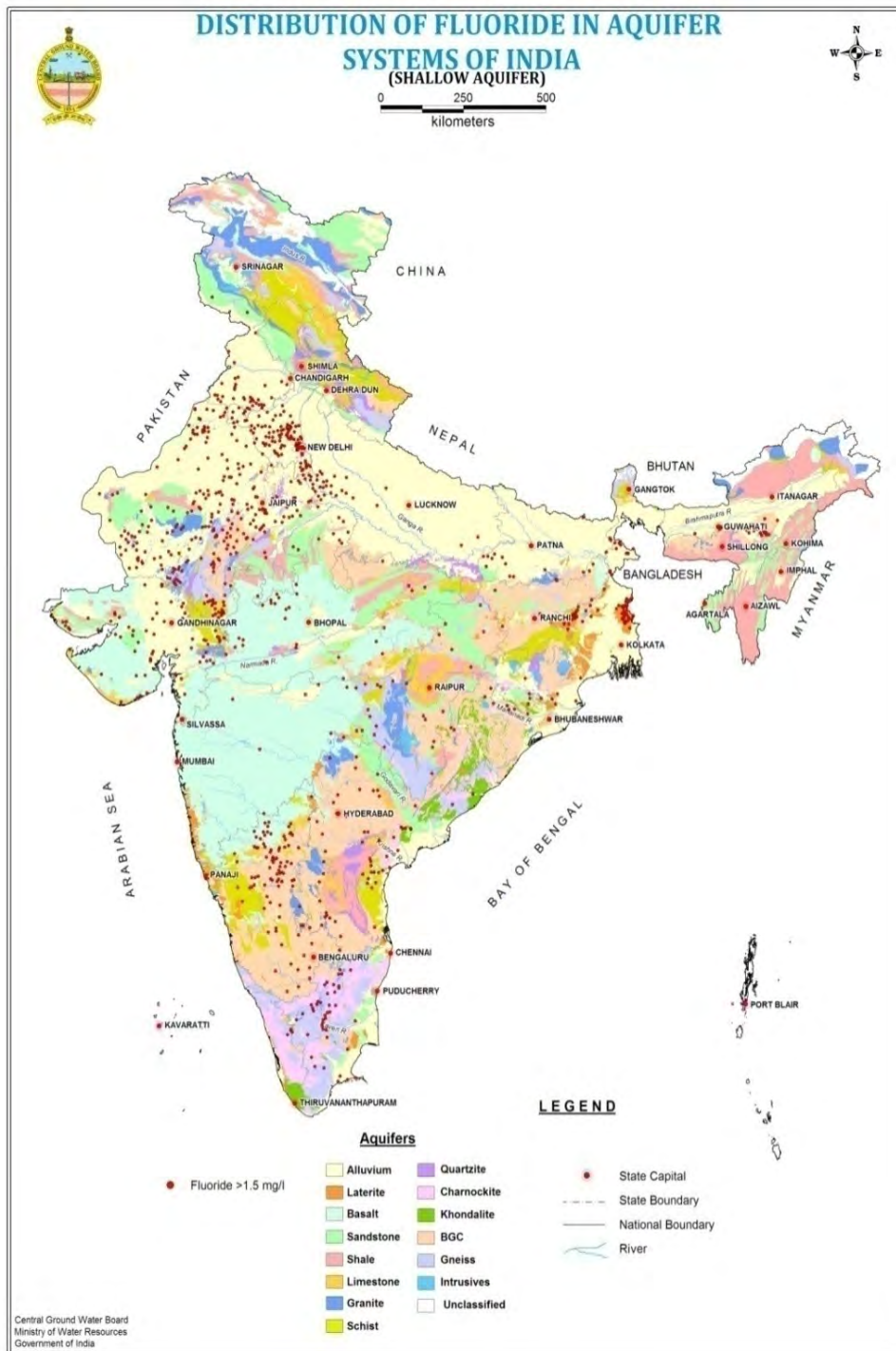
## 6.2.2 Health Hazard

Low level fluoride is required by human system as it is helpful in preventing dental carries, while consumption of high concentrations of fluoride can lead to serious health issues. The long exposures and use of ground water having high fluoride in excess of 1.5 mg/l results in *Fluorosis*, The types of fluorosis are dental, skeletal as well as non-skeletal type.



**Fig 10** Symptoms of Fluorosis mottled teeth and knocking knees

The dental fluorosis is the loss of luster and shine of the dental enamel. The discoloration starts from white, yellow, brown to black. It affects both the inner and outer surfaces of the teeth. Skeletal fluorosis is due to excessive quantity of fluoride deposited in the skeleton, which is more in cancellous bones compared to cortical bones. The disease is generally diagnosed at a developed stage. Fluoride poisoning leads to severe pain associated with rigidity and restricted movements of cervical and lumber spine, knee and pelvic joints as well as shoulder joints. Crippling deformity is associated with rigidity of joints and includes Kyphosis, Scoliosis, flexion deformity of knee joints, Paraplegia and Quadriplegia. Skeletal fluorosis affects both young children as well as adults. Non-skeletal type of Fluorosis includes ill effects on skeletal muscle, Erythrocytes, Gastro-Intestinal system, ligaments or combination of all. Fluorosis is irreversible and no treatment exists for it.



**Fig 11** The distribution of fluoride in Principal Aquifer Systems of India

### 6.2.3 Remedial measures

The fluoride remedial measures broadly adopted are ex-situ techniques. They can be classified into three major categories (NEERI 2011, Shrivastava & Vani 2009, Piddenanavar and Krishnappa, 2013).

#### (a) Adsorption and ion exchange

This technique functions on the adsorption of fluoride ions onto the surface of an active agent such as activated alumina, red mud, bone char, brick pieces column, mud pot and natural adsorbents where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix.

**Activated alumina:** Activated alumina is a highly porous aluminium oxide exhibiting high surface area. Alumina has a high preference for fluoride compared to other anionic species, and hence is an attractive adsorbent. The crystal structure of alumina contains cation lattice discontinuities giving rise to localized areas of positive charge which makes it attract various anionic species. It also does not shrink, swell, soften nor disintegrate when immersed in water. The maximum absorption capacity of activated alumina for fluoride is found to be 3.6 mg F/g of alumina.

**Red mud** Red Mud is a very fine material mainly composed of iron oxides and a variety of elements and mineralogical phases. It is produced during the Bayer process for alumina production. It is the insoluble product after bauxite digestion with sodium hydroxide at elevated temperature and pressure.

**Brick pieces column** The soil used for brick manufacturing contains Aluminium oxide. During burning operation in the kiln, it gets activated and adsorbs excess fluoride when raw water is passed through.

**Mud pot** These are the raw pots which are subjected to heat treatment as in the case of brick production and thus act as an adsorbent media.

**Natural adsorbents** Many natural adsorbents from various trees have been tried as defluoridation agents. Seeds of the Drumstick tree, roots of Vetiver grass and Tamarind seeds were few among them.

**Ion-Exchange resins:** Synthetic chemicals, namely, anion and cation exchange resins have been used for fluoride removal. Some of these are Polyanion (NCL), Tul-sion A - 27, Deacedite FF (IP), Amberlite IRA 400, LewatitMIH - 59, and AmberliteXE - 75 . These resins have been used in chloride and hydroxy form. The fluoride exchange capacity of these resins depends upon the ratio of fluoride to total anions in water.

#### (b) **Coagulation-precipitation**

Precipitation methods are based on the addition of chemicals (coagulants and coagulant aids) and the subsequent precipitation of a sparingly soluble fluoride salt as insoluble. Fluoride removal is accomplished with separation of solids from liquid. Aluminium salts (eg. Alum), lime, Poly Aluminium Chloride, Poly Aluminium Hydroxy sulphate and Brushite are some of the frequently used materials in defluoridation by precipitation technique. The best example for this technique is the famous Nalgonda technique.

#### **Nalgonda Technique**

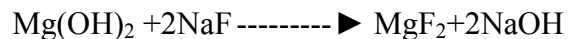
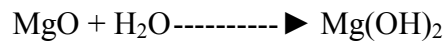
Nalgonda technique (Nawlakhe et al 1975) involves addition of Aluminium salts, lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection. It is opined that this technique is preferable at all levels because of the low price and ease of handling, is highly versatile and can be used in various scales from household level to community scale water supply.

The Nalgonda technique can be used for raw water having fluoride concentration between 1.5 and 20 mg/l and the total dissolved solids should be <1500 mg/l, and total hardness < 600 mg/l. The alkalinity of the water to be treated must be sufficient to ensure complete hydrolysis of alum added to it and to retain a minimum residual alkalinity of 1 - 2 meq/l in the treated water to achieve a pH of 6.5 - 8.5 in treated water.

Several researchers have attempted to improve the technique by increasing the removal efficiency of fluoride using Poly Aluminium Chloride (PAC) and Poly Aluminium Hydroxy Sulphate (PAHS)

**Methodology developed by IISc, Bangalore( Rao and Mamatha, 2004)**

This technique uses Magnesium oxide, lime and Sodium bisulphate. Magnesium oxide removes dissolved fluoride ions from water samples by precipitating fluoride as insoluble Magnesium fluoride.



Due to MgO, the pH of treated water rises to 10-11 which is adjusted to desirable levels (6.5 to 8.5) by adding 0.15 to 0.2 g of Sodium bisulphate per litre water. If bicarbonate ion concentration of water is more than 200 mg/l, it interferes with the function of Sodium bisulphate. To overcome this bicarbonate interference, 0.3 mg of lime and 0.8 mg of MgO are added per liter water.

**(c) Membrane techniques**

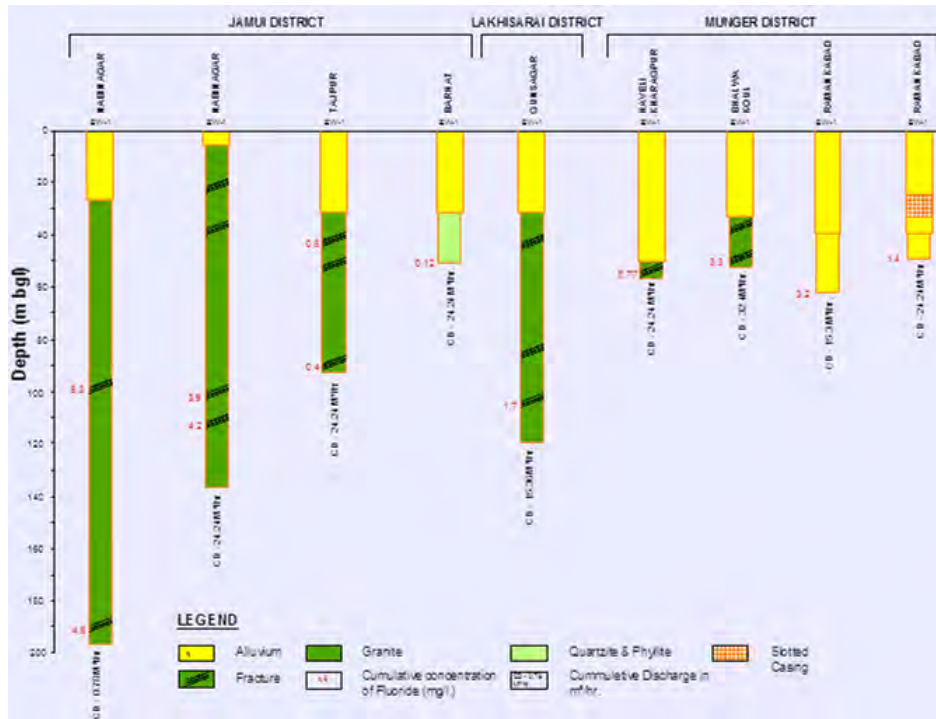
Reverse osmosis, nanofiltration, dialysis and electro dialysis are physical methods that have been tested for defluoridation of water. Though they are effective in removing fluoride salts from water, however, there are certain procedural disadvantages that limit their usage on a large scale.

***Is potable water supply possible in affected areas through Fluoride-safe aquifers?***

The question remains that like in case of arsenic, is there fluoride-safe aquifers in contaminated areas? The exploration and hydrogeochemical analyses of ground water under CGWB studies taken up in fluoride affected areas have shown no predictable relationship with depth. As such, there are very limited options for management of fluoride contaminated aquifers.



**Fig 12** Drilling by DTH rig in a fluoride affected village



**Fig 13.** Vertical distribution of Fluoride in exploratory wells of Bihar

As there is no positive correlation between the fluoride concentration and depth of occurrence of ground water, fluoride-safe aquifers are not prevalent like arsenic-safe aquifers. This has been amply demonstrated by CGWB exploratory drilling in fluoride contaminated areas. In one such area like the marginal alluvial areas of South Bihar Plain, the alluvial envelop as well as the hard rock below contain high fluoride in ground water. If we try to correlate the depth of ground water occurrence in alluvial as well as in various fracture zones in hard rocks no correlation has been found (**Fig 13**). The mitigation options therefore largely lean towards the dilution through artificial recharge. However, an integrated hydrogeological investigation for thorough characterization of the local hydrogeological set-up is an essential pre-requisite in successful adoption of dilution through artificial recharge as a remedial option for fluoride mitigation.



In one such study in fluoride affected Nalgonda District of Andhra Pradesh, to induce groundwater recharge, a check dam was constructed on upstream of capture well of 3 m dia with 5 m depth. The groundwater from capture well (**Fig 14**) has been envisaged to be transferred through pipe bypassing the delineated hydraulic barrier using gravity-siphon system for augmenting the main drinking water supply well source during lean period.



**Fig 14** Capture well rejuvenated by recharged water

## 6.3 Salinity

Salinity is a measure of the amount of dissolved particles and ions in water. The contents of dissolved solids in groundwater vary highly from one location to another, both in terms of specific constituents (e.g. halite, anhydrite, carbonates, gypsum, fluoride-salts, and sulphate-salts) and regarding the concentration level. The latter, often called salinity level is a convenient macro-parameter for a first general characterization of water quality. It is usually expressed as Total Dissolved Solids (TDS) – i.e. milligrams dissolved solids per liter of water, but use of chloride content (mg/l) or the electrical conductivity (EC, in  $\mu\text{S}/\text{cm}$ ) is also widespread in expressing salinity. The main contributors to water are: chloride ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), nitrate ( $\text{NO}_3^-$ ), calcium ( $\text{Ca}^{+2}$ ), magnesium ( $\text{Mg}^{+2}$ ), bicarbonate ( $\text{HCO}_3^-$ ), and sulfate ( $\text{SO}_4^{-2}$ ). The concentrations of boron (B), bromide (Br), iron (Fe), and other trace ions can be of local importance.

### 6.3.1 Occurrence and hydrogeochemistry

Groundwater contains naturally-occurring salts from dissolving rocks and organic material. Some rocks dissolve very easily; groundwater in these areas can naturally be very high in salinity. In some coastal areas under favourable hydrogeological conditions, groundwater overdraft (overpumping) has caused the natural groundwater gradient to reverse and has allowed seawater to intrude coastal aquifers that thereby increase overall salinity of the area.

Geogenic source of elevated levels of dissolved solids can be grouped into following categories

1. *Deposition under marine environment*: During this process, seawater fills the voids of the sediments (connate water). Often it remains trapped inside the sediment matrix for a very long period, even long after the marine environment has seized.
2. *Sea level variations*: Rising sea levels may cause flooding of coastal land by seawater, either for a long period (marine transgressions) or a short one (storm flood events, tsunamis). Reduced sea levels, like those prevailing on a global scale during the Pleistocene, create conditions for intensified flushing of coastal saline groundwater domains.

3. *Sea water intrusion*: In coastal area where aquifers are hydraulically connected to the sea, over-development of fresh water aquifer cause landward intrusion of saline water through aquifer from sea.
4. *Meteorological processes and the hydrological cycle*: On a worldwide scale, evaporation contributes steadily to the formation saline groundwater, in particular by producing evaporates. Rainfall, on the other hand, tends to have an opposite effect and activates those parts of the hydrological cycle that may flush and refresh bodies of saline groundwater.

In addition the climate change (admittedly, not an entirely 'natural' phenomenon) is assumed to be causing a global rise in atmospheric temperatures and rising sea levels. This will intensify the risks of sea water intrusion. Especially in areas where in addition the rainfall becomes less, salinity levels of groundwater may increase by intensified evaporation and by stronger anthropogenic pressures.

In India vast inland landmass is affected by ground water salinity. Their origin belongs to dissolved salts from the aquifer matrix due to long residence time of ground water, evaporite deposits in sedimentary sequence etc. Water logging and over-irrigation causes the water table to rise and so causes the water to go saline due to contact with sources of salts, as well as due to a much greater rate of evaporation near the surface. Water logging of fields causes higher salinisation of ground water in arid or semi-arid areas where the rate of evaporation is quite high.

In many areas, salt leached from the surface accumulates in an unsaturated zone between the soil surface and the groundwater table. With increased 'leakage' of water from the surface and rising groundwater tables, salt in this zone may leach into the groundwater causing groundwater salinity to increase.

The ground water chemistry in saline areas may range from Ca-HCO<sub>3</sub> type in many fresh ground-waters to Na-Cl type in many brackish and saline ground waters to Ca-Cl type in some brine environments. The specific chemical composition is dictated by the geochemical history of the groundwater. For example, it can undergo precipitation or dissolution of halite, gypsum or carbonate minerals, each leaving a different signature on the chemical composition.

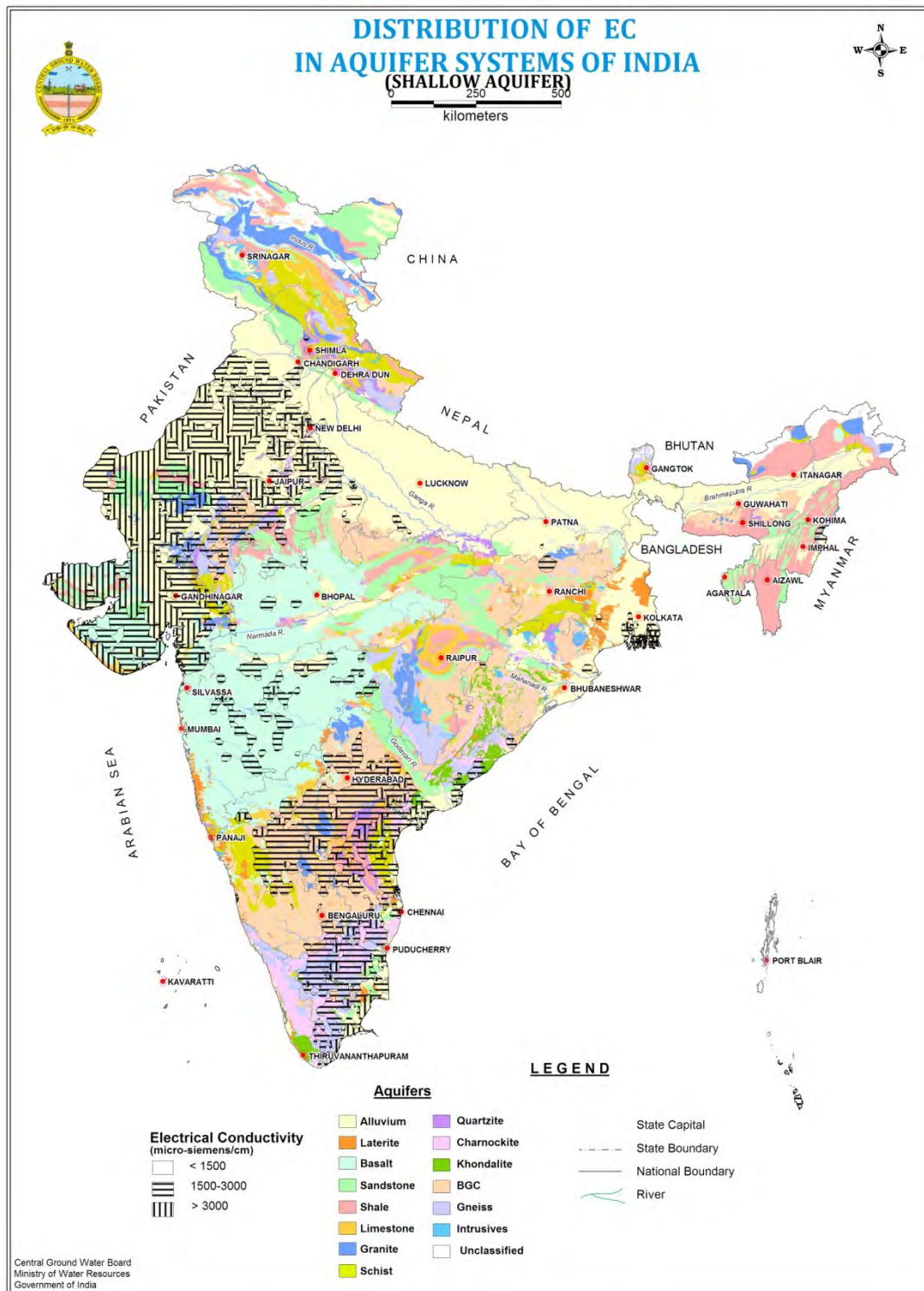
Saline water intrusion is also causing ground water salinity in coastal areas. They are related to overpumping of freshwater lying over the saline water and hence the origin will be anthropogenic. However in some coastal areas the salinity may be geogenic also. The isotope study made by CGWB under SIDA project Kerala, indicated that the brackishness in parts of the Tertiary aquifer is not due to mixing of sea water with fresh ground water but it is due to the diffusion of salinity from the intercalated clay layers.

The distribution of EC in different Principal Aquifer Systems of India is shown in **Fig 15**

### **6.3.2 Health Hazard**

High concentrations of salts can damage crops, affect plant growth, degrade drinking water quality, and damage industrial equipment. Most salts do not naturally degrade, and can remain in groundwater for decades.

High concentrations of chloride (a major constituent of total dissolved solids) can make water unfit for human consumption and for many industrial uses, but the human health-related problems have not been critically observed yet. However, high concentrations of sodium ion can contribute to certain heart disease or high blood pressure, particularly in susceptible individuals. Excessive concentration of chlorine has bad effects on the environment as well: it can produce leaf burn and even defoliation in sensitive crops; in lakes can increase the presence of metals in waters and prevent the distribution of oxygen and nutrients and thus harm aquatic life.



**Fig 15** The distribution of EC in different Principal Aquifer Systems of India

### 6.3.3 Remedial Measures

Traditionally, distillation has been the method used for desalting water for human consumption or other use. Membrane methods have emerged through the last 50 years and now predominate among the desalination practices. The following describes each of the various methods used for water desalination treatment.

#### 1. Distillation Methods

There are several variations in distillation technology used in desalination. They are all based on the vapourization of liquid water when brought to its boiling point. The nearly pure water vapour produced is condensed and collected for use, while dissolved salts remain behind in the remaining liquid feed water. Some of the methods by which distillation is practiced are as follows:

- multi-stage flash;
- multiple effect;
- vapour compression;
- membrane distillation; and
- solar humidification.

#### 2. Membrane Technologies

Membrane processes involve passing of impaired feed water through a semi-permeable material which can filter out unwanted dissolved or undissolved constituents, depending on the size and treatment of the openings. Membrane technologies identified include:

- Reverse Osmosis;
- Microfiltration/Ultrafiltration/Nanofiltration;
- Electrodialysis Reversal; and
- Forward Osmosis.

#### 3. Other Technologies

**Freezing** : During the freezing process, dissolved salts are naturally excluded during the initial formation of ice crystals. Before an entire mass of water has been frozen, the mixture is washed to remove salts adhering to the ice crystals. The ice is then melted to produce fresh water which is collected as product. This process can be used to desalinate seawater, however, it has not been a commercial success (Buros, 2000).

**Hybrid Facilities:** A method of reducing overall costs of desalination can be the use of hybrid systems using both RO and distillation processes. Such a system could provide a more suitable match between power and water development needs (Buros, 2000).

## 6.4 Iron and Manganese

### 6.4.1 Iron

Although iron is the second most abundant metallic element in the Earth's outer crust, concentrations present in water generally are small. The chemical behavior of iron and its solubility in water depend strongly on the oxidation intensity and pH in the system in which it occurs. Igneous rock minerals whose iron content is relatively high include the pyroxenes, the amphiboles, biotite, magnetite, and, especially, the nesosilicate olivine. For the most part, iron in these minerals is in the ferrous,  $\text{Fe}^{2+}$ , oxidation state, but ferric ( $\text{Fe}^{3+}$ ) may also be present, as in magnetite,  $\text{Fe}_3\text{O}_4$ . Under reducing conditions when sulfur is available, the ferrous polysulfides such as pyrite, marcasite, and the less stable species mackinawite and griegite may occur. Where sulfur is less abundant, siderite ( $\text{FeCO}_3$ ) may form. In oxidizing environments the sedimentary species will be ferric oxides or oxyhydroxides such as hematite,  $\text{Fe}_2\text{O}_3$ , goethite,  $\text{FeOOH}$ , or other minerals having these compositions. Freshly precipitated material may have poorly developed crystal structure and is commonly designated ferric hydroxide,  $\text{Fe}(\text{OH})_3$ .

Magnetite tends to resist attack by water and is commonly present as a residue in resistate sediments. Iron is a common constituent of sulfide ores of other metals, and ferrous sulfide is generally associated with coal seams. Availability of iron for aqueous solution is strikingly affected by environmental conditions, especially changes in degree or intensity of oxidation or reduction. High concentrations of dissolved ferrous iron can occur in solution at the sites of either reduction of ferric oxyhydroxides or oxidation of ferrous sulfides. Iron is present in organic wastes and in plant debris in soils, and the activities in the biosphere may have a strong influence on the occurrence of iron in water. Micro-organisms are commonly involved in processes of oxidation and reduction of iron, and some species may use these reactions as energy sources.

Iron is an essential element in the metabolism of animals and plants. If present in water in excessive amounts, however, it forms red oxyhydroxide precipitates that stain laundry and plumbing fixtures and, therefore, is an objectionable impurity in domestic and industrial water supplies.

#### **6.4.1.1 Occurrence and hydrogeochemistry**

The extent to which Fe dissolve in groundwater depends on the amount of oxygen in the water and to a lesser extent upon its degree of acidity, i.e. its pH. Iron can occur in two forms: as  $\text{Fe}^{2+}$  and as  $\text{Fe}^{3+}$ . When levels of dissolved oxygen in groundwater are greater than 1- 2 mg/L, iron occurs as  $\text{Fe}^{3+}$ , while at lower dissolved oxygen levels, the iron occurs as  $\text{Fe}^{2+}$ . Although  $\text{Fe}^{2+}$  is soluble,  $\text{Fe}^{3+}$  is insoluble in normal pH water.

If in groundwater the dissolved oxygen is less, iron (also manganese) will dissolve readily, particularly if the pH of the water is acidic. Dissolved oxygen content is typically low in deep aquifers, and also if the aquifer contains organic matter. Decomposition of the organic matter depletes the oxygen in the water and the iron dissolves as  $\text{Fe}^{2+}$ . When this water is pumped to the surface, the dissolved iron reacts with the oxygen in the atmosphere, changes to  $\text{Fe}^{3+}$  (i.e., is oxidized) and forms rust-colored iron minerals.

#### **6.4.1.2 Health Hazard**

High iron makes the water taste astringent. The water may appear brownish due to the precipitation of ferric hydroxide. It may stain utensils, laundry and equipment. The EPA cautions that although iron in drinking water is safe to ingest, but the iron sediments may contain trace impurities or harbor bacteria that can be harmful.

The most well-known role that iron plays in human nutrition is in the formation of the protein haemoglobin, which transports oxygen to all cells of the body. Iron is also used in cellular metabolism and is found in many of the body's enzymes. Low iron stores in the body can lead to iron deficiency, anaemia and fatigue. The immune system is also affected. In young children this negatively affects mental development, leads to irritability and causes concentration disorder.



Chronically consuming excess amounts of iron can lead to a condition known as iron overload. This condition is usually the result of a gene mutation. Left untreated, iron overload can lead to haemochromatosis, a severe disease that can damage the body's organs. Early symptoms include fatigue, weight loss, and joint pain, but if haemochromatosis is not treated, it can lead to heart disease, liver problems and diabetes.

## **6.4.2 Manganese**

Manganese is considered to be the 12th most abundant element in the biosphere. Although manganese is one of the most abundant metallic elements, there is only about 1/5<sup>th</sup> as much manganese in the earth's crust as there is iron. The chemistry of manganese is somewhat similar to that of iron as both metals participate in redox processes in weathering environment. Many igneous and metamorphic rocks contain manganese as a minor constituent but in basalt it is a significant constituent. Lateritic weathering process produces manganese oxide accumulation in economic proportion. It is widely distributed in soil, sediment, water and in biological materials. Although manganese is essential for humans and other species of the animal kingdom as well as for plants, at higher level it is toxic.

### **6.4.2.1 Occurrence and Hydrogeochemistry**

The levels of manganese in groundwater from natural leaching processes can vary widely depending upon the types of minerals present at the aquifer. Manganese is not an essential constituent of any of the common silicate rock minerals, but it can substitute for iron, magnesium, or calcium in silicate structures. Manganese can form a wide variety of mixed-valence oxides and has three possible valence states in such environments rather than two (2+, 3+, and 4+) but the 3+ species are unstable. Many igneous and metamorphic minerals contain divalent manganese as a minor constituent. It is a significant constituent of basalt as it is present in minerals such as olivine, pyroxene and amphibole. Small amounts are commonly present in dolomite and limestone, substituting for calcium. Manganese are more commonly found in deeper wells where the water generally remains in contact with rock for a longer time. In coal mining regions this metal may also be presented as a consequence of both deep and surface mining activities. Manganese often occurs together with iron in groundwater but it usually occurs in much lower concentrations than iron. It is present in soil as a result of mineral weathering and

atmospheric deposition, originating from both natural and anthropogenic sources. The divalent ion is the only form that is stable in soil solution, while Mn(III) and Mn(IV) are only stable in the solid phase of soil. Manganese mobility in soil is extremely sensitive to soil conditions such as acidity, wetness, organic matter content, biological activity etc. The solubility of soil manganese is thus controlled by redox potential and soil pH, where low pH or low redox potential favour the reduction of insoluble manganese oxides resulting in increased manganese mobility. At soil pH above 6, manganese forms bonds with organic matter, oxides and silicates thereby its solubility decreases. Manganese availability and solubility is thus generally low at high pH and high organic matter content, while in acid soils with low organic matter content its availability is high. The solubility of manganese is also high in anaerobic conditions at pH above 6, as well as in aerobic conditions at pH below 5.5.

#### **6.4.2.2 Health Hazard**

Manganese is easily concentrated in the brain, especially in the basal ganglia, and can cause an irreversible neurological syndrome similar to Parkinson's disease. Relatively high doses of manganese affect DNA replication and causes mutations in microorganism and mammalian cells. In mammalian cells, manganese causes DNA damage and chromosome aberrations. Large amounts of manganese affect fertility in mammals and are toxic to the embryo and foetus. The risk of damage to the central nervous system is of greater importance

#### **6.4.3 Remedial measures for Iron and Manganese**

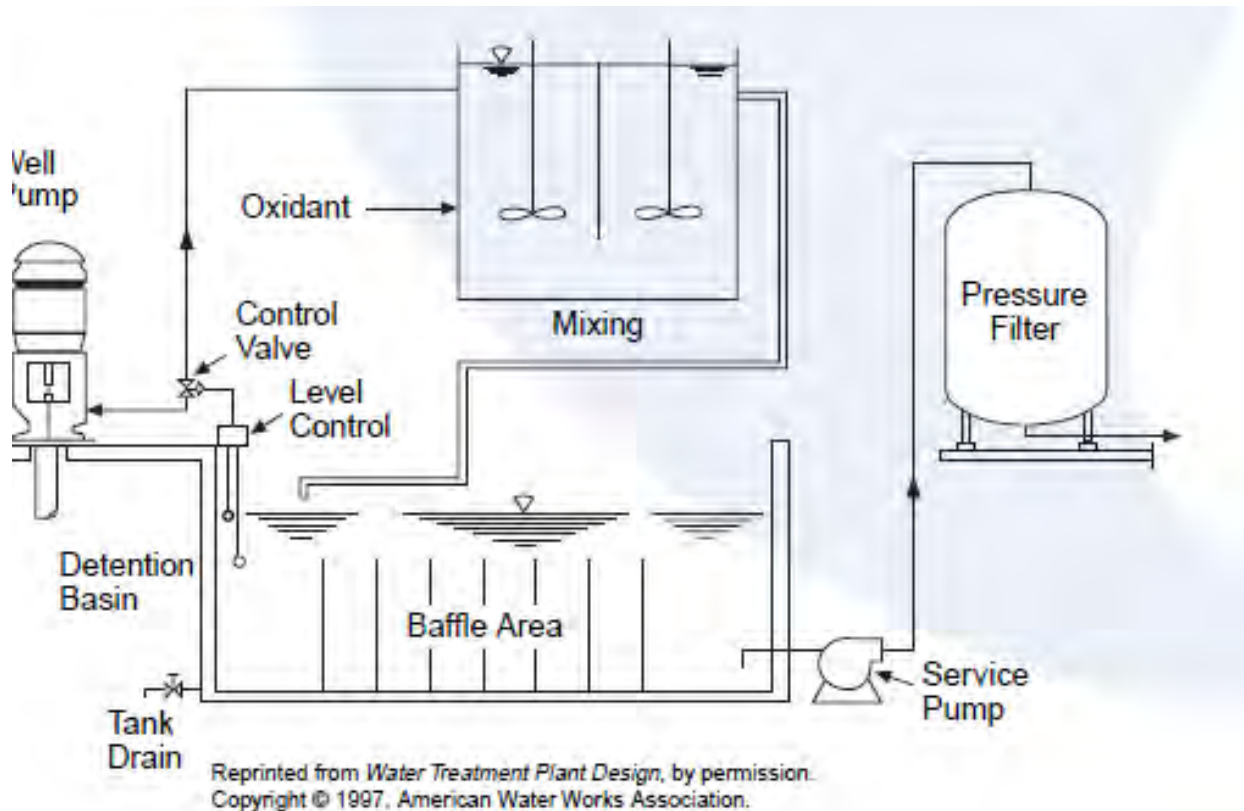
Because of the similar chemical behaviour the removal technologies of both the contaminants are the same. One of the most popular and widely used techniques is oxidation followed by filtration/sedimentation.

- a) **Oxidation and filtration** Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Ferrous iron ( $\text{Fe}^{2+}$ ) is oxidized to ferric iron ( $\text{Fe}^{3+}$ ), which readily forms the insoluble iron hydroxide complex  $\text{Fe}(\text{OH})_3$ . Manganese ( $\text{Mn}^{2+}$ ) is oxidized to ( $\text{Mn}^{4+}$ ), which forms insoluble ( $\text{MnO}_2$ ). The common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate and ozone. The dose of potassium permanganate, however, must be

carefully controlled. Too little permanganate will not oxidize all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color.

Ozone may be used for iron and manganese oxidation. Ozone may not be effective for oxidation in the presence of humic or fulvic materials. If not dosed carefully, ozone can oxidize reduced manganese to permanganate and result in pink water formation as well. Manganese dioxide particles, also formed by oxidation of reduced manganese, must be carefully coagulated to ensure their removal.

A low-cost method of providing oxidation is to use the oxygen in air as the oxidizing agent. Water is simply passed down a series of porous trays to provide contact between air and water. No chemical dosing is required. This method is not effective for water in which the iron is complexed with humic materials or other large organic molecules.



**Fig 16:** Oxidation and Filtration Method for Fe and Mn Removal from Ground Water

In general, manganese oxidation is more difficult than iron because the reaction rate is slower. A longer detention time (10 to 30 minutes) following chemical addition is needed prior to filtration to allow the reaction to take place. Manganese greensand is by far the most common medium in use for removal of iron and manganese through pressure filtration. Greensand is a processed material consisting of nodular grains of the zeolite mineral glauconite. The material is coated with manganese oxide. The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation reduction reactions necessary for iron and manganese removal. This coating is maintained through either continuous or intermittent feed of potassium permanganate. Anthra/sand (also iron-man sand) are other types of media available for removal of iron and manganese. They consist of select anthracite and sand with a chemically bonded manganese oxide coating.

Electromedia is a proprietary multi-media formulation which uses a naturally occurring zeolite and does not require potassium permanganate regeneration. Finally, macrolite, is a manufactured ceramic material with a spherical shape and a rough, textured surface. The principal removal mechanism is physical straining rather than contact oxidation or adsorption. Each medium has its advantages and disadvantages. Selection of a medium and oxidant should be based on pilot testing in which all necessary design criteria can be determined.

- b) **Ion Exchange** Ion exchange should be considered only for the removal of small quantities of iron and manganese because there is a risk of rapid clogging. Ion exchange involves the use of synthetic resins where a pre-saturate ion on the solid phase (the “adsorbent,” usually sodium) is exchanged for the unwanted ions in water. One of the major difficulties in using this method for controlling iron and manganese is that if any oxidation occurs during the process, the resulting precipitate can coat and foul the media. Cleaning would then be required using acid or sodium bisulfate.
- c) **Combined Photo-Electrochemical (CPE) Method** Different processes, such as electrochemical (EC), photo (UV), and combined photo-electrochemical (CPE) methods are used. A cell containing aluminium electrode as anode, graphite electrode as cathode and UV lamp are used and filled with waste water enriched with iron and manganese as an electrolytic solution. A limited quantity of sodium chloride salt is added to enhance

the electric conductivity through the solution. A comparison between different methods was undertaken to evaluate the applied conditions and the efficiency of Fe and Mn removal at different times and initial concentrations. The results revealed that CPE method was the best choice for the simultaneous removal of both iron and manganese in a short time < 10 min (Talaat et al., 2010).

- d) **Sequestration** Sequestration is the addition of chemicals to groundwater aimed at controlling problems caused by iron and manganese without removing them. These chemicals are added to groundwater at the well head or at the pump intake before the water has a chance to come in contact with air or chlorine. If the water contains less than 1.0 mg/l iron and less than 0.3 mg/l manganese, using polyphosphates followed by chlorination can be an effective and inexpensive method for mitigating iron and manganese problems. No sludge is generated in this method. Below these concentrations, the polyphosphates combine with the iron and manganese preventing them from being oxidized. Any of the three polyphosphates (pyrophosphate, tripolyphosphate, or metaphosphate) can be used. Applying sodium silicate and chlorine simultaneously has also been used to sequester iron and manganese. However, while this technique is reliable in the case of iron treatment, it has not been found to be effective in manganese control.

## 6.5 Uranium

Uranium is found at an average concentration of 0.0003% in the Earth's crust. The levels of uranium in natural igneous rocks and sedimentary rocks may vary from 0.5 to 4.7 µg/gm. In carbonate rocks, the average level is 2.0 µg/gm. There are only three known primary uranium ore minerals (uraninite (UO<sub>2</sub>), pitchblende (U<sub>3</sub>O<sub>8</sub>) and davidite ((Fe, Ce, U)<sub>2</sub>(Ti, Fe, V, Cr)<sub>5</sub>O<sub>12</sub>)). Sometimes they are altered to form the bright-colored secondary uranium minerals (complex oxides, silicates, phosphates, vanadates). Also specific micas contain uranium in the form of sulphates, phosphates, carbonates and arsenates, which are products of the weathering of original uranium ores. Uranium of natural isotopic composition consists of three isotopes: <sup>238</sup>U, <sup>235</sup>U and <sup>234</sup>U, all of them are radioactive. <sup>238</sup>U is an alpha emitter, decaying through the 18-member uranium natural decay series into <sup>206</sup>Pb. The decay series of <sup>235</sup>U (the actinouranium series) has 15 members that ends in stable <sup>207</sup>Pb. This series includes only two long lived (> several days) radioactive members, namely <sup>231</sup>Pa (T = 3.28years) and <sup>227</sup>Ac (T = 21.77days). Only <sup>235</sup>U is a

valuable fuel for electricity production. The residue of depleted uranium, which contains about 0.2%  $^{235}\text{U}$ , is used chiefly in armor piercing shells and for counterweights because of its pyrophoric properties and its high density. Uranium is fast acquiring notoriety as a radiological hazard. In fact, its radiotoxicity is known to be low. However, its chemical toxicity should not be ignored. Generally, only dissolved uranium is chemically toxic. In its most common and bio available forms uranium exists as a uranyl ion.

### **6.5.1 Occurrence and Hydrogeochemistry**

The chemical behavior of uranium in aqueous solution is influenced by its inclination towards complex formation, hydrolytic process and redox properties. In naturally occurring waters it is also dependant on sorption process to surface of minerals and/or colloids. Four oxidation states of uranium are soluble namely  $\text{U}^{3+}$ ,  $\text{U}^{4+}$ ,  $\text{UO}_2^{2+}$ (V) and  $\text{UO}_2^{2+}$ (VI). The U(IV) and U(VI) states are stable in aqueous media although tetravalent ion is only stable under reducing conditions.

The most prevalent form of uranium in aqueous medium is the uranyl ion ( $\text{UO}_2^{2+}$ ) which can form compounds such as carbonate, chloride and sulphate. In concentrations below  $10^{-6}\text{M}$ ,  $\text{UO}_2(\text{OH})^+$  is the dominant species, while above this concentration polymeric forms occur. Carbonate and mixed hydroxo carbonate complexes are formed in geological environment as  $\text{CO}_2$  in air or closed ground water plays a significant role in their formation. Dissolved uranium can also form stable complexes with naturally occurring inorganic and organic ligands such as phosphate complexes.

### **6.5.2 Health Effects**

In ancient times uranium was used to produce yellow glazes in ceramic. Water containing low amounts of uranium is usually safe to drink. Because of its nature, uranium is not likely to accumulate in groundwater, In fish or vegetables uranium that is absorbed and enter in human body is eliminated quickly through urine and faeces. Uranium concentrations are often higher in phosphate-rich soil, but, concentrations often do not exceed normal ranges for uncontaminated soil. Plants absorb uranium through their roots and store it there. Root vegetables such as radishes may contain higher than usual concentrations of uranium as a result. It is possible that

intake of a large amount of uranium might damage the kidneys. There is also a chance of getting cancer from radioactive uranium. The provisional guideline by WHO (2004) of Uranium for drinking water is 15 µg/L. The guideline value is designated as provisional because of outstanding uncertainties regarding the toxicology and epidemiology of Uranium.

### 6.5.3 Remedial Measures

**Ex situ** Treatment of radioactive contaminants in ground water fall into following categories

1. *Adsorption or ion exchange*: The water soluble contaminants are captured by sorption onto a solid support that can be natural or synthetic material.
2. *Reactive sorption*: is based on reaction of contaminant with solid substrate. It is often applied in situ as a barrier wall that the contaminant is forced through and is trapped.
3. *Precipitation*: This is mostly practiced above ground and involves addition of alkali to raise the pH & precipitate the oxide or hydroxide.
4. *Reverse osmosis*: Water is transported through a high pressure gradient through a membrane essentially non permeable to the contaminant.
5. *Stripping*: Only applicable to volatile contaminants like radon.

Remedial strategies based on **in-situ** chemical stabilization are as effective as the geochemistry of the site permits. Such chemical technologies may be generally grouped according to the following paradigm.

1. *Redox Technologies*: These technologies attempt to manipulate oxidation-reduction conditions of the subsurface to reduce uranium to uranous (uranium IV) forms. The techniques include in-situ redox manipulation using sodium dithionite, zero-valent iron, microbial induced reduction, and calcium polysulfide technologies. The common deficiency of technologies in this category is that the reduced environment and corresponding uranium precipitate is easily re-oxidized over time. Consequently, over time the “treated” uranium is remobilized.
2. *Co-precipitated Iron Oxyhydroxide*: This technology affects only temporary stabilization because the reaction is reversed as the precipitate ages.

3. *Phosphate Precipitation Technologies*: These technologies apply and modify phosphate with uranyl (uranium VI) forms to remove soluble uranium and prevent further dissolution of uranium by sequestration, immobilization, or precipitation. The resulting reaction seeks to create a stable, long-lasting reaction that removes the source of ongoing uranium contamination to the groundwater. However, this group of technologies requires further development.
4. *Flushing Technologies*: This group of remediation technologies uses a variety of leaching solutions to dissolve solid-phase uranium and hydraulic extraction techniques to remove the solubilized uranium. Subsurface stratigraphic heterogeneities make comprehensive treatment difficult to attain. Hydraulic capture and capture of the mobilized uranium can be problematic.

### **Pilot Study Cases**

1. Bioremediation of uranium-contaminated groundwater: (Williams et al., 2012) Microbial reduction of soluble U(VI) to insoluble U(IV) by U(VI)-reducing capacity of the *Geobacter* species that are naturally present in subsurface environments can be simply and effectively stimulated with the addition of an acetate solution to the groundwater. This precipitates uranium from the groundwater preventing its further mobility and concentrations uranium dispersed in a large volume of groundwater into a discrete zone for subsequent removal.
2. Uranium removal from groundwater by natural zeolites :It is found that adsorption on clinoptilolite manganese oxide coated zeolite (MOCZ) may be useful for uranium removal.
3. Permeable Reactive Barriers Installation of Permeable reactive barriers (PRBs) like bone char phosphate, zero valent iron or ferric iron across the flow path of the contaminant plume has consistently lowered the input U concentration in the pilot studies.

### **6.6 Radon**

Radon is produced by the radioactive decay of radium-226, which is found in uranium ores, phosphate rock, shales, igneous and metamorphic rocks such as granite, gneiss, and schist



and to a lesser degree, in limestone. However, not all granitic regions are prone to high emissions of radon. Being a gas, it usually migrates freely through faults and fragmented soils, and may accumulate in closed caves or water. Owing to its very short half-life (3.8 days for  $^{222}\text{Rn}$ ), radon concentration decreases very quickly when the distance from the production area increases. Radon concentration varies greatly with season and atmospheric conditions. For instance, it has been shown to accumulate in the air if there is a meteorological inversion and little wind.

### 6.6.1 Occurrence and Hydrochemistry

Every square mile of surface soil, to a depth of 6 inches (2.6 km<sup>2</sup> to a depth of 15 cm), contains approximately 1 gm of radium, which releases radon in small amounts to the atmosphere. Natural radon concentrations in the Earth's atmosphere are so low that radon-rich water in contact with the atmosphere will continually lose radon by volatilization. Hence, ground water has a higher concentration of  $^{222}\text{Rn}$  than surface water, because radon is continuously produced by radioactive decay of  $^{226}\text{Ra}$  present in rocks. Likewise, the saturated zone of a soil frequently has a higher radon content than the unsaturated zone because of diffusional losses to the atmosphere.

Despite its short lifetime, it can be found in some spring waters and hot springs. Radon is sparingly soluble in water, but more soluble than lighter noble gases. Radon oxides are among the few other reported compounds of radon only the trioxide has been confirmed. Radon carbonyl  $\text{RnCO}$  has been predicted to be stable and to have a linear molecular geometry.

Larger concentrations of  $^{222}\text{Rn}$  are typically associated with granitic rocks that contain elevated concentrations of  $^{238}\text{U}$  (typically ten or more parts per million). Larger than average  $^{222}\text{Rn}$  have also been measured in other  $^{238}\text{U}$  naturally enriched sites such as phosphate bearing rocks. The observably enhanced concentrations of  $^{222}\text{Rn}$  in waters in granite suite of rocks are due to the moving out of radon gas from the parent rock. The solubility coefficient of radon in water is 0.254 at 20 °C. Its occurrence and distribution in groundwater vary among different rock types and can vary considerably within the same geologic formation depending upon mineralogy, uranium content, grain size, permeability, the nature and extent of fracturing in the host rock, and its tectonic history. Rocks such as schist typically contain higher concentrations of

uranium than rocks such as limestone and hence, higher groundwater radon concentrations are expected in schistose rocks.

Radon concentration in groundwater may vary with time because of factors such as dilution by recharge and changes in recharge area due to pumping etc. The seasonal changes may be high or low depending on the factors responsible for enrichment of radon in groundwater. A study on radon concentration in tube wells by Sonkawade et al.(1984) found that de-ionisation of water reduces the radon concentration. Also, the concentration of radon was found to be inversely correlated with the pH value of water samples.

### **6.6.2 Health Hazard**

An internationally prescribed radioactivity exposure limit is one mSv/year. Radiological effects owing to ingestion of dissolved radon in drinking water are defined in terms of effective radiation dose received by the population during habitual consumption of water. A study conducted in USA estimates that 12% of lung cancer deaths (Grans, 1985) are linked to radon (radon-222 and its short-lived decay products) in indoor air. Erlandsson *et al.* (2001) estimated approximately 100 fold lesser risk from exposure to radon in drinking-water.

Radon present dual pathways of exposure for individuals - through drinking water and inhalation of air containing radon released from groundwater. Research on health effect through drinking water pathways is scanty, however considerable research has been done on affect through inhalation. When an individual is exposed to radon the part of the body that receives the highest dose of ionizing radiation is the bronchial epithelium, although the extra thoracic airways and the skin may also receive appreciable doses. In addition, other organs, including the kidney and bone marrow, may receive low doses.

The primary adverse health effect associated with chronic exposure to radon is lung cancer Other harmful respiratory effects associated with chronic exposure to radon include emphysema, pulmonary fibrosis chronic interstitial pneumonia silicosis & respiratory lesions. Radon also has the potential to generate genotoxic effects- higher incidence of chromosomal aberrations.

### 6.6.3 Remedial Measures

There are two principal ways to remove radon from ground water best supplies.

1. *Aeration*: which forces radon from the water to air. It can be highly effective. Bubble plate aeration and diffused bubble aeration as point-of-entry units are capable of achieving removal efficiencies in excess of 99% at loading rates of 185 Bq/l and more (Dixon et al., 1991; Kinner et al., 1993). The low-tech spray jet aeration technique, which is the most practical aeration method for small community water supplies, removes between 50% and 75% of the radon (Dixon et al 1991; Chapman et al., 1990). One concern with aeration is the possibility of creating a large source of air-borne radon.
2. *Adsorption*: through granular activated carbon, with or without ion exchange, can also achieve high radon removal efficiencies (upto 99.7%, depending on the loading rate) (Kinner et al., 1993).

## 6.7 Strontium

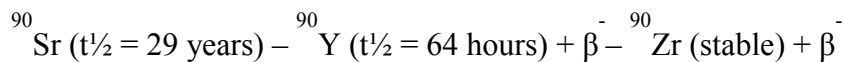
Strontium is a soft, silver-yellow, alkaline-earth metal. It has three allotropic crystalline forms and in its physical and chemical properties it is similar to calcium and barium. Due to its extreme reactivity to air, this element always naturally occurs combined with other elements and compounds. The half-life of  $^{90}\text{Sr}$  is 29 years. Eventually, all of the radioactive strontium will be converted to stable zirconium. Strontium is commonly occurs in nature, forming about 0.034% of all igneous rock and in the form of the sulfate mineral celestite ( $\text{SrSO}_4$ ) and the carbonate strontianite ( $\text{SrCO}_3$ ). Strontium compounds that are water-insoluble can become water-soluble, as a result of chemical reactions. The water-soluble compounds are a greater threat to human health than the water-insoluble ones. Fortunately its concentrations in drinking water are usually quite low.

### 6.7.1 Occurrence & Hydrochemistry:

The most significant strontium mineral is celestite (strontium sulphate,  $\text{SrSO}_4$ ), followed by strontianite (strontium carbonate,  $\text{SrCO}_3$ ). Strontium compounds can be water soluble.

Seawater contains 8 mg/lstrontium on average. River water generally contains about 50 µg/L of strontium and in oyster tissue 10 mg/L of strontium (dry mass) was found.

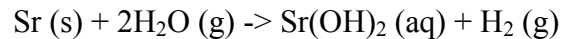
When dissolved in water, strontium mainly occurs as  $\text{Sr}^{2+}$ . The other possible form is  $\text{SrOH}^+$ . Because strontium is an element, its atoms do not degrade by environmental processes such as hydrolysis or biodegradation. However, radioactive strontium is subject to radioactive decay and transformation to other elements. Eventually, all of the radioactive strontium will be transformed into stable zirconium by the process of radioactive decay:



Both radioactive and nonradioactive strontium compounds are subject to both biotic and abiotic transformation mechanisms.

In surface water and groundwater, strontium exists primarily as a hydrated ion. Strontium can form ionic complexes with other inorganic or organic substances. It is relatively mobile in water and reacts with water quicker than calcium and slower than barium.

The following reaction in aqueous solution is applicable:



However, the formation of insoluble complexes or sorption of strontium to soils can reduce its mobility in water. Strontium sorbs to soils by ion-exchange, and tends to be more mobile in soils with a high concentration of exchangeable ions or in soils with low cation exchange capacities.

### 6.7.2 Health Hazards

The human body contains approximately 4.6 mg/kg strontium. It has no specific function, but it is absorbed because of its similar chemistry to calcium. Consequently, the larger part of absorbed strontium is inserted in bones. Strontium is non-toxic and a daily intake of about 0.8-5 mg is harmless, when it only contains non-radioactive strontium. The risk of radioactive strontium intake is mainly based on its carcinogenic and mutagenic mechanism, problems that occur in cell division, and possible increased infant mortality.  ${}^{90}\text{Sr}$  decays to radioactive Yttrium,

which accumulates in hypophysis and ovaries, and subsequently disrupts infant hormonal development, and infant growth. The only strontium compound that is considered a danger to human health, even in small quantities, is strontium chromate. The toxic chromium that it contains mainly causes this. Strontium chromate is known to cause lung cancer, but the risks of exposure have been greatly reduced by safety procedures in companies, so that it is no longer an important health risk

### 6.7.3 Remedial Measures

The removal technologies of strontium are given below

- a) **In situ Chemical Barrier** A pilot study using underground chemical barrier of calcium phosphate, was conducted near Hanford's N Reactor, USA. As radioactive strontium in groundwater flows through the barrier, it binds to the calcium phosphate (also called apatite). This technique is promising.
- b) **Zeolite Treatment Wall** Laboratory and modeling studies were conducted to assess the potential performance of a permeable reactive barrier constructed of a natural zeolite material in a demonstration Project in western New York State, USA. The results of laboratory column tests indicated that the barrier material would be effective at removing strontium from groundwater under natural gradient conditions.

## 6.8 Chromium

Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 mg/kg. Chromium compounds are found in the environment, due to erosion of Chromium-containing rocks and can be distributed by volcanic eruptions. The concentrations range in soil is between 1 and 300mg/kg, in sea water it is 5 to 800 µg/liter, and in rivers and lakes it varies from 26 µg/litre to 5.2 mg/litre. It is a transition element with possible oxidation states from -2 to +6, but only the 0 (elemental), +2, +3 and +6 states are common. Divalent compounds are relatively unstable as they are readily oxidised to the trivalent form. Trivalent compounds are stable and most naturally occurring chromium is in the trivalent (chromic) state. Although hexavalent chromium (chromate) rarely occurs naturally, it is produced from

anthropogenic sources. The pentavalent and tetravalent compounds are generally unstable; an exception is tetravalent chromium in the dioxide,  $\text{CrO}_2$  (widely used in magnetic recording tape).

### 6.8.1 Occurrence and hydrogeochemistry

In India the chromium contamination is reported to be mostly anthropogenic, however at local scale the contamination is geogenic. In Sukinda area, the lateralization process involving oxidation and alternation of the serpentines creates alkaline pore water which facilitates the generation of Cr (VI) from the inert chromites and causes hazardous chromium pollution of water (Godgul and Sahu 1995) in and around the area.

Chromium is an element that primarily exists in trivalent and hexavalent oxidation states. Cr(VI) is far more mobile and toxic than Cr(III) and more difficult to remove in water. The most common Cr(VI) forms are chromate ( $\text{CrO}_4^{2-}$ ) and hydrogen chromate ( $\text{HCrO}_4^-$ ). The relative amount depends on pH. Dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) can also occur. The equilibrium concentration of dissolved Cr (III) in natural water is small as compared to Cr(VI) concentration. In water Cr(III) is mostly in the free-ion form, although these ions associate with hydroxide ions in a pH dependant manner forming  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})_2^+$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_4^-$ . The solid precipitate  $\text{Cr}(\text{OH})_3(\text{s})$  will equilibrate with the dissolved species.  $\text{Cr}^{3+}$  also complexes with organic and inorganic ligands such as  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{CN}^-$ . These are major Cr species found in aqueous solution. At  $\text{pH} < 6$  and  $\text{Eh} > 0.6 \text{ V}$ ,  $\text{HCrO}_4^-$  can also be dissolved in water.

The equilibrium distribution of Cr is in between the two oxidation states Oxidation kinetics depends on a variety of factors and make actual ratio complicated. Kinetics are a function of biochemical conditions, including pH, redox and nutrient levels that govern microbial activity. Cr(VI) is converted to less mobile Cr(III) by reduction reaction.

### 6.8.2 Health Hazards

Water insoluble Chromium (III) compounds and Chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Chromium (VI) have been known for a long time.

Because of the specific transport mechanisms, only limited amounts of Chromium (III) enter the cells. Several *in vitro* studies indicated that high concentrations of Chromium (III) in the cell can lead to DNA damage. Acute oral toxicity ranges between 1.5 and 3.3 mg/kg. The proposed beneficial effects of Chromium (III) and the use as dietary supplements yielded some controversial results, but recent reviews suggest that moderate uptake of Chromium(III) through dietary supplements poses no risk.

The acute toxicity of Chromium (VI) is due to its strong oxidation properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions.

### 6.8.3 Remedial Measures

The various remediation strategies for chromium that have been developed and used are as follows

#### a) *Reduction of Toxicity*

**Chemical Reduction:** It is abiotic in-situ or ex-situ reduction with electron donor such as S, Fe(II) or Fe(0). The Cr (III) thus formed from Cr(VI) then precipitates out of the solution. Ex-situ reduction has high costs as system must include sedimentation or filtration. In-situ reduction is dependent on site specific conditions like pH, permeability, lithology, water depth, concentration of metals in water and salinity.

**Microbial Reduction:** Microorganisms capable of reducing Cr(VI) to Cr(III) include bacteria (Pseudomonas, Micrococcus, Escherchia, Enterobacter, Bacillus, Aeromonas, Achromobacter and Desulfomamaculum), algae, yeasts and fungi. External reduction reaction that are biologically mediated still require the presence of electron donor. such as Fe, Mn, or oxidized organic matter.

**Phyto remediation:** This includes phytoaccumulation, phytostabilisation, phytoextraction and Rhizofiltration. Like biological and chemical reduction, phytoremediation is a multi-faceted approach towards Cr remediation.

**Phytoaccumulation** one of the most common forms of Cr(VI) phytoremediation, consists of the uptake of the Cr from the soil to the plant roots and ultimately into the above ground parts of the plants. Some plants can accumulate very large amounts of a specific metal, such as Cr. The plant, *Leptospermum scoparium* was found to contain soluble Cr in the leaf tissue as the trioxalatochromium(III) ion  $(Cr(Cr_2O_4)_3)^{3-}$ . The function of the chromium-organic acid complex was to reduce the toxicity of the Cr.

**Phytostabilization** Plant and other biological secretions can stabilize Cr in the root zone. These can change pH or complex the Cr as Cr(III). In addition, plant roots minimize erosion and the migration of contaminated sediment. Phytostabilization is most useful for low concentration contamination or large polluted areas, when conventional chemical–physical methods are most expensive. Phytostabilization can be combined with best management practices such as phosphorus amendments, lime, or organic matter to enhance immobilization and avoid leaching.

**Phytoextraction** refers to taking up of Cr as organic material/Cr complexes. Complexation with organics was identified as facilitating Cr availability to plants in lab-scale experiments (Cervantes et al., 2001). The sulfate transport system is apparently involved as it is for bacteria. In most experiments, Cr(VI) is preferentially taken up over Cr(III). Roots take up 10 to 100 times more Cr than shoots and other tissues.

**Rhizofiltration** refers to the uptake of Cr from wastewater by plant roots. Terrestrial plants with long fibrous roots and high surface areas are typically used because sorption onto the surface of roots provides an additional uptake mechanism. Indian mustard seedlings grown in aerated water accumulated Cr(VI) by a factor of 100 to 250 times the concentration in water (Salt et al., 1997). *B. juncea* and *B. nigra* had the highest metal-accumulating ability and Cr had the highest extraction coefficient (followed by cadmium (Cd), nickel (Ni), Zn and Cu) (Kumar et al., 1995). The mechanism(s) for uptake are not yet clear. Neither are the effects of organic matter and other soil amendments on uptake efficiency, possibly owing to the uncertainty associated with the mechanisms of uptake and/or precipitation.

## **b) Removal technologies**



**Ex-situ technologies:**

- Ion-Exchange
- Granular Activated Carbon
- Adsorbents
- Membrane filtration

**In-situ technologies:**

- In situ soil flushing
- Electrokinetics

c) ***Containment technologies*** Containment technologies are used to either physically stop the spreading of groundwater plumes or to chemically immobilize contaminants in a nonexchangeable, insoluble form. Most containment technologies are performed in-situ, with the exception of soil vitrification prior to landfill disposal. Groundwater containment technologies involve the construction of a physical, chemical, or hydraulic barrier that isolates the impacted zone, either directing impacted water through a treatment zone or stopping its migration. Soil contaminants are either physically isolated by a barrier or chemically treated to tightly bind and immobilize contaminants onto the soil.

- Barrier Technologies
- Vitrification
- Solidification

## **6.9 Selenium**

Selenium was first recognized as an element by a Swedish chemist Jons Jacob Berzilius in 1817. It is a metalloid (an element intermediate in properties between the metals and the nonmetals) that is widely distributed throughout the world, but only in small quantities. It

generally occurs uncombined, usually in conjunction with free sulfur. It is more commonly found together with the sulfides as the selenides in ores of such metals as iron, lead, silver, and copper.

### **6.9.1 Occurrence & Hydrogeochemistry**

In its compounds selenium exists in the oxidation states of -2, +2, +4, and +6. It manifests a distinct tendency to form acids in the higher valences. Although the element itself is not poisonous, many of its compounds are extremely toxic. Selenium combines directly with hydrogen, resulting in hydrogen selenide,  $H_2Se$ , a colourless, foul-smelling gas that is poisonous. It also forms selenides with most metals (e.g., aluminum selenide, cadmium selenide, and sodium selenide). Selenite complexes with common soil components such as ferric and aluminium sesquioxides. Selenate does not form such complexes and is easily leached from soil to groundwater.

Acidic and reducing conditions reduce inorganic selenites to elemental selenium, whereas alkaline and oxidizing conditions favour the formation of selenates. Because selenites and selenates are soluble in water, selenium is leached from well-aerated alkaline soils that favour its oxidation. In contrast, elemental selenium and selenides are insoluble in water; therefore, selenium tends to be retained in wet, poorly aerated soils, the reducing conditions of which favour those forms. Thus, selenium in alkaline soils is available for uptake by plants, whereas the availability of selenium in acidic soils tends to be limited by the adsorption of selenites and selenates to iron and aluminium oxide sols (NRC, 1983).

Temperature, moisture, concentrations of water-soluble selenium, the climate, organic matter content and microbial activity determine its mobility. Agriculture not only increase the selenium content in soil; it can also increase selenium concentrations in surface water, as selenium is brought along in irrigation drainage water.

### **6.9.2 Health Hazards**

There is evidence selenium can accumulate in the tissues of organisms and can then be passed up through the food chain. Usually this biomagnification of selenium starts when animals eat a lot of plants that have been absorbing large amounts of selenium. Due to irrigation run-off

concentrations of selenium tend to be very high in aquatic organisms in many areas. When animals absorb or accumulate extremely high concentrations of selenium it can cause reproductive failure and birth defects.

In north western India selenium toxicity has been observed in form of snow white chlorosis in wheat and sugar cane plants and chronic selenosis in animals and human beings. The most consistent clinical manifestation indicated by animals is losing body condition and loss of hair, necrosis of the tip of the tail, reluctance to move, stiff gate, overgrowth of hoof followed by development of cracks and abnormalities in horn growth. Complaints of premature abortion have also been recorded.

Exposure to Selenium in humans takes place either through food or water with typical symptoms like loss of finger toe nails and hair and progressive deterioration of health. Majority of the population complained of nausea, headache and also exhibited tooth decay, staining of teeth and nails with brittleness and longitudinal streaks.

### **6.9.3 Remedial Measures**

Several techniques may be used to reduce the level of selenium from drinking water:

1. Ion exchange,
2. Activated alumina (AA),
3. Reverse osmosis (RO), and
4. Distillation.

Ion (anion) Exchange can reduce selenium by 90-95%, where the selenate ion is strongly preferred. Although Se (IV) is more difficult to oxidize as compared to As (III) which is oxidized to As (V), this can readily be accomplished with free chlorine. The optimal rate of oxidation is found to be between pH 6.5 and 8.0 where Se (IV) can be converted to Se (VI) within 5 minutes at a free chlorine concentration of 2 mg/l. At pH 9.0, only 15% of the Se (IV) has been found to be converted with 2 mg/L of free chlorine. Pure oxygen was found to be ineffective at oxidizing

Se (IV) to Se (VI). Other techniques used for selenium removal include distillation (> 98% reduction), reverse osmosis (RO) (> 90% reduction), and activated alumina (85-95% reduction).

### **Pilot Trial Cases**

Chemical clarification with lime, ferric sulfate or aluminum sulfate and activated carbon adsorption are moderately effective in removing selenite from water and ineffective at removing selenate. (Culp/Wesner/Culp, 1986).

Selenium adsorbed onto iron oxide-coated sand. Practically complete removal of Se (IV) from a 10 mg/L solution in contact with 100 gm/L coated sand was achieved within 10 min, whereas Se(VI) removal required about 90 min (Lo & Chen, 1997). Similar results were reported using aluminium oxide-coated sand, although the adsorption capacities were lower (Kuan et al., 1998).

Pilot plant trials:It is reported that activated alumina adsorption using Alcoa F-1 can lead to selenium removals of 98% at pH 5 (Flemming, 1986).

Cellulose acetate and cellulose triacetate membranes were effective at removing both selenite and selenate; removals in excess of 95% were achieved (Huxstep & Sorg, 1987). A 95% removal of selenium was achieved by nanofiltration of highly contaminated agricultural drainage water during laboratory studies (Kharaka et al., 1996)



## 7.0 A NOTE ON NITRATE

Nitrate, the end products of the biologic nitrification process, is the most ubiquitous chemical contaminant in the world's aquifers and the concentration levels are increasing. The distribution of  $\text{NO}_3^-$  in groundwater is controlled by a number of factors. They include source availability, thickness and composition of the vadose zone, precipitation, irrigation, ground water flow, aquifer heterogeneity, dissolved oxygen concentrations and electron donor availability and dispersion. Examples of nitrogen compounds found in naturally occurring waters include ammonia ( $\text{NH}_3$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), and the ammonium ion ( $\text{NH}_4^+$ ). Nitrogen is also found in many organic compounds such as proteins and protein derivatives including purines and pyrimidines, and urea. Generally, inorganic nitrogen salts are quite soluble in natural waters.

### 7.1 Occurrence and Hydrogeochemistry

Molecular, atmospheric nitrogen may be transformed into organic nitrogen by nitrogen fixing bacteria and algae. Therefore, natural waters may contain dissolved nitrogen gas ( $\text{N}_2$ ), ammonia ( $\text{NH}_3$ ), in addition to ionic forms such as ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ) as well as organic nitrogen compounds. Sources of ammonia include decomposition of dead plant and animal material, release from organic soils, and complex photochemical reactions in the lower atmosphere. Rainfall generally contains larger amounts of ammonia than oxides of nitrogen.

Elemental nitrogen occurs as a diatomic molecule  $\text{N}_2$ . Gaseous nitrogen is considered inert chemically. Ammonia is highly soluble in water. When ammonia reacts with water, it forms ammonium and hydroxide ions. Nitrite nitrogen is a rather unstable nitrogen species which will generally be reduced or oxidized. Nitrate nitrogen is quite soluble in water and is not significantly absorbed by clay-rich soils. It represents the stable end product of the nitrification process. Nitrates are quite stable unless they are biologically denitrified under anaerobic conditions or taken up by plants. In the absence of oxygen, nitrates may be reduced to nitrites by heterotrophic bacteria. This process is called denitrification, and the end product is molecular nitrogen.

Most of the ground water samples with elevated nitrate concentrations were in direct or indirect hydraulic continuity with decaying plant or animal material, agricultural fertilizers, domestic sewage, areas of high density animal confinement, or geologic materials containing soluble nitrogen compounds. Nearly all the reported cases of excessive nitrate build-ups in shallow ground waters appear to be related to the downward leaching of nitrogen by surface water. The downward leaching of surface water requires a relatively open geologic profile between the ground surface and the water table. Once the nitrates reach the water table, they generally form a thin layer (usually <3m) capping the shallow ground water body. Literature survey indicates that deep wells (>150 m) show little or no evidence of nitrate contamination. Most of the reported instances of nitrate contamination appear to be related to irrigated agriculture and the use of chemical fertilizers or to domestic sewage.

Non-agricultural sources cannot affect the aquifers regionally, however, locally they can cause nitrate pollution (Hudak 1999). In India, higher  $\text{NO}_3$  concentration in ground water has been reported from different hydrogeological terrain (Somasundaram et. al., 1993, Namade and Srivastava 1997, Datta et. al., 1997). Nitrate contamination in the ground water of the Gangetic plains has been extensively studied by various workers such as Handa (1983), Pandey and Mukherjee (1994) and Saha et. al(2008).

Nitrate and nitrite anions are not absorbed by clay soils because both the soil particles and the anions have a negative charge. The ammonium ion however, carries a positive charge and is adsorbed on the surface of negatively charged soil particles. Ammonium ions electrostatically bound to negatively charged clay particles may be oxidized via the action of microorganisms, and resulting negatively-charged nitrite or nitrate ions are then free to migrate with the percolating soil waters. Nitrate reported in a chemical analysis would include nitrate originally present in the water but, also, could include oxidized ammonia, ammonium, and nitrite originally present. Ammonium has been found in thermal waters, and, unless proper sampling and analysis techniques are used, will tend to oxidize and be reported as nitrate.

Contribution of bedrock nitrogen to nitrate concentrations in water has been recognized by many investigators (Mansfield and Boardman, 1932; Power and others, 1974; Boyce and others, 1976; Holloway and others, 1998). Ammonium-bearing aluminosilicate minerals have

been identified in a number of geologic settings worldwide. Little is known regarding the influence of ammonium-bearing bedrock on soil and water quality (Holloway and Dahlgren, 1999). Nitrogen exists in rock as relict organic matter associated with sedimentary rock or as ammonium substituting for potassium in sedimentary, igneous, and metamorphic rock (Stevenson, 1962). Sedimentary rocks that form in an organic-rich depositional environment can include nitrogen as residual organic matter or as ammonium minerals (Holloway and others, 1998). Coal deposits are a geologic regime with notable occurrences of geologic nitrogen. On a localized scale, release of nitrogen through weathering of nitrogen-bearing rock can potentially affect the quality of water and soil (Holloway and others, 1998). Geologic nitrogen can also be affected by biological processes. Biochemical transformation can influence the release of nitrogen in bedrock to streams and ground water (Holloway and Dahlgren, 1999). Natural nitrate is also associated with sediments typical of arid environments such as playa lake, alluvial-fan, and braided-stream deposits, primarily associated with atmospheric nitrogen.

## **7.2 Health Hazards**

Ingestion of  $\text{NO}_3$  in drinking water has caused met-hemoglobinemia in infants under 6 month of age. This disease is caused by the bacterial reduction of nitrate to nitrite in the intestinal tract. The nitrite then enters the blood-stream and combines with the hemoglobin to form methemoglobin, which reduces the blood's capacity to transport oxygen. Severe met-hemoglobinemia may result brain damage and death. Prolonged intake of high level of nitrate is linked to gastric problems due to the formation of nitrosamines in adult human. Nitrosamines compounds have been shown to cause cancer in test animals.

## **7.3 Remedial Measures**

For removal of nitrate both non-treatment techniques like blending and treatment processes such as ion-exchange, reverse osmosis, biological denitrification and chemical reduction are useful. The most important thing is that neither of these methods is completely effective in removing all the nitrogen from the water.

**a) *Methods involving no treatment:*** In order to use any of these options the nitrate problem must be local-scale. Common methods are –



- i) Raw water source substitution
- ii) Blending with low nitrate waters
- iii) Connection to an existing regional system
- iv) Organizing a regional system

This greatly reduces expenses and helps to provide safer drinking water to larger numbers of people.

***b) Methods involving Treatment:***

They are as follows

- Adsorption/Ion Exchange
- Reverse Osmosis
- Electrodialysis
- Bio-chemical Denitrification (By using denitrifying bacteria and microbes)\
- Catalytic Reduction/Denitrification (using hydrogen gas or formic acid)

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**Annexure-I**

**State wise names of the districts (partly affected) from where ground water contamination (Fluoride, Nitrate, Arsenic, Iron,Salinity and Trace elements) have been reported**

S. No.	State/UT	Fluoride (above 1.5 mg/l)	Nitrate (above 45 mg/l)	Arsenic (above 0.05 mg/l)	Iron (above 1.0 mg/l)	Salinity	Trace elements
1.	Andaman& Nicobar				Andaman		
2.	Andhra Pradesh	Adilabad, Anantpur, Chittoor, Guntur, Hyderabad, Kadapa, Karimnagar, Khammam, Krishna, Kurnool, Mahabubnagar, Medak, Nalgonda, Nellore, Prakasam, Rangareddy, Visakhapatnam, Vizianagaram, Warangal, West Godavari	Adilabad, Anantpur, Chittoor, Cuddapah, East Godavari, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mahabubnagar, Medak, Nalgonda, Nellore, Nizamabad, Prakasam, Ranga Reddy, Srikakulam, Visakhapatnam, Vizianagaram, Warangal, West Godavari		Adilabad, Chittoor, Cuddapah, Guntur, Hyderabad, Karimnagar, Krishna, Kurnool, Mahabubnagar, Medak, Nalgonda, Nellore, Nizamabad, Ranga Reddy, Vishakhapatnam	Adilabad, Ananthapur, Chittoor, East-Godavari, Guntur, Kadapa, Karim Nagar, Khammam, Krishna, Kurnool, Medak, Mehboob Nagar, Nalgonda, Nellore, Nizamabad, Prakasam, Srikakulam, Visakhapatnam, Warangal, West-Godavari	Se- in parts of Ranga Reddy district (by Purushotham et al) U-Nalgonda (brindha etal,2011 Sr-Maheshwaram Watershed,Ranga Reddy District U-Cuddapah dist, Chandagiri dst, Tirupati,Nayadupet,Chitto or, Nellore(by AMD)
3.	Assam	Goalpara, Kamrup, Karbi Anglong, Naugaon, Golaghat, Karimganj		Sivsagar, Jorhat, Golaghat, Sonitpur, Lakhimpur, Dhemaji, Hailakandi, Karimganj, Cachar, Barpeta,	Cachar, Darrang, Dhemaji, Dhubri, Goalpara, Golaghat, Hailakandi, Jorhat, Kamrup, Karbi Anglong, Karimganj, Kokrajhar, Lakhimpur, Morigaon, Nagaon,		



				Bongaigaon, Goalpara, Dhubri, Nalbari, Nagaon, Morigaon, Darrang & Baksha	Nalbari, Sibsagar, Sonitpur		
4.	Bihar	Aurangabad, Banka, Bhagalpur, Gaya, Jamui, Kaimur( Bhabua), Munger, Nawada, Rohtas Sheikhpura, Nalanda, Lakhisarai	Aurangabad, Banka, Bhagalpur, Bhojpur, Darbhanga, Kaimur(Bha bua), Patna, Rohtas, Saran, Siwan	Begusarai, Bhagalpur, Bhojpur, Buxar, Darbhanga, Katihar, Khagaria, Kishanganj, Lakhisarai, Munger, Patna, Purnea, Samastipur, Saran, Vaishali	Aurangabad, Begusarai, Bhojpur, Buxar, East Champan, Gopalganj, Katihar, Khagaria, Kishanganj, Lakhisarai, Madhepura, Muzaffarpur, Nawada, Rohtas, Saharsa, Samastipur, Siwan, Supaul, West Champan		
5.	Chhattisgarh	Bastar, Bilaspur, Dantewada, Dhamtari, Janjgir-Champa, Jashpur, Kanker, Korba, Koriya, Mahasamund, Raipur, Rajnandgaon, Surguja	Bastar, Bilaspur, Dantewada, Dhamtari, Jashpur, Kanker, Kawardha, Korba, Mahasamund, Raigarh, Raipur, Rajnandgaon	<i>Rajnandgaon</i>	Bastar, Dantewada, Kanker, Koriya,	Durg, Bilaspur, Kawardha, Janjgir Champa, Raigarh and Raipur	U –Bastar, Dantewada,Raigarh,Mah asamund(by AMD)
6.	Delhi	East Delhi, New Delhi, North West Delhi, South Delhi, South West Delhi, North Delhi, West Delhi	East Delhi, Central Delhi, New Delhi, North Delhi, North West Delhi, South Delhi, South West			New Delhi, North , South, East, West, North West, South West	

			Delhi, West Delhi				
7.	Goa				North Goa, South Goa		
8.	Gujarat	Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Junagadh, Kachchh, Mehesana, Narmada, Panchmahals, Patan, Porbandar, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara	Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Jamnagar, Junagadh, Kachchh, Kheda, Mehesana, Narmada, Navsari, Panchmahals, Patan, Porbandar, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara		Ahmedabad, Banaskantha, Bhavnagar, Kachchh, Mehesana Narmada,	Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Jamnagar, Junagadh, Kachchh, Kheda, Mahesana, Navsari, Patan, Porbandar, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara, Narmada	
9.	Haryana	Bhiwani, Faridabad, Fatehabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Karnal, Kurukshetra, Mahendergarh, Panchkula, Panipat, Rewari, Rohtak, Sirsa, Sonapat, Yamuna Nagar	Ambala, Bhiwani, Faridabad, Fatehabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Karnal, Kurukshetra, Mahendargarh, Panchkula, Panipat, Rewari, Rohtak, Sirsa, Sonipat, Yamuna Nagar	Ambala, Bhiwani, Faridabad, Fatehabad, Hissar, Jhajjar, Jind, Karnal, Panipat, Rohtak, Sirsa, Sonapat, Yamunanagar.	Ambala, Bhiwani, Faridabad, Fatehabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Karnal, Kurukshetra, Mahendargarh, Panipat, Rohtak, Sirsa, Sonipat, Yamuna Nagar	Ambala, Bhiwani, Faridabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Karnal, Mohendragarh, Panipat, Rewari, Rohtak, Sirsa, Sonapat	U-Mahendragarh(by AMD)
10.	Himachal Pradesh		Una, Solan, Hamirpur, Kangra, Mandi, Kullu				U- Kumaon Rn-Palampur & Dalhousie stations in Kangra & Champa valley

							(Virk et al,2000),Kasol(KUlu district) U-Una(by AMD)
11.	Jammu & Kashmir	Rajaori, Udhampur	Jammu, Kathua, Anantnag, Kupwara		Baramulla, Budgam, Kathua, Kupwara, Pulwama, Srinagar		
12.	Jharkhand	Bokaro, Giridih, Godda, Gumla, Palamu, Ramgarh, Ranchi	Chatra, Garhwa, Godda, Gumla, Lohardaga, Pakur, Palamu, Paschimi Singhbhum, Purbi Singhbhum, Ranchi, Sahibganj	Sahebganj	Chatra, Deoghar, East Singhbhum, Giridih, Ranchi, West Singhbhum		
13.	Karnataka	Bagalkot, Bangalore, Belgaum, Bellary, Bidar, Bijapur, Chamarajanagar, Chikmagalur, Chitradurga, Davanagere, Dharwad, Gadag, Gulburga, Hassan, Haveri, Kolar, Koppal, Mandya, Mysore, Raichur, Tumkur	Bagalkot, , Bangalore, Belgaum, Bellary, Bidar, Bijapur, Chamrajnagar, Chikmagalur, Chitradurga, Davanagere, Dharwad, Gadag, Gulburga, Hassan, Haveri, Kodagu, Kolar, Koppal, Koorg, Mandya, Mysore, Raichur. Shimoga, Tumkur, Udupi, Uttar Kannada		Bagalkot, Bangalore, Belgaum, Bellary, Bidar, Bijapur, Chikmagalur, Chitradurga, Dakshina Kannada, Davanagere, Gulburga, Hassan, Haveri, Kodagu, Kolar, Koppal, Mysore, Raichur, Shimoga, Tumkur, Udupi, Uttar Kannada	Bagalkote, Bangalore-Rural, Bangalore-Urban, Belgaum, Bellary, Bijapur, Chamarajnagara, Chikballapur, Chikmagalur, Chitradurga, Dakshina Kannada, Davanagere, Dharwad, Gadag, Gulburga, Hassan, Haveri, Kodagu/ Coorg, Kolar, Koppal, Mandya, Mysore, Raichur, Ramanagara, Shimoga, Tumkur, Udupi, Uttara	u-Kolar (Sridhar Babu et al), Chikmagalur Gulbarga(by AMD)

						Kannada, Yadgi	
14.	Kerala	Palakkad, Alappuzha, Idukki, Ernakulam, Thiruvananthapuram.	Alappuzha, Idukki, Kollam, Kottayam, Kozhikode, Malappuram, Palakkad, Pathanamthitta, Thiruvananthapuram, Thrissur, Wayanad		Alappuzha, Ernakulam, Idukki, Kannur, Kasaragod, Kollam, Kottayam, Kozhikode, Malappuram, Palakkad, Pathanamthitta, Quilon, Thiruvananthapuram, Thrissur, Wayanad	Trivandrum, Kollam, Kottayam, Ernakulam	
15.	Madhya Pradesh	Alirajpur, Balaghat, Barwani, Betul, Bhind, Chhatarpur, Chhindwara, Datia, Dewas, Dhar, Dindori, Guna, Gwalior, Harda, Jabalpur, Jhabua, Khargon, Mandla, Mandsaur, Morena, Narsinhpur, Rajgarh, Satna, Sehore, Seoni, Shahdol, Shajapur, Sheopur, Sidhi, Singrauli, Ujjain, Vidisha	Alirajpur, Anuppur, Ashok Nagar, Balaghat, Barwani, Betul, Bhind, Bhopal, Burhanpur, Chhatarpur, Chhindwara, Damoh, Datia, Dewas, Dhar, Dindori, Guna, Gwalior, Harda, Hoshangabad, Indore, Jabalpur, Jhabua, Katni, Khandwa, Khargon, Katni, Mandla, Mandsaur, Morena, Narsimhapur, Neemuch, Panna,		Balaghat, Barwani, Betul, Bhind, Bhopal, Chhatarpur, Chhindwara, Damoh, Datia, Dewas, Dhar, Dindori, Guna, Gwalior, Hoshangabad, Indore, Jabalpur, Jhabua, Khandwa, Katni, Mandla, Mandsaur, Narsinghpur, Neemuch, Panna, Raisen, Rajgarh, Ratlam, Rewa, Sagar, Satna, Sehore, Seoni,	Balaghat, Bhind, Chhatarpur, Gwalior, Indore, Jhabua, Khargone, Morena, Neemuch, Ratlam, Rewa, Satna, Sehore, Sheopur, Shivpuri, Ujjain	U-Seoni, Betul(AMD)

			Raisen, Rajgarh, Ratlam, Rewa, Sagar, Satna, Sehore, Seoni, Shahdol, Shajapur, Sheopur, Shivpuri, Sidhi, Singrauli, Tikamgarh, Ujjain, Umaria, Vidisha		Shahdol, Shajapur, Shivpuri, Sidhi, Tikamgarh, Ujjain, Umaria, Vidisha, East Nimar		
16.	Maharashtra	Amravati, Beed, Chandrapur, Bhandara, Dhule, Gadchiroli, Gondia, Jalna, Nagpur, Nanded, Ratnagiri, Sindhudurg, Yavatmal	Ahmednagar, Akola, Amravati, Aurangabad, Beed, Bhandara, Buldana, Chandrapur, Dhule, Gadchiroli, Gondia, Hingoli, Jalgaon, Jalna, Kolhapur, Latur, Mumbai, Nagpur, Nanded, Nandurbar, Nasik, Osmanabad, Parbhani, Pune, Sangli, Satara, Solapur, Wardha, Washim, Yavatmal		Ahmednagar, Amravati, Beed, Buldana, Chandrapur, Dhule, Gadchiroli, Jalna, Kohlapur, Latur, Nandurbar, Nashik, Osmanabad, Parbhani, Ratnagiri, Satara, Thane, Wardha, Washim, Yavatmal	Ahmednagar, Akola, Amravati, Aurangabad, Beed, Bhandara, Buldhana, Chandrapur, Dhule, Jalgaon, Jalna, Nagpur, Nasik, Pune, Raigard, Sangli, Satara, Solapur, Thane, Yavatmal	
17.	Manipur			Bishnupur, Thoubal	Bishnupur, Thoubal		
18.	Meghalaya				East Garo Hills, East Khasi Hills, Jaintia Hills		
19.	Orissa	Angul, Balasore, Bargarh, Bhadrak,	Angul, Balasore, Bargarh, Bhadrak,		Balasore, Bargarh, Bhadrak, Cuttack,	Balasore, Bhadrak, Ganjam, Jagatsingpur,	Chromium (Hexavalent) - Sukinda valley in

		Baudh, Cuttack, Deogarh, Dhenkanal, Jajpur, Keonjhar, Khurda, Mayurbhanj, Nayagarh, Nawapara, Sonpur	Bolangir, Baudh, Cuttack, Deogarh, Dhenkanal, Gajapati, Ganjam, J.Singhpur, Jajpur, Jharsuguda, Kalahandi, Kendrapara, Keonjhar, Khurda, Koraput, Malkangiri, Mayurbhanj, Nawapada, Nayagarh, Phulbani, Puri, Sambalpur, Sundergarh, Sonpur		Deogarh, J.Singhpur, Jajpur, Jharsuguda, Kalahandi, Kandmahal, Keonjhar, Kendrapara, Khurda, Koraput, Mayurbhanj, Nayagarh, Puri, Rayagada, Sambalpur, Sundergarh, Sonpur	Jajpur, Kendrapara, Puri	Sukinda block of Jajpur District Mn-Khurda
20.	Punjab	Amritsar, Barnala, Bhatinda, Faridkot, Fatehgarh Sahib, Firozpur, Gurdaspur, Jalandhar, Ludhiana, Mansa, Moga, Muktsar, Patiala, Ropar, Sangrur, Tarn-Taran	Amritsar, Barnala, Bhatinda, Faridkot, Fatehgarh Sahib, Firozpur, Gurdaspur, Hoshiarpur, Jalandhar, Kapurthala, Ludhiana, Mansa, Moga, Muktsar, Nawan Shahr, Patiala, Ropar, Rupnagar, Sangrur, Tarn-Taran	Mansa, Amritsar, Gurdaspur, Hoshiarpur, Kapurthala, Ropar.	Bhathinda, Faridkot, Fatehgarh Sahib, Firozpur, Gurdaspur, Hoshiarpur, Mansa, Rupnagar, Sangrur	Bhatinda, Faridkot, Ferozpur, Gurudaspur, Mansa, Moga, Muktsar Patiala, Sangrur	Se in Nawanshahar ,Hoshiarpur (Dhillon and Dhillon,1991and2003),Taran Taran district(Dept. of Water Supply and Sanitation, Govt. of Punjab) U-Moga, Barnala,Bathinda,Ferozpur,Ludhiana,Sangrur and Fazilka* * Source not identified Rn-Bathinda & Gurdaspur (Virk et al,2001)

21.	Rajasthan	Ajmer, Alwar, Banswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chittaurgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajsamand, Sirohi, Sikar, Sawai Madhopur, Tonk, Udaipur	Ajmer, Alwar, Banswara, Baran, Barmer, Bundi, Bharatpur, Bhilwara, Bikaner, Chittaurgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhalawar, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Partapgarh, Rajsamand, Sirohi, Sikar, Swai Madhopur, Tonk, Udaipur		Ajmer, Alwar, Banswara, Baran, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chittaurgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhalawar, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Pratapgarh, Rajsamand, Sikar, Sawai Madhopur, Sirohi, Tonk, Udaipur	Ajmer, Alwar, Baran, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chittorgarh, Churu, Dausa, Dhaulpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhalawar, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajsamand, Sawai-Madhoper, Sikar, Sirohi, Tonk, Udaipur	U- Nagaur, Jodhpur, Pali and Sikar(AMD)
22.	Sikkim						Rn-Swastik Burtu village near Gangtok
23.	Tamil Nadu	Coimbatore, Dharmapuri, Dindigul, Erode, Karur, Krishnagiri, Namakkal, Perambalur, Pudukotai, Ramanathanpuram, Salem, Sivagangai, Theni, Thiruvannamalai, Tiruchirapally, Thirunelveli, Vellore,	Chennai, Coimbatore, Cuddalore, Dharmapuri, Dindigul, Erode, Kancheepuram, Kanyakumari, Karur, Madurai, Namakkal, Nilgiris, Perambalur, Pudukotai,		Namakkal, Salem	Chennai, Coimbatore, Cuddalore, Dharampuri, Dindigul, Kancheepuram, Karur, Nagapattinam, Namakkal, Perambalur, Pudukkottai, Ramnathapuram, Salem, Sivaganga, Thanjavur, Theni, Thiruvallur, Tirunelveli, Trichchirappalli,	Manganese: Tiruvallur, Kancheepuram, Vellore, Cuddalore, Dindigul, Erode, Tiruppur

		Virudhunagar	Ramanathanpuram, Salem, Sivagangai, Theni, Thiruvannamalai, Thanjavur, Tirunelveli, Thiruvallur, Trichy, Tuticorin, Vellore, Villupuram, Virudhunagar			Tuticorin, Vellore, Villupuram, Virudhunagar	
24.	Tripura				Dhalai, North Tripura, South Tripura, West Tripura,		
25.	Uttar Pradesh	Agra, Aligarh, Etah, Kashiram Nagar,, Firozabad, Jaunpur, Mahamaya Nagar, Mainpuri, Mathura, Mau, Sonbhadra, Varanasi and Unnao	Agra, Aligarh, Allahabad, Ambedkar Nagar, Auraiya, Azamgarh, Badaun, Baghpat, Balrampur, Banda, Barabanki, Bareilly, Basti, Bijnor, Bulandsahr, Chitrakoot, Etah, Etawah, Fatehpur, Firozabad, GB Nagar, Ghaziabad, Ghazipur, Hamirpur, Hardoi, Hathras, Jaunpur, Jhansi, Kannauj, Kanpur Dehat, Lakhimpur, Mahoba,	<i>Bahraich, Balia, Balrampur, Bareilly, Basti, Bijnor, Chandauli, Ghazipur, Gonda, Gorakhpur, Lakhimpur Kheri, Meerut, Mirzapur, Muradabad, Rai Bareilly, Sant Kabir Nagar, Shajahanpur, Siddarthnagar, Sant Ravidas Nagar, Unnao</i>	Azamgarh, Ballia, Balrampur, Etawah, Fatehpur, Gazipur, Gonda, Hardoi, Kanpur Dehat, Kanpur Nagar, Lakhimpur, Lalitpur, Mau, Siddartnagar, Unnao	Agra, Aligarh, Firozabad, Hamirpur, Kashganj, Kanpur Nagar, Mathura, Rae Bareli, Unnao	Manganese: Lakhimpur, Hardoi, Badaun and Kushinagar



			Mathura, Meerut, Mau, Moradabad, Muzaffarnagar, Mirzapur, Raebarelli, Rampur, Sant Ravidas Nagar, Shajahanpur, Sitapur, Sonbhadra, Sultanpur, Shravasti, Siddarth Nagar, Unnao				
26.	Uttarakhand		<i>Dehradun, Haridwar, Udham Singhnagar</i>				Ra in Dehradun city(Ramola et al, 1999)
27.	West Bengal	Bankura, Bardhaman, Birbhum, Dakshindinajpur, Malda, Nadia, Purulia, Uttardinaajpur, South 24 Praganas	<i>Bankura, Bardhaman</i>	<i>Bardhaman, Hooghly, Howrah, Malda, Murshidabad, Nadia, N-24 Parganas, S- 24 Parganas</i>	Bankura, Bardhaman, Birbhum, Dakshindinajpur, E. Midnapur, Howrah, Hugli, Jalpaiguri, Kolkatta, Murshidabad, N-24 Parganas, Nadia, S-24 Parganas, Uttardinaajpur, West Midnapur	Howrah, N 24 Parganas, Purba Medinipore, S 24 Parganas	Manganese : isolated pockets of North and South 24 Parganas, Murshidabad, Nadia and Malda U- Purulia(by AMD)



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