CHAPTER-II

REVIEW OF LITERATURE
The assessment of the water quality involves a careful examination of the delicate interface between Physics, Chemistry and Biology. The biological methods show the degree of ecological imbalance, whereas the chemical methods measure the concentration of the pollutants. The assessment and evaluation, as well as devising methods for abatement of pollution, require a study of these three components (Rana and Palria, 1998).

The international and national contributions on the study of quality of the water, vis a vis Physico-chemical and heavy metal contamination of the water sources are enumerated below. A review of the detailed literature on this subject provides an insight into the deterioration of the water quality in the surface and groundwater sources.

**International findings**

Ishaku and Ezeigb (1979) investigated the seasonal variation in heavy metal contamination of groundwater in the Jimeta- Yola area was investigated. The objectives of the study were to determine the seasonal variation in heavy metal contamination and to determine the influence of anthropogenic activities on heavy metal contamination. Groundwater samples were collected from hand-dug wells and boreholes between the dry season and rainy season periods. The water samples were analyzed using the DR/2010 spectrophotometer, TDS/conductivity meter and membrane filtration method. The results revealed that chromium hexavalent and copper enrichment occurred in the rainy season in the order of Cr+6.
Maroof et al (1986) studied the concentrations of Calcium and Zinc in different drinking water supplies of Dhaka City, Bangladesh. They reported that the concentration of Cadmium was below the detection limit (51 micrograms per litre) in source water. A range of 1.03 to 1.58 and 1.71 to 2.24 ppb, in supply water (tap water and tube well water) respectively and that the corresponding Zinc content ranged from 0.013 to 0.30, 0.018 to 3.8 and 0.042 to 0.37 mg/L.

Thomas et al (1986) reported that the waste water from a disposal site at Koszalim, in Poland, to be the cause of increased groundwater pollution, particularly by heavy metals and that a decrease in the concentrations of Zinc, Copper, Lead and Manganese in the effluents during certain period was reflected in the lower levels of their concentrations in the ground water.

Langanegger (1987) studied the groundwater quality in Accra of Ghana. He reported that apart from the igneous and metamorphic rocks, the aquifer materials in these plains contained micas, hornblende and feldspar, which might be responsible for high concentrations of Lead, Chromium in the ground water and that the galvanized pump parts contributed significantly to the amount of Iron in the moderately to highly corrosive ground water aquifers.

Pelig Ba et al (1998) measured the concentrations of Mercury, Lead, Copper, Zinc, Cadmium, Iron, Manganese, Chromium and Arsenic in the ground water from the upper west and upper east region and the Accra plains in Ghana. He found that the mean Cd, Mn and Cu concentrations for all the study areas fell within the WHO limits, whereas the values of Pb, Cr and Fe exceeded the WHO limits for drinking water. From the available chemical data of rocks in the area he
the suggested and that the local bedrock was the dominant source of the trace elements found in the ground water.

Middelkoop. (2000) was found the spatial variability of heavy metal on floodplains of the lower Rhine river in the Netherlands contain large amounts of heavy metals, which is a result of many years of deposition of contaminated overbank sediments. The metal pollution varies greatly between the various floodplain sections as well as in vertical direction within the floodplain soil profiles. The lowest metal pollution is found in the distal parts of floodplain sections with low flooding frequencies, where average sedimentation rates have been less than about 5 mm/a. The largest metal accumulations occur in low-lying floodplain sections where average sedimentation rates have been more than 10 mm/a.

Jensen et al (2000) evaluated the quality of groundwater at scrap recycling localities in Denmark. They reported that 25 years of this anthropogenic activity elevated the concentration of metals such as Zinc and Cadmium in the soil and soil water, upto 3 m below the ground surface. They found low pH values, presumably caused by disposal of car batteries. They pointed out that the risk of metal migration in the groundwater was limited as long as the pH remains high, above 6.5

Lee et al (2005) evaluated variations in heavy metal contamination of stream waters and ground waters. Results of an exploratory investigation of stream waters in 2000 indicated substantial contamination with heavy metals
including zinc (Zn), iron (Fe) and arsenic (As) for at least 6 km downstream from the mine. The decreases in the heavy metals contents in the groundwaters associated with reduced rainfall were quite different from the increases observed for the stream waters.

Nouri et al. (2006) evaluated regional pattern of heavy metal concentrations and agricultural activities in the southern Iran. Analyzed with the flame atomic absorption spectrometry and Cu, Zn and Ni concentrations have been shown below the EPA standards respectively, but Cd concentrations of all the samples were recorded higher than EPA standards. The heavy metals concentrations is more pronounced in the south part than northern part of the studied area. Absent confining layers, proximity to land surface, excess agricultural and industrial activities in the south part and ground water flow direction that is generally from north to south parts in this area makes south region of Shush plain especially vulnerable to heavy metals pollution and other contaminants.

Cempel and Nikel (2006) conducted experiments on toxicity of nickel on humans as well as animals. They found that nickel in the air, water and food causes health risks. The toxicity and carcinogenicity of some nickel compounds (in the nasal cavity, larynx and lungs) in experimental animals, as well as in the occupationally exposed population as summarize the current overview of the occurrence and sources of nickel in the environment, and the effect of this metal and its compounds on living organisms.
Nasrullah et al. (2006) conducted the analysis of pollution load in industrial effluent and ground water. The results obtained from heavy metals determination in Industrial effluents showed that all the results of ground water were compared with US-EPA and WHO standards, from the findings it was concluded that all ground water samples were safe for drinking purpose.

Tariq et al. (2006) analysed the heavy metal contamination in various industrial effluents of Hayatabad industrial Estate (HIE) at Peshawar in Pakistan. They studied a total of 12 samples including 7 from industrial effluents at the discharge point of each industry, 1 from main drain receiving effluents of all industries and 4 from tube or dug wells in the Vicinity of the Estate. They reported that the characteristics of effluents varied with the industry; Cadmium, Chromium, Copper, Manganese, Nickel and Lead were above the permissible limits; varying results were also obtained for various parameters in the underground water samples; the pH, TSS, TDS, Iron and Zinc were within the permissible limits in all, but Cadmium, Chromium, Copper, Manganese, Nickel and Lead were above the permissible limits in one or more water samples compared with the WHO and US-EPA standards established for drinking water.

Salmasi and Tavassoli (2006) aimed to find out ground water pollution of south of Tehran because of ten years irrigation with Ni, Cd and Pb borne waste water. Heavy metal concentrations (Pb, Cd and Ni) were measured by atomic absorption spectrophotometer by use of HNO3 4N solution. They determined that, because of high sorption capacity of these elements to soils, these metals were accumulated in surface layer of the soils.
Suman et al (2006) analyzed water samples from Leachate and groundwater for various physico-chemical parameters including heavy metal (Cd, Cr, Cu, Fe Ni, Pb and Zn) concentration and microbiological parameters. Total coliform (TC) and faecal coliform (FC) were determined in groundwater and leachate samples. Results, likely indicate that groundwater quality is being significantly affected by leachate percolation.

Singh (2006) was assessed the levels of heavy metal like arsenic, fluoride, iron, nitrate, cadmium, copper, lead, nickel and zinc were detected at elevated levels in drinking water of north-eastern states. These chemical constituents enter into the water and cause pollution of surface water and groundwater. These metals also destroy the ecosystem in which they enter.

Duruibe et al (2007) explained about some heavy metals having bio-importance as trace elements and the biotoxic effects of many of them in human biochemistry. Poisoning and toxicity in animals occur frequently through exchange and co-ordination mechanisms.

Gobel et al (2007) studied the degradation of groundwater near roads, sidewalks, commercial and residential structures in Munster, Germany and reported that the quality of surface water, seepage water and groundwater was influenced by the pollutants that collected on the impervious surfaces and that are carried by the urban runoff and heavy metals such as Lead , Zinc, Copper, Cadmium , Polycyclic Aromatic Hydrocarbons (PAH) , Mineral Oil
hydrocarbons (MOH) and readily soluble salts in the runoff contributed to the degradation of water.

Winkel et al (2008) examined the Arsenic contamination in the densely populated river deltas of Southeast Asia (Bengal, Red River and Mekong deltas). The showed that Holocene deltaic and organic – rich surface sediments were the key indicators for the arsenic risk areas and that the combination of the surface parameters was a successful approach to predict the groundwater Arsenic contamination.

Saeed and Shaker (2008) assessed the concentrations of heavy metals including Iron, Zinc, Copper, Manganese, Cadmium and Lead (Fe, Zn, Cu, Mn, Cd and Pb) in water, sediments and fish organs from Lake Manzala showed greater concentrations of most of the studied metals than those from Lake Edku and Lake Borollus. They concluded that Nile tilapia caught from these two Lakes may pose health hazards for consumers.

Mark et al (2009) assessed concentrations of heavy metals in the wells and municipal springs, represents the major source of potable water for the human population outside major urban areas in northwestern Romania. Sampling of groundwater in northwestern Romania has indicated areas of potential concern for human health, where heavy metal concentrations exceed accepted environmental quality guidelines.

Bronius and Lynikien (2009) discussed heavy metal contamination from leachate of landfill area of industrial waste material influenced order of the main
pollutants: the most important elements in this case are Cu, Ni, Zn, Pb, Mn, Cr and other ions, the sulphides of these metals and other toxic compounds. Results showed that the iron concentration is the greatest exceeding even 200 times the admissible value allowed (Norm HN 24:2003). The leachate processed in purification devices is released to the Third stream. Heavy metal concentrations in waters of this stream are low and they further decrease downstream because the pollutants are diluted.

Derwich et al (2009) carried out studies in eight wells located in the vicinity of Fez stream and Sebou River which waters. The obtained results showed high concentrations of heavy metals mainly in wells drilled inside the alluvial aquifers and on the meadows of the Fez stream and Sebou River. The comparison of the contents of heavy metals between shallow aquifers and surface waters along Sebou River indicated a very narrow correlation which can be explained by hydrogeologic interaction between these waters.

Rizwan et al (2009) assessed the groundwater quality of Sialkot, an industrial city of Pakistan, for physico-chemical parameters and heavy metal concentrations. Cluster Analysis (CA) grouped all sites into four zones based on spatial similarities and dissimilarities of physiochemical properties. The study was done for identification of groundwater quality parameters with concentration above the allowable limits of WHO and to find out potential areas where water treatment plants/technologies can be targeted in Sialkot.

that the groundwater of the study area cannot be considered of good quality as it is highly turbid (57% of total sites) with high level of Zn, Fe and Pb, which were above WHO and PSQCA permissible limits.

Heredia and Cirelli (2009) studied the distribution of trace elements in the soil pore water and groundwater in Buenos Aires, Argentina. They observed a trend of diminishing Manganese content with increasing depth below the ground as well as higher concentrations of trace elements in shallow aquifers. They suggested that these are indicative of the effects of anthropogenic activities.

Ololade et al (2009) analysed the effects of household wastes on the surface and groundwater in Ondo state in Western Nigeria and found that the surface sources and unlined wells were vulnerable to contaminants and the concentrations of Lead, Nickel and Cadmium were high.

Momodu and Anyakora (2010) analyzed the groundwater in a middle-class neighborhood in Lagos, Nigeria, where it is the only source of water for the population, they detected Lead in 60% of the samples with 36.7% cases being in excess of the maximum contamination level (MCL); Calcium in 38% of the samples with 32.65% being above the corresponding MCL and Aluminum in 94% of the samples but below the MCL. They concluded that in general, the local population was at significant risk, since other sources of water were absent there.

Makkasap and Satapanajaru (2010) evaluated the distribution patterns of Cd, Zn and Hg in groundwater by geospatial interpolation. Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was used to measure the concentrations of Cd, Zn, and Hg in groundwater samples. Most of the heavy
metals concentrations were exceeded groundwater quality standards as specified in the Ministry of Natural Resources and Environment, Thailand. The trend distribution of heavy metals were high concentrations at the southeastern part of the area that was especially vulnerable to heavy metals and other contaminants.

Vasilatos et al (2010) has revealed high concentrations of hexavalent chromium in groundwater systems by using the GFAAS for total chromium, diphenylcarbazide-Cr(VI) complex colorimetric method for hexavalent chromium, and flame-AAS and ICP-MS for other toxic elements in several groundwater samples. The contamination of water by hexavalent chromium in central Euboea is mainly linked to natural processes, but there are cases that it is associated with anthropogenic activities.

Oyeku and Eludoyin (2010) mainly focused to create awareness on the effect of dumpsite on groundwater in developing countries, especially Nigeria., pH and conductivity were determined using a pH/conductivity meter (Jenway model), while the concentrations of the heavy metals (Co, Fe, Pb and Cu) were determined using atomic absorption spectrophotometer (AAS). The study concluded that the groundwater sources within 2 km radius of a major landfill will be vulnerable to the effect of landfill, if they are not adequately protected.

Odukoya and Abimbola (2010) did geochemical analyses of groundwater and streams flowing around abandoned and active dumpsites in Lagos, Southwestern Nigeria. Trace elements like silver, arsenic, beryllium, bismuth, cerium, cobalt, chromium, lithium, selenium, tellurium, titanium, uranium, vanadium, tin and yttrium were below detection level for all the water samples
while tungsten, thallium, molybdenum and lead were only present in surface and groundwater close to the dumpsites and also display values higher than recommended standards while copper, zinc, aluminum, barium and strontium respectively while the water around most of the dumpsite areas exceeded the acute and chronic effect levels proposed by the United States Environmental Protection Agency in 2007.

Momodu and Anyakora (2010) assessed that about forty nine well and borehole water samples were analyzed using Atomic Absorption Spectrophotometer for their Aluminium, Cadmium and Lead content and their levels compared with the WHO the Maximum Contaminant Level (MCL) for Aluminium, Cadmium and Lead are 0.2, 0.003 and 0.01mg/L respectively. The results obtained from this study suggest a significant risk to this population given the toxicity of these metals and the fact that for many, hand dug wells and bore holes are the only sources of their water supply in this environment.

Ikenaka et al (2010) evaluated the spatial distribution of heavy metals in main areas of Zambia to understand the characteristics of the pollution in each area. The results indicate that heavy metal pollution in Zambia has strong regional differences. However, areas geographically distant from mining beds had only moderate or low heavy metal concentrations, although the concentrations of Pb and Zn were highly correlated with the populations of each town. Our findings indicate that heavy metal pollution in Zambia is still increasing, due to human activities, especially mining.
Lei et al. (2010) explored heavy metals contamination in the metal sulfide mine in the arid district, through studying the acidification and the heavy metals distribution and evolution of groundwater in the black swan (BS) nickel sulfide mine (Western Australia). The groundwater samples were collected from the drilling holes situated in the vicinity of tailings storage facility (TSF) and in the background of the mine (away from TSF), respectively, and. It may be due to the percolation of tailings waste water from mill processes, which leads the tailings to oxidize and the deep groundwater to acidify and contaminate with heavy metals. They concluded that the heavy metals concentration in groundwater may be controlled by pH mainly.

Momodu and Anyakora (2010) analysed heavy metal concentrations in groundwater and the results suggest a significant risk to this population given the toxicity of these metals and the fact that for many, hand dug wells and bore holes are the only sources of their water supply in this environment.

Armah et al (2010) presented their studies on application of multivariate statistics for the interpretation of surface and groundwater data from Tarkwa, a mining community in the Western region of Ghana. This study underscores the value of multivariate statistical analysis for evaluation and interpretation of the data with a view to stimulating better policy outcomes and decision-making that positively impacts water quality and thus prospectively diminishes the pollution caused by hazardous toxic elements in mining environments.

Olusegun (2010) investigates possible contamination of untreated and treated groundwater by lead, faecal coliform and Escherichia coli in a hundred
randomly selected boreholes from different parts of Ibadan metropolis, located in South-West Nigeria. The results obtained supported previous findings that severe environmental degradation, which is readily observable in most parts of Ibadan city, could possibly contribute to pollution of ground water source like boreholes. Supply of adequately treated water from public waterworks to the teeming population in Ibadan city is an important problem that must be solved by the government.

Moraki (2010) carried out tests concerning the contamination of the groundwater at the area of Avlida. The results of the remediation testing, aiming to the assessment of the contamination in groundwater at that area, and propose ways for the water remediation.

Laniyan et al., (2011) investigated groundwater samples and leachate around the dump site, the samples acidified with two drops of concentrated nitric acid before it was sent for analysis. The results revealed dominance of Pb, Fe and, Mn when compared with WHO standard, while all the metals were found high in the leachates, Fe and Pb were extremely high in the groundwater. Thus, Pb, Fe and Mn if not checked could lead to major health problems like tooth discoloration, low mental development and kidney problems on the public.

Adelekani and Abegunde (2011) determine the concentrations of heavy metals, in soil and groundwater at automobile mechanic villages located in Ibadan. Soil and groundwater samples from 7 automobile mechanic villages and a control site in Ibadan, Analyzed for selected heavy metals namely: Cd, Cu, Pb, Cr and Ni. Soil samples were obtained in triplicates and at depths while water
samples were obtained from dug wells at the sites. Compared to the limits set by WHO for drinking water, values measured in the groundwater samples were lower than those limits and the exception of Cu where all the values were higher than the limits.

Nkansah et al (2011) tested the groundwater samples of Kwahu west district of Ghana and reported that all elements except Iron, Lead and Nickel were well within the safety limits recommended by WHO and that the level of industrialization in the study area had kept the water relatively from heavy metal contamination.

Pastor and Hernandez (2011) analysed the pollution levels in 15 old urban solid waste landfills in Madrid region of Spain. They reported the presence of heavy metals and salts in the soil and surface waters and updated the situation in respect of the risks for the health of the ecosystem and human and wildlife close to the landfills.

Kargar et al (2011) studied heavy metal concentrations in ground water and the spatial difference among sampling stations can be attributed to the existence of faults and diaclases in the geologic structure of Miduk region which causes the groundwater sampling sites to be impressed by different contamination sources (toe seepage and upper seepage water originated from different zones of tailings dump).

Liu et al (2011) assessed the impact of long-term electroplating industrial activities on heavy metal contamination in agricultural soils and potential health
risks for local residents. Results Hazardous levels of Cu, Cr, and Ni were observed in water and paddy soils at sites near the plant. Water, paddy soil, and rice from the studied area have been contaminated by Cu, Cr, and Ni. Cu and also Ni are the key components contributing to the potential health risks.

Wang et al (2011) investigated in order to understand current metal contamination due to industrialization and urbanization in Xiamen, China. The data suggested that copper-rich suspended solids contributed substantially to copper accumulation by M. iridescens and played a critical role in the pathway of copper into the food chain. The conclusions of this investigation are likely to be applicable to other relevant scenarios.

Chib et al (2011) studied spatial and temporal occurrence of heavy metals (Al, Cd, Pb, Zn, Cr, Co, Cu, Fe, Mn and Ni) in water and sediment samples in a sub-basin in the southeast of Brazil (São Carlos, SP). All samples were analysed using the USEPA adapted metal method and processed in an atomic absorption spectrophotometer. The source of contamination was probably diffuse, due to products such as batteries and fluorescent lamps, whose dump discharge can contaminate the bodies of water in the region in the rainy season.

Adelekanl and Abegunde (2011) determine the concentrations of heavy metals, in soil and groundwater at automobile mechanic villages located in Ibadan, Nigeria, the values measured in the groundwater samples were lower than those limits for the heavy metals with the exception of Cu where all the values were higher than the limits. The recommendations of the study include execution of some form of phyto-remediation measures at the villages; strict compliance to
regulatory limits in sludge to be released from these villages into the environment and the enforcement of other environmental protection regulations to arrest the ongoing buildup of these metals on those locations.

Akoteyon et al (2011) examined groundwater contamination around municipal landfill site in Alimosho Local Government Area of Lagos State, Nigeria. The result showed that the mean concentrations of all measured parameters except Cr and Mn conform to the maximum permissible limits of WHO standards for drinking water quality. He suggested that there should be adequate maintenance and adherence to world standard of landfill operation in order to safeguard the health of the populace.

Dermatas et al (2012) investigated the potential contribution of geogenic chromium (Cr) to a contaminated aquifer of a heavily industrialized area in Greece. Many cases resulted in serious soil and groundwater contamination incidents. Preliminary results indicate that the Cr(VI) plume in the study area is likely caused by a combination of geogenic and anthropogenic sources.

Ying et al (2012). The analysis of ecological risk assessment based on sediment quality guidelines suggested that heavy metals in most sediments from the Honghu Lake had moderate toxicity, with Cr being the highest priority pollutant. The results showed that the average concentrations of heavy metals in surface water were ranked as: As>Zn>Cu>Cr>Pb>Ni>Cd>Hg.

He et al (2012) investigated the application of our recently developed DNA-based luminescence methodology for the rapid and sensitive detection of
mercury (II) ions in real water samples. The results showed that the system could function effectively in real water samples under conditions of low turbidity and low metal ion concentrations. However, high turbidity and high metal ion concentrations increased the background signal and reduced the performance of this assay.

Maxwell and Jonathan (2012) examined the concentration of lead, a toxic element in rural groundwater of Benue state. Lead concentrations in the boreholes were noted to be higher in the wet season when compared to that of the dry season. The possible cause of lead concentrations in the study may be attributed to the increased use of chemical fertilizers on farms that find their way into groundwater sources.

Okoro et al (2012) analysed the suitability of the water for human consumption and domestication purposes. The measured heavy metals concentrations exceeded the World Health Organization (WHO) standard guideline for potable water usage. The result reflects probable pollution from the industrial effluent which are often released into storm water runways without further treatment. Analysis of variance (ANOVA), Pearson correlation and principal component (PCA) analysis were used to describe the data.

A comprehensive study has been carried out with respect to chromium, manganese, zinc, copper and nickel contamination of groundwater in Dhemaji district of Assam, India. Twenty groundwater samples were collected from tube well and ring well in both dry and wet seasons. The metals were analysed by
using Atomic Absorption Spectrometer, Perkin Elmer AA 200 model. Normal distribution and correlation analysis have been employed to find out the distribution pattern of the metals in the area. It is ascertained that a sizeable number of groundwater samples contain chromium, manganese and nickel at toxic level. Copper and zinc content of groundwater was found to be within the guideline value of WHO. High concentrations of all the trace metals except for chromium were recorded in the dry season than in the wet season. Statistical analyses of the data reveal that the distribution of various metals in the study area is widely off normal. The metal concentration of groundwater in the district follows the trend Zn>Mn>Cr>Cu>Ni in both the seasons.

A study was carried out to assess the water quality situation of groundwater sources in Kathmandu Valley, Nepal. Groundwater has remained a major water supply source for a population of 1.5 million at present in the valley. The focus of this study was to evaluate the extent and sources of groundwater contamination. Water sampling was carried out in selected deep wells and shallow sources. The level of pollution was evaluated by comparing the water quality results with WHO guidelines. The major problems with the dug wells, hand pumps and spouts were found to be the elevated nitrate and mercury contents. The deep wells located on the central aquifer were found to have a serious threat of ammonia pollution. Deep wells were also found to have iron, manganese and mercury concentrations exceeding the guideline values. Multivariate statistical analysis was carried out to cluster the sampling sources and identify the common factors describing the potential sources and possible mechanisms associated with
the contaminants. The results suggested that disintegration of the sediment organic matter under strong reducing environment leads to the origin of the unusual water qualities at the central confined aquifer. This process may be microbially mediated and occurs with the simultaneous reduction of species such as arsenic, iron, manganese and sulfate. Both natural and anthropogenic water quality problems were observed in the groundwater system of Kathmandu valley. Attention should be focused to consider distinct strategies to address these problems.

The physio-chemical characteristics of mercury have made it a favourable component for many industrial and agricultural applications. Significant anthropogenic Hg sources include fossil fuel combustion, the chloralkali industry and pharmaceuticals. Modifications to industrial practices countered by the increased use of Hg for gold amalgamation, particularly in tropical, developing countries. Under any of these circumstances, varying quantities and forms of Hg have been inevitably released to environments where it can pose a risk to human and ecological health. Given the unique behaviour of Hg, remediation of Hg contaminated sites can be complicated and costly. This paper reviews commonly employed and emerging techniques to mitigate Hg pollution and describes key design considerations and concerns associated with each method. Well-established ex-situ (external) techniques, such as physical separation and thermal treatment of excavated materials, are discussed in theory and practice. Potential in-situ (i.e. in place) Hg recovery methods, such as soil vapour extraction combined with soil heating and the use of leaching agents, are also explored.
Finally, containment strategies are described for sites where more conclusive measures cannot be employed.

The Trace metals contamination of water samples from various samples surface water in and around Akot city was assess. The sampling points were selected on the basis of their importance. The heavy metals like Cd, Cr, Pb, Cu, Ni and Zn were analyzed in surface water samples of rivers lake and field water pond. The results were compared with standards prescribed by WHO and ISI. It was found that the surface water was contaminated. Some sampling sites showed trace elements contamination above the water quality standards and the quality of water is very bad and it is unfit for drinking purpose.

A study was conducted to evaluate the heavy metal contamination status of groundwater in Brahmaputra flood plain Barpeta District, Assam, India. The Brahmaputra River flows from the southern part of the district and its many tributaries flow from north to south. Cd, Fe, Mn, Pb, and Zn are estimated by using atomic absorption spectrometer, Perkin Elmer AA 200. The quantity of heavy metals in drinking water should be checked time to time; as heavy metal accumulation will cause numerous problems to living being. Forty groundwater samples were collected mainly from tube wells from the flood plain area. As there is very little information available about the heavy metal contamination status in the heavily populated study area, the present work will help to be acquainted with the suitability of groundwater for drinking applications as well as it will enhance the database. The concentration of iron exceeds the WHO recommended levels of 0.3 mg/L in about 80% of the samples, manganese values exceed 0.4 mg/L in
about 22.5% of the samples, and lead values also exceed limit in 22.5% of the samples. Cd is reported in only four sampling locations and three of them exceed the WHO permissible limit (0.003 mg/L). Zinc concentrations were found to be within the prescribed WHO limits. Therefore, pressing awareness is needed for the betterment of water quality; for the sake of safe drinking water. Statistical analysis of the data was carried out using Special Package for Social Sciences (SPSS 16).

**Indian Findings**

Subba Rao (1983) who studied the Hydrogeology and Hydro-Chemistry of Visakhapatnam urban area, India observed that the groundwater quality was affected by sea water intrusion along the eastern coastal belt and by industrial effluents in the western part of Visakhapatnam.

Sarma and Swamy (1986) studied the water quality in Visakhapatnam basin, India and found that contamination was due to natural geological formations, industrial effluents and urbanization.

Lakshmanan et al (1986) investigated the quality of water supplies in and around the twin cities of Hyderabad and Secunderabad, India (especially with respect to pH, TDS, Cl, NO₃, and F). They found that out of the 75 dug wells and 35 tube wells sampled, about 76% dug wells and 40% tube wells have high nitrate content exceeding the WHO standard. They concluded that in the absence of fertilizer applications and geological deposits, the high nitrate (>300 mg/L)
observed in the wells within the twin cities area were due to lack of good sanitary practices and improper drainage systems in the area.

Subbarao (1988) carried out iron concentrations in the Visakhapatnam were ranges from 400 to 780 μg/l. A comparison of groundwater data with rock and soil chemistry suggests that the concentration of iron (400–530 μg/l) in the groundwaters is derived from the rocks and soils due to geogenic processes. Results that indicates the impact of anthropogenic activities on the ground water system and causing the health disorders.

Narayana and Suresh (1989) analysed the chemical characteristics of groundwater of Mangalore city, Karnataka, India and reported the following combinations of inorganic ions: (I) Na-Ca-Cl (II) Na-Ca-CO₃ (III) Na-Ca-Cl-HCO₃ and (IV) Ca-Mg-Cl.

Garg et al. (1990) studied the various water quality parameters of ground water of Roorkee city. A systematic calculation of correction coefficient ‘r’ for eight water quality parameters of 72 samples collected from 6 different places of water supply sources (Tube Well) for 12 months and the result show that, large positive correlation between BOD and Permanent Hardness (r = 0.991) and for BOD and Total Hardness is r = 0.989.

Rao et al. (1991) studied the ground water of Musunur Mandal of Krishna district (A.P) and found that, the Physico- Chemical parameters like Nitrates, Fluorides, Phosphates, Iron and Sulphates were found to be within the permissible limits.
Ravichandran and Pundarikanthan (1991) studied the groundwater quality of Madras, India in the context of polluted waterways of the city. They reported that the multiple regression analysis indicated that the areas around the wastewater ways were contaminated with the nitrates and phosphates, while pH and electrical conductivity were beyond the acceptable limits.

Dhanaselvan and Lakshmanaperumalsamy (1991) examined the groundwater of Kanpur city, Uttar Pradesh, India and reported that it was contaminated by both industrial and domestic sewage.

Rao et al. (1992) a studied the Physico-Chemical parameters of 23 bore wells and dug well of 23 villages of Challapalli Mandalam. The quality of well water was assessed by comparing with existing standards for important parameters, correlation coefficient ‘r’ among various water quality parameters were determined and found that, there is high incidence of Fluoride.

Hegde et al (1992) analysed the groundwater samples from the vicinity of sewage courses in Hubli, Karnataka, India for major anions and cations. They reported that the was clearly discernable, with the results showing high values of Cl, Na, Ca and TDS.

Rao et al (1992) monitored the physic chemical and bacterial parameters of water in the bore wells and dug wells of challapalli, Andhra Pradesh, India and determined the correlation coefficient amongst them.

Subba Rao (1993) studied the chemical quality of the groundwater in the industrial zones of Visakhapatnam, India. They reported that 15% of the industrial
well waters recorded more than 3000 S/cm level of conductivity; major ions crossed the safe limits at many places; and the toxic elements including lead, chromium, arsenic, zinc, cobalt have been traced in large amounts in the groundwaters of the industrial zones, with a zinc plant being identified as the worst offender.

Somasundaram et al (1993) investigated groundwater quality in Madras, India to determine variations in the major ions and nitrate concentration and heavy metal and bacterial pollution in the groundwater sources adjacent to a severely polluted water course. They found that a combination of inadequate sanitation and industrial discharges to be the contributing factors and numerous sources in the environment, such as atmospheric, geological and anthropogenic as well as nitrogen present in soil contribute to the total nitrogen content of the natural waters.

Ozha et al (1993) examined the nitrate concentration in the groundwater in Barmer and Churu of Rajasthan, India. They reported that the major nitrate contributing sources for the groundwater appear to be of geologic origin, especially the rock fossils and nitrate deposits; and the nitrate concentration increased with total hardness, calcium and magnesium and decreased as the depth of the water table increased.

Vijay Kumar et al (1993) studied the relationship of nitrates and the other Physico chemical constituents of the groundwater sources in Medchal, A.P, India. They found increase in nitrate concentration with decreasing pH and increasing hardness.
Patel et al 1994 studied the 21 Physico-Chemical parameters for the ground water samples from 14 rural areas of Rourkela Industrial Complex and found that all the rural areas are perfectly fit for drinking.

Ramesh et al (1995) studied on groundwater for eight ultra-trace elements (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn). The mobility, concentration and geoaccumulation of these metals are important indices to quantify the levels of pollution. Elements such as Mn, Cr and Zn exceed the maximum permissible limits at certain locations.

Rengaraj (1996) assessed the nitrate levels in the groundwaters of suburban localities of Madras (Chennai), India and concluded that the high nitrate concentration might be due to leaching of domestic wastes from sewage lines and septic tanks as also the use of various nitrogenous fertilizers in the nearby agricultural lands.

Jain et al (1996) studied the Physico chemical characteristics of the groundwater in different villages of district Haridwar, Uttar Pradesh, India, to classify on the basis of different standards. They reported that higher values of certain constituents at a few places indicated that the water was not suitable for domestic application.

Viswanadham and Murali (1996) of Pedana town in Krishna Dt, India analysed the groundwater pollution and found that the domestic sewage along with industrial effluents polluted the groundwater.
Panda and Singh (1996) studied the major inorganic anions such as Nitrate, Sulphate, Fluoride, Chloride, and Phosphate in drinking water collected from 5 different sources in Port City Paradeep and the results showed seasonal fluctuations.

Kumar et al (1997) studied the pollution status of aquatic system of central part of Jharia coalfield with reference to heavy metal content in water like Cd, Pb, Fe, As and Se and found that the levels are higher than limits prescribed by BIS for drinking water due to run off from mining areas, overburden dumps, mine fires, domestic effluents, industrial effluents etc. are probably the sources of this heavy metal content.

Naidu et al (1997) studied the water quality parameters in the coastal towns of Andhra Pradesh, India to assess their suitability for domestic and other needs and found pollution by industrial waste water and sewage.

Mittal and Verma (1997) analysed the groundwater quality in Patila, Punjab, India. Higher concentrations of various inorganic ions were observed by them in the close vicinity of sewers. They reported that leaching of contaminants from the sewers was the only cause of groundwater pollution of that area.

Rao and Prasad (1997) analysed the samples of soils and weathered rocks of Vamsadhara river basin in Andhra Pradesh, India for their water-soluble phosphate and other chemical parameters. They determined that the water-soluble phosphate in the fertilizers being used for agriculture. From their studies they
concluded that the geological sources dominate over the fertilizer sources in contributing \( \text{PO}_4 \) to the groundwaters.

Gnanasundar and Elango (1998) tested groundwater in the coastal aquifer in the urban zone to the south of Chennai (Madras) city, India. They found a freshwater ridge in the central part of this zone as well as sea water intrusion of upto 200 to 300 meters from the coastline. They attributed the poor quality of groundwater at certain locations to their proximity to the Buckingham Canal, which functions as a drain for the urban wates.

Mishra and Sahoo (2003) evaluated the quality of the ground water in and around Deogarh, India. They concluded that the groundwater with higher concentrations of magnesium causes laxative effect and excess fluoride causes severe bone fluorosis to human beings.

Mohapatra and Singh (1998) studies for the determination of inorganic anions such as Nitrate, Sulphate, Chloride, Fluoride and Phosphates in drinking water collecting from 6 different sources in the City of Cuttack and the results of the inorganic anions obtained were well within the permissible limits recommended by WHO, ISI and ICMR.

Naidu et al. (1998) studied the water quality parameters in 3 north coastal town of Andhra Pradesh and the results indicate that, the water of Mindi Industrial Zone, Old Post Office and Jalaripet of Visakhapatnam, Kothapeta, Vakumpeta and Mayuri, theatre areas of Vizianagaram and Kothapeta and complex areas of Srikakulam towns are polluted either by industrials waste water or by sewage and saline waters.
Kaplay et al. (1998) studied the quality of Bore Well and Dug Well water around the industrial areas of Tuppa region of Nanded City, Maharashtra and the study reveal that, the ground water is contaminated due to industrial effluent and Total Hardness, Salinity, Calcium and Magnesium content as per Indian standards for drinking water. Crop production; and human and cattle lives are adversely affected by this pollution.

Rambabu et al. (1998) studied the water quality parameters, like pH, Electrical Conductance, Total Hardness, Chloride, Sulphate, Nitrate and Fluoride and metals like Na, K, Ca and Mg of Chiral Town Open Wells, Prakasam District and found that out of 13 Open Wells 7 Open Wells are polluted in nature.

Koushik et al. (1999) collected water samples from three lentic water bodies (Motijhil, Surajajkund and Ranital of Gwalior region and analysed for some heavy metal like Cu (0.017 to 0.09 mg/l), Zn (0.065 to 0.120 mg/l) Ni (below detection limit 0.001 mg/l to 0.004 mg/l) Co (0.003 to 0.009 mg/l) Pb (0.002 to 0.009 mg/l) Mn (0.009 to 0.016 mg/l) Cr (0.020 to 0.048 mg/l) Cd (0.009 to 0.019 mg/l) and As (all the value are below the detection limit 0.001 mg/l). Seasonally lowest and highest value of all the parameters except Arsenic were recorded during summer and rainy season respectively in all the three water bodies and all the value of all the heavy metal parameters are found below the limit prescribed by different agencies.

Balsankar and Nagrajan (2000) collected ground water samples at different location in an around Cuddalore SIPCOT are analysed for their Physico-
Chemical characteristics and found that, there is a wide variation in water quality from sample to sample and most of the water samples have high Total Dissolve Solids and unpleasant odour.

Garg et al. (2000) studied the Physico-Chemical parameters of 30 ground water samples in eastern part of Hisar city and found that, on an average all most all the samples had one or the other chemical constituent beyond WHO permissible limits.

Garg et al. (2000) studied the Physico-Chemical parameters of 30 ground water samples in eastern part of Hisar city and found that, on an average all most all the samples had one or the other chemical constituent beyond WHO permissible limits.

Someshekar et al. (2000) collected 48 Tube Well water from Channapatona Town and surrounding and found that, quality of 80% of well is unsuitable for drinking in term of Hardness, 50% in terms of Magnesium and 20% in term of Nitrates and Calcium.

Tyagi et al. (2000) reported that, some Physico-Chemical parameters of ground water like Colour, Hardness, COD, BOD, Fluoride, Chloride, Sulphate, Calcium, Nitrates, Phenols, Cyanide etc in the industrial areas of India was much higher than the permissible limits of WHO (1993) and ISI (1991) drinking water standards.

Abdul et al (2001) dealing with toxic metal contamination of soil, aqueous waste streams and groundwater causes major environmental and human health
problems. Now-a-days phytoremediation is the use of plants to extract, sequester and/or detoxify pollutants and is a new and powerful technique for environmental clean-up. In the present review, current knowledge about metal accumulation and detoxification mechanism in plants is discussed. The importance and potential commercial applications of the phytoremediation are described.

Sohani et al. (2001) collected 16 ground water samples from the Bore Wells of different colonies of Nandurbar Town (Maharashtra) and analysed for 15 parameters related to water quality and found that some Physico-Chemical parameters within the permissible limit and some are beyond the permissible limit of drinking water standards. High Iron content (0.0 to 5.80 mg/l) has been detected.

Tiwari et al. (2002) studied the drinking water quality of residential colony, SAIL Satellite Township and four other sources of drinking water in Ranchi and found higher values of Nitrate, Chloride, Calcium and Magnesium are obtained.

Jeyras et al. (2002) studied the Physico-Chemical parameters for water samples collected from 15 Bore Well situated in different streets of Bharati Nagar and found that, the water is Saline and Hard.

Abdull et al. (2002) studied the 20 Physico-Chemical parameters of 20 sampling stations and found that all the water bodies are contain high levels of Inorganic Salts and Total Hardness with high Electrical Conductance.

Kaplay and Patode (2002) and Baber et al (2002) in tuppa area near Nanded in Maharashtra, India. Investigated the impact of the industrial waste on
the groundwater and soil characteristics. They reported that the groundwater was contaminated by lead and iron in that area.

Guruprasad (2003) studied the physic-chemical and bacteriological quality of groundwater in Tadepalli mandal of Guntur district, India to assess the impact of pollutants due to agriculture and human activities on the water quality. They reported that high levels of nutrient load and pollution was indicated in the hand pumps.

Rani et al. (2003) studied the drinking water quality of five rural places in and around Thittagudi, Tamilnadu and found most of the water samples have high TDS values and high Alkalinity.

Padmavathy et al. (2003) studied the water pollution of well waters taken from Ariyalur area in Tamilnadu and found that, the WQI values below 90.

Mishra and Sahoo (2003) studied the ground water quality in and around Deogarh and found that, the Physico-Chemical parameters like pH, Conductance, TDS, TH, Na, K, Mg, Ca, Cl, SO4 and HCO3 indicate that, the ground waters are suitable both for domestic and irrigation purpose.

Prakasan (2004) studied the ground water quality of Kerala with special reference to Kollam District and found that, the ground water in Mayyanad Panchayat is slightly acidic (pH=5.4 to 7.7) which is unsafe for drinking where as in Kollam Corporation area is not problematic.

Ramachandramoorty et al (2004) analysed the fluoride ion concentration in the groundwater of Tiruchirapalli, Tamilnadu, India. They reported that low
calcium content and high alkalinity increased the fluoride level in water; lower the total hardness higher was the fluoride ion concentration; and that groundwater was contaminated by the industrial activity and application of large amount of fertilizer around the area.

Potawary and Bhattacharya (2005) studied the groundwater samples of coal mining area of Assam, India and found that pH values were lower than the WHO prescribed limit and the concentration of major cations and anions was appreciable.

Rao and Nagaprapurna (2005) studied the correlations among various groundwater quality parameters and data from 63 groundwater samples collected from Jeedimetla industrial estate in Hyderabad city, India. They classified groundwater based on hydrochemistry to ascertain their suitability for various purposes and described various mechanisms that influence the ground water chemistry.

Misra et al (2005) evaluated the effect of industrial effluents on the ground and surface water due to the steel plant and other major industries at Rourkela in Orissa, India. Their analytical data of the physico-chemical parameters indicated that the river water was contaminated mainly due to the industrial and municipal effluents and the ground water of some of the analyzed areas was contaminated due to municipal and industrial solid waste dumping.

Poonkothai and Parvatham (2005) carried out physico–chemical and microbiological studies of automobile wastewater in Nammakkal, Tamil Nadu, India and found that the values for physico–chemical parameters were on the
higher side of permissible limits of BIS and also that bacteria were present at high concentrations.

Lingeswara Rao et al (2005) analyzed groundwater samples, covering all geological formations, collected from 100 drinking water sources all along the Nellore coast, Andhra Pradesh, India, for major physical and chemical parameters. They reported that the analysis of correlation coefficients among different chemical constituents indicated that the quality of groundwater in the study area was saline and consisted of high sodium chloride, magnesium bicarbonate and sodium sulphate.

Prakash and Somashekar (2006) tested 1,206 groundwater samples from 272 villages in Anekal Taluk near Bangalore, India and found that water quality was better in the deeper borewells and was also influenced by the rock formations.

Harish Babu, et al (2006) studied the physico–chemical characteristics of the groundwater at Tarikere Taluk, Karnataka, India. They compared the values with BIS and WHO and inferred that the areas near the industrial estate showed higher, TDS, total hardness and nitrates.

Anusha et al (2006) carried out a physico–chemical study of the groundwater samples from the bore wells and dug wells at Nacharam Industrial area of Hyderabad, India and found that the pollutants were above the acceptable limits.
Mukherjee and Nelliyat (2006) examined the effects of disposal of industrial effluents on the groundwater at Mettupalayam in Tamil Nadu, India. They reported that the pollution has stopped using the untreated water.

Jadeja et al (2006) studied the quality of groundwater in the industrial area of Dharmapur in Porbandar city of Gujarat, India. They reported that by examining various physico-chemical and bacteriological characteristics. TDS was above the desirable limit and all the samples were rated as unacceptable for their taste on the basis of total hardness.


Abida et al. (2009) found that water, plankton, fish and sediment in the Cauvery River water downstream is contaminated by certain heavy metals. Heavy metal concentration in water was Cr > Cu > Mn > Co > Ni > Pb > Zn. Although, the quality of Cauvery River may be classified as very good based on the salt and sodium for irrigation, Zn, Pb and Cr concentration exceeded the upper limit of standards. Metal concentrations in the downstream indicate an increase in the pollution load due to movement of fertilizers, agricultural ashes, industrial effluents and anthropogenic wastes. An immediate attention from the concerned authorities is required in order to protect the river from further pollution.

Borah et al (2009) has been carried out experiments on heavy metal contamination of groundwater with respect to cadmium, manganese, zinc and copper in the tea garden belt of Darrang district, Assam, India. The study reveals
that the groundwater of the area is highly contaminated with cadmium and also found to contain manganese at an alert level. Copper and zinc in the groundwater of the area are within the guideline values of WHO.

Buragohain et al (2009) has carried out studies on chromium, manganese, zinc, copper and nickel contamination of groundwater in Dhemaji district of Assam, India. Groundwater samples contain chromium, manganese and nickel at toxic level and copper and zinc content of to be within the guideline value of WHO. High concentrations of all the trace metals except for chromium were recorded. The metal concentration of groundwater in the district follows the trend Zn>Mn>Cr>Cu>Ni in both the seasons.

Puthiyasekar et al (2010) investigated the pollution vulnerability of bore water in the coastal region of Tirunelveli and Thoothukudi in the state of Tamilnadu, India. Samples were analyzed to find the concentrations of sodium, magnesium, aluminium, potassium, calcium, copper, cadmium, mercury and lead. The level of contamination is higher than the WHO limits of drinking water standards; but copper and aluminium content are within the limit.

Mahadev et. al., (2010) evaluated water quality parameter and heavy metal of upstream and KRS Dam. Results revealed that in three rivers of upstream (Hemavathi, Cauvery and Laxmanatheertha) carried high loads of Arsenic, Iron, Nickel in Upstream. In other word, Arsenic is a dominant risk too more than maximum permissible standard of water quality and is a risk factor in this river.
Mridul et al (2010) studied seasonal variations in the concentrations of groundwater with respect to arsenic, lead, cadmium and aluminium in Dhemaji district of Assam, India. The concentrations of aluminium, lead and cadmium in groundwater were found to be significantly elevated. High concentrations of all the metals were recorded in the dry season than in the wet season.

Patil and patil (2010) studied water samples of Amalner town in Maharashtra, India for 15 parameters. Quality of the groundwater was found to be inferior to that of water in the municipal supply. They concluded that proximity to a sewage pond and large floating sewage were the probable causative factors for the poor quality of groundwater.

Veena Choudary et al (2010) studied the groundwater samples of different villages in Indira Gandhi, Bhakra and gand canal catchment area of North-West Rajasthan, India and found fluoride, boron and nitrate contamination. They concluded that in the absence of industrial pollution in the study sites, availability of these compounds in the groundwater was due to natural reasons and by the use of chemical fertilizers.

Rafi et al (2011) analyzed groundwater collected from different areas in and around the Jammalamadugu Mandal of YSR District, India and analyzed for their physicochemical characteristics. The results of this analysis were compared with the water quality standards of WHO and CPHEEO. In this analysis the various physical chemical parameters such as pH, electrical conductivity, turbidity, total dissolved solids, Cl-, F-, SO42-, NO3-, Na+, K+, Fe,Cr, calcium and magnesium etc., were determined using standard procedures. The quality of
groundwater samples were discussed with respect to these parameters and thus an attempt were made to ascertain the quality of groundwater used for drinking and cooking purposes in the sampling areas.

Sameer et al 2011; Chlorides are important in detecting the contamination of groundwater by sewage. The groundwater in Belgaum city was analyzed for their chloride content and other related parameters in January and May month during the year 2010. In present study twenty five groundwater samples collected from open wells and analyzed for chloride content. The chloride concentration varied from 34.86 mg/l to 333.05 mg/l during the month of January and 31.77 mg/l to 297.86 mg/l during the month of May. High concentration of chloride was observed downstream of Lendhinala. High coefficient of variance indicates a great variability of chloride concentration in groundwater. A positive correlation of chloride with calcium, magnesium and sodium indicates non carbonate hardness and with TDS and EC indicates salinity. It is observed that, there is increase in chloride concentration (based on data from 2002 to 2010) in various parts of the city indicates mixing of sewage and groundwater. The regression equations have been developed between chloride and other water quality parameters.

Nabanita and Sarma (2012) evaluated the heavy metal contamination status of groundwater in Brahmaputra flood plain Barpeta District, Assam, India. Cd, Fe, Mn, Pb, and Zn are estimated by using AAS and concentration of iron, manganese, lead and Cd is reported three of them exceed the WHO permissible
limit (0.003 mg/L) except Zinc. Therefore, pressing awareness is needed for the betterment of water quality; for the sake of safe drinking water.

Jameel et al (2012) aimed at detecting the possibilities of ground water quality deteriorations due to the improper solid waste dumping with special reference to heavy metal pollution. From the data, it is shown that except Pb, the other heavy metals are present within the permissible limit. Our study suggests the preventive measures which are to be adopted to control the contamination of excess Pb present in the ground water around this region.

Byragi Reddy et al (2012) determined concentrations of heavy metals in ground water and results were like Al (0.0449 ppm), Cr (0.096 ppm), Mn (0.144 ppm), Fe (1.569 ppm), Ni (0.203 ppm), Cu (0.508 ppm), Zn (2.814 ppm), As (0.036 ppm), Cd (0.284 ppm), Hg (0.011 ppm) and Pb (1.084 ppm) results respectively. The moderately high concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg and Pb in groundwater, likely indicate that groundwater quality is being significantly affected by leachate percolation.
Study Area

Visakhapatnam, “The City of Destiny”, is bounded on the South by East Godavari district, on the West by Orissa state and on the East by Bay of Bengal. On account of rapid industrialization, there has been significant migration into the city. The city was originally a small fishing village but due to its natural harbor it developed into a major port serving several industries, including steel, petroleum refining and fertilizer. With the formation of “Greater Visakhapatnam” in 2005 the city’s development is set for a quantum leap.

Topography

The metropolitan city Vishakhapatnam located on East Coast of India is one of the fastest growing industrial cities in Asia. It is located at 17o43’ N latitude and 83o17’ E longitude (Fig.1). Vishakhapatnam urban area comprises Vishakhapatnam Municipal Corporation covering 111 km2 and Gajuwaka Municipality with an area of 97 kms. It is proud of having a natural harbor. It is 21st largest town in India (population wise), and 2nd in the state of Andhra Pradesh. As per census 2001, the population of Vishakhapatnam metropolitan city is 13, 29,472. The city map has been shown in Figure.

Physiography and Drainage

The area has four major hill ranges viz., Kailassa, Yarada, Naraka and Kambalkonda. The rest of the area is characterized by undulating topography. The hill ranges Kailasa and Yarada running parallel to each other occur North and South of the city respectively and extend roughly in east-west direction. The area is mainly drained by rivers like Hanumanthavoka, Naravagedda, Peddagedda and numerous other minor
Figure-1: Map showing the study area

streams taking their origin in the adjoining hills and follow general slope of the area. Besides these major streams, numerous other streams originate from local hills slopes and uplands and join the sea directly. The drainage is generally dendritic to sub-dendritic. Drainage density is more in hills and low in plains. The main course of stream, appear to be structurally controlled. A series of springs also occur in Kailasa hill range, they are perennial in nature and appear to be structurally controlled. In addition to main water
bodies and reservoirs numerous/small tank exists in peripheral villages whereas in urban areas tanks might have been filled due to development activity. The important geomorphic units of the area are hills, alluvial plains, mud flats, buried pediment, colluvial plain and coastal plain.

**Climate**

The climate of the Vishakhapatnam urban area is characterized by high humidity throughout the year with aggressive summer and pleasant winter. Visakhapatnam comes under the temperate climate and owing to its proximity to the sea, the humidity is usually high in the atmosphere. The temperature is observed to fluctuate. The rise in temperature is higher during dry season than in the monsoon season. The temperature rises progressively from February to May and during the winter season it is less. The significant observation in the mean temperatures is the gradual increase in the temperature with the effect of industrialization and denudation of vegetation cover in many parts of city and surrounding areas.

The most important feature of the climate is the alternation of seasons known as the monsoons. Based on these monsoons Indian meteorologists recognized the following seasons. 1. The North-West monsoon (Dec- February) 2. The hot weather season (March – May) 3. The South-West monsoon (June – September) 4. The retreating South-West monsoon (October- November). During September- November depressions result in storms and heavy rains. The coastal part of Visakhapatnam is prone to cyclones, storms and high winds during cyclonic season. Significant diurnal variations in hydro-meteorological parameters like precipitation, temperature and relative humidity also exist.

**Geology**
The area forms a part of Eastern Ghat tectonic complex of Archaean age which include khondalites, charnockite and migmatite groups. These are overlain by laterites of subrecent age. The unconsolidated sediments of recent age comprising red sediments, streams borne alluvium, colluvium and coastal sands also occur. The rock formations are steeply dipping with dips ranging between 60° and 80° strike and dip joints are well developed in Khondalites. In hard rocks, the occurrence and movement of ground water is limited to secondary porosity developed through weathering and fracturing. Ground water occurs under water table conditions in weathered residuum and semi-confined to confined conditions deeper fracture zones. Varying lithology of the geological formations considerably influences the groundwater conditions in all alluvial parts. The main sources of water, which sustains groundwater body in fine to coarse grained sands, is rainfall; the other sources of groundwater replenishment are infiltration from river, return seepage from irrigation and inflow from neighboring areas.

**Potential of Ground Water**

The thickness of weathering varies from 5 m to as high as 45 m. The weathered zone is porous and thick in Khondalites compared to other rock formations except in Kaolinised zones. The mode of ground water abstraction is mostly by means of dugwells or shallow borewells and is used mostly for domestic purposes. The dug wells range in depth from 2 to 21 m, while the general depth being 8 to 10 m. The depth of borewells varies from 15 to 60m. The depth to water level ranges from 0.7 to 19.20 m. The average seasonal water level fluctuation is of the order of 1.33 to 6.39 m. The long term water levels do not show any significant trend. In hard rocks, higher yields are observed in Khondalites than in quartz – feldspathic gneisses and charnockites. It is also observed that whenever quartz veins/quartz rich intrusive occur, such wells have recorded higher yields. In Narava tidal flat and peripheral areas ground water is not suitable for
development. In areas close to Kailasa hill and Waltair high lands, water levels are deep. Exploitation is done through deep open wells and deep borewells. In area like MVP Colony, Isukathota, parts of Lawsons Bay, Mudasaralova valley ground water prospects are good. Dug wells are feasible in these zones. A preliminary assessment of ground water resource indicate that ground water recharge due to rainfall infiltration is estimated to be 16.75 MCM/Year. The ground water draft from all sources is to the tune of 16.11 MCM/ Year. The ground water recharge and draft are almost equal. However, the groundwater development is less in semi-urban areas.

**Water Supply**

With the increased industrialization and urbanization during the last three decades there has been a lot of thrust on water resources in the urban area. Consequently there is a big gap between water supply and demand. During summer the situation becomes worse. The demand for water may further increase in future since the limits of city are expanding along with the increase in population. The principal sources of water supply in VMC are surface water and ground water. At present the water supply is around 37 MGD of which 21 MGD is utilized for drinking and domestic purpose and 16 MGD consumed by industries. The important sources of water in VMC are surface water reservoirs built across the river/streams around the city. The average per capita water supply is 19 GPCD. There is a deficit to the tune of 12 GPCD obviously the gap is met by tapping ground water. Thus, the ground water abstraction bridges the gap between demand and supply.

**Status of Industries**

Vishakhapatnam is very famous for industries in Andhra Pradesh, since it is having natural resources, water facility and handling facilities of many industries. It is well connected by sea, rail and air. Since it has a major Port, Vishakhapatnam has developed into a major industrial zone. Some of the major Industries of Vishakhapatnam
are Hindustan Zinc Ltd, Hindustan Shipyard Ltd, Hindustan Polymers, Vishakhapatnam Steel Plant, Vishakha Refinery, Coromandal Fertilizers, Bharath Heavy Plates and Vessels, Vishakhapatnam Port Trust, Naval Dock Yard, Dredging Corporation of India etc.

**Wind Direction**

The wind direction is mostly from South-West with a wind speed of 5.15, 10.3, 13.84 and 6.92 kms per hour in January, May, August and November respectively. Sky clearance factor is 50 to 70 except in the rainy season, which is above 20. Evaporation rate is about 250cms per year and the average rainfall is 120 cms per year.

**Demography**

Visakhapatnam is currently ranked as the second largest urban agglomeration in Andhra Pradesh. The Greater Visakhapatnam Municipal Corporation (GVMC) consists of the Municipal Corporation of Visakhapatnam (MCV), 32-merged Villages and the erstwhile Gajuwaka Municipality. The population of Visakhapatnam urban agglomeration increased from 1.05 million in 1991 to 1.32 million in 2001. The growth of the population was more than 80% during 1971-81 and 37.11% during 1991-2001.

Due to formation of GVMC and merger of surrounding villages, several well established urban components of the city are located within the GVMC. The details of the population of the Municipal Corporation of Visakhapatnam and now functioning as the Greater Visakhapatnam Municipal Corporation are given in Table 1.

**Table 1: Population Trends – Greater Visakhapatnam Municipal Corporation**

<table>
<thead>
<tr>
<th>Area</th>
<th>Population</th>
<th>Density</th>
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<tbody>
<tr>
<td></td>
<td>(Sq Km)</td>
<td>(Lakhs)</td>
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<td>------------------</td>
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<tr>
<td></td>
<td>2001</td>
<td>2006</td>
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<tr>
<td>Greater Visakhapatnam</td>
<td>111</td>
<td>540</td>
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</table>

(Source: Greater Visakhapatnam Municipal Corporation)

Sampling

Water samples were collected in the morning hours between 7 am and 9 am for a period of two years during March-May 2010 and March-May 2011. Sampling in the month of March was chosen since it was onset to summer season where most of the aquifers are under saturated condition with high concentrations. The summer season was also selected to avoid dilution if any due to rainy season. Water was collected in sterilized glass bottles labeled with sample code and transported to the laboratory in an ice box. The changes that occur in the bacterial content of the water on storage were reduced to a minimum by ensuring that the samples were not exposed to light. They were maintained under low temperature preferably between 4° to 10°C, but not frozen. After sampling, analysis was done immediately in Environmental Microbiology Laboratory of Andhra University, Visakhapatnam. The samples were processed and analyzed scrupulously by following the appropriate methods.
Figure 2: Sampling points
Figure 3: Sampling points
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Location</th>
<th>Total Depth (Mbgl)</th>
<th>Depth To water level (Pre monsoon)</th>
<th>Depth To water level (Post monsoon)</th>
<th>Annual Fluctuation (m)</th>
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</thead>
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<td>3.00</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td>2</td>
<td>Opp V.S Organics</td>
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<td>3.00</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>Colony at R city</td>
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<td>3.00</td>
<td>2.00</td>
<td>1.00</td>
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<td>2.00</td>
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</table>
**Physico-chemical parameters**

The physico-chemical analysis was performed by following the standard methods.

The brief details of analytical methods and equipment used in the study are given in Table-3.

**Table 3: Analytical methods and equipment used in the study (APHA, 2005)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Instruments/Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>pH Meter</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Electrometric</td>
<td>Conductivity Meter</td>
</tr>
<tr>
<td>TDS</td>
<td>Electrometric</td>
<td>Conductivity/TDS Meter</td>
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<tr>
<td>Alkalinity</td>
<td>Titration by H\textsubscript{2}SO\textsubscript{4}</td>
<td>-</td>
</tr>
<tr>
<td>Hardness</td>
<td>Titration by EDTA</td>
<td>-</td>
</tr>
<tr>
<td>Chloride</td>
<td>Titration by AgNO\textsubscript{3}</td>
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</tr>
<tr>
<td>Sulphate</td>
<td>Turbidimetric</td>
<td>Turbidity Meter</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Ultraviolet screening</td>
<td>UV-VIS Spectrophotometer</td>
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<tr>
<td>Phosphate</td>
<td>Molybdophosphoric acid</td>
<td>UV-VIS Spectrophotometer</td>
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<td>Fluoride</td>
<td>SPADNS</td>
<td>UV-VIS Spectrophotometer</td>
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<tr>
<td>Sodium</td>
<td>Flame emission</td>
<td>Flame Photometer</td>
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<td>Potassium</td>
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<tr>
<td>Calcium</td>
<td>Titration by EDTA</td>
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<td>Magnesium</td>
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<tr>
<td>BOD</td>
<td>5 days incubation at 20°C followed by titration</td>
<td>BOD Incubator</td>
</tr>
<tr>
<td>COD</td>
<td>Digestion followed by titration</td>
<td>COD Digester</td>
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</table>
Chemicals, Reagents & Instruments

The chemicals, reagents and solvents used for carrying out the analysis were of analytical grade, procured from BDH, England/India; E. Merck, Germany/India; Qualigens, India; SD Fine Chemicals, India; Fluka, Switzerland; Hi-Media, India; Sigma Aldrich USA and USEPA Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

The solvents were distilled before use, Triple distilled water was generally used for the preparation of solutions and for carrying out the experiments. The glassware used was of Borosil, India, the burettes and pipettes being of class-A grade. The instruments used are listed in Table 4.

Table 4: Instruments used

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH Meter</td>
<td>Digital pH Meter, Model 362, Systronics (India)</td>
</tr>
<tr>
<td>Electrical Conductively Meter</td>
<td>Digital Conductivity Meter, Model 306 Systronics (India)</td>
</tr>
<tr>
<td>UV-Visible Recording</td>
<td>Thermo Spectronic Unicam UV 500 (USA)</td>
</tr>
<tr>
<td>Spectrophotometer</td>
<td>Systronic UV-Visible Spectrophotometer</td>
</tr>
<tr>
<td>Ion Selective Electrode Meter for the determination of fluoride</td>
<td>WTW inoLab Level 3 (Germany), with fluoride ion selective electrode</td>
</tr>
<tr>
<td>ICP-MS, for the determination of trace metals in water</td>
<td>Perkin Elmer Sciex ELAN DRC II</td>
</tr>
</tbody>
</table>
Parameters to be analyzed:

**pH (Direct Measurements)**

All the solutions used for pH measurement were prepared with carbon dioxide free water and all the buffer solutions were prepared afresh after every four weeks. 0.05 M potassium hydrogen phthalate buffer solution which shows a pH of 4.00 at 25°C, 0.01m potassium dihydrogen phosphate which exhibits at pH of 6.85 at 25°C, 0.05m borax buffer solution, which yields a buffer solution of pH 9.18 at 25°C were prepared with triple distilled water.

The pH meter was standardized against the buffer solutions of known pH values and in the required range. (pH=4.00, 6.85, 9.18). The electrode was kept immersed in the sample taken in a beaker and the pH of the sample was recorded. pH electrode was rinsed thoroughly with every sample before making the measurements.

**Electrical Conductively (Direct Measurement)**

All the solutions used for electrical conductively measurement were prepared with conductively water with conductively less than 1 µmhos/cm and 0.01m, standard
potassium chloride solution with a conductively of 1413 µmhos/com at 25°C. These were carefully diluted further to 0.001m and 0.005m to give 141.3 and 717.8 µmhos/com, at 25°C. The cell constant of the conductively meter was adjusted by immersing the cell in a standard 0.001m KCl solution to a conductance of 147.0 µmhos/cm. The functioning of the meter was further checked by another standard 0.005m KCl solution which gave a conductively of 717.8 µmhos/cm. The cell was thoroughly washed twice or thrice with de-ionised water and then with sample. Thereupon, conductivity of the sample was measured and recorded.

**Total Dissolved Solids (TDS)**

The sample for total dissolved solids (TDS) measurement was thoroughly mixed by shaking and then filtered through standard glass fibre filters. A clean porcelain dish was dried at 180±2°C for one hour, cooled in a desiccators and weighed. A sample of required volume (250mL) was taken in the dish and carefully evaporated to dryness. The dish was dried for one hour, again at 180±2°C, cooled in a desiccators and weighed. The weights of the empty dish as well as the dish containing the dissolved solids were recorded after getting the constant weights by repeatedly drying desiccating for cooling and weighing. TDS was calculated from the difference in weights and volume of dried sample.

**Total Hardness (EDTA Titrmetric Method)**

0.01m standard calcium solution: 1.000g calcium carbonate was quantitatively transferred and dissolved in minium volume of 1:1 hydrochloric acid and made up to 1000ml with distilled water. 0.01m ethylene diaminetetraacetic acid disodium salt solution, pH 10.0, Buffer solution, 1.0m sodium hydroxide solution 0.5% Erichrome Black-T indicator solution were prepared. Solid murexide was used in the titrations.
20.0ml of standard calcium solution was diluted to 50ml with distilled water. 2.0ml ammonium chloride ammonium hydroxide buffer solution (pH 10) and 2 drops Eriochrome Black-T indicaor solution were added. It was slowly titrated with EDTA solution with continuous stirring until the colour changed from wine red to blue. The same procedure was performed for the reagent blank. Concentration of EDTA was calculated from the titre values.

20.0ml of sample was diluted to 50ml with distilled water to which 2ml ammonium chloride-ammonium hydroxide buffer solution and 2 drops Eriochrome Black-T indicator solution were added. It was slowly titrated with standardised EDTA solution with continuous stirring until the colour changes from wine red to blue. Total hardness was calculated from the titre values.

Determination of calcium: 20.0ml of sample was diluted to 50ml with distilled water to which 2.0ml sodium hydroxide buffer solution and 0.4g murexide indicato were added. It was slowly titrated with standardised EDTA solution with continuous stirring until the colour changed from red to blue violet. The same procedure was adopted for reagent blank. The amount of calcium was calculated from the titre values.

Determination of magnesium: Magnesium was calculated by using the formula after appropriately convertint he data: Amount of Magnesium=Total Hardness minus Total calcium.

**Alkalinity (Titration Method)**

Carbon dioxide free distilled water was used for the preparation of all the solutions as well as for conducting the experiments for the determination of alkalinity.

0.01m standard sodium carbonate solution, 0.02m hydrochloric acid solution 0.5% phenolphthalein indicator solution 0.05% methyl orange indicator solution were prepared. To a 20.0ml of standard sodium carbonate (0.01m) solution drops of methyl
orange indicator was added and diluted to 100ml with distilled water. The solution was
titrated with hydrochloric acid solution to be standardised with continuous stirring until
the colour of the solution turned from yellow to pink. The same procedure was adopted
for reagent blank. The concentration of hydrochloric acid was calculated.

20.0ml of sample was taken without filtration or alteration to which 3 drops of
phenolphthalein indicator solution was added and diluted to 100ml with distilled water.
The solution was titrated using standardised hydrochloric acid until the pink colour of the
solution disappears. Next, 3 drops of methyl orange indicator were added. The titration
was continued slowly with continuous stirring until the solution colour changed from
yellow to pink. The same procedure was adopted for blank also. Total alkalinity (T-
alkalinity) was calculated from the titre values.

**Chloride (Argentometric Method)**

0.01m standard sodium chloride solution 0.01m silver nitrate solution 5%
potassium chromate indicator solution were prepared. To a 20.0ml of standard sodium
chloride solution 1.0ml potassium chromate indicator solution was added and diluted to
100ml with distilled water. It was titrated with silver nitrate solution to be standardised
with continuous stirring until the red precipitate of silver chromate was just observed.
The same procedure was carried out for reagent blank. The concentration of silver nitrat
was calculated using the titre values.

20.0ml of sample was taken and pH of the sample was adjusted to 7.0. To this
1.0mlo potassium chromate indicator solution was added and diluted to 100ml with
distilled water. It was titrated against standardised silver nitrate solution with continuous
stirring till the formation of red silver chromate precipitate was just observed. The
amount of chloride in the sample was calculated using the titre values.

**Sulphate (Turbidimetric Method)**
1000mg/L $\text{SO}_4^{2-}$ stock sulphate solution 100mg/L $\text{SO}_4^{2-}$ working sulphate solution were prepared. Barium chloride crystals of 20-30 mesh were used.

30g magnesium chloride 5g sodium acetate, 1.0g potassium nitrate and 20ml acetic acid in 500ml distilled water were mixed and made up to 1000ml buffer solution. A series of standard solutions containing 0 to 50.0mg/L $\text{SO}_4^{2-}$ were prepared from standard sulphate solution in 25ml volumetric flasks. 100ml of sample was taken in 250ml Erlenmeyer flask to which 20ml buffer solution was added and mixed in a stirring apparatus. Barium chloride crystals were added while stirring. The same procedure was adopted for sulphate standard solutions and reagent blank. The turbidity of the solution was measured. A calibration curve was plotted for the concentrations of sulphate in the standards against their corresponding turbidities. The amount of sulphate present in the sample was determined from the calibration curve after developing turbidity of the samples in a similar way.

**Nitrate (Cadmium Reduction Method)**

1000mg stock nitrate solution 20mg/L $\text{NO}_3^{-}$ intermediate nitrate solution 1 mg/L $\text{NO}_3^{-}$ working nitrate solution 6m hydrochloric acid 2.0% copper sulphate solution 0.05m stock ammonium chloride EDTA solution were prepared in nitrite free tripled distilled water.

Copper-Cadmium granules: 25g 40-60 mesh cadmium granules were washed with 6.0m hydrochloric acid. The washed cadmium granules were swirled with 2.0% copper sulphate solution until blue colour partially fades. Copper sulphate solution was decanted and the process was repeated for several times with fresh portions of copper sulphate solution 0.5% sulphanilamide solution 0.3% N-(1-naphthl) ethylenediamine dihydrochloride (NEDA) solution were prepared.
Preparation of Cadmium Reduction Column: Glass wool plug was inserted into the bottom of a reduction column. The column was then filled with distilled water. Sufficient copper cadmium granules was placed to produce 18.5 cm long column. Proper care was taken to avoid entrapment of air while filling up the column with granules. The column was washed with 200ml dilute ammonium chloride – EDTA solution and activated by passing a mixture of 75ml dilute ammonium chloride EDTA solution and 25ml 1 mg mg/L NO$_3^-$ standard nitrate solution at a rate of 5 ml/min through the column.

A series of standard nitrate solution were prepared in the required range (0.04 to 0.4mg/L NO$_3^-$) by diluting working nitrate solution to 25.0ml. A series of standard nitrate solutions were prepared in the required range (0.2 to 2.0mg/L NO$_3^-$) by diluting working nitrate solution to 10ml. The pH of a known volume of the sample (20.0L) was adjusted to 7 with dilute hydrochloric acid. 75.0ml dilute ammonium chloride – EDTA solution was added to the sample and made up to 100ml. It was passed through the column at the rate of 5ml/min. 20.0ml was collected after discarding the first 35ml of the eluent. Whenever necessary the sample was first properly diluted before it was passed through the reduction column. The reduction of nitrate standards and blank was carried out exactly as described for the sample.

Within 15 minutes after the collection of eluents of the sample and the standards 1.0ml sulphanilamide solution together with 1.0ml N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) solution were added and diluted to 25ml. the result was a reddish purple colour. The same procedure was adopted for reagent blank. The absorbance of the colour developed for the sample and reduced nitrate standards were measured at 543 nm against reagent blank. A standard curve was prepared by plotting absorbance of standards against their corresponding nitrate concentrations. The concentration of nitrate in the sample was determined directly from the standard curve.
The efficiency of the reduction column was checked for confidence as follows: standard solutions of nitrite were prepared in the same concentrations as that of nitrate standards used. The reagents were added to the nitrite standards as explained above and the colour was developed. The absorbance of the solutions was measured and compared with that of nitrate standard solutions. The nitrate and nitrite standards of same concentrations resulted in almost same absorbances. The reduction column was freshly prepared whenever there was a discrepancy.

**Fluoride (Ion-Selective Electrode Method)**

All the fluoride standard solutions were preserved in polyethylene bottle and all the determinations of fluoride were carried out in polythene containers only. 1000mg/LF stock fluoride solution 100mg/L F intermediate stock fluoride solution, 10 mg/L F working fluoride solution and 6 m sodium hydroxide solution were prepared.

Total ionic strength adjustment (TISAB) buffer: 57.0 ml glacial acetic acid 58.0g sodium chloride and 4.0g 1, 2-cyclohexylenediamine tetra acetic acid (CDTA) were dissolved in approximately 500ml distilled water in a beaker. The beaker was kept in a cool water bath and about 125ml of 6m sodium hydroxide was slowly added with constant stirring till the solution attained a pH of 5.3-5.5. The solution was transferred to a 1000ml volumetric flask and made up to the mark with distilled water.

A series of standards (0.5, 1.0, 2.5, 5.0mg/L F') were prepared from the working fluoride solution in 50ml volumetric flasks 20.0mL of the sample was taken in a 50ml polythene beaker and equal volume of TISAB buffer was added. The fluoride selective electrode and the reference electrode (Single junction electrode) were thoroughly washed with distilled water. Reference electrode was filled with the single junction electrode filling solution. Both the reference and fluoride sensitive electrodes were immersed in
the reagent blank. After attaining stable reading the meter was set for zero concentration. Then the reagent blank was replaced by fluoride standard. The instrument was set for the concentration of that standard. Again the electrodes were placed in the second standard. The concentration of the second standard was achieved by adjusting the slope. The calibration of the instrument was checked by an intermediate of the two standards. The concentration of fluoride in the samples was measured directly after getting a satisfactory result.

**Dissolved Oxygen (Iodometric Method)**

0.01m standard potassium dichromate solution 0.0025m sodium thiosulphate solution 10% potassium iodide solution 1.0% starch indicator solution and 16% manganous sulphate solution.

Alkali-Iodide-azide reagent: 125g sodium hydroxide and 33.75g sodium iodide were dissolved in 250ml distilled water 2.5g sodium azide was dissolved in 10ml distilled water and the solution was added to alkali-iodide solution.

Standardisation of sodium thisulphate solution: 20ml iodate free 10% potassium iodie solution and 2.0g sodium hydrogen carbonate were taken in a glass stoppered flask. 6.0ml concentrated hydrochloric acid was added and diluted and 100ml with distilled water. 20.0ml of 0.01m, standard potassium dichromate solution was added and mixed thoroughly. It was stoppered and kept in dark for 5 minutes. The liberated iodine was slowly titrated with sodium thiosulphate solution with constant stirring until the solution acquired a yellowish-green colour. Then 2.0ml starch solution was added and titration was continued with constant stirring until the titrant solution colour changed from greenish-blue to light green. The same procedure was adopted for reagent blank. The concentration of sodium thiosulphate solution was calculated.
Trace Metals in water samples

Methyl isobutyl metone (MIBK): Methyl isobutyl ketone was distilled and used for extraction of metals. Ammonium pyrroldinedithiocarbamate (APDC) solution, 4%, Nitric acid solution 4.0 M, Nitric acid solution 1.0 M, Sodium hydroxide solution 1.0 M were prepared.

Determination of Trace Metals

The determination of trace metals in the samples was carried out by using ICP-MS. The determination of the metals consists of four parts.

a) Complexation of metals with APDC and extraction with MIBK
b) Back extraction of the metals with 4N HNO₃
c) Removal of MIBK by evaporation and the metals were redissolved in 2% HNO₃ solution and made up to 25mL.
d) Determination of trace metals in HNO₃ using ICP-MS

500mL of the sample was taken and pH was adjusted to 2 using either dilute supra pure dilute nitric acid or dilute sodium hydroxide solution. The sample was then transferred to a one liter separating funnel, to which 2mL 4% APDC solution and 15mL MIBK were added. The contents were shaken vigorously for sufficient time. After visualizing the separated aqueous and organic layers clearly, the organic layer (MIBK) was collected in another separating funnel. To ensure complete extraction of the metals from the samples, the extraction was repeated 3 times by adding similar fractions of APDC and MIBK. All the MIBK fractions were in another separating funnel. The metals were back extracted into 4 M HNO₃ by extracting with small portions of 4mL the acid for 3 times. All the acid fractions were added together and the solution was made up to 25mL. A similar procedure was adopted for the standards and the reagent blank. The HNO₃ solution containing trace metals was evaporated to almost dryness so that the MIBK was completely removed. Then 20mL
of 2% HNO₃ was added to the beaker and gently heated and contents were carefully transferred to a 25mL volumetric flask and makeup to the mark using 2 % HNO₃ solution.

**Standard reference sample** (NIST 1640) and Sigma – Aldrich Trace metals mixture : standard water reference sample NIST 1640, obtained from National Institute of Standard and Technology(NIST), USA were used for evaluating the accuracy of the analysis.

**Accuracy of the Analytical Data:**

The errors in the estimation of the chemical parameters involving gravimetric estimations are less than 1.0% and the estimations involving volumetric methods may be up to 2.0%, GC, ICP-MS, Ion selective electrode meter and flame photometer, the errors are in the range of 1.0-5.0%.

**Table 5: Operating conditions of ICP-MS**

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<th>Parameter</th>
<th>Value</th>
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<td>Argon gas-flow</td>
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<td>Nebulizer</td>
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<tr>
<td>Auxiliary</td>
<td>1.2 L/min</td>
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<tr>
<td>Plasma</td>
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<tr>
<td>Lens Voltage</td>
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<tr>
<td>Sample uptake rate</td>
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</tr>
<tr>
<td>Measuring mode</td>
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<tr>
<td>Number of sweeps</td>
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<td>Integration time (ms)</td>
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<tr>
<td>Replicates</td>
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<tr>
<td>Internal standard</td>
<td>^{103}Rh</td>
</tr>
</tbody>
</table>

a At an overall concentration of 20 ng/mL .........

Concentrations of dissolved trace metals were analyzed by direct-injection Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) with corrections for ion
interfer-ences. Documentation and quality assurance for the ICP-MS method for low-level trace-element analysis is described in Garbarino and Taylor (1994) and Garbarino (1999). Concentrations of metals in field blanks collected for this study were typically not detected except for one blank sample collected on May 23, 2001 that may have had contamination either in the blank water or in the fixing acid. This sample was recollected in August 2001 and was clean the second time. High concentrations of trace metals that were detected in the contaminated blank were within the range of back-ground levels in the August sample, and therefore did not affect the interpretation. Analytical precision for dissolved metals was better than ± 5 percent for samples collected at well DG-2 on June 13, 2000. Precision was not as good for a set of replicates collected from well DG-5 on May 16, 2001, possibly due to large spatial gradients in the concentrations of some metals, particularly lead, in the ground water near the drop zone. The well-purging process may have caused or exacerbated the problem by drawing water from around the well annulus where there was likely a large gradient in the concentration of lead. Analysis of a third sample from this well, collected on August 23, 2001, also indicated substantial variability in the concentrations of lead and other metals at this site.