CHAPTER 4

DISCUSSION
4. DISCUSSION

Various Acts of Parliament have generally brought under tight control the discharge of objectionable industrial wastes into water courses. Even so, some loopholes remain and various pollutants find their way into the rivers and lakes in our country. Untreated industrial wastes in surface waters, can bring about a rapid deterioration of their physical, chemical and biological qualities. Hence various physico-chemical tests were conducted routinely to estimate the general level of pollution in river Tungabhadra at Kumarapatnam (Karnataka). Data on such aspects, apart from adding to the existing information on Indian rivers, would serve as a baseline upon which the impact of any future effect could be assessed and also would provide a background for any future studies.

The impact of pollution mainly depends on the natural chemistry of the receiving water course. Reference to the natural conditions is important for the assessment of water quality and the ecological impacts of pollutants. A general approach involving all the important factors is complicated but needed if ecological information is to be used as an aid to optional river management, which involves drinking water supply, the needs of industry, agriculture and navigation and finally maintenance of ecological equilibrium (Descay & Empain 1984).
4.1 PHYSICO-CHEMICAL CHARACTERISTICS

Physico-chemical analysis forms the basis of interpretation of the quality of water in relation to source, geology, climate and use. There exists a notion that water quality only be defined for a specific function or use of water. In fact, water quality is the consequence of a complex of physical, chemical and biological properties of the water, important for all uses and functions of the water (Biswas 1978 Lyklema 1979). The following pages give the most important water quality aspects of River Tungabhadra at Kumarapatnam, Dharwad District, Karnataka State. The main emphasis has been on determining and documenting the degree and load of pollution.

4.1.1 Colour

Colour indicates the general physical appearance of a water sample and it may result from the presence of natural metallic ions (Iron and manganese), humus and peat material, plankton weeds, and industrial wastes containing phenols, amines, excessive chlorine etc. Colour is a rough measure of organic matter. In some highly coloured industrial waste waters, colour is contributed principally by colloidal or suspended material (APHA 1980).

Many industrial effluents are coloured. For example, pulp and paper mill effluents and HPF effluent are dark
brown in colour. This colour may be discerned by the people using the receiving water for various purposes. The colour value of water is extremely pH dependent and invariably increases as the pH of water is raised.

Colour is known to carry COD and toxicity with it. General observations suggest that the intensity of colour in a waste stream is reflected by its COD most of the times. Hence, colour is removed to make waste suitable for general and industrial applications. The colour values could be used as an approximation of the content of organic substances (Borg 1983).

In the present study, the upstream water remained clear and normal except in the wet season. During wet season, the water became muddy or slightly coloured because of washings of soil particle, organic matter, silt etc., from the catchment area. However, the effluents remained coloured throughout the study period. GRF effluent was pale blue in colour and HPF effluent was highly dark brownish in appearance. This is due to the presence of high amount of lignin, its derivatives, carbonaceous materials (Joshi & Datta 1987) and other pollution indicating factors (specially Cl, SO_4, O.M., TH, TS, and D.S.). Sudhakar & Venkateswarlu (1989) also observed highly dark brown coloured effluents in case of paper mills of Andhra Pradesh.
It was found that the high molecular weight chlorolignins, produced during the bleaching of pulp using chlorine water, contributes most of the dark colour to the effluents. It is believed that overall first stage of the caustic extraction effluent contributes about 70% of the typical kraft mill's total effluent colour loading. Effluent colour is largely due to lignin degradation products such as aromatic and quinoid nuclei, carbonyl and ethylenic groups.

Colour is thought to contribute negatively to the aesthetic value of water. However, biologists are increasingly concerned about the effect of reduced light transmittance on organic productivity as well as toxic effects (Soniassay et al 1975). Rosehart (1985) has discussed the colour removal process in kraft pulp and paper mill effluent in detail.

Kongovi et al (1986) observed pale brown colour even in the downstream water of river Tungabhadra at Airani (9.6 km downstream from the discharge point of HPF effluent) and Hirebidari (12.0 km downstream) during the study period (Feb 1985 to March 1986).

It is obligatory to remove these pollutants from the effluent before it discharges into the receiving water because it creates environmental problems due to its colour and toxicity (EPA 1974). There are no standards for colour
in waste waters. It is, however, recommended that colour should be removed as far as possible (ISI Standards IS-2724-1983).

4.1.2 pH

Measurement of pH is one of the most frequently used tests in water chemistry because practically every phase of water supply and waste water treatment is pH dependent. The pH or hydrogen ion concentration indicates the intensity of the acidic or basic character of a solution, at a given temperature. No suggestive correlation could be drawn between pH of the effluents and the seasons. However, the lowest pH was recorded in rainy season. Most natural waters have a pH in the range 5.0 - 8.2 (Kongovi et al 1986). It is rare to find strong mineral acids in natural waters due to the natural balance maintained between excess $CO_2$ and $HCO_3^-$ ions. Most Indian rivers have moderately alkaline waters (Ventakeswarlu 1986).

The pH of upstream water was alkaline in nature ranging between 7.2 to 8.9. The lowest value was recorded in July 1986 as there was dilution by increase in the level of water due to rains. The rain water decreases the pH of the river water. Both the effluents also remained alkaline during the entire monitoring period except for few months. This may be attributable for the basic nature of the effluents.
The narrow ranges of fluctuations in pH of HPF effluent indicate that the effluent possess a relatively high buffering capacity which prevents abrupt changes in their pH value. However, in case of GRF, the range was wide or large indicating poor buffering capacity. Similar conditions were noticed in case of the Blue Nile and White Nile of Africa by Sinada & Karim (1984). Kongovi et al (1986) have recorded a pH range of 7.1 to 8.9 in case of upstream water and the effluents of HPF and GRF 6.2 to 10.6 between Feb 1985 - March 1986.

According to Zingde et al (1981), primary production respiration and mineralization are able to alter the pH of the aquatic systems due to the changes in oxygen and carbonate concentrations and this might be predominant in Narmada river because of high turnover rates. Moreover natural turbulence with concomitant aeration can also influence the pH, though to a limited extent. Verma et al (1988) concluded that the high pH value of paper mill effluents was due to the presence of carbonates, caustic soda and bleaching powder used in the processing of raw materials.

pH is known to have a pronounced effect on the toxicity of many materials to fish. The toxicity of ammonia (Hemens 1966) and Zinc (Mount 1966) is increased at alkaline pH
values, whereas hydrogen sulfide (Sano 1976) is more toxic at acid values. Moreover, Katz (1971) has stated that the alkalies of kraft pulping wastes may increase the pH of rivers and lakes to a level too high for fish survival.

Generally, pH values outside the biological range of 6-8 are regarded as inimical to aquatic fauna. The lower lethal limit of pH to fish is about 4, whereas the upper lethal limit is between 10 and 11 (Lloyd and Jordan 1964, Robinson et al. 1976). A number of studies have shown that the pH of pulp mill wastes as discharged to receiving water can contribute appreciably to the toxicity (McLeay et al. 1979). Howard & Walden (1965) estimated that up to 75% of the toxicity of kraft mill effluent is attributable to adverse pH.

Considering the chemical equilibria which limit the concentration of trace metals in fresh water, a decrease in pH would favour a prolonged retention time for some metals in the free water (Borg 1983) Dickson (1980) has recorded negative correlations between pH and Cd, Zn, Pb and Mn.

4.1.3 Temperature

Generally, the surface water temperature follows the ambient air temperature fairly closely. It was found to be true in the present study also. At Station I, the upstream water temperature was always lower by 3 to 6°C in comparison
to the atmospheric temperature except during hot summer and winter. In case of HPF also, the effluent temperature was lower by 0 to 5°C, whereas GRF effluent sometimes exhibited higher temperature (1 to 6°C) than the atmospheric temperature. It may be due to the nature of the effluent or a case of little thermal pollution.

Moreover, the water temperature was higher during dry season than that of the wet season. This is because latitude, altitude, degree of isolation, substrate composition, turbidity, ground or rainwater inflows. Wind and vegetation cover can also influence the temperature of water in rivers. Because of its influence on the physiological processes of aquatic animals, temperature is yet another frequently quoted water quality variable. The solubility of oxygen is affected nonlinearly by temperature and increases considerably in cold water (Venkateswarlu 1969a, Manikya Reddy 1984, Verma et al. 1988). Pinter and Backhaus (1984) have observed that periods of low flow coincide with warm weather in case of Neckar river, which is a tributary of River Rhine in Germany. The temperature of the river water used to reach exceptionally higher level of 27°C during the extremely hot summer.

4.1.4 Electrical Conductivity

Conductivity is a measure of the total amount of ions present in a waterbody and is useful approximation to
chemical richness. It is a numerical expression of the ability of an aqueous solution to carry an electric current which in turn depends on the presence of ions, their total concentration, mobility, valence and relative concentrations and on the temperature measurement (APHA 1980).

Conductivity value for natural waters generally falls in the range of 85 to 120 μS cm⁻¹ (Allen et al 1974). The annual mean of values was 243.6 μmhos/cm at Station II (mean 1828.67 μmhos/cm) and Station III) mean 3678.25 μmhos/cm). This is because the industrial effluents have a very large quantities of dissolved ions in them. In general, minor seasonal variations found in the upstream water contrast deeply with the daily fluctuations in polluted waters. The conductivity values were much higher in summer and lower in rainy season in the upstream water.

The chemical composition of river water depends on a wide variety of physical, chemical and biological features, but three basic mechanisms control surface water chemistry, precipitation, the nature of the bed rock and the evaporation-crystallisation process (Gibbs 1970).

The upstream water (BKM) derives its ionic composition primarily from the rain and the rock or sediments over which the river flows. The rate of evaporation and crystallisation of hot arid regions of the Station I exerts
the main influence over conductivity in summer. Secondary influence on the ionic composition is exerted by macrophytes and phytoplankton and to an increasing extent by the various agricultural and domestic human activities.

According to Welcome (1985) the combined effects of following factors tend to produce higher conductivities in the dry season than in the wet:

1. Dilution effects, whereby flood or rainwater with weak ionic concentration reduces conductivity.
2. Solution effects, the 'shore factor' whereby salts locked on previously dry land by decaying vegetation, animal dung, ash from burnt vegetation etc. enter solution as the flood water extend over longer areas.
3. Wash-out effects, whereby nutrients rich ground water is displayed into the river channel by increased infiltration.
4. Concentration by evaporation and
5. Absorption by living components of the system.

Schmidt (1972) noted consistently higher ionic concentrations during the dry season in Amazon river as compared to the rains. Pinter and Backhaus (1984) reported very high conductivity value (750 $\mu$S Cm$^{-1}$) in case of Neckar river, a tributary of Rhine river, Germany due to increased
mineral components as a result of the geology of the catchment area.

4.1.5 TOTAL SOLIDS (TS), TOTAL DISSOLVED SOLIDS (TDS) AND TOTAL SUSPENDED SOLIDS (TSS):

Total solids refer to both dissolved and suspended solids in the effluent. Waters with high dissolved solids are generally of inferior palatability and water with high suspended solids may be aesthetically unacceptable for various purposes. Waters with high total solids may induce unfavourable physiological reaction in the transient consumer. Thus, the quantity of solids is proportional to the degree of pollution. The total solids were highest at Stations II and III than the upstream Station I. This confirms the degree of pollution at different stations.

The contents of solids provide a widely applied water quality criterion, which in solution exert only a biological influence at high levels of total dissolved solids (TDS) that are more characteristic of marine environments. Dissolved solids do not change the appearance of a waterbody in the same manner as suspended solids (TSS). Owing to this effect on turbidity and colour and in the case of domestic and industrial wastes, also on the oxygen demand more attention is diverted to suspended solids than the total dissolved solids.
According to Allen et al. (1974) the finer suspended matter in natural waters is usually of an organic nature representing colloidal matter which has been fluctuated under the influence of bacteria and protozoa. Inorganic suspended matter is chiefly restricted to material of silicious nature; resulting from the erosion of mineral soils.

The primary ecological effect of inert suspended solids is essentially physical in nature, in which the particulate load in suspension is abrasive, the effective light penetration is reduced and sedimentation occurs.

According to Prasad and Manjula (1980) and Manikya Reddy (1984), the total solid content vary directly with the rate of water flow, since surface runoff adds more and more solids during the rainy season to the water. In contrast, a reduction in flow leads to sedimentation of suspended material. In the present investigation also high values of total solids were recorded during the rainy season at all stations.

Suspended solids concentration is almost solely dependent on the physical considerations of the stream flow velocity and the nature of the stream bed. Runoff increases the amount of suspended material due to terrestrial and shoreline erosion and a resuspension of river sediment.
through increased turbulence. Delfino and Byrnes (1975) noted that the changing hydrological conditions, for example discharge or flow, affected the concentrations of both the dissolved and suspended constituents in Missouri river of Nebraska, USA. A number of parameters including total phosphorus, total organic nitrogen, oxygen demand and certain metals correlated with the increased solids.

In the present case, the surface run off of rain water might have carried the solid waste particles (fly ash or local ash used by boilers) dumped adjacent to the effluent canals, as the land exhibited slope towards the canal and river Tungabhadra (Fig.6, 1C). Soil erosion is high at the catchment area due to sparse vegetation (Acharyulu 1991).

Kongovi et al (1986) during their earlier investigations from Feb 1985 to March 1986 noticed higher concentrations of total solids in the effluents than the river water of Tungabhadra at Kumarapatnam near to Harihar (Karnataka). The values of total solids in the effluents were generally in thousands of mg/l level (upto 9800 mg/l). In the present study (Msay 1986 to April 1987) also higher quantities of total solids i.e. range of 320.0 - 3302.0 mg/l and 11310 - 9898.0 mg/l of total solids in HPF and GRF effluents respectively, were recorded. In the upstream the annual average of total solids was 264.37 mg/l.
with a range of 96.0 - 534.0 mg/l. The GRF effluents exhibited higher amount of total solids.

In the present investigation, the total dissolved solids were always more than the total suspended solids as observed by earlier studies (Manikya Reddy 1984, Balakista Reddy 1989) in other South Indian rivers. They may consist mainly the dissolved mineral contents and organic matter. Temperature will also affect the concentration of dissolved solids. Higher temperatures first of all permit higher solution rates of soluble materials. This can be further aggravated in downstream areas of tropical rivers where precipitation is low and evaporation is high leading to increases in the concentration of dissolved materials. While this is most evident in the concentration of dissolved salts, other soluble materials also show a tendency to increase. In the present study, maximum concentration of total dissolved solids (TDS) was recorded in May 1986 at all the three sampling stations.

The marked fluctuations observed in case of HPF effluent may be attributed to the characteristics of the polluted waste water. In Sundays river, Eastern Cape, South Africa, the chemical characteristics of the water and the raised TDS levels were obviously due to geological effects and geographical nature of the catchment (Forbes and Allanson 1970).
Seasonal fluctuations in TDS levels were noticed by Edwards & Brooker (1984) in river Wye of South Britain. TDS was lowest in winter season and highest during summer. At Harihar, the highest value was noticed in summer at all stations. Edwards et al (1984) noticed higher average suspended solids exceeding from 400 mg l⁻¹ in river Ebbw of Great Britain derived from coal wastes. In case of Italian peninsula river PO, the suspended materials varied markedly and influenced by meteorological events. The main value ranged between 45 - 450 mg/l with a maximum value of 6400 mg/l (Chiaudani & Merchetti 1984). Similar marked seasonality in the fluctuation of total residue was noted by Sinada and Abdel Karim (1984) in the Blue Nile river of Sudan. During rainy season it received great quantities of silt, clay and fine sand carried by its numerous tributaries.

Limited concentrations of suspended solids in suspension are detrimental to aquatic fauna such as fish only when their shape is sharp or irregular. For example, because of their needle like shape, fibres contained in pulp and paper wastes have an apparent toxicity to fish. Sublethal effects are compatible with an interference with respiration (Kramer & Smith 1965). Betts & Wilson (1967) stated that the suspended solids in the effluent discharge should be very low, of the order of 36 ppm, but with the
proviso that this standard might be lowered still further. Sprague & McLeese (1968) have stated that plugging of gills by particulate matter has been found to be one important reason for fish death. This was supported by Pearson (1972).

Suspended solids will also increase the turbidity of the receiving water and this can interfere with conditions that favour "good fish fauna" (EIFAC 1964). In a lake or similar site, this can contribute to "lignotrophic" condition (Eloranta 1970), in which the reduced penetration of sunlight affects the phytoplankton. Suspended solids can also lead to benthal deposits McKeown et al (1968) which produce mats on the bottom of receiving waters, with resultant destruction of fish food and spawning grounds (Wilber 1969). Pearson (1972) and Waldichuk (1962) also opined in similar patterns. Waldichuk (1962) has reported that, as a result of such bottom sediments crabs and other invertebrates are wiped out. Moreover sediments generate $\text{H}_2\text{S}$ and when dredging operation stir up the bottom, a fish kill may occur. Recent reports of Alabaster (1972) Pearson (1972) have emphasized that settleable solids can contribute to deoxygenation of water, with consequent elimination of oxygen dependent species in the affected zone.
4.1.6 Chemical Oxygen Demand (COD):

The two main determinations for assessing the level of water contamination by chemical species which can undergo biological and chemical oxidation are: the standard BOD, which is an estimate of the amount of $O_2$ needed to stabilize the organic material in the sample, and the standard COD, which gives a measure of the amount of organic material that is chemically oxidized. This chemical test is less subject to errors and has the advantage of being rapid and uses strong oxidising agents, thus providing a measure of the oxygen equivalent of water samples (Goodwin et al 1977).

The five-day BOD determination (APHA 1980) is an empirical test, conducted under standardized laboratory conditions which measures the oxygen required by bacteria to metabolize the available organic material in the sample. The test provides an estimate of the potential drain placed upon the DO resource of a waterbody. The controversy as to the value of the BOD test has arisen principally from its misuse. The most notable example of inappropriate use has been the transfer of in-bottle BOD decay rates to predict in-stream deoxygenation (UN 1990). Another disadvantage is the time allowed for the test is usually five days, and the difficulty arises out of the use of some of the $O_2$ oxidising ammonium and organic nitrogen to nitrates and nitrites. Moreover a number of workers have advised against over
reliance on 5 day BOD as a means of assessing long term demand in receiving waters. Gates and Ghosh (1971), Raabe (1968) and Razzel (1972). Because of all these considerations BOD tests were not undertaken during the present investigation.

COD is a more realistic measurement of total oxygen demand and it analyses both diodegradable and non biodegradable organic matter. For samples from a specific source, COD can be related experically to BOD, organic carbon or organic matter content (APHA 1980). The COD of waste is generally higher than the BOD because more compounds can be chemically oxidised than can be biologically oxidised.

In the present investigation, the COD of HPF and GRF effluents were always higher than in Upstream water. This may be due to higher concentration of toxic substances and oxidizable organic matter in the effluent. Similar results were recorded by Verma et al (1988) in the effluents of Aryabhattach Paper Mill, near Kosi, Darbhanga (North Bihar). Srivastava et al (1988) observed high concentration of COD, BOD, sulphate and total solids in the effluent of Orient Paper Mill, Amlai (M.P), upto 30 km downstream from the mill.
The COD values exhibited marked fluctuations in case of HPF and GRF effluents during the period of monitoring. It may be attributed to the fluctuations in the concentrations of various parameters responsible for oxygen demand throughout the study period (Table 1,2,3). Friedrich and Miller (1984) too observed an increase in COD values on passing down the river Rhine (Central Europe) due to the presence of toxic substances from industrial household sources and also from numerous non-point sources originating from streets or agriculture. According to Joshi and Dutta (1987) the dark coloured waste water of Orient Paper Mill, Amlai (M.P) contain major pollutants such as lignin, its derivatives and various carbonaceous substances dissolved from the raw material (Bamboo etc) during pulping process.

Fujiya (1961) reported severe histological and histochemical changes in fish caged near Kraft pulp mill outfalls. He has documented pathological changes occurring to Sparus microcephalus on 12-24 h exposures in receiving waters containing kraft pulp mill effluent. When COD was 10ppm, the ribonucleic acid content of the pancreas declined and at COD values exceeding 50 ppm, nacrosis and disquamation of intestinal epithelia occurred.

4.1.7 Dissolved Oxygen (DO)

Dissolved oxygen estimation is one of the most important parameters in water quality studies. The
distribution of DO within the aquatic ecosystem is one of the main factors influencing the distribution of fish (Welcomme 1985) In order to be an asset and support life, a river must contain adequate DO so that a balanced spectrum of aquatic life can survive.

The impact of low concentrations or anaerobic conditions reflects in an unbalanced ecosystem, fish mortality odours and other aesthetic nuisances. The three main sources of DO in any aquatic ecosystem are:

1. Aeration from the atmosphere
2. Photosynthetic oxygen production and
3. DO in incoming tributaries.

The oxygen content of surface waters has a strong influence on the diversity of species of fish in the aquatic populations. It influences the distribution and abundance of algal and other aquatic plant populations also. If a stream is severely polluted, the DO may disappear entirely and the anaerobic organism dominate to produce toxic conditions as well as foul odour. The river becomes deoxygenated or even anoxic due to the decomposition of organic material, the oxygen demand of fish and increased temperatures. In deoxygenated water, $\text{H}_2\text{S}$ concentration may build up through the decomposition of bottom mud and detritus.
In the present study, the upstream water at Station I recorded significant levels of DO (more than 6.30 mg/l) during the period of monitoring. The annual mean value remained 9.85±3.57 mg/l which is suitable to support diverse biota, substantially higher than those of the two effluents. This may be attributed to the aeration of water from the atmosphere due to turbulence and wind action, photosynthetic oxygen production and DO in incoming tributaries. The maintenance of DO levels depends mainly on temperature, oxidizable organic matter and biota. Katz (1971) emphasized that the saturation solubility of O$_2$ in water is 9-1 ppm at 20°C and 7.5 ppm at 25°C.

In the present investigation the DO content of the effluents was much less than that of unpolluted upstream water. Kongovi et al. (1986) too reported drastic depletion of DO in HPF and GRF effluents as well as in downstream region, nearly 200 yards from the discharge point. In case of effluents, the variation in DO level was quite irregular and the difference between the maximum and minimum concentrations was quite appreciable. In several occasions the minimum level fell to zero and rarely exceeded 2 mg/l. The annual mean DO values of HPF and GRF effluents were 2.11±2.32 mg/l and 2.19±2.09 mg/l respectively. Seasonal variations were not evident here, as their mean values indicated the effluents were poorer in DO content and may cause adverse effects on aquatic organisms.
The upstream water exhibited higher DO content in winter and summer seasons and lower in rainy season. Similar conditions were recorded by Delfino and Byrnes (1975) in Missouri River of Nebraska (USA) where the low DO saturation level (64%) in July 1972 was due to increased oxygen demand loading observed during a heavy rainfall-stimulated high discharge period. Berner (1951) ascribed the low DO values reported during the periods of very high turbidity to the in situ oxidation of the organic fraction in the suspended material. Rather than seeing a decrease in oxygen demand due to dilution of a steady-state stream oxygen demand, the increased discharge, by causing higher suspended solids and turbidity levels, created higher oxygen demand concentration. A very high correlation coefficient was observed between TSS and the three oxygen demand parameters (BOD, COD, TOC). Further studies pointed the influence of organic enriched soils (from terrestrial run-of and resuspension of bottom sediments) on the water quality of the Missouri River. This probably explains the occurrence of low DO in rainy season, in the present investigation. The higher DO level during summer may be due to the greater availability of oxygen in fresh water attributed to photosynthesis by phytoplankton and algae. Among processes adding oxygen to the water, phytoplankton photosynthesis is predominant in summer and the oxygen production depends on
algal biomass and factors influencing its photosynthesis. Natural aeration is very little at times of low flow.

Higher DO level in winter season could be due to the higher solubility of gas at low temperature and increased photosynthesis. In general, the solubility of oxygen is affected nonlinearly by temperature and increases considerably in cold water (Venkateswarlu, 1969 a, Sampath Kumar 1977, Manikya Reddy 1984 and Verma et al. 1988). Heise (1984) observed similar results in case of River Gudena of Denmark. It dropped from a winter level of above 8 mg/l $O_2$ to a summer level of below 5 mg/l.

The reduction in the DO level at Station I in the month of May 1986 may be due to the rise in temperature. The increase in temperature not only decreases the dissolution rates of gaseous oxygen but also increases the rate of oxidation of organic matter and hence the rate of oxygen consumption (Zingde et al. 1981).

Edwards et al. (1984) recorded negligible DO content in river Ebbw of Great Britain despite the higher reaeration capacity of the river, which was associated with its shallow and generally fast current. The natural $O_2$ supply from the air is reduced because of lower current speeds and the water depth of 3 m. Depletion of oxygen is particularly marked in summer when temperatures are still higher and algal
photosynthesis is less effective (Pinter and Backhaus 1984). In Neckar river, a tributary of river Rhine (Germany) they observed that the higher temperatures favour microbial, oxidative breakdown of organic materials, thus reducing the O$_2$ content of water.

The higher values of DO in case of HPF and GRF effluents in the month of August 1986, may be attributed to the rains. As the rain water increases the level of water in the river, there is initial rise of dissolved oxygen concentration due to the combined effects of factors such as increased turbulence, low temperature and aerating action of wind. The increased turbulence brings about better mixing of air with river water.

In dry season, DO conditions are linked to a number of factors including the size of the waterbody or pollutants, degree of thermal stratification, vegetation cover, phytoplankton development and wind action. In general, there is a tendency for even comparatively shallow bodies of water to stratify with higher DO concentrations near surface. This may explain the higher DO levels noted in summer season at Station I. In shallower water bodies, which lack vegetation cover, wind action may ensure mixing through the whole water column (Schmidt, 1973). Chiaudani and Marchetti (1984) observed a vertical gradient of DO content under the
conditions of intense solar radiation in case of river PO (Italian Peninsular river). The oxygen deficit at some stations was attributed mainly to plankton respiration and at others to benthic respiration.

In general, the effluents require oxygen for decomposition, the higher the amount of such wastes, the greater will be the demand for oxygen from the receiving waters. As the amount of wastes becomes very large, the stress imposed on all the aquatic organisms will be very serious.

In deoxygenated water, \( \text{H}_2\text{S} \) concentration may build up through the decomposition of bottom mud and detritus. Their decomposition may deplete the DO in the waterbody completely that is vital for aquatic life. The presence of even a small quantity of \( \text{H}_2\text{S} \) (1.0 ppm) is toxic to aquatic lives especially fish (Doudoroff and Katz 1950). Probably this was the reason behind the total absence of fish in paper mill waste water (Verma et al. 1988). Mass fish mortalities have been recorded from Brazil (Brinkmann & Santos, 1973), Gudina Heise 1984) and the Kafue flats (Tait 1967). In both the cases, the mortalities were attributed to sudden reduction in temperature cooling the surface water which coupled with strong winds caused a rapid breakdown of stratification, abrupt deoxygenation and contamination with \( \text{H}_2\text{S} \) to lethal
levels. In river Tungabhadra also mass fish kill took place several times. For example, major fish kill of 14th Feb. 1984, 8th March 1986, 20th June 1986 followed by recent episode from 16th March 1992 to 18th March 1992 (Fig. 21,a,b).

Normally a high level of DO is required to sustain the performance of various fish species. According to Katz (1971) the Salmonoid fish require a DO level of 7 to 8 ppm to carry out all their necessary activities. It is widely accepted that a DO level of 3 to 5 mg/l is the minimum required to support a balanced population of aquatic flora and fauna. It must be kept above zero in order to avoid foul odours or other nuisances (Palange & Zevala 1987).

4.1.8 Free Carbon dioxide

Surface waters normally contain less than 10mg/l of free carbon dioxide while some ground waters may easily exceed this concentration. Recarbonation of a supply during the last stages of water softening is a recognise treatment process (APHA 1980). The CO$_2$ content of a water may contributed significantly to corrosion.

The CO$_2$ system is the principal source of dissolved inorganic carbon, which is of great importance to primary productivity by plankton algae. CO$_2$ dissolves in water to form a weak acid which greatly increase the ability of water
According to Hutchinson (1957) high pH favours the conversion of CO\textsubscript{2} into CO\textsubscript{3}, whereas at low pH, the conversion is reversed in favour of CO\textsubscript{2}. Moreover, pH, carbonates, bicarbonates and carbon dioxide form a complex in the medium and the fluctuations in one may reflect on the other thereby showing either a direct or inverse relationship between any two of these factors (Sudhakar 1989). At the same time, living organisms contribute the CO\textsubscript{2} concentration through respiration.

In the present study, the effluents always recorded higher CO\textsubscript{2} concentration than the upstream water. Aerobic degradation of organic matter might have contributed to the higher levels of carbon dioxide at Stations II and III (HPF, GRF) than that of Station I (BKM). Among effluents, the HPF effluent had four times CO\textsubscript{2} concentration than that of GRF effluent.

4.1.9 Chlorides

Chloride (Cl\textsuperscript{-}) is one of the major inorganic anions present in water and waste water. In the presence of sodium it imparts salty taste to the water. In drinking water, the salty taste produced by chloride concentration is variable and dependent on the chemical composition of water. Their concentration in industrial waste water is higher than in the raw water. It also may be increased by industrial processes (APHA, 1980).
A high chloride content may harm metallic pipes and structures, as well as growing plants. Its importance in plants is associated with ionic balance and osmosis although it is believed to have catalytic function as well.

Earlier workers have explained that its major source is sewage (Venkateswarlu 1969a, Rajagopalan et al. 1970, Rai 1974a, Whitton and Crisp 1984, Manikya Reddy 1984). Chloride's principal source is animal matter, sewage or drainage. Sampath Kumar (1977) has reported increased concentration of chlorides at polluted station sin River Moosi and less values in unpolluted stations.

In the present study also, higher concentration of chloride content was observed in the effluents of HPF and GRF industries. The concentration of chlorides was always many times higher than that was present in the upstream water (BKM). Moreover higher chloride contents were recorded during summer at all stations while the lowest were observed during rainy seasons. The maximum values were noted during low water flow of dry season whereas the minimum during the higher level and flow of rainwater. The marked fluctuations observed in HPF and GRF effluents may be due to the increased industrial pollution. In River Ebbw of Great Britain, Edwards et al. (1984) reported the higher concentration of chlorides derived from sewage discharges.
and coal wastes. They were not markedly flow-dependent. Many other workers have reported higher concentration of chlorides in various rivers. Sudhakar & Venkateswarlu (1989), Huff & Horkan (1984) and many others have reported high chloride content due to pollution. Pinter & Backhaus (1984), Prat et al. (1984) and Bass & Harrel (1981) have reported high chloride content as a result of the geology of catchment composition of geological substration and oil field brines respectively.

In the present study, the chloride content in the effluents was always higher than that of the upstream water. It may be ascribed to the industrial pollution or processes.

4.1.10 Carbonates and Bicarbonates

Inorganic carbon constitutes a major nutrient of photosynthetic metabolism by algae. The total inorganic carbon concentration in fresh water depends on pH, which is governed by reactions involving the carbonate system. When CO$_2$ gas dissolves in water carbonic acid is formed. This in turn dissociates to HCO$_3^-$ and CO$_3^{2-}$ ions. All these reactions are reversible. At pH 5 and below, free CO$_2$ dominates in water and above pH 9.5, CO$_3^{2-}$ is quantitatively significant. Between 7.0 and 9.0 pH, HCO$_3^-$ dominates (Wetzel 1975). According to Hutchinson (1957), high pH favours the conversion of CO$_2$ into CO$_3^-$ whereas at low pH, the conversion is reserved in favour of CO$_2$. 
One might have a rough judgement of the water composition after determining total hardness, the concentrations of $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, $\text{Cl}$, $\text{SO}_4^{2-}$ and pH. In the present study carbonates were found to be absent at all stations throughout the period of monitoring except for Feb. 1987 in case or Upstream and June 1986 in GRF effluent. The HPF was characterised by the complete absence of carbonates. The absence of carbonates in the upstream water may be ascribed to the geology (see section 2.1), where the red loamy soils are characterised by the absence of lime and free carbonates.

According to Sudhakar (1989) pH, carbonates, bicarbonates and $\text{CO}_2$ form a complex in the medium and the fluctuations in one may reflect on the other, thereby showing either direct or inverse relationship between any two of these factors. In the present study, the maximum and minimum values of bicarbonates were recorded during summer and rainy seasons respectively in the case of Upstream water (BKM) whereas it exhibited well marked fluctuations in the two effluents (HPF and GRF). The latter recorded higher values for bicarbonates than the former.

The carbonates were found to be not detected in a similar study by Sinada and Abdel Karim (1984) in White Nile and Blue Nile rivers of Khartoum, Sudan. Here the total
alkalinity was primarily due to bicarbonate ions and seasonal variations were reported. The alkalinity values increased gradually and steadily during the dry season, but decreased during the wets season. A similar finding has been observed in several African rivers (Hall et al. 1977, Balon & Coche, 1974). Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate and hydroxide content it is taken as an indication of the concentration of these constituents. However, Edwards & Brooker (1984) reported that the seasonal changes in the concentration of bicarbonate were lowest during the winter and highest during the summer in case of a Southern Great Britain river, Wye. This was attributed to the seasonal pattern of flows, and simple concentration flow regression of this major ion.

Even though the carbonates were absent foremost of the period of monitoring at all the stations, CO₂ was present in these months at all the stations. This can be attributed to the conversion of soluble calcium carbonate to insoluble form in the presence of CO₂. Similar findings were reported in River Manjira (AP) by Sheshadri (1989), Manikya Reddy (1984), Zingde et al. (1981), Sudhakar & Venkateswarlu (1989), Kongovi et al. (1986) have reported high quantities of bicarbonates at polluted stations. Kongovi et al. (1986) reported very high bicarbonate content in all the water
samples collected from the GRF discharge point up to Kuruvatti (42.0 km downstream from discharge point). According to them water is unfit for irrigation.

According to Sinada and Abdel Karin (1984) the high value of alkalinity of White Nile and Blue Nile rivers of Sudan imply a large reserve of total CO₂ which reflects an adequate supply of inorganic carbon for the support of algal populations. However, in case of Neckar river, a tributary of Rhine (Germany), Pinter and Backhaus (1984) have ascribed the high concentrations of bicarbonates to the geology of the catchment area. According to Prat et al. (1984) the high concentrations of carbonates and bicarbonates along the whole length of the river Llobregat, a typical mediterranean river of North East Spain, was due to the composition of the geological substratum of the river.

4.1.11 Calcium

The presence of calcium (5th among the elements in order of abundance) in water supplies results from passage through or over deposits of limestone, dolomite, gypsum and gypsiferous shale. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating. However appreciable quantities of calcium salts breakdown on heating to form harmful scale in boilers, pipes and cooking utensils.
The concentration of Ca ranges usually encountered are as follows (Allen et al. 1974).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral soils</td>
<td>0.5 to 2% (Excl. calcareous)</td>
</tr>
<tr>
<td>Soil extraction</td>
<td>10 to 200 mg.100 g$^{-1}$ (excl. calcareous)</td>
</tr>
<tr>
<td>Rain waters</td>
<td>0.1 to 3 mg/l</td>
</tr>
<tr>
<td>Fresh water</td>
<td>1 to 100 mg/l</td>
</tr>
</tbody>
</table>

Ca contributes to the total hardness of the water. It is a required nutrient for normal plant metabolism. Calcium is essential for the maintenance of the structural and functional integrity of the cell membranes. It is the second most dominant cation in river waters. Ca is essential for apical and root tip development and accumulation in cell walls as calcium pectate. It is one of the dominant elements in the skeletal structures of many animal groups.

Some waters are relatively rich in Ca and tests for hardness (which also includes Mg) are essential for water treatment. Kongovi et al. (1986) have observed low Ca and Mg contents in the effluents of HPF and GRF and there was no appreciable increase in their contents during the study period. However, they recorded slight increase from Feb. to May. In the present study, higher values were recorded in summer whereas lower values in rainy and winter seasons at all the stations. Moreover, effluents recorded higher values
than the upstream water of Tungabhadra indicating its origin due to pollution by industries. The upstream recorded annual mean value of 28.32±9.67 when compared to those of HPF and GRF effluents, 90.86±25.75 and 115.03±61.18 respectively.

Similar results were recorded by others in effluents of GRASIM Complex at Nagda, Ujjain (MP) also. Trivedi (1979) recorded 221mg/l of Ca (17.71 tons/day of Ca) and 63mg/l of Mg (i.e. 5 tons/day of Mg) in Chambal river whereas Narendra Dad (1981) reported to 50 mg/l of Mg in River Chambal at Nagda (MP) due to GRASIM industries.

Calcium is a dynamic ion and can exhibit marked seasonal and spatial dynamics. In the present investigation also seasonal variation was noted. Higher calcium content was noted as a result of pollution in many cases. (Somashekar & Ramaswamy 1982-83, Sudhakar & Venkateswarlu 1989, Manikya Reddy & Venkateswarlu 1986). Moreover Somashekar et al. (1984) observed a substantial reduction in the germination percentage of paddy seeds, which they attributed to the presence of higher amounts of Ca/Mg and other dissolved salts present in the effluents of paper mill, textile mill and food and chemical industries.

Similar results were noted in other countries also. Edwards & Brooker (1984) recorded lower and higher calcium and magnesium contents in river Wye (Southern UK) in winter
and summer seasons respectively and they attributed this
difference to the seasonal pattern of flows and simple
correlation flow regression of these ions. Pinter and
Backhaus (1984) in Neckar, a tributary of Rhine (Germany)
recorded the higher $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ contents as a result of
geology of its catchment. The upstream water in the present
case might have received its $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ from the geology
of its catchment, run-off from agricultural fields etc.
Kawecka and Szcesny (1984) observed high values for Ca and
total alkalinity along the whole length of Dunajec river of
Poland as a result of the $\text{CaCO}_3$ type of water of the river.

Soils vary greatly in their calcium content. It may
range from zero to several hundred milligrams per 100 gms.
The annual mean values of calcium content was found to be
five times more in case of sediments of HPF canal and
approximately nine times more in case of sediments of GRF
effluent canal than in the unpolluted upstream sediment
samples. The maximum and minimum were observed during summer
and rainy seasons. This finding coincided with the seasonal
variation of Ca content in case of the upstream water
samples. However, will marked fluctuations were observed in
case of sediments of effluent canals.

4.1.12 Magnesium

$\text{Mg}$ ranks 8th among the elements in order of abundance
and is a common constituent of natural water. They are
important contributors to the hardness of water and when heated Mg salts normally breakdown to form scale in boilers. Moreover, concentrations greater than 125 mg/l may exert a cathartic and diuretic action (APHA 1980). The concentration may range from zero to several hundred milligrams per litre depending on the source.

The concentration ranges generally encountered are as follows (Allen et al. 1974).

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral soils</td>
<td>0.2 to 3%</td>
</tr>
<tr>
<td>Soil extractions</td>
<td>4 to 50 mg·100g⁻¹</td>
</tr>
<tr>
<td>Rain water</td>
<td>0.1 to 2.0 mg/l</td>
</tr>
<tr>
<td>Fresh water</td>
<td>0.5 to 20 mg/l</td>
</tr>
</tbody>
</table>

Mg has been accepted as being a major nutrient and is needed by all organisms since it activates many enzyme systems and is involved in phosphorus transfer processes. It is an essential constituent of the chlorophylls.

Its concentration is always lower than that of calcium in natural waters (Dakshini and Soni 1979, Manikya Reddy & Venkateswarlu 1986, Manikya Reddy 1984, Sudhakar 1989, Sheshadri 1989). In the present case also similar result was observed at all stations. Lower values were observed during the wet season whereas maximum values were found to be more erratically fluctuated at Stations II and III. The lower
values were due to dilution during the rainy season. In the upstream station, higher values were recorded in winter season. The fluctuations in the effluents can be ascribed to the different degrees of pollution load of the industries. Prasad & Manjula 1980, Manikya Reddy 1984 and others have suggested that the fluctuations in case of CA and Mg were due to different degrees of dilution of water discharged from the paper mill.

Higher concentration of Mg in effluents were reported by many earlier workers (Somashekar & Ramaswamy 1982-1983, Somashekar et al 1984, Somashekar et al. 1983 and Verma et al. 1988).

Magnesium is present in many primary silicate minerals (biotite, amphibolites and olivines) and also occurs in dolomite and certain salts. It is widely distributed in soils and is particularly associated with clays. In general, availability is higher in basic and neutral soils and lower in acid soils.

In most soils much of the Mg is fixed in primary and secondary minerals such as micas, carbonates etc. Plants appear to be relatively sensitive to a slight deficiency or excess of this element (Jacob 1958). The higher and lower values of sediment samples coincided with the values of water samples. The greater Mg concentration of GRF sediments
(Station III) than the BKM and HPF sediments also found to be coinciding with the values of the water samples. It shows that Mg was deposited in the sediments in considerable number.

### 4.1.13 Total Hardness

Hardness is defined as the sum of calcium and magnesium concentrations, both expressed as $\text{CaCO}_3$, in milligrams per litre. Hardness in water is due to the presence of divalent metallic ions (the principal ones are calcium and magnesium) and is expressed as the equivalent quantity of $\text{CaCO}_3$. Hardness is mainly due to the presence of bicarbonates of calcium and magnesium or to sulphates and chlorides of Ca and Mg. Carbonates and bicarbonates are believed to contribute to the temporary hardness of water whereas permanent hardness is due to sulphates and chlorides of calcium and magnesium (Sudhakar 1989). The hardness may range from zero to hundreds of mg/l in terms of $\text{CaCO}_3$ depending on the source.

Sawyer (1960) considered water with less than 75mg/l of $\text{CaCO}_3$ as soft and above 75mg/l of $\text{CaCO}_3$ as hard. Hardness in water forms scale on pipes and fittings in water supply system, then reducing or elimination corrosion. But excessive hardness can lead to the partial blocking of pipes and additionally reacts with soap to form a curdy precipitate.
In the present study, the upstream water of Tungabhadra the total hardness ranged between 16.0108 - 123.55 mg/l. with an annual average of 71.65±31.65 mg/l. Except for the month of Jan. 1986, Nov, Dec, March and April 1987, the total hardness values were lower than 75 mg/l level. The higher values of total hardness may be due to the presence of bicarbonates of calcium and magnesium. The maximum and minimum values were seen in the dry and wet seasons respectively. They corresponded with the low and high rate of flow in the river. The carbonates were lacking while sulphates and chlorides were in low concentrations. When compared to the unpolluted upstream zone, the HPF effluent and GRF effluent were having four and five times more total hardness as shown by their annual mean values. (HPF mean 237.93±145.71 mg/l and GRF mean 347.57±301.49 mg/l). This increase in total hardness may be attributed to the increased concentrations of bicarbonates, sulphates, chlorides along with calcium and magnesium due to industrial processes.

In effluents fluctuations were marked. The higher concentration was observed during the dry season at all stations. The lower values found to be varying in case of effluents. It may be due to different degree of dilution of water discharged from the mill or physico-chemical characteristics of the effluents. This was in agreement with

Higher hardness of water may affect the health of people adversely. According to Amavis et al. (1976), earlier studies in Europe and North America have shown an inverse correlation between the hardness of drinking water and the incidence of cardiovascular disease (heart disease, hypertension and stroke). A similar inverse correlation between the hardness of water and the risk from several non-cardiovascular cases of death was indicated by other studies.

4.1.14 Sodium

Sodium ranks sixth among the elements in order of abundance and is present in most natural waters. Hard waters which are softened by the sodium exchange process may have relatively higher concentrations. A high sodium ratio affects the soil permeability adversely and the ratio of sodium to total cations is important in human pathology and in agriculture. Sodium contributes to the ionic balance of the cell fluid and is essential for animals, through apparently not for plants. The concentration ranges
generally encountered (excluding saline soils) are given below (Allen et al. 1974).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Mineral soil</td>
<td>0.1 to 5%</td>
</tr>
<tr>
<td>Soil extraction</td>
<td>2 to 20 mg.100g⁻¹</td>
</tr>
<tr>
<td>Rain water</td>
<td>0.5 to 15 mg/l</td>
</tr>
<tr>
<td>Fresh water</td>
<td>2 to 100 mg/l</td>
</tr>
</tbody>
</table>

In the present investigation, the effluents recorded significantly higher sodium content than the upstream water. The higher quantity of sodium in effluents may be due to the pollution by industries. They use sodium salts for their manufacturing process. The higher and lower concentrations were recorded in dry and wet season respectively. During summer the reduction in flow and higher rate of respiration always favour a higher value for sodium. Increased river discharge caused by run off during rainy season decreased the concentrations of major dissolved ionic constituents in the river. Specially, increased discharge led to lower concentrations of sodium chloride, calcium and sulphate. Delfino and Byrens (1975) observed similar results in case of Missouri River (USA).

Many earlier workers too observed greater concentrations of sodium and a wider range of fluctuations than potassium in water and effluents (Sinada & Abdel Karim 1984; Somashekar & Ramaswamy 1984, Kongovi et al. 1986,
Seshadri (1989). Moreover, Sinada and Abdel Karim (1984) noted that the maxima of Na and K in Blue and White Nile rivers of Sudan coincided with the end of the dry season, which is in agreement with our results also.

Although sodium is present in certain silicate minerals, the levels in non-saline soils are relatively low. The sodium content of saline soils is very high since the salts of sodium are readily soluble. The optimum sodium content for different soils may be considered to be in the range of 5-20mg.100g⁻¹ soil. According to Chanakya (1981) the HPF effluent with high sodium and electrical conductivity values affected soil even upto 25 cm depth. It is in this zone that the plant roots depend for their nutrition. Somashekar et al. (1984) recorded that the Na and K content increased in all the soil types after irrigation with the effluents of paper and textile mills which resulted in poor germination of paddy seeds. Kongovi et al. (1986) reported higher Na and K contents from soil samples collected from Nalavagal village which is in the vicinity of the industry. Similar results were obtained in the present study also.

The sodium content was higher in sediments of the effluent canals when compared to that of upstream water. Higher values were recorded in summer whereas lower Na contents in winter and rainy seasons. All these observations
clearly coincided with the values of the water and effluents flowing over these sediments. The higher content was due to the industrial processes where compounds like sodium sulphate, sodium hydroxide and sodium carbonate (See 1.1.4) are used in large quantities.

4.1.15 Potassium

Eventhough potassium ranks 7th among the elements in order of abundance, its concentration rarely reaches 20mg/l in most drinking waters. Potassium is essential to all plants for cell and membrane organization and protein synthesis. It appears to be the only major ion without a structural function in living organisms (Allen et al. 1974).

The concentrations generally encountered are as follows:

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<tr>
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</thead>
<tbody>
<tr>
<td>Mineral soil</td>
<td>0.1 to 2%</td>
</tr>
<tr>
<td>Soil extraction</td>
<td>5 to 50 mg.100g⁻¹</td>
</tr>
<tr>
<td>Rain water</td>
<td>0.1 to 1.0 mg/l</td>
</tr>
<tr>
<td>Fresh water</td>
<td>0.5 to 10 mg/l</td>
</tr>
</tbody>
</table>

In the present study, potassium was always less than sodium content. Several workers have reported similar results (Mitra 1982, Manikya Reddy & Venkateswarlu 1986, Venkateswarlu 1986, Somashekar et al. 1984, Somashekar & Swamy 1984, Somashekar et al. 1983 and Delfino and Byrnes 1975). Edwards and Brooker (1984) observed seasonal changes,
particularly higher contents in summer and lower contents in the winter season. He attributed them to the seasonal pattern of flows in the river.

In the present investigation, the concentration of potassium exhibited narrow variations during May 1986 to April 1987 at all stations. In the upstream water seasonal fluctuation due to the changes in flow rate was observed.

Although K is present in relatively large amounts in most soils, its soil chemistry is very complex and most of it is fixed in a form not available to plants.

Potassium is a structural element of many soil minerals (notably feldspars and micas). In addition it undergoes fixation and releases phenomena associated with clay minerals including illite which is itself a source of the element. Some of these "fixed" potassium is moderately available to plants but the readily available fraction includes that held by soil colloids and some in true solution. Mobile potassium is readily leached from light soils and also from the organic matter.

In case of sediment samples, the values almost coincided with the trend of potassium concentration fluctuation of water samples. The sediments of HPF and GRF effluents recorded higher values of K content from the
upstream sediment. They might have received them from the effluent samples flowing over them.

4.1.16 Sulphates

Sulphate is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per litre. Sulphur is widely distributed in rocks, being present as sulphides in unweathered igneous types. Weathered material, particularly sedimentary rocks may contain significant amounts of sulphate. Mineral sulphur in soils is normally sulphate but sulphide and sulphites may be present under reducing conditions. Precipitation may contribute a significant amount of sulphate to the soil solution and this is of both maritime and industrial origin. The concentration range generally encountered in rain water is 0.4 to 4 mg/l and in fresh water it varies between 2 to 150 mg/l (Allen et al. 1974).

Sulphur itself is almost never a limiting factor in aquatic ecosystems. The normal level of sulphates is more than adequate to meet plant needs. Odorous conditions are easily created when water is overloaded with organic waste. In the presence of organic matter, certain bacteria may reduce sulphate to sulphide producing $\text{H}_2\text{S}$ and a rotten egg smell.
The major sources of sulphur in natural waters are rocks, fertilisers and water discharges from industries. Moreover, sulphates are also derived largely from human activities sewage and fertilisers. According to Skullberg & Lilliehammer (1984) the source of sulphates in the river Gama was due to precipitation of air pollutants.

In the present investigation, the sulphate content was always higher in the effluents than in the upstream water. In the upstream water it remained low whereas an case of HPF and GRF effluents, the lower value was noted in July when compared to the consistently higher values of the remaining period. The GRF effluent recorded three times more sulphates than that of HPF effluent. The higher concentration of sulphates in both the effluents can be ascribed to the various chemicals used in viscose process (See 1.1.4). The wastes from the spinning bath of the industry in general contains sulphuric acid, sodium sulphate, zinc sulphate, hydrogen sulphide and carbon disulphide in them. Moreover, the pulping processes use sulphur-containing compounds (See 2.2). The industry produces sulphuric acid, carbon disulphide and sodium sulphate in large quantities along with the grasilene fibre. All these may contribute to the higher sulphate concentration of the effluents, particularly in GRF effluent. In the wet season July (1986), the effluents get diluted as a result of rain and may receive
the run-off water from the solid waste (coal ash or fly ash) dump also. In summer due to evaporation and decreased flow and the industrial processes, the sulphate concentration remained always higher.

Various other workers also reported higher sulphate concentration in different rivers as a result of pollution (Sheshadri 1989, Sudhakar 1989, Trivedi 1979, Narendra Dad 1981, Manikya Reddy & Venkateswarlu 1986, Somashekar et al. 1983, 1984, Kongovi et al. 1986). Kongovi et al. (1986) have reported a range of 90 - 669 mg/l of sulphates in the effluents of Grasilene factory. Trivedi (1979) recorded 1021 mg/l of sulphates in river Chambal released by GRASIM complex at Nagda, Ujjain (MP) and later Narendra Dad (1981) recorded similar data at Nagda (MP). This industry is a sister concern of HPF belonging to GRASIM. According to Sudhakar (1989) the increased concentration of sulphates in paper mill effluents was due to: 1) discharge of effluents containing sulphates and 2) decomposition of organic matter. These two processes might have played a prominent role in the present investigation also. High value of sulphates was observed in summer where as low in winter.

Sinada & Abdel Karim (1984) observed that the seasonal variation in sulphate content in the two rivers (Blue Nile and the White Nile of Sudan) differed considerably from each
other. In Blue Nile the high and low values were noted in dry and wet seasons respectively. The reverse was observed in case of White Nile. The low value was attributed to the removal of sulphates in the swamp region by the activity of SO$_4$ reducing bacteria under the conditions of O$_2$ deficiency as suggested by Talling (1957). Holden & Green (1960) observed that the absence of sulphate in a Nigerian river, Sokoto was a limiting ion for the phytoplankton. Johnson (1968) described maximum values (150-700 mg/l) of sulphate is water due to flowing over limestone deposits of Malaysia. Sulphates are more common in the Malaysian water than those of South America and Africa. In South America it is virtually absent in many black waters and in Africa it is present only in those waters flowing from volcanic regions (Welcomme 1985).

4.1.17 Sulphites

Sulphites are one of the common oxidised forms of sulphur and are widely used in bleaching and food preservation. Effluents of paper and pulp mills are characterised by sulphites and may also occur in boiled and boilers fed waters. They may occur in natural waters or waste wates as a result of industrial pollution, and in treatment plant effluents dechlorinated with sulphur dioxide. Excess sulphite ion in boiler water is deleterious because it lowers the pH and promotes corrosion (APHA 1980).
Moreover, it causes anxiety, nausea, eye strain, headache and asthma etc. Sulphur reduces the DO content and COD of water, which is harmful for the aquatic species (Preeti Kaur et al. 1988).

Control of sulphite ion in waste water treatment and discharge may be important environmentally, principally because of its toxicity to fish and other aquatic life and its rapid oxygen demand (APHA 1980).

In the present investigation, the concentration of sulphite is greater in HPF effluent than the GRF effluent as well as the upstream water. Its concentration was more or less uniform throughout the study period at Station I and III, whereas it fluctuated markedly within a range of 2.0 - 26.0 mg/l in case of HPF effluent. Higher and lower values were observed during dry and wet seasons respectively. The higher sulphite content may be attributed to the acidic bisulphite used in the manufacturing process (See 1.1.4). In sulphite pulps or paper and pulp industry bisulphites such as ammonium calcium, magnesium and sodium are commonly used. During man made fibre manufacturing sodium sulphite is widely used.

According to Wilson (1972) the sulphite waste liquor (SWL) can also affect the DO i.e. lowering the DO by approximately 1 mg/L for each increment of 1000 ppm SWL, particularly in a water whose original DO was 8.5.
4.1.18 Lignin

Lignin is a plant constituent that often is discharged as a waste during the manufacture of paper pulp and man-made fibres. In the present investigation lignin content was determined in samples which were stored in polythene container at laboratory temperature. The known chemical properties of wood extract component and the studies of Rogers et al. (1971) on pulp chips show that the toxicity of wood extractives decreases on storage, whereas the fibre components, cellulose and lignin are chemically stable if stored at room temperature, in darkness and under nitrogen (Nikitin 1966).

Lignin is a major component of perennial plants and as such is probably the second most abundant of all the continuously cycled organic materials on earth (cellulose is presumably the most abundant). Lignin is a common name for a heterogeneous group of phenolic polymers that together with hemicellulose and pectin fill the space between cellulose fibrils in woody cell tissues.

Lignin is a three dimensional aromatic polymer composed of basically three different types of p-hydroxycinnamyl alcohols. The relative amount of these alcohols determine the types of lignin. Softwood lignins are mainly polymers of coniferyl alcohol, hardwood lignins are mixed of coniferyl
and sinapyl alcohols and grass lignins are mixed polymers of all the three alcohols (Leisola and Fiechter 1985).

Lignin functions as binding material between cell wall components. It gives rigidity to the plant cell wall and protects woody lants from mechanical stress. As a major by-product of pulp manufacture, lignin is also one of the largest industrial waste materials (Kirk 1971).

In the present investigation very low lignin content was observed at Station I (Upstream water) and it remained more or less uniform throughout the period of monitoring. In the effluents they were in higher concentration during summer and lower in rainy season. Among the two effluents under investigation, the HPF effluent always recorded higher lignin content throughout the study period. The dark brown colour of the effluent is due to the presence of high lignin content, its derivatives and other organic compounds. Except for April 1987, lower concentration of lignin was observed in GRF effluent (See 1.1.4).

Degradation of lignin was found to occur only under aerobic conditions. A high percentage of $O_2$ is found necessary for this process. It was found that after 30 to 35 days, 45% conversion to CO$_2$ was observed in one soil sample while in one water sample, 30% conversion to CO$_2$ was noted (Anjali Roy 1987).
Biological degradation of lignin is an important part of biospheric carbon-oxygen cycle. Lignin is either directly degraded to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) or converted to humus which is very resistant to biological degradation. Complete degradation of lignin is believed to be a result of cooperative action of various fungi (such as fungi belonging to Basidiomycetes, Ascomycetes, Fungi Imperfecti etc.) and bacteria such as Bacillus (Leisola & Feichter 1985).

4.2 HEAVY METALS

Heavy metals include all metals with Atomic Number greater than 23 and specific gravity more than 5.0 (Arceivala 1991). The effects of various metals in waste wates range from beneficial through troublesome to dangerously toxic (APHA 1980). Some are required as trace elements by living organisms, though others (Hg, Cd and Pb) are not necessary. The anthropogenic inputs have now overwhelmed the natural biogeo-chemical cycles of trace metals in many ecosystems. At least 11 heavy metals, such as Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se, Ni and Sn are known to be essential for living organisms (Schroeder et al. 1970, O'Dell and Campbell 1971). Essential metals always function in combination with organic molecules and most commonly with proteins, either tightly bound in metal proteins or more loosely bound in metal protein complexes (Vallee & Wacker
1970). In addition, according to Vallee (1959), a wide range of enzymes form more loosely bound metal enzyme complexes and cannot achieve full catalytic activity in the absence of a specific metal or metals. Although some heavy metals are essential at suitable concentrations for enzymatic activity, they may become enzyme inhibitors when their natural concentrations are exceeded. At more than natural levels, these are frequently toxic to aquatic organisms due to selective inhibition of particular crucial enzymes. Consequently, most heavy metals, whether essential or not, are potentially toxic to living organisms.

In many rivers and lakes, the human input of trace metals is many times greater than the natural input (Nriagu et al. 1979). According to Nriagu (1978), Moore & Ramamoorthy (1984) and Adriano (1986), trace metals are released into the environment by wide spectrum of natural and anthropogenic sources like atmospheric fall out, liquid effluent discharge by industries and leaching of metal bearing minerals (Vanloon 1977). Regardless of their source, most metals eventually end up in surface and ground waters (Arceivala 1991).

The current rate of industrial inputs greatly exceed the baseline burdens of trace metals in the average lake and river. The present study of pollution of River Tungabhadra at Kumarapatnam (Karnataka) by the effluents of polyfibre
industry in a classic example of heavy metal pollution of rivers in our country.

The pollution of surface waters by various heavy metals is usually hazardous for the living organisms. They are considered to be toxic when they are present in the aquatic environment, whether in solution, in the bottom sediment or in living organisms, at concentrations which interfere with the intended use of the waterbody, because of their negative effect on human health or on the aquatic ecosystem as a whole. The levels at which such negative impacts are likely to become significant are indicated by World Health Organisation (WHO) Water Quality Guidelines. Serious pollution by such toxic substances has been identified in numerous important rivers, lakes and reservoirs of our country (Patil 1977, Chawdhry 1977, Jhingran & Tripathi 1977).

The heavy metals are the micropollutants of special interest as they have health and ecological significance because of their persistence, toxicity and bio-accumulation characteristics. Metal pollutants present in rivers and lakes, partly enter the bottom sediment and partly overflow to the coastal waters. Once they enter the food chain, a considerable amount of biomagnification can take place and eventually the edible plants and fish containing the metal
pollutants in substantial concentrations can affect human consumers. Though their concentration may be low, because of their accumulation abilities, which can be revealed in living organisms they must be prevented from entering inland fishery waters. They can also constitute a long term risk to human health. Moreover, an accumulation of toxic pollutants in bottom sediments, which do not undergo biodegradation processes, may prevent the use of such waters for fisheries and drinking water supply for many years.

Natural as well as anthropogenic sources are possible origin for heavy metals. To distinguish between the two sources is not very easy except in heavily industrialised or urbanised areas. Pollutants that are not water soluble are taken up the sediments, either directly or indirectly through biological processes and may remain in the water sediment system more or less indefinitely, depending on the extent of recycling between the uppermost sediment and the overlying water.

The downward movement of metals to the bottom of natural water bodies results from scavenging by suspended solids and concomitant sedimentation. Distribution and transport of metals in aquatic environments are primarily controlled by the sediment and water column respectively.
Toxic substances contained in the effluents can be considered from the point of view of toxicity of individual chemicals or on the basis of total effluent toxicity. Furthermore, environmental factors interact with one another and in these circumstances, it is exceedingly difficult to analyse the effect of any one factor on any one component of the ecosystems. Water can act as a medium which can carry toxic chemicals and other hazardous metals from its source for a long distance in the ecosystem.

Although sediments act as a 'sink' for heavy metals, the latter may still be potentially mobile. For example, release of these metals into the overlying water may be effected by changes in the physico-chemical conditions such as pH and oxidation potential (Eh). Movement of metals out of sediments may also be achieved by biotic factors such as uptake through rooted plants (Harding & Whitton 1978). From here, the metals may enter food chains, or be released into the water by the plants themselves. The microorganisms which are associated with river and lake 'sediments', may compete very effectively with the sediments in accumulating metal and have a significant effect on their mobilisation into food chains.

When there is a direct uptake by heavy metal ions in solution, the toxic action eliminates many plants, with only
resistant species surviving eg: Lemanea (a red algae) which is resistant to Zn and Pb in running water and Stigoclonium (a filamentous green alga) resistant to Cu and Zn. Fish may also disappear no doubt, largely due to the direct uptake of heavy metals from solution by the gills.

In view of the known hazards from metals such as Hg in natural waters it is essential that the effects of increasing metal concentrations should be assessed before conditions are allowed to deteriorate further. Although the behaviour of the metals in sediments is not fully understood the earlier studies showed that under suitable conditions some metals are returned to the overlying water following remobilization and upward diffusion. As a result, contaminated sediments may persist as sources of metals when the original source has been removed (Bryan 1976). According to Bryan (1976) in river waters where rate of deposition are relatively rapid, analysis of sediments has considerable value as indicators of general levels of contamination. If areas are free from disturbance by currents and burrowing animals, sediment cores can be used to obtain as historical record of metal contamination. Further, the toxicity of pollutants depends more on interaction with their constituents and the physico-chemical nature of water body. Physico-chemical factors such as pH, Eh, inorganic cations and anions, organic minerals, clay minerals and metal
oxides, influence the speciation of heavy metals and hence their bioavailability and ultimately their toxicity to microbiota.

The solubility of the metal is of central importance and is largely controlled by pH and temperature. Negative correlations were found between pH and Cd, Zn, Pb and Mn (Dickson 1980, Borg 1983). Moreover, considering the chemical equilibria which limit the concentration of trace metals in fresh water, a decrease in pH would favor a prolonged retention time for some metals (Borg 1983). It is also known to a little extent that a particular pollutant executes its toxicity depending upon the form in receiving waters (Lloyd 1960; Sprague 1964). Physico-chemical parameters like pH (Mount 1966, Borg 1983), hardness (Howarth & Sprague 1978, Wong 1980, Chapman 1978) and alkalinity (Miller and Mackay 1980, Borg 1983) carbonate ions (Rai et al. 1981, Shehata and Whitton 1982) largely modify the toxicant in their toxic action. According to Borg (1983) the main controlling factors for trace metals are pH, humus content and alkalinity.

The pH may affect the metabolic state of the cell or the chemical speciation of metals (Richter and Theis 1980) or the extent of complexing of metals to the organic constituents of the medium (Babich & Stotzky 1980). The
cations like Ca\textsuperscript{++}, Mg\textsuperscript{++} in the environment may reduce the toxicity of metals because of competition for sites on cell surfaces between these cations normally present in an environment and the cationic speciation form of heavy metals (Shehata & Whitton 1982, Hart et al. 1979, Rai et al. 1981). Inorganic anions exert an influence on the speciation of metals and hence their toxicity to the microbiota. Heavy metal cations form coordination complexes not only with hydroxyl ions, but also with inorganic ligands such as Cl\textsuperscript{−}.

Most waste waters from industrial installations have a complex chemical composition; consequently it is important to know not only the toxicity of individual components, but also their combined effect. The combined effect of the various components of waste waters may be manifested in the form of synergism, antagonism or an independent combined effect. For example, combination of heavy metals (Cu & Zn, Cu & Cd, Ni & Zn) ammonia and phenol, ammonia and chlorine, formic acid and sulphates etc. are synergistic. Chlorination of certain medium toxic compounds leads to a sharp increase in their toxicity.

The microbial response to individual metals may differ from the response to stress from multiple metals as indicated by several studies on antagonistic, synergistic or additive interaction between multiple metals. The metal-
combination is dependent on the relative concentration of the toxicants (Shehata & Whitton 1982, Prasad & Prasad 1982).

It was proposed by Jenne (1968) that the hydrous metal oxides of Mn and Fe act as a sink for heavy metals. They are nearly ubiquitous in soils and sediments, both as partial coatings on other minerals and as discrete oxide particles. It has been found that the uptake and release of heavy metals is influenced by the pH of the solution and by the presence of organic and inorganic complexes. According to them the natural water organic matter plays a significant role in uptake and release of heavy metals on hydrous oxide coatings or discrete particles. There is no doubt that hydrous metal oxide are important sinks and modes of transport for heavy metals in the environment, the quantitative magnitude of this role is not known for a variety of natural water conditions.

4.2.1 Zinc

Zinc is an essential microinorganic element required in trace amount for plant growth. Concentrations above 5 mg/l may cause a bitter astringent taste and and opalescence in alkaline waters. Zinc enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. The heavy metal zinc occurs in many types of industrial wastes, particularly in metal plating and the
manufacture of organic constituents such as acrylic fibre, rayon, cellophane and special synthetic rubbers.

The concentration of zinc in plants ranges from as low as 1 ppm to as high as 10000 ppm on a dry weight basis. Commonly encountered concentration lies between 20 and 100 ppm (Katyal & Randhawa 1983). In rain water normally a range of 1-15 µg.l⁻¹ and in case of fresh water a range of 5-50 µg.l⁻¹ are observed (Allen et al. 1974). In industrial areas much higher values have been recorded.

Zn mainly functions as the metal component of a series of enzymes like carbonic dehydrogenase, alkaline phosphases and a number of other dehydrogenases. More than 20 different zinc metalloenzymes have been identified. Moreover, it plays an important role in the biosynthesis of nucleic acids, RNA polymerases and DNA polymerases (Moore & Ramamoorthy 1984). Its deficiency is thought to restrict RNA synthesis, which in turn inhibits protein synthesis. Zinc deficient plants are thus poor in protein. Zinc is also involved in auxin production in plants.

In the present investigation, higher concentration of zinc was noted in GRF effluents than HPF and the upstream water. The upstream water was characterised by low zinc content when compared to the HPF and GRF effluents. This higher concentration of zinc in the effluents, particularly
in case of GRF effluent can be attributed to the raw materials used (Zinc Sulphate) as well as to the manufacturing process. The range of Zn in case of GRF was found to be marked and fluctuations were exhibited. Similar results of higher zinc level were also recorded by Cabrera et al. (1987) in river Guadiamar of Spain (Holland & Harding 1984) in River Mersey of Britain (Harding & Whitton 1981 Say et al. 1981, Van Urk 1984) in lower Rhine-Meuse (Mathis & Cummings 1973).

According to Whitton & Diaz (1980) the highest Zn levels usually occur at the lowest pH values, where zinc tends to be less toxic. A marked +ve correlation was observed between Cd and Zn. High levels of Zn occur associated with a wide range of Ca and Phosphate -P levels.

Eventhough the total content is relatively low in many soils, in rare cases it may be high enough to be toxic to some species. Bulk of the Zn in soil exists in the primary mineral structure i) in the terromagnesian minerals, augite, hornblende and biotite, ii) salts such as sphalarite (Zns) Smithsonite (ZnCO₃), Zincite (ZnO) and Willemite (ZnSiO₃ and ZnSiO₄). Zinc is associated with various igneous minerals, but in soils is generally held in the lattice of clay minerals and thus retained by the soil colloids as the clay weather. It is freely available to plants over a wide pH range but less so in very acid soils.
In the present investigation, sediments of Stations II and III exhibited higher Zn content than the unpolluted upstream sample. These fluctuations more or less coincided with the fluctuations of Zn level in case of water samples. The higher zinc content of sediment samples were due to deposition and accumulations of the metal from effluents.

Zn is unusual in that it has low human toxicity but relatively high toxicity to fish, so that water, which is suitable as a potable supply, having upto 5 mg Zn/litre would be highly toxic to most fish species (Hellawell 1988). Under conditions of elevated concentration however, the normal enzyme-zinc mechanism may be significantly altered, giving rise to toxicity. Antagonistic or synergistic interactions may also alter zinc toxicity. According to Whitton (1970), a medium rich in nutrient such as phosphorus, may lower the toxic effects of heavy metals. Toxicity of zinc to aquatic plants is highly variable, with LC$_{50}$'s ranging from 0.0076 to 750 mg/l. An increase in the Ca and Mg content of water reduces toxicity to most species. As with other heavy metals, toxicity is modified by environmental factors, including hardness, temperature, dissolved oxygen concentrations and the presence of suspended solids or organic matter.

It was observed that the contents of Zn were within limits prescribed by W.H.O. (1971) and I.S.I. (1983).
Table 41: Standards for Physical and Chemical Quality of Drinking Water

<table>
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<tr>
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<tbody>
<tr>
<td></td>
<td>Highest Desirable</td>
<td>Max. permissible</td>
<td>Highest Max. Permissible</td>
<td>Desirable</td>
</tr>
<tr>
<td>Colour</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Taste and Odour</td>
<td>Unobjectionable</td>
<td>-</td>
<td>Unobjectionable</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>7.0-8.5</td>
<td>6.5-9.2</td>
<td>6.5-8.5</td>
<td>8.5-9.2</td>
</tr>
<tr>
<td>Temperature °F (°C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Specific conductance µ.S.cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40.0 mS·cm⁻¹</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>120.0 mg/l</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.0 mg/l</td>
</tr>
<tr>
<td>Sodium</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.0 mg/l</td>
</tr>
<tr>
<td>Potassium</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.0 mg/l</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg/l)</td>
<td>500</td>
<td>1500</td>
<td>500</td>
<td>1500</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>200</td>
<td>600</td>
<td>250</td>
<td>1000</td>
</tr>
<tr>
<td>Calcium (mg/l)</td>
<td>75</td>
<td>200</td>
<td>75</td>
<td>200</td>
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<tr>
<td>Magnesium (mg/l)</td>
<td>150</td>
<td>30</td>
<td>100</td>
<td>50.0</td>
</tr>
<tr>
<td>Total hardness as CaCO₃ (mg/l)</td>
<td>100</td>
<td>500</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>Sulphate (mg/l)</td>
<td>200</td>
<td>400</td>
<td>150</td>
<td>200</td>
</tr>
</tbody>
</table>

**U.S. Maximum Contaminant Level mg/L**

- Sulphate: 30 mg/l
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Highest Desirable</td>
<td>Max. permissible</td>
<td>Highest</td>
<td>Max. Permissible</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>5.0</td>
<td>15.0</td>
<td>5.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Copper (as Cu) (mg/l)</td>
<td>0.05</td>
<td>1.5</td>
<td>0.05</td>
<td>1.5</td>
</tr>
<tr>
<td>* Lead (mg/l)</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>No relaxation</td>
</tr>
<tr>
<td>* Cadmium (mg/l)</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
<td><em>do-</em></td>
</tr>
<tr>
<td>Iron (as Fe) (mg/l)</td>
<td>0.05</td>
<td>1.5</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Manganese (as Mn)(mg/l)</td>
<td>0.1</td>
<td>1.0</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Cobalt (µg/l)</td>
<td>NS</td>
<td>NS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel (µg/l)</td>
<td>NS</td>
<td>NS</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: * These concentrations are mandatory upper limits and should not be exceeded.
NS Not stated.
standards for drinking water in case of upstream water as well as HPF effluent. However, in case of GRF effluent Zn levels were found to be more than the highest desirable levels of 5.0 mg/l. Zn, prescribed by both the above standards, particularly in the month of Sept. and Oct. 1986.

4.2.2 Copper

Copper is the most common and one of the most toxic of heavy metals. It is widely distributed in nature in free state and in sulphides, arsenides, chlorides and carbonates. Copper complexes of oxidation status (+1), (+2) and (+3) are known though Cu (+2) is most common. Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes and to catalyze the oxidation of manganese. Copper is essential to humans and the adult daily requirement has been estimated at 2.0 mg.L⁻¹ (APHA, 1980). It activates certain enzyme systems in plants, especially those linked with oxidation process. It is also essential for animals. Copper is known to be associated with a number of metal proteins. The essential metabolic role of Cu is evident from its presence in cytochrome oxidase and chlorophyll. Some of its biological important is related to the ability to oscillate between the cuprous and cupric state i.e. the ability to accept or donate electrons. The ease of organocomplex formation coupled with the high stability of many resultant complexes, gives Cu the
potential to interact strongly with organic compounds in living tissue or in the immediate abiotic environment.

Speciation of copper in natural water is determined by the physico-chemical, hydro-dynamic characteristics and the biological state of water (Moore & Ramamoorthy 1984). Imhoff et al. (1980) reported that in case of Ruhr River, copper showed a small range of variation in concentration even with changing flows and this was attributed to the geochemical origin of non-point sources. Soluble Cu levels in uncontaminated fresh waters usually range from 0.5 to 1.0 mg/l increasing to ≥ 2 µg.L⁻¹ in urban areas.

Copper is a highly toxic heavy metal posing great threat to aquatic organisms when present in levels higher than the maximum acceptable toxicant concentration (Rajkumar & Das 1991). Cu concentration in plants generally vary between 5 and 20 ppm. It is believed that in excess of 20 ppm may harm the plants. The most prominent symptoms of Cu toxicity is chlorosis, superficially resembling Fe deficiency (Katyal & Randhawa 1983).

Copper is highly toxic to most aquatic plants. Inhibition of growth generally occurs at 0.1 mg/l, regardless of test conditions and species. Sublthal effects of Cu intoxication includes in initial loss of K due to increased permeability of the cell. There may also be
Inhibition of $O_2$ evolution, assimilation of carbon and decrease in the rate of photosynthesis. Copper may increase the permeability of the cell wall in aquatic plants thereby increasing susceptibility to other pollutants. Blue green algae are particularly susceptible to Cu because of the inhibition of nitrogen fixation. Many algal species and invertebrates can adapt to high copper levels in water. Other examples include Crustacea, Mollusca, Oligochaetes, insects and macrophytes (Hellawell 1988).

Copper is usually more toxic to freshwater fish than any other heavy metal except mercury. $LC_{50}$'s range from 0.0017 to 1.0 mg/l under most conditions. Acute toxicity to fresh after fish depends largely on water hardness. Copper ions precipitate gill secretions, causing death by asphyxiation (Tsai 1979). Necrotic kidney cells, faulty degeneration of the liver and brain haemorrhage have been reported for exposed fish.

Although combinations of copper/lead and copper/cadmium are antagonistic in their effects on algae, combinations of copper/nickel act synergistically. Synergism has also been noted for combinations of Cu & Mn and Cu & Zn (Moore & Ramamoorthy 1984).

Copper is not toxic to humans. There is no indication that copper is carcinogenic or mutagenic to humans (Moore & Ramamoorthy 1984).
In the present investigation, the concentration of Cu was more or less in the same range at all the sampling stations. There were no considerable variation in the mean values of the upstream water and effluents except GRF recorded slightly higher Cu content. This clearly indicated that there was no much copper discharge as pollutant to the river Tungabhadra. GRF effluent was found to be contributing small amount to the river water. The Cu content noticed in the upstream is attributed to the geology of the catchment area (See 2.1).

The content of Cu at Station I (Upstream water) was within the highest desirable levels prescribed by W.H.O. International Standards (1971) as well as I.S.I. Standards (1983). It was slightly more in the month of June 1986. In case of HPF effluent, it was found to be exceeding slightly the highest desirable level set by WHO and ISI Standards in the months of June - Aug 1986, Nov. 1986 and April 1987. However, in case of GRF effluent, Cu level was slightly more in the months of June - Aug. 1986, Oct. Nov and March - April 1987 than the set standards.

4.2.2.1 Copper in sediments

Cu occurs in nature chiefly as sulphides the most abundant of these in chalcopyrite (CuFeS$_2$). The largest fraction of total Cu is present in the crystal lattices of
primary and secondary minerals. It also occurs in soils in organic combinations and are exchangeable cation on soil colloids and a minute fraction in soil solution (less than 0.001 ppm). It is almost entirely present as complexed with organic matter and in soils it varies from 10-200ppm with an average value around 55 ppm. According to Allen et al. (1974) the concentration ranges generally noticed are as follows:

<table>
<thead>
<tr>
<th>Mineral soils</th>
<th>5-100 µg.g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil extractions</td>
<td>0.1-3 µg.g⁻¹</td>
</tr>
</tbody>
</table>

In the present investigation well marked fluctuations in Cu content was recorded in the sediments of effluent canals. Naturally they were more mode in case of effluent canal sediments than the upstream sediment and this may be due to the pollution load. The higher Cu level of GRF sediments coincided with the higher values of the effluent of the GRF unit. More Cu content was found to be absorbed to the sediment.

Similar higher Cu levels in sediments were also noticed by Mathis and Cummings (1973) in Illinois River (USA), Boyden et al. (1979) in Restronguet Creek (U.K.) and Pagenkopf and Cameron (1979) in Natural Creek, Montana (USA). Unpolluted freshwater sediments generally contain levels of 20 mg.Kg.⁻¹
Normally, the Cu content is sorbed rapidly to sediments, resulting in high residue levels. Rate of absorption varies with the type of clay/presence of ligands and Fe/Mn oxides (Moore & Ramamoorthy 1984). Depending on the factors like pH, salinity, presence of natural and/or synthetic chelating agents, desorption from sediments into the bulk water takes place.

The point of concern for us is that one soil application of Cu produces a strong residual effect and its usefulness lasts at least for 2-8 years. Hence its repeated application may bring about a toxic accumulation in soils (Katyal & Randhawa 1983). These are to be avoided because it may lead to accumulation of Cu in the agricultural land on the banks of Tungabhadra near the study area, thus affecting agricultural productivity.

4.2.3 Lead

Lead is a member of the Group IV elements of the periodic classification. Lead has a stable (+2) and (+4) oxidation status. Lead forms alkyl and aryl compounds. It is one of the oldest metals known to man and since medieval times has been used in piping, building materials, solders, paint, type metal, ammunition, castings etc. Recently lead is being used in storage batteries, metal products, chemicals and pigments. Tetra ethyl lead is widely used as
an antiknock agent in gasoline. Lead is widely distribute through its use in batteries, dying and glass and in combination with arsenic ink sprays (Lad arsenate).

Lead is a serious cumulative body poison. Natural waters rarely contain more than 20 μg/l, although values as high as 400 μg/L have been reported. Lead in a water supply and soil may come from industrial, mine and smelter discharges or from the dissolution of old lead plumbing. Plants and soils on roadside verges are high in lead. Anthropogenic inputs greatly exceed those from natural sources which have tetraethyl lead as an antiknock ingredient. Mining contributes substantially to lead containing solid wastes in the environment. With the exception of nitrate and acetate, most lead salts (+2) are insoluble in water. The concentrations generally encountered are:

<p>| | |</p>
<table>
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<tbody>
<tr>
<td>Soil</td>
<td>2 - 20 μg.g⁻¹</td>
</tr>
<tr>
<td>Fresh water</td>
<td>2 - 20 μg.g⁻¹</td>
</tr>
</tbody>
</table>

Lead forms moderately strong chelates with organic ligands containing S, N and O donor atoms. Physico-chemical speciation of lead in drinking water indicates little or no free ionic lead. A significant portion of lead is bound to colloids, either as hydrous iron oxides or organic macromolecules depending on the composition of water. A substantial fraction is non-ion exchangeable.
Lead is toxic to many plant species although a few are relatively tolerant. Because there is often good correlation between lead levels in water and plant tissues, several major species have been used as biomonitors of environmental contamination (Moore & Ramamoorty 1984). These include fresh water representatives of *Elodea*, *Cladophora*, *Myriophyllum* and estuarine *Fucus*, *Laminaria* and *Ascophyllum*. Absorption rates are species dependent and increase with exposure concentration. Lead is a cumulative poison to mammals. There is often little accumulation of lead in marine and fresh water species. Consequently lead is not a threat to fisheries resources except in cases of extreme pollution. Methylation of lead is rare under natural conditions and consequently organo lead is seldom found in fish tissues. These compounds are, however, produced industrially in large quantities and inevitably escape into the environment. Although currently rare in the aquatic environment, organo leads are highly toxic and therefore may pose an eventual threat to fisheries resources. The 96h LC$_{50}$ for total lead generally falls within the range 0.5 - 10 mg/l. Chronic effects on long term exposure to lead nitrate (not found in natural water) may appear at concentrations as low as 8 µg.L.$^{-1}$.

Inorganic lead is less toxic to aquatic plants than mercurials and copper. Many environmentally important lead
compounds such as halides, sulphates, phosphates and hydroxides are in soluble and thus are of relatively low toxicity in aquatic systems. In humans the major source of lead is through the respiratory tract. For e.g. lead in urban airborne particles. Inorganic lead compounds induce renal carcinoma in rats and mice.

Present investigation recorded alarming levels of lead in the months of June, Nov 1986 and Apr. 1987 when it exceeded even the maximum permissible level fixed by WHO International Standards (1971) and ISI Standards (1983). They were found to by several times more than the upper limit for drinking water quality. Moreover lead levels were always more than the highest desirable level prescribed by both the Standards, for most of the monitoring period. Only on Aug. 1986 it was low at station I.

Manikya Reddy and Venkateswarlu (1985) reported very high lead content in the effluent channel than River Tungabhadra, exceeding WHO Standards.

4.2.3.1 Lead in sediments

Sorption of lead by river sediments is correlated to organic content and grain size. According to Forstner and Whittman (1981) concentrations of soluble lead in uncontaminated fresh water are generally \( \leq 3 \text{ \( \mu g.L^{-1} \)} \).
However, much higher levels often occur near highways and cities due to the combustion of gasoline. For example, residues in rivers in Southern France and Lake Naini Tal (India) were 3.5-53 and 20-89 μg.L⁻¹ respectively (Servant & Delapart 1979, Pande & Das 1980). Although comparable range occurs in major industrial zone rivers the discharge of liquid mine wastes may produce ≥ 500 μg. PbL⁻¹ in receiving wastes (Imhoff and Koppe 1980).

Total levels in precipitation generally range from 1-50 μg.L⁻¹ (Eisenreich 1980).

According to Pagenkopf & Cameron (1979), sediments of Creek, Montana (USA) recorded a mean of 295 mg kg⁻¹ dry wt. due to metal mining.

Other industrial/municipal sources generally produce residues in sediments of ≤ 500 mg/kg. In uncontaminated areas concentrations range from 2-50 mg.kg⁻¹ depending on the nature of the underlying bedrock.

High residues are often reported for attached plants in habitat polluted waters. It was suggested that the plankton settled on contaminated bottom sediments during winter and resuspended during the spring.

The increased lead content of sediments were corresponding with the higher values of the effluent samples.
4.2.4 Cadmium

Cadmium is the second member of the Group IIb triad (Zn, Cd, Hg) in the periodic classification of elements. The chemistry of Cd is homologous to that of Zn and different from Hg in both the properties of the element and its compounds. The stable state of cadmium in the natural environment is Cd (+2). Cd(+2) is present totally as the divalent species upto pH 8, in the absence of any precipitant anions such as phosphate and sulphide. It begins to hydrolyse at pH 9, forming Cd(OH)$^+$ species. In the absence of any precipitant anions (Cd(-2) will be available for adsorption on to suspended solids and complexation with organic matter and will be transported in those forms. Cd forms moderately stable complexes with a variety of organic compounds.

Measurable amount of Cd occurs in many soils and plant materials. Cd is also introduced into the environment through its use in pigments, electroplating, galvanizing and alloy manufacture and as an industrial waste product. It generally becomes concentrated in some organs where it can exceed 100 $\mu$g g$^{-1}$. It is usually discharged as an effluent into drainage courses or into the atmosphere. The concentrations generally encountered are:

- Soils: $0.03 - 0.3 \mu$g g$^{-1}$
- Fresh water: $1 - 50 \mu$g L$^{-1}$
Cadmium is highly toxic and its intake even in minute quantity are suspected of being responsible for adverse changes in arteries of human kidneys. A Cd concentration of 200 μg/L is toxic to certain fish (APHA 1980). There is much concern about the levels present in the environment, mainly because it is a cumulative poison effect to mammals. Since the metabolism of cadmium is closely related to zinc metabolism, cadmium seems to displace zinc in many vital enzymatic reactions, causing disruption or assation of activity (Moore & Ramamoorthy 1984).

Dissolved Cd levels in fresh water generally range from 10 to 500 μg.L⁻¹. However, in case of extreme pollution, concentration may exceed 17000 ngL⁻¹. It has been suggested that aquatic organisms incorporate Cd in their tissue and transport it to deeper waters through sinking of their detritus and debris (Moore & Ramamoorthy 1984). Bioccentration of Cd in plants has been reported by Page et al. (1981). The influence of several external physical and chemical factors on the uptake of Cd is noticed.

Cd is usually less toxic to plants than methyl mercury and copper and similar toxic to Pb, Ni and Cr(+3). Depending on species and test conditions, inhibition of growth and photosynthesis generally occurs at 0.02-1.0 mg/L. However, chronic effects have been reported for concentration as s
low as 1 μg/L. The toxicity of Cd may be attributed to the displacement of zinc from carrier proteins, consequently the addition of zinc to media significantly reduces all loss. Selenium may act as a synergist to Cd, whereas Cd may inhibit copper toxicity.

Exposure of 3 species of green algae to CdCl₂ resulted in the formation of intra mitochondrial granules containing cadmium (Silverberg 1976). Swelling, vacuolization and degeneration of mitochondria were observed implying significant cytotoxicity. Cd concentrations 0, 0.01; 0.1 mg.L⁻¹ also reduces the concn. of ATP chlorophyll in many species and decreases O₂ production (Moore & Ramamoorthy 1984).

4.2.4.1 Cadmium in sediments

Adsorption to sediments increases with pH and beyond a threshold point (pH > 7 for Cd) virtually all the metal ion is sorbed. Correlation of Cd sorption to organic content occurs in a variety of soils and sediments. According to Gardiner (1974) sorption desorption of Cd from river muds was rapid and humic acid was responsible for the sorption. Cd residues in freshwater sediments are highly variable, ranging from 0.1 mg.Kg⁻¹ dry weight to 3000 mg.Kg⁻¹. Release of sorbed Cd into the bulk water is dependent on the partition coefficient, which is related to sediment characteristics and water quality parameters.
4.2.5 Iron

Iron is a major component of most soils. The predominant iron minerals are the oxides but iron is also present in many other minerals (notably carbonates, micas, amphibolite and clay). Although it is widely distributed, iron deficiencies can occur due to its low solubility in alkaline (calcareous) soils and phosphate fixation.

The concentration of iron normally encountered are:

- Mineral soils: 0.5 - 107
- Soil extraction: 0.02 - 0.5%
- Rain water: 5 - 150 μg.l\(^{-1}\)
- Fresh water: 50 - 100 μg.l\(^{-1}\)

In filtered samples of oxygenated surface waters iron concentrations rarely reach 1 mg/l. Some ground waters and acid surface drainage may contain considerably more iron. Iron in water can cause staining of laundry and porcelain. A bittersweet astringent taste is detectable by some persons at levels above 1 or 2 mg/l (APHA 1980).

Under reducing conditions, it exists in the ferrous state. In the absence of complex forming ions ferric iron is not significantly soluble unless the pH is very low. On exposure to air or addition of oxidants, ferrous iron is oxidised to the ferric state and may hydrolyze to form insoluble hydrated ferric oxide. This is the predominant
form found in most laboratory samples unless the samples are collected and maintained under anoxic conditions to avoid oxidation. The growth of bacteria in the sample during storage may alter the form of iron present.

Iron may be in true solution, in a colloidal state that may be peptized by organic matter, in inorganic or organic iron complexes or in relatively coarse suspended particles. Iron is an essential plant nutrient but levels are so high in most soils that a value for extractable iron is not very meaningful. Iron occurs in the respiratory pigment porphyrin which is required in electron transfer (Cytochrome) processes in plants and animals. It also activates some oxidases and is considered to be necessary for chlorophyll synthesis.

Iron plays a key role in several enzyme systems in which the haem or haemin function as the prosthetic group. These enzyme systems comprise the catalans, peroxidases and several cytochromes. Among non-haem Fe enzymes is ferredoxin which regulates oxidation-reduction reactions. Its role in photosynthesis, NO$_2^-$ and SO$_4^{2-}$ reduction and N$_2$ assimilation underlines the vital function Fe performs in overall plant metabolism (Katyal & Randhawa 1983).

Iron deficient plants lack chlorophyll and are chlorotic even though Fe is not part of the chlorophyll. However, it is indispensible for its biosynthesis.
Its concentration usually ranges from 50-100ppm in plants. In general, legumes are richer in Fe than grasses. Iron toxicity in crops is rare. The threshold concentrations for incidence of Fe toxicity are thus not thoroughly known.

The Fe content was found to be far exceeding the maximum permissible level of Fe prescribed by both WHO (1971) and ISI (1983) Standards for drinking water in the months of June 1986, Nov. 1986 and April 1987 at Station I (Upstream water). There was rain and higher flow of water in the month of June and Nov 1986. The high values coincided with rain and consequent flow of water in the river. For the remaining periods it was found to be more than the highest desirable level of Fe. However, it was found to be absent in the month of May 1986. The higher level of Fe may be ascribed to the geology of catchment area of River Tungabhadra (See 2.1.).

In HPF effluent, the Fe level was exceeding the maximum permissible levels prescribed by WHO (1971) and ISI (1983) Standards from drinking water quality in the month of June, Sept. 1986 and March 1987. For the remaining periods of monitoring, Fe level was almost above highest desirable level except in May 1986. In case of GRF effluent, the same results were noticed. In June, Sept, Oct and Nov 1986 it
crossed the maximum permissible level whereas in the remaining periods it was more than the desirable level.

4.2.5.1 Iron in soils

Iron, among the micronutrients, has the distinction of being most abundant in soils, which ranks 4th in content among the chemical elements which make up the earth's crust. On the average, soils contain about 5% Fe by weight. Total Fe contents in soils generally do not regulate the Fe nutrition of crops. Like excessive P, high levels of Cu, Mn, Mo and Zn interfere with Fe uptake and utilisation. These, then may promote Fe deficiency. Fe and P are mutually antagonistic. Soils with high amounts of P and heavy metals like Mn, Cu, Zn etc are deficient in iron (Katyal & Randhawa 1983).

4.2.6 Manganese

Although Mn in ground waters generally present in the soluble divalent ionic form because of the absence of oxygen, part of all of the Mn in a water treatment plant may be in a higher valence state. Determination of total Mn normally does not differentiate the various valence states. There is evidence that Mn occurs in surface waters both in suspension in the quadrivalent state and in the trivalent state in a relatively stable, soluble complex. Although rarely present in excess of 1 mg/l, it imparts objectionable
and terracious stain to laundry and plumbing fixtures. Mn occurs in domestic waste water, industrial effluents and receiving streams.

Mn is an essential plant and animal nutrient which activates several enzyme systems, though its specific involvement in any enzyme is not thoroughly understood. The role of Mn in photosynthesis is clearly identified through its absolute necessity for water splitting during Hill's reason. Mn is also important in CO$_2$ assimilation and in nitrogen metabolism (Katyal & Randhawa 1983). For plant nutrition Mn$^{2+}$ fraction is important. Mn$^{2+}$ represents the entire water soluble Mn.

The concentrations of Mn normally encountered are:

- Mineral soils 200-300 µg.g$^{-1}$
- Soil extraction 5-500 µg.g$^{-1}$
- Rain water 0.4 - 3.0 µg.g$^{-1}$
- Fresh water 1.0 - 80 µg.g$^{-1}$

It ranges from 200 to 500 ppm on a dry qt. basis. Plant Mn contents are drastically reduced as the pH becomes alkaline. Apart from the Mn concentration, the incidence of Mn deficiency or toxicity is regulated by the level of Fe in the plant.
The most significant point is that the Mn content was found to be exceeding the highest desirable level of Mn prescribed by both WHO International Standards (1971) and ISI Standards (1983) at all the stations. However, they were within the maximum permissible level. The higher Mn levels may be attributed to the geology of the catchment area (See 2.1). Gradual weathering of the ores and conversion to soluble salts in the catchment area might have concentrated to the higher Mn content of the upstream water of River Tungabhadra (See 2.1).

4.2.6.1 Manganese in sediments

The levels of Mn in many soils are extremely low, possibly limiting in sandy soils. It is widely distributed in soils derived from igneous and sedimentary rocks. Its availability is generally the highest in mildly acid soils but can be very low in strongly acid peats. Like iron, its availability drops in calcareous soils.

The prominent Mn soil fractions are Mn$^{2+}$ and a series of manganese oxides in which Mn exists in trivalent or tetravalent forms. Mn is also associated with soil organic matter.

Total Mn contents between 200-300 ppm are most common in soils. These can vary from a trace to as high as 10% or even more. However, total Mn content of a soil is a poor
index of Mn availability to plants. High availability of Fe, Zn or Cu make soils Mn deficient. Crop variation exhibits differential tolerance to Mn toxicity.

4.2.7 Nickel

Nickel occurs widely in nature, particularly in ultra basic rocks. The average concentration in the earth's crust is estimated to be 60-90 mg/kg. The sulphide ores are often exploited, the metal being used in electroplating, alkaline storage batteries and the production of alloys. Nickel is released into the environment during mining, smelting, manufacture and the combustion of fossil fuels (EIFAC Report 1984).

The predominant oxidation state of Nickel in natural waters is the divalent cation, Ni$^{2+}$ and in waters of pH 5 to 9 this ion is almost the only form present. Complexes of naturally occurring ligands are formed to a small degree. Many stable complexes occur with organic ligands and the metal can also be absorbed on to clay minerals, leading to the concentration in the finest fraction. Due to that property sediments could be regarded as a possible reservoir of Nickel, as for many other metals. Morris (1975) reported that metals tend to dissolve out of the sediments and not the water under field condition at low pH and high Eh. Nickel can therefore occur in the aquatic environment as its
soluble salts, adsorbed on suspended solids and in the form of organic complexes. The contribution to toxicity of the two forms is difficult to predict. Nickel concentrations in natural waters vary from 0.005 mg/l. Nickel interacts with only five essential elements, Ca, Co, Cu, Fe and Zn in plants, animals and microorganisms. Nickel powder and its compounds cause a variety of cancers in rodents and are listed as possible curative agents for occupational or environmental cancer in man (Moore & Ramamoorthy 1984).

In the present investigation, the Ni level was found to be more or less same at all the stations during the period of monitoring. It was slightly higher in case of the HPF effluent. The lowest value was in May 1986 at all the 3 stations where as highest values were observed on different months of sampling. For eg. Oct 1986 at Station I, Feb. 1987 at Station II followed by June at Station III. The higher values at Station I or upstream may be due to the geological characteristics of the area (2.1) where as in case of effluents, the slight increase may be due to the pollution load of the wood based industries.

Further, for Nickel level, the WHO International Standards (1971) as well as the ISI Standards (1983) have not stated their guidelines. They are yet to be prescribed. Hence their toxicity should be considered by the limited
No precise descriptions of the biochemical basis of the toxicity of nickel have been made, but the metal is known to bind to a variety of molecule structures such as nucleic acids and proteins effects on several enzymes have been reported. Nickel is generally less toxic to invertebrates and fishes than Cu, Hg, Pb, Zn, Cd, Ag, Cr and As depending on the conditions. In short-term tests in soft water the most sensitive species of fresh water fish are killed by exposure to concentrations of about 4 to 20 mg/l. Higher LC$_{50}$ values of nickel to different species of fish have been found in harder waters, from about 30 to 80 mg Ni/l. From the limited data available it appeared that hardness had the greatest effect on toxicity while other determinants have not been proved to have a significant effect (EIFAC Report 1984).

Additive effects on toxicity have been reported for mixtures of Ni and Cu and Ni, Cu and Zn. Even though nickel has little capacity for accumulation in all the fish studies, this relatively low concentration of nickel in tissues can cause biochemical damage (EIFAC Report 1984).

A concentration of 0.1 mg/l harmed the macrophyte Lemna but green algae were affected much lower concentrations.
However under most test condition, Ni is less toxic to aquatic plants than Hg, Tu, Cd, Ag etc., but more toxic than Lead & Zinc. Significant reduction in growth and photosynthesis generally occur at 0.1 - 0.5 mg Ni/l (Moore & Ramamoorthy 1984).

4.2.8 Cobalt

The importance of cobalt to plants is not fully understood, but it is necessary for enzyme activation in nitrogen fixation process. It is also needed by algae, fungi and bacteria. Its deficiency seems to depress fixation of N₂. The essentiability of Co for the growth of higher plants has not been satisfactorily established. However, Co is absolutely essential for the growth and development of animals. Several animal diseases are attributed to Co deficiency in herbage (Katyal & Randhawa 1983).

The amounts of Co in most soils are normally very low, but may increase in soils associated with basin, igneous and some sedimentary rocks.

Cobalt has been included in the "Grey List" substances of EEC and are regarded as less dangerous as their impact may be local. Most plant species contain less than 1 ppm Co in the dry tissue. It is evident that considerably higher levels of Co are found in legumes than grasses. Plant
species show remarkable differences to excess Co. In general, several crops may suffer from excess Co if they contain more than 15 ppm Co, but such instances are rare.

The W.H.O. International Standard (1971) and I.S.I. Standard Institution (1983) have not stated a limit for the level of cobalt in drinking water. However, it may become toxic if it is added continuously without any control.

In the present investigation, the GRF effluent recorded higher Co level than the HPF effluent as well as the upstream water. The upstream always exhibited lower values for Co content, thereby indicating the addition of Co as a pollutant in the former cases. In sediments, the level of Co was not available. The level of Co in upstream water may be of lithogenic origin.

According to Borg (1983) the concentration of humic substances influences the distribution of Co, as shown by its positive correlation with the total concentration of Co.

Manikya Reddy & Venkateswarlu (1985) estimated the level of Co in the paper mill effluent and Tungabhadra River. It fluctuated between 0.03 - 0.20 ppm & 0.05 - 0.16 ppm in the effluent channel and river water respectively. Paul & Pillai (1978) have noticed high Co level in Periyar River.
4.3 CHROMOSOME ABERRATION TEST

Human activity has inevitably increased the levels of metal ions in many of our natural water systems. Mine drainage, industrial and domestic effluents, agricultural run off, acid rain and the like have all contributed to the increase of metal loads in these waters. One of the common sources of heavy metal pollution is the discharge of industrial effluents which are continuously released into the environment (Nriagu 1980). Heavy metals are toxic pollutants and their presence in the environment especially in water is a current major concern. They pose great threat to the ecosystem as well as human health.

The metals and their different compounds form a major portion of hazardous chemical pollutants. Their toxicities range from mildly harmful to lethal in extreme cases. Their common feature in relation to biological life is that, in excessive quantities they are poisonous and can cause death of most living organisms (Antonovics et al. 1971). Even though, their role in various physiological functions in higher plants have been worked out in detail, their impact on cell division and chromosome system is relatively less known.

The heavy metals enter the ecosystem through certain industrial effluents, and in the form of solid waste
deposits. Various processes like precipitation, wind etc. are responsible for their transport to a great distance away from their source in aquatic environment.

Metals seem to affect the chromosome structure as well as number in higher plants in addition to the induction of mutations (Singh & Sharma 1980). *Allium cepa* is an efficient system to detect typical alterations in chromosomes by different chemicals. Several aspects of mutagenesis have been reviewed in higher plants by Ehrenberg (1971).

In onion root tip cells studied from the control materials (Upstream water), cell division was almost normal and only a few aberrations were noted. In the treated bulbs a number of cytological abnormalities were encountered. These abnormalities remained dose dependent. The effluents (both HPF and GRF) depressed the mitotic rate and induced mitotic abnormalities in a dose dependent manner in the root tip cells of *Allium cepa*. The mitoclassic effects (on the spindle) included diplochromosomes metaphase, arrest, stickiness, precocious movement of chromosomes, unequal separation during anaphase, scattered chromosomes, laggards multipolarity, C-mitosis, polyploidy etc. Single or multiple breaks or fragments, gaps, anaphase bridges and laggards constituted the chromatoclassic (on the chromosomes) or clastogenic effects. The frequency of these aberrations increased with the increase in treatment duration.
Interphase cells with di-, multi and micronuclei were also observed rarely. The occurrence of various types of abnormalities have been recorded in section 3.7.

From the results mentioned earlier (3.7), it has become clear that the HPF and GRF effluents were highly capable of inducing various types of cytological abnormalities in the root tip cells of *Allium cepa*. These abnormalities include spindle as well as chromosomal aberrations. The frequency of cell division was also affected drastically bringing down the mitotic index (mitodepressive) resulting in complete antimitotic effect where the mitotic division was totally arrested.

### 4.3.1 Mitotic arrest

In the present investigation, inhibition of cell division in the root tip meristems was the primary effect of industrial effluents. The inhibitory effect on mitosis was observed to increase with the increase in concentration of the effluents. At the lowest concentration used (25%) a good percentage of cells was found to complete the mitotic cycle even though several cytological abnormalities were present. In the next higher concentrations 50% and 75% most of the cells could not complete the cell cycle because of mitotic arrest manifested in the form of acute clumping of chromosomes, stickiness and structural aberrations of
chromosomes. We can observe variation in different months depending on the variations in the physicochemical variables and heavy metal contents of the effluents. They are found to be highly correlated to each other. Materials treated with the highest concentration of the effluents (100%) or in other words without any dilution, the cells could not even enter into the M-phase because of the arrest at $G_2$ phase resulting in the cell death although few cells survived to proceed in M-phase for sometime but could not complete the cycle because of the acute chromosome aberrations. At certain months, the roots lost their turgidity and consequently started deteriorating. They became black and rotting of the roots as well as the lower portion of the onion bulbs took place at higher treatment duration of the concentrated effluents (without dilution).

According to Kihlman (1966), antimitotic substances are able to prevent cells from entering into mitosis and they inhibit the division of cell, nucleus and the chromosomes. Edmunds (1964) has opined that doubling of DNA is not only the requirement for cell division, but inhibition of DNA synthesis will generally result in an inhibition of cell division. According to Singh (1982) antimitotic substances act through different means, producing some active radicals which finally create imbalance in the nucleic acid and protein metabolism resulting in the induction of chromosomal abnormalities.
Cellular damages caused by waste waters of industrial origin, particularly of polyfibre, paper and pulp mills are not well understood. Eventhough there are earlier reports of inhibitor effect of the polyfibre factory, paper and pulp mill effluents on plants in our country, they have been restricted only to the actual damage caused by these effluents and they have not explained the factors responsible for the induction of various aberrations in *Allium cepa*. They include studies of Oblisami & Rajannan (1978), Ravindran & Ravindran (1978), Rangaswamy et al. (1980), Shanthamurthy and Rangaswamy (1979). The mutagenicity and genotoxic activity of pulp and paper mill effluents have been worked out by Nestmann & Lee (1985). They have dealt with the factors responsible for mutagenicity of the effluents of pulp mills in detail.

From the present results it is quite clear that the effluent (HPF and GRF) have inhibitory effect on cell cycle as evidenced by the reduction in mitotic index values with increasing concentration of the effluents and also from the induction of severe cytological abnormalities in the treated onion bulbs. However, it is difficult to predict whether DNA synthesis was blocked or not since further studies have not been undertaken in this regard. On the otherhand, the various types of spindle disturbances observed during the present investigation indicate that there could have been
the inhibition of protein synthesis, since in the functioning of the mitotic apparatus and kinetochores, protein synthesis is essential. According to Shanthakumari and Stephen (1988) absence of chromosomal DNA and RNA synthesis was the cause of mitotic inhibition induced by holothurin.

4.3.2 Spindle Abnormalities

The spindle abnormalities observed in the present study ranged from change in the orientation of the spindle to complete inactivation (Stathmokinesis). In activation of spindle apparatus implied the impairment of the microtubular systems and according to Sharma & Sahu (1977) the malfunction of the microtubules was ascribed to the inhibition of DNA dependent RNA polymerase involved in microtubule protein synthesis or the direct action on tubule protein.

The preponderance of abnormalities attributable to spindle disturbances indicates that the action of HPF/GRF effluents is mainly on the spindle proteins (Mukherjee & Sharma 1988). The effluents may become potent spindle inhibitors in Allium root tip cells. Various effects on spindle apparatus (or mitoclasic effects) included clumping of chromosomes, laggards, unequal separation of chromosomes at anaphase, scattering of chromosomes at metaphase and
anaphase, multipolar spindle formation, C-mitosis, polyploidy etc.

The change in the orientation of the spindle axis was the result of shifting of the poles of the mitotic apparatus and was frequently recorded in cells at metaphase, anaphase and telophase stages of cell division. In such cases, the direction of the spindle axis frequently does not coincide with the direction of the cell axis. It may be oblique or diagonal in direction.

In certain cells we can see the scattered chromosomes from the equatorial plate of metaphase cells. Here the chromosomes are fully contracted and appeared to be scattered all over the cell instead of being arranged in the equatorial plate from a metaphase plate (Pseudo-spindle mitosis, Deysson 1968). According to Deysson (1968) several antimitotic agents are known to induce this abnormality. Another type of important abnormality noticed occasionally in treated cells was lagging chromosomes or lagging fragments and these are believed to have less active kinetochores. According to Reider (1982) lagging chromosomes may arise as a result of chromosome deletion or inactivation as well. Singh (1982) suggested that the reasons for these lagging chromosomes at anaphase might be due to the inactivation of spindle fibres that were attached to them.
Barthelmees (1957) attributed the phenomenon of lagging chromosomes to hindrance of prometaphase movement of chromosomes accompanied by adhesion of the centromeres to the nuclear membrane or to the surrounding surface of the plasma. The presence of lagging chromosomes also indicate that was impaired but not completely inhibited due to the action of the effluents on the mitotic apparatus (Grant 1978). Similar abnormalities have been induced by several herbicides (Badr 1979, Pandita 1986, Shehab 1980).

Frequently C-metaphases were observed in certain cases and these resulted from disturbance of the spindle fibres. Here the daughter chromosomes do not move to the opposite poles and a restitution tetraploid nucleus is formed. Arrested metaphases may also lack the normal orientation of the chromosomes on the equatorial plate. In the present study diplo chromosomes preparations and polyploidization were encountered.

C-mitosis is one of the consequences of inactivation of spindle apparatus connected with the delay in the division of centromere. Deysson (1968) suggested that this may lead to polyploidy and cells thus formed degenerate without further division.

The effluents also suppressed cell plate formation or cytokinesis without affecting chromosome or nuclear division.
resulting in binucleate cells. Disfunction of spindle structure can lead to the formation of scattering of chromosomes, polyploid cell and binucleate cells (Somashekar et al. 1983). This leads to the conclusion that effluents can cause a partial delay to the onset of mitosis and completely inhibits spindle formation at 24 h treatment of all the concentrations. Polyploid cells were observed at higher concentrations and durations. After 48 h treatment of 75% and 100% effluents, total cyto-toxicity was observed in certain months suggesting a total inhibitory action of the chemical on the onset of mitosis.

A rather rare process of polyploidization is spindle fusion in binucleate cells were the two nuclei enter mitosis, simultaneous bimitosis (D'amato 1989). Here the binucleate cells on recovery after treatment showed biprophase. Biprophase was also reported by Sharma & Sahu (1977). In the present study binucleate cells proceeding in prophase have been encountered. However, later stages could not be traced out.

This was followed by disturbed anaphase giving rise to tripolar and tetrapolar cells. Sometimes splitting of functioning spindle lead to multipolar divisions. Somashekar et al. (1984) observed similar results in case of Allium cepa when treated with a fungicide Topsin. Multipolar
spindle was observed by Singh (1982) during treatment with IAA and MH on Allium cepa roots.

The inhibition of spindle formation has been shown to lead to more abnormalities such as stickiness, unequal distribution of chromosomes at anaphase, multipolar anaphase, chromosomal bridges and laggards. The important effect of both the effluent treatments were partial or entire inaction of spindle mechanism followed by scattering of chromosomes.

4.3.3 Chromosome Stickiness

Another class of anomalies observed in chromosomal stickiness is induced by several agricultural chemicals (Grant 1978). Stickiness is generally regarded as a physiological effect on chromosomes during division. It appears in the longer durations and high concentrations due to adhesion or clumping of chromosomes. The predominance of stickiness indicates the toxicity of the chemicals and heavy metals present in the effluent at the chromosome level (Sathaiah et al. 1985). The sticky meta-anaphase cells resulted due to the jointing of the chromosome arms, were observed in majority of the cells. There has been a long controversy regarding the molecular mechanism of stickiness. It was the view of Darlington (1942) that stickiness results from a breakdown of chromosomal nuclei acid to a depolymerized and fluid condition.
Kaufmann (1956) considers that it is due to partial dissolution of nucleoprotein. Hsu et al. (1965) proposed that stickiness may be due to RNA containing particles which coat the surface of chromosomes. However, McGill et al. (1974) suggested that chromosomes stickiness arises due to improper folding of chromosome fibres into single chromatid and chromosome. Stripping of protein covering DNA in chromatin has also been suggested to be responsible for stickiness (Stephen 1979).

Sticky bridges were encountered in some cells at anaphase. These bridges differ from chromatid and chromosome bridges in the fact that acentric fragments are absent in the cytoplasm of the same cell (McGill et al. 1974). Sticky bridges are unstable and eventually break apart and dissolve out. In some instances sticky bridges present at anaphase may persist at the telophase stages and hinder separation of chromosomes (Evans 1962).

4.3.4 Gaps or Achromatic Lesions

The occurrence of achromatic lesions were observed as a rare feature with GRF effluent. Chromosome erosions leading to banded appearance have been described as achromatic lesions (Kihlman 1966) or gaps (Brinkley & Hittleman 1975). A gap is expressed as a severe attenuation or achromatic region along the chromatid arm (Brinkley & Hittleman 1975).
When observed by light microscopy, gaps may appear as complete breaks or display a thin connection across the lesion. But under electron microscope the continuity of chromatin fibre is maintained by these regions. Sax and Sax (1966) suggested that gaps might represent points where reunion of broken ends are being occurred.

Hsu (1982) claims that fine threads can sometimes be seen running across the nonstaining region. However, these sites are obviously so delicate that breakage is easily possible. The continuity of chromatin through gaps is very well evidenced by anaphase preparation in which daughter chromosomes occur with several gaps as single chromosome.

4.3.5 Chromosome Breakage

Treatment with effluents induced structural chromosome changes including breaks, fragments and bridges. Extensive fragmentation was observed at higher concentration and treatment duration. The number of fragments in a cell usually varied from 1 to 4.0. Occasionally cells showing 10 to 15 fragments per cell were also observed. But the frequency of cells showing breakage was very low. Generally the fragments were seen lagging in the centre during anaphase separation. Chromosome fragmentation has been frequently observed in different materials following treatment with chemicals (Kihlman 1966).
There has been considerable controversy over the mechanism of which chromosome breaks are formed. Various explanations have been offered to explain the mechanism of chromosome breakage. Metal ions form some constituent part in the structure of the chromosomes acting as bonds between nucleoprotein blocks of chromosomes (Steffensen 1961, Kihlman 1966). The occurrence of chromatid breaks at all intervals would suggest that the chemical acted at the $G_2$ or late S-phase of DNA synthesis or after the reproduction of chromosomes at the interphase nucleus.

Dustin (1947) holds the view that the mode of action of breakage inducing chemical is mainly through an affect of sulfhydryl groups. A generally held view is that a disbalance in the metabolic set up of the chromosome, especially with relation to the surrounding medium, is responsible for chromosome breakage as proposed by Sharma & Sharma (1960). They also suggest that fragmentation may often result from a non-specific manifestation of stickiness which may ultimately cause difficulty in chromosome disjunction resulting in breakage at certain loci. One means of explaining the case by which chromosomes are broken is to concede that they consist of molecular aggregates bonded together by relatively weak bonds (Steffensen 1961).
4.3.6 Anaphase Bridges

Both the effluents produced anaphase bridges mostly single or occasionally double bridges and rarely multiple ones. Chromatid bridges and sticky bridges were obtained at all the concentration and treatment durations. The present results point out that there is a considerable incidence of reunion of broken chromosomes. Bridge at anaphase showed that breakage and reunion of broken chromosome ends had occurred in $G_1$ phase. Sister chromatids stick together either at the ends or in the middle and form bridges when they would separate at anaphase (Darlington 1942).

Bridges without fragments are more common on those with bridge and fragment. Such abnormalities also have been reported by Ravindran & Ravindran (1978) in their studies on the effect of textile factory waste waters on *Allium cepa* and *Ornithogalum virens*.

Breaking up of chromosomes followed by proximal chromatid reunion evidently results in dysenteric chromosomes which turn to characteristic anaphase bridges (Grant 1978), or these anaphase bridges may be attributed to the general stickiness of chromosomes (Abraham & Koshy 1979). These are of genetic interest because it may ultimately lead to loss of genetic material.
4.3.7 Micronuclei

Micronuclei are true mutagenic effects (Auerbach 1962). A smaller number of incidence of micronuclei was observed in the somatic cells of Allium cepa. Acentric fragments produced as a result of treatment were not transported to the spindle poles during anaphase and as a rule, they do not become incorporated in the daughter nuclei; instead they remain in the equatorial region of the cell, where they form the so-called micronuclei (Kihlman 1966). Micronuclei eventually disappear due to the action of cytoplasmic nucleases and proteases, but they persist for a considerable period of time.

Micronuclei formation suggests the direct action of the chemical on genetic material, i.e. a damage at the chromosome level (Banerjee et al. 1986). They may appear as a result of either clastogenic or mitotic events.

4.3.8 Diplochromosomes

They are the characteristic abnormalities induced by GRF effluent treatment at higher concentrations. The daughter chromatids held together only at the centromeric region and these are referred to as diplochromosomes. This is possibly due to the inactivation of the spindle apparatus and consequent delay of division of centromere. They were almost lacking in the HPF effluent treated cells.
4.3.9 Polyploidy

Disfunction of the spindle apparatus can lead to the formation of polyploid cells or changes in chromosomes number (Somashekar et al. 1983). The complete separation of chromatids along with the division of the centromere had resulted in polyploid cell with double the normal number of chromosomes due to the breakdown of spindle mechanism and non disjunction of chromosomes at anaphase followed by subsequent duplication of chromatids into chromosomes. Grant (1978) opined that polyploid cells were the result of an action of the effluents on the mitotic apparatus. Hence both the effluents act as polyploidy agents in rare cases.

4.3.10 Cytomixis

Cytomixis were normally observed in cells treated with effluents for longer duration (72 h) and concentration (100% effluent). This phenomenon is characterised by transmigration of nuclear substances between adjacent cells through chromatin and cytoplasm strands.

Although cytomixis is recorded in many genera and species as a general phenomenon, the underlying cause is not very clear. It may be due to genetic or physiological disturbances or both. Many nongenetic factors are responsible including mechanical pressure applied during squashing. The phenomenon of cytomixis in the pollen mother
cells of *Plantago ovata* Forsk, (Plantaginaceae) may be due to genetic or physiological disturbance or both (Singh 1986).

The amount of migrating chromatin varied greatly in different meocytes ranging from a portion of chromatin material to the centre genome complement of a nucleus. However, the probability of inclusion of migrated chromosome into the nucleus of recipient cells and the degree of viability of donor cell are still unknown.

The cytomixis resulted in cells having chromosome number deviating from the diploid number. George & Geethamma (1985) presented the method of speciation through the process of cytomixis in the shoot meristems of *Jasminum* sp. It resulted in cells with different levels of ploidy but more commonly aneuploidy. Such numerical alteration of chromosomes by means of cytomixis in the shoot bud has played a distinct role in the origin of some sps. of *Jasminum*.

In sexual cells (PMCs), cytomixis results in the degeneration and ultimate sterility of pollen. On the other hand, in the vegetative cells of the shoot tip where mitotic abnormalities are rare, cytomixis evidently had numerical variation of chromosomes alone and consequent origin of new species.