CHAPTER-VI

Results and Discussions

Photo 6.1: View of Ujjani Reservoir backwater at Daund

‘Water bears a more complex character than its life-supporting function – not only for basic human needs, but for livelihood.’ **Pratibha Mehta, UN Resident Coordinator**
CHAPTER-VI

Results and Discussions

6.1 Introduction

Worldwide water bodies are the primary means for disposal of waste, especially the effluents, from industries that are functioning near the dam. These effluents from industries have a great deal of influence on the pollution of the water body. These effluents can alter the physical, chemical and biological nature of the receiving water body (Sangodoyin, 1991). Economic development and population growth require stable water and hydroelectric power supplies. However, because of the relative scarcity of natural lakes, the tropical countries are constructing reservoirs for their economic development. When industrial, domestic and agricultural wastes are added to these water, these reservoirs get heavily polluted (Lewis, 2000). Reservoirs often receive water from river drainages and are, therefore, vulnerable to changes in the hydrology or water quality of rivers in their downstream (Lewis, 2000).

The quality of dam water is dependent on variety of factors such as:

1) Geological formation of area;
2) nature of drainage pattern;
3) type of development activities in the sphere of agriculture, industrialization and urbanization;
4) creation / operation of anti pollution activities.

The parameters required to evaluate the quality of a water body are multi-variable and all can not be readily categorized or determined. One very general classification groups the parameters into three broad categories i.e. physical, chemical and biological. These categories are very general and the parameters often involve complex relationships, where one parameter might influence upon the system in several ways. Some of the parameters, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, etc., are commonly analyzed but not precisely defined.
It needs to be clarified that identification of specific characteristics (physical, chemical and biological) is not the ultimate goal in practical consideration of quality. It is rather an important step by which suitability of water for human usage is identified. They provide certain useful information for judging whether water quality in resources is suitable or not and, if not, which specific changes might be necessary to make it so.

For the purpose of above consideration, in situ monitoring and analyses were carried out to determine: (a) temperature, (b) pH, (c) conductivity, (d) Total Dissolved Solids (e) Turbidity and (f) dissolved oxygen (DO) concentration. These parameters profoundly influence the life present in any lake or reservoir, its distribution and adaptability. To understand the changing pattern of water quality of Yeshwantsagar reservoir there is a need to monitor and find out the sources and types of water pollutants. The findings are discussed below.

6.1.1) Temperature

In tropical systems, marked variations in temperature and rainfall between seasons influence the physical and chemical characteristics of water bodies (Adebisi, 1981). The greatest source of heat in water is solar irradiance by direct absorption. Transfer of heat from air and the sediments takes place but this input is usually very small as compared to direct absorption of solar radiation by water, suspended particulate matter and dissolved organic compounds. Changes in water temperature can result from climatic phenomenon or from the introduction of industrial waste or discharge of cooling water used by power stations and many other industries. Stream temperature may also be increased by irrigation practices and return agricultural drainage. Temperature is basically important for it affects on certain chemical and biological activities in the organisms within aquatic media. The temperature in most of the water bodies ranges between 7.8 to 38.5°C in Indian subcontinent (Singhal et al., 1986)

The temperature is an important factor for many uses of water and its suitability as a habitat for aquatic life. Chlorination is more effective in summer. Thus, the high temperature influences the efficiency of water purification and treatment. The water temperature is important to use it in various industries, for
example, in paper and pulp industry. Cold water is used in steel industry and rayon manufacturing. Water having temperature more than 32\(^0\)C affects rice plants. Water having temperature less than 16\(^0\)C is preferred for use in farms and dairy factories. Water temperature more than 27\(^0\)C is less useful for cooling purpose (CWPRS, 2002). Warm water accelerates corrosion in pipelines and cooling system. Temperature also controls behavioural characteristics of organisms’ solubility of gases and salts in water. No other factor has so much influence like temperature (Welch, 1952).

There is relatively less information about optimum temperature requirement for growth and reproduction of aquatic flora and fauna. Diatoms, an important constituent of aquatic food chain, grow best at 15\(^0\)C to 25\(^0\)C. Green algae, a primary producer, grow best at 25\(^0\)C to 35\(^0\)C; and noxious blue green algae at 30\(^0\)C to 40\(^0\)C (Carins, 1956b). The effect of temperature is a complex one because temperature influences the rate of both, photosynthesis and respiration. The amount of growth achieved depends on the balance between these two processes. The growth of rooted plants is often enhanced by temperature increase. Prolonged increase in water temperature might contribute the spread of nuisance plants. The maximum temperatures that an adult fish can tolerate vary with the species of fish, prior acclimatization, oxygen availability and synergistic effects of other pollutants, etc. For spawning and hatching of eggs, lower temperatures are required. Above certain levels, rise in temperature seems to become abruptly lethal for many organisms. A sudden change in temperature is deleterious to fish life.

Temperature of water is an important parameter in detecting pH, EC and dissolved ions present in water. The water of a reservoir is usually warmer in the winter and cooler in summer than it would be without a dam. As this water flows into its river, the altered temperature also affects the temperature of the river. It impacts the plant and animal life present in both the reservoir and the river. Temperature also affects forms of alkalinity, kinetics of chemical reaction and pattern of microflora influencing biological reactions and chemical equations. Due to increase in temperature DO decreases. High temperature is usually assumed to cause a pollutant to be more toxic (Sprague, 1970) and resistance to disease become lower (Jones, 1964). The sensitivity of fish to toxic substances and disease increases at high temperature, basically due to
decrease in oxygen concentration. More water passed over gills and, therefore, more toxic material passes over the permeable membrane (Miller, 1977).

During initial phase of monsoon (June, 2008) daytime atmospheric temperature at Ujjani was 28°C to 33°C. In this season of monsoon surface water temperature of Ujjani reservoir water varied from 26.3°C to 28.6°C. It was 26.4°C, near intake point of the dam and increased marginally up to Palasdev nala. In shallow areas the water temperature was marginally more as compare to deeper areas. Near Bhigwan Takrarwadi, when air temperature was 33°C then the water temperature near bank was 28.5°C (Fig.6.1).

During Nov.2009, the field checks and survey are repeated when the sky remained partially covered by cloud. The day time air temperature was approximately 26°C to 30°C. As a result, the surface water temperature was slightly less, 23.3°C to 26.1°C, as compared to the June 2008. Gole (1993) reported that during their study shallower portion of Ujjani reservoir temperature was 35°C. He also added that it was uncomfortable to wade through such warm water. Such high temperature is an unfavorable situation for fish and many other aquatic species. The water temperature becomes more than 30°C is detrimental to many fish species. During the present study period, a large number of dead fish were noticed in certain areas of this reservoir. One of the reasons could be high temperature of water. Along bank of the reservoir where bottom water temperature was more as compare to deeper areas a large number of floating dead fish was noticed.

The surface water temperature was 32°C in the upstream areas of Bhigwan Takrarwadi but atmospheric temperature was 36°C. The surface water temperature during study period of May, 2009 remained more or less same from dam area upto Daund. It varied between 27°C near Canal Head and Bhigwan Takrarwadi. Thick growth of vegetation and hence more biological activity might have caused higher temperature (30.2°C) near Ajoti Village. The reason may be cloudy sky condition, the variation in water temperature during daytime, both longitudinally and vertically, was marked less inspite of being summer season. Day time temperature of the reservoir water remained same when sky condition was cloudy during December 2009.
Fig. 6.1: Values of temperature in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.2: Mean values of temperature in 20 sampling stations in pre-monsoon and post-monsoon.

\[ R^2 = 0.157 \]
As reported by Gole (1993), during winter of 1992 Ujjani reservoir water temperature during daytime varied between 20°C and 25°C, which is comparable with the present findings. The average temperature of Pune Municipal Corporation (PMC) water was 22°C. The present study indicates that during summer period thermal stratification may occur in certain areas of Ujjani reservoir; and particularly, in the shallow part of the reservoir, the water temperature may become unfavorably high for fish. This reservoir water may not prove useful for cooling purpose in industries. Therefore, as the temperature of Ujjani reservoir water during summer rises up to 30°C or more, discharge of warm water into this reservoir should not be allowed. Fig.6.2 shows that there is no much variation trend with time.

6.1.2) pH

pH is a measure of the acidity or basicity of an aqueous solution. Pure water is said to be neutral, with a pH close to 7.0 at 25 °C (77 °F). Natural pure water has pH 7 which indicates an equal number of H⁺ and OH⁻ ions while acidic water has a pH less than 7, indicating the preponderance of H⁺ ions. It is the negative logarithm (base 10) of the molar concentration of dissolved hydronium ions (H₃O⁺). Not only is the hydrogen ion a potential pollutant in itself but it is also related intimately to the concentrations of many other substances, particularly the weakly dissociated acids and bases. The concentration of weakly dissociated acids and bases not only affect the pH value, determine the ease with which it can be altered. But pH should not be confused with acidity or alkalinity.

pH is considered as an important chemical parameter in river water since most of the aquatic organisms are adapted to an average pH. Stream water usually ranges from pH 6.5 (slightly acidic) to a pH of 8.5, an optimal range for most organisms. pH values varied from 7.2 to 8.7 are suitable for aquatic organisms (Subbamma and Rama, 1992 and Klein, 1973). Most of the biological processes and biochemical reactions are pH dependant. pH is considered as an indicator of overall productivity that causes habitat diversity (Minns, 1989). The pH of natural waters is governed to a large extent by the interaction of hydrogen ions arising from the dissociation of H₂CO₃ and from OH⁻ ions, resulting from the hydrolysis of bicarbonates. For most limnological purposes, the approximate neutrality at pH 7 is sufficiently accurate. Owing to the great variety of substances which occur in water or
make contact with it, many compounds may be present which contribute ionise hydrogen. Waters containing larger amounts of dissolved matters are more likely to show higher buffer effect, while low buffering capacity is to be expected in waters low in dissolved materials.

Soft water lakes, hence, generally have low buffering action, and the sudden changes in pH which sometimes occur are due to this reason. Hard water lakes, on the other hand, have higher buffering capacity and a similar inflow would have a much smaller effect. Ordinarily, the surface water of large lakes, due to more dilution, undergoes relatively smaller change in pH from season to season (Welch, 1952). Special circumstances surrounding smaller lakes may impose pH changes in greater magnitude. In deeper water, however, changes can be expected in relation to over turns, stagnation periods, nature of bottom materials and other reasons. If the water is in vigorous motion the moving water dilutes and distributes the products of photosynthesis and respiration causing pH changes less distinguishable.

The measurement of pH has wide applications in water and wastewater management. Usually domestic sewage is neutral or slightly alkaline with a strong buffering action. Industrial wastes, on the other hand, can be strongly alkaline or acidic that may have a marked effect upon the pH of the receiving water. Since, many waste waters are treated biologically or added to streams or waters where biological systems must be protected pH measurement and control are very significant. However, pH is required to be considered in chemical coagulation, disinfection, softening and corrosion control. Water having low pH (less than 6) can corrode pipes and concrete. High pH water, on the other hand, hastens scale formation in water heating apparatus and also reduces the germicidal potential of chlorine. Water acquires a sour taste at pH 3.9 or below. Neutral to slightly alkaline water is recommended for many industries.

The optimum pH for irrigation water depends on the type of crops to be grown and the physical and chemical properties of the soil. It is obvious that where alkaline soils are predominant water with low pH value is preferred. Water of moderately high pH is not detrimental for most crops in acid soils. It is known that the hydrogen ion concentration has a relation with living matter, but its exact nature was not adequately observed. It is believed that pH may have some effects on the ability of cells to absorb
and utilize oxygen and to give off carbon dioxide. It may work through some modification of the permeability of the cell membranes. Organisms and tissues respond differently to conditions of neutrality, acidity or alkalinity. pH is known to have a conditioning influence upon certain enzymes, growth relations and the performance of some functions in plants. Each organism has its tolerance range of pH terminated by a maximum, minimum and possesses an optimum at some intermediate position.

Extreme pH can result in rapid fish kills, alteration in flora and fauna and harmful secondary reactions such as change in nutrient solubility and formation of precipitates in a lake or reservoir or other water bodies. There is a reason for believing that the unfavorable effects attributed to low dissolved oxygen may be due to an accompanying too high or low pH conditions. The ability of some fish species to extract oxygen from water gets seriously affected at pH below 5 and above 9 (Welch, 1952). Well developed fish in unpolluted waters can tolerate pH between 5 and 9, certain species can tolerate even above 10, at least for a day. But, even within this range pH can have a marked effect upon toxicity of certain compounds. Fish that can tolerate pH values as low as 4.8, die even at pH even 5.5 if the water contains 0.9 mg/L of iron (Bandt, 1948). Eventhough, direct lethal effects of pH on fish are not produced usually within the range of 5 to 9.5 but from the point of view of productivity the pH range of 6.5 to 8.5 is considered to be safe. When pH falls below 5.0 specialized flora and fauna may develop and some species have been observed at pH value as low as 2.9.

Neutral to slightly alkaline water supports growth of all natural aquatic life whereas most plants have an optimum pH between 6 and 7. Gole (1993) reported that the pH value of Ujjani reservoir water in 1991 remained above 7 and in some shallow areas as high as 9 or more. The pH of so in the vicinity of the reservoir was found to be basic (pH 7.4 to 8.6). Sharma (1993), regarding pH of river reported that between August 1992 and February 1993 the pH value of Bhima river at Pargaon varied between 6.9 and 8.0. The pH value of the Mutha river water varied between 6.2 and 8.8 while flowing through Pune city area during winter of 1986-87(Wagh et.al., 1987). In 1992, the students of Bharti Vidyapeeth observed that the ground water along the Mutha river had pH values between 6.2 and 7.2. The lake water was always
alkaline as pH constantly remained above 7. The earlier studies showed that the range of pH of a majority of lakes and reservoirs lies between 6 and 9. This is in accordance with earlier reports by Wetzel (1975) who reported that the value of pH ranges from 8 to 9 units in Indian waters.

The value of pH is high during the monsoon which may be due to addition of solids from the runoff water. Marker (1977) has made the same observation. Alkalinity and pH are the factors responsible for determining the amenability of water to biological treatment (Manivasakam, 1980). pH showed a strong positive correlation with dissolved oxygen. Increasing levels of dissolved oxygen in aquatic systems are usually associated with eutrophic and productive water bodies (Egborge, 1994). Ujjani reservoir water should show stronger buffering capacity due to its large area and high salinity. Hence, due to addition of limited quantity of wastes its pH value is not likely to change rapidly. However, high density planktons and aquatic plants can have influence on its pH value, at least in certain zones, particularly where exchange of water is low. As the soil around this reservoir is basic in nature (Gole, 1993), its water too is expected to be alkaline.

In the month of June 2008 Ujjani reservoir water pH values varied between 7.04 and 8.24, i.e. remained marginally alkaline (Fig.6.3). During the period of post monsoon (November, 2008) the range of pH values were observed from 7.76 to 9.17. In general the pH values were higher in winter than other seasons. The variation can be due to the exposure of river water to atmosphere, biological activities and temperature changes (Adebowale et al., 2008).

Kannan and Jog (1980) also reported higher pH values in rainy season and lower in summer. Low pH in summer may probably be due to high rate of organic matter decomposing activities by microbes which release acids. Even during monsoon and winter seasons the reservoir water remained marginally alkaline. However, in November 2008 the pH value 9.17 was noticed in Galandewadi. Growth of plankton and fall in reservoir water level might be the contributing factors towards increased pH in water during this period.

During May 2009 the pH values were more near Ganjevalan and less Palasdev village, varied between 8.64 and 7.17. In summers, the high temperature enhances microbial activity causing excessive production of CO₂ and reduced pH. Khan and
Khan (1985) and Narayani (1990) also reported similar results at Seikha Jheel in Aligarh and eutrophic wetlands of lower lake (Bhopal) respectively. However, Tripathi and Srikandar (1989) found neutral pH in case of polluted water in their studies indicating that neutral pH alone need not necessarily be an index of purity and pH 7 will have to corroborate with other parameters.

In the month of December 2009 pH values varied between 7.68 and 9.15 in Ujjani reservoir water i.e. remained marginally alkaline and the pH values were more near Chandgaon Village and less Bhigwan Nala which varied between 9.15 and 7.68. Ghose and Sharma (1988) also recorded relatively high pH of water in the months of the winter in their study of the Ganga river attributing high pH to increased primary-productivity. Hence, throughout the study period, this reservoir water was found to be marginally alkaline. The basic nature of the soil in the area must be an important contributing factor towards alkaline pH of this reservoir water. In general there was no significant variation in pH value, either longitudinally or vertically.

As water of the reservoir is alkaline in nature, it is more useful for irrigation purpose in acidic soils. Its alkaline pH may cause some problems in industrial uses and water treatment plants. Because, such water hastens scale formation and lowers the germicidal potential of chlorine. There may not be any direct lethal effect but such alkaline water is not ideal for rapid growth of fish population. An advantage of comparatively high pH value is removal of certain pollutants by precipitation. For example, a heavy metal like lead, which comes from vehicular exhausts, remains insoluble in water when pH value is above 8 (Hall, 1937). Under high pH condition such pollutants are less available to aquatic life and hence create less toxic action.

The desirable limit of pH for drinking water is 6.5 to 8.5 (BIS, 1991; WHO, 1992) and drinking water supplied by Pune Municipal Corporation (PMC) had average value of 7.8. Mean values of pH are presented in Fig.6.4 which shows no variation of pH with different seasons.
Fig. 6.3: Values of pH in different sampling stations in pre-monsoon and post-monsoon

Fig. 6.4: Mean values of pH in 20 sampling stations in pre-monsoon and post-monsoon
6.1.3) Turbidity

Turbidity is a principal physical characteristic of water and is an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample. It is caused by suspended matter or impurities that interfere with the clarity of the water. It is, therefore, commonly regarded as the opposite of clarity. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble coloured organic compounds, plankton and other microscopic organisms. Human activities, such as construction, can lead to high sediment levels entering water bodies during rain storms. Areas prone to high bank erosion rates as well as urbanized areas also contribute large amounts of turbidity to nearby waters. Some industries like quarrying, mining and coal recovery can generate very high levels of turbidity from colloidal rock particles. The turbidity of water is a very important parameter in water treatment process to calculate the quantity of coagulants and provides an estimate of un-dissolved substances (Rizwan et al., 2009). In water bodies such as lakes, rivers and reservoirs, high turbidity levels can reduce the amount of light reaching lower depths, which can inhibit growth of submerged aquatic plants and consequently affect species which are dependent on them such as fish and shellfish. High turbidity levels can also affect the ability of fish gills to absorb dissolved oxygen. The water qualities of the reservoir have negative impact due to discharge of sewage and municipal wastes into water bodies (Mohapatra and Singh, 1999).

The turbidity of surface water is usually between 1 NTU and 50 NTU. When turbidity is above 5 NTU one can see the cloudiness in water. Aquatic plants need light to grow. When turbidity is high solid particles prevent sunlight from reaching plants below the surface and photosynthesis decreases. When it occurs plants are in danger. Their growth is reduced and they may even die. When turbidity is high, particles absorb heat from the sun and it raises temperature of water. In warm water dissolved oxygen level drops (warm water holds less oxygen than cold water). With less photosynthesis plants also produce less oxygen. Low oxygen levels affect growth and reproduction of animals and plants. It may even cause their death. Particles in water clog fish gills which can cause serious problems to them. Poor water clarity blocks light and limits their movement which makes it difficult to see their prey.
Cloudy water also makes it difficult for predatory birds to see their prey. Poor water clarity can make water unsuitable to drink and swim in. Some suspended particles support bacteria growth. The cost of filtering and disinfecting polluted water can be very high. Reservoirs often receive water from large areas (river drainages) relative to their size and are, therefore, especially vulnerable to changes in the hydrology or water quality of rivers (Lewis, 2000).

Nephlo Turbidimeter was used for the measurement of turbidity in the present study. The presence of turbidity has a significant effect on photosynthetic zone due to constant hindrance in transmitting the light. Particulate matter, whether organic, inorganic or excessive growth of biota is responsible for the change in water quality rendering it unfit for drinking. As water turbidity is mainly caused by the presence of suspended matter, turbidity measurement has often been used to calculate fluvial suspended sediment concentrations (Norsaliza and Ismail, 2010).

The turbidity of Ujjani reservoir during June 2008 (pre-monsoon) varied between lowest 2.3 NTU at dam wall and maximum 18 NTU at Bhigwan Takrarwadi. The highest value of turbidity was also found i.e. 15.5 NTU at Daund (Fig.6.5). The values are high in the dry seasons. The higher values during the dry seasons are due to the absence of floodwater, surface runoff and settling effect of the suspended solids due to secession of rainfall (Kolo, 1996). At Bhigwan Takrarwadi and Daund the abnormal values of turbidity are usually due to discharge of water due to floating sediments carried by the river from catchment areas. Mathew et al. (1992) have however reported order of turbidity as summer > rainy > winter in the study of water pollution in rural pond near Mandula (M.P)

The turbidity values of Ujjani dam during Post-monsoon (November 2008) were found to be in between 4.3 NTU and 26.6 NTU. Significantly higher turbidity recorded during post-monsoon season was at sampling locations Palasdev nala, 18.6 NTU and Daund, 23.2 NTU. It may be due to heavy rainfall leading to an increase in phytoplankton abundance and decay of organic matter in suspension in addition to surface runoff from adjacent streams carrying heavy sand and silt into the water. Lewis (1978) opined that phytoplankton biomass influences water transparency and therefore turbidity.
Fig. 6.5: Values of Turbidity in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.6: Mean values of Turbidity in 20 sampling stations in pre-monsoon and post-monsoon.
During pre-monsoon season of 2009 (May) as compared to post-monsoon, the turbidity value was slightly lower. The turbidity values during pre-monsoon (May, 2009) varied between 3.2 and 21.9 NTU. The turbidity value near dam wall was 3.2 NTU. The higher values of turbidity were found at the sampling locations: Bhigwan Nala, Bhigwan Takrarwadi and Daundi i.e. 15.13 NTU, 21.9 NTU and 18.7 NTU respectively. Values obtained are compared with those of waters of most tropical rivers and Lakes (Olaniran, 2000; Kolo, 1996; Khana and Ejike, 1984). The desirable limit of turbidity for drinking water is 5 NTU (BIS, 1991; WHO, 1992) and drinking water supplied by Pune Municipal Corporation (PMC) had average value of 0 NTU.

The turbidity values of Ujjani reservoir during Post-monsoon (December 2009) vary between minimum 4.1 NTU and maximum 28.5 NTU. The turbidity values marginally remain same near the dam wall (4.1 to 4.9 NTU). The values obtained are within the acceptable values of 4.1 and 28.5 NTU according to Ayodele and Ajani (1999) for fish production. The turbidity value increases from Palasde village, 20.1 NTU to upstream most point Bhigwan Takrarwadi, 28.5 NTU. The mean concentration of turbidity in surface water exhibits an increasing trend June-08, Nov.08 and Dec.09 (Fig.6.6).

6.1.4) Electrical conductivity:

The ability of substances/water to conduct an electric current is called conductivity. Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. Salts that dissolve in water break into positively and negatively charged ions. Conductivity is the ability of water to conduct an electrical current and the dissolved ions are the conductors. The major positively charged ions are sodium (Na$^+$), calcium (Ca$^{++}$), potassium (K$^+$) and magnesium (Mg$^{++}$). The major negatively charged ions are chloride (Cl$^-$), sulphate (SO$_4^{2-}$), carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$). Nitrates (NO$_3^-$) and phosphates (PO$_4^{3-}$) are minor contributors to conductivity although they are biologically very important.

Special electric conductivity is conductance by a cubic cm of a substance at 25$^0$ C or at a specified temperature. Conductivity of water, therefore, gives an idea about the
total dissolved ionizable solids in it. Naturally conductance of water increases with an increase of concentration of dissolved and dissociable substances.

The ability to conduct a current depends upon the presence of ions, their total concentration, mobility, valence, relative concentrations and on the temperature of measurement. Hence, determination of conductivity of water is a quick way for measuring the approximate total ion concentration in it. Purer the water lower the EC value. Instead of providing any qualitative identification, conductance permits approximate estimation of total ionic population. The simplicity and speed of the technique make it attractive for the estimation of the overall quality of water which otherwise would have to be obtained by summarizing the results of the numbers of specific analytical determinations. The conductivity increased with the increase in total dissolved solids and water temperature (Entz, 1973). The lower conductivity values recorded for the dry season may be due to the utilization of such allochthonous materials by the phytoplanktonic organisms of the reservoir. High conductivity values have been reported to be indicative of an increase in the amount of polluting particles (Oben, 2000).

However, it needs to be made clear that conductivity may bear no simple relationship to the concentration of dissolved solids and an equality of conductance between two samples does not necessarily imply an equality of total dissolved solids. In practice, it has been found that the conductance at 25°C, multiplied by a factor between 0.65, can be used to predict the concentration of dissolved solids unless the water is of an unusual composition. Thus, EC is used as a popular general measure of total quantity of dissolved salts i.e. salinity in given water. The salinity of reservoir water is governed not only by inputs of dissolved ions of influents from runoff but also by the fate of these materials due to evaporation of water.

The total salt content, stated in terms of EC, is an important criterion for many uses of water including municipal water supply, industrial water supply, irrigation water, water for stock, wild life, fish and aquatic life. The limit for domestic supply is based primarily on taste thresholds. The international standard for drinking water with respect to total dissolved solids, recommended by WHO, is 1500 mg/L (maximum permissible level) and 500 mg/L (minimum desirable level). In industries, particularly
for using in boilers, water having much less EC or less dissolved solids are required to prevent corrosion and the deposition of scale.

The direct effect of total salt content on aquatic life is osmosis. All substances in water collectively exert osmotic pressure on the organisms living in it. The total ionic salinity composed almost entirely of the eight major ions is of major importance in osmotic regulation of metabolism and biotic distribution. The distribution of biota in fresh waters has been influenced by long evolutionary processes of physiological adaptation to a wide range of salinities or mechanism for osmotic regulation. Osmotic regulation functions primarily in the maintenance of a difference in concentrations of ions inside and outside of the cells at appropriate physiological level. Most aquatic species can tolerate some changes in the relative amount of salts normally present in the water they habitat if the total concentration does not change significantly. However, wide variations in the total salinity or in the concentrations of individual salts can have far reaching effects upon aquatic fauna. It is noticed that a good number of different species of fresh water fish are usually not found in waters with EC greater than 2000 µs/cm (CWPRS, 2002).

Conductance is one of the most important criteria for the classification of irrigation water. The rate of water entry into plants depends on water potential gradient and the root resistance. Excessive level of salinity may also alter the hormone balance of plants (Bernstein, 1975). It may damage plant cells and cytoplasmic organelles (Meiri and Shalhevet, 1973). Salinity generally reduces growth rate and ultimate size of plants. In case of root crops, salinity reduces the yield of root storage organs more than it does vegetative or root growth.

Waters containing high dissolved salts become increasingly more hazardous for irrigation of salt-sensitive crops or for application to fine textured soils because of which water passes with difficulties. Due to all these reasons knowledge about EC and concentrations of major ions is important for irrigational use of waters to know their suitability while using on different types of soils for different kinds of crops. For irrigation purpose, the EC limit suggested by McKee and Wolf (1976). However, good drainage of the soil may be a more important factor for crop growth than the salts in the irrigation supply. Even when excellent waters are used, poorly drained
land may sometimes go out of production. On the other hand moderately saline water may sometimes be used on open well-drained soils.

The EC being an unstable parameter, its value changes with time after collection of samples. It needs to be determined in situ or immediately after collection of samples. In the source regions of the river Bhima and its tributaries the salinity is very low (Sharma, 1993) indicating less water-rock interaction and less human interference in these areas. This is expected because the rate of rock weathering depends upon temperature. Therefore, in tropical areas usually strongly weathered soils are drained by water. Such waters, hence, carry fewer electrolytes and a large part of their total composition is constituted by Silica. Moreover, the rivers flowing through the alluvial, laterite and red soil areas have a lower soluble salt content than the rivers which flow through black cotton soil areas (CWPRS, 2002).

It is obvious that while crossing the city areas, the EC of the Mutha river increases due to effluents and wastes discharged into it, in addition to leaching of minerals from soil. During 1986-87 winters, Wagh et al. (1987) observed that the EC of this river water increased from 200 µs/cm to 600 µs/cm since it flows through the city area. Wagh (1999) during 1994-95 too noticed a similar trend, the EC value increased from 220 µs/cm to 520 µs/cm. Patil (1996) observed the EC value of the canal water from Khadakwasla reservoir up to the city area varied between 90µmhos/cm and 390 µs/cm. Whereas, EC of the Mutha river basin ground water studied by a group of students of Bharti Vidyapeeth’s Engineering College, was as high as 1330 µs/cm and 1520 µs/cm during monsoon of 1996 and early summer of 1997 respectively. And the values showed an increasing trend along the stretch of the river towards downstream. During 1992, Sharma (1993) observed that the electrical conductance of the Bhima River at Pargaon changed significantly with time during rainy season i.e. from 130 µs/cm during first week of August to 400 µs/cm during end of August, showing effect of initial rains carrying soluble salts. The value gradually reduced and remained at approximately 300 µs/cm till October. But, as the dry season commenced, the EC value of the river water at Pargaon increased four-folds. In the middle of February 1993 it was 1300 µs/cm. The EC value of Ujjani reservoir water was found to be considerably high.
In the month of June 2008, (Pre-monsoon) the surface water EC values varied between 400 µs/cm and 1135 µs/cm from dam wall to Daund. The highest EC 1135 µs/cm was found at Daund and lowest value 400 µs/cm at Padasthal Village.

Increased conductivities could result from low precipitation, higher atmospheric temperatures resulting in higher evapotranspiration rates and higher total ionic concentration and saline intrusions from underground sources. It could also be due to a high rate of decomposition and mineralization by microbes and nutrient regeneration from bottom sediments (Egborge, 1994). However, the value was somewhat more in some of the areas such as Shahaville village (671 µs/cm), Ajoti Village (629µs/cm) and further upstream. Slow and restricted flows of stagnation favour the concentration of dissolved salts were to increase the Conductance (Prather et al., 1982).

During post-monsoon season of 2008 (November), compare to summer, the EC values were marginally high. The EC values during post-monsoon (Nov.2008) varied between 422 µs/cm and 2472 µs/cm. The highest EC was 2472 µs/cm found at Bhigwan Takrarwadi and lowest EC 422 µs/cm in upstream areas at Chandgaon village. The EC of surface water varied marginally lower during summer (May 2009) also and remained between 392µs/cm and 1518µs/cm. In some areas, water had marginally higher EC values, up to 1518 µs/cm at Bhigwan Takrarwadi and 1057 µs/cm at Daund, i.e., in this zone the water was more saline compare to other study areas. One of the reasons of higher salinity in this area is input of domestic water from Daund town and Bhigwan. Washing and cleaning activities at this point were also noticed during the present study (Fig.6.7). It was observed during post-monsoon December, 2009 that there was a marginal to significant decrease in EC over previous study periods. It may be as an effect of high rain fall during the year 2009. Hence, more dilution and less evaporation. The EC values during post-monsoon (December.2009) varied between 379 µs/cm and1129 µs/cm. The mean concentrations of EC in surface water exhibit an increasing trend only in Nov.2008 (Fig.6.8). Average electrical conductivity measured for PMC water was 70 µs/cm. Therefore, EC values of Ujjani reservoir water indicate that this water usually remains within ‘permissible’ range (except few locations) for agricultural use during most part of a year.
Fig. 6.7: Values of EC in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.8: Mean values of EC 20 sampling stations in pre-monsoon and post-monsoon.

$R^2 = 0.031$
But, to use such water for irrigation purposes adequate drainage facility is required for protection of soil against water logging and salinity problem. This moderately saline water needs pre-treatment for many of the industrial uses. During summer, especially if the rainfall of the previous year remained scanty, the water even after conventional treatment may taste saline.

6.1.5) Total Dissolved Solids (TDS)

Total Dissolved Solids (often abbreviated TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in: molecular, ionized or micro-granular (colloidal sol) suspended form. Total dissolved solids are normally discussed only for freshwater systems as salinity comprises some of the ions constituting the definition of TDS. The principal application of TDS is in the study of water quality for streams, rivers and lakes. Though, TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants. High values of TDS in surface water are generally not harmful to human being but high concentration of these may affect persons who are suffering from kidney and heart diseases (Gupta et al., 2004).

In general, the total dissolved solid concentration is the sum of the cations and anions in the water. Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The chemicals may be cations, anions, molecules or agglomerations on the order of one thousand or fewer molecules so long as a soluble micro-granule is formed. More exotic and harmful elements of TDS are pesticides arising from surface runoff. Certain naturally occurring total dissolved solids arise from the weathering and dissolution of rocks and soils. It is well established (Fausey et al., 1995) that the mineral content of the water expressed as TDS can be used as a rough indicator of the edaphic conditions which play a fundamental role in determining the biological productivity of water bodies.

Therefore, the TDS test provides a qualitative measure of the amount of dissolved ions but does not tell us the nature or ion relationships. In addition, the test does not
provide us insight into the specific water quality issues, such as: elevated hardness, salty taste, or corrosiveness. Therefore, the TDS test is used as an indicator test to determine the general quality of the water. Total concentration of dissolved solids is normally obtained from the weight of dry residue remaining after evaporation of the volatile aliquot of water sample. The value so obtained denotes various types of mineral species dissolved in water.

The TDS in water samples is estimated by multiplying EC by an empirical factor. This factor may vary from 0.55 to 0.90 depending upon the nature of soluble ionic components, their concentration and the temperature of water (Hem, 1970). Rainwater and Thatcher (1960) have reported the value of the multiplying factor as 0.65± 0.1. Day and Nightingale (1984) reported the value as 0.527 to 0.570 for groundwaters of Fresnol Wisalie and Bakersfield in USA. Reddy et al. (1993) have reported that the multiplying factor ranges from 0.61 to 0.64 for surface and groundwater of Tirupati region, Andhra Pradesh (AP). Kefford et al. (2003) have expressed salinity in terms of EC and arrived TDS using the formula EC = 0.754 TDS for the Barwon river, Victoria, Australia. These varied values of the multiplying factor reported by various researchers clearly indicate that the multiplying factor depends upon the hydrogeology of the area and is not related on a one-to one basis. Therefore it is an important parameter to the water quality standard. The higher the concentration of TDS in water poorer is its quality. According to drinking water standards prescribed by United States Public Health Services (USPHS, 1962) TDS should not exceed 500mg/L beyond which they may influence toxicity of heavy metals and organic compounds in fish and other aquatic life (McKee and Wolf, 1976).

The TDS of Ujjani reservoir during pre-monsoon (June 2008) varied between 256 mg/L to726 mg/L. The high values of TDS were found 726 mg/L at Daund and also at Bhigwan Takrarwadi, 330 mg/L. At Bhigwan Takrarwadi and Daund the sudden increase observed in the level of TDS. It was contribution from the industrial waste. Alkalinity of all sampling stations of the river has helped in increasing TDS in agreement with Fritsch and Rich (1983); Rawson, (1951); Rao (1953). The low value of TDS was found 270 mg/L at U/S Dam and also near dam wall was 272 mg/L.
Fig. 6.9: Values of TDS in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.10: Mean values of TDS in 20 sampling stations in pre-monsoon and post-monsoon.
The TDS values ranges between 270mg/L (Chandgaon Village), 1582 mg/L (Bhgwan Takrarwadi) and Daund(848mg/L) during postMonsoon (November 2008). The level of TDS in groundwater increased due to high concentration of salts (Din et al., 1997). However, near dam and some other nearby areas the values were not so high. It remained around minimum 330 mg/L to maximum 237 mg/L. During pre-monsoon season of May 2009 as compare to post-monsoon the TDS value was slightly lower. The TDS values during premonsoon (May 2009) varied between 250 mg/L to 971mg/L. The TDS value near dam and immediate downstream surface water was 254 mg/L. In upstream areas the highest TDS was 971 mg/L found at Bhigwan Takrarwadi and also at Daund, 676mg/L. The desirable limit of TDS for drinking water is 500 mg/l (BIS, 1991) and 1000 mg/L (WHO, 1992). The drinking water supplied by Pune Municipal Corporation (PMC) had average value 50 mg/L.

The TDS values of Ujjani dam during Post-monsoon (December 2009) were marginally less as compared with November 2008 (Post-monsoon). The TDS values during post- monsoon (December 2009) varied between lowest 232 mg/L to highest 722 mg/L. The low value of TDS 232mg/L was found at Kalthan no.2 and high value 722 mg/L was found at Daund. Fig. 6.9 shows TDS in Ujjani reservoir was lower than the maximum recommended value of 500 mg/L, except Bhigwan Takrarwadi (19) and Daund. One of the reasons of higher TDS in this area is input of domestic water from Daund town and Bhigwan. Washing and cleaning activities at this point were also noticed during the present study. Tahir and Bhatti (1994) supported that high level of TDS and total hardness in surface water was due to discharge from polluting industries and untreated wastes. Figure 6.10 clearly shows that the increasing of TDS trend over period of Nov.08 and May 08 whereas the Nov.08 and Dec.08 remain same.

6.1.6) Total Hardness (TH)

Hard water usually has high mineral contents. Generally, such waters have higher levels of dissolved calcium and or magnesium minerals. These minerals may occur in ground water passing through chemically susceptible rocks like limestones or other rocks with calcium minerals. Such waters precipitate soaps, hindering lather formation, may also cause a hard scale in boilers and other hot water distribution systems. Polyvalent salts of the long-chain fatty acids present in soap are insoluble in
water, whereas, monovalent cations like Na and K form soluble salts. Water hardness is generally expressed as equivalent CaCO$_3$ in mg/L and is not a pollution parameter but simply indicates water quality (Mahadev and Gholami, 2010).

The level of hardness is related to the amount of dissolved mineral in the water. It is defined as concentration of multivalent cations such as Ca$^{2+}$ and Mg$^{2+}$. But, in true sense of the term, any substance that forms an insoluble curd with soap gives rise to hardness. Apart from Ca and Mg, many other polyvalent metal ions, (e.g. iron, manganese, copper, barium, lead, zinc and aluminum) also precipitate soap. But, they are usually absent in appreciable concentration in natural waters and hardness is attributed to only Ca and Mg ions. Hence, Ca, Mg and total hardness in the water are interrelated (Palanisamy et al., 2008).

The principal natural sources of hardness in water are the chemically more susceptible sedimentary rocks, seepage and runoff from soils. In general, hard waters originate in areas with thick top soil and limestone formations (Sawyer and McCarty, 1967). Groundwater is generally harder than surface water. Groundwater which is rich in carbonic acid and dissolved oxygen usually has a high solvating power, therefore, the rocks contain appreciable amounts of minerals such as calcite, gypsum and dolomite. Hardness may have levels up to several thousand milligrams per litre (Sawyer and McCarty, 1967; De Fulvio and Olori, 1975).

Hardness in water may also result due to the natural accumulation of salts from contacts with soil and geological formations or it may enter anthropogenically. Soft water refers to the water containing low salinity and is usually derived from drainage of acidic igneous rocks or as a result of large concentrations of alkaline earths derived from drainage of calcareous deposits (Wetzel, 1975). In addition to the natural sources, industrial discharges and return flow from irrigation drainage may also increase the hardness of water.

Soap will neither cleanse nor lather until all the hardness of water is precipitated as insoluble salts of the fatty acid. Prior to usage of synthetic detergents washing was being done with soaps and the problem of hard water was more of a nuisance than it is today. As detergents have polyvalent metal salts and contain polyphosphates that tie up the Ca Mg and Fe ions these do not result in to precipitation (CWPRS, 2002).
Excessive hardness is undesirable in water for laundries, carbonate beverages, metal finishing, dyeing and textile industries, food processing, paper and pulp, bottle washing, photography, leather goods and many other industrial processes. But, very soft water, though good for their usage in laundries, dish washing or boilers, may be corrosive to water pipes and may cause disintegrating effect on Portland cement. Water with less than 10 mg/L of hardness may also attack concrete but, hard water may not cause harm for irrigation purpose. No injuries are (McKee and Wolf, 1976) observed to plants grown in calcareous soils or from watering them with hard water. Some of the workers have even mentioned that hard water is superior to soft water for irrigation.

Although hardness may have significant aesthetic effects, its tolerable limits have not been established as public acceptance of hardness may vary considerably with reference to the local conditions. Soft water was found to cause substantial loss of all essential elements from food (e.g., vegetables, meat and cereals) when used for cooking. Such losses may reach up to 60% for magnesium and calcium or even more for some other microelements (e.g., copper, manganese and cobalt). In contrast, when hard water is used for cooking, the loss of these elements is much lower and in some cases higher calcium contents have been reported in food as a result of cooking (WHO, 1978; Haring and Van Delft, 1981; Oh et al., 1986 and Durlach, 1988).

Water hardness can influence the composition of the aquatic flora and fauna (Persoone, 1979). It is known for a long time that there are definite and fairly clear-cut biological differences between hard water and soft water biota. According to Hawkes (1979), in hard waters rich macrophytic-flora develop while the invertebrate fauna are dominated by crustaceous and molluscs. Waters having hardness values of 15 ppm or above are satisfactory for the growth of fish while values less than 5 ppm CaCO₃ result into slow growth, distress and eventual death of fish (Gupta and Gupta, 2006). Wetzel (1975) has observed that that hard water lakes, in which high calcareous inputs are sustained over long period of times, show reduced productivity as a result of decreased nutrient availability. Growth rate of bacteria of metabolism also remain low because of low concentrations and turnover of easily decomposable organic compounds which can further reduce synthesis of organic micronutrients. Hard waters, however, do not show appreciable harmful effects upon the health. The
role of hard water in the formation of urinary concentrations is controversial (McKee and Wolf, 1976). Several reports indicate the negative correlation between hardness of drinking water of an area and the death rates from degenerative cardiovascular diseases. But, in India such waters cause problems in digestive system and the possibility of forming calcium oxalate crystals in urinary track have also been reported (Sonawane and Khole, 2010).

Howe (1976) has documented the role of relative deficiency of hardness of water in the production of myocardial and chronic renal diseases in U.S.A. and Japan. Studies done by Salvato (1972) have also revealed that there are higher mortality rates from cerebrovascular and cardiovascular diseases in people provided with soft water than in those provided with hard water. But, the actual causative factors responsible for higher mortality remained unexplained. As the salt content of soft water is low, there is some possibility that such water remains deficient in certain essential trace elements, which may be a contributory factor towards such diseases. Water hardness affects on toxicity. The laboratory tests have shown that the hard water reduces the toxic effects of heavy metals on fish. According to McKee and Wolf (1976), copper sulphate is less harmful to fish than in soft water. Their study indicates that cadmium, lead, titanium, vanadium, etc. are more toxic in soft water than in hard water environment. Salvato (1972) has proved that water softer than 50 mg/L corrosive whereas water harder than 80 mg/L allows greater usage of soap. Hence, the water hardness may be classified as follows.

<table>
<thead>
<tr>
<th>Type</th>
<th>Hardness Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft water</td>
<td>&lt; 17 mg/L</td>
</tr>
<tr>
<td>Slightly hard</td>
<td>17-60 mg/L</td>
</tr>
<tr>
<td>Moderately hard</td>
<td>60-120 mg/L</td>
</tr>
<tr>
<td>Hard</td>
<td>120-180 mg/L</td>
</tr>
<tr>
<td>Very hard</td>
<td>&gt; 180 mg/L</td>
</tr>
</tbody>
</table>

The hardness values mentioned below are expressed as milligram equivalent CaCO₃ per liter of water. The present study reveals that Ujjani reservoir water is harder than its upstream feeder channels but the degree of hardness is seasonal. The hardness values of this reservoir water varied between 129 mg/L and 466 mg/L during pre-monsoon June 2008. It is also observed that near the dam wall, the hardness was less
as compared to its upstream areas. From upstream of dam to Galendewadi the
hardness was found to be approximately < 180 mg/L. From Palasdev nala to Daund,
the hardness increases and the higher values were met at Bhigwan nala-306 mg/L,
Bhigwan Takrarwadi - 466 mg/L and at Daund - 427 mg/L. i.e. it means the hardness
increased gradually towards the upstream direction, during rainy seasons (Fig.6.11).
However, the hardness was found to be very high during post-monsoon (November
2008). But it varied between 205 mg/L and 524 mg/L. The hardness values were less
than 300mg/L from the upstream of Dam to Kandalgaon village. It suggests that the
hardness of Ujjani reservoir water were marginally more during post-monsoon as
compared to earlier periods of pre-monsoon. The higher values of hardness were
again found at Bhigwan Nala-370 mg/L, Bhigwan Takrarwadi - 524 mg/L and Daund
-398 mg/L. It suggests that the hardness increased towards upstream direction. Similar
observations have also been reported by scientists of CWPRS (2002).

The hardness values of the reservoir water varied between 156 mg/L and 501
mg/L during Pre-Monsoon (May, 2009). As compared to previous year the Pre-
Monsoon hardness values were marginally more. Similarly, higher values for water
hardness were also found at Dalaj No.1-303 mg/L, Bhigwan nala-327 mg/L, Bhigwan
Takrarwadi - 501 mg/L and Daund-357 mg/L. However, no specific trend in relation
to variation of total hardness values according to distance was observed.

The concentration of calcium (Ca) in Ujjani reservoir water were marked high at
restricted locations thereby increasing the hardness values of water samples during
post-monsoon (December 2009). The hardness values of the reservoir water during
this survey varied between 221 mg/L and 644 mg/L. The hardness values observed
from the collected water samples were as follows- Palasdev village–385 mg/L,
Palasdev Nala - 357 mg/L, Dalaj No.1-406 mg/L, Bhigwan Nala- 472 mg/L, Bhigwan
Takrarwadi - 644 mg/L and at Daund -529 mg/L. Other than these locations, the water
hardness was found to range between 221 to 342 mg/L. Hence, it may be inferred that
the water is mostly moderately hard to very hard. However, a few water samples were
found to be of very hard water category. The desirable limit of total hardness for
drinking water is 300 mg/l (BIS, 1991; WHO, 1992). The drinking water supplied by
Pune Municipal Corporation (PMC) had average value 50 mg/l.
Fig. 6.11: Values of TH in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.12: Mean values of TH in 20 sampling stations in pre-monsoon and post-monsoon.
Therefore, the water is not suitable for usage in boilers, heating appliances, laundries, dyeing, textile mills, paper and pulp manufacturing and food processing. The use of such water would require more soap and may lead to formation of scales on the surface of utensils when used for domestic and heating purpose. Temporary hardness (i.e. carbonate hardness) can be removed by boiling the water. But, for removal of permanent hardness, there are two principal methods lime or lime-soda treatment and ion exchange method (zeolite method). For industrial applications, it requires relatively low hardness.

The lime-soda process may be strengthened by increasing the temperature. The selection of lime-soda treatment or ion exchange procedure is decided on the basis of raw water quality and the local cost of the softening chemicals (Singley, 1971). The concentration of TH at all sampling stations exhibit an increasing trend over a period of monitoring June-08, Nov.08, May-09 and Dec.09. It is clearly seen from the mean concentration of TH over four seasons (Fig.6.12). The hardness of Ujjani reservoir water is mainly responsible for the growth of more macrophytic-flora and molluscs.

6.1.7) Total Alkalinity (TA)

Alkalinity is a measure of buffering capacity of water and is important for aquatic life in a freshwater system because, it equilibrates the pH changes that occur naturally as a result of photosynthetic activity of phytoplankton (Kaushik and Saksena, 1989). Alkalinity of water is its capacity to neutralize a strong acid and is characterized by presence of all hydroxyl ions capable of combining with hydrogen ions (Koshy and Nayar, 1999). Alkalinity is used as criteria for determining the nutrient status of waters (Sorgensen, 1948 and Moyle, 1949). In pure natural waters alkalinity is mostly due to dissolved CO₂ or bicarbonate ions and it represents the main carbon source for assimilation during photosynthesis. These constituents result from dissolution of mineral substances in the soil and atmosphere (Mittal and Verma, 1997).

\[
\text{Alkalinity} \quad \text{A}^- + \text{HOH} \rightarrow \text{HA} + \text{OH}^-
\]

Most of the alkalinity of natural waters is formed due to dissociation of CO₂ in water:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]
Carbonate and bicarbonate may originate from microbial decomposition of organic matter also. Total alkalinity is caused by bicarbonates, carbonates, OH ions, borates, silicates and phosphates (Kataria et al., 1995). Due to alkaline nature of Ujjani reservoir water, presence of bicarbonates is observed in most of the water samples. The total alkalinity of surface water from Ujjani reservoir varied from 218.1mg/L to 485.1mg/L during Pre-monsoon (June 2008) and no particular trend in its values or variations could be noticed. The alkalinity values were higher at Ganjevalan-353 mg/L, Bhigwan nala-399.5mg/L, Bhigwan Takrarwadi-485.1 mg/L and Daund-412.9 mg/L. While at the other sampling sites, these values remained around < 300 mg/L. The source of bicarbonate ions in ground water is from the dissolution of carbonate rocks and from carbonate species were present (calcium plagioclase) (Taylor, 1958). It was found that amount of Ca is higher than Mg and bicarbonate is the most dominant ion in Ujjani reservoir. According to Ruttner (1963) in lakes, calcium bicarbonate is the most dominant buffer, a fact which normal lakes share with most of the hard water lakes.

The total alkalinity values, during November 2008 (post-monsoon) varied from 290.3 mg/L to 460.5 mg/L. The TA was higher during this period than the previous surveys. Enhanced rock-water interaction during Post-Monsoon could have contributed towards this increase (Pawar, 1993). Osborne et al. (1987) observed that an increase in concentration of cations was balanced by increase in concentration of bicarbonates and the increase in bicarbonate in a reservoir is probably due to absorption of atmospheric CO₂ if pH increased during the period.

Figure 6.13 shows the total alkalinity values of Ujjani reservoir water were found to be in the range of minimum 249.4 mg/L to maximum 480.5 mg/L during May 2009 (Pre-monsoon). The higher values of alkalinity were recorded at the following sampling stations Kalthan No.2-387.4 mg/L, Dalaj No.1-370.4 mg/L, Bhiwan nala – 468.1 mg/L, Bhigwan Takrarwadi–480.5mg/L and Daund-389.5 mg/L.
It may be worth mentioning that during this period, the EC of the reservoir water was very high especially at Bhigwan Takrarwadi and Daund. However, the increasing trend for EC values was much more effective for HCO$_3^-$ concentrations have also been made by (CWPRS, 2002). The minimum values of TA were recorded at the sampling stations of U/S of dam-253.9 mg/L, at canal head-249.4 mg/L and D/S of dam-268.1 mg/L. Kaul and Handoo (1980) found that with increase in atmospheric temperature and the consequent increase in the photosynthetic process in hot season, alkalinity values usually decrease in summer. They observed significant difference in alkalinity between surface and bottom waters: lower in surface waters than in the bottom, in Nilnag Lake, Kashmir.

The concentration of total alkalinity varied from 266.7 mg/L to 491.8mg/L during Post-Monsoon (December 2009). The lowest values of TA were found at Kalthan No.1-266.7mg/L and maximum 491.8mg/L was found at Bhigwan Takrarwadi. Therefore, no particular trend in its value or variations could be noticed. The most probably, dilution occured due to rainwater and the HCO$_3^-$ concentration during this period was marginally less as compared to other seasons. Venkateswarlu (1969a) also observed that alkalinity is affected by rain fall. In the Lake, total alkalinity was solely due to bicarbonates and no carbonate alkalinity could be traced at any station during the entire period of study.

However, when the alkalinity level is used as a criterion for assessing the nutrient status (Sorgensen, 1948 and Moyle, 1949) the reservoir water is highly nutrient rich. According to their classifications, waters were grouped into three different nutrient status groups on the basis of alkalinity: (a) 1 to 15 mg/L as nutrient poor, (b) 16-60 mg/L as moderately rich, and (c) more than 60 mg/L as nutrient rich. The WHO acceptable limit for total Alkalinity is 200 mg/L. beyond this limit taste may become unpleasant. Total alkalinity of the surface water during all the seasons in general showed a decreasing tendency from the pre-monsoon period to the post monsoon during the entire period of study. It may be assumed that as the monsoon progresses the alkalinity content decreases or water quality stabilizes in the Lake. Figure 6.14 clearly shows the slightly increasing of TA trend with time over the four seasons.

The desirable limit of total alkalinity for drinking water is 200 mg/l (BIS, 1991) and 500 mg/l (WHO, 1992).
Fig. 6.13: Concentrations of TA in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.14: Mean values of TA in 20 sampling stations in pre-monsoon and post-monsoon.
The drinking water supplied by Pune Municipal Corporation (PMC) had average value 75 mg/l. In Ujjani reservoir, the surface water of Bhigwan Takrarwadi and Daund as compared to other stations, showed a higher alkalinity in all seasons during entire period of study. It is at this station the sewage of Bhigwan Takrarwadi and Daund township join the surface water of the reservoir. Hence, the increase in alkalinity in surface waters at this site was a sign of anthropogenic impact on the system.

6.1.8) Calcium (Ca\(^{++}\)) and Magnesium (Mg\(^{++}\))

Calcium contributes is the fifth most common element found in most natural waters. Water becomes hard when it comes in contact with soluble, divalent metallic cations, especially, calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)). The sources of calcium are minerals such as amphiboles, feldspars, gypsum, aragonite, calcite, pyroxenes, dolomite and clay mineral (Obiefuna and Sheriff, 2011). Calcium salts and calcium ions (Ca\(^{2+}\)) are among the most commonly encountered substances in fresh water. Actual concentration of Ca in fresh water ranges from almost zero to several hundred milligrams per litre which results from the leaching of the soil, passage of water through rocks with calcium bearing minerals through sewage and industrial wastes. The Ca\(^{2+}\) ion concentration is most strongly influenced by metabolism and biotic requirements. Generally, calcium concentration is low as the rate of decomposition of igneous rock minerals (anorthite) is slow and this is shown in balanced reaction of its decomposition (Hem, 1985). Plagioclase feldspar and secondary carbonates are the principal sources of calcium in basalts. Calcium contributes not only to hardness of water but it is also instrumental in buffering the pH of water. When river water is impounded in a storage reservoir it may get modified due to calcium carbonate (CaCO\(_3\)) precipitation. The increased pH may bring about super saturation and result in precipitation around the edge of the water body.

Human body requires approximately 0.7g to 2.0g of Ca per day as food element (Taylor, 1949). Calcium ions (and also magnesium) are important in the preservation of integrity of the cell membrane in higher forms of life. Approximately, 99% of the Ca and 70% of Mg in the mammals are found in skeletal structures. Calcium is essential for normal plant growth for the maintenance of good tilth in the soil and is
desirable in water for irrigation. It maintains the structural and functional integrity of cell membrane and holds plant cells together. Calcium is useful in the growth and population dynamics of fresh water flora and fauna in numerous ways. It forms skeletons of vertebrates, calcareous shells and structures of many other species. Ca is required as nutrient for normal metabolism of higher plants. The requirement of Ca is usually provided by green algae (Wetzel, 1975). Calcium reduces the toxicity of many chemicals to fish and other aquatic fauna. A concentration of 50mg/L of Ca was found to suppress the toxic effect of 2mg/L of Zn, and 0.7mg/L of Pb upon some species of fish (Jones, 1938). According to Hart et al. (1945), of the U.S. waters supporting a good mixed fish fauna, ordinarily have about 5% had less than 15mg/L of Ca; 50% had less than 28mg/L and 95% had less than 52mg/L. The lethality of very high concentrations of Ca on fish indicate that fish can survive from one to three days at concentrations of 2500 mg/L to 4000 mg/L of Ca.

Ca is beneficial in water and it tends to inhibit corrosion of cast iron and steel (Larson and Skold, 1957). It forms a protective coating inside of steel pipes and boilers. But its higher concentrations lead to harmful scale formation, salt precipitation due to waste of soap, difficulties in electroplating, rinsing operations and drastic reduction in fermentation processes. The calcium ion concentrations in Ujjani reservoir water were high in both the pre and post-monsoon seasons. Its calcium values varied between 22.77 mg/L and 89.16 mg/L during Pre-Monsoon (June 2008). The calcium concentrations were recorded from 26.30 to 33.23 mg/L at the sampling points from U/S of dam wall to Shaha village but higher concentrations have been recorded at the sampling sites Dalaj No.1-50.2 mg/L, Bhigwan Nala-55.61 mg/L, Bhigwan Takrarwadi – 89.16 mg/L and Daund-78.35 mg/L.

During (Post-Monsoon), November, 2008 Calcium ion values varied between 36.12 mg/L and 98.39 mg/L. The higher concentrations were found again at Shaha village-60.16mg/L, Kalthan No.1-64.20 mg/L, Bhigwan Takrarwadi -98.39 mg/L and Daund -79.26 mg/L. The Ca ion concentrations in other sampling points are between 40 to 60 mg/L. These analyses reveal that the Ca content increases during the winter and decreases during the monsoon due to dilution factor and comparatively high temperature values during monsoon tend to reduce Ca solubility in water (Wagh, 1998).
In the consecutive year too similar trend continued. During May 2009 (Pre-Monsoon), the Calcium ion concentrations ranged from 34.12 mg/L to 94.27 mg/L. The water level of this reservoir had gone down considerably and hence high Ca concentration was recorded (e.g., between 40 to < 94 mg/L) (Fig.6.15).

During (Post-Monsoon) December 2009 the Calcium ion concentration varied between 40.46 mg/L and 111.5 mg/L. The higher concentrations were found at Bhigwan Takrarwadi and Daund i.e. 115.5 mg/L and 105.3 mg/L respectively. The calcium ion concentration of Ujjani reservoir water was higher during pre-monsoon as compared to post-monsoon. The calcium concentration was found between 40 to 50 mg/L near the dam. The Ca concentrations were marginally higher, varied from 50 mg/L to < 100mg/L in further upstream areas. The concentration of Ca at all sampling stations exhibit an increasing trend over a period of monitoring June-08,Nov.08,May-09 and Dec.09 which is clearly noticed from the mean concentration of Ca over four seasons (Fig.6.16). The permissible limit for calcium in drinking water is 75 mg/l (BIS, 1991) and 150 mg/l (WHO, 1992). The drinking water supplied by Pune Municipal Corporation (PMC) had average value 4 mg/L.

This reservoir water being hard, the reduction in Ca concentration is expected which is the result of precipitation of CaCO$_3$ during summer months. Moreover, the concentration of CaCO$_3$ in natural waters depends upon a number of factors such as, temperature, pressure, concentration of carbon dioxide in water, pH, biological factors and presence of other ions. CaCO$_3$ is also known to bring about precipitation of inorganic nutrients, removal of humic acids and other organic compounds by adsorption. The study also reveals that the Ujjani reservoir waters contained a moderately high concentration of Calcium throughout. But, it is interesting to note that reservoir contained a good number of shells and mollusks. It indicates that a part of Ca was used for the formation of calcareous shells. However, significant seasonal variation in dissolved Ca concentration in this reservoir water was not noticed which may be due to maintenance of equilibrium between dissolved and calcareous Ca.

Magnesium is one of the most common elements in the crust of earth. But, when it is present in natural waters is chemically very active and therefore not observed naturally in an elemental state. It contributes to water hardness and its
sources in natural water are rocks containing magnesium (e.g., carbonate, silicate, sulphate and chloride) Obiefuna and Sheriff (2011). Its abundance in water is less than calcium (Pitter, 1999). Minerals which contribute magnesium to freshwaters are amphiboles, olivine, pyroxenes, dolomite and magnesite. The dark coloured ferromagnesian minerals (olivine, pyroxene and amphiboles) contain major constituent that is magnesium in igneous rocks. It is also found in sedimentary minerals i.e. magnesite, hydromagnesite, hydroxide brucite and mixture of magnesium with calcium carbonate (Hem, 1985). Even though both contribute towards water hardness to the property of hardness Mg compounds are more soluble than Ca compounds. Hence, Mg rarely gets precipitated and its demand in metabolism is minor in fresh waters. Therefore, their concentrations are of conservative type and show less fluctuation (Wetzel, 1975).

Magnesium is essential for both plants and animals. The inclusion of Ca and Mg ions in the tissues of vertebrates is primarily a reflection of their presence in bone. Mg$^{2+}$ plays an important role in many of the enzymatic reactions as an activating ion. Magnesium in waters serves as a cofactor and activator for enzymatic reactions such as glycolysis, ATP metabolism, transport of elements through cell membranes, synthesis of proteins, nucleic acids, neuromuscular excitability and muscle contraction, etc. It also acts as a natural antagonist of calcium. Magnesium deficiency increases risk to humans. It develops various pathological conditions such as vasoconstrictions, hypertension, cardiac arrhythmia, atherosclerotic vascular disease, acute myocardial infarction, eclampsia in pregnant women, diabetes and osteoporosis (Rude, 1998; Innerarity, 2000; Saris et al., 2000). The concentration of Mg at all sampling stations exhibit an increasing trend over during the period of monitoring i.e. June-08, Nov.08, May-09 and Dec.09 which is clearly observed from the mean concentration of Mg over these four seasons (Fig. 6.18). High magnesium diets with low in Ca can cause rickets (Shohl, 1939). But, Mg in water is not considered as a public health hazard because the taste of water becomes quite unpleasant before the waters reach their maximum toxicity. Concentrations of Mg greater than 125 mg/L can have a cathartic and diuretic effect. Its concentration in ground and surface waters may vary widely but rarely exceeds 30 mg/L. Mg and Ca cations in irrigation water tend to keep the soil permeable and in good tilth.
Fig. 6.15: Concentrations of Ca in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.16: Mean concentrations of Ca in 20 sampling stations in pre-monsoon and post-monsoon.
Fig. 6.17: Concentrations of Mg in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.18: Mean concentrations of Mg in 20 sampling stations in pre-monsoon and post-monsoon.
The exchange of soil complex normally contains much more Ca than Mg. It is the only metal contained in chlorophyll and hence when the element is deficient it results chlorosis (Gilbert, 1957). Therefore, loss of green colour, especially in leaves, suggests an inadequate Mg supply in plants. The relative concentration of Mg and Ca in water controls the distribution of certain fish food organisms (Hedgpeth, 1944). Doudoroff and Katz (1953) reported that fish can tolerate up to 1000 mg/L of Mg in lake water. Mg ions are vital in water quality assessment because of their hardness reaction and its salts form scale in boilers and cause deposition within pipes.

During Pre-Monsoon i.e. in June 2008, Mg ion values of Ujjani reservoir water varied between 14.18 mg/L and 48.49 mg/L. The higher concentration of magnesium was found at Bhigwan Nala, Bhigwan Takrarwadi and Daund i.e. 40.72 mg/L 48.49 mg/L and 33.62 mg/L respectively. The Mg ion concentrations of Ujjani Dam water of other sampling stations were found <30 mg/L. The Mg ion concentrations during Post-Monsoon i.e. in November 2008 noticed varied between 26.17 mg/L and 67.11mg/L. Surprisingly, the higher concentrations were noticed at Shaha Village, Bhigwan Nala, Bhigwan Takrarwadi and Daund, i.e. 43.48 mg/L, 53.12 mg/L, 67.11 mg/L, 54.47 mg/L respectively. The ionic composition of most water bodies is directly related to the rock types on the catchment (Bennion et al., 1997). Similar trend was noticed in the next year during Pre-Monsoon i.e. May 2009, the magnesium ion concentration ranged between 17.29 mg/L and 64.6 mg/L. The higher values of Mg$^{2+}$ was found at the sampling points Dalaj No.1, Bhigwan Nala and Bhigwan Takrarwadi 44.54 mg/L, 43.23 mg/L, 64.6 mg/L respectively. The Mg ion concentration found near the dam was from 17.29 to 26.73 mg/L. During Post-Monsoon i.e. December 2009, Ujjani reservoir water the Mg$^{2+}$ concentration varied between 29.15mg/L and 8.92 mg/L (Fig.6.17). The permissible limit for magnesium in drinking water is 30 mg/l (BIS, 1991) and the drinking water supplied by Pune Municipal Corporation (PMC) had average value 4 mg/l. The higher concentrations of magnesium were found at Dalaj No.1- 59.10 mg/L, Bhigwan Nala- 81.45 mg/L, Bhigwan Takrarwadi - 88.92 mg/L and Daund - 64.82 mg/L. Near the dam the Mg$^{2+}$ value varies from 29.15 to39.15 mg/L. Mg concentration was found to be higher than the previous periods.
Hence, throughout the study period, variation in Mg concentrations in this reservoir water was not significant. And the reservoir water contained enough Mg for supporting a good growth of fish fauna.

6.1.9) Sodium (Na\(^+\)) and Potassium (K\(^+\))

Sodium is an alkali-metal element which has a strong tendency to exist in the ionic form and constitutes 2.6 percent of the Earth’s crust (Weast, 1972). It is the sixth most abundant element on the Earth. It is a soft, silvery-white, highly reactive metal that is never found in nature in the uncombined state. Potassium is an essential element in humans and occurs widely in the environment including all natural waters.

Sodium is also abundant cation in the extracellular fluid. It is largely associated with chloride and bicarbonate in regulation of acid–base equilibrium. Maintenance of the osmotic pressure of body fluid and prevention of excess fluid loss, are another important functions of sodium preserving the normal irritability of muscle and permeability of cells. According to WHO (1984), approximately 50 mg of sodium is essential in the minimum sodium chloride requirement of 120 mg/day.

Potassium, one of the active metals, is not found in a free state in nature but occurs only in ionized or molecular state. Its concentration in fresh waters seldom reaches 20 mg/L due to its strong coherence into silicate minerals. The concentration of K is more than a few tens of milligrams per liter in water with high dissolved solids or from hot springs. It is found that Potassium is mainly used in fertilizers, manufacturing of soaps (both liquid and soft), glass industry and in matches. Sodium is ubiquitous in the water environment. Its concentration varies considerably depending upon hydrological, geological, local and regional conditions. The seasonal fluctuations and salt utilization patterns also bring about changes in its concentration. All natural waters contain sodium ions (Na\(^+\)) and its concentrations are below 200 mg/L. But, its higher concentrations in inland waters are normally associated with pollution from industrial discharges, sewage effluent and sea water intrusion.

The anthropogenic sources of sodium, which contribute significantly to the surface water, include road salt, water treatment chemicals, domestic water softeners and
sewage effluents. Water treatment chemicals including sodium fluoride, sodium silicofluoride, sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium phosphate, sodium silicate and sodium hypochlorite prove harmful when used together as their total concentrations may go up to 30 mg/L (WHO 1979).

In natural waters sodium ion \((\text{Na}^+)\) is introduced due to weathering of rocks, industrial effluents, domestic sewage and irrigation. Especially, the reused water during irrigation has much higher Na concentration than the original water. Many sodium salts are used in industry and so is one of the most common ions in the process of wastes. However, sodium and potassium concentration in lakes mostly remain uniform with a very little seasonal variation indicating the conservative nature of these ions. But, due to needs and greeds of human beings, the Na and Cl contamination of groundwater and surface water have increased multifold especially in urban areas (Mason et al., 1999). The PMC water showed average value of \(\text{Na}^+\) and it was 4.1 mg/l. Excessive sodium in drinking water greater than 200 mg of Na is harmful to persons suffering from cardiac, renal and circulatory diseases (McKee and Wolf, 1976). But its harmful effects may be camouflaged by Ca, Mg or other elements. Adequate intake of potassium, calcium, and magnesium with essential requirement of sodium is useful as a healthy diet for heart, weight and stress reduction (Whitney et al., 1987). Potassium is an essential nutritional element and though required in low concentrations, it is vital for plants and animals. \(\text{K}^+\) ion occupies animal cells as a principal inorganic cation whereas \(\text{Na}^+\) ion is a constituent of extracellular tissue fluids. They serve as essential activating ions for specific enzyme systems. Potassium plays a major role in synthesis and respiration processes, even more importantly, regulates the hydration of tissues. However, excessive quantities of K are cathartic.

Potassium consumption from drinking-water through large single dose usually induces vomiting and affects health (Gosselin et al., 1984). Sodium influences the physicochemical properties of plasma and water supply. The salts of sodium, potassium, calcium and magnesium are essential in natural waters. But, their individual toxicities are naturally countered balanced to produce a physiologically balanced situation in the presence of other ingredients.
Hence, a discharge with an excess of an ion upsets the balance to create toxic conditions (Hawkes, 1979). However, the toxicity of Na on aquatic life depends largely on the anions involved. Na is, therefore, not a desirable element (Welch, 1952) which serves the following roles: (1) as a conservator of potassium; (2) for replacement of potassium as a plant nutritive element; (3) providing of silt adsorbed potassium to plants; and (4) antidote against certain toxic salts. The monovalent cations Na\(^+\) and K\(^+\) are involved primarily in ion transport and exchange. The spatial and temporal distribution of these two cations in lakes usually remains uniform with very little seasonal variation. Potassium has been observed to stimulate plankton growth. The toxicity of K to fish is reduced by Ca. Several investigators found that K could be toxic to fish in soft waters when concentrations are more than 50 mg/L (McKee and Wolf, 1976).

Sodium is required in limited amounts for the growth of most of the plants. Na is not only toxic to plants but deleterious to soil conditions in high concentrations. The suitability of water for irrigation is not only decided by total salt contents but also on the basis of composition of salts. Hence, the existence of particular ions may have toxic effects on crops on the basis of salt composition. At the same time, the balance among some ions may also be harmful to the growth properties of soils. For example, the ratio of sodium to total cations is vital not only in agriculture but also in human pathology. The suitability of river water for irrigation, therefore, decreases with increasing solute content and not only because of the greater salt burden. The presence of sodium in soils leads to swelling that closes the pores of the soil, reduces the soil permeability and increases the pH of the soil solution to dangerous levels. Waters with sodium carbonate or bicarbonate, as predominant salts, are more harmful to plants than water with other sodium salts. However, the action of sodium (and potassium) ions on soil largely depends upon the concentrations of some other ions, mainly Ca and Mg. However, the Potassium absorption for most crops is dependent on highly specific low concentration mechanism which for the most crops can supply adequate K even in the presence of high concentrations of other cations (Epstein et al., 1963). So, the most crops are able to receive adequate K even under saline conditions. When Potassium is used as fertilizer will have no major effect on pH. It however, raises EC of the soils.
The requirement of Na is opposite to those of agriculture for some of the industrial and domestic purposes. Soft waters, relatively high in Na, low in Ca and Mg, are preferred for domestic and many industrial uses because they render little lime deposition in pipes and boilers. Municipal water supplies, therefore, are often softened by removal of some of the divalent cations. But the same water supply to be supplied for gardens and agriculture require higher degree of water softening. In industries for using in boilers more than 50 mg/L of sodium and potassium together may cause foaming. High concentrations of sodium chloride and other sodium salts also aid in corrosion of iron and steel plants.

The sodium ion concentrations in Ujjani reservoir water were high in both, (Fig.6.19) Pre and Post-monsoon. During June 2008 (i.e. pre-monsoon season), in the reservoir water sodium ion values varied between 60.20 mg/L and 140.8 mg/L. The higher values of Na ion were recorded at following sampling stations Bhigwan Nala-111.2 mg/L, Bhigwan Takrarwadi-140.8 mg/L and Daund-102.5 mg/L. During this period, the EC values of the reservoir were also very high. In the reservoir water several blue-green algae have been noticed. Wetzel (1975) is of the opinion that the growth of blue-green algae is favoured in water containing more than 40 mg/L of Na.

During November 2008 (i.e. post-monsoon season), in the reservoir water sodium ion values varied between 56.14 mg/L and 140.5 mg/L. The higher concentrations have also been recorded at Bhigwan Takrarwadi- 140.5mg/L and Daund -123.2 mg/L. Various metals from industrial, agricultural, domestic and urban wastes may enter into river and lake waters through leaching, runoff, effluents and dry deposition (Biney and Christopher, 1991; Okoye et al., 1991). A major share of these metal ions is also due to rock dissolution. However, the extent of rock dissolution effect on surface water chemistry has still not been fully understood (Katsuro and Ohmori, 2005).

The analyses of Ujjani reservoir water during May 2009 (i.e.pre-monsoon) reveal a Na concentration in the range from 60.29 mg/L to 109.8 mg/L. During this period, most of the sampling points the Na concentration remains in between 80 to < 100 mg/L., (except Bhigwan Takrarwadi-109.8 mg/L). Such high concentration of sodium is not expected from arable lands and appears to be influenced by wastewater flowing from local households (Wojciech and Pulikowski, 2008).
During December 2009 (i.e.post-monsoon season), in the reservoir water the Na ion concentration varied between 48.49 mg/L and 123.5 mg/L. Exceptionally higher concentrations of Na were recorded at Bhigwan nala-112.1mg/L, Bhigwan Takrarwadi-123.5 mg/L and Daund - 98.16 mg/L. But, this was reduced near the dam wall at Kalashi where it recorded between 50 to 60 mg/L. It is interesting to note that the concentration of Na decreased through the span of monitoring four seasons i.e. June-08, Nov.08, May-09 and Dec.09 (Fig.6.20). The Na ion concentrations in Ujjani reservoir water are moderately high and such water is not conducive for growth of useful aquatic fauna. At the same time, such high concentration of Na can also cause foaming in boiler water. The concentration of potassium ions (K+) in natural fresh waters is generally low (which is normally less than 10 mg/L) but sea water and brines may contain much higher concentrations. The potassium ion concentrations of Ujjani reservoir water remained more or less uniform throughout the study period.

During June 2008 (i.e.pre-monsoon season), water potassium ion values of Ujjani reservoir varied between 1.88 mg/L and 7.89 mg/L. The higher values were recorded at Bhigwan nala-4.56 mg/L, Bhigwan Takrarwadi-7.89 mg/L and Daund -6.14 mg/L. While these concentrations from U/S of Dam to Dalaj No.1 were as low as between 2 to <4 mg/L. During November 2008 (i.e.post-monsoon season), the reservoir water potassium ion values varied between 2.17mg/L and 7.40 mg/L. The higher concentration was found at Dalaj No.1- 4.34 mg/L., Bhigwan Nala -7.40 mg/L, Bhigwan Takrarwadi - 6.80 mg/L and Daund-5.47 mg/L. The minimum concentration of K ion was found near sampling stations i.e. from U/S of Dam to Palasdev nala and they were: 2.17mg/L to 3.95 mg/L (Fig.6.21), except Shaha Village-5.86mg/L.

The analyses of Ujjani reservoir water during May 2009 (i.e.pre-monsoon season), the K ion concentrations were found in the range of 2.72 mg/L to 6.77 mg/L. During this period, most of the sampling points the K concentration remained approximately between 4 and 6 mg/L. As a result of low rain fall in the year 2008 there was a drastic fall in reservoir water level. The water samples collected during May 2009 had a very high K ion concentration. As already mentioned, during this period, the EC values of this part of the reservoir were also high. Research has revealed that K contamination in surface water can result from the overuse of inorganic fertilizers. Figure 6.22 shows concentration of K increases only during summer season (May 2008).
Fig. 6.19: Concentrations of Na in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.20: Mean concentrations of Na in 20 sampling stations in pre-monsoon and post-monsoon.
Fig.6.21: Concentrations of K in different sampling stations in pre-monsoon and post-monsoon

Fig.6.22: Mean concentrations of K in 20 sampling stations in pre-monsoon and post-monsoon.
During December 2009 (i.e.post-monsoon season), in the reservoir water the potassium ion concentration varied between 2.18 mg/L and 6.79 mg/L. The average potassium value of Pune Municipal Corporation (PMC) water was 0.20 mg/l. The higher concentration of K ion was found at Shaha Village-5.2 mg/L, Bhigwan Nala - 6.79 mg/L and Bhigwan Takrarwadi -5.78 mg/L. Though, most of the source rocks contain approximately equal amounts of Na and K, and both are released during weathering, a part of the K go on into clay structure and thereby, its concentration gets reduced in water (Bohlke, 2002). This effect could be seen at the upstream zone i.e. near the river mouth of the reservoir. Otherwise, K being a conservative cation, its distribution in lakes should remain more or less uniform with very less seasonal variation.

The potassium ion concentrations of the reservoir water remained more or less uniform throughout the study period. The values in different seasons varied from 2 mg/L to 8 mg/L. marginally higher values (<5 mg/L) could be observed in the water samples collected during June 2008 and in a few samples collected from upstream part of the reservoir during May 2009.

6.1.10) Bicarbonate (HCO\textsuperscript{3}−)

Natural waters, which include the ocean and freshwater lakes, ponds and streams, act as a major interface between the lithosphere, biosphere and the atmosphere. Natural waters contain a variety of weak acids and bases which include the major elements present in living organisms (e.g., CO\textsubscript{2}, HCO\textsuperscript{3}− and CO\textsubscript{3}−\textsuperscript{2−}). Bicarbonates serve a crucial biochemical role in the physiological pH buffering system. Alkalinity of natural water is determined by the soil and bedrock through which it passes. The main sources for natural alkalinity are rocks which contain carbonate, bicarbonate and hydroxide compounds, along with borates, silicates, and phosphates. Limestone is rich in carbonates. So, waters flowing through limestone regions or bedrock containing carbonates generally have high alkalinity hence it has good buffering capacity. Conversely, areas rich in granites and some conglomerates and sandstones may have low alkalinity and therefore, poor buffering capacity.
In freshwater ecology, strong photosynthetic activity by freshwater plants in daylight releases gaseous oxygen into the water and at the same time produces bicarbonate ions. These shift the pH upward until it becomes toxic to some organisms. In darkness, when no photosynthesis occurs, respiration processes release carbon dioxide and no new bicarbonate ions are produced resulting in a rapid fall in pH. Alkalinity of water is the capacity to neutralize acidic nature and the presence of carbonates, bicarbonate and hydroxides are the main causes of alkalinity in natural waters. Accumulation of free carbon dioxide due to little photosynthetic activities of phytoplankton will lower the pH value of the water while intense photosynthetic activities of phytoplankton will reduce the free carbon dioxide content resulting in increased pH values (Egborge, 1994; Gupta and Gupta, 2006, Adebisi, 1981).

Carbon dioxide (CO$_2$) is one of the most vital substances required for the life of organisms. It is also required for bacteria and aquatic animals. However, the large quantities of CO$_2$ usually have a detrimental effect and may even become fatal if consumed in sufficiently high volumes. Its accumulations in unpolluted natural waters, however, usually do not reach up to such lethal amounts, owing to the ease with which it is released into the air or combine chemically. Under normal conditions, the solubility of CO$_2$ is approximately 0.4 mg/L at 30° C, 0.5mg/L at 20° C and 1.0 mg/L at 0° C (CWPRS, 2002).The solubility of CO$_2$ is independent of the pH. As CO$_2$ dissolves in water, the solution contains unhydrated CO$_2$ at about the same concentration by volume as in the atmosphere (Goldman et al., 1972). Free CO$_2$, dissolved in water combines in part with the water to form carbonic acid (H$_2$CO$_3$).

In addition to CO$_2$ hydration process, bicarbonate may reach water from many other sources and the decomposition of organic matter or they may be discharged by innumerable industrial processes (for bicarbonates are among the most commonly used salts). In combination with Ca and Mg, CO$_2$ also occurs in natural waters in two forms, viz., (a) a fixed carbon dioxide e.g., CaCO$_3$ or MgCO$_3$ and (b) as half bound of the two, the fixed CO$_2$ is a stable state and half bound CO$_2$ occurs as Ca(HCO$_3$)$_2$ or Mg(HCO$_3$)$_2$. In such a loose binding that algae are able to consume large part of it for their photosynthesis (Welch, 1952). Thus, HCO$_3$ ions in the water provide the main buffer system for regulating the H$^+$ ion concentration in water, and also provide the carbon dioxide for photosynthesis. Although, bicarbonates dominates the H$^+$ ion
distribution, the concentration of bicarbonates and carbonates in natural and polluted waters depends upon the temperature, pH and concentration of other dissolved solids.

Ruttner, (1948) studied the differential behavior of CO$_2$ or HCO$_3^-$ with Elodea (a vascular plant) and Fontinalis antipyretica (a water moss) and demonstrated that both the plants utilize free CO$_2$ at approximately the same rate. When free CO$_2$ gets exhausted, Fontinalis ceases its activity of photosynthesis while Elodea continues at a decreased rate with the help of available bicarbonates in water. But, bicarbonates are generally consumed when bicarbonate concentration exceeds that of CO$_2$ by more than 10 times. Hence, the affinity for bicarbonates may be taken as is an adaptive behavior of fresh water plants, particularly for submerged angiosperms (Wetzel, 1975). Algae also utilize bicarbonates directly or indirectly by dissociating them into CO$_2$ and in doing so cause an increase in the pH of the water and precipitation of CaCO$_3$.

The excessive bicarbonates, therefore, control the salinity and the total solid content of water and tend to form carbonates and scale at high temperatures. In irrigation water, the bicarbonates indirectly allow the sodium ratio to increase by helping the precipitation of CaCO$_3$. As a result, with more concentrated soil solutions, Ca and Mg precipitate as carbonates and the relative proportion of Na is increased. Many of the carbonates are insoluble in water, and such salts are removed from polluted waters by precipitation or adsorption. For this reason, chlorides or sulphates occur in excess than the carbonates in waters. As such carbonates or bicarbonates are not detrimental to fish life but their buffering action and effect upon pH usually contribute towards the toxicity, especially due to of high pH value (Hart et al., 1945).

Presence of bicarbonates is observed in most of the water samples due to alkaline nature of Ujjani reservoir water. During June 2008 (pre-monsoon), the HCO$_3^-$ contents of surface water from Ujjani reservoir varied from 218.1mg/L to 485.1mg/L and no particular trend in its values or variations could be noticed (Fig.6.23). The bicarbonate values were higher at Ganjevalan-353 mg/L, Bhigwan nala-399.5mg/L, Bhigwan Takrarwadi-485.1 mg/L and Daund-412.9 mg/L. While at the other sampling sites, these values remained around < 300mg/L. The source of bicarbonate irons in ground water is from the dissolution of carbonate rocks and from carbonate
species present (calcium plagioclase) (Taylor, 1958). The HCO$_3^-$ concentrations, during November 2008 (post-monsoon) varied from 290.3 mg/L to 460.5 mg/L. The bicarbonate concentration was higher during this period than the previous surveys. Enhanced rock-water interaction during Post-Monsoon could have contributed towards this increase (Pawar, 1993).

The bicarbonate values of Ujjani reservoir water were found to be in the range of minimum 249.4 mg/L to maximum 480.5 mg/L during May 2009 (i.e. pre-monsoon season). The higher values of HCO$_3^-$ were recorded at the following sampling stations Kalthan No.2-387.4mg/L, DalajNo.1-370.4 mg/L, Bhiwan nala–468.1 mg/L, Bhigwan Takrarwadi–480.5mg/L and Daund-389.5 mg/L. It may be worth mentioning that during this period, the EC of the reservoir water was very high especially at Bhigwan Takrarwadi and Daund. However, the increasing trend for EC values was much more effective for HCO$_3^-$ concentrations have also been made by (CWPRS, 2002). The minimum values of HCO$_3^-$ were recorded at the sampling stations of U/S of dam-253.9 mg/L, at canal head-249.4 mg/L and D/S of dam-268.1 mg/L. The concentration of HCO$_3$ at all sampling stations exhibit an increasing trend over a period of monitoring June-08,Nov.08,May-09 and Dec.09 which is clearly seen from the mean concentration of HCO$_3$ over four seasons (Fig.6.24). The drinking water supplied by Pune Municipal Corporation (PMC) had average value of HCO$_3^-$ 19 mg/l.

During December 2009 (post-monsoon season) the concentration of bicarbonates varied from 266.7 mg/L to 491.8 mg/L. The lowest values of HCO$_3^-$ were found at Kalthan No.1-266.7 mg/L and maximum 491.8 mg/L was found at Bhigwan Takrarwadi. No particular trend in its value or variations could be noticed. The HCO$_3^-$ concentration during this period was marginally less as compared to other seasons due to dilution which occurred because of rainwater. Bicarbonates are detrimental to aquatic life due to increase in salinity of the water. As mentioned earlier it increases the sodium hazard by aiding in the precipitation of CaCO$_3$ in irrigation water. It is, however, a main constituent which provides buffering capacity of natural water. The pH values of natural water largely depend upon the concentration of this parameter. In most natural waters where Ca$^{2+}$ is a predominating cation, the solubility product of CaCO$_3$ determines the amounts of Ca$^{2+}$, CO$_3^{2-}$ and HCO$_3^-$ which can co-exist in the solution.
Fig. 6.23: Concentrations of $\text{HCO}_3^-$ in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.24: Mean concentrations of $\text{HCO}_3^-$ in 20 sampling stations in pre-monsoon and post-monsoon.
6.1.11) Chloride (Cl\(^-\))

The sources of chloride in drinking-water are mainly from sewage, industrial effluents or saline intrusion. Excessive chloride concentrations increase the rate of metal corrosion depending on the alkalinity of the water. Although, no health-based guideline values are proposed for chloride in drinking-water, the chloride concentrations in excess of 250 mg/L in water can lead to detectable taste. Chlorine occurs in various oxidation states (from -1 to +7) and the chloride (Cl\(^-\)) form is the most significant in aerated water. Chlorides are found in practically in all natural waters and comparatively lesser concentrations in various rock types. The igneous rocks have lower concentrations of Cl\(^-\) in their circulating water, except in sea water contamination of underground supplies.

Human urine contains approximately 6 g Cl\(^-\) per person per day (CWPRS, 2002). Chloride is also present in rain and snow where physical processes contribute towards marine solutes in air near the sea and rain water may contain one to several tens of milligrams per litre of Cl\(^-\) but such concentrations decrease rapidly towards landward direction. The most common type of water in which Cl\(^-\) is dominant anion is one in which Na\(^+\) is the predominant cation.

Man made chloride pollution, however, has increased considerably in the recent years. Chloride is often the most dominant ionic species in ground water. It is highly mobile but as it is not involved in major oxidation-reduction and other common geochemical reactions that occur in aquifers it does not form solute complexes (Freeze and Cherry, 1979; Hem, 1985; Kleissen et al., 1990; Reynolds and Pomeroy, 1991; Peters and Ratcliffe, 1997). It is also not able to form salts of low solubility with most of the cations and is not significantly adsorbed on mineral surfaces. Hence, chlorides do not dominate the compositional variations of water chemistry. But, at the same time, it is a bulk anion which is required for all animals and plants and reasonable concentrations is not harmful to humans.

Chloride concentrations above 250 mg/L give a salty taste to water but not if the Ca or Mg cations are also present. Therefore, the maximum recommended concentration of Cl\(^-\) is generally 250 mg/L for public usage. However, the ‘saltiness’ of water depends to some extent upon the associated cations. For example, a salty taste can be detected
in 250 mg/L of NaCl. The Cl\(^-\) concentration up to 1500 mg/L is reported to be safe for cattle, sheep, swine and chickens (McKee and Wolf, 1976). Excessive consumption of drinking-water containing sodium chloride at concentrations above 2.5 g/L has been reported to produce hypertension (Fadeeva, 1971) and congestive heart failure (Wesson, 1969). However, research done by the (Department of National Health and Welfare, Canada 1978) has revealed that most of the ill effects of excessive NaCl in water are related to the sodium and not the chloride ion.

Surprisingly, in the water stressed regions, the chloride concentrations up to 2000 mg/L have been utilized by the humans without development of adverse effects. Hence, it may be concluded that the source of chlorides should be given due consideration while judging the quality of drinking and that any sudden increase in the Cl\(^-\) content of a supply should be suspected for the sake of adverse pollution effects. Chlorides are considered to be among the most troublesome anions in irrigation water because they pose more toxic effects than sulphates to most plants, including lemons, alfalfa, fruit trees, potatoes, woody vines and berry crops. Even the usage of sprinkler irrigation for fruit crops is often hazardous as leaves absorb Cl\(^-\) and Na\(^+\) directly and accumulate these ions. Sodium and Cl\(^-\) contamination within a wetland’s watershed and recharge areas can destroy rare and endangered plant species (Wilcox, 1986a; Grootjans et al., 1988; Panno et al., 1998, 1999b, 2000). Chlorides are also known to increase the rate of corrosion of steel and aluminium. The higher concentrations of chloride contain waters lead to the electrolytic corrosion of pipes and boilers. McKee and Wolf (1976) have presented the following concentrations of chlorides for specified beneficial use:

Domestic water supply (250 mg/L), Industrial water supply (50 mg/L), Irrigation (100 mg/L) and Stock and wild life (1500 mg/L). The drinking water supplied by PMC had average value 60 mg/L. The chloride content in the Mutha river water increases sharply as the river flows through the populated areas after Khadakwasla reservoir. Wagh et al. (1987) observed that during 1986-87 winters the Cl\(^-\) concentration of this river water increased manifold due to receiving of domestic effluents from the city area. During winters of 1994 and 1995, again, Wagh (1999) observed that the concentration of chlorides increased while the river traversed through Pune city. Gole (1983) found that the Cl\(^-\) concentration of Khadakwasla reservoir water was 14 mg/L.
and that of the Mutha river was 8 mg/L at upstream of Vitthalwadi. During his study period (October 1982 to March 1983), the increase in Cl\(^-\) concentration was not very high and it increased up to approximately 50 mg/L. Patil (1996) observed low variations in the Cl\(^-\) concentrations of Mutha right bank canal water which varied from 6.7 mg/L to 18.8 mg/L.

Similar observations were made by the group of students of Bharti Vidyapeeth’s college of Engineering (Pune) for the water quality along the Mutha River. Sharma (1993) found that the Cl\(^-\) ion concentration of the Bhima river water near Pargaon, upstream of Ujjani varied between approximately 20 mg/L and 60 mg/L. During monsoon of 1992, it was as high as 186 mg/L. Removal of Cl\(^-\) from water supply is usually not an option because of the enormously high expense of desalination. Increasing concentrations of these ions in groundwater and surface water can adversely affect environmentally sensitive areas such as wetlands. During June 2008, the Cl\(^-\) ion concentrations in Ujjani reservoir water varied between 45.22 mg/L and 160.4 mg/L. During pre-monsoon, the samples collected from the reservoir had more Cl\(^-\) content at Bhigwan Takrarwadi and Daund. Their chloride concentrations were 160.4 mg/L and 140.3 mg/L respectively. Otherwise, the concentrations of Cl\(^-\) on an average remained 100 mg/L in all other study regions.

During November 2008 (post-monsoon), the concentrations of chloride remained between 42.54 mg/L and 119.3 mg/L. The concentration of Cl\(^-\) ion in Ujjani reservoir water remained low throughout the study area. Only a few samples had slightly higher Cl\(^-\) content (e.g., Bhigwan nala- 80.13 mg/L, Bhigwan Takrarwadi- 119.3 mg/L and Daund-89.40 mg/L). The chloride contents normally increases as the mineral contents increase (Dubey, 2003). During May 2009 (pre-monsoon) the concentration of chlorides from upstream of dam upto Daund remained between 38.36 mg/L and 72.4 mg/L. The water samples collected from Kalashi, Bhigwan nala, Bhigwan Takrarwadi and Daund had high Cl\(^-\) content (from 60.1 mg/L upto 120.3 mg/L).

Increase in chloride concentration during the rainy season may be due to the entry of allochthonous material into the reservoir along with rain water from catchment area as has been opined by (Hutchinson, 1957; and Sehgal, 1980). Other than these sites, the Cl\(^-\) concentrations in adjoining regions varied from approximately 38.36 mg/L to 58.90 mg/L.
Fig. 6.25: Concentrations of Cl in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.26: Mean concentrations of Cl in 20 sampling stations in pre-monsoon and post-monsoon.
During December 2009 (post-monsoon), the Cl\textsuperscript{-} content in this reservoir water was found to be almost uniform (36.42 mg/L to 101.0 mg/L) at all the observation sites. High concentrations of Cl\textsuperscript{-} were, however, observed near Bhigwan nala- 80.13 mg/L and Bhigwan Takrarwadi- 101.0 mg/L and Daund-68.19 mg/L. Such an increase may be attributed to higher volumes of runoff which increase the amount of pollutants entering the rivers and streams draining that watershed (Kauffman and Brant, 2000).

The chloride concentration near Bhigwan nala, Bhigwan Takrarwadi, and Daund remains high in both pre and post-monsoon seasons (Fig.6.25). The present study reveals that sufficient stress from nonpoint source pollutants has degraded and threatened the quality of surface waters. It is important to note that elevated chloride level is only one indicator of poor water quality; chloride alone is not a threat to aquatic systems. The mean concentrations of chloride in Ujjani reservoir water exhibit decreasing trend in both seasons i.e. pre-monsoon and post-monsoon season (Fig.6.26).

6.1.12) Sulphates (SO\textsubscript{4}\textsuperscript{2-})

There are several sources of sulphate in water. Decaying plant and animal matter may release sulphate into water. Numerous chemical products including ammonium sulphate fertilizers contain sulphate in a variety of forms. The treatment of water with aluminum sulphate (alum) or copper sulphate also introduces sulphate into a water supply. Most of natural waters contain sulphates (SO\textsubscript{4}\textsuperscript{2-}) but their concentration varies. These occur in almost all natural surface water and the origin of most sulphate compounds in the study area is through the industrial wastes.

The most frequent source of sulphur in fresh water are; (1) the sulphate (SO\textsubscript{4}\textsuperscript{2-}) ions in combination with common cations and (2) hydrogen sulphide (H\textsubscript{2}S). Other sulphides SO\textsubscript{4}\textsuperscript{2-} ions are also released which appears in water as a result of either (1) leaching of sulphate compounds from sedimentary formations in the drainage area; (2) as the final oxidized stage of sulphides, sulphites and thiosulphates; (3) due to oxidation of organic matter in the sulphur cycle; (4) form anthropogenic sources such as discharges from domestic sewage, agriculture lands and numerous industrial wastes,(e.g., tanneries, paper and pulp mills and textile mills) or (5) from the rains (McKee and Wolf, 1976). Magnesium, Potassium and sodium sulphate salts are all soluble in water. Calcium and barium sulphates are not very easily dissolved in water.
Sulphates are also leached out of certain igneous-rock minerals but the most extensive and important occurrences are in evaporating sediments. Hence, calcium sulphate (gypsum or anhydrite) is common in evaporate-rock. Sulphates are also associated with minerals like barite (BaSO₄), epsomite (MgSO₄·7H₂O) and gypsum (CaSO₄·2H₂O) Greenwood and Earnshaw (1984). These dissolved minerals contribute to the mineral content of many drinking waters. The weathering of sulphide minerals in aerated waters allows to get the sulphur oxidized to SO₄²⁻ ions which are water soluble. However, yet surface waters are generally low in SO₄²⁻, except in regions locally rich with SO₄²⁻ ion and in close basins where evaporation raises the concentration.

The sulphur in most soils occurs in the organic rather than inorganic state. Only approximately 1% to 3% of organic sulphur in soils is normally converted into inorganic sulphate each year (mineralization). At the same time, some inorganic sulphates are reduced to the organic matter. During the process of soil formation, the sulphides of primary minerals are converted to sulphates. The sulphates, in turn, are changed to many and varied organic compounds by microorganisms, plants and animals. Organically bound sulphur in soils is decomposed and transformed as sulphate by various natural processes. Microorganisms, plant roots and some of the enzymes release inorganic SO₄²⁻ in soil from organically bound sulphur (Ferney and Stevenson, 1966). The growth of plants in soils also gives rise to increased mineralization of sulphur from the organic matter (Ferney and Spencer, 1960). The decomposition of organic sulphur compounds may result in the accumulation of mercaptans and H₂S under anaerobic conditions..

Sulphur pollution of natural waters is a result of either discharge of domestic sewage, industrial wastes, mine water, urban and road drainage, leaching of sulphur containing fertilizers, weathering of coal and sulphide ore minerals, spillage of sulphur products or atmospheric burning of fossil fuels. Anthropogenic sources now account for 20% to over 90% of the sulphur in surface waters. Therefore, the sulphur contents of natural waters are increasing because of pollution (Nriagu and Hem, 1978). Approximately 50% of sulphur compounds are used as fertilizer (e.g., ammonium sulphate, superphosphate, calcium sulphate, sodium sulphate and potassium sulphate). In developed countries, the elemental sulphur and calcium
sulphate are used as amendments on salt-affected soils in amounts as high as several tons per hectare. The remedial method replaces Na with Ca and brings down the pH of the soil to almost neutrality. Sulphide also originates from the sewage or industrial wastes of tanneries, paper mills, textile mills, chemical plants or gas manufacturing processes. Concentration of SO$_4^{2-}$ ion in natural waters may increase as a result of ground water contact with gypsum deposits on the oxidation of sulphide containing minerals (pyrites).

Rainwater is a significant source of sulphur in lakes and rivers of the industrialized zones. The sulphur compounds from burning of fossil fuels, decomposition and combustion of organic matter, sea salt or volcanoes are transported and mixed in the atmosphere by winds and are redeposited on the ground after precipitation. The atmosphere, therefore, serves as a means of transport for sulphur from various sources into the sinks, on the earth’s surface (Kellog et al., 1972). Most of the emission of sulphur from man made activity the atmosphere is in the form of sulphur dioxide (SO$_2$). Present contribution of human being to the SO$_2$ emission is approximately one half as much as nature to the total atmospheric burden of sulphur compounds. In addition SO$_4^{2-}$, H$_2$S volatile organic sulphides or thiols produced by microbial action on dead organic matter or excreta also are the contributors (Bowen, 1977). Hence, in the atmosphere, SO$_2$ comes not only from burning of fossil fuels and other industrial discharges but also as a product of oxidation of organic sulphur and H$_2$S.

Sulphur dioxide in atmosphere is oxidized to sulphur trioxide (SO$_3$) by photochemical or catalytic processes, and in the presence of moisture, the SO$_3$ is converted to sulphuric acid or a sulphate salt, which later and soon precipitates out of the atmosphere. Hence the retention time of SO$_2$ in the atmosphere is usually for a few days and this is the reason that the proportion of SO$_2$ in the atmosphere is significantly small as compared to annual emission (Robinson and Robbins, 1970). But, during this time, SO$_2$ gets transported several hundred kilometers from its point of emission.

The background concentration of sulphur in natural waters also gets altered due to evaporation and the endogenic cycling of the sulphur. Each aquatic ecosystem contains a large inorganic sulphur pool and small but active organic sulphur pool.
 Nearly all the assimilation of inorganic sulphur in oxic water occurs as SO$_4^{2-}$ whereas; in decomposition of organic matter sulphur is released largely as H$_2$S. Thus, in general, the most oxidized (SO$_4^{2-}$) and the most reduced (sulphide) states are commonly available forms of sulphur in natural waters. Intermediate oxidation states are occasionally reported in grossly polluted water but never as dominant species. Under oxic conditions, H$_2$S is oxidized rather rapidly leaving only little traces of H$_2$S in aerated regions of aquatic systems.

Microbial sulphate reduction is an important biogeochemical process which accounts for the sulphides in the sediments. Reduction of sulphur to H$_2$S occurs upon decomposition of organic material by heterotrophic bacterial metabolism where bacteria reduce compounds such as, sulphite, thiosulphate, hyposulphite, and basic sulphur to H$_2$S. These heterotrophic and anaerobic sulphate reducing bacteria use the sulphur compounds as a hydrogen acceptor in the oxidative metabolism (Wetzel, 1975). Hence, lakes receiving rich sources of SO$_4^{2-}$ from inflowing water often contain high concentrations of H$_2$S in their deeper stratum of water which is perennially stagnant (Stuiver, 1967). Thus, a large fraction of SO$_4^{2-}$ in lakes may get lost from the deeper zones especially at the sediment water interface.

Loss of sulphur by the escape of H$_2$S by diffusion or gas bubbles to the atmosphere is usually small, except in marshes. The transport of sulphur by means of sedimentation of biological materials or through production of H$_2$S by biodegradation of organic matter is quantitatively not so significant, except in organic-rich ecosystems. Oxidation of sulphide by dissolved oxygen is a common reaction in natural water. The oxidation of aqueous sulphide by oxygen is a complex function of several factors, including initial sulphide and dissolved oxygen concentrations, temperature, pH, presence or absence of catalyst or inhibitors, as well as, biological activity. Several groups of bacteria also oxidize H$_2$S and other sulphides to sulphur, and sulphur to sulphate. The sulphide, produced by biological activity in anaerobic waters, is oxidized via chemical and biological reactions when the anaerobic waters are mixed with oxygenated waters.

The studies of the rate of oxidation of aqueous sulphide by (Chen and Morris, 1972) reveal that in acidic solutions, with pH less than 6, the oxidation rate is very slow. The rate increases rapidly as pH increases to a maximum of 8 but falls till the
value of pH reaches almost 9, and again increases 11. With regard to the metals, their catalytic effects occur in the following sequence: Ni^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Ca^{2+} or Mg^{2+} cations. These cations increase the sulphide oxidation rate by 5 folds to more than 100 folds in the pH range of 7 to 9. Organic compounds can also modify the oxidation reaction rates and the reaction products. Inhibition and catalysis of sulphide oxidation by metal ions and organic ligands have important environmental consequences.

In oxidized systems, where sulphur exists in SO_4^{2-} form, an important set of solubility control involves the alkaline earth metals. Ca is the most abundant of these in most aqueous systems which forms gypsum (CaSO_4, 2H_2O), anhydrite (CaSO_4) and some other species of similar compounds. These are moderately soluble compounds. As the ionic strength of water is increased by other more soluble ions, such as Na^+ and Cl^-, the effective solubility of gypsum is increased. Gypsum has a maximum solubility near 30°C, and its solubility decreases at higher temperature.

Sulphate is ecologically important in natural waters because it plays important role in protein metabolism and is incorporated virtually in all proteins. It is involved in a numerous biochemical and inorganic reactions in aquatic systems. When utilized in protein synthesis and photosynthetic and animal metabolism SO_4^{2-} is reduced to sulphhydryl (-SH) form. Short supply of SO_4^{2-} can inhibit the development of phytoplankton population and thereby reduces the total production.

Importance of sulphur cycle in aquatic sediment is the release of phosphorous. The presence of iron sulphide is required for insoluble phosphorus to be converted into soluble forms which are more mobile and available for utilization by plants. Primary production is, thus, directly dependent on the sulphur cycle both for the availability sulphate and further release of phosphorus (in form of phosphate) from the sediments (CWPRS, 2002). The sulphates and sulphides can have significant effects on various beneficial uses of water. The recommended drinking water standard for SO_4^{2-} is 250 mg/L or less except where a suitable supply is not available. This limit is based basically on the laxative action and not on any serious physiological effects. SO_4^{2-} less than 1000 mg/L is considered to be physiologically not harmful.
Sulphate is somewhat less toxic than Cl\(^-\) in irrigation waters. In high concentrations, \(\text{SO}_4^{2-}\) ion may cause precipitation of Ca. The concentration of \(\text{SO}_4^{2-}\) less than 4 meq/l (i.e. 192 mg/L) in irrigation water is not likely to cause any harmful effect under most conditions and that between 4 to 12 meq/l is usually acceptable. The proportion more than that is hazardous (McKee and Wolf, 1976). Gypsum is soluble in distilled water up to 30 meq/l and its solubility increases markedly in the presence of other salts. Soils containing substantial quantities of precipitated gypsum are, therefore, not normally susceptible to sodium damage. \(\text{SO}_4^{2-}\) added to the soils leaches downward either very slowly or very quickly, depending on the factors such as amount of rainfall, the soil texture and the ability of the soil to retain adsorbed \(\text{SO}_4^{2-}\).

High \(\text{SO}_4^{2-}\) concentration in water in contact with hydrated cement not only increases the rate of leaching from the cement but may result in the disintegration of the hydrated cement (Camp, 1963). However, Hammerton (1945) observed that the reactions towards concrete were low when the concentration of \(\text{SO}_4^{2-}\) was less than 300 mg/L. At concentrations more than 1000 mg/L the attack was rapid. Domestic sewage and waste waters are usually harmless to concrete, the \(\text{SO}_4^{2-}\) concentrations being generally less than 300 mg/L. When the sewage becomes anaerobic, however, the formation of even low levels (2 mg/L) of \(\text{H}_2\text{S}\) has a marked deleterious effect on the concrete sewer (Bizok, 1964). \(\text{H}_2\text{S}\) also blackens lead paint, copper and brass objects and causes corrosion of concrete and hence, its presence in industrial waste waters is deleterious. The presence of \(\text{H}_2\text{S}\) in lakes and other water bodies is toxic action to fish, detrimental to flora and fauna in addition to giving foul odour.

The toxicity of sulfate in humans is in the form of diarrhea in infants exposed to water containing sulphate at concentrations ranging from 630 to 1150 mg/L (Chien, 1968). However, the diarrhoea could not be explained as being solely due to exposure to high sulfate levels and other factors may have played a role. He also reported that humans can adapt to higher concentrations with time.

Ingestion of 8 g of sodium sulphate and 7 g of magnesium sulphate caused catharsis in adult males due to \(\text{MgSO}_4\) (Cocchetto and Levy, 1981; Morris and Levy, 1983). Cathartic effects are commonly reported by people consuming drinking-water containing sulphate in concentrations exceeding 600 mg/L. Dehydration has also been
reported as a common side-effect following the ingestion of large amounts of magnesium or sodium sulphate (Fingl, 1980).

During June 2008 (pre-monsoon), the $\text{SO}_4^{2-}$ ion concentration in Ujjani reservoir water ranged from 60.40 mg/L to 205.9 mg/L. The maximum concentrations of $\text{SO}_4^{2-}$ were recorded at Bhigwan Takrarwadi-205.9 mg/L, Daund-195.2 mg/L, Dalaj No.1-107.1 mg/L and Bhigwan Nala-180.1 mg/L. In other sampling stations, the surface water $\text{SO}_4^{2-}$ content varied between 60.40 mg/L and 93.43 mg/L. During June 2008, when the reservoir water went to a very low level, as a consequence of low rainfall and a long dry spell, a major change in $\text{SO}_4^{2-}$ content occurred in Ujjani reservoir water.

During November 2008 (post-monsoon), the $\text{SO}_4^{2-}$ ion concentration in this reservoir water increased remarkably. Its values, during this period, varied between 69.33 mg/L and 251.5 mg/L. The highest values of $\text{SO}_4^{2-}$ found at Bhigwan Takrarwadi-251.5 mg/L, Daund-213.7 mg/L, Dalaj No.1-218.0 mg/L and Bhigwan Nala-236.7 mg/L. During Post-Monsoon, as an effect of light rains and mixing with some runoff waters, the $\text{SO}_4^{2-}$ concentrations in some of the areas of the Ujjani reservoir were found to be marginally more as compared to Pre-Monsoon. Similar observation has been made by (CWPRS, 2002). However, the $\text{SO}_4^{2-}$ concentrations of other locations were ranging from maximum 125 mg/L to minimum 69.33 mg/L.

The sulphate concentrations of Ujjani reservoir during May, 2009 (Pre-Monsoon) were in the range of 60.98 mg/L and 183.2 mg/L. The water samples collected from the areas between Bhigwan Takrarwadi-183.2 mg/L, Daund-160.1 mg/L, Bhigwan Nala-138.4 mg/L and Dalaj No.1-109.4mg/L. During the summer season, the sulphates concentrations of the other sampling stations were less than 100 mg/L.

During December 2009 (Post-Monsoon), the $\text{SO}_4^{2-}$ concentrations of the collected water samples varied between 75.50 mg/L at D/S of Dam tail point and 281.4 mg/L at Bhigwan Takrarwadi.

The $\text{SO}_4^{2-}$ concentration of Ujjani reservoir after monsoon was higher than summer season. It may be due to exposure of some of the submerged areas, and hence causing of oxic condition (Fig.6.27). In addition, due to the inflow of wastes, the concentration of $\text{SO}_4^{2-}$ ion increased markedly in some of the areas. As a result,
during this observation period, the SO$_4^{2-}$ content in water remained more than 100 mg/L, except few sampling stations.

The rivers contribute to sulphur compounds from three major sources: rocks, fertilizers and the atmosphere. In many irrigated areas, the concentration of residual matter increases in the root zone of cultivated fields resulting from evapotranspiration and causes calcite and gypsum to precipitate. Inorganic sulphates usually occur as calcium sulphate (gypsum) of the soil. In saline soils, soluble sulphate is an inherent part and may be present in large amounts (Nyborg, 1978). In such soils, SO$_4^{2-}$ occurs in part as Na$_2$SO$_4$ (sodium sulphate) which can move within the soil profile with the movement of water. When an area of low rainfall is reclaimed by irrigation the increased water supply tends to leach away the accumulated solutes and they appear in drainage water or return flow. Even where the soil is fairly free from soluble salts, the SO$_4^{2-}$ and Cl$^-$ concentrations of the residual draining from an irrigated area are generally much higher in the original water supply. The concentration of SO$_4^{2-}$ at all sampling stations exhibit an increasing trend over a period of monitoring June-08,Nov.08,May-09 and Dec.09. It was clearly seen from the mean concentration of SO$_4^{2-}$ over four seasons (Fig.6.28).

Exposure of bottom materials or formation of oxic conditions can cause oxidation of insoluble sulphide to soluble sulphate. Thus, the SO$_4^{2-}$ concentration in lake water may increase markedly. The favorable pH of Ujjani reservoir water (approximately 8), growth of plants, and increase in ionic strength of water also might have resulted in increased concentration of SO$_4^{2-}$ along with oxidation and solubilisation sulphur compound in the reservoir water. The desirable limit for sulphate in drinking water is 200 mg/L (BIS, 1991) and 250 mg/L (WHO, 1992). The PMC water has average value of SO$_4^{2-}$ containing 7 mg/L.

Thus, only during post-monsoon (Nov.2008 and Dec.2009), the SO$_4^{2-}$ ion concentration was high in most parts of the reservoir, however its concentration remained mostly less than 100mg/L during pre-monsoon (June, 2008 and May, 2009), except few locations.
Fig. 6.27: Concentrations of $\text{SO}_4^{2-}$ in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.28: Mean concentrations of $\text{SO}_4^{2-}$ in 20 sampling stations in pre-monsoon and post-monsoon.
This reservoir water, in general, is not likely to cause direct adverse effect due to excessive sulphate concentrations. But under anaerobic or low oxygen conditions a part of $\text{SO}_4^{2-}$ may get reduced to $\text{H}_2\text{S}$ which has foul smell and toxicity.

### 6.1.13 Nitrate ($\text{NO}_3^-$)

Nitrogen constituting up to 78% by volume of the atmosphere, is vital for plants which succumb to lack of nitrogen. It is required only as a limiting ingredient for plants and other living beings if natural resources are converting molecular nitrogen ($\text{N}_2$) into ammonium ($\text{NH}_4^+$) or nitrate ($\text{NO}_3^-$) forms, which are then readily taken up by plants. Hence, nitrate serves as the most important nutrients in an ecosystem (Chandaluri et al., 2010). Nitrates are added to surface waters through igneous rocks, inorganic nitrate fertilizers, land drainage as well as from plant and animal debris.

When influenced by human activities, surface water can have nitrate concentration up to 5 mg/L $\text{NO}_3^-$ but often less than 1 mg/L of $\text{NO}_3^-$. However, the World Health Organization (WHO) has recommended 50 mg/L as the limit for $\text{NO}_3^-$ in drinking water (Chapman, 1996). The determination of nitrate in surface water gives a general indication of the nutrient status and the level of organic pollution.

All living beings require nitrogen for building of proteins and a variety of other essential compounds. It is central to all ecosystems because they play a vital role along with carbohydrates, fats and other major constituents of living substances in the synthesis and maintenance of proteins. It is also one of the major constituents of cellular protoplasm along with phosphorous, carbon and hydrogen.

Most organisms cannot use gaseous $\text{N}_2$ and in order to manufacture protein the organisms need nitrogen in “fixed” form, i.e., incorporated in compounds. Certain species of bacteria and blue-green algae use nitrogen to combine with hydrogen to form ammonia ($\text{NH}_3$) which spontaneously reacts with water to form ammonium ion and undissociated hydroxide. These reactions provide the nitrogen the necessary metabolic processes in building proteins and other organic molecules. These processes together give rise to “nitrogen-fixation”. $\text{NH}_3$ and ammonium ions are also used by other soil bacteria which convert them to nitrate ($\text{NO}_3^-$), during a process of “nitrification”. Other nitrogen compounds such as ammonia and urea are also utilized both in natural systems and as fertilizers in agriculture. It is reported that some
nitrification in soil is also activated chemically by sunlight in the absence of biological agencies (Welch, 1952).

The proteins manufactured by plants undergo a number of chemical modifications in the food web. At each trophic level, due to mainly excretion, the nitrogen is returned back to the environment. Hence, organic nitrogen compounds are used by the microbes of decay, which allow nitrogen molecules to break down to NH$_3$. At the same time, during known as “denitrification process” NO$_3^-$ is reduced to molecular N$_2$. Thus, the organic nitrogen is returned in the form of the atmospheric nitrogen and the nitrogen cycle is completed.

Chemical and biological processes that circulate nitrogen within the lithosphere, atmosphere, hydrosphere and biosphere constitute the nitrogen cycle. Under natural conditions, nitrogen lost from ecosystems by denitrification, volatilization, leaching, erosion, wind flow aerosols and transportation out of the system is balanced by biological fixation and through other sources. In relatively stable and undisturbed ecosystems nitrogen inputs and outputs are almost balanced.

Intervention of human being in the nitrogen cycle has either imbalanced the steady state or shifted the system into a new steady state. Modification of land use patterns, in the form of cultivation of grasslands has caused a steady decline in the nitrogen content of the soil (Jenny, 1933). Simultaneously, other agricultural activities such as removal of harvested crops, timbers, mixing and breaking up of the soil also have increased the nitrogen losses. On the other hand, the use of commercial fertilizers has increased the nitrogen contents of soil. The invention of industrial process for artificial fixing atmospheric nitrogen has also modified the nitrogen cycle. Now, it is realized that unless the required quantity is properly applied, a considerable nitrogenous portion is lost as NO$_3^-$ nitrogen to the ground water. Automobile exhausts and industrial combustions add nitrous oxides to the atmosphere, which are finally carried to the soil and water in due to precipitation. Animal and human wastes (sewage effluents), also contribute towards nitrate pollution.

All these nitrogen pollution mechanisms finally give rise to eutrophication of rivers, lakes and estuaries. Global estimates suggest that nearly 1.5 billion people lack safe drinking water and that at least 5 million deaths per year can be attributed to
waterborne diseases (Scheelbeek, 2005). NO$_3^-$ or NH$_3$ nitrogen added to soil, as fertilizer, undergoes following modifications. If not assimilated by microbes or plants, it will usually be lost from soil, either by volatilization (NH$_3$) or by leaching (mainly NO$_3^-$). The extent of leaching depends chiefly on soil texture and on the quantity of water that penetrates the soil before the crops can assimilate the nitrogen (CWPRS, 2002). The nitrogen from lake is lost to the atmosphere or sediments by (a) effluent outflows from the basin; (b) reduction of NO$_3^-$ to N$_2$ by bacterial denitrification (return of N$_2$ to the atmosphere) and (c) permanent loss of inorganic and organic nitrogen-containing compounds to the sediments.

Various reports indicate that nitrogen compounds in natural waters range from nil to more than 100 mg/L of NO$_3^-$. And nitrogen in surface water ranges from nil to 1000 mg/L of NO$_3^-$ nitrogen in ground water. In surface water, however, NO$_3^-$ nitrogen seldom exceeds 5 mg/L in unpolluted areas and often the concentration is less than 1 mg/L (Hem, 1959). According to Reid and Wood (1976), in unpolluted fresh waters the average concentration of NO$_3^-$ nitrogen is 0.30 mg/L all over the world. NO$_3^-$ nitrogen is the most available form of nitrogen for green plants rooted in the substratum or floating in the water (Reid and Wood, 1976). For all practical purposes, the nitrogen cycle of lakes is mainly microbial in nature; bacterial oxidation and reduction of nitrogen compounds are coupled with photosynthetic assimilation and utilization by algae and larger aquatic plants. The role of animals in the nitrogen cycle of lakes is rather small, but under certain conditions it can influence periodic population responses of photosynthetic utilization rates of nitrogen compounds (Wetzel, 1975).

Nitrate, the end product of aerobic stabilization of organic nitrogen, occurs in polluted waters that have undergone self-purification or aerobic treatment process. Due to overuse of fertilizers nitrate is abundant in natural surface waters. Photosynthetic action constantly utilizes NO$_3^-$ and converts it to organic nitrogen in plant cells. The amount of NO$_3^-$ in solution, at a given time, is determined by metabolic processes in water, i.e., production and decomposition of organic matter. Most algae have relatively high protein content, often exceeding 50% of their dry weight. Their nitrogen requirements are, therefore, quite considerable. In most of the lakes, phosphorous is a limiting nutrient. The additional nitrogen and phosphorous
accelerate nutrient enrichment or eutrophication which is increased multifold by human activities. Chemically, during nitrate-water reaction, the nitrates are converted into nitrites and cause for several types of diseases. But, mostly it depend on duration and quantity of nitrite consumption (Mondal et al., 2008). The consumption of nitrate rich water also causes a large number of diseases like dizziness, abdominal disorder, vomiting, weaknesses, high rate of palpations, mental disorder and even stomach cancer (Perlstein and Attala, 1976; Reddy, 1981; Thind, 1982 and Burt et al., 1993).

The WHO drinking water standards for nitrates have recommended a limit of 45 mg/L which was established because of the relationship between high NO\textsubscript{3}\textsuperscript{−} in water and infant methemoglobinemia i.e. blue-baby disease (Ferrous ion in hemoglobin, when oxidized, forms methemoglobin). In normal human blood approximately 2% of total haemoglobin is methemoglobin which does not combine with oxygen molecule. In the digestive system, certain bacteria can convert NO\textsubscript{3}\textsuperscript{−} to NO\textsubscript{2}\textsuperscript{−} which reacts with hemoglobin forming methemoglobin. Its appearance in appreciable quantities in human blood is an indication of a disease, whose symptoms include labored breathing and occasional suffocation results, especially in human infants. Serious and occasional fatal poisoning in infants has occurred following ingestion of well waters containing high concentrations of NO\textsubscript{3}\textsuperscript{−}. Very high concentration of NO\textsubscript{3}\textsuperscript{−} may also cause irritation of the mucous lining of the gastrointestinal tract and bladder, with symptoms of diarrhea and dieresis. Drinking 1 lit of water containing 500 mg/L of NO\textsubscript{3}\textsuperscript{−} can cause such symptoms even in adults (McKee and Wolf, 1976). Nitrate poisoning has also been reported among cattle’s, following their consumption of hay containing very high concentrations of NO\textsubscript{3}\textsuperscript{−}. An excess of NO\textsubscript{3}\textsuperscript{−} tends to reduce soil permeability and due to osmotic reactions it sometimes accumulates to toxic concentrations in soil solutions (McKee and Wolf, 1976). Nitrate containing waters are harmful to dyeing of woolen silk fabrics and also to fermentation processes. For brewing, the NO\textsubscript{3}\textsuperscript{−} concentration of water should be less than 15 to 20 mg/L (Pfeil, 1959).

But is beneficial in lower concentrations (2mg/L of NO\textsubscript{3}\textsuperscript{−} in water) where it protects metal in boilers from intercrystalline cracking. Nitrate waters, by stimulating growth of planktons, indirectly accelerate the fish production (Hart et al., 1945). The leaching of nitrates from agricultural and domestic use allows runoff septic tanks, poor dug
wells and defective sewerage systems to concentrate nitrates in the groundwater systems (Piskin, 1973; Canter, 1997, Lindsay, 1979).

During pre-monsoon period (June, 2008) the NO$_3^-$ concentration varied from 0.24 mg/L, to 8.65 mg/L. The maximum value being at Station Daund and minima at U/S of dam and Shaha village. The high concentrations of these ions can indicate contamination of water by agricultural run-off, refuse dump leachate and through human or animal wastes (Anonymous, 1993 and 2001; Hudak, 1999; Fytianos and Christophidis, 2004). The high concentration of NO$_3^-$ form Ganjevalan, Bhigwan Takrarwadi and Daund can be attributed to the use of fertilizer and surface runoff. Similar result was obtained by Esmail et al. (2009) for the leachate and groundwater pollution due to municipal solid waste landfill of Ibb City, Yemen. However, near the dam wall, the NO$_3^-$ concentration was found to be low, possibly due to dilution of water to a large extent. The environmental problems have reached an alarming stage throughout the world, largely because of anthropogenic activities in their catchment areas (Young et al., 2004).

The NO$_3^-$ ion concentration varied from 0.0 mg/L to 17.72mg/L in post-monsoon period (November 2008). The nitrate concentrations after monsoon were relatively higher than pre-monsoon season, which could be due to leaching and surface run off of nitro-phosphates fertilizers from adjoining fields as well as, domestic sewage, similar observation made by (Mustapha and Omotosho, 2005). Near the dam wall to Shaha village the NO$_3^-$ ion concentration was minimum (about 0.22mg/L to 1.33mg/L) while at sampling sites, Chandgaon Village and Palasdev Nala, these were not detected. The lower values of nitrate concentration may be due to utilization by phytoplanktons as evidenced by high photosynthetic activity (Das et al., 1997).

During May, 2009(Pre-Monsoon) field study, the nitrate concentrations of Ujjani reservoir water remained comparatively low (from 0.38 mg/L to 6.63 mg/L). The other sampling stations the nitrate concentration was less than 3 mg/L. (Swaranlatha and Rao, 1998) have also reported that nitrates are in low concentration in summer and high during monsoon which might be due to surface run off dilution due to and rains.
Fig. 6.29: Concentrations of NO$_3^-$ in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.30: Mean concentrations of NO$_3^-$ in 20 sampling stations in pre-monsoon and post-monsoon.
The NO$_3^-$ ion concentration during December 2009 (Post-Monsoon), varied from 0.44 mg/L, to 15.4 mg/L. The nitrate concentration after monsoon of Ujjani dam water was high as compared to summer season (Fig.6.29).

The nitrate concentration of Ujjani reservoir near dam was low in both Pre and Post-Monsoon seasons. The growth of aquatic plants and algae was prominently observed in backwaters of Ujjani reservoir. In the present study, the main origin of nitrate is from agricultural fertilizers, contributed effectively to ground waters in the form of nitrates, added either diffuses and point pollution mechanisms.

Diffused pollution is associated with farmers’ agricultural practices. The higher values of nitrate recorded during monsoon season are due to variation in phytoplankton excretion, reduction of nitrate and by recycling of nitrogen through bacterial decomposition of planktonic detritus present in the environment (Govindasamy et al., 2000). Another possible way of nitrate entry is through oxidation of ammonia form of nitrogen to nitrite and then consequently to nitrate (Rajasegar, 2003). The desirable limit for nitrate in drinking water is 45 mg/L (BIS, 1991) and 50 mg/L (WHO, 1992). The PMC water has average value NO$_3^-$ content was 0.12 mg/L.

This study showed maximum level of nitrate occurred in Post-monsoon and minimum during Pre-Monsoon. Baring a few exceptions, the concentrations of NO$_3^-$ at all sampling stations exhibit an increasing trend over a period of June-08 to Dec.09 (Fig.6.30).

6.1.14) Phosphate (PO$_4^{3-}$)

The lower phosphorous contents of ground water have an average concentration of 20 µg/l which is due to the effectiveness of the high insolubility of phosphate containing minerals and the scavenging of surface phosphate by biotic removal and soil percolation (Wetzel, 1975). But, higher concentrations in ground waters have been recorded when leaching from excessive fertilizers or recharges of cooling waters are met with (McKey and Wolf, 1976). Phosphorous is mainly observed in igneous rocks and sediments. Roughly 0.12% of the earth’s crust is composed of combined phosphorus (Welch, 1952). Phosphorous being an active element does not occur free in nature and is found in the form of phosphates in several minerals. The main source
of phosphate in water is due to chemical and mechanical weathering along with erosion of rocks. During erosional processes phosphates are mobilized partly as dissolved inorganic phosphate and partly as adsorption by or even into the clay particles. Most of the chemical industries produce wastes containing toxic heavy metals and also hazardous organic and inorganic effluents. These chemicals are contaminated with the ground water and severely pollute the ground water (Rajendran and Mansiya, 2011).

Phosphate contamination comes from disposal of detergent contaminated sewage and due to washing of clothes in water. Inorganic phosphorus or orthophosphates play a dynamic role in water bodies as they are readily taken up by the phytoplankton (Krishnamoorthi et al., 2011). According to Golterman (1975), the increased application of fertilizers, use of detergents and domestic sewage play major roles in the phosphorus contamination in water. Phosphorous can occur at oxidation states ranging from -3 to +5, but fully oxidized states as phosphate, characterizes most natural water systems. Reduced forms of phosphorous are present in certain synthetic organic chemicals (e.g., pesticides and insecticides). These synthetic organic compounds are mostly unstable in aerated water but may under in reducing environments, which exhibit toxicity to many forms of life, especially pesticides.

The phosphorous cycle begins as phosphate ions are absorbed from the soil into plants and get incorporated into organic molecules. Man influences this cycling by using phosphate containing rock as a fertilizer and by manufacturing number of industrial products. Surface drainage often contributes to phosphorous dumping into the streams and lakes. The quantities of phosphorous entering surface drainage are influenced by the amount of phosphorous in soils, topography, vegetative cover of the area, quantity and duration of runoff flow, land use and also pollution. Over use of the phosphate fertilizers allows them to be washed by rainfall and irrigation water into the streams. On the topographic sinks or reservoir such as lake, phosphorous enters the cycle from the catchment area or sediment release. It leaves the cycle when it is washed through the outflows or is incorporated permanently into sediments as detritus or precipitates. Before it reaches the sea, some of the phosphates may get trapped in the sedimentary rock formations which preserve them in considerable quantity.
Phosphates trapped in this way may get recycled and return to phosphate cycle again due to reworking of sediments.

The second most important source of phosphate is human excreta and detergents. Levels of phosphorous of several hundred mg/m$^3$ are not uncommon in flowing waters that receive wastewater discharges. It is estimated that approximately 2 gm of phosphate-phosphorous per person per day is excreted. Adding to this quantity, another 2 gm of triphosphate-phosphorous (derived from washing detergents) gets released per day per person. As a result the use of fresh water experiences alarming increase in the phosphate concentration. Due to urbanization, the increase in phosphorous discharge to surface waters is almost by direct proportion to the population densities (Weibel, 1969). The studies have also revealed that phosphates mostly come from the detergents (Nebel and Kormondey, 1981) and only about 30% come from human excreta. Industrial phosphorus inputs, especially those associated with food processing and water-softening agents are also exceedingly high. Phosphates have been used in municipal water works and especially in boiler feed water treatment to prevent scale formation and to inhibit corrosion. All these soluble phosphates join the flow of sewage into the streams.

Agriculture is another source of phosphorous which includes leaching and drainage of fertilizers and other soil nutrients. Even though the use of phosphate fertilizers has a potential for increasing the dissolved phosphorous content of drainage, due to its limited mobility in soils or sediments, its concentration usually remains low. Even these small quantities of phosphate loaded runoff waters from agricultural activities contribute to eutrophication. However, inadequately treated sewage is most harmful (Kimball, 1978). Phosphates adsorbed on clay may remain in water suspension or get precipitated into the sediments. The clays may release phosphate, especially if the soluble phosphate concentration is low, due to the growth of algae. The sedimentary part of the phosphate may dissolve again in certain circumstances or it may be extracted from sediments of shallow lakes by algae, bacteria or other organisms. The reductions of such phosphorous fractions are replaced by regeneration of solubilised phosphorous fractions from decomposition at depth and by release of phosphorous from sediments.
The phosphorous cycle does not involve gaseous phases and also does not have a major retention time in the atmosphere. This is because phosphorous does not form any stable volatile compounds. The only ways of it are in the atmosphere as small particles of dusts. The fall out of such particulate material of the atmosphere is from dust generated over the land, from soil erosion and from urban and industrial atmospheric contamination. The phosphorous contents of such precipitation are highly variable, but generally low (Wetzel, 1975). Total phosphorous in lake water may be grouped into two components: soluble phosphorous (phosphate form) and organic phosphorous (contained in planktons and other organic matter in the water). The only significant form of inorganic phosphorous is orthophosphate (OP) in natural waters which contain OP and polyphosphate anions. The OP is the final dissociation product of phosphoric acid. The OP species are thermodynamically most stable and the concentration of inorganic OP varies widely in different lake waters. Algal growth may reduce it to values below the detectable limit by chemical analysis. A portion of the phosphorus of lake water is bound organically and in cellular constituents in the living matter or variously associated with or adsorbed to inorganic and dead particulate organic matter.

The total phosphate concentrations in non polluted natural waters extend over a very wide range, from less than 1µg/l, to extreme levels in closed saline lake, with more than 200 mg/L. Their concentrations in solution in natural water are normally low, due to low solubility of most of its compounds and its use by biota as nutrients. Variation is usually in accordance with the geochemical structure of the region. Phosphorous levels usually increase in low-land water derived from sedimentary rock deposits (Wetzel, 1975). Organic phosphorous compounds synthesized by plants and animals may contribute a significant fraction of the dissolved and particulate phosphorous in many natural water bodies. Phosphorous participates either due to organic activity (inner cycle) or while getting transported in a global cycle. In the global cycle, allows recycling it to terrestrial ecosystems the sea only by two mechanisms. One is through sea birds that harvest through marine food chains and may return it to land in their excrement. The other one is the slow geological uplifting of ocean sediments to form land, requiring a time span of millions of years.
In smaller cycles, organic matter in plant debris or animal excrement is decayed and phosphorous becomes available for uptake by plant roots and reincorporates into organic matter. After passing through food chains, it once again passes to the decomposers and the cycle is closed. When the plant is consumed or decomposed, some phosphate ions are released back to the environment, as the consumers break down organic molecules in respiration. Others become part of the consumer’s tissues. This process is repeated at successive trophic levels until finally all the molecules containing phosphate are broken down.

Water leaches phosphorous not only from phosphorous-containing rocks but also from the soil. Once within a lake, the phosphorous enters into a complicated cycle involving various physical, chemical and biological processes these processes tend to keep the phosphorous in the lake water, either in soluble or organic form by a continuous series of conversions into one another. Inorganic phosphate is eliminated from aquatic solutions when it is used by growing algae. Similarly the phosphorous added to the open waters is consumed by the phytoplanktonic algae and bacteria. This uptake rate is dependent upon factors such as pH, presence of various ions and compounds availability of micronutrients, light intensity, internal cellular biochemistry and external substrate concentrations (Wetzel, 1975). Most of the phosphates are released back into the water after the death of algae. The dead algae cells also contain some phosphates which are then broken down by bacteria.

Majority of the phosphate salts and organic-phosphorous compounds have low solubility. Therefore, phosphorous appears in the suspended matter or sludge. Hence, the lake sediments usually contain higher concentrations of phosphorous than the water. Increasing pH also leads to formation of CaCO₃, which co-precipitates phosphate with carbonate whereas high phosphate adsorption by clays is favoured by low pH levels (Otsuki and Wetzel, 1972). Such an exchange of phosphorous between the sediments and overlying water is dependent on physical, chemical and metabolic factors to the sediments and the rapidity of process of regenerating the phosphorous.

Some of the bottom deposit phosphorous is returned to the circulation when bacteria are playing an important role in the dynamics of phosphorous cycling in the water. Restoration of phosphorous to the upper water is also brought about by inflow of phosphate rich waters rich in phosphate or by the return or circulation of
phosphorous contained in the dead phytoplanktons. The rate of phosphorous release from the sediment increases markedly if the sediments are disturbed by agitation from turbulence (Zicker et al., 1956). The phosphorous is not only abundant in the bodies of animals (in protoplasm, nerve tissue and bones) and plants but also is a constituent of fertile soils. It is an essential nutrient for plant and animal growth and is also part of cycles of decomposition and photosynthesis. Although in relatively small proportion it plays an important role in photosynthesis and cellular respiration. The productivity of soil is increased if the amount of phosphorous availability in the soil is increased (McKee and Wolf, 1976).

Being a nutrient, phosphates in irrigation water is usually beneficial in increasing the fertility of the soil. But accumulation of phosphorous in soil over a long period of time may potentially interfere with plant growth (Powell, 1975). Nutrient imbalance in the plants is caused by high phosphorous levels in the soils which reduce the availability of some crop micronutrients. Hence, an excessive concentration of phosphorous (more than 60 mg/l) shows signs of incipient iron chlorosis. Ecologically, phosphorous initiate its major role in biological metabolism. Compounds play a major role in nearly all phases of metabolism when energy transformation is required during photosynthesis. Phosphorous is also required in the synthesis of nucleotides, phosphatides, sugar phosphates and other phosphorylated intermediate compounds. Phosphate is also bonded (usually as ester), in a number of low molecular weight enzymes and vitamins, essential for algal metabolism.

Along with tremendous release from the domestic usage the loading of phosphorous into streams has increased tremendously as a result increased agricultural fertilizers, industrial wastes and detergents. Much of the wastewaters in developing countries are discharged into waterways with improper treatment. The sewage treatment is also done without removal of appreciable amount of phosphate. Obukov (1948), reported that presence of more than 0.2 mg/L of phosphorous in ground or surface water suggestive of phosphorous, of sewage origin. Due to the lack of data the concentration of phosphorous that produce eutrophication cannot be estimated.

The studies made by (Lawson and Brisbun, 1970) reveal that algal blooms occur even at phosphorous concentration of less than 0.1 mg/L, if other essential
elements are present. (Connell, 1966) demonstrated that 0.3 mg/L of phosphate is probably the critical tolerance range, above which excessive growth occurs. (Vollenweider, 1968) is of the opinion that depending upon the yearly loading per unit area of the lake. There would be rapid eutrophication it loading increases due to natural or anthropogenic causes.

Phosphates form complexes, chelates and insoluble salts with a number of metal ions. The extent of complexing and chelation between various phosphates and metal ions in natural waters depend upon the relative concentrations of the phosphates, metal ions, the pH and the presence of other ligands (\(\text{SO}_4^{2-}\), \(\text{CO}_3^{2-}\), fluoride, organic species) in the water. Due to lower phosphate concentrations the formations are generally low and complexes have little effect on the major cation distribution but play a vital role in the phosphate distribution (Golachawska, 1971). Phosphates, in raw-water sources, interfere with coagulation, flocculation and lime soda treatment of water (Hatch and Rice, 1941). \(\text{PO}_4^{3-}\) concentration in Ujjani reservoir varied from 0.01 mg/L, to 0.62 mg/L, in pre-monsoon period (June 2008). The maximum values being recorded at Station Daund and minimum at Kandalgaon Village. The phosphate concentration of Ujjani reservoir was low during Pre and Post-monsoon seasons (Fig.6.31). Phosphorus is normally very low (< 1 mg/L) in clean potable water sources and usually not regulated (John et al., 2008).

During post-monsoon period (November 2008), the \(\text{PO}_4^{3-}\)concentration varied from 0.0 mg/L to 1.32 mg/L. The phosphate concentration after monsoon was relatively higher than pre- monsoon season, but all the values were well within the limits. This increase could be due to agricultural runoffs from the fields. Similar observations were made by (Muduli and Panda, 2010). Near Palasdev village the phosphate concentration was not detected. Most of the sampling stations from dam wall to Chandgaon Village, the \(\text{PO}_4^{3-}\) concentration was on higher side (from minimum 0.20 mg/L to maximum 1.32 mg/L.

During May 2009 (Pre-Monsoon), the phosphates concentrations of surface water remained comparatively low and varied from 0.01 mg/L to 0.99 mg/L. The minimum concentration of phosphate was 0.01mg/L at Dalaj No.1 while maximum value recorded were 0.99 mg/L at Bhigwan nala. As per Allen (1972), in exceedingly soft water lakes, inorganic carbon may be the limiting nutrient, even though in most lakes
diffusion of carbon dioxide from atmosphere is adequate to sustain carbon requirement of phytoplanktonic populations.

The $\text{PO}_4^{3-}$ concentration during December 2009 (Post-Monsoon), varied from 0.02 mg/L, to 1.69 mg/L. The phosphate after monsoon of Ujjani dam water was high except Bhigwan Takrarwadi - 0.025 mg/L. It was higher at the sampling sites, at Canal Head - 1.69 mg/L, Ganjevalan - 1.06 mg/L and Kalashi- 1.25 mg/L. The growth of aquatic plants and algae were abundant in the Ujjani reservoir. The introduction of phosphorus, in the form of phosphates, in aquatic environment is a major cause of eutrophication (Wagner, 1974).

CWPRS (2002) compared $\text{PO}_4^{3-}$ concentrations of Ujjani and Panshet reservoirs and concluded that due to higher concentrations of $\text{PO}_4^{3-}$ the growth of aquatic plants and algae growth of blue-green algae is far more common in Ujjani reservoir. The present study also revealed that Panshet reservoir receives phosphates mostly from natural sources, whereas it is Ujjani reservoir which receives a major part of phosphates as a result of human activities. The literature review indicates that the role of phosphorous, as a limiting factor in the growth of plankton algae, is of diverse type.

Morphology of the reservoirs, the degree of slope and sources of phosphorous which enter into the lakes also influence upon the algal growth. Golterman (1973), has also opined that phosphate from natural sources is much less available for algal growth as compared to that from human activities. The concentration of $\text{PO}_4^{3-}$ at all sampling stations exhibit an increasing trend over the period of monitoring June-08,Nov.08,May-09 and Dec.09 which is clearly observed from the mean concentration of $\text{PO}_4^{3-}$ during four seasons four seasons (Fig.6.32). The PMC water has average value of phosphate content 0.01 mg/L. The phosphate concentrations in the Mutha river water increases sharply when it crosses Pune city area. The Mula river too traverses a large industrial belt and the combined Mula-Mutha rivers flow through densely populated agricultural areas. As a result of admixture of a number of nutrients, including phosphorous in the Mutha and Mula rivers, the growth of aquatic weeds is intense in some parts of the river stretches.
Fig. 6.31: Concentrations of $\text{PO}_4^{3-}$ in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.32: Mean concentrations of $\text{PO}_4^{3-}$ in 20 sampling stations in pre-monsoon and post-monsoon.
6.1.15) Dissolved Oxygen (DO)

Dissolved oxygen analysis measures the amount of gaseous oxygen (O₂) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration and also as a waste product of photosynthesis. Adequate dissolved oxygen is necessary for good water quality and is an essential for sustainable aquatic life.

The surface water usually contains dissolved oxygen concentrations ranging from about 5 to 14.5 mg O₂ per liter depending on the water temperature, salinity and altitude. The dissolved oxygen (DO) concentration present in water reflects atmospheric dissolution, as well as autotrophic and heterotrophic processes that respectively produce and consume oxygen. It is, therefore, the factor that determines whether biological changes are brought by aerobic or anaerobic organisms. Thus, its measurement is vital for maintaining aerobic treatment processes intended to purify domestic and industrial wastewaters. The optimum value for good water quality ranges from 4 to 6 mg/L of DO. It ensures healthy aquatic life in a water body (Parmar and Parmar, 2010).

The sources of oxygen (from atmosphere and photosynthetic inputs) and the hydro mechanical distribution of oxygen are counter balanced by consumption metabolism of living organisms. Some of the oxygen uptake also occurs due to purely chemical or photochemical oxidation reactions. The concentration of DO is greatest near surface, when there is a direct interchange between the water and the atmosphere and also stirring due to by wind. Natural stream purification processes require adequate oxygen levels in order to preserve aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/L, aquatic life is put under stress. Oxygen levels that remain below 1-2 mg/L for a few hours can result in large fish kills.

The degree of solubility of atmospheric O₂ is a function of temperature and pressure. At normal atmospheric pressure, the solubility is 11.33 mg/L at 10°C, 10.2 mg/L at 15°C, 9.2 mg/L at 20°C and 8.4 mg/L at 25°C (Gaikwad, 2000). With increase in local average temperature of Ujjani, at more than 30°C reduces O₂ solubility to less than 7 mg/L. DO is key parameter reflecting the quality of water and hence used in classifying its quality, particularly of water which receives domestic and industrial waste. Its consumption during decomposition of organic matter reduces its
concentration to zero. Hence, DO reflects the degree of organic pollution in water. Therefore, if the water bodies receive large amount organic pollutants, oxygen level falls even to zero and aerobic organisms are completely destroyed (Gupta and Sharma, 1994; Singh and Singh, 1994).

As a result of large loads of organic waste, the balance between oxygen producing and oxygen consuming processes has resulted into lowering of DO values at various sampling sites in Ujjani dam. At the same time there is a reduction in self-purification capacity of the Bhima river due to inadequate volume of natural flow of water to dilute the pollutants. Consequently it gives rise zooplankton and algal blooms and has given rise to eutrophication of water. Such an eutrophication is also observed at Mula-Mutha and Bhima confluence where almost stagnant water conditions result into black flower formation and effusion of methane.

The measurement of DO is vital for designating the quality of aquatic environment. It is a measure of the capacity of water to receive organic matter without causing nuisance. The anthropogenic factors such as loading of nitrogen and phosphorus from industrial, municipal and agricultural sources and increased production of aquatic plants have contributed to decline in dissolved oxygen (Smith et al., 1999). The DO in water, at equilibrium with a normal atmosphere, is a function of temperature, pressure and salinity of the water. Natural waters, however, are seldom at equilibrium or are saturated with DO as temperatures vary with seasons. At the same time, due to variation in physical, chemical, biochemical or biological activities the, DO gets modified or reduced.

The palatability of water gets enhanced due to the presence of DO. But, the zero DO would inhibit corrosion, especially in cooling waters. DO in a river or reservoir is also essential to assimilate waste water and other oxygen demanding biochemical processes such as decomposition of organic matter, algal respiration and photosynthesis, nitrification, oxidation of iron, etc. Absence of oxygen will result in the predominance of an anaerobic microbial population whose end products are associated with severe nuisance conditions such as offensive odors and dark sludge accumulations. When the DO concentrations fall below permissible limits for any life form it gives rise to:
1) An upward migration of life forms into overlying and better oxygenated waters; 
2) onset of diseases in fish; and 
3) fish kill instances in summer.

The anaerobic situation as a result of reduced DO also gives rise to release of iron and manganese from their insoluble oxidized state to reduced and soluble state. These reduced states are more soluble than the oxidized forms and such a geochemical concentration toxic to the aquatic life. Moreover, the intensity of toxicity of many pollutants, including heavy metals, increases in low oxygen conditions. Under extreme condition the lethal effects of lower DO values become hazardous and form stressful situations in river, lake and reservoir environments.

The oxygen requirements of fish vary with the species and their age, prior acclimatization, temperature, and the concentrations of the other substances in the water, etc. Respiratory distress develops if fish remain in water with low DO. They usually recover quickly when they go back oxygenated water. (Ellis et al., 1946) showed that with lower DO values of 3.0 mg/L or less prove to be hazardous or lethal to the fish. The optimum condition of dissolved oxygen concentration should remain at 5.0 mg/L or higher. As per the norms of CPCB (1992), the minimum value of DO should be 4.0 mg/L for fisheries. However, carp species, which are sluggish in movement, can withstand lower oxygen concentrations than fish. Oysters also show considerable resistance to oxygen deficiencies (Clark, 1933).

The lower values of DO at the confluence of Mula-Mutha rivers with Bhima river were brought to limelight only after the incidence of mass fish mortality, during May 2008 and April 2009. It raised the eyebrows not only of the press but also the scientific community. Fish habitat in fresh water lakes is strongly constrained by water temperature and available dissolved oxygen (Xing et al., 1998). The Mula and the Mutha rivers carry a huge load of chemicals and sediments and discharge their pollutants into the river Bhima due to the outburst of rapid industrialization and urbanization in Pimpri-Chinchwad and Pune cities.

The region is a cluster of 2,800 industries. Out of which 2,520 are engineering units, 75 chemical, 6 textile and dying, 25 pharmaceuticals and 77 are electronics (CPCB Report, 2001). The effluents generated by these industrial zones from are approximately of the range of 40 MLD. As thermal stratification was observed in
some of the areas during summer, the DO concentrations in its water was studied in detail. Gole, (1993) reported seasonal variations in DO contents of Ujjani reservoir water. He observed that DO values were high during monsoon months and dropped during the post monsoon period. These values also rose slightly in winter and dropped significantly again till June. There was rise in DO values again in late June, presumably due to wind mixing.

During Pre-monsoon (June 2008) when the present study was conducted, Ujjani reservoir surface water contained 1.48 mg/L to 6.45 mg/L of DO. The DO values near the dam wall were 4.67 mg/L. It was due to mixing of water with atmosphere. During this period the lowest DO was 1.48 at Daund and highest DO of 6.45 mg/L was observed at Kalashi Village. The high oxygen concentration of 6.45 mg/L was recorded at Kalashi Village during the Pre-monsoon season. It was due to enhanced photosynthetic activities and reduced turbidity during the dry season. Similar observations were reported by (Vander-Heide, 1982).

During November 2008 (Post-Monsoon), the DO concentration ranged between 4.2 mg/L to 6.93 mg/L. The lower values of DO during November 2008 were probably due to addition of organic matter, industrial waste, as well as, agricultural run-off. At most of the sampling locations, the dissolved oxygen is less than 5mg/L such as at D/S of dam- 4.57 mg/L, at Ajoti village-4.97 mg/L, at Kalthan No.1- 4.85, at Palasdev nala- 4.2 mg/L. The drop in DO concentration in November could also be as a result of the vertical mixing due to low surface water temperatures (Araoye, 2009).

A concentration of 5 mg/L DO is recommended for optimum fish health. Sensitivity to low levels of dissolved oxygen species is specific; however, most species of fish are distressed when DO falls to 2-4 mg/L. Mortality usually occurs at concentrations less than 2 mg/L (Araoye, 2009).

During May 2009 Ujjani reservoir water DO values varied between 2.21mg/L and 5.63 mg/L. The DO values were more at D/S of dam-5.63 mg/L, at Canal Head-5.24 mg/L and Kalashi-5.55 mg/L. The DO values of other sampling stations were below 5mg/L (Fig.6.33). Oxygen depletion events can occur due to various reasons but, they are most likely to cause fish kills during hot summers. The reduction in oxygen production may be caused by cloudy weather. Heavy populations of plants or algae
are the most important producers of oxygen in the system, but they are also the most important users of oxygen.

The thermal and DO stratification at Kalshi village was studied by (CWPRS, 2002). The study showed a DO variation from 7.5 to 0.1 at depth 0.3m to 10m respectively. Warm water is less capable of holding oxygen gas in solution than cool water. Muggy, overcast summer days often result into oxygen depletions. During cloudy weather, the intensity of light reaching surface waters is greatly diminished, resulting in a marked decrease in oxygen production from photosynthesis. Lake water temperature and DO concentrations are considered as the most significant water quality parameters affecting survival and growth of fish (Fry, 1971; Magnuson et al., 1979; Coutant, 1987, 1990; Christie and Regier, 1988).

Surface waters warm up more rapidly than deeper during hot weather. As the difference in temperature increases between warm surface water and cool bottom water a thermocline develops. A thermocline is an area of rapid temperature change that acts as a physical barrier between warm water at the surface (epilimnion) and cold water at the bottom (hypolimnion). When a thermocline is present there is no mixing of surface and deep layers of water. As the process of photosynthesis and oxygen production occurs only near the surface, water in the deep layer becomes oxygen deficit and develops an oxygen demand. The thermocline can be broken by heavy wind and cold rain, common during summer thunderstorms. When the thermocline breaks down, the oxygen-rich surface waters mix with oxygen-deficient bottom waters. If the oxygen demand is sufficient, all DO present will rapidly be removed from the water column, resulting in severe oxygen depletion and a fish kill.

The DO value of Ujjani reservoir water was found to be considerably high during Post-monsoon (December 2009) as compared to pre monsoon (May-2009). The surface water DO values varied between minimum 3.78 mg/L to maximum 6.11mg/L. Out of 20 sampling locations 11 locations had DO values more than 5mg/L while at 9 sapling sites the DO values were less than 5mg/L.
Fig. 6.33: Concentrations of DO in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.34: Mean concentrations of DO in 20 sampling stations in pre-monsoon and post-monsoon.
The addition of sewage from the metropolitan cities of Pune and Pimpri-Chinchwad and the agricultural discharge from irrigated regions contribute towards the chemical quality of Mutha river water (Pawar et al., 1992; Pawar and Shaikh, 1995; Wagh, 1999). The PMC tap water had average DO content of 8 mg/L. The concentrations of DO at all sampling stations exhibit decreasing trend over the period of monitoring June-08, Nov.08, May-09 and Dec.09. It is clearly noticed from the mean concentration of DO during four seasons (Fig.6.34).

It is obvious that return flow movement and mixing of water were more near the dam. Nearer to the dam a better mixing of air and exchange of the surface water with the deep water could have been responsible for this trend. In Panshet reservoir also a somewhat similar situation was observed by CWPRS (2002) during summer (April 2000). It indicates that a rapid fall in DO with depth is a common phenomenon in both the reservoirs during summer. The warmer and lighter surface water does not mix efficiently with the deep water during day time and as a result the DO contents were found markedly less in deep waters.

### 6.1.16) Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a chemical procedure for determining the amount of dissolved oxygen. It is essential for aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. It determines the strength in terms of oxygen required to stabilize domestic and industrial wastes.

Microorganisms, such as bacteria, are responsible for decomposing organic waste. When organic matters such as dead plants, leaves, grass clippings, manure, sewage or even food waste are present in water body, bacteria begin the process of breaking down this waste. When it happens most of the available dissolved oxygen is consumed by aerobic bacteria snatching the oxygen demand of the other aquatic organisms. The test was found to be more sensitive for organic pollution. Since BOD is a measure of biodegradable material in water, increase in the organic matter causes increase in the BOD level. Greater values of BOD are indicative of more rapid oxygen depletion in the water (Krishnamoorthi et al., 2011). Rapid urbanization and industrialization in the developing countries like India pose severe problems in
collection, treatment and disposal of effluents. This situation leads to serious public health problems.

Human activities can affect the oxygen content of the air but it is not true for the aquatic environment. But, many of the streams and lakes suffer periodic shortages of DO. Many times the shortage is so severe that certain aquatic organisms can no longer survive for want of oxygen. The added organic matter supplies carbon and other nutrients and stimulates the growth of microbial population. Biochemical Oxygen Demand and Dissolved Oxygen are inversely related. Lower BOD values indicate that the water system has low population of oxygen consuming pathogens (Rajendran and Mansiya, 2011). For the degradation of oxidizable organic matter to take place minimum of 2 to 7 mg/L of DO level is to be maintained at laboratory experimentation or is required to be present in the natural waters (De, 2003).

In a slow sluggish stream, BOD of only 5 mg/L might be sufficient to produce deoxygenation resulting in anaerobic conditions whereas a stream descending from hill slope may easily offset even 50mg/L of BOD without appreciable depletion of DO. It is only when oxygen demand for the biochemical oxidation process exceeds the ability of water body to replenish its oxygen and then the depletion of oxygen takes place. BOD, therefore, becomes vital important but low DO conditions occur when subsequent growth of saprophytic bacteria takes place. If sufficient oxygen is lost it leads to degradation of water quality. Hence, one of the most important indicators of water pollution is BOD. If other conditions remain same higher the BOD of a stream or lake water then less oxygen is likely to be available for the organisms for their survival.

The domestic water must possess a BOD of not more than 2 mg/L as per Indian standards. For commercial fishing and aesthetic purpose 5 mg/L of BOD has been considered as maximum acceptable limit. The tolerance limit of BOD for the industrial effluents is 30 mg/L whereas for that of COD it is 250 mg/L (IS: 2490, part-I, 1918). However, BOD is not considered as a critical factor for irrigation water. In poorly drained and poorly aerated soils the additional depletion of oxygen by oxidisable organic matter may be deleterious. Therefore, it has been suggested that the use of water with high BOD for irrigation should be restricted to may well drained and well aerated soils (Rhoades and Bernstein, 1971).
From the analyses of BOD data of Ujjani reservoir water samples it appears that while flowing towards Ujjani much of the dissolved oxidisable organic matter of the Bhima and Mula-Mutha rivers gets removed from water. It manifests due to adsorption by the particulate matter present in the rivers and subsequent precipitation or by microbial degradation. The research has shown that the major portion of the organic compounds in river water remains associated with particulate matters (Andelman and Caruso, 1971). Hence, the precipitation of particulate matters causes removal of major portion of organic matter from water. While entering into a reservoir system, due to rapid fall in flow rate, much of the particulate matter settles near the entrance. The Mula-Mutha rivers while flowing through Pune city area towards Ujjani, a major part of the dissolved oxidisable organic matter gets diluted and oxidized due to natural processes like reaeration, photosynthetic action and dilution. Thus, the Mula-Mutha and Pavna rivers in spite of receiving a large amount of organic effluents from Pune and Pimpri-Chinchwad city area get self purified. It could be due to these reasons. Therefore, the BOD values of Ujjani reservoir water have remained moderately low. Moreover, the large volume of water and vast surface area of this reservoir also helps in lowering the BOD. This also allows rapid reaeration and hence rapid oxidation of the decomposable load. However, it is obvious that within the reservoir itself some BOD load is generated due to the presence of dead algae, plants and other species.

Biochemical Oxygen Demand depends on temperature, extent of biochemical activities, concentration of organic matter and such other related factors (Muduli and Panda, 2010). Before monsoon (Fig.6.35) June 2008 the highest BOD value of 6.24 mg/L in the surface water of Ujjani reservoir was noticed at Bhigwan Takrarwadi and near the river mouth (i.e., at Daund area-5.88mg/L). Other values recorded were 5.14 mg/L near Galandewadi and 5.59 mg/L near Bhigwan nala. During these seasons the surface water temperature of Ujjani reservoir ranging from was 26\(^0\)c to 27.8\(^0\)c. The highest BOD was due to the enhanced biological activity at higher temperature. The level of pollutants from the nearby domestic or industries added to the rivers was same throughout the year. This view was in agreement with the work of (Paramasivam and Sreenivasan, 1981). The lower values of BOD during pre-monsoon found at sampling sites were from 1.22 mg/L to 1.62 mg/L near Dam Wall,
Ganjevalan-2.11mg/L, Palasdev village -1.31mg/L and Palasdev nala-1.87mg/L. The lower value of BOD near dam wall and nearby area is due to organic load enters into this reservoir gets normally diluted to low concentrations by a large volume of water.

During the study period, Nov. 2009 (post-monsoon) the BOD values ranged from 0.79 mg/L to 8.46 mg/L. The highest BOD values of during post- monsoon season were observed near Bhigwan Takrarwadi-8.1mg/L and Daund-8.46 mg/L. Similarly, the higher BOD values are found at Galandewadi- 6.41 mg/L and Dalaj No.1- 6.36 mg/L. Increase in dissolved organic matter consumes large amounts of oxygen. A reduced pH condition along with abundance of E.coli also results in enhancement of BOD (Talib et al., 2009). The lower values of BOD were observed at Palasdev nala-0.79 mg/L, U/S of dam-1.68 mg/L, Chandgaon Village-1.93 mg/L and Palasdev village-1.55 mg/L. However, in most of the other areas the BOD values of Ujjani reservoir water have remained between 2.07 mg/L and 5.84 mg/L. But the water supplied by PMC has nil BOD.

During summer (May 2009), the higher BOD values were recorded at Dalaj No.1- 6.88 mg/L, Bhigwan Takrarwadi-7.89 mg/L and Daund-7.62 mg/L. However, in some of the other areas these values have remained less than 4 mg/L. At the sampling locations of Kalthan No.1, Ganjevalan, Chandgaon Village and Palasdev village, the BOD values were < 2 mg/L. The BOD values <3mg/L are considered within the permissible limits. The maximum for BOD values were observed during pre-monsoon period due to the maximum biological affinity at elevated temperature while lower values were met with during winter and at reduced flow of river water (Ghavzan et al., 2006).

The BOD concentration during December 2009 (post-monsoon) varied from 0.65 mg/L to 10.89 mg/L. After monsoon these values were more than 5 mg/L at sampling stations, Dalaj No.1, Bhigwan nala, Bhigwan Takrarwadi and Daund. During the study period (pre and post-monsoon) the BOD values of Ujjani reservoir from U/S of Dam to Shaha Village were less than 3 mg/L. The low value of BOD clearly indicates the low level of biodegradable material (Paramasivam and Sreenivasan, 1981). The concentration of BOD at all sampling stations exhibit an increasing trend over the period of monitoring from Nov.08 to Dec.09. It was clearly observed from the mean concentration of BOD over four seasons (Fig.6.36).
Fig. 6.35: Concentrations of BOD in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.36: Mean concentrations of BOD in 20 sampling stations in pre-monsoon and post-monsoon.
6.1.17) Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) test is commonly used to measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g., lakes and rivers). It makes COD a useful measure of water quality. However, Chemical Oxygen Demand does not differentiate between biologically available and inert organic matter. Therefore, it is a measure of total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. It, therefore, gives a quantitative value of water quality.

The COD is a measure of the amount of oxygen consumed by the organic material within a water sample that is oxidized by a strong chemical oxidant such as potassium dichromate ($K_2Cr_2O_7$). Increasing number and amount of industrial, agricultural and commercial chemicals discharged into the aquatic environment lead to various deleterious effects on the aquatic organisms (McGlashan and Hughies, 2001).

Virtually all organic matter in the sample to be tested is oxidized in this method and some of which may not be susceptible to bacterial decomposition. For example, some naturally occurring compounds like cellulose and lignin along with some synthetic organic chemicals are resistant to bacterial action. These are either non-decomposable or are degraded at a very slow rate by bacteria. These organic compounds are also oxidized along with the decomposable compounds by a strong oxidizing agent and catalysts. BOD test, therefore, measures only biochemically decomposable or degradable organic matter while COD measures total organic matter. Therefore the values of COD in some of the samples are more than their corresponding BOD values. For decomposable domestic wastes and industrial wastes, the value for COD are approximately 2.5 times of that the corresponding value for BOD. This ratio is still higher for unpolluted surface and ground water. Further the COD test results are unaffected by toxic pollutants for unpolluted surface and ground water. Hence, the COD test may be considered as the most reliable method for assessing the organic matter in the sample. BOD test is, therefore, used in stream pollution control management and in evaluating the capacity of self-purification of the stream. COD values provide a measure of the oxygen equivalent to that portion of the organic matter in a water sample that is susceptible to oxidation under test condition (Bertram and Balance, 1996). Most of the water samples collected from Ujjani reservoir
showed high COD values. These values ranged from a maximum of 71 mg/L to a minimum of 6.54 mg/L.

It is observed from the COD analyses of data of Ujjani reservoir water samples that while flowing towards Ujjani reservoir much of the dissolved oxidisable organic matter from the Bhima and Mula-Mutha rivers gets separated from the stream flow. It may be due to adsorption by the particulate matters present in the rivers, subsequent precipitation and also by microbial degradation. The earlier research has illustrated that the major portion of the organic compounds in river water remains associated with particulate matter (Andelman and Caruso, 1971). Hence, precipitation of particulate matter causes removal of major portion of organic matter from the water. While entering into the reservoir system, due to rapid fall in flow rate, much of the particles settle near the entrance.

Figure 6.37 shows that the COD values of Ujjani reservoir during pre-monsoon (June 2008), ranged from the maximum of 50.5 mg/L to minimum of 6.54 mg/L. The higher values of COD were of found at sampling stations Bhigwan Nala, 48.5 mg/L and Bhigwan Takrarwadi, 50.5 mg/L. Like other parameters, the COD values were noticed higher at the upstream most point Bhigwan to Daund. The lower values of COD were found at the Kalashi-8.88 mg/L and Palasdev Village, 6.54 mg/L.

Dead fish were found at Bhigwan Takrarwadi, Daund and Pargaon during the middle of May (2009). High BOD and COD values are also associated with high fish mortality. It suggests the impact of BOD and COD on respiratory metabolism (Venkataraman, 1996).

As per the chemical analyses of water during November 2008 (post-monsoon), the COD values were observed between minima of 11.4 mg/L at Canal Head and maxima of 68.6 mg/L at Bhigwan Takrarwadi. In the present study, COD values were higher in the surface water samples as surface waters (rivers and lakes) are wide open to flooding which carry various organic contaminants that are susceptible to oxidation. However, the substance soil strata (layers) may act as filter to underground water (John et al., 2008). The lower concentrations of COD were found at Kalashi-13.8 mg/L and Palasdev Village-12.9 mg/L. The lowest value for COD 11.4 mg/L was found at Canal head. The COD concentrations of Ujjani reservoir during May 2009 (pre-monsoon) were found to be comparatively lower than Post-Monsoon seasons.
The lower values of COD 11.0 mg/L during pre-monsoon were found at Kalashi while the higher values were recorded at Bhigwan Takrarwadi-56.4 mg/L, Bhigwan Nala-49.3 mg/L, Kandalgaon Village-39.1 mg/L, Galendewadi-36.2 mg/L, Padasthal Village, 38.04 mg/L and Gangevalan -36.0 mg/L.

The higher values in the dry seasons may be due to submerge of woody (organic) matter at the river sites. Therefore, the decay of organic matter favoured by high temperature of the dry seasons led to high values of COD in the dry seasons as compared to wet seasons (Ajibade et al., 2008). Due to the higher pollution environment in the Mula-Mutha and Pavna rivers, to domestic untreated sewage and industrial waste being dumped into the rivers, the higher values of COD were recorded in Pune and Pimpri-Chinchwad municipal corporation areas (MPCB Report, 2004-05). The COD concentration during December 2009 (post-monsoon) varied from 16.8 mg/L, to 71.9 mg/L. The PMC tap water had the COD content of 0 mg/L.

The higher concentration of COD was found at the sampling points Kandalgaon village-36.4 mg/L, Gangevalan-36.4 mg/L, Bhigwan Nala, 46.4 mg/L, Bhigwan Takrarwadi, 71.9 mg/L, and Daund, 29.8 mg/L. The high values of COD indicated that most of the pollution caused by industrial effluents in the upstream of the rivers is at alarming speed. Similar results were also reported by Pande and Sharma (1998). However, the lower values of COD from 16.8 mg/L. to 16.9 mg/L at near dam wall are suggestive self purification process being active.

The highest COD during the study period (pre and post-monsoon) was due to the level of pollutants which were added by domestic sewage and industry throughout the year. The results for the chemical oxygen demand and biochemical oxygen demand indicated presence of non biodegradable source of pollution which might be micro pollutants in nature or reduced form of salts (Rao, 2006a and 2006b; Pandey et al., 2006; Capkin et al., 2006). The concentrations of COD at all sampling stations exhibit an increasing trend over a period of monitoring i.e. June-08, Nov.08, May-09 and Dec.09. It was clearly observed from the mean concentration of COD during four seasons (Fig.6.38).
Fig. 6.37: Concentrations of COD in different sampling stations in pre-monsoon and post-monsoon

Fig. 6.38: Mean concentrations of COD in 20 sampling stations in pre-monsoon and post-monsoon
6.1.18) Sodium Adsorption Ratio (SAR)

Sodium Adsorption Ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation. It is determined by the concentration of solids dissolved in the water. It is also a measure of the sodicity of soil. Higher is the sodium adsorption ratio in water less suitable it is for irrigation. Saline soils pose a serious concern to irrigated agriculture in arid and semi-arid regions of the world (Tanwir et al., 2003; Ahmad et al., 2006). Soil salinity mainly increases due to the application of poor quality irrigation water used in farming. It allows salts to accumulate in the root zone which negatively affects plant growth, where the root zones hinder the plant roots and prevent from withdrawing water from surrounding soil. It lowers the amount of water available to the plant regardless of the amount of water actually in the root zone (Seilsepour and Rashidi, 2008).

If irrigation water, with a high SAR, is applied to soil over the years then sodium in the water can displace the calcium and magnesium of the soil. It results in the ability of soil to form stable aggregates as well as loss of soil structure and tilth. It will decrease in infiltration and permeability of the soil to water leading to problems with crop production in humid zones. Rainfall is the main source of soil waters. But, in arid or semi arid zones soil waters may be derived primarily from the irrigation waters. Hence, in arid or semi arid zones most of irrigation water is lost by root water uptake or by evapotranspiration. As a consequence, the volume of soil water reduces and the concentration of soil solution increases. Subsequently, as most of salt is left behind in the soil and salt concentration increases in the remaining volume of water. When enough salts accumulate in the effective crop root zone they negatively affect plant growth.

Depending on the frequency of irrigation, the amount of water applied and the available drainage facility, the concentration of salts in the water drained from the root zone may increase by two to ten times that of the irrigation water. On an average, such an increase of about 50 cm depth is two to three times than that of the irrigation water (Shainberg and Oster, 1978).
Soil is a complex natural material made of disintegrated rocks and decayed organic material. It provides nutrients, moisture, and support for the land plants. Salts can create a build-up of exchangeable sodium in the soil. This build-up results in the dispersion of soil colloidal particles and an increase in soil pH to almost greater than 8.5. As soil colloidal particles disperse it soil becomes increasingly resistant to water infiltration and percolation. These sodium-affected soils become hard and compact when it becomes dry and very resistant to water penetration due to dispersion and swelling when wet.

The physico-mechanical properties of soils are mainly dependent on quantity, size and the strength of soil aggregates and their stability in water (Tajik et al., 2003). Soil water acts as a solvent, reactant, medium for chemical reactions, plastising agent as well as acts as a reservoir of nutrients for plant. When processes like precipitation, dissolution, mineral weathering or uptake of salts by plants are neglected then irrigation water enters the soil and it becomes more concentrated without changes in composition. But, due to the above mentioned chemical processes, also due to the introduction of fertilizers and pest-regulating chemicals the solute content of soil water gets modified along with concentration. As it is difficult to predict quantitatively the effect of irrigation water on the ultimate composition of the soil solution, the predictions regarding it are too limited and are pertaining to very special conditions (Rhoades and Bernstein, 1971).

Calcium and magnesium are the most prevalent cations in soil solutions and Na sometimes becomes the dominant cation in the soil solution and a part of exchangeable Ca and Mg is replaced by Na. Divalent ions (mainly Ca) impart good condition of tilth and structure while opposite is true when Na predominates. The effect of K on soil structure is similar to that of Na but the concentration of K is generally very small in water K is often omitted for calculations of resultant Na-hazard. The suitability of water for irrigation purposes deteriorates with increasing solute content not only because of greater salt burden but also because of the increased Na-hazard associated with changes of SAR.

A steady state condition within agricultural soil is attained in which the SAR value of the soil solution approximates the SAR value of the applied irrigation water.
A major factor known to affect the final soil water SAR value (SAR$_{SW}$) is the loss of Ca from solution as a result of lime precipitation. An additional factor which also influences the SAR$_{SW}$ value is the introduction of Ca and Mg into the soil water from weathering of soil minerals. Since it is the SAR of the soil water rather than that of irrigation water, per se, that affects the exchangeable Na content of soils, any attempt made to evaluate Na hazard of waters for irrigation purposes should take these factors into account (Bower et al., 1968).

Even if the Na percentage or relative composition does not change, due to increase in total salt concentrations of soil water by evapotranspiration the SAR value increases proportionally to the square root of the total concentration. Thus if the total cation concentrations are doubled and if the proportion of Na, Ca and Mg remains same, the SAR value will increase by a factor of 1.41. If the concentrations are quadrupled, the SAR value will be doubled, etc. As the salt concentration in the soil solution increases with depth, there is a corresponding increase in the SAR of the soil solution in the same direction. Hence, relatively high SAR values exists relatively deep in the soil profile. But it may not always produce much reduction in soil permeability, because of the simultaneously presence of high salt concentrations. However, subsequent passage of low-salt water through the soil may lower the permeability, as excess of salt is removed from the high sodium zone (McNeal, 1981). In managing irrigation waters and drainage waters for salinity control, it is generally desirable to maintain the SAR of the irrigation water below 10. A value as high as 15 to 20 may be approached for some coarse-textured soils without noticeable effects on soil permeability. But waters of low salt concentrations (less than 50 mg/L total dissolved salt) may disperse soil even at lower values.

The SAR values of all the water samples collected from Ujjani reservoir were below 4, in pre and post-monsoon seasons, the acceptable limit for irrigation. During June 2008 (Pre-Monsoon), the SAR values of Ujjani reservoir water varied between 2 and 3.47. The higher values of SAR were found at Kalthan No.2- 3.42, Kalashi-3.09, Chandgaon village-3.47 and Palasdev village-3.28. The SAR values of other sampling sites are less than 3. During November 2008 (post-monsoon) the SAR values of Ujjani reservoir water remained almost between 1.65 and 3.37 as compared to June 2008 when the SAR values were found less.
Fig.6.39: Values of SAR in different sampling stations in pre-monsoon and post-monsoon.

Fig.6.40: Mean values of SAR in 20 sampling stations in pre-monsoon and post-monsoon.
The higher values were recorded at D/S of tail point. The SAR values of Ujjani reservoir water remained within 3 from other sampling sites. During May 2009 (pre-monsoon) the reservoir water level had dropped considerably due to long dry spell and the SAR values of the samples collected from Shaha village and Kalthan No.2 were 2.67 and 2.70 respectively. Similarly, at other locations the values of Ujjani reservoir water, during this period, varied between 1.01 and 2.58 (Fig.6.39). All these values are well within the acceptable value of 10.

During December 2009 (post-monsoon), the SAR values of this reservoir water were found varied from 1.17 to 2.25. However, slightly higher SAR values were recorded at the Bhigwan Nala-2.25.

It is, therefore, concluded that the Ujjani reservoir water will not affect the soil permeability when used for irrigation purpose. As per U.S. Salinity Laboratory classification of irrigation water Ujjani reservoir water falls under the category of C$_2$-C$_1$ class (i.e., of low sodium hazard and medium salinity hazard category). Except these samples, all water samples were of C$_2$-S$_1$ category (i.e. not likely to cause sodium hazard if used for irrigation purpose). But, as mentioned earlier, the SAR values of soil solution remain same as that of the irrigation water. But, with repeated irrigation the salt concentration of soil solution increases gradually. As a remedial action, the excess water is required to be leached out the salt, where natural leaching by winter rains does not occur (Shainberg and Oster, 1978). Moreover, sodium hazard depends upon the soil texture and its composition.

The concentration of SAR at all sampling stations exhibit decreasing trend over a period of monitoring June-08,Nov.08,May-09 and Dec.09 which is clearly observed from the mean concentration of SAR during four seasons (Fig.6.40).

6.1.19) Heavy metals

6.2.1) Introduction

As a result of industrial development and urbanization, metal pollution in water bodies has become a serious environmental problem, threatening not only aquatic ecosystems but also human health through contamination of drinking water and bioaccumulation along the food chain (Chaohua et al., 2007).

Lakes and surface water reservoirs are the most important freshwater resources which mainly cater to the needs of drinking water and agriculture. They are also the sources
for renewable energy (hydro power) and are essential resources for the industries. Lakes provide favourable breeding grounds for fish; provide social and economic benefits through tourism and recreation. Lakes also play an equally important role in flood control (Oyewale and Musa, 2006).

Heavy metals include the group of metallic elements which have relatively high atomic weight and their specific gravity is either 5 or more. The heavy metals that are considered to be the most toxic as water pollutant are: mercury (Hg), lead (Pb), arsenic (As) and a toxic pollutant in ground water. These are present in small concentrations in the natural water systems. Their occurrence in groundwater and surface water can be due to dissolution of naturally occurring minerals containing trace elements in the soil zone aquifer material or due to human activities like mining of fuels, smelting of ores and improper disposal of industrial wastes (Jinwal et al., 2009).

Heavy metal pollution in Indian rivers has been studied by number of researchers. Ajmal and Ahsan (1987) have determined the distribution of heavy metals in water, sediments, plants and fish samples collected from river Hindon (tributary of river Ganga) and river Yamuna. The adverse effects of waste materials become acute in inland water systems due to their traditional role as receiving bodies for effluents. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms. Due to hazardous effects, heavy metals have been studied in detail, with respect to their toxicity and potential bioaccumulation (Pourang et al., 2005).

Metal pollution poses two main environmental aspects: (a) the public health aspects, associated with ingestion by man toxic levels of contaminants, as contaminated water used for domestic and other uses and; (b) the environmental considerations associated with maintenance and diversity of biomass. Toxicity of metals may give rise to reversible or irreversible metabolic changes in the biological systems. They also affect the suitability of water for various beneficial uses. Metals such as lead, mercury, cadmium and copper are cumulative poisons causing environmental hazards (Ellen et al., 1990).

The trace metals become toxic when their concentration levels exceed the permissible limits. The impact of heavy metals on aquatic organisms depends upon:
(1) the concentrations and availability of trace elements to organisms; (2) time/dose effects; (3) behavior of organisms which may be significant in determining the distribution of populations; (4) sensitive phase of the life history; (5) growth as a measure of integrated physiological responses; (6) aggravating and ameliorating effects of variation in environmental parameters on toxic effects; (7) interaction between toxins; (8) concentration in organisms and routes of entry of foreign molecules into organisms; (9) indirect effects of toxins involving effects on predation (Lockwood, 1979). The toxicity of most metals varies enormously with the environmental conditions, mainly because of their effects on the chemical speciation of the metals. (Fogg and Westlake, 1955) reported that most metallic micronutrients are toxic when in excess or when their availability exceeds the tolerance limits. The toxic effects are elevated when an organism is subjected to physiological stresses, by modification temperature, salinities, oxygen deficiency or bordering the limits of its physiological capabilities (Lockwood, 1979).

Different species may show a different selective accumulation of different trace metals. For example, clams show selectivity for Zn, oyster for Cu, and cockles for Ni. This tendency is apparent in many species of both plants and animals (Langford, 1983). Phytoplanktons tend to accumulate trace metallic elements in the order: Fe > Zn > Cu > Co > Mn (Wetzel, 1975). Due to synergistic effect, even small concentrations of some metal salts in mixture may become toxic to some organisms. There is no good reason to expect that industrial wastes will contain only one toxic component. Mixed solution of two or more metals may be more toxic than the sum of the toxicities of individual solutions of single metals of corresponding concentration. For example, sulphates of Zn and Cd, Ni and Co in mixed solution of the 2 salts are additive. Whereas, the toxicity of mixtures of Ni and Zn, Cu and Zn, Cu and Cd, are greater than would be expected if toxicity were additive (Katz, 1971).

The pH value of water often plays a dominant role in exchange reactions. Processes like sorption-desorption, precipitation-solubilisation, redox and complexation reactions often depend on the solution pH. Adsorption process of heavy metals on to clay minerals depends upon the pH value. The hydrogen ions compete with heavy metal cations for exchange sites in the system, thereby partially releasing the latter. Organic substances possess a high degree of selectivity for divalent ions as
opposed to monovalent ones. The affinity of heavy metal ions is greater than that of alkaline earth (Ca, Mg) and alkali (Na, K) ions, as illustrated by the series: Pb > Cu > Ni > Co > Zn > Mn > Ca > Mg > K > Na (Forstner and Wittmann, 1983).

Singer (1977) summarized the influence of dissolved organics on the distribution of metals and dissolved organic matters are capable of (1) complexing metals and increasing metal solubility; (2) altering the distribution between oxidized and reduced forms of metals; (3) alleviating metal toxicity and altering metal availability to aquatic life; (4) influencing the extent to which metals are adsorbed on suspended matter; and (5) affecting the stability of metal containing colloids.

It is very much likely that the Mutha and the Mula rivers receive considerable quantity of pollutants including heavy metals while passing through the city and industrial areas. These rivers have been carrying a large amount of heavy metals in dissolved state and as particulate matter with sediments. For the present study, hence, the concentrations of some of the heavy metals in water and sediment samples collected from Ujjani reservoirs during different seasons were estimated. The heavy metals analyzed are: Mn, Cu, Zn, Co, and Pb. Significant concentration of As in water has not been reported in Pune region. Hence, as analysis was not included in the present work. It might be mentioned here that the high levels of As in West Bengal and Bangladesh occurred most probably due to geologic reasons and not due to anthropogenic addition. Same is the most probably true in case of fluoride contamination in certain water sources of India.

However, it needs to be noted that water and food are not the only sources of human exposure to heavy metals. The air is another important source of exposure because of metal discharges into the air due to incineration of trash, burning of coal and vehicular exhausts. The toxicity and other characteristics of the heavy metals investigated in the present study are mentioned below in brief:

6.2.2) Zinc (Zn)

Zinc is an essential plant and human nutrient. Small amounts of Zn are needed for nutrition by most crops, but toxicity results when concentration exceeds. All readily soluble salts of Zn have an unpleasant taste, and the taste can be detected in less-than-
dangerous amounts of Zn in drinking water. In many countries, the Zn standard in domestic water is based upon its taste threshold. As Zn is usually physiologically harmful to man except at very high concentrations, WHO has sets its maximum concentration value to be 15 mg/L. The solubility of zinc depends on temperature and pH of the water in question. When the pH is fairly neutral, zinc in water insoluble, Solubility increases with increasing acidity, above pH 11, solubility also increases (Solai et al., 2010).

Zn exhibits greatest toxicity towards fish and aquatic organisms. The sensitivity of fish to Zn varies with species, age and condition of the fish, as well as with the physical and chemical characteristics of water. The water pollution research board, U.K., reported that there was little toxic action of the Zn precipitated from solution in alkaline water, almost all of the toxicity being attributed to the Zn remaining in solution (McKee and Wolf, 1976). The presence of Cu appears to have a synergistic effect on the toxicity of Zn (also mentioned under Cu). On the other hand, Ca is antagonistic towards Zn toxicity. Jones, (1938) reported that for mature fish the lethal limit for Zn in water containing 1 mg/L of Ca is only 0.3 mg/L; but in water with 50 mg/L of Ca, as much as 2 mg/L of Zn is not lethal.

In Ujjani reservoir, Zn in moderate concentration was detected in few samples. During June, 2008 samples contained 0.05 mg/L or less Zn. During summer season significant concentrations of Zn could not be detected in most of the water samples. Water analyses during May, 2009, Zn varies from 0.124 to 0.01 mg/L. However, in most of the samples the concentration of Zn was not detected (Fig.6.41). The desirable limit for Zn in drinking water is 5 mg/L (BIS, 1991) and 3 mg/L (WHO, 1992). Although the water supplied by PMC has nil Zn.

During November, 2008 and December, 2009(Post-Monsoon), Zn concentration varies 0.15 to 0.01 mg/L near the dam. The concentration of Zn near the dam after monsoon was found to be little higher. However, in most of the samples, the concentration of Zn remained less than 0.01 mg/L. The concentration of Zn at all sampling stations exhibit an increasing trend over a period of monitoring June-08, Nov.08 and May-09 which is clearly seen from the mean concentration of Zn over the seasons (Fig.6.42)
Fig. 6.41: Concentration of Zn in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.42: Mean concentration of Zn in 20 sampling stations in pre-monsoon and post-monsoon.
6.2.3) Manganese (Mn)

Like Fe, Mn occurs in more than one valent forms and its cycling is dictated largely by the oxidation-reduction conditions of lakes. It forms soluble complexes with $\text{HCO}_3^-$, $\text{SO}_4^{2-}$, $\text{Cl}^-$ and $\text{NO}_3^-$. But the oxides, $\text{CO}_3^{2-}$ and $\text{OH}^-$ (hydroxides) are only sparingly soluble. For this reason Mn ions are seldom present in natural surface waters in high concentrations. When divalent Mn is released in aqueous solution during weathering, it shows somewhat more stability towards oxidation than is ferrous iron. But when contacted with atmosphere, it gets precipitated at site where the pH of water is high enough, as a crust of Mn$^{4+}$ oxide. The encrustation generally contains a substantial quantity of co-precipitated Fe and sometimes some other metals as well. In ground water, subject to reducing conditions, Mn can occur in high concentrations. Like Fe, organic molecules can form stable complexes with Mn$^{2+}$. Organic complexing plays a role in retention of Mn in a complexed dissolved form for transport once the redox conditions are altered by microbiare and plant metabolism.

Manganese is an undesirable impurity in water supplies, mainly owing to a tendency to deposit black oxide stains. Its limit in domestic water is, therefore, established more due on the basis of aesthetic and economic consideration rather than physiological hazard. It is undesirable in domestic water because it causes unpleasant taste, deposits on food, stain and discoloration laundry, growth of some microorganisms in distribution systems. In concentrations not causing unpleasant taste, Mn is regarded to be of no toxicological significance in drinking water. Some reports, however, indicate that chronic exposure to higher concentrations of Mn may cause hallucination, insomnia, metal confusion and even impotency.

Although manganese is essential to both plants and animals, its higher concentrations in aquatic systems cause harm, the extent of which varies both with the species of plant and composition of water. More than 1 mg/L of Mn is inhibitory to blue-green and green algae (Patrick et al., 1977). The toxicity of Mn towards fish is dependent upon many factors. It appears to be somewhat antagonistic to the toxic action of Ni towards fish. Its metabolism is closely related to that of Ca, P, Fe, Cu and possibly other minerals. During the study period of June, 2008 and May, 2009 (Pre-Monsoon), the Mn concentrations in Ujjani reservoir varied 0.013 mg/L to 0.541 mg/L.
Fig. 6.43: Concentration of Mn in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.44: Mean concentration of Mn in 20 sampling stations in pre-monsoon and post-monsoon.
Analyses of water during study period at most of the sampling stations, the Mn concentration were higher (Fig.6.43). During May, 2009, when a large area of the reservoir got exposed due to fall in water level, a moderate amount of Mn >0.5 mg/L detected in water collected from upstream areas of the reservoir. The concentrations of Mn at all sampling stations exhibit decreasing trend over a period of monitoring June-08, Nov.08 and Dec.09. The mean concentration of Mn during May 09 increases (Fig.6.44). The desirable limit for Mn in drinking water is 0.1mg/L (BIS, 1991; WHO, 1992) and the PMC tap water had the Mn content of 0 mg/L.

During post- monsoon (November, 2008 and December, 2009), the water sample collected from Ujjani reservoir contained approximately 0.01 mg/L to 0.09 mg/L of Mn. Most of the Water sample during this period did not contain any significant amount of Mn.

6.2.4) Copper (Cu)

Copper is comparatively a heavy metal. Copper occurs in traces and is required for nutrition. It is not considered poisonous, like Pb or Hg only because very little of Cu is retained by the body. Very high concentration of Cu is dangerous to human beings. High concentrations of Cu give water a disagreeable taste, and hence, not considered to be a hazard in domestic supplies. Minute quantity of Cu is beneficial or essential for plant growth. But more than 0.2 mg/L concentrations may show toxic symptoms to some plants like sugar beets and barley (McKee and Wolf, 1976).

Excess of Cu is highly toxic to algae, sea plants and invertebrates but is only moderately toxic to mammals. Its toxicity to aquatic organisms varies significantly not only with the species, but with the physical and chemical characteristics of water. It causes synergistic effects with some other metal ions. For example, the sulphates of Cu and Zn, and Cu and Cd are synergistic in their toxic effect on fish (Doudoroff, 1952). Synergism also exists between Cu and Hg. Cu concentrations varying from 0.1 mg/L to 1.0 mg/L have been reported to be toxic for many fish species. Like Hg and Cd, Cu affects production of eggs of fauna.
Fig. 6.45: Concentration of Cu in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.46: Mean concentration of Cu at 20 sampling stations in pre-monsoon and post-monsoon with an $R^2 = 0.279$. 

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6.2.5) Cobalt (Co)

Cobalt is an essential trace element. It is the central metallic element of vitamin B12. It is a relatively low toxic heavy metal to man. In concentration of more than 0.1 mg/L it may cause injury to some plants, such as tomatoes. Mn can reduce Co injury (McKee and Wolf, 1976). Trace amount of Co ion appears to stimulate the growth of some aquatic organisms. At higher concentrations however, Co ions may cause toxic effects (Hermann, 1959).

In Ujjani reservoir water, the presence of Co was not detected in the samples collected during June, 2008, November, 2008, May, 2009 and December, 2009.

6.2.6) Lead (Pb)

It is a very toxic element, which accumulates in the skeletal structure of man and animal. Under normal conditions, lead does not react with water. However, when lead comes in contact with moist air its reactivity with water increases. A small lead oxide (PbO) layer forms at the surface of the metal. When both oxygen and water are present, metallic lead is converted to lead hydroxide (Solai et al., 2010).

The natural mobility of Pb is low owing to its low solubility of its salts. Its adsorption on organic and inorganic sediment surfaces and co-precipitation with Mn-oxide also tend to maintain its low concentration levels in surface and ground waters. Due to its extensive use in petrol, its presence in the environment has increased multifold. The rocks and soils in nearby areas of lead ore (galena) possess appreciable concentration of Pb in natural waters. Leaching of Pb from the older water supply pipes also is a source of Pb concentration in drinking water. However, the modern manufacturing of water supply pipes do not repair Pb. Lead compounds are also used in printing, dying and paints and hence, it may find its way through effluents of such processes.

Lead enters into human body and is retained as a cumulative poison. Lead poisoning is accompanied by symptoms of intestinal cramps, nerve-paralysis, anemia and kidney abnormalities. Lead poisoning among human beings is reported to have been caused by drinking of water containing Pb in the concentrations varying from 0.042 mg/L to
1.0 mg/L or more (Fourcade and Caron, 1957). The safer limits of Pb toxicity are not stated clearly as its accumulation, retention in human body and varying sensitivity of individuals towards Pb toxicity differ considerably (McKee and Wolf, 1976). BIS (Burro of Indian Standards) have set allowable concentration of Pb in drinking water as 0.05 mg/L. WHO international standard for Pb is 0.1 mg/L, which is prescribed in India for inland surface waters of class-C type. But there are certain reports which indicate that daily ingestion of even 0.1 mg Pb over the years cause lead poisoning. Inorganic Pb salts in irrigation water are toxic to plants. It can cause delayed germination, as well as, death of plants. Farm animals are poisoned by Pb from various sources, including paint. Chronic Pb poisoning among animals have been caused by more than 0.5 mg/L of Pb in soft water.

In water, Pb-salts form a film of coagulated mucus on fish, because Pb reacts with organic constituent of mucus. The coagulated mucus deposited over the gills of fish causes their death by suffocation as a result of this obstructive layer. The toxicity of Pb in soft water is more as compared to hard water. Moreover, the presence of Ca at a concentration of 50 mg/L can offset the toxic effect of 1 mg/L of Pb (McKee and Wolf, 1976). The water supplied by PMC had average Pb content of 0.35 mg/L. During June, 2008 and May, 2009 (Pre-Monsoon) Pb concentration in Ujjani waters varied between 0.012 mg/L and 0.32 mg/L (Fig.6.47). The higher concentration of Pb (< 0.1mg/L) was found at Canal Head, Shaha Village, Padasthal Village, Kalthan No. 1, Chandgaon Village, Bhigwan nala and Daund. During November, 2008 and December, 2009 (Post-Monsoon), Pb concentration varies 0.01 mg/L to 0.42 mg/L. The higher concentration of Pb was found at Gangevalan - 0.42 mg/L and Daund-0.334 mg/L. At U/S of Dam, Near Dam Wall, Canal Head and D/S of Dam Tail Point the dissolved Pb concentrations in this reservoir water remained mostly below detection limit. The concentrations of Pb at all sampling stations exhibit stable trend over a period of monitoring June-08, Nov.08 and May-09 whereas it decreased during Dec.09 (Fig.6.48). There were no significant variations in the concentrations of the trace metals between water samples of various seasons and also no distinctive distribution patterns in heavy metal contents in the samples collected within the sites of Ujjani reservoir.
Fig. 6.47: Concentration of Pb in different sampling stations in pre-monsoon and post-monsoon.

Fig. 6.48: Mean concentration of Pb at 20 sampling stations in pre-monsoon and post-monsoon.