2. REVIEW OF LITERATURE

The literature pertaining to the present investigation has been reviewed and presented under the following sections and subsections:

2.1 Use of wastewater in agriculture and its composition
   2.1.1 Wastewater reuse in agriculture
   2.1.2 Different types of wastewaters and their composition

2.2 Effect of wastewater application
   2.2.1 Ground water quality
      2.2.1.1 Chemical composition of groundwater quality
      2.2.1.2 Heavy metals contamination in ground waters
      2.2.1.3 Water quality parameters
      2.2.1.4 Water quality indices
      2.2.1.5 Irrigation water quality
   2.2.2 GIS techniques for groundwater quality characterization

2.3 Plant growth and development
   2.3.1 Seedling emergences
   2.3.2 Enzyme activity
   2.3.3 Yield and Morphological parameters

2.1 USE OF WASTEWATER IN AGRICULTURE AND ITS COMPOSITION

2.1.1 Wastewater reuse in agriculture

The use of urban wastewater in agriculture is a centuries-old practice which has started receiving renewed attention concomitant with the increasing scarcity of freshwater resources in and around many cities of arid and semiarid regions of the world. Driven by rapid urbanization and growing wastewater volumes, it is now widely considered useful in urban and peri-urban agriculture despite the health and environmental risks associated with this practice. Though pervasive, this practice is largely unregulated in low-income countries, and the cost and benefits are poorly understood.
Wastewater reuse in agriculture: Internationally

The reuse of wastewater for irrigation has been reported in many countries of Asia, Middle East, Mediterranean, South America and the USA. Of the 9700 ha irrigable land in Tehran, about 6900 ha area is being irrigated with wastewater. It has been widely used for agricultural irrigation in many countries around the world (Friedel et al., 2000; Barbagallo et al., 2001), including cities or provinces in China, such as Beijing (Liu et al., 2005), Shanghai (Chen et al., 2007), Liaoning (Sun et al., 2008), Hebei (Wu et al., 2003). The wastewater generated from domestic, industrial and commercial activity in Jordan was estimated to be 109 MCM (Million cubic meters) in 1985 and was projected to be 189 MCM in the year 2000, out of which some 80 MCM of treated wastewater would be available for restricted use in 8000 ha.

Wastewater in the United States at the time of discharge must generally conform to secondary standards in respect of biological oxidation and disinfection. At this treatment level, US Environment Protection Agency (EPA) guidelines for water use are intended to minimize human exposure. Water reuse alternatives considered appropriate include surface irrigation for orchards and non-potable aquifers, wetland augmentation and industrial processing (Shuval, 1991).

Wastewater use in agriculture has been practiced for conservation strategy. The volume of treated wastewater in 1988 was 78 Mm$^3$ with only 1750 ha under irrigation with treated wastewater in Tunisia and the volume of treated wastewater was expected to exceed 125 Mm$^3$ by 2000 (FAO, 1992). In Portugal, treated wastewater is a considered as a valuable potential resource for irrigation. It was estimated that treated wastewater in a dry year would be expected to irrigate nearly 60,000 ha of orchards, vineyards, and golf courses depending upon storage capacity in southern Portugal. An area of 1000 ha was planned to be irrigated with tertiary treated wastewater near Lisbon (Angelokis and Bontoux, 2001). South Korea is a densely populated country and has water shortages. Increasing sewage discharge due to growing population is degrading water quality of receiving water bodies (Yoon et al., 2001). Mexico has a population of 97 million, out of which 87% of the population has access to water supply and 73% population has access to sewage system. However, only 22% of the 5.8 BCM (billion cubic meters) municipal
wastewater generated received some treatment before reuse or discharge into the environment (Jimenez et al., 2002).

In Damascus, Syria, 177 million m$^3$/year of treated wastewater are reused for irrigating 9,000 hectares. Both treated and untreated wastewater is normally disposed into rivers, valleys or to the sea (WHO, 2005). With the advent of water-borne municipal sewage in the mid-nineteenth century, sewage farms were increasingly seen as a solution for the disposal of burgeoning volumes of wastewater from many rapidly growing cities of Europe and the United States including London, Paris, and Berlin. The benefits cited included the prevention of river pollution and the provision of water and nutrients to agriculture. With the development around 1913 of biological wastewater treatment processes, such as trickling filters and activated sludge, that require much less land, sewage farms fell into decline in urbanized industrialized countries (Asano et al., 2007).

In many European and North American cities wastewater was disposed of in agricultural fields before the introduction of wastewater treatment technologies, to prevent pollution of water bodies. In Paris, for instance, the use of partially treated wastewater was common until the second part of the 1900s (Asano et al., 2007). In China, Mexico, Peru, Egypt, Lebanon, Morocco, India and Vietnam, wastewater has been used as a source of crop nutrients over many decades if not centuries (Shuval et al., 1986; AATSE, 2004; Jiménez and Asano, 2008). Thus, agricultural use of untreated wastewater has been associated for centuries with both environmental protection through land application and crop production (Keraita et al., 2008).

In a cross section of 14 countries from MENA, including Israel, where 60% of its sewage effluent is reclaimed for use, between 16–100% of the treated wastewater is recycled for agriculture. But the volumes treated represent anything between 10% and 90% of the generated wastewater volumes (author’s construct), which implied that significant amounts of untreated wastewater are also used. Data reported from 34 countries across the world show that the volumes of treated wastewater used for agriculture could vary anywhere between 38 m$^3$/day and 4.5 million m$^3$/day (Jiménez and Asano, 2008).

There is evidence that around 600 BC the Romans collected urine in public urinals and sold it to dyers, tanners and other merchants. Cesspits were emptied daily
and the contents were used as fertilizers (Bahri, 2009). In a cost–benefit analysis of greywater reuse systems constructed in residential schools in India, the internal and external benefits far outweighed the costs (Godfrey et al., 2009).

**Wastewater reuse in agriculture: Nationally**

It was estimated that in India about 73,000 ha of per-urban agriculture is subject to wastewater irrigation (Strauss and Blumenthal, 1990). The survey conducted by CPCB in 1994-95 indicated that most cities did not have organized wastewater collection and treatment facilities in India. The status of wastewater generation, collection, and treatment in urban areas has been given by Kulkarni (2003). It was also found that the class I cities and class II towns of Maharashtra, Uttar Pradesh, West Bengal and Gujarat, including National Capital Territory, New Delhi contribute to 59% of the total wastewater generated in the country, According to Ministry of Environmental and Forests, out of the total 6684 Million cubic meter (Mm$^3$) wastewater generated from the cities and towns, 4755 Mm$^3$ (71%) was collected annually and only 1496 Mm$^3$(22%) was treated prior to release and remaining disposed untreated.

Forty-nine cities have primary and secondary treatment facilities while twenty-seven cities have only primary treatment facilities. In India, it estimated that in 2003, 22,900 million litres per day (MLD) of domestic wastewater was generated from urban centers against 13,500 MLD of industrial wastewater (Central Pollution Control Board, 2003). It is estimated that the domestic and municipal fresh water (both from surface and groundwater) demand in India by 2025 and 2050 will be about 55 and 90 Bm$^3$, respectively (NCIWRD, 1999) and about 80% of the supplied volume will be returned as wastewater.

However, it is not known precisely as to how much quantity of treated/untreated wastewater is being used presently for irrigating crops. From the available information on status of wastewater generation, collection and treatment in the country, it appears that there is a considerable scope for enlarging present wastewater irrigated area. Assuming net irrigation requirement (NIR) of a seasonal crop as 400 mm ha$^{-1}$ and an overall conveyance and water application efficiency as 50%, one Mm$^3$ of wastewater could irrigate about 125 ha (Kulkarni, 2003).
It can be assumed that about 50% of the wastewater generated in class I and class II cities could be treated to a level acceptable for irrigation. While selecting a water application method for wastewater irrigation, factors such as contamination of plants and harvested products, direct contact of farm workers with wastewater and impact on the environment need to be considered. Use of grated pipes for wastewater application to furrows was tried out at Aurangabad, as it reduced direct contact of the field workers with wastewater (Kulkarni, 2003). In areas like Vadodara, Gujarat, which lack alternative sources of water, one of the most lucrative income-generating activities for the lower social strata is the sale of wastewater and renting pumps to lift it (Bhamoriya, 2004). It has been reported that irrigation with sewage or sewage mixed with industrial effluents results in saving of 25 to 50 per cent of N and P fertilizer and leads to 15-27% higher crop productivity, over the normal waters (Anonymous, 2004). In peri-urban areas, farmers usually adopt year round, intensive vegetable production systems (300-400% cropping intensity) or other perishable commodity like fodder and earn up to 4 times more from a unit land area compared to freshwater (Minhas and Samra, 2004).

Presently about 15% of India’s water resources are consumed by the domestic and industrial sectors and the share of these two sectors will grow to about 30% by 2050. Since the consumption of these sectors is only 15-20% against 80% in agriculture, the production of domestic and industrial effluents will multiply in quantity with more contaminants of organic compounds, dissolved toxins and heavy metals. The first sewage farm in India was established in Ahmedabad in 1896 followed by Poona in 1918 and Madurai in 1928. Now there are more than 300 sewage farms with an area of more than 50,000 ha across India. The cause of concern is the irrigation practice with crude and irrational manner which is causing many environmental and health implications (Minhas, 2006).

A large area in and around Bhubaneswar city is irrigated with Gangua nala which receives municipal sewage of the city. A number of crops viz., paddy, vegetables and sugarcane, are grown using Gangua water. A study in DWM on impact of long term urban wastewater irrigation on soil did not indicate any soil degradation (Weckenbrock et al., 2009).
2.1.2 Different types of wastewaters and their composition

In recent years, the disposal of industrial effluents has become a problem of increasing importance throughout the world. The wastewater generated in the tropical cities of developing world such as Mexico City, Rio-de-Janerio, Cairo, Delhi, Calcutta, Karachi, etc. is a cause of serious concern as this wastewater is a mix of human waste and industrial effluents and thus, it is very difficult to classify it. The industries that use a major amount of water include distilleries, paper mills, tanneries and textiles. Also coal washaries, automobiles and food processing industries use considerable amount of water and discharge the polluted water into the nearby rivers or discharge it on land (Chhonkar et al., 2000). The wastewater applied to agriculture is supposed to be the safest option as it provides nutrients to plant and has economic advantages over other means of disposal but composition of wastewater varies with the type of industries, thus, they have both advantages and disadvantages when they are used for irrigation.

As far as Indian scenario is concerned, there were 285 distilleries in India (All India Distilleries association circular (AIDA), 1995). Most of these distilleries are concentrated in the states of Maharashtra, Uttar Pradesh and Karnataka. According to an estimate, the alcohol production in India has reached 2.7 billion liters mark. The proportion of wastewater, generally known as spent wash is nearly 15 times of the total alcohol production. This massive quantity, approximately 40 billion liters of the effluents, if disposed untreated, can cause considerable contamination of water resources, leading to widespread damage to life (All India Distilleries Association Circular, 1995).

The distillery effluents carry a very high organic load of 50,000 mg L$^{-1}$ BOD and 95,000 mg L$^{-1}$ COD as has been recorded in spentwash, whereas the post-methanation effluents had considerable lower organic load (5,000 mg L$^{-1}$ BOD and 25,000 mg L$^{-1}$ COD). The spent wash contained 1,000 mg L$^{-1}$ nitrogen, 40 mg L$^{-1}$ phosphorus, 11,000 mg L$^{-1}$ potassium and 1,500 mg L$^{-1}$ sulphate with 15 dS m$^{-1}$ electrical conductivity (EC) and 4.5 pH. The nutrient concentration and EC decreased while pH increased in post methanation effluents as compared to those in spent wash (Joshi et al., 1996). The metals (in mg L$^{-1}$) like Fe-34.8, Mn-12.7, Zn-4.61, Cu-3.65, Cr-3.65, Cd-0.48 and Co-
0.08 were also found in spentwash with electrical conductivity in the range of 15-23 dS m$^{-1}$ (Zalawadia and Raman, 1994).

Water requirement is high in paper industry and it varies from 250 to 350 m$^3$ per ton of the product. The major chemicals used by paper and pulp mills are sodium carbonate, sodium hydroxide, sodium sulphide, sodium carbonate, and calcium hypochlorite and magnesium bisulphate. Obviously, the wastewater also contains these chemicals in various amounts. Large paper mills (LPM) generate 220 m$^3$ of wastewater per ton of paper produced which contains 168 kg suspended solids, 65 kg BOD load and 246 kg COD load. The relatively high pollution is associated with small paper mill (SPM) due to non-recovery of chemicals from black liquor which is reported to be uneconomical. As such it is estimated that each ton of paper made in SPM generates 2.65 times the pollution load discharged per ton of paper made in LPM (Upadhya and Singh, 1991).

Lignine and its derivatives responsible for the brown colour in the wastewater, are not readily biodegradable and, thus, constitute recalcitrant pollutants particularly, pulp washing and contribute to a number of toxic pollutants. These include resins, acids, chlorinated lignin and chlorofatty acids. Other toxic pollutant includes tri- and penta-chlorophenols used in slimicide and biocide formulations in the mills. Besides these, on an average LPM and SPM effluents contain N, 6; P, 1.5; K, 10; Ca, 200; Mg, 35 and Na, 75, all expressed in mg l$^{-1}$ (Upadhya and Singh, 1991).

The quantity of effluents discharged from tannery industry amounts to about 30-40 liter/kg of skin/hide processed and in the case of finishing units, the quantity is about 50 litter/kg of raw skin/hide (Aggarwal and Aggarwal, 1990). There were about 3000 tanneries in India mostly spread over Tamilnadu, West Bengal, Uttar Pradesh, Maharashtra, Karnataka, Punjab and Rajasthan (Sujatha and Gupta, 1996). A large number of tanneries (about 433) are located in Tamilnadu and their contribution is about 70 % in the total export of leather and leather products of the country.

Two types of tanning processes are mainly followed in India, viz., vegetale tanning and chrome tanning. There is a lot of difference between the pollution loads of the effluents generated from the vegetables and chrome tanning processes. The effluents from chrome tanning generally contain much higher concentrations of chromium, TDS<
suspended solids, chlorides etc., as compared to vegetables tanning however, sulphate is not present in chrome tanned effluents (Manivasagam, 1987).

The effluents (vegetable tanning) emanating industry near Dindigul, Tamilnadu, showed that they were very complex, slightly acidic (pH 6.0) with a variety of dissolved cations and suspended particles (57 mg L\(^{-1}\)), tannin (127 mg L\(^{-1}\)), Mg (1.5643 mg L\(^{-1}\)), K (6.48 mg L\(^{-1}\)), Ca (4 mg L\(^{-1}\)), Mn (0.67 mg L\(^{-1}\)) and Pb (0.23 mg L\(^{-1}\)) concentrations were very low while Cu and Fe were not detected (Manivasagam, 1987). Similarly, chemical analysis of effluents samples collected from Unnao, Uttar Pradesh revealed the alkaline nature (pH 8.67) of effluents having high BOD (980 mg L\(^{-1}\)), COD (2080 mg L\(^{-1}\)) and total dissolved solids (835 mg L\(^{-1}\)) (Vajpayee \textit{et al.}, 1995).

In India, the major textile mills are located at Ahemadabad, Mumbai, Coimbatore and Chennai. However, medium and small units are distributed throughout the country. In the textile industry, chemicals such as sodium carbonate, sodium nitrite, sodium silicate, sodium oxychloride, sodium sulphide, sulphuric acid, hydrogen peroxide, bleaching powder, acetic acid, tannin acid, detergents, malt or enzymes, dyes, mordents, starch, gum etc. are used (Gupta and Nathawat, 1992).

The composition of wastewater varies among individual sections of textile factory. For example, effluents emanating from Buckingham and Carnatic textile mills were alkaline, except for sizing and fancy dyeing sections which were acidic in reaction. The effluents from de-seizing had higher BOD, COD and low suspended solids. Wastewater from khaki dyeing had high total dissolved solids in addition to 860 mg L\(^{-1}\) of chromium. Pollution load was high from sizing, de-sizing and fancy dyeing sections (Govindan, 1982).

There are about 769 hand processing textile units in Pali city alone which discharge about 1.8 million liter of effluents per day. The effluents emanating from hand processing units of Pali (Rajasthan) were characterized with high salinity (SAR, 82), BOD (400-800 mg L\(^{-1}\)), COD (900-1500 mg L\(^{-1}\)), excessive concentrations of sodium and carbonate ions (RSC: 42 meq L\(^{-1}\)), high alkalinity (pH: 10-11.5) and unduly low concentrations of calcium. The total chromium and phenolic compounds in the effluents of Pali were found to be 0.18 and 0.24 mg L\(^{-1}\), respectively, whereas, the mixed industrial effluents (mainly textiles) were reported to have pH ranging from 9.0-10.0, EC
from 5-10 dS m\(^{-1}\), RSC from 10-40 meq L\(^{-1}\) and SAR from 60-150. The lack of calcium ions and appreciable occurrence of magnesium ions in concentration of lesser than 2 meq L\(^{-1}\), and excess of carbonate ions (as high as 30 meq L\(^{-1}\)) have also been observed in these effluents (Gupta and Nathawat, 1992).

Apart from these specific industrial effluents, sewage effluents, generated out of the mixture of domestic and industrial waste waters, are other important metal contributors to the environment. The concentration of micronutrients and heavy metals in sewage effluents emanating from the different cities in many-folds higher than that of tubewell waters (Rattan et al., 2002). Heavy metals content in the effluents exhibits considerable variation depending upon the sources of their origin and season of their generation. For example, concentration of metals, except Fe, in the effluents emanating from Kolkata city was lower during the monsoon than in winter due to dilution effects; higher concentration of Fe during monsoon was due to addition from land along with the runoff (Mitra and Gupta, 1999). Concentration of Zn, Cu, Fe, Mn, Ni, Cr and As was 4 to 2300 times higher in sewage water emanating from Jalandhar, Punjab than the groundwater (Brar et al., 2000).

Asano (1994) reported that about 20-100 mg L\(^{-1}\) N, 4-15 mg L\(^{-1}\) P, 20-150 mg L\(^{-1}\) K and 10-130 mg L\(^{-1}\) free ammonia in sewage water. It was high (100-750 mg L\(^{-1}\)) in BOD that was a measure of decomposable organic matter present in domestic sewage. Typical raw sewage contains 107-109 Coliforms per 100 mL. Industries may further contribute toxic ions like Cd, Ni, Cr, Pb etc. to sewage water. Yadav et al. (2002) reported that the sewage effluents contained 20-179, 93-1130, 50-535, and 92-1357 µg L\(^{-1}\) Cd, Cr, Ni and Pb, respectively. At Central Soil Salinity Research Institute, Karnal, sewage water was collected in a pump through gravity and was pumped into a unlined pond every 24 hours (Minhas and Samra, 2004). The amount of sewage water was around 83000 L day\(^{-1}\). The quality of this domestic wastewater was pH: 7.93, EC: 0.98 dS m\(^{-1}\), BOD: 198 mg L\(^{-1}\), COD: 249, NH\(_4\) -N: 12.9 mg L\(^{-1}\), NO\(_3\) -N: 2.43 mg L\(^{-1}\), HCO\(_3\): 7.89 meq L\(^{-1}\), P: 4.06 mg/l, K: 0.29 meq L\(^{-1}\), Na: 2.38 meq L\(^{-1}\), Ca: 2.19 meq L\(^{-1}\), Mg: 3.20 meq L\(^{-1}\), Zn: 0.24 mg L\(^{-1}\), Fe: 0.94 mg L\(^{-1}\), Mn: 0.03 mg L\(^{-1}\), Pb: 0.16 mg L\(^{-1}\), Cd: 0.01 mg L\(^{-1}\), E. Coli: 10\(^{10}\) per 100 mL and total suspended solids 100 mg L\(^{-1}\).
Rattan *et al.* (2005) reported that P, K and S contents in sewage effluents emanating from Keshopur effluents contained 5.5, 3.6, 2.6, 6.4 and 1.3 times higher amounts of Zn, Cu, Fe, Mn and Ni, respectively, compared to groundwater. There were no appreciable variations between these two sources of irrigation water in respect of Pb and Cd. The sewage effluents contain appreciable amounts of useful major plant nutrients *viz.*, P, K and S, which was also reflected in the appreciable built-up of these nutrients in sewage irrigated soils in periurban area of west Delhi.

Rattan *et al.* (2005) also determined some selected physico-chemical parameters in sewage and effluent samples in periurban areas of Delhi, where sewage effluent was applied for agricultural crops. The results indicated that the sewage water samples were acidic in reaction with pH values ranging from 5.8 to 6.5. The tolerance limit of pH of irrigation water ranged from 6.0-9.0 (Rattan *et al.*, 2005). All the effluent samples were within the permissible limit. Electrical Conductivity of sewage effluents in all samples exceeded 1.00 dS m$^{-1}$ (1.36-2.88 dS m$^{-1}$) indicating that these effluents were saline in nature. The carbonates and bicarbonates contents in effluents samples varied from traces to 0.8 and 4.4 to 9.8 meq L$^{-1}$, respectively. The values of residual sodium carbonate (RSC) varied from traces to 1.2, *i.e.* RSC in all samples were below 1.25 meq L$^{-1}$ (Safe limit for irrigation water). These effluents can safely be used for irrigation purpose as far as RSC is concerned.

According to Singh *et al.* (2012), hydrochemical groundwater evaluations revealed that most of the groundwaters belong to the Na$^+$- K$^+$-Cl$^-$-SO$_4^{2-}$ type followed by Na$^+$-K$^+$-HCO$_3^-$ type. Salinity, chlorinity and SAR indices indicated that majority of groundwater samples can be considered suitable for irrigation purposes in the villages of Lutfullapur Nawada, Loni, District Ghaziabad, U.P., India.

### 2.2 EFFECTS OF WASTEWATER APPLICATION

#### 2.2.1 Ground water quality

**2.2.1.1 Chemical composition**

The composition of effluents is quite variable depending upon the contributing source, method and time of collection and treatment adopted. In our country most of the
waste waters are a mixture of domestic, commercial and industrial activities. Therefore, a large proportion of this waste water is organic in nature and contains essential nutrients but sometimes toxic elements are also present in appreciable amounts (Kansal, 1994; Venkateswara Rao et al., 1996; Siddaramaiah et al., 1998; Srinivasachari, et al., 1998; Patel et al., 2003). These waters are used for irrigating crops grown in the immediate surroundings of their disposal sites. The long-term use of this water for irrigating crops may cause accumulation of heavy metals in soils to such an extent that they may become toxic to plants. The uptake of heavy metals by plants is governed by their concentration in the soil solution. Thus, the crops grown in contaminated soils may accumulate heavy metals in excess quantities, which, in turn, may cause clinical problems in animal and human beings.

The major constituents of groundwater are chloride, sulphate, carbonate and bicarbonate as anions and sodium, calcium, magnesium as well as potassium as cations. However, nitrate is also present in appreciable amounts in some cases. Besides these, following elements may be found in minor quantities depending upon the location of groundwater. There are fluoride, copper, iron, zinc, cobalt, nickel, manganese, lithium, silicon, bromine, iodine, rubidium, beryllium, barium, titanium, zirconium, vanadium, chromium, lead, molybdenum, selenium, arsenic, antimony, bismuth, phosphate and organic ions. The chemical composition of groundwater reflects the effects of chemical processes occurring between the minerals and flowing waters. Most of inland areas of Indian subcontinent are Ca-Mg-HCO$_3$ type (Bartariya, 1993; Datta and Tyagi, 1996). Alteration trends, in turn, may be related to natural and anthropogenic factors. Broadly speaking, the intake of major and minor ions is related to solid water interaction (Bartariya, 1993; Subba Rao, 2002).

Datta and Tyagi (1996) indicated that in the overexploited aquifer conditions, groundwater of south western parts of Delhi was primarily saline and secondary alkaline, and in the remaining parts the waters were primarily alkaline and secondarily saline, having different compositions. viz., Na-Mg-Cl, Na-Cl-HOC$_3$ and Na-Cl type. Huaming and Yanix (2004) reported that mineral dissolution or hydrolysis, ion exchange and industrial, agricultural contaminations are the major hydgeochemical processes in
shallow Quaternary aquifers. Subramani et al. (2005) inferred that in the Chithar River basin, Tamil Nadu, the abundance of major ions in groundwater was of the following order:

Na > Ca > Mg > K = Cl > HCO$_3$ > SO$_4$ > NO$_3$ > CO$_3$

The study further revealed that most of the groundwater samples were Ca-Mg-Cl type of waters. The trilinear diagram suggested that alkaline earths (Ca and Mg) significantly exceeded the alkalies (Na+K) and strong acids (Cl and SO$_4$) exceeded the weak acids (HCO$_3$ and CO$_3$). Umar et al. (2006) studied the groundwater hydrochemistry in Kali Hindon watershed in Muzaffarnagar district the pH value of which varied from 7.4 to 8.1, hence, the groundwater was neutral to slightly alkaline in nature. Their investigation revealed existence of six different groups characterized by distinct chemical compositions.

Singh et al. (2006) evaluated the groundwater sources in the Gangetic alluvium aquifer region (Unnao) and concluded that the groundwater in the region is classified as moderately hard, normal chloride and sulphate type. In less than 19 percent of the samples, levels of TDS, hardness, Cl, F, SO$_4$, Ca and Mn exceeded their respective permissible limits and were mainly concerned with unpleasant taste and adverse effect in domestic use.

Kaya et al. (2007) carried out a study with a different approach to detect the spread of groundwater contamination and locate possible pathways of leachate plumes that resulted from an open waste disposal site of Canakkale municipality. Interpretations of DC resistivity geoelectrical data showed a low resistivity zone (<5 ohm-m), which appears to be a zone, that is fully saturated with a leachate from an open dumpsite.

Kashetrimayum and Bajpai (2012) interpretation of hydrochemical analysis of groundwater quality and evolution of hydrochemical facies in the Markanda river basin revealed that concentrations of the major ions (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, SO$_4^{2-}$, CO$_3^-$ and HCO$_3^-$) and important physical parameters were within the permissible limits for irrigation based on calculated indicies (SAR, Na%, PI).
2.2.1.2 Heavy metals contamination

The density of heavy metals is more than 6 cm$^{-3}$ and atomic weight more than that of iron (Alloway, 1990). The example of heavy metals includes chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), cadmium (Cd), lead (Pb) and mercury (Hg) etc. They are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. Human activity has drastically changed the biogeochemical cycles and balance of some of these heavy metals. They are stable and persistent environmental contaminants since they cannot be degraded or destroyed (Adriano, 1986).

Heavy metals are also known to have adverse effects on the environment and human health (Nriagu, 1978). Heavy metals are released into the ground water from a wide spectrum of natural and anthropogenic sources (Ramamoorthy, 1964). Many researchers (Chakraborti et al., 2002; Singh, 2004; Sia Su, 2007; Das et al., 2009; Borah et al., 2009a,b; Buragohain et al., 2010) have reported heavy metal pollution of drinking water resources from the different parts of the world.

Natural sources of heavy metals

Weathering of rocks is the principal source from which soils derive their heavy metals. In the Canadian Shield, where there has been a widespread mineralization of the bedrock, trace metal pollution has been a serious problem. In India, Arsenic (As) poisoning due to drinking of geologically enriched As-ground waters has been reported for various parts of West Bengal (Sanyal and Mukhapatra, 2000). Geologically driven selenium toxicity of fodder has also been reported from some pockets of Punjab (Dhillon et al., 1992). Analysis of geo-chemical data for China, United States, Tibet and Alaska has revealed regional variations in the abundance of trace elements in soils (Chen et al., 1991). In general, the sequence for regional variations in various divisions of Mainland China has been reported as: Southwest China> Tibetan Highland> Xinjiang-Mongolia> Northern China> Northeast China> Sotheast China. Correspondingly, the metal contents in soil samples belonging to Lithosol order was observed to be in the order of Cold-highland soils > Inceptisols > Aridisols = Mollisols > Ultisols > Alfisols > Oxisols. This trend was apparently a result of climatic influence on soil genesis, with the oxisols (high
rainfall areas with highly weathered and highly leached soils) yielding the lowest elemental mean values. The highest mean values for most trace metals in the lithosols were a result of its relatively high indigenous elemental contents as well as chemical properties of the bedrock from which the soils were formed. Thus regional variations in heavy metal concentrations in soils are primarily governed by the diversity and nature of in-situ parent material. In general, metamorphic rocks are the richest source of heavy metals. The sedimentary and igneous rocks follow. Among the rock samples analyzed by Wedpohl (1974), Zn, Cu, Mn and Fe concentrations were found highest in green schist (a metamorphic rock) and lowest in sandstone (a sedimentary rock). Of the three sedimentary rocks (*i.e.* sandstone, shale and limestone), Zn and Mn contents were the highest in limestone. Shale had comparatively higher Cu and Fe contents than limestone. However, their Mn concentrations were almost the same. Granite, an acid igneous rock, showed Zn, Cu and Mn contents close to those present in gneiss (a metamorphic rock) and limestone. These were lower than those present in basalt, a basic igneous rock (Taylor, 1954). Arsenic contents have been reported to be much higher in the sedimentary rocks (Boyle and Jonasson, 1973).

Soil reflects the composition of the parent rock from which they are derived. Parent material is, therefore, responsible for the accumulation of heavy metals in the soil and its nature is responsible for the differential levels of these metals in the soils. A number of trace metals accumulate by the differential levels of these metals in the soils. A number of trace metal concentrations can vary widely in different soils derived from different parent materials. More basic ingenious parent materials potentially contribute highest quantity of Cr, Mn, Co and Ni to soils (Levinson, 1974; and Alloway, 1990), while amongst the sedimentary parent materials; shales potentially contribute the highest quantity of Cr, Ni, Co, Zn and Pb. The rate of weathering of minerals determine the release of these elements into the soil initially in the form of simple or complex inorganic ligands, depending on mineral solubility under prevailing soil pH and EC conditions. Studies have shown that for Mn, Ni and Cr, the main source in soil is the parent material which can lead to their accumulation at high rates in subsoil.

The availability of trace metals to plants depends on the ease of weathering of rocks. Many trace metals are most commonly found in sulphide ores, like galena (PbS),
Cinnabar (HgS), Chalcopyrite (CuFeS₂), Sphalerite (ZnS) and pentlandite (NiFe). Since many minerals contain trace metals, which are insoluble and resistant to weathering, higher concentrations can be found in tropical soils where longer and more intensive weathering regimes prevail. The contents of Zn, Cu, Fe and Mn were highest and lowest in green schist and sandstone, respectively. Generally sedimentary rocks have higher Arsenic content than igneous and metamorphic rocks. Arsenic content in coal can be as high as 2000 mg/kg (Onishi, 1969) while sandstone and carbonate rocks contain 1 mg/kg.

Environmental pollution by heavy metals is very prominent in areas of mining and old mine sites and pollution reduces with increasing distance away from mining sites (Peplow, 1999). These metals are leached out and in slopy areas, they are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (Garbarino et al., 1995; INECAR, 2000). During mining processes, some metals are left behind as tailings scattered in open and partially covered pits; some are transported through wind and flood, creating various environmental problems (Habashi, 1992). Heavy metals are basically recovered from their ores by mineral processing operations (Peplow, 1999; Lenntech, 2004; UNEP/GPA, 2004; United States Department of Labor (USDOL), 2004). Cadmium is released as a by-product of zinc (and occasionally lead) refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth’s crust. Generally, metals are emitted during their mining and processing activities (Lenntech, 2004). As Pb-containing minerals are less soluble in water, its concentration is generally low in natural water (Venugopal et al., 2009). Groundwater may be contaminated by lead due to enrichment from either natural or anthropogenic activities in the soil and, in some cases, mineral weathering (Buragohain et al., 2010). Metal ions contamination in groundwater is mainly due to the rock minerals weathering, sewage discharge and other waste effluents on land and runoff water. Some heavy metal ions viz., cobalt and copper, are extremely essential for humans, but if present in large quantities, may cause physiological disorders. Cadmium, chromium and lead are highly toxic even in trace concentrations (Jain et al., 2010). In
general, WHO (2011) mentioned chromium (Cr) is widely distributed in Earth’s crust. Cr (VI) is a carcinogen via the inhalation route, although an NTP study has shown evidence for carcinogenicity via the oral route at high doses only.

**Anthropogenic sources**

Certain heavy elements, such as Hg and Pb, are difficult to relate to any climatic or soil formation factors as these elements are widely introduced into the environment through anthropogenic (e.g. agricultural/ industrial) sources (Semu et al., 1985; and Rieuwerts et al., 1998). For most metals, the magnitude of their input to environment is: soil> water> air (Nriagu and Pacyna, 1988). It has been observed that metal loading on the surface soils closer to industrial areas is usually higher than in residential and natural reserve areas (Zhou et al., 1997). The principal anthropogenic sources of trace metals in soils and natural waters were the dumping of urban/animal/agricultural waste and discharge of domestic and industrial (including mine and smelter) waste waters/waste waters/sewage sludge (Prahaldad and Seenayya, 1989).

**Industrial effluents**

There have been several reports on the extensive pollution of ground waters of Aligarh city (U.P.) with Fe, Mn, Cl\(^-\) and NO\(_3\)\(^-\) due to the surface disposal of sewage wastes and wastes from metal processing industries (Ajmal and Rajiuaddin, 1986). Industrial effluent from an insecticide (Paris green) producing industry led to acute As-contamination of soils and ground waters of Behala in West Bengal (Chatterjee et al., 1993). Lake Hussain Sagar in Hyderabad (AP) is a typical example of an industrially polluted lake. More than 400 industrial units, which manufacture chemicals, drugs, paints and machine tools, are located on its banks. A recent study on the Pb, Cd, Ni and Zn contamination of ground waters around Hussain Sagar lake has shown varying hazardous levels of contaminants which decreased with increasing distance from the lake (Srikanth et al., 1993). Discharge of fly ash leachates from ash disposal ponds in the vicinity of Indraprastha Power Station and Rajghat Power House have also led to elevated levels of Cd and Co in soils (Mehra et al., 1998). Another study alongside the dry riverbed of river Ganga near Kanpur industrial area (Farooq et al., 1999) has
revealed extensive heavy metal pollution of soil and fruits/vegetables of the region. DTPA extractable Cr in effluent irrigated soils around carpet manufacturing units of Gopiganj and Bhadohi areas of eastern U.P. have also been reported to be ranging between 0.84 to 19.03 mg kg$^{-1}$ (Singh et al., 2001). In general, steel producing industries are a larger source of heavy metal emissions than the refineries (Ndiokwere and Ezihe, 1990).

Zaheeruddin and Khursid (2004) revealed that the polluting load in the Yamuna basin is mainly caused by agricultural activities and discharge of industrial effluents without proper treatments. Presence of high amounts of various major ions and heavy metals in the vicinity of a leather processing zone in Dhaka city was reported by Zahid et al. (2006).

Shyamala et al. (2008) determined that the effluents from dyeing units play a vital role in toxicating the groundwater quality. According to Prashant et al. (2012), increased need for groundwater has extensively risen due to urbanization and industrialization. In addition, the growth in industries, particularly tanneries, has led to generation of enormous amount of wastes, which is distinguished by its strong colour, odour, high biological oxygen demand (BOD), high chemical oxygen demand (COD), high pH, high total dissolved solids (TDS) and high total suspended solids (TSS), and even heavy metals such as chromium and lead, leading to pollution of surface waters (Sousaslan et al., 2008). In addition to mining, contamination of the environment by radioactive elements has also occurred from extractive industries, such as those for iron, phosphorus, coal, mineral sands textile processing, pulp and paper milling and oil (Tinker and Nye, 2000; Tabrez and Ahmad, 2009 & 2010; (Omotayo et. al., 2011; Gupta and Ahmad, 2012).

**Sewage Effluents**

In cultivated lands around Ludhiana city (Punjab), increase in total Cd, Ni and Co contents in sewage effluent irrigated soil has been reported to be about 36, 86 and 46 per cent over that in tube well irrigated soils (Azad et al., 1986). In sewage effluent irrigated soils around Kolkata, maximum build up recorded was that of Zn (80 times) followed by Cd (75 times), Pb (25 times), Cu (16 times) and Cr (4 times) over non-
sewage irrigated soils (Mitra and Gupta, 1999). Under Keshopur Effluent Irrigation System of Delhi, where sewage irrigation has been practiced for last two decades, the DTPA extractable soil- Zn, Cu, Fe and Ni concentrations have been reported to be about 253, 202, 337 and 153 per cent more than the tube well irrigated soils (Rattan et al., 2000). In a similar study conducted on IARI farm being irrigated with sewage water emanating from the institute complex since three decades, DTPA-extractable Zn, Cu, Fe, Mn, Ni and Pb contents increased by 127, 200, 22, 247, 100 and 29% over adjacent soils irrigated with tube well (Datta et al., 2000). A study of sewage irrigated crop fields in the adjoining areas of Lucknow (UP) was also conducted to find heavy metal concentrations in the soils and vegetables by Singh et al. (2000). The study indicated that the fields irrigated with sewage water contained considerably higher quantities of Cd, Cr, Pb, Ni and Zn in both soil and vegetable crops samples than the canal water irrigated fields. A similar study was conducted in Yamuna canal command area of Faridabad, Haryana and it was observed that soils irrigated with polluted Yamuna canal water had higher quantities of trace elements (Fe, Mn, Zn and Cu) as compared to that with tube well irrigated soils (Gurjar and Yadav, 2005).

**Agrochemicals, Fertilizers and Soil amendments**

Fertilizers, soil amendments and agrochemicals are the other anthropogenic sources of heavy metal contamination of agro-ecosystems (Jones and Saymon, 1987). On an average, the annual Cr in the effluents emanating from ammonia and urea producing industries has been assessed at 4.8 tons (Swaminathan, 1993). Phosphatic fertilizers are a rich source of Cu, Zn, Cr, Cd and Pb. However, their concentrations in commercial fertilizers are far lower than those found in organic manures. Organic manures richness in heavy metals may be categorized as sewage-sludge > municipal solid waste > FYM > pig manure > poultry manure (Verloo and Willaert, 1990).

Coata et al. (2002) studied groundwater contamination in a rural setting, where potential contaminant sources include inorganic fertilizer. These results show that high fertilization rates and irrigation lead to increased hazards of groundwater pollution. Mukherjee et al. (2005) assessed the suitability of groundwater quality for drinking and agricultural purposes in the South 24-Parganas district of West Bengal. The results
showed that the pollution with respect to chloride, nitrate and fluoride is mainly attributed to the extensive use of fertilizers and large scale discharge of municipal wastes into the open drainage system of the area.

Ju et al. (2006) studied the annual nitrogen (N) budget and groundwater nitrate-N concentrations in the field in three major intensive cropping systems i.e., wheat-maize, greenhouse vegetables and orchard systems in Shandong province, north China. Nitrate leaching was evident in all three cropping systems and the groundwater in shallow wells (15 m depth) was heavily contaminated in the greenhouse vegetables production area, where total N inputs were much higher than crop requirements. Ju et al. (2007) further compared the effects of excessive fertilizer and manure applications on the soil environment in greenhouse vegetables systems shifted from wheat-maize rotations 5-15 years previously and in wheat-maize rotations. The study revealed that due to excessive fertilizer applications in greenhouse vegetables production in northeast China, excessive salt and nitrate concentrations may accumulate and soil quality may deteriorate faster than in conventional wheat-maize rotations.

2.2.1.3 Water Quality Parameters

The water quality is the summation of all physical, chemical, and biological properties of water, which may determine its suitability for domestic and industrial purposes. There are four basic criteria for characterization of irrigation water quality. These criteria known as water quality parameters are: (1) Total soluble salt content (Salinity hazard as EC_{iw} dS/m); (2) Relative proportion of cations and anions in terms of (i) Sodium adsorption ratio (SAR), (ii) Residual sodium carbonate (RSC), (iii) Ratio of Ca^{2+} to Mg^{2+}; and (3) Concentration of toxic elements (Heavy metals).

**Total Salt Content, EC_{iw} (dS m^{-1})**

The major constituents present in ground water are chloride, sulphate, carbonate, bicarbonate, nitrate and fluoride as anions and sodium, calcium, magnesium, potassium and some heavy metals as cations. The surface water has low salt concentration as compared to ground water due to presence of dissolved salts in tube well water (Ayers and Westcot, 1976).
Paliwal and Yadav (1976) reported that in groundwater of Delhi State, the sodium content increased with salinity while that of potassium was constant. Sodium per cent increased with salinity up to a maximum of 55 per cent while calcium was maximum at low salinity and then decreased regularly. The percentage of magnesium was less than sodium but higher than calcium and followed no definite trend with increase in salinity. In general, Delhi’s ground water was of Na-Mg-Ca type.

Paliwal and Gandhi (1976) reported that in addition to sodium, magnesium is likely to act additively in increasing sodium hazard and continuous usage of such waters was likely to show more adverse effects on the physico-chemical properties of even light textured soils.

Datta and Tyagi (1996) reported that ground water of Najafgarh and Nangloi blocks of Delhi State had higher contents of sodium and magnesium as compared to Alipur and Mehrauli blocks. At all salinity levels, relative order of dominant cations was Na>Mg>Ca. In case of anions, the percentage of chloride increased and that of carbonate and bicarbonate decreased non-uniformly with increase of salinity while sulphate content remained nearly constant (Paliwal, 1972). The precipitation of carbonate and bicarbonate ions as insoluble carbonates of calcium and magnesium at higher salinity levels appears to be responsible for such a decrease of bicarbonate as well as those of calcium and magnesium. Hence, the calcium content of the waters has been observed to be less and was nearly half that of the magnesium (Girdhar and Yadav, 1982).

2.2.1.4 Water sodicity indices

After analysis of water samples for different parameters like total salt (EC), cations and anions, it is imperative to calculate some indices in order to assess water quality and its subsequent effect on soils. Important sodicity indices used to assessment for water quality are given in the following sub-sections.

**Sodium adsorption ratio (SAR)**

High sodium in irrigation water can cause severe soil permeability problems. Meeting the crop water demand under these conditions may become extremely difficult. In addition, other problems such as seed germination, soil aeration, disease and weed
control due to surface water ponding and stagnation may need special consideration. The most commonly used index to evaluate sodicity potential of irrigation water has been the Sodium Adsorption Ratio (SAR). It is expressed as:

\[
\text{SAR} = \frac{\text{Na}}{[(\text{Ca}+\text{Mg})/2]^{1/2}}
\]

in which the concentration of cations is in me/L.

Based on the values of SAR, irrigation waters can be rated into different categories of sodicity (Richards, 1954):

- **Safe** < 10
- **Moderately safe** 10-18
- **Moderately unsafe** 18-26
- **Unsafe** > 26

**Residual sodium carbonate (RSC)**

This index is important for carbonate and bicarbonate rich irrigation waters. Permeability problems, however, are also related to the carbonate ($\text{CO}_3^{2-}$) and bicarbonate ($\text{HCO}_3^-$) contents in irrigation water which is not considered in the SAR concept. When drying of the soil occurs between irrigations, a part of the $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ precipitates as sparingly soluble carbonates of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ thus removing $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ from the soil solution and increasing the relative proportion of $\text{Na}^+$ on soil exchange complex which would increase the sodicity hazard (Eaton, 1950; Richards, 1954). RSC is calculated as under:

\[
\text{RSC (me/L)} = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})
\]

Concentrations of both cations and anions is in me/L. Alkalinity hazard in terms of RSC is categorized as under (Richards, 1954):

- **Safe** < 1.25
- **Moderate** 1.25-2.5
- **Unsafe** > 2.5
However, based on extensive survey of RSC waters regarding their effect on crop growth and soil properties, Paliwal and Yadav (1976) observed that waters up to 5.0 me/l RSC can be used for irrigating wheat crops on sandy loam soils in areas having mean annual rainfall of 600 mm or more. Paliwal and Yadav (1976) further reported that only 30 per cent Delhi ground water samples had residual sodium carbonate problem. Water samples having EC values between 2-4 dS m\(^{-1}\) had RSC value up to 5 me/L. However, in more saline waters (EC >4 dS m\(^{-1}\)), there was no RSC (Minhas, 1994; Minhas and Tyagi, 1998). Recently, Banerjee (1999) reported no residual sodium carbonate (RSC) in Delhi area adjoining Yamuna river basin. Gurjar et al. (2005) has also reported no RSC in tubewells of Yamuna canal command area at Faridabad, Haryana.

**Adjusted SAR**

For assessing the effect of SAR and RSC together, the index of adjusted SAR is considered. It is calculated by the formula:

\[
\text{Adj. SAR} = \text{SAR} \left[1 + (8.4 - \text{pHc})\right]
\]

Where Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) of SAR are in me/L from water analysis and pHc is the calculated pH of irrigation water in contact with lime under equilibrium conditions. \((8.4 - \text{pHc})\) is the Langelliar's saturation index in which 8.4 is substituted as pH of a buffered soil in place of water pH (pHa).

\[
\text{pHc} = (pk2' - pkc') + \text{p (Ca + Mg)} + \text{p (Alk)}.
\]

Here, pk2' and pkc' are negative logarithms of the second dissociation constants of carbonic acid (H\(_2\)CO\(_3\)) and the solubility product of CaCO\(_3\), respectively. pCa+Mg is negative logarithm of calcium and magnesium concentration in water (m mol/L) and p(Alk) is negative logarithm of the titrable bases (CO\(_3^{2-}\) + HCO\(_3^{-}\)) of the water (m mol/L). Standard tables are available for the values of these parameters in relation to water analysis.

Ayers and Westcot (1985) reported that Adj. SAR predicts more correctly and precisely the hazardous effect than do the older SAR and RSC indices. Based on the
nature of clay minerals in the irrigated soils, they suggested the permissible limits of Adj. SAR under increasing degree of the hazards.

**Adjusted Sodium Ratio (adj. R\textsubscript{Na})**

Ayers and Westcot (1985) gave the term adjusted R\textsubscript{Na} (Adjusted Sodium Ratio) as an improvement over the older Sodium Adsorption Ratio (SAR).

\[
\text{Adj. R}_{\text{Na}} = \frac{N_{\text{a}^+}}{\sqrt{C_{\text{a}^{2+}} + M_{\text{g}^{2+}}}}
\]

In which,

\(N_{\text{a}^+}\) = Sodium in irrigation water (meq/L)

\(C_{\text{a}^{2+}}\) = Effective calcium concentration

\(C_{\text{a}^{2+}}\) represents Ca in the applied irrigation water but modified due to salinity of the water (EC) and HCO\textsubscript{3}/Ca at estimated partial pressure of CO\textsubscript{2} in the soil surface (PCO\textsubscript{2})=0.0007 atm.

\(M_{\text{g}^{2+}}\) = Magnesium in irrigation water (meq/L)

**Magnesium:Calcium ratio**

It has now been established that calcium and magnesium do not behave equally in a soil system and magnesium deteriorates soil structure, particularly when waters are sodium-dominated and highly saline. High level of Mg usually promotes higher development of exchangeable Na in irrigated soils (Girdhar and Yadav, 1982). Based on ratio of Mg to Ca, waters are categorized as shown below:

- Safe \(<1.5\)
- Moderate \(1.5-3.0\)
- Unsafe \(>3.0\)

While formulating the equation for SAR, it had been assumed (Richards, 1954) that calcium and magnesium ions behave alike in ion exchange reactions and influence the adsorption of sodium equally. But it has been shown by Singh and Ramamoorthy (1964), Paliwal and Maliwal (1971), Paliwal (1972), Ramamoorthy et al. (1972), Prasad (1973) and Paliwal and Gandhi (1976) that calcium and magnesium in irrigation water
do not behave alike in cation exchange reactions in all types of soils and clay minerals. At the same level of salinity and SAR but with varying proportion of calcium and magnesium, higher adsorption of sodium by soils and clay minerals was observed at higher Mg:Ca ratios (Gandhi, 1973). It is because the bonding energy of magnesium is generally less than calcium and, therefore, allowing more sodium to be adsorbed. Hence, it induces more ESP at the same level of SAR if the water contains higher proportion of magnesium to calcium.

Paliwal and Yadav (1976) reported that in 64 percent water samples of different blocks in Delhi State, magnesium was more than calcium and magnesium: calcium ratio in some cases was as high as 9. However, 54 per cent of the samples had Mg:Ca ratio in the limited range of 3: 1. Datta and Tyagi (1996) also reported more magnesium than calcium in Delhi groundwater and Mg:Ca ratio in some cases was as high as 10. But, 70-80 percent cases showed ratio in the range of 2-4. However, Mg:Ca ratio did not show any correlation with salinity.

2.2.1.5 Irrigation water quality

USSL classification of irrigation water

It is based on the electrical conductivity of water in micromhos per centimeter (EC) and the sodium adsorption ratio (SAR) (Richards, 1954).

The curves were drawn by following empirical equations:

Upper curve  \[ S=43.75-8.87 \log C \]
Middle curve  \[ S=31.31-6.66 \log C \]
Lower curve  \[ S=18.87-4.44 \log C \]

Where, \( S \) = sodium adsorption ratio; \( C \) = electrical conductivity in \( \mu \)mhos/cm; \( \log \) = logarithm to the base 10. However, soil, plant and climatic parameters were not considered in this concept.

Ramamoorthy (1964) modified the USSL scheme in the higher range of salinity by introducing soil texture and salt tolerance characteristics of the plant and extended the salinity range \( C4 \) from 2,250 to 6,750 and \( C5 \) from 6,750 to 20,250 \( \mu \)mhos/cm.
maintaining the dependence of class on the logarithm of the electrical conductivity of irrigation water as originally proposed by the USSL staff. Keeping in view the chemical composition of water, soil properties, water table conditions and salt tolerance characteristics of the crop plants, a water quality classification was proposed by Bhumbla and Abrol (1972). Ayers and Westcot (1985) suggested relatively more comprehensive classification. Hence, water quality related problems were grouped in 3 headings, \textit{viz.}, (i) salinity, (ii) water infiltration and (iii) specific ion toxicity. Each of the water quality problems was further classified into three categories based upon the degree of restriction on their use. Using "none" restriction category waters implies no soil or productivity problems are expected to arise. Careful selection of crops and other management practices can maintain the yields when utilizing "slight to moderate restriction" category waters. For "severe restriction" category waters, soil problems are bound to originate and potential yields cannot be achieved even after following special management practices.

\textbf{2.2.2 GIS Techniques in Groundwater Quality Characterization}

Geographic Information System (GIS) are now recognized as a powerful tool for mapping and analyzing spatial environmental data (Sweeney, 1999; Tjandra \textit{et al.}, 2003). Praharaj \textit{et al.} (2002) investigated the levels of metal contamination in groundwater due to particulate matter fallout and leaching from ash pond and assigned contaminated indices for the adjacent localities around an ash disposable site using GIS. The study further suggested that the zone of attenuation for Ba, Fe, Cu, Mn, S and Zn in groundwater is about 600-900 m from the ash pond. Anbazhagan and Nair (2004) used GIS for groundwater quality mapping of Panval Basin of Raigarh district, Maharashtra. The final output provided a pictorial representation of suitability of the groundwater for drinking and irrigation purposes on a spatial scale.

Babiker \textit{et al.} (2007) developed a GIS-based groundwater quality index (GQI) which synthesized different available water quality data (e.g., Cl$^-$, Na$^+$, Ca$^{2+}$) by indexing them numerically as per the World Health Organization (WHO) standards. It also displayed the natural (depth of groundwater table, geomorphologic structures)
and/or anthropogenic (land-use and population density) controls over the spatial variability in the basin.

Singh and Lawrence (2007) prepared a groundwater quality map of Chennai city using GIS which synthesized groundwater quality parameters such as Hardness, pH, TDS, HCO₃, SO₄, NO₃, Ca, Mg, Cl and F by contouring methods with Arcview 3.2a. Nas (2009) prepared a GIS based for groundwater quality map of Konya, Turkey by taking 156 samples from of the wells which synthesized different groundwater quality parameters such as pH, electrical conductivity, Cl⁻, SO₄²⁻, hardness, and NO₃⁻ concentrations by ordinary Kriging method by indexing them numerically as per the World Health Organization, U.S. Environment Protection Agency and Turkish Standards Institute drinking water guidelines.

Chatterjee et al. (2010) attempted spatial distribution maps of hardness, pH, TDS, HCO₃, SO₄, NO₃, Ca, Mg, Cl, and F using GIS contouring methods with Arc view 3.2a including WQI of Dhanbad district. Idoko et al. (2012) studied the influence of changes in a season on heavy metal concentrations in rural groundwater of Benue State by taking 26 water samples from rural community boreholes and analyzed there for heavy metal concentrations (Fe, Mn, Zn, Pb, Cu) based on the WHO standards as well as their variability for both wet and dry seasons. The results showed Zn that values were higher in the dry season, while the other metals investigated had higher concentrations in the wet season. This implies that as climate becomes either wetter or drier, in concentrations of heavy metals are likely to respond appropriately.

2.3 PLANT HEALTH GROWTH AND DEVELOPMENT

It is well known that there is a wide difference among the various plant species due to genetic character with respect to absorption rate of nutrients and response to the toxic elements as well. The use of industrial effluents as irrigation caused either beneficial or toxic effects on growth and yield of different crops depending upon the loading rate of the metal salts in different effluents.

Water pollution by toxic chemicals present in industrial wastewater is a worldwide problem now. Plants exposure to micro-pollutants may occur naturally (geochemical pollution) or result directly from contaminated industrial charges or from
the discharge of effluents. All these pathways are of interest from the point of view of transfer of micro-pollutants into the human food chain following plant uptake. The influence of waste waters on the germination and early growth, yield and uptake of nutrients and micro-pollutants has been reviewed in this section. Some trace elements are essential in plant nutrition, but plants growing in the nearby zone of industrial areas displayed increased concentration of heavy metals, serving in many cases as biomonitor of pollution loads (Mingorance et al., 2007).

2.3.1 Seedling emergence

The influence of wastewaters on the growth and seedling germination had been assessed and reported by many workers (Dutta and Boissy, 1997; Siddaramaiah et al., 1998). In the majority of studies dealing with the changes of endogenous phytohormones and functioning related substances associated with pollution, generally a decrease has been reported (Reddy and Borse, 2001). Gadallah (1996) observed that the waste waters from fertilizer, oil industries and sewage had significant phyto-toxic effects on radicle growth and retarded the growth of sunflower plants. The fertilizer factory effluent inhibited 100% radicle growth resulting in the death of sunflower seedlings due to high acidity in waste waters and high content of \( \text{PO}_4^{3-} \), \( \text{Zn}^{2+} \) and \( \text{Fe}^{2+} \). The seed germination and growth of maize significantly increased up to 25% concentration of effluent but decreased at higher concentrations (Choudhary et al., 1987).

Ajmal and Khan (1983) reported that the germination in the water irrigated soil was 100%, whereas it ranged between 91 to 99% at various effluent concentrations. Germination was the quickest in water irrigated soil and soil treated with 25% effluent, whereas the seed treated with 100% effluent germinated at the end. Shoot length of plant was the highest in the control (no effluent) and 25% effluent and least in the soil treated with undiluted effluent. Further they reported that the pH of soil increased gradually with the increase in the concentration of the effluent. Hence, this alkaline effluent may be used in acidic soils. For best results, it was suggested that sugar factory effluent must be diluted before use. As observed by Bahadur and Sharma (1989) and Bhattacharya and Mukherjee (1995), a combination of heavy metals present in industrial effluent acted
synergistically and brought about overall reduction in vegetative and reproductive growth.

Srivastava (1991) evaluated the paper mill and chlor-alkali plant effluent (CAP) on seed germination of healthy seeds of radish and onion in different dilutions of effluents and revealed that the percent germination was more with lower concentrations of the effluents when seeds were treated for one to five days each. In the case of radish, at 10% concentration of the effluents, there was a significant decrease in mean root length, shoot length and secondary roots as compared to control, while no secondary root could emerge out in 100% concentration of CAP effluent. Low dissolved oxygen associated with high mercury and residual chlorine content in effluent adversely affected the germination and subsequent growth of seedlings. In okra, the germination percentage increased by 15% with tap water and 25% with spentwash (Hari et al., 1994). Gomathi and Oblisami (1992) stated that pulp and paper mill effluent could also be used for irrigating tree crops after proper dilution. Germination percentage decreased from 100 to 75% due to irrigation with paper mill effluent at 100% concentration. The length of the root and shoot and vigor index of the tree species viz., Azadirachta indica, Milletia pinnata and Tamarindus indica, decreased considerably. But on application of effluent at concentrations of 25, 50, 75 and 100% at 100 mL day\(^{−1}\), the effluent had no inhibitory effect on germination at 25 and 50% concentrations, 25% effluent was equal to that of normal water for irrigation.

Pandey and Soni (1994) stated that the lower concentration (10%) spentwash had enhanced germination in Areca catechu and Dalbergia sissoo. Muthalagi and Mala (2007) found that 100% sewage concentration on Trigonella foenum (Fenugreek) reduced the germination, length of root and shoot from 42 to 32%, 2.10 to 1.49 cm and 2.08 to 1.49 cm, respectively. This study indicated that 10% sewage showed maximum germination, shoot length and root length. Devrajan and Oblisami (1995) reported that sugarcane (Var. Co-853) is tolerant to saline conditions and, hence, it performed well at 50, 40, 30 and even at 20 dilutions of distillery effluents. Devarajan et al. (1993) also reported significantly higher cane yield in Co-771 at 50, 40, 30 and 20 times diluted effluent irrigations than water. The grain yield of rice was not affected by the effluent irrigation. The effluent used for irrigation had an EC around 3.0 dS m\(^{−1}\) and SAR around
9.0, which the rice crop could have tolerated due to its ability to withstand highly saline conditions. Moreover, as the effluent contained appreciable amounts of N, P, K, Ca, Mg and micronutrients, it would have enhanced crop growth (Srinivasachari et al., 1998). Early seedling growth and dry biomass were found to be better at 25 % concentration with continuous application. The rice seeds collected from effluent affected areas were less viable and even viable seeds showed delayed germination over control areas. The effluent having pH 8.6, BOD 870 mg L\(^{-1}\) and COD 980 mg L\(^{-1}\) inhibited germination and growth of seedling at higher concentration \(i.e.\) 90 and 100 % of effluent (Dutta and Boissy, 1997).

An increase in germination of soyabeans, black gram and green gram by 24.9, 12.0 and 34.5 per cent, respectively, was observed as a result of effluent irrigation over normal water irrigation. Similarly, shoot and root length as well as vigour index were also increased with effluent irrigation over normal water irrigation. Among the oilseed crops, good germination per cent, shoot and root length and vigour index were recorded in sunflower crop, while these parameters were reduced in groundnut, castor and gingelly crops due to effluent irrigation (Udayasoorian et al., 1999). The germination per cent, root and shoot growth of vegetables \(v\text{iz.}\) ladies finger, brinjal, tomato, amaranthus, bitter gourd, beet root and moringa were better in treated effluent as compared to raw effluent. Plant growth characters of these vegetables were higher under effluent irrigation than well water irrigation and further increase in growth was observed with the increase in the proportion of water for diluting the effluent (Malathi, 2001).

Reddy and Borse (2001) reported increase in germination count, root and shoot length of methi (Trigonella foenumgraeeum) at 25 % effluent concentration, whereas decrease was observed above 25 % effluent concentration. The effluent had high alkalinity (pH-10.8), BOD (2000 mg L\(^{-1}\)), COD (5300 mg L\(^{-1}\)) and total dissolved solids (5100 mg L\(^{-1}\)). A negative correlation was observed between germination, early growth and increase in concentration of effluent in radish and onion (Srivastava, 1991). Heavy metal rich effluent (TDS 2790 to 14988.5 mg L\(^{-1}\), Ni 16.3 to 116.8 mg L\(^{-1}\), Pb 13.6 to 282.7 mg L\(^{-1}\), Cr 12.3 to 146.4 mg L\(^{-1}\) and Co 2.3 to 56.4 mg L\(^{-1}\)) reduced percentage germination and survival of seedlings at and above 50% concentration in chilli (Capsicum annuum L.) (Siddaramaiah et al., 1998). Mariappan et al. (2001) reported that
even with the treated tannery effluent the shoot length was affected and abnormal structure was observed in the root system. The pronounced inhibition of shoot and root length was the main cause for the decrease in fresh weight and dry weight of seedlings. It was further observed that the chlorophyll content, carotenoids, carbohydrate and protein contents were reduced with increasing concentration of treated tannery effluent. With the increase in the levels of the concentration of treated tannery effluent, L-proline increased in the leaves of the plant. Mahankale and Dauore (2001) reported that in polluted water applied plot, the yield was less than unfertilized plot because the polluted water released from the tannery plant may have contained some growth inhibiting components. Further, they described that the polluted water had depressed the growth of plant due to low pH and the presence of solids in the form of dissolved solids as well as suspended solids beyond the IS standards for disposal of industrial waste water.

Mishra and Pandey (2002) observed that concentrations of effluent (10 to 50%) and 5% dilution of 20% concentration of leachate of flash light factory sludge with Hoagland solution was beneficial for the growth of the root and shoot in case of the seeds of Cicer arietinum. However, 100% concentration of effluent/leachate was inhibitory. The translocation of heavy metals viz., Cd, Cr, Ni etc., was more in roots and leaves of cabbage and pearl millet, whereas only a small amount was translocated to edible parts in cabbage head and grains of pearl millet. The contents of the metals in cabbage head were comparatively lower than those recorded in pearl millet grain. Further, results of dry sorghum fodder analysis indicated higher quantity of metals in fodder due to irrigation with effluents followed by treated and its alternate use with tube well water.

Ramana et al. (2002) conducted a laboratory experiment to study the effect of different concentrations (0, 5, 10, 15, 20, 25, 50, 75 and 100%) of distillery effluent (raw spentwash) on seed germination (%), speed of germination, peak value and germination value in some vegetable crops viz., tomato, chilli, bottle gourd, cucumber and onion. The distillery effluent did not show any inhibitory effect on seed germination at low concentration except in tomato, but in onion, the germination was significantly higher (84%) at 10% concentration as against 63% in the control. Irrespective of the crop species, at highest concentrations (75 and 100%), complete failure of germination was
observed. The rate of germination, peak value and germination value also followed a similar trend and a concentration of 5% was found to be critical for seed germination in tomato and bottle gourd and 25% in the rest of the crops. Based on the tolerance to distillery effluent, the crops studied have been arranged in the following order: cucumber > chilli > onion > bottle gourd > tomato. So the effect of the distillery effluent is crop-specific and due care should be taken before using the distillery effluent for pre-sowing irrigation purposes.

Sharma et al. (2002) conducted bioassay studies to assess the toxicity of raw and diluted distillery effluent on seed germination, seedling growth and pigment content of sugarbeet by collecting effluent samples from the main whole of the Sri Ganganagar Sugar Mill Factory, in Rajasthan. Seeds kept moist in different dilutions (1, 5, 10, 20 and 30%) of effluent solution, along with double distilled water, which served as the control, revealed that higher concentrations (>5%) of effluent were toxic, however, the effluent can be used for irrigation purpose after proper dilution. Sharma et al. (2002) studied the effect of fertilizer factory effluents (0, 1, 2, 5, 10, 25, 50 and 100%) on seed germination of tomato cultivars PED, Pusa Ruby and Rupal-I. The percentage germination step by step decreased with rising concentration of effluents. Germination increased with 25% effluent concentration. Higher concentrations (50 and 100%) showed adverse impact on germination. Dixit (2003) studied the effect of fertilizer factory effluents (0, 1, 2, 5, 10, 25, 50 and 100%) on seed germination of tomato cultivars PED, Pusa Ruby and Rupal-I. The percentage germination gradually decreased with increasing concentration of effluents. Germination increased with 25% effluent concentration. Higher concentrations (50 and 100%) showed a negative impact on germination.

Bansal (2004) revealed that the soils and plants under sewer water irrigation had higher concentrations of Zn, Cu, Cd, Pb, Cr, Ni and Mn as compared to fields irrigated by underground water. He stated that judicious use of sewer water in soils of Aligarh district for a long period would increase the metal concentration in crops much beyond the toxic limit. Heavy metal contamination in the environment is becoming a serious problem from the human health point of view. A number of factors are responsible for this type of pollution viz., geo-climatic conditions of the region, rate of industrialization, rate of urbanization, improper waste management, other anthropogenic causes etc.
Almost all the trace elements that contaminate the system get readily absorbed by the plants and are then passed on to animals and are toxic at levels slightly above those required for maintaining normal metabolic activities of the body (Chakraborty et al., 2004). Jaja et al. (2004) observed the effect of Pb, Cu and Fe compounds on germination and early seedlings growth of two tomato seed varieties (NHLe 158-3 and ROMA VF). Lead and Copper indicated higher inhibitory tendencies to the germination and growth of the tomato varieties than the ferric compound. NHLe 158-3 variety is more tolerant to metallic compounds pollutants than the ROMA VF. Similar results were observed in *Pisum sativum* (Kevresan et al., 2001), *Paspalum distichum* and *Cynodon dactylon* (Shua et al., 2002), *Lens culinaris* (Kiran and Munzuroglu 2004), *Plantago major* (Kosobrukhov et al., 2004) and *Albizia lebbeck* (Farooqi et al., 2009).

Thiruvanuldevi et al. (2006) evaluated the seed quality characters of neem with industrial effluents *viz.*, tannin, textile dyeing, cement, rayon pulp and automobile both as raw and in different dilutions (10-50%) and found that on irrigation with raw material the reduction in germination was minimal due to tannin and rayon pulp irrigation, whereas the irrigation with dyeing and automobile effluent inhibited the germination completely. Continuous irrigation with effluent was, however, found to cause seedling damage, which was severe with textile dyeing, tannery and automobile effluents. However, the diluted effluent increased the germination and seedling vigour compared to raw effluent. Lie et al. (2008) observed that Cadmium is a highly toxic contamination that affects *Jussiaea rapens* metabolic process. Shafiq et al. (2008) observed the effect of various concentrations like 25, 50, 75 and 100 ppm of lead and cadmium on seed germination and seedling growth of *Leucaena leucocephala*. They reported that the rate of seed germination, root growth and dry weight decreased from 75 ppm, 50 ppm and 25 ppm in both metals as compared to control. Cadmium showed comparatively more pronounced effects at 100 ppm in *Leucaena leucocephala* seedlings as compared to lead.

Rehman et al. (2009) reported that the effect of soil extract of korangi and landhi industrial areas prominently suppressed seed germination, shoot length, and root length, etc. in some vegetables (*Hibiscus esculentus* L. and *Cyamopsis tetragonoloba* L.) and flowering plants (*Zinnia elegans* Jacq and *Helianthus annus* L.). Ogunwenmo et al. (2010) observed the effect of various concentrations like 50% and 100% of brewery,
textile and paint effluent on germination and seedlings growth of leafy vegetables namely, *Amaranthus hybridus* and *Celosia argentea*. They reported that brewery effluent improved seed germination in *Amaranthus hybridus* while textile mill was only effective at lower concentration up to 50% at 2 h presoaked period. Paint effluent would require clean-up, maximum dilution and short presoaking period below 30 min to yield any appreciable result in *Amaranthus hybridus*. None of the effluent was suitable for *Celosia argentea* but may be slightly tolerant to paint diluted effluent where water is scarce. Generally, Paint and textile wastewater inhibited seed germination and became toxic at higher concentrations. Ling *et al.* (2010) studied the impact of mercury on germination, seedlings growth and root elongation of vegetables (*Brassica oleracea* and *Brassica campestris*). They observed the detrimental effect on germination, seedlings growth, coleoptile growth and root elongation with increase in concentration of mercury. Mercury stress was more sensitive to vegetables in terms of coleoptile growth and root elongation than seed germination.

Akinci *et al.* (2010) investigated the effects of chromium on seed germination and early seedling growth of melon (*Cucumis melo* L.) with different concentrations (0, 2.5, 5, 10, 25, 50, 75, 100, 200 and 300 mg l\(^{-1}\)) at germination stage, and (0, 2.5, 5, 10, 20, 30, 40, 50, 60 and 70 mg l\(^{-1}\)) at early seedling stage. Overall germination rate, germination index, mean germination time and germination uniformity index values decreased with increase in the concentration of chromium at germination level but radicle length, radical fresh and dry weight, hypocotyl length, hypocotyl fresh and dry weight, growth tolerance index and seedling relative growth rate were negatively affected by increased chromium concentrations at the seedling stage. Rahman *et al.* (2010) observed a reduction in seed germination and seedling growth in chickpea treated with 50, 100, 200 and 400 ppm of nickel and cobalt. Houshmandfar *et al.* (2011) studied the effects of mixed cadmium, copper, nickel and zinc on seed germination and seedling growth of safflower with different concentrations (0 60, 120, and 180 mg kg\(^{-1}\)) which were made up of equal amounts of cadmium (¼), copper (¼), nickel (¼), and zinc (¼). Results showed increasing the concentration of heavy metal mixture to 180 mg kg\(^{-1}\) significant decreased seed germination as compared to control treatment (p<0.01). A negative response of root and shoot length of safflower to heavy metal mixture
application relative to control treatment was observed at 120 mg kg\(^{-1}\) (p<0.01). The heavy metal mixture treatment of 60 mg kg\(^{-1}\) exhibited the lowest percentage of tolerance in germination and seedling growth characteristics of safflower as compared to control.

Aswani et al., (2011) conducted a study on accumulation of heavy metals (Cd, Zn, Fe, Ni and Pb) in seed oil of medicinal plant - *Momordica charantia* (bitter gourd). The concentrations of metals Cd (0.09*10^3µg/L), Fe (104.35*10^3µg/L), Cu (3.53*10^3 µg/L) and Ni (8.94*10^3 µg/L) were observed. The presence of trace metals such as Cu, Fe, Cd, Pb, and Ni is known to have adverse effects on the plants and human health.

Valasange et al. (2012) conducted a study to evaluate the effect of mixed chromium, copper and lead on seed germination and seedling growth of maize variety 'Safed Ganga', under controlled light and temperature conditions. Treatments included 0 (control), 60, 120, and 180 mg/kg which were made by equal amounts of chromium, copper and lead. The heavy metal mixture treatment showed toxic effects on seed germination and seedling growth of maize. Increasing the concentration of heavy metal mixture to 180 mg/kg showed a significant decrease in seed germination as compared to control treatment.

2.3.2 Enzyme activity

Heavy metals stress can induce three possible types of metabolic modification in plants: (i) alterations in the metabolic pool to channelise the production of new biochemically related metabolites which may confer resistance or tolerance to Cr stress e.g., phytochelatins, histidine (Schmfger, 2001); (ii) alteration in the production of pigments which are involved in the life sustenance of plants e.g., chlorophyll, anthocyanin (Boonyapookana et al., 2002); and (iii) increased production of metabolites e.g., glutathione, ascorbic acid as a direct response to heavy metals which may cause damage to the plants (Shanker, 2003).

Low concentration of copper treatment resulted in an increase in the seedlings while the reverse was true at higher concentrations (Deef, 2007). Amylase activity showed lower level in plants with increase in concentration of heavy metals (Devi et al.,
So, it resulted in accumulation of soluble saccharides and polysaccharides in seeds due to their negative effect on amylase activity.

Cu and Mn treated seedlings of maize showed inhibited amylase activity which may be due to enhanced peroxidant status (Ahmed and Trifu, 1980). Heavy metals stress affected the enzyme activity by reducing the antioxidant glutathione pool and affecting the iron mediated defence processes (Pinto et al., 2003). Heavy metal effect on proteolytic system cannot be generalized, however, impairment of proteosomes functionality and decreased protease activity seems to be a common feature involved in metal toxicity in plant (Mishra and Dubey 2006; Pena et al., 2008). Zinc (Zn) causes a decline in protein content and a corresponding rise in the activity of hydrolytic enzymes such as protease due to heavy metal stress. It is likely that heavy metals stress induced senescence through enhancement of catabolism of key metabolites such as chlorophyll, protein and RNA (Khudsar et al., 2004). Plants responded to oxidative stress by distinct antioxidative defence mechanisms. The key components include enzymatic and nonenzymatic antioxidants. The enzyme components include superoxide dismutase (SOD), catalase (CAT), peroxidase and enzymes of ascorbate glutathione cycle (Bowler et al., 1994).

Induction and activation of superoxide dismutase (SOD) and of antioxidant catalase are some of the major metal detoxification mechanisms in plants (Prasad, 1998; Shanker et al., 2003). Gwozdz et al. (1997) found that at lower heavy metal concentrations, activity of antioxidant enzymes increased, whereas at higher concentrations, the SOD activity did not increase further and catalase activity decreased. A similar increase in lipid peroxidation, in terms of malondialdehyde formation, was observed with these treatments. In E. colona plants supplemented with Cr at 1.5 mg L^{-1}, activities of peroxidase and catalase were higher in tolerant calluses than in non-tolerant ones (Samantaray et al., 2001).

Samantaray et al. (1999) used peroxidase and catalase activities as enzyme markers for identifying Cr tolerant mung bean cultivars. In wheat cultivar, cv. UP2003, the application of 0.05–0.5 mM Cr decreased activities of both enzymes (Sharma and Sharma, 1996). Sen et al. (1994) observed a decrease in catalase activity and increase in peroxidase activity at concentrations above 10 µg L^{-1} Cr(VI), whereas the enzyme
activities were least affected by Cr(VI) at lower concentrations. The calli derived from *L. leucocephala* growing on contaminated soil when supplemented with 15 AM Cr, exhibited higher catalase and peroxidase activities than those from the uncontaminated soil. This provided evidence that plant material from contaminated sources were physiologically distinct from the uncontaminated ones (Rout *et al.*, 1999). The increase in antioxidant enzymes activity observed might have been in direct response to the generation of superoxide radical by Cr induced blockage of the electron transport chain in the mitochondria. The higher increase noticed due to Cr (VI) indicated that Cr (VI) addition probably generates more singlet oxygen than Cr (III). The decrease in the activity of the enzyme as the concentration of the external Cr increased may be because of the inhibitory effect of Cr ions on the enzyme system itself. Stimulation of reduced glutathione (GSH) biosynthesis was observed under stress conditions in poplar trees (Noctor *et al.*, 1998).

Toppi *et al.* (2002) reported that GSH levels ranged from about 30 nM SH g\(^{-1}\) fresh weight (FW) of root extracts to 300 nM SH g\(^{-1}\) FW of leaf extracts in maize, tomato and cauliflower plants following a Cr(VI) treatment at concentrations of 5 and 10 mg L\(^{-1}\), which were higher than control levels. Glutathione pool dynamics of sorghum was affected in terms of GSH and GSSG and the GSH/ GSSG ratio, by Cr speciation stress, indicating that there is a possible role of this pathway in countering Cr stress (Pathmanabhan, 2004). There was a marked decline in the GSH pool under Cr speciation stress, more severely in roots. Several authors have observed oxidation of different cellular thiols such as GSH and cysteine by Cr (VI) in *in vitro* studies (McAuley and Olatunji, 1977). Dichromate reacts with GSH at the sulphydryl group forming an unstable glutathione CrO\(_3^-\) complex (Brauer and Wetterhahn, 1991). Thiolate complexes of Cr (VI) with g-glutamylcysteine, Nacetylcysteine and cysteine have also been described (Brauer *et al.*, 1996). The interconversion of reduced and oxidised forms of glutathione to maintain redox status of the cell as well as to scavenge free radicals could have caused a decrease in GSH. Metal-binding peptides like metallothionein have increased under Cr (VI) stress (Shanker *et al.*, 2004).

Bhardwaj *et al.* (2009) investigated the effect of excess Pb on physiological and biochemical attributes of *Phaseolus vulgaris* L., and observed that the activity of
antioxidative enzyme as ascorbate peroxidase (APX; EC 1.11.1), glutathione reductase (GR; EC 1.6.4.2) was increased while Catalase (CAT; EC 1.11.1.6) activity decreased with increasing concentration of Pb. Anjum et al. (2012) reviewed about modulation of glutathione and its related enzymes in plants in response to toxic metals and metalloids. A differential degree of increase in GR activity (3-5 folds) was reported by Reddy et al. (2005) in Macrotyloma uniforum and Cicer arietinum to 200, 500 and 800 ppm concentration of Pb when compared to the respective controls. Morsy et al., (2012) reported that accumulation of heavy metals induced oxidative stress in both species Zygophyllum species (Z. album and Z. coccineum). Both Zygophyllum species alleviated oxidative stress via increased antioxidant enzyme activities. The root PM lipid composition of Zygophyllum species was altered in response to heavy metal pollution. Some of the PM lipid changes may be in a direction favorable to restore optimum membrane properties and functions. Increased antioxidant enzyme activities as well as PM lipid alterations may enable both Zygophyllum species to withstand the prevailing stressful environment.

2.3.3 Yield and Morphological Parameters

Crops like sugarcane have been found to withstand the application of concentrated paper mill effluents without showing any adverse impact on the yield, whereas cereals like wheat and rice grow only after dilution to BOD levels of 500-10000 mg L⁻¹. Significant higher yields of sugarcane and the increase in available N content of soil were obtained with 200 kg N per ha supplied through spentwash; however, the yield and available N decreased when 300 kg N/ha was applied through spentwash (Agarwal and Dua, 1976).

Chu and Wong (1987) reported accumulation of Cd, Cu, Mg, Pb and Zn in many vegetable crops like Brassica chinensis, Daucus carota and Lycopersicum esculentum grown in polluted areas with sewage sludge. Pande (1994) determined the physiochemical characteristics of sugar factory effluents and distillery vanishes at Nawabganj and also studied the fresh and dry biomass of crops (gram, maize, pigeon-pea and wheat) in relation to the dilution of the effluents (0%, 5%, 10%, 25%, 50%, 75% or 100%) used in irrigation. Both effluents had poor transparency and tended to be warm with no
dissolved oxygen particularly in vanishes, dissolved CO$_2$ concentration was low while BOD and COD were high. Sugar factory effluent was rich in sulphate and bicarbonate, while vanishes had low pH and high conductivity, total nitrogen and calcium content plus considerable amounts of ammonia and phosphate. Adverse effects on crop yield was noted at doses of 25-100%, 5% or 10% sometimes had beneficial effects with the impurity content acting like normal fertilizer.

The total dry matter production of different crops showed considerable variation in the response to the application of spentwash at varying dilutions. With the exception of onion, there was a regular increase in the yield with the decrease in the dilution of spent wash. In case of onion, maximum yield was obtained at 50 times dilution level (Zalawadia and Raman, 1994; Raman and Zalawadia, 1997). Athar et al. (2001) investigated the toxic effect of certain heavy metals (Cd, Pb Ni, Mn, Zn and Cr) on the growth and grain yield of wheat (*Triticum aestivum* L.). Heavy metals significantly reduced growth and grain yield with Cd being the most toxic metal followed by other heavy metals. Cui et al. (2004) defined the metal transfer factor (TF) from soil to crop as the metal concentration in the crop (dry weight) divided by the metal concentration in the soil (dry weight) in which the crop was grown. Rattan et al. (2005) computed metal transfer for various crop grown in sewage irrigated soils. In case of Zn and Fe, MTFs (metal transfer factors) for the crops grown on sewage effluent irrigated soils were lower than that for crops irrigated with tubewell water. There was no linear relationship between crop uptake and metal content to food chain (Plants) is concerned, Ni has greatest potential, followed by Zn, Fe, Mn and Cu.

Rattan et al. (2005) studied the long term impact of sewage irrigation on the uptake of metals by various crops grown on sewage irrigated soils of west Delhi. Rice grain accumulated much higher amount of Zn and Cu grown on sewage – irrigated soils compared to tube well water-irrigated soils, while slight increase in Ni content was recorded. Manganese content in rice grain for sewage-irrigated soils was much lower than that for tube well water-irrigated soils. Although sewage effluents- irrigated soils exhibited much higher amount of DTPA-Fe, it was not reflected in Fe content of rice grain. Wheat had elevated contents of Zn, Cu, Fe, Mn and Ni grown on sewage-irrigated soils compared to that produced with tube well irrigation. Sorghum accumulated higher
amount of Fe, Cu and Ni on sewage effluents irrigated soils, while Zn and Mn contents were lower than its background level. Maize showed higher accumulation of all the elements on sewage effluent irrigated soils. Spinach grown on sewage-irrigated soils accumulated higher amount of Zn, Cu and Ni than those grown on tubewell water-irrigated soils, whereas the trends was reverse for Fe and Mn (Rattan et al., 2005).

Liu et al. (2005) reported that MTF for Cd varied greatly between the crops. The MTF values for Cr and Pb are similar. The high values of Cd and Zn from soil to crop indicated a strong accumulation of both by crops. In some crops (Lactuca sativa L., Brassica oleracea), Cd concentration was much higher. They suggested that heavy metals transfer from soils to plant was a key pathway to human health exposure to metal contamination. Soundarrajan and Pitchai (2007) found that application of spentwash diluted at higher level (50 times) increased germination percentage, growth, fruit yield and fruit quality of okra in a pot culture experiment. In a study conducted by Yadav, and Meenakshi, (2007) to assess the toxicity of effluent on seedling germination, seedling growth, biomass and crop yield of Raphanus sativus var. Pusa Chetki (Raddish) and Hibiscus esculentus, Versha uphar (Okra), it was observed that the germination percent decreased with increased in the effluent concentration.

Muhammad et al. (2008) studied the impact of heavy metals (Pb, Cu, Cr, Zn and Cd) on different parts of the vegetables (spinach, coriander, lettuce, radish, cabbage and cauliflower) grown in an effluent irrigated field in the vicinity of an industrial area of Faisalabad, Pakistan. The leaves of spinach, cabbage, cauliflower, radish and coriander contained higher concentrations of heavy metals as compared to other parts (stems, roots) in each vegetable. Quishlaqi et al. (2008) reported that the crops cultivated on wastewater irrigated soils around Shiraz suburban area of SE Iran showed high level of heavy metals as compared to those grown on tube well water-irrigated soils. However, no significant variation was found in the levels of these metals among the examined crops is found. The results indicated that the highest transfer values belonged to Cd (1.4-34.2) compared to Zn (0.21-0.28). The high transfer factor values for Cd from soil to crop indicated a significant accumulation of this element by vegetables confirming its high phytoavailability in soils. This also indicated that as far as entry of these heavy metals into the food chain is concerned, spinach and lettuce have the greatest potential
for Cd human exposure risk assessment. It is clear that an elevated level of metal accumulation in edible parts of vegetables plants is mainly from their growth media like water and soil. Long-term consumption of these metal-contaminated vegetables can cause different disease like thalassemia, dermatitis, brain and kidney damage, as well as cancer in the human body. Similar trends of bioconcentration factor for heavy metals in different vegetables studied were in the order Cu > Pb > Zn > Cd > Ni > Fe > Cr, which were more or less similar to the reported values (Khan et al., 2008).

John et al. (2009) investigated the effect of heavy metal toxicity (Pb and Cd) on plant growth, biochemical parameters and metal accumulation of Brassica juncea L. with different concentrations of Cd (0 µM, 150 µM, 300 µM, 450 µM, 600 µM, 750 µM, and 900 µM) and Pb (0 µM, 150 µM, 300 µM, 600 µM, 900 µM, 1200 µM, 1500 µM). Overall growth of plant exhibited a decline in growth, chlorophyll content and carotenoids with Cd and Pb. However, the content of protein was decreased by Cd (900 µM) to 95% and by Pb (1500µM) to 44% at the flowering stage. Proline increased at lower concentration of Cd and Pb but at higher concentrations, it showed a decrease. More Cd and Pb were accumulated in roots than shoots. Ahmad et al. (2010) conducted a study to investigate the concentration of heavy metals (Cu, Zn, Pb, Cr, Cd, Fe and Ni) in soil and vegetables grown in an industrial area in Bangladesh. The order of metal concentration was Fe>Cu>Zn>Cr>Pb>Ni>Cd in contaminated irrigation water, and a similar pattern Fe>Zn>Ni>Cr>Pb>Cu>Cd was observed in soil.

Yaqvob et al. (2011) conducted a study to evaluate the response to two tomato varieties (Barakat and Local tomato) to ordinary heavy metals (Fe, Pb and Cu) in northern of Iran. They observed that some heavy metals in higher doses may cause metabolic disorders and growth inhibition for most of the plant species. Borah et al. (2012) investigated the effect of heavy metal toxicity (Cu, Zn and Pb) on the growth, development, chlorophyll and proline content of Pisum sativum with different concentration of Cu, Zn and Pb (100, 200 and 400 mg/kg). Overall growth of plant exhibited a decline in growth and development with Cu, Zn and Pb. However, drastic fluctuations were observed in Chlorophyll content, regarding the concentration of chlorophyll a and b in the treatment plants, compared to control. In the first estimation (after 30 days of germination of seeds), high proline content was observed in all the
treatment plants compared to the control (except Cu 100 mg/kg and Zn 200 mg/kg), and in the second estimation (after 60 days of germination of seeds), the amounts decreased except in a few of the treatments compared to the data obtained in first estimation. Experiment showed that higher the concentration of heavy metals the more is the toxic effect to *Pisum sativum*. Zinc and Lead were more toxic to the plant compared to Copper.