CHAPTER 1

INTRODUCTION

1.1 Background

Since the awareness of global pollution, various studies have been undertaken on wet precipitation, dry deposition, cloud water, moss analysis, dew and snow samples to assess the atmospheric pollution. These studies have provided useful information on environmental status of places around the world. With rapid economic and industrial development, environmental status has been degraded and at the same time efforts have been made to restore it. Study of wet and dry deposition has become very important benchmark for measuring environmental purity.

In advanced countries, studies related to environmental degradation and restoration have began in early sixties, much before it was apprehended in underdeveloped countries. Most of the earlier studies were undertaken in the USA, Europe, UK, and later also in the Southeast Asian countries. Several studies used bulk samplers, some used wet only samplers. Sample duration varied from seasonal to sub-event, but most of the works reported event-based sampling. Parameters estimated included major anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, HCO$_3^-$, etc.) and cations (Na$^+$, K$^+$,Ca$^{2+}$, Mg$^{2+}$, etc.). Dissolved materials were measured in some cases. Some studies concentrated on only trace element measurement. Important aspects of the study of wet precipitation and runoff quality are briefly reviewed below.
1.2 Literature Review

1.2.1 Chemical Composition Of Wet and Dry Deposition

Urban dust resuspended by winds and vehicular traffic and other human activities was presumed to be a strong source of dry particle deposition in cities. In Athens, wet only values for calcium and potassium were high compared to other European cities. Dikaikos et al.(1990) attributed the high calcium content to limestone, which was predominant constituent of soil and air borne dust in Athens and potassium was attributed to marine sources.

In early times most of the studies were made on rain water acidity and SO$_2$ and NO$_x$ as criteria. In the relatively clean coastal locality in Northeast England, the rainfall pH was found to be related to local SO$_2$ concentration in the atmosphere. There was evidence that between 1978 and 1982 rain water acidity decreased with a decrease in the SO$_2$ level slightly. Corelation coefficients for pH with SO$_2$ are -0.5 and -0.45 for two sites.(Wharfe et al.,1985).

The variation of precipitation quality at rural sites in Northern Europe from one year to another had been attributed to meteorological factors. Declining trends in the concentration of sulphate in precipitation was most pronounced at Eskedalemuir in Scotland, conforming to the reduction of SO$_2$ in United Kingdom.(Semb and Dovland, 1986).
The diurnal and seasonal variation in chemical composition of wet precipitation was studied at Long Island, New York, during 1983-'85. Among the ions NO$_3^-$ showed strong diurnal variations (maximum at around noon), but lacked a seasonal dependence. In highly concentrated samples NO$_3^-$ was more abundant than SO$_4^{2-}$. Sulphate on the otherhand showed a weaker diurnal and seasonal variation than NO$_3^-$. Both Na$^+$ and Cl$^-$ exhibit seasonal variation, high in winter. Chemical composition of precipitation data showed a much narrower distribution in summer than in winter and there was the possibility of more metal cation involvement with NO$_3^-$/SO$_4^{2-}$ in winter (Lee et al., 1986). Measurement of precipitation chemistry at Shimane, on the Japan Sea coast revealed that major ion concentrations were very close to each other in the three stations except in sea salt concentration. Nearly 70% of sulphuric and nitric acids were neutralized by ammonia and calcium content in precipitation. Maximum concentration was observed in winter and minimum in summer e.g. mean concentration of calcium in January was 89.1 µeq/l and 4.4 & 3.2 µeq/l in June –July. (Yamaguchi et al.1991). At Dhahran in Western Arabian Gulf Coast, Nitrate and sulphate contribute equally to precipitation acidity and Ca and Mg in alkaline suspended particulates had the major contribution in buffering the acidity of precipitation (Ahmed et al. 1990). The diurnal and seasonal variations in chemical composition of wet precipitation were studied at Long Island, New York during 1983-85. In Washington State, bulk precipitation was studied at two high elevation sites during winters of 1983-85. The precipitation content had low SO$_4^{2-}$/NO$_3^-$ concentration, (SO$_4^{2-}$ concentration at Stevens Pass site were 5 0-7.0 µeq/l in 1983-84 and 7.4-13.0 µeq/l in 1984-85) despite having an urban industrialized region in the studied area, which was due to an interplay of the meteorological and washout factors unique to the region (Duncan et. al, 1986).
In Albany, New York, precipitation was acidic during the period 1986-88. Major contributions to acidity were $\text{SO}_4^{2-}$ and $\text{NO}_3^{-}$. Maximum $\text{SO}_4^{2-}$ concentration 713 μeq/l and $\text{NO}_3^{-}$ concentration of 176 μeq/l were observed during June and April respectively. Among the cations $\text{NH}_4^+$ and $\text{Ca}^{2+}$ had the highest concentration of 186 μeq/l and 51 μeq/l respectively. Acidity increased in summer and spring and decreased in winter. $\text{NH}_4^+$ and $\text{Ca}^{2+}$ were the major neutralizing component for these acids. High acidity of precipitation was attributed to a combination of direct influences from fossil fuel combustion and long range transport of pollutants (Khwaja and Husain, 1990).

In Mount Carmel, Israel, during the period 1989-92, the wet precipitation was found to be strongly acidic in about 40% of cases and distinctly alkaline in about 12% of the events. $\text{SO}_4^{2-}$, responsible for acidity was believed to be imported from Central or Eastern Europe via Mediterranean Sea. In contrast, bulk sample on the same site had a higher pH 6.35 in bulk fall, compared to 4.33 in wet fall due to high $\text{Ca}^{2+}$ 87 μeq/l to 42 μeq/l in wet fall and $\text{K}^+$ concentration in the local aerosols emanating from calcareous soils. (Singer et al. 1993). Marine rainwater was also studied during 1986-88 at a coastal site in western Mediterranean Sea and during a Trans Atlantic cruise. Acidity was due to $\text{NO}_3^{-}$ and $\text{SO}_4^{2-}$; the relative contribution of $\text{NO}_3^{-}$ was higher in Atlantic Ocean site than those in Mediterranean site. Acidic (pH-4-5) rains were attributed to anthropogenic $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$. High values (pH-6-7) were explained by neutralization of strong acids by natural alkaline dust, such as calcite, transported from desert area of African continent (Losno et al. 1991).
In 1987, bulk precipitation in suburban area of Tokyo, Japan was studied and origin of soluble species were evaluated and showed that solutes were derived from three sources, viz sea salt, acid substance and CaSO_4. Excepting Na, Mg, Ca most of other measured ionic component concentration increased in summer than the corresponding spring values (Tsurumi et al.1990). In contrast to the above works; the rainwater acidity in the Central Amazon, Brazil was attributed to organic acid. The study during the period 1988-’89, and comparison with earlier works revealed that atmosphere over the Central Amazon had a considerable capacity to dilute the byproducts of large-scale deforestation. The composition of rain appeared to be derived from a constant source of oceanic and rain forest aerosols and not significantly influenced by local biomass burning (Williams and Fisher, 1997).

Some studies had been undertaken to assess the pollution effect in urban and suburban areas and enhanced precipitation weighted concentrations (PWCs) for the urban sites in most of the major ions have been observed. Sodium and sulphate, ions were found approximately equal in both urban and suburban (3.3 for both Na\(^+\) and 75.8-76.9 for SO_4\(^{2-}\) \(\mu\)eq/l . [H\(^+\)] was lower at urban than at suburban (68.4 for urban and 74 for suburban). When the suburban site was upwind of the urban site, concentrations of all major ions except Na\(^+\) were higher at urban site (Sisterson and Shanon, 1990).

Though studies on seasonal variation are limited, literature showed two distinct trends in Europe and in the U.S. European measurements showed highest H\(^+\) concentration values in winter, whereas in U.S., highest concentrations were in summer. The differences in concentrations and seasonal variations of major ions in Manchester, U.K.
The role of atmospheric conditions in influencing the biochemical cycles in forests has been well recognized. Atmospheric conditions to which forests are exposed differ regionally. One such study of atmospheric deposition in conifer forests in U.S. and in Federal Republic Of Germany during year 1987 revealed that precipitation concentration of all ions except $H^+$ were higher at German site than in U.S. site, most significantly for the nitrogen species. The weighted mean concentrations for $NO_3^-$, $NH_4^+$ were 24 and 17 μeq/l in U.S. site and 41 & 52 μeq/l in German site. The concentration differences of sulfate, potassium and magnesium ions in wet precipitation at two sites in U.S., Germany were of the same order as their atmospheric concentrations in aerosols (Lindberg et al., 1990). Successive rain samples were analyzed in two forest areas in Denmark and Netherlands. Results revealed highest concentrations of many ionic species ($Na^+$, $Cl^-$, $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$ and $NO_3^-$) in the initial fraction of most rain events, followed by decreasing concentrations in subsequent samples (Hansen et al. 1994) When atmospheric deposition covering large areas in Western Switzerland was studied, inputs of major and trace elements were not found to be statistically different in space. Factors contributing to homogeneity of the region were also studied during the period 1990-1991. Among the ionic components $Ca^{2+}$ (0.81mg/l) was most abundant, followed by $SO_4^{2-}$ (0.58mg/l) and $Cl^-$ (0.56mg/l), $N-NO_3^-$ (0.48mg/l) (Atteia, 1994). In Ankara, Turkey, study of chemical composition of wet precipitation during the period 1993-94 showed substantial contribution of surface soil on acidity of precipitation during summer, indicating significant neutralization of
acidity due to high atmospheric loading of CaCO$_3$ in summer. Annual average pH in precipitation was 4.7, episodic rain events showed fairly low pH. During summer, soil was identified as the source of some of the pollution derived elements. The total volume weighted average concentration of Ca$^{2+}$ was 2.64 mg/l and SO$_4^{2-}$ was 2.5 mg/l, followed by NO$_3^-$ (2.2 mg/l) (Kaya and Tuncel, 1997).

Among the studies of seasonal variations in precipitation chemistry, the one during 1992-95 in La-Selva, Costa-Rica, with high volcanic activity provided a better understanding of the true seasonal patterns in a region. The study revealed seasonal increase in the marine aerosol and nutrient content of precipitation during dry season and that sometimes-seasonal pattern were only present when conditions became extreme, such as during severe dry periods. Na$^+$ and Cl$^-$ were most abundant and varied from 2.2 - 165 µeq/l and 3.0 - 203.0 µeq/l respectively (Eklund et al., 1997). Wet precipitation was studied in Wales during 1995 and the precipitation chemistry was found to be dilute (overall mean conductivity of 23 µs/cm) acid (overall mean p$^H$ 4.88) and dominated by sea salts. Maximum concentration of sea salts occurred in first three months of the year and maximum excess sulphate (2.94 mg/l), nitrate (0.38 mg/l) and ammonium (0.57 mg/l) concentration occurred during summer months. Excess sulphate was a significant component of the acid anion loading in wet precipitation (Reynolds et. al., 1999). In Amman, Jordan, wet precipitation had marine influences as well as desert dust influence. High levels of Ca (average concentration 293.9 µeq/l) and SO$_4^{2-}$ (average concentration 248.8 µeq/l) were attributed to desert dust (Jaradat et. al. 1999). In Istanbul, Turkey same study revealed mostly neutral to alkaline character of precipitation. High concentrations of sulphate (0-150 mg/l) and nitrate (0-70 mg/l) during
December to March was for urban heating demand. Ammonium and calcium predominated in the summer period neutralizing the acidity (Gülsoy et. al. 1999).

Precipitation samples were studied along altitudinal gradient in the northern Pennines in U.K. during the period 1993 - 1995 Na\(^+\), Mg\(^{2+}\), Cl\(^-\) and marine SO\(_4^{2-}\) in bulk precipitation showed maximum values in spring and minimum in summer, indicating a consistent seasonal pattern. Precipitation chemistry at the lowest elevation site was found to be strongly influenced by local sources (Taylor et al., 1999). In Caecilian basin (1996-97), northeastern Mediterranean Sea, 28% of rain samples were acidic against a 58% of alkaline character. Acidity was highly variable with pH range 3.5-7.6. Mineral dust from arid regions contributed significantly to the neutralization of acidity with its high CaCO\(_3\) content. Precipitation pH varied with the influence of air trajectories (Ozsoy and Saydam, 2000). Fossil fuel combustion and agricultural activities led to high levels of NO\(_3^-\) (400 kg N Km\(^{-2}\) y\(^{-1}\)) and NH\(_4^+\) (310 kg N Km\(^{-2}\) y\(^{-1}\)) deposition in the northeastern part and central part respectively of Mississippi river basin. The study indicated that about half of the nitrogen emitted within the basin possibly be transported eastward to be deposited outside the basin (Lawrence et al., 2000).

Besides wet precipitation, fog water, cloud water, snow, dew, and moss species emerged as a subject of study to assess the environmental status of a region. They have quite good relations with wet precipitation chemistry. Southern Californian fogs were frequently found to be hundred times more acidic than rain in the same area (Hileman, 1983). The fog water collected at river site California had high concentration (26000 μM of NH\(_3\), 29000 μM of NO\(_3^-\) and 6200 μM of SO\(_4^{2-}\)) (Munger et al., 1990). Fog water
analysis allowed the identification of two probable sources of acidity in Strasbourg, France, to be automobile traffic and a refuse incinerator near the town (Millet et al., 1996). The solubility of polyvalent cations in fog water was studied in Strasbourg, France and observed that the variation in solubility could possibly be due to the presence of organic acid in fog water (Millet et al., 1995). When rain and snow samples from same regions were analyzed, the values were found comparable to each other. Concentration in rain samples were higher than the snow samples for some elements viz. Ca, Si, Mg, K, NO₃⁻ and SO₄^{2-}, B, V, Mn, Ba and Pb (Atteia, 1994). Substantial work had been done on chemical composition of snow (Naik et al., 1995; Hautala et al., 1995; Loranger et al., 1996) and yielded very useful information regarding environmental impact of air pollution sources and transport, deposition of air pollutants.

On the other hand, cloud water research revealed that ionic species in cloud water were generally five times more concentrated than in rainwater. Mean SO₄^{2-} concentrations were 84 μeq/l and 13 μeq/l, Cl⁻ 478 μeq/l and 62 μeq/l, Na⁺ 316 μeq/l and 46 μeq/l in cloud water and rain samples respectively (Vong et al., 1997). The sulphate concentration in cloud water was lower than in rain in Dhahran, having significant anthropogenic sources of sulfur. Excepting Na⁺, Cl⁻, SO₄^{2-}, NO₂⁻, other ion concentrations were similar in cloud water and wet precipitation samples (Schemenauer and Cereceda, 1992)

Chemical composition of dew was studied in Amman, Jordan and was compared with contemporary rain samples. Both rain and dew were found to be of neutral acidity with
the buffering effect of CaCO₃. Total dissolved solids were higher in dew than rain samples of same period (Jiries, 2001).

1.2.2 Trace elements in wet precipitation

Natural processes and anthropogenic processes along with industrial processes, such as metal refining and fossil fuel combustion have led to a substantial increase of trace elements in the atmosphere. Toxic effects of various elements to terrestrial and aquatic ecosystem are well known and therefore their estimation in our environment has become essential. With the introduction of sophisticated instruments / equipment, precise estimation of these elements has become possible. Atmosphere, via wet and dry deposition, is a significant source of many trace elements to ecosystem. Since the elemental concentrations are significantly influenced by human activities, their study is of crucial importance for environmental management.

From time to time, various studies had been undertaken on the trace element composition of rainwater all over the world. Some studies concentrated on only one element. Montiel, (1974) studied vanadium in wet precipitation and found that in Paris region, V content in rainwater was proportional to quantity of fumes present in atmosphere. In cold season, the V content in rainwater in Paris region rose to around 135 µg/l. It was found that V content was inversely proportional to the depth of precipitation event. With lead, the fallout of V from the atmosphere was found very rapid. Sulphur and iron can be used as indicators to assess the general chemical status of precipitation and quantitatively correlated with deposition rates of host of elements. The low boiling point elements and compounds As, Br, Cd, Cl⁺, F⁻, K⁺ & NO₃⁻ were best
correlated with S and these were highly enriched in smoke and fumes from igneous processes as combustion, metallurgical operations etc. The terrigenic elements such as Ba, Ce, Co, Cr, Cs, Se, Sn and Th were found to be better related with Fe. Again Fe and S were significantly correlated ($r = 0.55$) (Hallet et al., 1985).

Among the trace elements, atmospheric lead concentration correlates strongly with petrol lead in Perth, Western Australia during the period 1982-87. The relation describing the regression line is given as

$$\text{Pb (Atmos)} = a \cdot \text{Pb(Petrol)} + b,$$

where Pb(Atmos) was mean annual average atmospheric Pb concentration in $\mu g/m^3$ Pb(petrol) was the annual petrol-Pb consumption in Tonnes.

The coefficients $a$ and $b$ were $3.86 (0.07) \times 10^{-3}$ and $-1.83(0.07)$ respectively. (O'Connor et al., 1990). The high degree of correlation confirmed the claim of O'Connor et al.(1977) that atmospheric Pb in Perth Central Business District must be dominated by vehicular emitted Pb. In Sweden, the trace metal concentration in atmospheric precipitation was highest in southern Sweden and decreases northward. Enrichment factor indicated anthropogenic origin of these elements and believed to be derived from long range transport from the rest of Europe. Fe was most abundant (Max 350 $\mu g/l$) among the metals studied. Cd was less abundant (Max 0.77 $\mu g/l$). Cd, Pb, Zn concentrations had similar seasonal variations, being highest in February, March and April. On the other hand Cu, Fe, Mn peaked in spring (Ross, 1987). Generally, the levels of trace elements in wet precipitation and in air, found in South Holland were low. Compared to the toxic values for aquatic organisms, the Cd and Pb concentrations
in precipitation were too high in South Holland. The marked difference of Pb concentration from 167 μg/m³ to 38μg/m³ was believed to be due to introduction of unleaded petrol. There was a quite good relation between dry deposition and bulk precipitation of trace elements. Dry deposition constitutes about 10% to 50% of the bulk precipitation (Daalen, 1991). Observation from rain and snow studies in Western Switzerland revealed that concentrations and fluxes were typical for slightly contaminated European regions. Region was found to be homogenous despite difference in altitude and human influence. Most of the elements originated from sea water and continental crust, as also from human activities. In this study trace elements were categorized into three groups according to their concentration. Zn with an average concentration around 20μg/l Fe, Ba, Mn, B, Cu, Sr and Pb were abundant with their concentrations between 2 and 8.0 μg/l and Ni, Cr, V, Rb were found with their concentration lower than 1 μg/l (Atteia, 1994). Atmospheric input played a major role for some of the trace elements' fluxes - Cu, Pb, B, V and also Zn and Mn (Atteia et al., 1993).

Pb is one of the toxic metals that induce pollution on global scale. A major part of the lead burden of the biosphere appeared to be related to the commercial use of organolead compound in gasoline. Rainwater and snow from two sites in Croatia contained ionic alkyllead in the concentration range of 10-280 ng/l of Pb. Most abundant alkyllead compounds were found to be trialkyllead derivatives. An increased level of ionic alkyllead was observed during winter in rain, which was absent in snow. Organic and total lead deposited by wet precipitation in urban areas of Croatia represented only a small portion of lead compounds emitted from vehicles (Mikac and Branica, 1994). Wet deposition of metals over tropical north and South Atlantic Ocean
and parallel sampling of seawater enabled the estimation of recycling rates of sea salt components. This revealed a net trace metal flux from the atmosphere into ocean in the vicinity of inter tropical convergence zone. Recycling rates of Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn ranged from a minimum of $7 \times 10^{-4}$ % (Co) to a maximum of 75 % (Al). Trace metal concentration in southwestern Atlantic precipitation seemed to be connected to anthropogenic sources (Helmers and Schrems, 1995). In Norwegian background sites, the concentration of trace elements was found to be variable in space and time, reflecting distances to the major emission sources, wind direction and precipitation amounts. The concentration ranges of trace elements in Norwegian background stations were found to be similar to those found in western Europe by other investigations. However, the concentration of trace elements varied widely among the stations. V concentration in one station was 2-5 times the concentrations at other stations. The Pb contents (0.3-45 ng/ml) and (0.57-76.0 ng/ml) at two stations were 15 times than that measured in another stations (0.16-3.8 ng/ml). Majority of the elements showed their maximum concentrations in winter and spring seasons (Berg et al., 1994). The element concentration in precipitation in Ankara in Turkey was comparable with concentrations reported for other urban areas. Crustal elements showed high concentration during summer season, while anthropogenic elements did not show any well-defined seasonal cycles. The lack of industrial activity in Ankara had profound influence on temporal behavior of elements (Kaya and Tuncel, 1977). In Northern Europe, rainwater was studied at different distances and wind directions from the emissions of the Russian nickel ore mining and roasting–smelting industry. Regional variation in element content was found to be much greater than temporal variation. Concentration of elements reflected the distance from industrial plants. Majority of the heavy metals showed
enrichments of two to three orders of magnitude in their median levels close to industrial activity in Russia, compared to background levels in Finland. Median concentrations of Pb for composite summer sample varied in the range 0.56–6.3 µg/l. Maximum medium concentration of Cu, Cr, V and Mn were 231, 0.47, 3.51, 3.6 µg/l were observed (Reimann et al, 1977). In Amman, Jordan, heavy metal concentration varied considerably between stations and precipitation events. Zinc was most abandoned among the heavy metal and showed a significant correlation with lead (r = 0.80), indicating a common source for these two heavy metals. Maximum mean concentrations of Pb, Zn, Cu, Cd among the three stations observed were 135, 840, 100 and 82 ppb respectively (Jaradat et al, 1999).

Heavy metal and trace element content was studied in dew, snow as well as in cloud water and found to be useful tool, for assessing the level of contamination in an urban area. Heavy metal content in dew was highest in winter due to fossil fuel combustion for heating purposes. It was also found that heavy metal content in dew was lower than that in rain water during the same period (Jiries, 2001). Manganese and other trace elements were studied in snow at different distances from an expressway. Average concentrations of trace elements for the top layer were significantly higher near the expressway compared to increasing distances from the expressway. The average Mn concentrations in the top and bottom layers ranged from 0.003–0.035 mg/l. In decreasing order, the average concentrations varied in the top layer as follows: Na > Ca > Mg > Al > Fe > Zn > Cu > Mn > V and in the bottom layer Na > Ca > Mg > Al > Fe > Cu > Zn > Mn > V. The study revealed a direct contamination of the snow by road activities and an important deposition of trace elements near the roadway (Loranger et al, 1996).
In Arabian Peninsula, most of the trace elements in cloud water existed in one or two orders of magnitude less than the maximum concentration allowed by the drinking water guidelines. Majority of the elements had anthropogenic origin. In most cases the concentrations of trace elements were below the method detection limit (Schemenauer and Cereceda, 1992).

Along with wet deposition, several studies have been performed with regard to dry deposition – element concentration. In some cases, dry deposition and wet deposition rates have been studied. Chan et al., (1986) studied both wet precipitation and dry deposition in Ontario. He found that in general wet deposition was greater than dry deposition throughout all stations for all parameters. Geographically the wet deposition to dry deposition ratio was fairly constant for large particles (Fe, Al, Ni, Cu), but it increased in the case of fine particles (Pb, Mn, Zn, Cd) away from the source. The comparison of wet and dry depositions indicated that wet deposition processes remove higher amount of metal from the atmosphere than did dry deposition. This was found to be significant in case of Zn and Pb. The study reveal that air of Budapest was rather polluted even with elements emitted generally from the soil (Ti, Fe, Mn, K, Ca) and in the city other pollutants Pb, Zn, As were in higher concentration (203, 136 and 21.9 ng/m³) than those found in Hungarian background conditions (10.4, 21.8 and 3.69 ng/m³) (Molnar et. al, 1993). Most of the elements found in the air in southeast England were found to be crustal and anthropogenic origin. The relative low concentration of the elements in aerosols at a North Sea Coastal site was explained by the fact that transport from the west generally associated with greater wind speed and often with frontal systems and rainfall which efficiently remove contaminants resulting in lower
concentration of aerosols at this site. The concentration range of Pb (1.3-196 ng/m³), Cd (0.05-5.4 ng/m³), Zn (1.4-237 ng/m³), Mn (1.1-86 ng/m³) were observed (Yaaqub et al., 1991). Element concentrations were also studied in air in Wuhan, a city in Central China. Crustal elements such as Si, Al, Cu and Fe were found primarily in the coarse fraction and combustion related elements (Zn, Pd) were predominantly found in fine fractions. Some of the element concentrations in fine and coarse particles were Al (0.70 and 8.3 μg/m³), V (0.005 and 0.017 μg/m³), Pb (0.35 and 0.071 μg/m³) and Se (0.035 and 0.003 μg/m³) respectively (Waldman et al., 1991). At the Turkish coast of the North Eastern Mediterranean sea, the concentration of crustal elements (Al, Fe) in atmospheric particulate increased by an order of magnitude during March-May and October-November due to invasion of desert particles. The concentration of anthropogenic elements as Zn and Cd reached their maximum levels during the dry season (Kubilay and Saydam, 1995). Atmospheric Pb was widely studied in Brisbane, Australia during 1979-91, the monthly average Pb concentration increased in the winter and decreased in the summer season. It was noticed the Pb levels had markedly decreased since the introduction of unleaded patrol as fuel for vehicles. However close to roadways, the seasonal variations of Pb levels were weak (Simpson and Xu, 1994).

1.2.3 The Indian Situation

In India, several studies were made during 1965 and 1974. Rainwater pH was measured in Delhi during 1965 – 66 and found to be in alkaline range (Khemani et al., 1987). Total suspended particle and water-soluble components were measured in 1980 in Delhi (Khemani et al., 1985). In Bombay region, during 1974, rain samples were measured for major ionic components with acidity. All the rainwater was alkaline with
soil-oriented elements Ca and Mg except in the highly industrialized area of Bombay, where the pH was low (Khemani, 1974; Sequeira, 1976). The pH of rainwater in Delhi, which was in alkaline range during 1965-66 remained alkaline even after a period of 12 years (Khemani et al., 1985). During 1978, monsoon rain was found alkaline, pH values were in the range: 7.0 - 8.4 (Subramanian and Saxena, 1980).

Forest areas were also included for wet precipitation study. Rao et al. (1995) studied rainwater chemistry during 1989-'90 over a forest area in Silent Valley Forest in south India and found the precipitation pH to be slightly acidic, the average pH of rainwater was 5.31. They also studied the throughfall chemistry in the same forest and found that quality of precipitation falling on the forest was altered during a brief but significant interaction with plant surfaces, with an average pH of throughfall was 6.38 indicating that throughfall was more alkaline than that of rainwater.

With passing of period, the atmospheric conditions change over a place. The precipitation was acidic in Chembur, Trombay, in 1974 (Sequeira, 1976), which became less acidic in 1990 (pH 5.87 - 7.05). The variation was attributed to the change in use of fuel from high sulphur coal to natural gas and partly to the pollution control measures adopted by the industries (Khemani et al., 1994).

In India as early as 1982, wet deposition of some of the trace elements was studied at Deonar (Bombay). The power law exponent of 0.6 was found suitable to describe the relationship between Cd, Pb, and Cu in wet deposition and rainfall amount of monsoon rain. The concentration of Cd, Pb and Cu ranged from 0.05 - 0.2 µg/l, 0.35 - 3.2 µg/l, 0.5 - 19.7 µg/l respectively (Ashawa et al., 1985). Trace element concentrations in air at
an industrial area in eastern suburban Bombay (India) were found to be much higher. Concentration of some of the elements – Fe (2.95 and 5.06 µg/m³), Si (3.59 and 9.48 µg/m³), Na (5.87 and 8.20 µg/m³) were found to be quite considerable at two sites (Sharma and Patil, 1992). Earlier studies on wet and dry deposition on same place established that in general wet deposition was greater than the dry deposition (Chan, 1986).

**Quality of fog, snow, etc.**

Earlier studies observed that fogs were frequently 100 times more acidic than rain in the same area (California) (Hileman, 1983). The chemical composition of fog in Delhi, North India with reference to the influence of alkaline particulates was studied for the first time in 1985. The fog water was found alkaline (pH 6.4 – 7.6). The soil-oriented component Ca²⁺ was sufficient to neutralize the small amount of acidity in fog water (maximum concentration of Ca²⁺, Mg²⁺, Na⁺, K⁺ were 28.4, 6.3, 25.0 and 22.5 mg/l respectively (Khemani et al, 1987). Fog water was studied in Delhi during 1989 - 90 winters and it was found that Ca²⁺, Na⁺, Mg²⁺, K⁺ were the dominant species. It was slightly acidic (pH 6.2- 6.9). The presence of soil oriented components Ca²⁺, Mg²⁺, K⁺ were found in high concentrations (Maximum Concentrations were 2021 µeq/l, 337.4 µeq/l and 309.5 µeq/l respectively (Kapoor et al, 1993).

### 1.3 Surface Runoff Quality

From time to time, various studies had been undertaken from very early times to assess the impact on recipient water bodies from the pollutant contamination in urban runoff water. Urban runoff pollution can essentially be characterized by runoff quantities and
pollutant concentration. When a decision on the handling of storm water is to be made, it is of the greatest importance to have full knowledge of storm water quality. Urban storm water pollution loads on the receiving water are a matter of great concern in many developing and developed cities. Runoff from street surfaces contains significant loads of heavy metals and organic compound and these are generated by traffic activities, pavement degradation, and atmospheric deposition (Grottker, 1987; Sansalone and Buchberger, 1997).

Pope et al. (1978) attempted to quantify discrete materials arising from various sources and relate them to such variables, like storm intensity, storm duration, runoff volume, climatic condition and traffic volume using continuous monitoring procedures. A series of low intensity precipitation events within a short period of time removing soluble materials from the road surface in a 'gradual flush' leaving little to be removed in subsequent storm, thus 550% in flow velocity correspond to a net decrease of 32% in TDS. He also assumed a constant traffic flow, which inferred a constant rate of application of contaminants; hence the mean storm concentration of contaminants in the runoff after a given antecedent period will be dependent of total runoff volume. In early seventies, average urban storm water was found to have less contamination than the urban snow content from the same area, in Goteborg, Sweden. About 57% of the suspended solid and 31-65% of the heavy metals could be removed from the street surfaces by sweeping which otherwise enrich the runoff water. The difference in the Zn and Cu contents of fallout and storm water was explained by the corrosion of building materials and Pb from the lead emission by motor vehicles. For each of the parameters
analyzed, storm water content was much more enriched, as compared to atmospheric fallout in terms of precipitation amount (Malmquist, 1978).

Among the heavy metals Pb, Cd, Zn, Cu were studied in most of the investigations of surface runoff water. In Essen, Germany Pb concentration exhibited a reduction following the use of unleaded fuel. Zn concentrations were higher because of safety fences. Cu was more abundant in runoff than Cd. In dissolved portion, Cd content was highest. Nearly 85% of Cd was dissolved in highway runoff. Cu and Zn showed concentrations between that of Pb and Cd (Dierkes and Geiger, 1999).

Storm water runoff samples from highways were studied for petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAH) and a variety of trace elements. The study suggested that highway runoff could contribute over 50% of the annual pollutant load of solids, PAHs, Pb and Zn entering an adjacent river. The concentration of various pollutants in highway runoff varied within a storm event. All the pollutants, eg suspended solid, petroleum hydrocarbon, Pb, Cd, Cu, Fe exhibited high concentration during first flood. Pb & Fe and some other pollutants exhibited a subsequent concentration peak in the second flush and several pollutants showed a concentration peak between the flushes, which was explained by reduced dilution effect. The variation of concentrations of all pollutants was found unrelated (Hoffman et al., 1985).

Makepeace et al. (1995) reviewed several papers studying urban storm water qualities and its impact on receiving water bodies. His work presented all contaminants with their existing concentration ranges and compared with drinking water and aquatic guidelines.
The toxicity effect of the contaminants and their probable sources were discussed contaminant wise. Metals were found to be subjected to changing conditions in storm water systems like aerobic/anaerobic conditions and pH. Adsorption, precipitation, dissolution, deposition, dissociation, complexation, transformation and biochemical reactions were the different processes involved with the removal of the contaminants. The metals in a form(s) that is available to the biological population, only was of concern. Free metal ions and weak inorganic complexes tend to be the most toxic to aquatic life.

Urban runoff can be categorized into three different types, viz.,

(i) Runoff arising from roofs covering 54.5% of the urban surface area,
(ii) Runoff from streets - representing 23 % and
(iii) Runoff from courtyards, gardens and public areas, constituting the remaining 22.5 %.

All three categories of runoff were studied in Paris for S.S, COD, BOD₅, Hydrocarbon, Cd, Cu, Pb and Zn. Median concentrations for S.S. (92.5ppm), COD (131mg/l), BOD₅ (36mg/l), HC (508 µg/l) and Cu (61 µg/l) were highest for street runoff among roof runoff and yard runoff. Pb concentration (median) of 133 µg/l in street runoff was more than the maximum concentrations for level 2 water quality in France. The heaviest hydrocarbon load in street runoff was accounted due to traffic related origin. Solids were found to be main vector of pollution in street runoff (Gromaire-Mertz et al., 1999). Settling velocities of street runoff particles were much lower than these measured at
storm sewer outlets, median velocities varied from < 0.001 cm/s to 0.023 cm/s of street runoff against 0.2 cm./s on an average for storm sewer outlets (Chebbo, 1992).

In cities belonging to advanced countries like Japan, there have been combined and separate type sewer systems to cope with rainwater and sewerage. However during heavy showers, such systems cause problems at discharge destinations causing pollution of rivers and lakes. In such a situation, one study concentrated on characteristics of runoff water and discharge loads from separate type sewer systems during rainfall. Only BOD₅, COD, S.S, T-N and T-P of runoff and rainwater were evaluated. The analysis of rainwater was carried out to determine rainfall pollution levels. During initial rain, an extremely high concentrated first flush was observed. After the second peak, the concentration became low due to dilution decrease of remaining pollution load . The values of BOD, COD, S.S in rainfall were negligible with regard to discharge, but that of T-N and T-P couldn't be ignored (Uchimura et al, 1997).

Urban highway runoff was studied in heavily loaded urban roadway in Cincinnati, Ohio during the year 1995. It was found that runoff water from paved surfaces transported a wide variety of solids ranging from sub micron particles to gravel size aggregates. Particle size 9500 microns to 25 microns had been studied. Pb, Zn, Cu, Cd were analyzed on rainfall runoff and snow melt washoff. The study revealed that smaller particles (< 850 microns) were transported in snowmelt washoff. Cu, Zn, Pb concentrations increased with specific surface area (SSA) or equivalently decreased with particle size for all rainfall and snow events. Zn content on solids from rainfall events was significantly higher than for snow events. In contrast Pb concentrations were
higher on solids for the first snow event compared to solids in rainfall runoff, however the case was reversed in the second snow event. Cd was found to be very mobile element and mainly dissolved in street runoff. (Sansalone and Buchberger, 1997) In Taejon and Chongju cities of Korea, urban stormwater runoff was studied with the quality parameters BOD₅, COD, S.S., TKN, NO₃-N, Total P, PO₄-P, Pb, Fe and n-hexane, during the period 1995-97. It was revealed that pollutant concentrations in runoff of residential watershed were higher than those of the industrial watershed in case of most of the investigating parameters (Lee and Bang, 2000). In this study event mean concentration (EMC) was used to characterize runoff constituents and found that the relative magnitude of EMC in wet weather was 2 to 20 times higher than in dry weather for the constituents S.S. and n-hexane extracts, e.g. EMC for S.S. was 53.3 for dry weather, against 655.5 for wet weather and for n-hexane extracts 26.2 for dry weather against 216.2 in one station.

Urban stormwater runoff has been considered as a major source of heavy metals in receiving waters. Lead accumulation in our environment is a matter of concern. Therefore, Pb emerged as a subject of study in stormwater runoff. Pb in stormwater runoff arising from painted structures was studied in an urban setting. The study revealed that Pb concentration strongly depended on paint age and structure type. The concentrations were in the order (>10 y) > (5-10 y) > (0-5 y). All samples showed particulate Pb as a major fraction of the total Pb. It was found that Pb content in synthetic rainwater wash was contributed by the release of small Pb containing particulate. Maximum Pb concentration for wood and brick structures with more than 10 years old paint finishes were 1900µg/l and 28000µg/l (Davis and Burn, 1999).
The majority of constituents in road runoff was associated with particulate material and therefore accumulates in the sediments of receiving streams (Hewitt and Rashed, 1992). Quality of street runoff and its impact on receiving water bodies in Eastern England was studied during 1996. The study involved sediment and invertebrate samples from nine East Anglian Rivers near the trunk road crossings and found no major impact on macro invertebrate community in the test samples due to road runoff. There was no overall metal contamination (Pb, Zn, Cd) at sites downstream of the trunk roads as evident from sediment and invertebrate metal analysis. Stream sediment metal concentration had no consistent relationship with invertebrate metal concentration (Perdikaki and Mason, 1999).

1.4 Environmental impact of Wet Precipitation and Surface Runoff

Atmosphere plays a very important role in the biogeochemical cycles of elements in the environment. (Galloway et al., 1982). Atmospheric gaseous and particulate emissions from anthropogenic, natural and industrial sources are redistributed, transported and finally wet precipitated and dry deposited in areas away from their sources. S and N oxides are emitted to our environment from various sources and these are washed out by wet precipitation. Conversion of these gases into sulfuric and nitric acid is fast in rain droplets (NRC, 1983) resulting in acid rain. Acid precipitation has been one of the major problems to our environment. Acid rain damages vegetation, acidifies the lake water, deteriorates ancient monuments and marble structures. (Sullivan, 1985; Cheng et al., 1987; Vocom, 1979; Skoulikidis, 1983. Proton released by strong atmospheric acids induces progressive soil acidification (De Vries et
al., 1989). Trace elements in wet precipitation can be accumulated in the top soil (Ulrich, 1985), which raise the soil toxicity for living organisms. (Kabata-Pendias and Pendias, 1985). Acid rain could affect the solubility of trace metals, and consequently their availability for terrestrial or oceanic ecosystems.

Atmospheric pollutants are removed from the atmosphere by the scavenging action of rain and these pollutants end up at the surface of the earth and transported partially to the ground water. Therefore acid rain increases the soil acidity, enrich the soil with various constituents of rainwater.

Pollutant deposition on plant material is a possible cause of the forest disease observed in many parts of Europe and North America (Georgii and Pankranth, 1982; Ulrich and Pankranth, 1983). Such forest diseases cause forest decline and therefore lead to local climate change (White & Driscoll, 1987; Losno et al., 1988);

In semi arid region, Jordan's water resources depend mostly on rainwater for ground water recharges. Therefore, contaminants in rain water can tremendously affect the ground water reserves (Jaradat et al., 1999). A pH variation in wet precipitation could affect the solubility of some compounds and consequently their availability for the biological components (White and Driscoll, 1987; Losno et al., 1991). NH₃ and NO₃-N in rainwater were considered as a source of plant nutrients (Eriksson, 1959). Early studies linked the acidification of Scandinavian lakes and declining fish population with rainfall acidity, resulting from long range transport of Sulfur compounds in European atmosphere (Sweden, 1972; Fowler et al, 1980, as quoted in Ahmed et al., 1990). In Kingdom of Saudi Arabia, air pollution emission of SO₂ and NOₓ with other pollutants,
coupled with high concentration of suspended particulate, extremity of temperature and relative humidity were believed to be responsible for serious material corrosion problems affecting metal structures, concrete works and shortening the life expectancy of equipment and machinery (Graedel and Schwartz, 1977; KFUPMRI, 1983).

1.5 Aim of the present work

Wet precipitation has been the subject of intense study in developing countries. Guwahati city has been developing rapidly and in Guwahati city, such work on wet precipitation and surface runoff composition has not been made till date. In view of the city's thick population, congested streets, haphazard growth of industries, it has become essential to make such a study so that evaluation of the change in environmental quality can be monitored in due course of time. Overcrowded streets and roadside garbage contribute significantly to the enrichment of runoff water. Garbage disposal of the city is inadequate to keep the city in a clean environment. Certain major ions and heavy metals are seen to enrich runoff water significantly. Thus it is felt worth analyzing both rain and runoff water in certain points covering most of the city.

The principal objectives of this study were therefore:

(a) Determination of major ions e.g. Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻, F⁻ in wet precipitation and surface runoff during individual rain events,

(b) Determination of trace elements viz. Fe, Mn, Zn, Pb, Cu, Sb, Se, Ni, Cr, V, B, Ba, Sr in wet precipitation and surface runoff as above,
(c) Characterization of wet precipitation and surface runoff with respect to conductivity, alkalinity and hardness, etc.,
(d) Elucidation of the probable sources of the pollutants and the trace elements,
(e) Drawing conclusion about the general quality of wet precipitation and runoff in Guwahati and
(f) Suggesting measures for maintaining environmental purity with respect to precipitation and also for related research work to be undertaken in future.

1.6 A Brief Description of the City Of Guwahati

The city of Guwahati is situated in a very picturesque scenario. On its north, there flows the river Brahmaputra, the south and the eastern sides are surrounded by two rows of semi circular hillocks. The cardinal points of Guwahati are 26°10' north latitude and 92°49' east longitude. Amingaon area on the northern bank of the river Brahmaputra is also included in greater Guwahati area. The master plan area of the city along with the principal physical features is shown in Fig. 1.1.

The old city lies in a horseshoe shaped valley surrounded on the north by the river Brahmaputra and on the other three sides by low hills comprising Kharghuli and Chunchali hills in the east (maximum height 216 m), Japorigog, Nilachal and Fatashil hills on the south and the famous Kamakhya hill on the west (maximum height 303 m). The average elevation of the valley is about 52 m from the Mid Sea Level, along with many higher and low pockets within this area. To the west of the city lies the Jalukbari-Azara plain, where the Deeparbeel and its adjoining low-lying areas are located. Amingaon -North Guwahati areas on the north of the river Brahmaputra is situated in
flat plain interrupted by some small rolling hillocks. Bounded by the hilly ranges on the north, Khashi-Jaintia hill ranges on the south and east and Fatasil hill on the west, lies the broad plain, with an extent 15 km from north east to south west and an average width of about 4km.

Guwahati is situated on the fringe of hard rock formations. There are two distinct geological formations. The alluvial plains of the Brahmaputra are interrupted by Inserbergs formed by gneisses and schist. The alluvial plains also include the marshy tract that comprises the Deepar beel area. The valley fill areas consist of clay, silt and sandy clay, sands and gravels.

The climate is homogenous over the city. The principal characteristics are cold and foggy winter, a moderately cool spring and a fairly hot and humid summer. The whole year can be divided into three periods. From February to May, the weather is, mainly dry and moisture less, heat is moderate. In the month of March, the northeast wind carries the dry sand from the river and makes the whole atmosphere dusty. In April-May, rain along with thunderstorms is very common. From June to October, there is sufficient rainfall and the heat is oppressive until August, with excessive humidity. From November to January, the weather is cool and foggy, with very little or no rain at all. The prevailing wind direction of Guwahati is from northeast to southwest during winter months, while it is from southwest to northeast during summer.

Early settlements centered in the Guwahati plain along the river Brahmaputra and gradually extended towards the south and west, to the hills as well as to the low lying.
areas, which have caused extensive water logging and drainage problems. Now the city has become very congested and heavy traffic on the narrow city streets pose a great problem to the inhabitants.

Main source of water supply for the city is the river Brahmaputra. Besides this, people have to depend on individual water supply from underground water reserves, as the city doesn't have any integrated water supply system to serve the entire city.

Guwahati city has no under ground sewerage system, with the exception of some individual townships. Majority of the areas within the Guwahati municipal corporation has individual septic tank system without any collective disposal of effluents. As regards the general garbage, the city does not have any scientific system. The city alone produces 600MT of garbage per day during the period 1998.

The natural topography of Guwahati is such that the rainwater of the whole area on the south bank of river Brahmaputra are carried by river Bharalu and river Basistha to Deepar Beel and ultimately discharged into the river Brahmaputra via Khana river on the west. However with the rapid increase in build-up areas, the capacities of these natural channels become inadequate resulting in frequent flooding in low-lying areas. The city does not have any scientific drainage system. The main drainage channel of the city, the Bharalu River is also been used for discharge of refinery waste.

The development of a city depends on the functional needs of the city, its problems and inadequacies. Till now various functions of Guwahati city are as follows:
(a) The city functions as a state capital,
(b) It functions as an administrative centre, holding administrative hierarchies of state, regional, divisional or zonal, district and local level,
(c) It functions as a trade and commerce center,
(d) The city functions as an industrial centre owing to its location, transportation facilities and operational advantages,
(e) It is an educational centre of special order,
(f) It functions as a transportation node, being the gateway of entire North- Eastern region of India comprising seven states

**Land use Plan 2001 for Guwahati City:** Considering the circulation pattern, topography of the city and various aspects of Guwahati City, the land use plan was proposed scientifically. Barring the hills areas and low lands, industrial, residential areas are scientifically distributed. In the proposed land use distribution, lands are allocated separately for residential, commercial, industrial, public and semi public uses, parks and play grounds, transportation, green belt, water bodies and hill areas and areas for special use of government.

Master plan for land use plan 2001 envisages distribution of residential areas in terms of self-contained residential entities, around major work centres. For residential purpose, an additional area was proposed in this plan to accommodate increasing population.
Total area earmarked for residential purpose comprises 29.42% of the total Master Plan area.

Commercial use. Various commercial sub centres and market places developed throughout city in addition to the commercial development along the major roads. Some shifting had occurred from the existing patterns and godowns in the Fancy Bazaar area has been proposed to be shifted gradually to the outskirts of the city. An additional area of 30 hectares was proposed for expansion of main city commercial centre at Fancy Bazaar. Along G.S. Road and H.B. Road, commercial development was anticipated. The total commercial area proposed under the plan accounts for about 2.5 % of the Master Plan area.

Public and Semi Public Use: This category is earmarked for multiple use like government and semi-government offices, educational institution, health facilities, socio-cultural and religious institutions etc. Unit no.2 (Fig. 1) has been earmarked for most of the major office complexes and an administrative complex for better coordination amongst the offices. For educational institutions, expansion is envisaged and lands for educational institutions are provided at planning unit and sectoral levels. No city level new hospitals are envisaged. It was proposed that each planning unit would have its own dispensaries and health centres to serve the communities of the unit. Cultural institutions of different orders are provided at all levels. Various recreational centres and parks have been developed in most of the units as proposed. There is state zoo cum botanical garden in unit 1, several swimming centres in units 1, 2, 3, 4 and 6, international level stadiums at unit 4 and 6, exhibition grounds in unit 3, 8, and 9 etc.
There are four industrial estates in Guwahati at Bamunimaidan, Bonda, Kalapahar and Rani for setting up of small scale and cottage industries.

**Circulation Pattern.** The valley area is surrounded by low hills comprising Kharghuli, Chunchali hills in the east, Japorigog, Nilachal, Fatasil hills on the south and Kamakhya hill on the west. Beltola plain, where the population has grown at a very high rate, is also surrounded by hills on all sides. Therefore emissions of all kinds in these valleys are circulated within the hilly boundaries, before being dispersed out of the valleys.

Guwahati city is having all kinds of transportation systems namely road, railway, air and water, of which road and railways play the predominant role. Among the roadways, the city consists of highways, as well as other state and district roads. The national highway, NH-37 links Guwahati with upper Assam and other neighbouring states like Nagaland, Meghalaya, Manipur, Tripura and also with the rest of India. Almost all-important places of the region are linked with Guwahati through roadways.

Guwahati is connected by rail linkages with the rest of the countries and all important places of Assam. The rail services run on diesel fuel. The main railway line goes through the heart of the busiest portion of the city, creating constant noise and disrupting road traffic on north-south direction. However, several overbridges and level crossings ease the traffic on the north-south direction to some extent.

The city and various localities have been connected through independent road pattern. There is no uniformity of road width and structure. Some roads are made of complete
earth; some are made of gravels and black topped with tar. The truck terminals are also near the busy city areas. The traffic volume is large enough and the city roads are inadequate to bear the traffic load, resulting in congested city roads and frequent traffic jams. Guwahati City is the main administrative centre, main business and educational centre of the entire Northeastern region, and therefore generates considerable road traffic. All kinds of traffic, such as, heavy trucks, buses, three wheeled carrier transports, four wheeled cars, and two wheeled motorcycles and scooters and auto-rickshaws ply on the city roads. The slow moving cycle rickshaws are still a part of urban transportation system. The pulling carts and pony carts are still in use in the transportation of goods for short distances.

The city bus service is the best mode of mass transportation operating in the city. The shuttle trains service and ferry service on the river Brahmaputra for mass transportation within the city has been abandoned. Therefore, the city bus service is the only service, catering to the needs of mass transportation.