

A STUDY OF CHEMICAL CHARACTERISATION OF FOG IN DELHI

Dissertation submitted to the Jawaharlal Nehru
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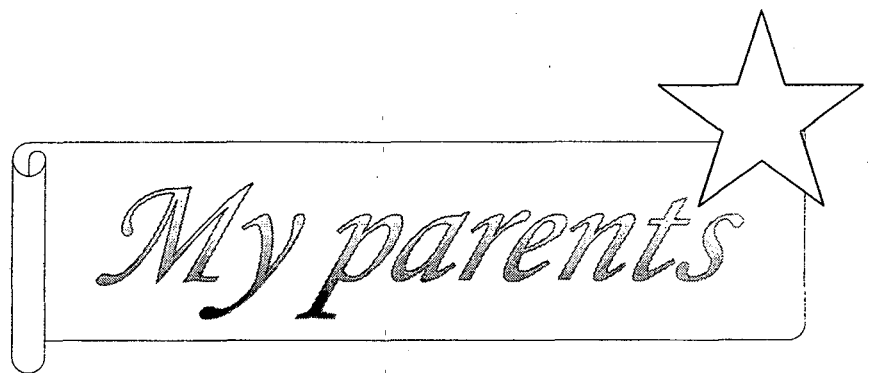
MASTER OF PHILOSOPHY

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**SCHOOL OF ENVIRONMENTAL SCIENCES
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI-110067
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2004**

Dedicated to.....





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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "A Study of Chemical Characterisation of Fog in Delhi" has been carried out in this school for the partial fulfillment of the award of the degree of master of philosophy. This work is original and has not been submitted in part or full for any other degree or diploma in any other University.

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List of Figures

<i>Figure</i>	<i>Title</i>	<i>Page No.</i>
Figure 2.1:	Nylon Fibre Active Cloud Water Collector	19
Figure 3.1:	Frequency of the various fog categories observed	26
Figure 3.2:	The relative fog frequency for winter season	26
Figure 3.3:	Variation of ph, Conductivity and TDS over different fog categories	28
Figure 3.4:	Variation of ph, Conductivity and TDS in Fog water and precipitation	28
Figure 3.5:	Variation in pH, Conductivity and TDS with water content in fog	29
Figure 3.6 (a):	Variation of water content as a function of Temperature for Fog	30
Figure 3.6 (b):	Variation of water content as a function of Temperature for Mist	30
Figure 3.6 (c):	Variation of water content as a function of Temperature for Haze	30
Figure 3.7:	Concentration of Cl ⁻ ion in various fog categories	31
Figure 3.8:	Concentration of SO ₄ ²⁻ ion in various fog categories	31
Figure 3.9:	Concentration of NO ₃ ⁻ ion in various fog categories	32
Figure 3.10:	Concentration of NH ₄ ⁺ ion in various fog categories	32
Figure 3.11:	Concentrations of Na ⁺ metal ion in soluble and insoluble fraction of fog water among various fog categories	34
Figure 3.12:	Concentrations of K ⁺ metal ion in soluble and insoluble fraction of fog water among various fog categories.	34
Figure 3.13:	Concentrations of Ca ²⁺ metal ion in soluble and insoluble fraction of fog water among various fog categories	35

Figure 3.14: Concentrations of Mg^{2+} metal ion in soluble and insoluble fraction of fog water among various fog categories	35
Figure 3.15: Concentrations of Cu^{2+} metal ion in soluble and insoluble fraction of fog water among various fog categories	36
Figure 3.16: Concentrations of Pb^{2+} metal ion in soluble and insoluble fraction of fog water among various fog conditions	36
Figure 3.17: Concentration of Cl^- ions in fog and precipitation	37
Figure 3.18: Concentration of SO_4^{2-} ions in fog and precipitation	37
Figure 3.19: Concentration of NO_3^- ions in fog and precipitation	38
Figure 3.20: Concentration of NH_4^+ ions in fog and precipitation	38
Figure 3.21: Concentrations of Na^+ metal ions in soluble and insoluble fraction of fog water and precipitation	39
Figure 3.22: Concentrations of K^+ metal ions in soluble and insoluble fraction of fog water and precipitation	39
Figure 3.23: Concentrations of Ca^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation	40
Figure 3.24: Concentrations of Mg^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation	40
Figure 3.25: Concentrations of Cu^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation	41
Figure 3.26: Concentrations of Pb^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation	41
Figure 3.27: variation in Cl^- ion concentration with water content in fog	44
Figure 3.28: variation in SO_4^{2-} ion concentration with water content in fog	44
Figure 3.29: variation in NO_3^- ion concentration with water content in fog	45

Figure 3.30: variation in NH_4^+ ion concentration with water content in fog	45
Figure 3.31: variation in Na^+ metal ion concentration in soluble and insoluble fraction with water content in fog	46
Figure 3.32: Variation in K^+ metal ion concentration in soluble and insoluble fraction with water content in fog	46
Figure 3.33: Variation in Ca^{2+} metal ion concentration in soluble and insoluble fraction with water content in fog	47
Figure 3.34: Variation in Mg^{2+} metal ion concentration in soluble and insoluble fraction with water content in fog	47
Figure 3.35: Variation in Cu^{2+} metal ion concentration in soluble and insoluble fraction with water content in fog	48
Figure 3.36: Variation in Pb^{2+} metal ion concentration in soluble and insoluble fraction with water content in fog	48
Figure 3.37: Fog sulphate and nitrate concentrations observed at each sampling events	50
Figure 3.38: Sulphate /Nitrate concentration ratio (equivalent/ equivalent) observed in fog on each sampling events	50
Figure 3.39: $\Sigma\text{cation} / \Sigma\text{anion}$ ratio observed on each sampling events	51
Figure 3.40: $\Sigma\text{Cations}$ and ΣAnions in different fog categories	51
Figure 3.41: Fog Na^+ and Cl^- concentrations on each sampling events	52

List of Tables

<i>Table</i>	<i>Title</i>	<i>Page No.</i>
Table 1.1:	Classification of fog condition with visibility	05
Table 2.1:	Fog events with meteorological parameters	17
Table 3.1:	Ionic concentrations in fog water and precipitation	27
Table 3.2:	Mean concentration and range of various ions in different fog categories and precipitation.	33
Table 3.3:	Concentration ratios of different ions.	42
Table 3.4:	Ionic concentrations of fog water in Delhi - A comparison with previous studies.	52

Contents

Certificate

Acknowledgement

List of Figures

List of Tables

<i>Chapters</i>	<i>Page No.</i>
(I) INTRODUCTION	1-14
(II) STUDY AREA AND METHODOLOGY	15-24
(III) RESULTS AND DISSCUSUSSION	25-53
(IV) CONCLUSION	54-55
REFERENCES	56-64

CHAPTER -I

INTRODUCTION

INTRODUCTION

Air pollution has become a great menace to the human life in this era of rapid industrialization, urbanization and unplanned development. Air pollution kills more than 2.7 million people annually, of which over 40% of such deaths occur in developing countries and 2/3 of these in Asia (UNDP, 1998). There are ranges of air pollutants which create nuisance, but we are mostly concerned with criteria pollutants, viz. CO, SO₂, NO₂, and TSP, which have significant effect on human health. Out of these pollutants TSP constitutes the major part of aerosols, which influences many atmospheric processes including visibility variation, fog and cloud formation, radiation balance and also the human health (Pueschel et al, 1986; Shaw, 1987; Pandis et al, 1995). It has also been observed that high particulate matters are usually associated with dense winter fogs (Chow, et al, 1993), although the fogs may be instrumental in the removal of particles from the atmosphere (Pandis & Seinfeld, 1989; Lillis et al, 1999; Collett jr. et al, 2000).

Fog comprises a complex physico - chemical system that plays a fundamental role in global geochemical processes. The word "FOG" refers to cloud of smoke particles, ice particles or mixture of these components, or cloud of small water droplets near ground level and sufficiently dense to reduce the visibility to less than 1000 meter (3,281 ft.). Thus, macroscopically, FOG is nothing but a layer cloud with sufficiently long surface contact to dampen vertical motions. These surface contacts significantly perturb the microscopic and chemical properties that differentiate fog from other clouds. Because of the occurrence of dissimilar optical phenomena, condensed water aerosols with a horizontal visibility between 0.5 to 1 km have been termed as MIST (Eldridge, 1969) and visibility between 1 to 10 km have been termed as HAZE (Heintzenberg, 1998). It provides a crucial temporal and spatial venue to the hydrological cycle affecting both the energy and material transport phenomenon of

the atmosphere (Dasch, 1988; Schemenaur and Cereceda, 1994; Breijnzeel, 2001). It interacts with both the incoming solar radiation as well as outgoing terrestrial radiation, hence affecting the global energy budget. It also reduces the visibility and causes disruption to the rail, road and air traffic.

[1.1] FORMATION OF FOG

Fog is formed due to the condensation of water vapour on condensation nuclei that are always present in natural air. Whenever the air is cooled, by any means whatever, below its dew point, a portion of the water vapour present separates out on such dust particles or other condensation nuclei as may happen to be present. If this process happens to occur at the surface of the Earth, it is called fog, no matter how shallow or how deep it may be. Fogs are likely to form along rivers and large creeks in the mountain valleys of all but arid regions in the later part of any still cloudless night of summer or autumn. During these seasons, the streams and humid soils are warm specially when exposed to sunrise, and hence evaporate much moisture into the lower atmosphere, where in great measure it remains when there is no wind to blow it away. Throughout the night, however the surface of the soil and the adjacent humid air, by virtue of its humidity, lose heat rapidly by radiation to the colder atmosphere above and to the sky, or empty space beyond. If there is no sunrise in the next forenoon to make good such loss – the inevitable consequences is a lowering of the temperature. Hence, during calm, clear nights, the temperature of the humid surface air often falls below the dew point and a fog of corresponding depth and density is formed.

Another source of numerous fogs is the drifting of relatively warm humid air over places much colder, such as the drifting of onshore winds over snow banks. In this way the humid air frequently gets cooled below its dew point and fog {“winter fog” or “sea fog”} is produced. Likewise heavy fogs are often formed when the wind is blown from warm to cold water. Fogs also frequently occur when cold air slowly flows in

over warm water. This explains the “frost smoke” of polar seas and the “steaming” of rivers and lakes on cold frosty mornings. In these cases, the relatively warm water goes on evaporating into the cold air even after it becomes saturated and thereby produces a water droplet or a minute ice crystal about every one of the myriads millions of nuclei present.

But if the sky is overcast, there commonly is enough radiation from the clouds back to the earth to prevent the cooling of the surface air to the dew point and consequent formation of fog. Neither does fog form when there is considerable wind, partly because humid lower air is mixed with upper dry air and the surface dew point thereby lowered, and partly because this mixing distributes the heat loss through a large amount of air instead of leaving it confined essentially to that near the ground. Hence, fogs – radiation fog, summer fog, land fog, valley fog – seldom occur either when sky is cloudy or the night windy.

[1.2] TYPES OF FOG

In respect to the ways in which they are formed, fogs may be divided broadly into two classes.

Radiation Fog:

It forms due to the cooling of the lower air below the dew point, partly by its own radiation and partly by contact with the surface, which itself had cooled by radiation. This type of fog is common along streams and valleys.

Advection fog:

It forms by the advection or horizontal movement of air from one place to another, such as drifting of relatively mild air from the ocean inland over snow banks, or from a warm current to a cold one; and the flow of frosty air over open water. Furthermore, any fog when shifted to a new position may then be called “*advection fog*”.

Other classifications:

- a) **Dry fog:** A fog, which because of the small amount of water content, does not wet our clothing – evaporates as fast as caught up – or else meaning as we often do, a haze caused by forest fire, dust storm, or volcanic explosion.
- b) **Wet fog:** A fog containing, so much water that it makes at least the surface of one's clothing damp.
- c) **Sea fog:** Fog originating on the ocean, whether remaining there or drifting on shore.
- d) **Land fog:** One occurring in the continent and which quickly evaporates, as its nuclei are slightly hygroscopic.
- e) **City fog:** One occurring over the city, especially those where large amount of soft coal has been used but have few smoke consumers. It is generally slow to evaporate, owing jointly, presumably to the hygroscopic nature of the nuclei and to the oil in the unburned sooty smoke.
- f) **Black fog:** This containing a great amount of soot, such as which occasionally forms over large smoky cities.
- g) **Pea – soup fog:** A local name given to those London fogs that contain only a moderate amount of smoke particles – just enough to give the fog distinctly yellowish colour.
- h) **Ice fog or frost smoke:** The fog of polar seas, caused by the drifting of very cold air over them.

[1.3] PROPERTIES OF FOG:

Fog plays an important role as processors of atmospheric aerosols and soluble gases. It affects the fate of some atmospheric species via both chemical and physical processes. They play the role in new particle production e.g. Uptake and oxidation of $\text{SO}_{2(g)}$ to $\text{SO}_4^{2-}_{(aq)}$ in drops, and particle removal (e.g. via particle scavenging and removal by fog deposition). The drop surface also provides an important reaction site. For example, the presence of a wet surface layer on atmospheric aerosol particles has been associated with the production of $\text{HONO}_{(g)}$ (Notholt, et. el., 1992). Fog also interacts with the incoming short wave radiations as well as long wave radiations. Hence, it reduces visibility which disrupts air, rail and road traffic. The transportation system comes to standstill during foggy conditions, which have a very serious implication for Indian economy. Foggy conditions have been classified according to the visibility status in the atmosphere.

Table 1.1: classification of fog condition with visibility (Eldridge, 1969; Heintzenberg, 1998)

Fog condition	Visibility range (Km)
Dense fog	0 – 0.5
Mist	0.5 – 1.0
haze	1.0 – 10

Furthermore, fog interception by vegetation is considered to be a significant component of the hydrological budget of the mountain forests that are frequently immersed in dense fog. It is considered as a major source of water influx to the mountain as well as coastal and forest ecosystems (Dasch, 1988; Gordon et al, 1994;

Schemenaur & Cereceda, 1994; Walmsley, et al, 1996; Breinzeel, 2001). It has been reported that in Colombia 48% of the annual water input to a cloud forest was from fog precipitation (Cavalier and Goldstein, 1989). In upper reaches of the mountain, fog (or cloud) water can provide a good alternative source of water for the mountains where conventional water supply system does not work, as well as for the area where water availability is scarce.

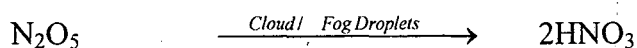
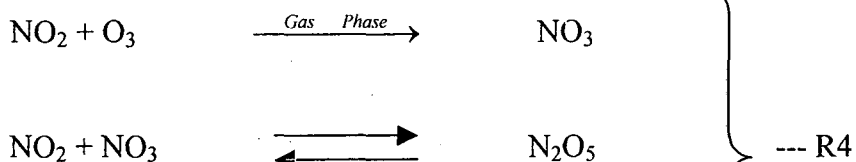
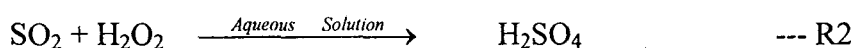
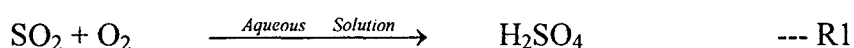
[1.4] PREVIOUS STUDIES:

Many studies have been made on fog in diverse locales, e.g. coastal areas where fog is frequent as a result of the advection of sea fogs at low elevations; and high elevation sites due to the advection of clouds over the terrain, or the generation of orographic clouds on certain topographic features. Despite many field experiments, the use of a variety of fog collectors, and a wide multidisciplinary acceptance of the importance of fog deposition, it has largely been neglected as water input to be monitored on a continuous basis (Schemenaur & Cereceda, 1994).

In 1980s, the review of the forest dieback in the mountains of central Europe (Mclaughlin, 1985; Schutt & Cowling, 1985) put an emphasis on the chemical deposition of high elevation fog. In 1985, The Chemistry of High Elevation Fog (CHEF) project began and thereafter, in 1986, Mountain Cloud chemistry Project (NCCP) was initiated in USA. Early results from CHEF (Schemenauer, 1986; Schemenauer and Winston, 1988) and other projects (Mohnen and Kaleck, 1989; Saxena et al, 1989) indicated that fogs covering upland areas were both more acidic and had higher concentrations of major ions than did precipitation at the same sites. Schemenauer et al, 1995 reported the occurrence of high acid fog event in Quebec Canada. It points out the potential importance of high elevation fog as a major pathway for acid wet deposition in southern Quebec. The mean pH for all sites and seasons was found to be 3.79. The dominant anion was SO_4^{2-} followed by NO_3^- . The

dominant cation was NH_4^+ . The results also show that the mountain areas of southern Quebec have a potential for total wet deposition.

The works of Kelly and his co-workers (Kelly et al., 1989) suggested that oxidation processes of SO_2 and NO_2 are the most important acid formation processes in cloud and fog. Besides Kelly, other researchers such as Penkett et al., 1979; Schwartz, 1984a; Lee et al., 1986; Hill et al., 1986 also suggested, the following reactions as the most significant processes producing acidity in cloud and fog.



In view of Kelly et al (1989), R3 is considered to be the most important gas phase source of HNO_3 and play a significant role in daytime; Whereas R4 is probably the most important in nighttime when photolytic destructions of NO_3 & N_2O_5 couldn't occur.

Khemani et al. (1989) reported that Ca^{2+} , Na^+ , K^+ , Mg^{2+} were the most dominant cations present in the fog water at Delhi. The study also revealed that contributions from industrial sources were negligible.

Pandis et al. (1990) studied the distribution of acidity and solute concentration among the various droplet sizes in fog. The results show that the mass solute concentration in droplets larger than 10 μm diameter increased with size. The result also suggests that the gas and aqueous phase chemical processes tend to decrease the total solute mass concentration differences between the various droplet sizes.

Boreux and Guiot (1992) developed a fog-forecasting model for a deeply embanked valley. This was a statistical model using Bootstrap discriminant analysis method using eight predictors: river surface temperature, air pressure, air temperature at two elevations, wind speed and relative humidity at the same two locations. The model-predicted values of the number of foggy days were in good agreement with the observed fog events.

Kapoor et al. (1993) reported the chemical composition of the fog water in Delhi in the year 1989. The observations were compared to the earlier study carried out by Khameni et al. (1989). The results suggested that concentration of the ions (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , NH_4^+ , Cu^{2+} , Pb^{2+} , SO_4^{2-} , NO_3^- , Cl^-) enhanced significantly.

Ishizaka and Qian (1994) studied the individual aerosol particles and residues of fog droplets in Japan. They used electron microscope and two stage impactor to analyze the fog droplets. It was found that nitrate and sulphate ions coexist as internally mixed particles in acid fog. They also got direct evidence of nitrate scavenging and sulphate production in fog droplets.

Gorden et al. (1994) studied fog events at cloud forest in Venezuela and found fog to be a very important chemical input in these areas. They concluded that ion

concentrations in fog were up to 20 times higher than in precipitation at the same site. NO_3^- concentration accounted for a large proportion of the acidity, Pb and Zn concentrations were relatively higher, and their sources were thought to be anthropogenic.

Schemenaur et al. (1995) documents the occurrence of highly acidic fog events in Canada. The paper points out the potential importance of high elevation fog as a major pathway for acidic wet deposition in southern Quebec, Canada. The dominant cation was NH_4^+ and dominant anion was SO_4^{2-} . Elias et al, 1995 and Weathers et al, 1995 also studied the occult precipitation or cloud deposition at mountain sites, and reported that mountain areas have a potential for total wet deposition.

Minami and Ishizaka (1996) studied the chemical composition of fog water near the summit of Mt. Norikura in Japan. They also reported that fog water is highly acidic. The result also showed that the acidification progressed rapidly at the initial stage of fog formation, primarily due to SO_4^{2-} enhancement and secondarily due to NO_3^- formation.

Fuzzi et al. (1997) reported the occurrence of airborne biological particles (bacteria, yeasts and moulds) in fog water. The result showed that fog droplets act as a culture media for airborne biological particles, i.e. they represent an atmospheric source of secondary biological particles.

Monte and Rossi (1997) found that fog water deposits numerous minerals after evaporation. When fog water evaporation occurs in the field, such minerals, which are all hygroscopic and deliquescent, either do not form at all or have a brief life span. Kokaite is the only mineral which survives for few hours and tends to transform rapidly into Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). They, opined, therefore that gypsum was the only mineral remaining on the surface interacting with the fog. Also that through this

mechanism considerable amount of SO_4^{2-} and Ca^{2+} was removed from the atmosphere – hydrosphere cycle.

Eckardt and Schemenauer (1998) documents the ion concentrations and the enrichment relative to sea water, in Namib desert (Namibia) fog water. The works suggested that Namibian fog water is at least as clean as has been reported from other coastal deserts in South America and provides a source of very clean water for the coastal desert region of south – western Africa.

Tenberken and Bachmann (1998) reported the dependence of the concentration of solutes on the size of fog droplets by analyzing single drops. A new sampling technique based on electrostatic precipitation has been used. It has been observed that solute concentration decreases with increasing drop size. The result is in clear contrast with the previous study of Pandis et al, (1990).

Chung et al. (1999) studied the chemical composition related to fog, mist and haze and its effect on visibility in South Korea. The results showed that the number of days of low visibility (≤ 10 km) was significantly increased by the occurrence of fog, mist and haze. It was also observed that the increase in the frequency of low visibility days was related to the increase in anthropogenic air pollutants and water vapour. It was also suggested that the characteristics of yellow sand and soil dust occurring in spring appear to determine the pH values in hydrometeors occurring on the Korean peninsula.

Honma et al. (2000) reported the health effects of naturally occurring acid fog for the Koshiro city of Japan. The study concluded that epidemiologically fog was the most important positive factor contributing to increased hospital visits compared to other meteorological values and air pollutants. The results also suggested that inhalation of

naturally occurring acid fog resulted in eosinophilic inflammation which contribute to respiratory deterioration.

Wrzesinsky and Klemm (2001) studied the fog water chemistry at a mountainous site in central Europe. The study reported the variability in the chemical composition of fog as a function of wind speed and wind direction. An automated system for collection of fog water was developed based on visibility as a determining parameter. The study also revealed that fog played an important role in the water balance of the forests. Fog water chemistry at mountainous site has also been reported from various other locations (e.g. Aikawa et al, 2001; Igawa et al, 2001). These results also showed lower pH and higher ion concentrations at the respective sites.

Collett Jr. et al. (2001) examined the fog composition and deposition fluxes of fog water and fog solutes in radiation fog in California. The results revealed that the average deposition velocity of fog nitrate was less than those of fog sulphate and ammonium. All the three species generally exhibited smaller deposition velocities than the fog water. The species dependent trend in deposition velocities was consistent with preferential enrichment of these species in small fog drops (Nitrate > Sulphate > Ammonium).

Herkes et al. (2002) studied the chemical composition of fog water in the city of Strasbourg, France over a period for 10 years from 1990 to 1999. The analysis revealed a significant decrease in acidity. The study linked this decrease to the decrease in $\text{SO}_{2(g)}$ and the resulting decrease in SO_4^{2-} . Trace metals concentrations especially Pb concentrations were also found to have decreased over the 10 year period.

Blas et al. (2002) studied the pollutant concentrations in fog water at urban as well as mountainous sites. The result revealed low pH and low pollutant concentrations at

mountainous sites in comparison to urban sites. This discrepancy has been attributed to the various industrial and anthropogenic activities going on at the urban sites.

Ma et al. (2003) applied a newer technique for collection of individual fog droplets and used micro Particle Induced X-ray Emission (PIXE) technique for chemical analysis of individual fog droplets. The result shows a bimodal shape of number size distribution. Also crustal components and sulphur are found to be the major constituents present in the fog water.

Urquiza et al. (2003) developed an empirical model for estimating the concentration of SO_4^{2-} ion in fog at high elevation locations in North America. The result shows that ozone measured at the fog collection sites, was also found to be a potential useful predictor of SO_4^{2-} in fog.

Zimmermann et al. (2003) reviewed the air pollution and atmospheric deposition dynamics in Germany, central Europe. The results underline the large variations in fog water composition depending upon liquid water content, formation of fog water, surface interactions and air mass origin.

Burkard et al. (2003), studied fog water flux at forest canopy Lageren research site in Switzerland and observed two types of fog: radiation fog and fog associated with atmosphere instabilities. The results show that concentrations of pollutants in fog water during radiation fog was considerably higher, resulting in high nutrient deposition, which adds to the nutrient influx through other sources. As a consequence the critical load of annual nutrient-input were exceeded resulting in a significant over-fertilization at the Lageren site.

Lange et al. (2003) also studied the fog frequency and chemical composition of fog water over Erzgebirge mountain site in central Europe. The study inferred that the

forests themselves alter the ionic composition of fog water and a distinct trend was visible from open field deposition to forest interior sites.

Holder (2004), examined the fog precipitation in a tropical mountain cloud forest in Guatemala, and concluded that fog precipitation was one of the most significant hydrological inputs to the cloud forest there.

Moore et al. (2004) studied the drop size dependent chemical composition in clouds and fogs. They developed a 5-stage collector called California State University 5 – stage Cloud water Collector (CSU 5 - Stage). The results show “U” shaped profiles of major ion concentrations at mountainous sites and “L” shaped profiles for urban sites. It has also reported that nitrate concentrations were significantly higher in the larger droplets.

Recently, Deshpande and Kamra (2004) studied the atmospheric electric conductivity and aerosol concentrations during fog over Indian Ocean. The results showed an increase in concentrations of all particle sizes in warm fog. However, in cold fog the increase was mainly in the concentrations of the nucleation mode particles.

1.5 Indian Scenario:

A very limited number of studies have been carried out on fog water composition in India. It all started in mid 1980s. The samples of fog water were collected and analysed for the first time at Delhi during two consecutive winters (1985 & 1986) by Khameni et al. (1987). The results showed that the dominant ions were Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} which were released mostly from soil. The concentration of acidic components (SO_4^{2-} & NO_3^{-}) was found to be less. The study indicated that contributions from industrial sources were negligible. Later Kapoor et al. (1993) studied the fog composition in Delhi and reported significant increase in Ca^{2+} and

NO_3^- concentrations in fog water when compared to concentrations of these ions in the study of Khemani et al. (1987).

Recently on 27th march 2000, Central Pollution Control Board (CPCB) signed a Memorandum of Understanding (MOU) with National Physical Laboratory (NPL), New Delhi (Annual report, CPCB, 2000) with the objective to carry out the study of occurrence of fog and to develop an early warning system for fog. During January 2001 monitoring of various parameters influencing the onset of fog was carried out by NPL. Again in Nov 2001 & Feb. 2002 parameters like mixing height, temperature and relative humidity, pressure and size fraction of SPM, SO_2 , NO_2 were monitored. But the results are yet to be conclusive.

There is no reported study on chemical composition of fog in Delhi for almost ten years during which Delhi's environment has undergone major changes. With the arrival of Compressed Natural Gas (CNG) run vehicles in 2000, air pollution scenario of Delhi has changed significantly. The lack of study of fog water composition in recent years has prompted us to undertake this study with the following objectives:

1. To collect and quantify the fog water in urban environment.
2. To chemically characterize the concentration of anions and cations such as: Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Ca^+ , K^+ , Mg^{2+} , Na^+ , Cu^{2+} and Pb^{2+} .
3. To measure the pH and Conductivity of fog.
4. To measure Total Dissolved Solids (TDS) in fog.

A brief description of study area and the Methodology used in this study are given in chapter-II; Results are discussed in chapter- III. The conclusion is given in chapter- IV

CHAPTER -II

STUDY AREA AND METHODOLOGY

[2.1] General Description of Study Area:

The present study pertains to monitoring of fog in Delhi, the capital city of India. It is located between $76^{\circ} 56'$ E to $77^{\circ} 23'$ E longitude and $28^{\circ} 12'$ N to $28^{\circ} 53'$ N latitude on the banks of river Yamuna and in the lap of the Himalayas and the Aravali at an altitude of between 213.3m and 305.4m above the mean sea level. Hot summer with maximum temperature as high as 46°C - 48°C and cold winter with minimum temperature as low as 1°C along with the unreliable rainfall (~ 611.8 mm) are the characteristic of this city, which falls in subtropical belt with continental monsoon climate.

The predominant wind direction in most part of the year is from west (W) to north-west (NW) except during monsoon months (July – September) where, it is from south (S) to southeast (SE). The winter months are dominated by calm conditions with low inversion and low mixing height, thereby keeping pollutant level high.

Sampling site:

Fog water has been collected at the rooftop of School of Environmental Science (SES) building, during the months of December (2003) and January (2004) when fog was a common occurrence in Delhi's environment. The School is situated within the campus of Jawaharlal Nehru University, New Delhi. The university campus is stretched over a vast tract of natural vegetation covering an area of 1000 acres. This place is far off from major industrial activity. Traffic density is very low within the campus but it is surrounded by major roads carrying heavy vehicular traffic.

[2.2] Fog Events and general meteorological conditions:

Fog water was collected on a continuous basis during winter season. A total of 18 fog events consisting of 5 events in December 2003 and 13 in January 2004 were observed. The four meteorological parameters; viz, Temperature, Relative humidity, Wind speed and Wind direction, have been monitored during winter season of year 2003-2004. The temperature during the period varied between 7.5 to 10°C during nighttime when fog advents. However, in the daytime temperature surged up to 19°C. Fog usually started at night between 8.00 and 10.00 pm and in general disappeared by around 8.00 am to 12.00pm the next day. Relative humidity ranges was in the range from 83% to 94%. North Easterly and Easterly winds were predominant during this period with speeds usually ≤ 0.1 m/sec. Details of fog events, the quantity of fog water collected during 12 – 14 hour period and the meteorological parameters were presented table 2.1.

During the sampling period three rain events also occurred. The rain samples of these events were collected and analysed along with the fog samples.

[2.3] Sample Collection:

For fog water collection, a Nylon fibre active fog water collector has been designed and fabricated based on fog water collector described by Daube (1987). The details of the collector are given in a subsequent section [2.4].

Table 2.1: Fog events with meteorological parameters

Event	Date	Quantity (ml)	Duration (hour)	Temp. (°c)	RH. (%)	Wind Speed (m/s)	Wind direc tion
1	23-Dec-03	180	12	8	93.5	0.1	NE
2	24-Dec-03	80	13	10	89.3	0.09	NE
3	27-Dec-03	5	12	10	85	0.1	NE
4	28-Dec-03	55	12	9.7	89.3	0.1	E
5	30-Dec-03	40	12	9.5	90.2	0.1	NE
6	1-Jan-04	160	14	8.5	85	0.1	E
7	2-Jan-04	5	12	9.7	87	0.09	NE
8	3-Jan-04	40	12	9.4	90	0.12	N
9	5-Jan-04	100	13	7.93	83	0.1	NE
10	6-Jan-04	300	12	7.5	89	0.1	NE
11	13-Jan-04	250	12	7.9	94	0.1	E
12	14-Jan-04	125	12	8.15	91	0.1	E
13	14-Jan-04	100	12	8.2	89	0.09	NE
14	15-Jan-04	100	12	8.5	92	0.12	NE
15	16-Jan-04	20	12	8.9	88	0.1	NE
16	17-Jan-04	5	14	9.7	87	0.1	NE
17	20-Jan-04	150	12	7.92	90	0.1	NE
18	24-Jan-04	40	13	9.2	91	0.09	N

The fog collector was cleansed between events by rinsing all of its surfaces with de-ionized water ($< 1\mu\text{s cm}^{-1}$), sprayed from a polyethylene reservoir. The collector bottle was kept soaking in de-ionized water, when not in use. The samplers were exposed for 12 – 14 hours, at every night, from the time of onset of fog.

The onset of fog has been defined according to visibility criterion. When an object (a tall monument or a high-rise building or a distant light source) roughly 2-3 km away

is obscured from view, it is taken as a sign of onset of fog. The categorization of fog (i.e. Fog, Mist and Haze) is based on the criterion mentioned in table 1.1.

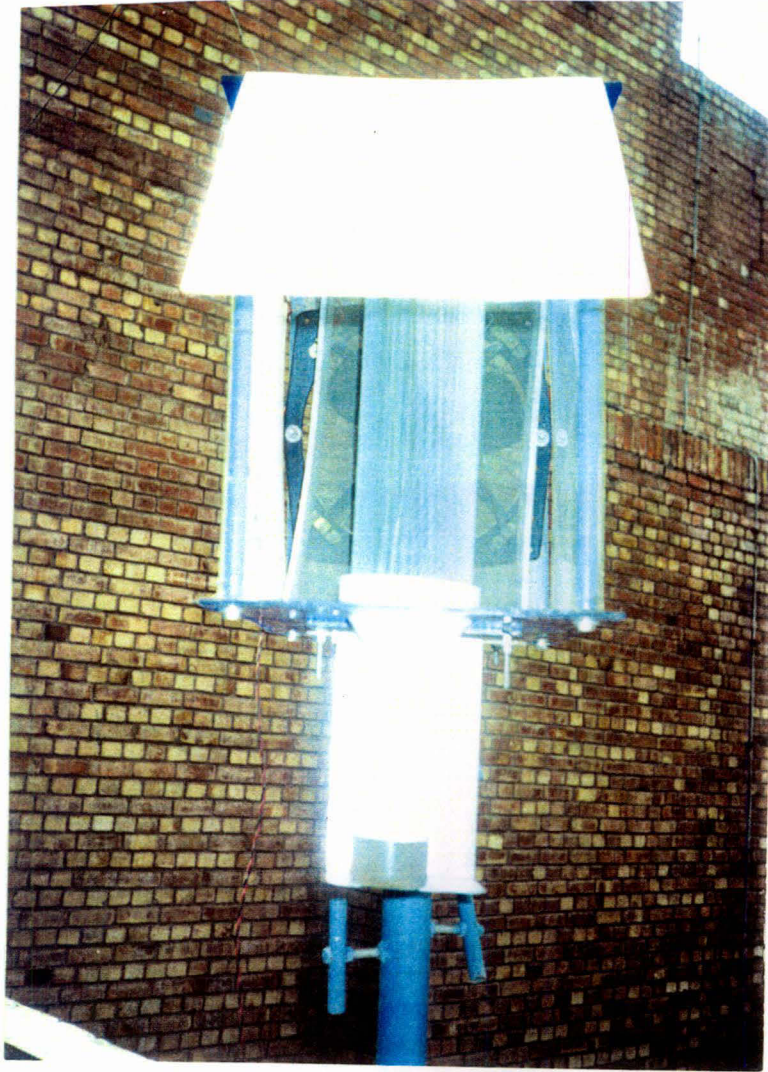
Fog and precipitation samples, collected in Teflon bottle, were transferred to 100 ml polyethylene bottle for storage and subsequent analysis. The storage bottles were pre-washed three times with de-ionised water and dried in an oven. Samples were not filtered at the time of collection, nor any preserving agents added. Samples were refrigerated (4⁰C) immediately after collection and kept cold until analysis.

[2.4] Apparatus:

Following apparatus have been used for fog water sampling, measurements of meteorological parameters and chemical analysis of fog samples.

- a. Nylon fibre Active fog water collector
- b. pH meter
- c. Conductivity and TDS meter
- d. Atomic Absorption Spectrophotometer
- e. UV/VIS Spectrophotometer
- f. Meteorological kit

(a) Nylon Fibre active fog water collector: the collector is modelled on the cloud water precipitator (CWP) described by Daube et al. (1987) (fig. 2.1). The fog collector consists of a 2 meter tall collection frame, with two identical horizontal annular disks (diameter 20 cm) fixed vertically at heights 40 cm apart. Between the disks, nylon strings (diameter 0.3mm) are stretched in double rows. The effective string length is about 500 m. The fog droplets, trapped on the strings, drips into a collection pan made up of Teflon and stored in a 500ml Teflon bottle. The whole collection unit is put into a rectangular case of dimension 56cm X 37cm X 40cm. This rectangular box is open at one end and at the other end a 220 Volt, 0.36-Ampere AC



(a)



(b)

Figure 2.1: Nylon Fibre Active Fog Water Collector

driven exhaust fan is fitted, which sucks the wind into this case. The hood above the collector prevents rain from diluting the fog sample.

To collect the precipitation a simple polyethylene funnel and bottle collector was used as a bulk sampler with an opening diameter of 20cm and collection area of 314cm². This sampler was also set up near the fog water collector. An arrangement has been made to protect it from direct radiation and light. One could expect no collector-induced differences in the chemistry of the fog water and precipitation.

Principle: Exhaust fan at the rear of the sampler creates vacuum within the rectangular case. As a result, moisture-laden air rushes inside the cavity and is impacted on the nylon string. There, tiny waterdrops stick to the string and trickle down under the influence of gravity and get collected in a Teflon bottle through a Teflon funnel.

(b) pH-Meter:

For pH measurements, a digital pH meter (Widson Scientific Works, Delhi Model No.DB1011) with combination electrodes is used. It has been calibrated using standard solution of strength 4.0 and 9.2.

(c) Conductivity & TDS Meter:

For electric conductivity and TDS measurement, a digital EC meter (Widson Scientific Works, Delhi Model No.DC610) has been used.

(d) Atomic Absorption Spectrophotometer (AAS):

For metal estimation, Atomic Absorption Spectrophotometer (Shimadzu, AA-6800, and Japan) was used. It consists of a hollow cathode lamp, monochromator, burner etc. In the burner air - acetylene gas mixture is used. The sample is injected through nebulizer. Different cathode lamps are used to analyse different metals.

(e) UV/VIS Spectrophotometer:

For estimation of anions (SO_4^{2-} , NO_3^- and Cl^-) and cation (NH_4^+) concentrations UV/VIS, Spectrophotometer (ECIL, India) was used.

(f) Meteorological kit:

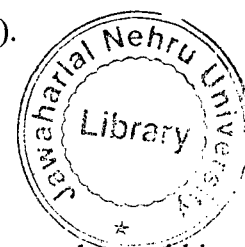
For monitoring of meteorological parameters viz. temperature, relative Humidity, Wind speed and Wind direction, meteorological kit (Dynamab, Pune, India), fitted on a Mobile Air Pollution Laboratory Van was used. This van was stationed near the sampling site during the course of study. This kit was attached to a computer, which recorded the data after every 5 minutes through software (ENVIDAS).

[2.5] Laboratory Procedure:

The pH, Conductivity and TDS measurements of collected samples were done within 1-2 hours of their collection. The collected samples of fog water and precipitation were then filtered by Whatman membrane filter (0.47 μm pore size). The filtrate is considered as a soluble fraction of fog water and the matter collected on filter is considered as insoluble fraction. Both the soluble and insoluble parts were analysed for cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Pb^{2+} and NH_4^+) and anions (SO_4^{2-} , NO_3^- and Cl^-). The analysis of cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and trace metals (Cu^{2+} and Pb^{2+}) were performed on AAS (Schimadzu, AA-600, Japan).

Measurements Using AAS:

Metal solutions: Standard metal solutions were prepared in the optimum concentration range by diluting the stock metal solution (1000 ppm). The stock solutions (1000 ppm) of different metals (ions) were prepared as per details given below.



Na: 2.542 gm of NaCl, dried at 140⁰C for one hour before weighing, was dissolved in 50ml de-ionized water and 1ml HCl. When all of NaCl is dissolved, it was diluted to 1000ml.

K: 1.907gm of KCl dried at 110⁰C for one hour before weighing, was dissolved in 50ml of de-ionized water and 1ml HCl. Thereafter it was diluted to 1000ml.

Mg: 1.658gm MgO was dissolved in 10 ml HCl and diluted to 1000ml.

Ca: 2.497 gm CaCO₃, dried at 180⁰C for one hour before weighing, was dissolved in minimum of HCl, and then diluted to 1000ml with de-ionized water.

Cu: 3.930 gm CuSO₄.5H₂O was dissolved in 50 ml de-ionized water and 5 ml 1:1 HNO₃. Then it was diluted to 1000ml.

Pb: 1.599 gm Pb(NO₃)₂ was dissolved in 50 ml de-ionized water and 5 ml 1:1 HNO₃. Then it was diluted to 1000ml.

After a warm-up time of the instrument, appropriate wavelength is set for the element to be analysed, and the slit width and air / acetylene ratio as given in the manual of the instrument were set. After igniting the flame, zero adjustment of AAS was done by annihilating the blank. Then the calibration solutions were allowed to be aspirated and the absorption signal was read out. After calibration 100 µl of Cs-La solution was added to 10 ml of the sample. The treated samples then were aspirated and absorption reading was recorded. The samples that are found to have the concentration higher than the upper limit of the concentration range of the standards were diluted into range and reanalysed.

Measurements Using UV/VIS Spectrophotometer:

The concentrations of NH_4^+ ion along with the anions (SO_4^{2-} , NO_3^- and Cl^-) were determined using UV/VIS Spectrophotometer. The procedure adopted for these measurements is given below.

NH_4^+ : For ammonium, ion estimation Indophenol Blue (EMEP, 1979) method was used. The detection range for this method is 0.04 – 2.0 mg/l

Principle: In alkaline solution (pH 10.4-11.5) ammonium ions react with hypochlorite to form monochloramin. In the presence of phenol and an excess of hypochlorite, the monochloramine will form a blue coloured compound, indophenol, when nitroprusside is used as catalyst. The concentration of ammonium is determined spectrophotometrically at **630 nm**.

SO_4^{2-} : Barium perchlorate – Thorin (EMEP, 1979) method is used for sulphate estimation. The detection range for this method is 0.05 – 4 mg/l.

Principle: $\text{Ba}(\text{ClO}_4)_2$ is added in excess to precipitate the sulphate as Barium Sulphate in an organic solvent (Dioxane). The organic solvent minimizes the solubility product of barium sulphate. The excess concentrations of Ba(II) ions in the solution is determined spectrophotometrically at **520 nm** through the reaction with Thorin (Na salt of (ortho-arsenophenyl-azo)-3-hydroxy-2,7-nepthalenedisulphonic acid).

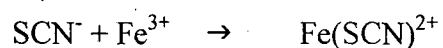
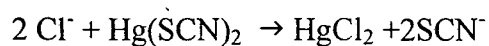
NO_3^- : For nitrate estimation, Griess method (EMEP, 1979) is followed. The detection range for this method is 0.02 – 0.23 mg $\text{NO}_3\text{-N/l}$ (0.1 – 1.0 mg NO_3/l).

Principle: Nitrate is reduced to nitrite using Cd treated with CuSO_4 as a reducing agent, in the presence of ammonium chloride.

Nitrite and sulphanilamid form a di-azo compound, which couples with N - (1-naphthyl) - ethylenediamine di-hydrochloride to form a red azo dye. The concentration in the solution is determined at **520 nm**

Cl⁻: Mercury Thiocyanate – iron (EMEP, 1979) method is applied for Cl⁻ estimation. Range for this method is 0.05 – 5mg/l.

Principle: Cl⁻ ion substitutes the thiocyanate ions in undissolved mercury thicyanate. The released thiocyanate ions react with iron thiocyanate complex. The absorbance is measured at **460 nm**.



CHAPTER -III

RESULTS AND DISCUSSION

From the observations of fog and subsequent analysis of collected fog samples, the fog frequency, liquid water content of fog and chemical composition of fog were determined.

[3.1] Fog frequency :

The characterization of fog frequency is often based on the number of recorded fog days. To improve accuracy, the number of fog hours needs to be recorded. However, due to non-availability of required equipment (Videograph), the exact duration (in hours) of fog could not be ascertained.

The categorization of fog is based on the criterion mentioned in table 1.1. As mentioned in section 2.2 out of a total of 18 fog events, 5 fog events were observed in December 2003 and 13 in January 2004 during the entire winter season (December, January and February). Fig 3.1 shows the number of fog days in each fog category (Fog, Mist & Haze).

The relative fog frequency in a given month is calculated by dividing the number of fog days in that month by the total number of fog days. The relative fog frequency for December and January months thus were found to be 27.77% and 72.22% respectively. Fig 3.2 shows the relative fog frequency for winter season. It is to be noted that in Delhi fog occurs only in the winter season and does not occur during remaining seasons (Pre-monsoon, Monsoon, and Post-monsoon). This was also the case in the year 2003-2004.

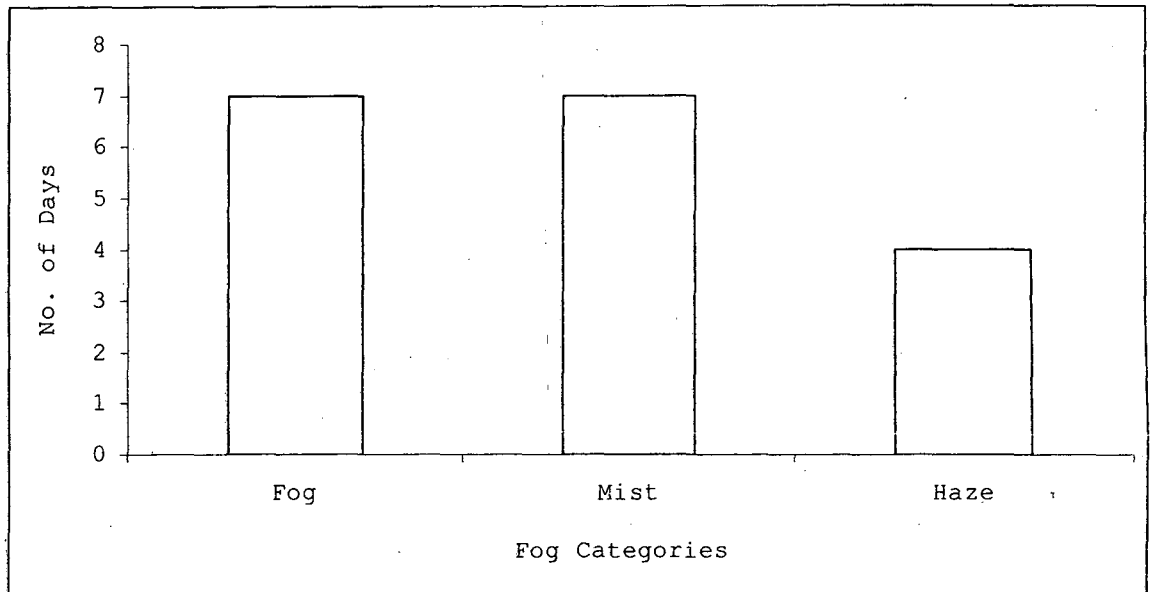


Figure 3.1: Frequency of the various fog categories observed.

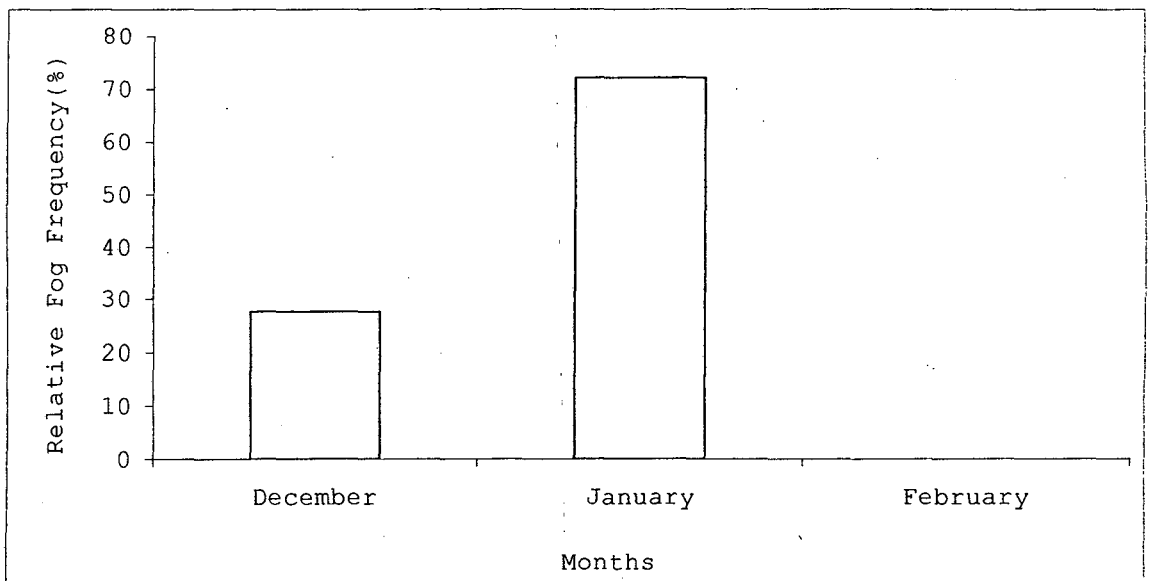


Figure 3.2: The relative fog frequency for winter season.

[3.2] Fog chemistry:

The chemistry of fog water collected during the winter season in Delhi is summarized in table 3.1. The pH, conductivity and TDS level for various fog categories is shown in fig 3.3. Fig 3.4 shows the mean pH, mean conductivity and mean TDS level for fog

and precipitation. The results show that pH, Conductivity and TDS were highly variable in all the samples collected as evident from their minimum and maximum values tabulated in table 3.2. The pH values vary from minimum of 5.43 to the maximum of 7.1 in fog water samples. pH value is minimum in fog condition and maximum in haze condition. In case of conductivity and TDS, the reverse trend is observed i.e. maximum values of these parameters in haze condition and minimum in fog condition. On comparison with the precipitation samples collected during the same period, mean pH value was higher in precipitation than in fog samples. The pH value in precipitation samples varies from 6.79 to 7.63. Thus, it has been found that majority of fog samples were slightly acidic in nature, in comparison to precipitation samples, which were either close to neutral or slightly basic in nature.

Table 3.1: Ionic concentrations in fog water and precipitation

Fog condition		Fog	Mist	Haze	Avg.	PPT. Av.
No.		7	7	4		
Temp. (°c)		8.02	9.18	9.58	8.82	
RH. (%)		90.21	89.26	86.75	89.07	
pH		6.73	6.28	5.81	6.35	7.20
Condt. (µs./cm)		1.03	2.27	4.65	2.32	0.49
TDS (mg/l)		0.47	1.48	2.52	1.32	0.26
Cl ⁻ (µeq./lit)		96.20	213.53	917.26	324.28	26.13
SO ₄ ²⁻ (µeq./lit)		3729.17	11671.41	39032.80	14663.07	2758.85
NO ₃ ⁻ (µeq./lit)		2615.15	7590.37	22042.67	8867.18	1112.75
NO ₃ ⁻ /SO ₄ ²⁻		0.77	0.78	0.75	0.77	2.48
NH ₄ ⁺ (µeq./lit)		54.41	21.62	0.00	29.57	276.73
Na ⁺ (µeq./lit)	soluble	199.94	429.36	1722.52	627.51	295.18
	insoluble	264.42	260.65	310.70	273.24	218.18
K ⁺ (µeq./lit)	soluble	174.21	330.96	1498.43	529.44	287.67
	insoluble	181.18	168.60	130.64	165.06	130.43
Ca ²⁺ (µeq./lit)	soluble	1440.27	2887.21	9889.47	3880.57	1639.61
	insoluble	259.10	376.55	164.06	283.65	126.68
Mg ²⁺ (µeq./l)	soluble	181.62	384.34	1568.10	568.56	213.96
	insoluble	134.38	129.19	124.42	130.15	91.30
Cu ²⁺ (µeq./l)	soluble	22.77	74.50	172.28	76.11	2.17
	insoluble	18.00	21.01	10.55	17.52	3.34
Pb ²⁺ (µeq./l)	soluble	0.00	0.00	0.00	0.00	0.00
	insoluble	4.29	4.91	4.02	4.47	2.38

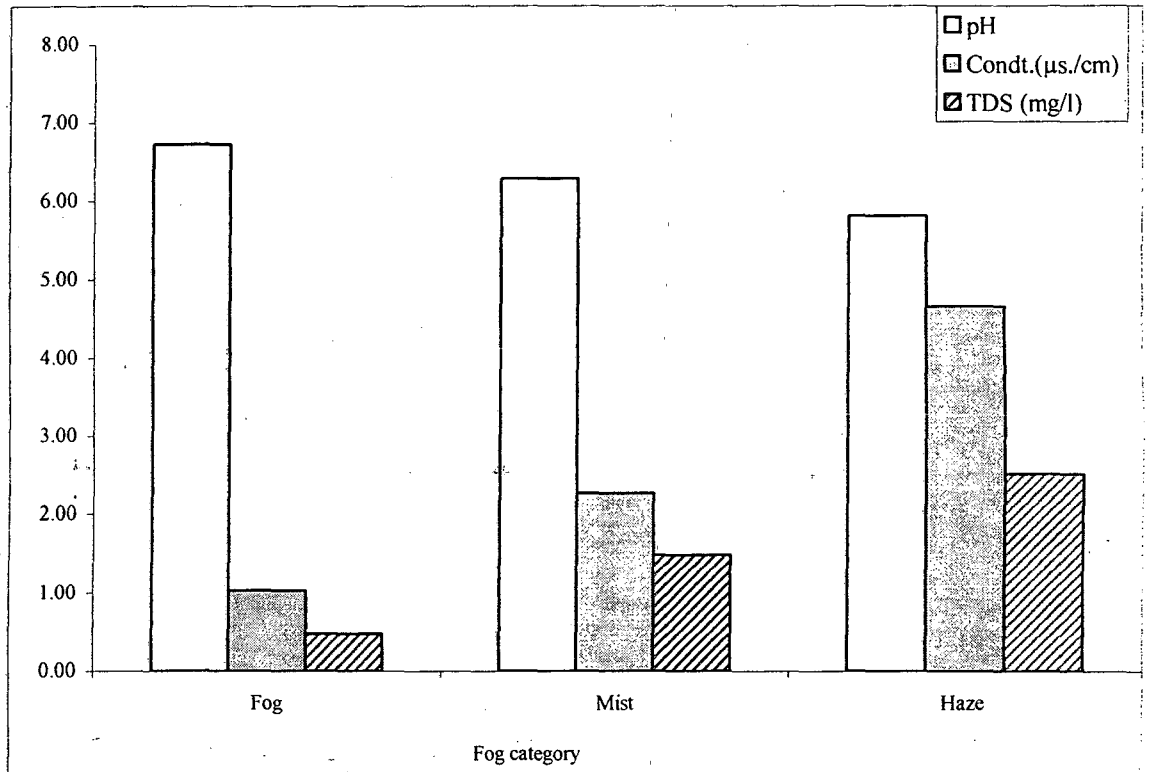


Figure 3.3: Variation of pH, Conductivity and TDS over different fog categories

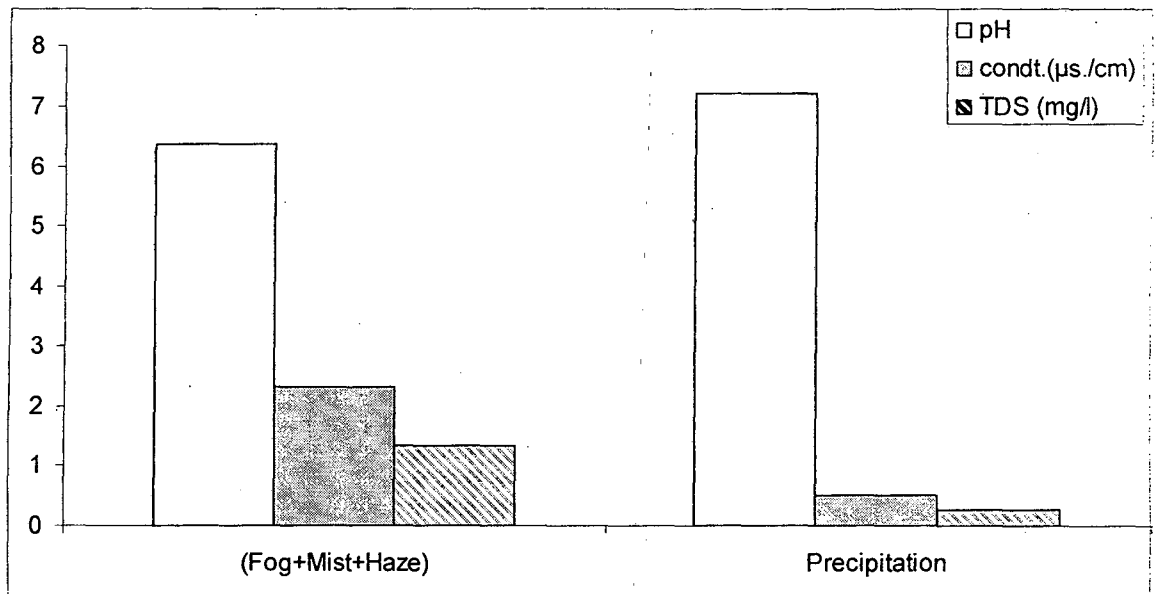


Figure 3.4: Variation of pH, Conductivity and TDS in Fog water and precipitation

Fig 3.5 shows the variation in pH, Conductivity and TDS with the water content. The trend revealed that as the water content increases pH increases slightly but

Conductivity and TDS decrease sharply. Fig 3.6 depicts the water quantity as a function of Temperature for different fog conditions. The RH (%) values associated with different temperatures are also indicated in figure 3.6. It reveals that water content of all categories of the fog is sensitive to even slight changes in temperature and RH.

Mean concentration, maximum and minimum concentrations of major ions in fog water and precipitation samples are given in table 3.2. Fig (3.7 - 3.9) show the anion (Cl^- , SO_4^{2-} , NO_3^-) concentrations and fig (3.10–3.16) display the cation (NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} and Pb^{2+}) concentrations over various fog categories. Concentrations of individual cations and anions averaged over all fog conditions and in precipitation are displayed in fig (3.17 - 3.26).

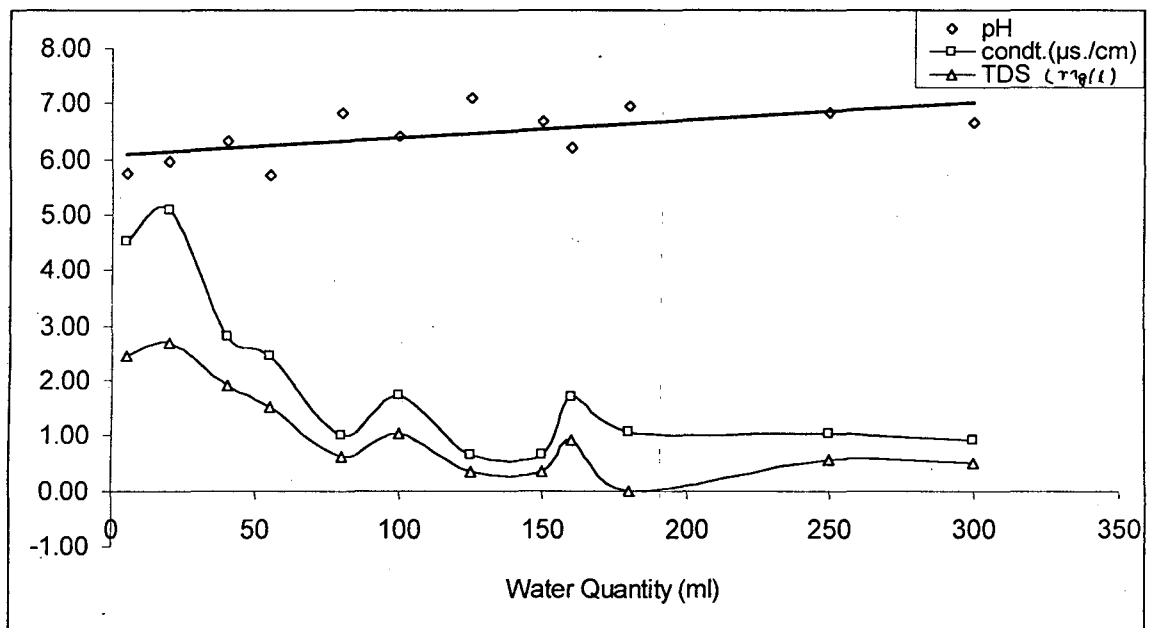


Figure 3.5: Variation in pH, Conductivity and TDS with water content in fog

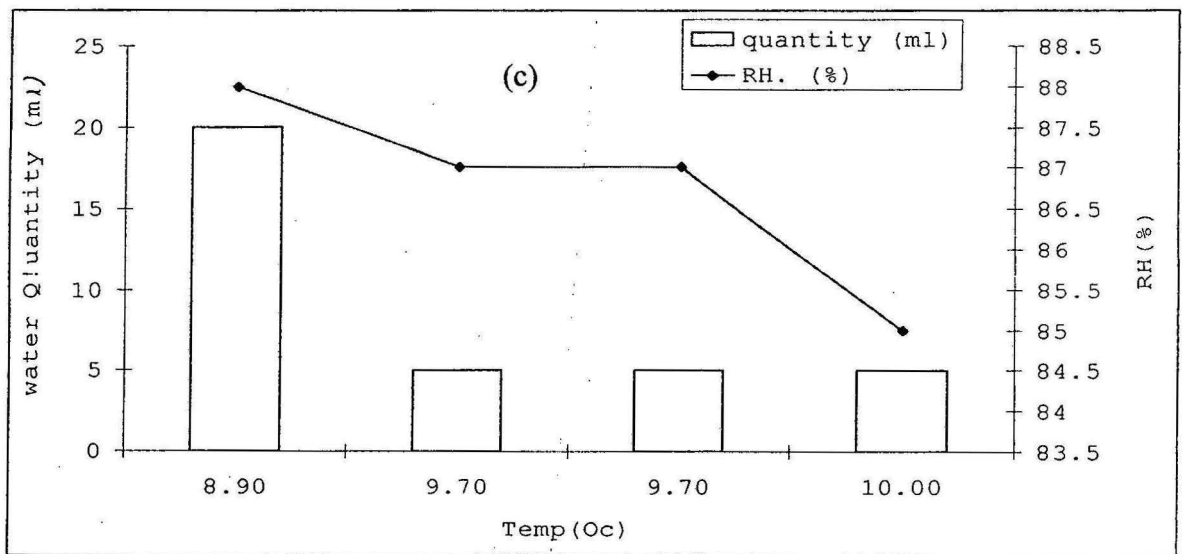
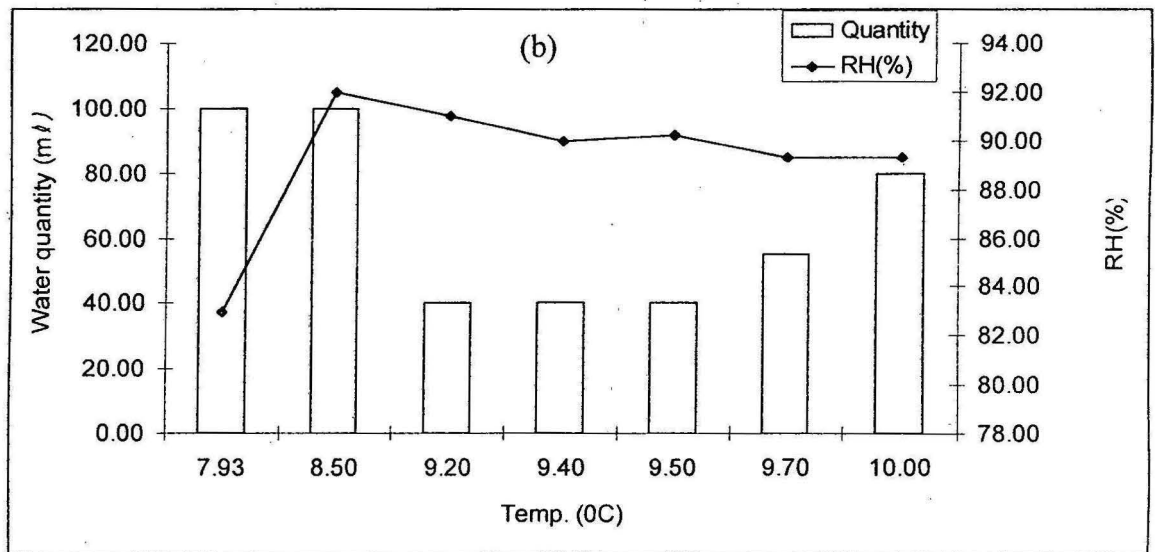
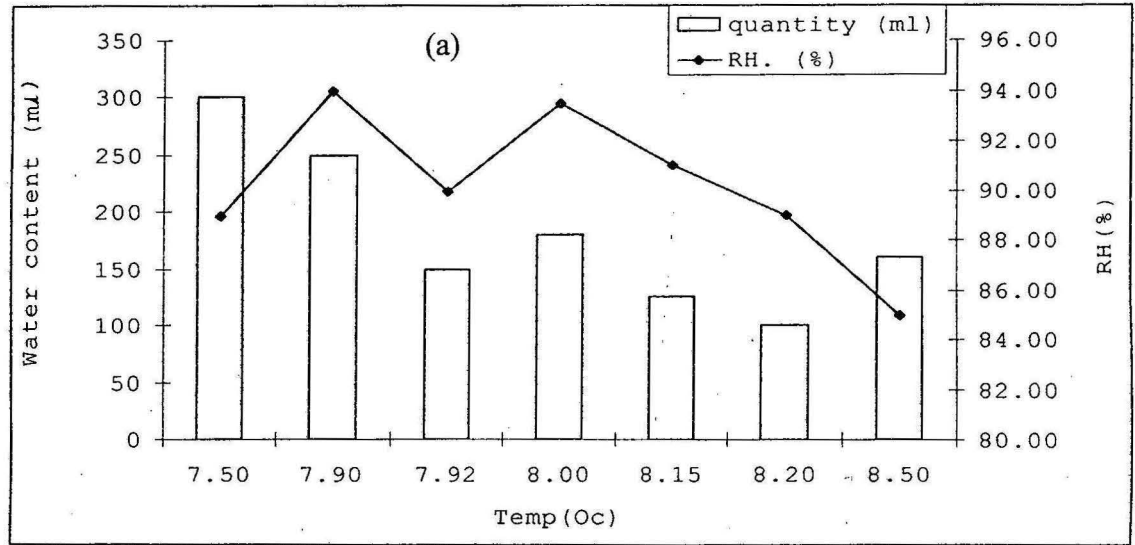


Figure 3.6: Variation of water content as a function of Temperature for (a) Fog; (b)Mist; (c) Haze.

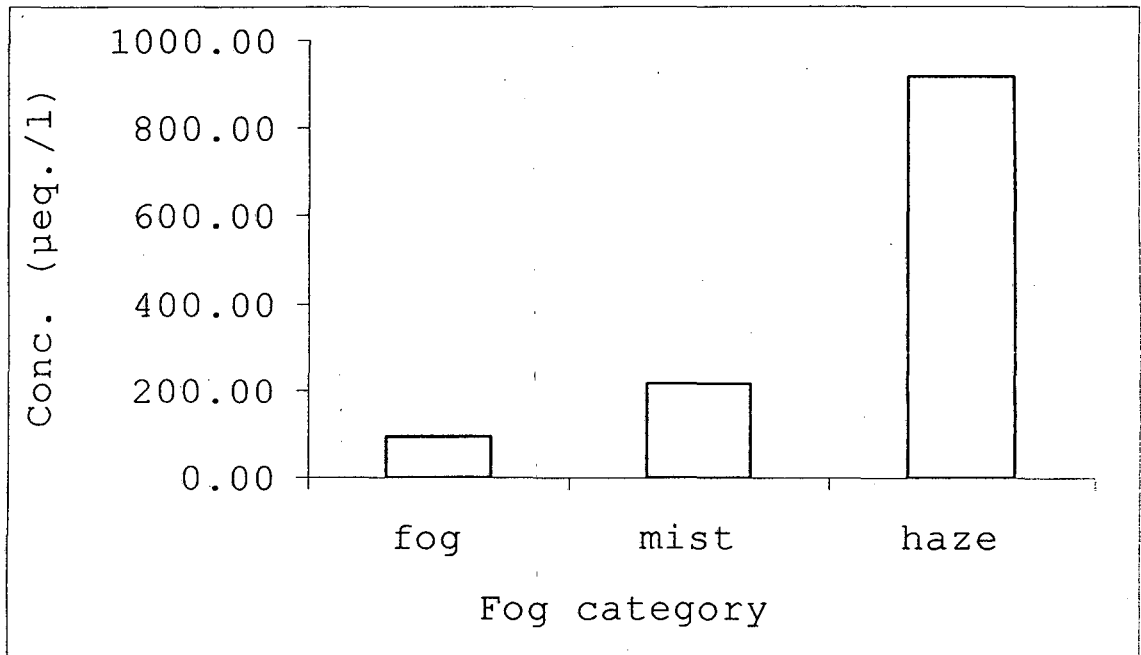


Figure 3.7: Concentration of Cl⁻ ion in various fog categories

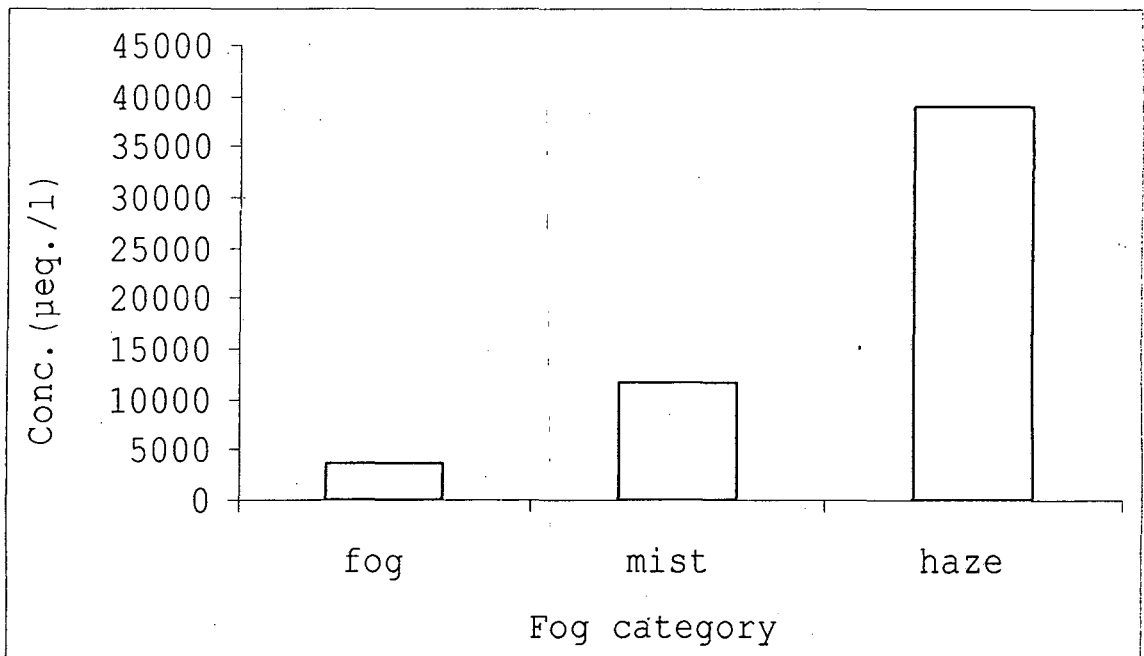


Figure 3.8: Concentration of SO₄²⁻ ion in various fog categories

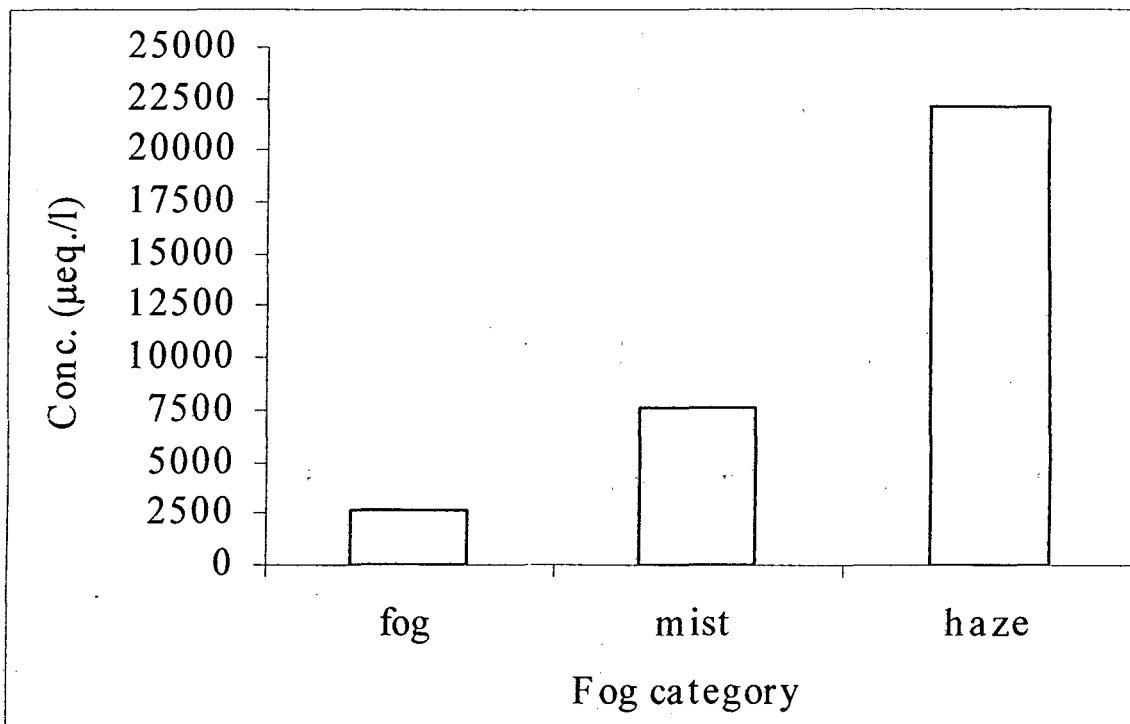


Figure 3.9: Concentration of NO_3^- ion in various fog categories

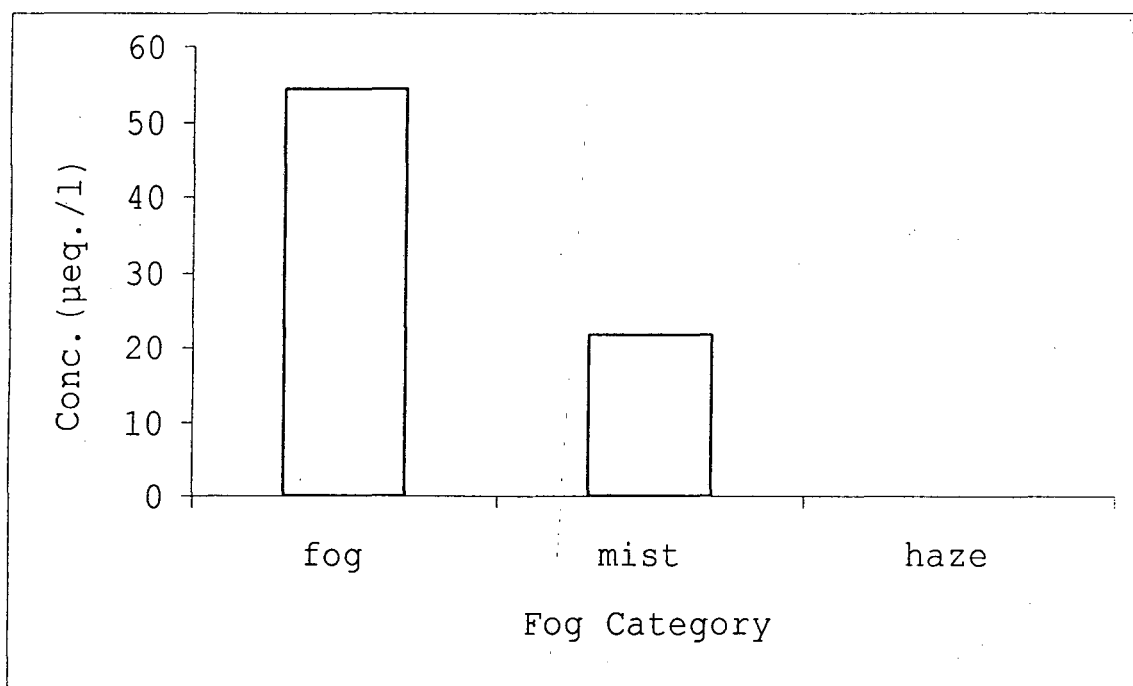


Figure 3.10: Concentration of NH_4^+ ion in various fog categories

Table 3.2: Mean, minimum and maximum values of concentrations of different ions in different fog categories and precipitation.

fog condition	Fog			Mist			Haze			Fog Average			PPT Avg.			
	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	
quantity (ml)	180.71	100.00	300.00	65.00	40.00	100.00	8.75	5.00	20.00	97.50	5.00	300.00	155.00	60.00	200.00	
pH	6.73	6.20	7.10	6.28	5.73	6.82	5.81	5.43	5.96	6.35	5.43	7.10	7.20	6.79	7.63	
condt.(μ s./cm)	1.03	0.65	1.70	2.27	1.01	5.08	4.65	5.08	13.52	2.32	0.65	13.52	0.49	0.49	0.98	
TDS (mg/l)	0.47	0.35	0.91	1.48	0.62	2.87	2.52	2.68	7.38	1.32	0.35	7.38	0.26	0.26	0.52	
Cl ⁻ (μ eq./lit)	96.20	48.80	136.68	213.53	115.15	326.79	917.26	219.30	1967.46	324.28	48.80	1967.46	26.13	19.17	89.27	
SO ₄ ²⁻ (μ eq./lit)	3729.17	1547.44	8487.34	11671.41	1982.54	21103.44	39032.80	18457.68	97429.01	14663.07	1547.44	97429.01	2758.85	764.25	6282.42	
NO ₃ ⁻ (μ eq./lit)	2615.15	1180.06	4239.22	7590.37	2695.86	20219.47	22042.67	15198.99	37612.41	8867.18	1180.06	37612.41	1112.75	243.02	3318.42	
NO ₃ /SO ₄ ²⁻	0.77	0.50	1.06	0.78	0.34	1.36	0.75	0.39	0.96	0.77	0.34	1.36	0.30	0.29	0.53	
NH ₄ ⁺ (μ eq./lit)	54.41	18.58	183.99	21.62	9.39	141.95	0.00	0.00	0.00	29.57	9.39	183.99	276.73	170.84	425.35	
Na ⁺ (μ eq./lit)	soluble	199.94	89.49	292.57	429.36	207.05	675.88	1722.52	715.01	3187.96	627.51	89.49	3187.96	295.18	22.21	916.75
	insoluble	264.42	155.55	312.19	260.65	149.11	307.13	310.70	298.86	318.94	273.24	149.11	318.94	218.18	218.18	298.24
K ⁺ (μ eqv./lit)	soluble	174.21	136.50	200.56	330.96	167.59	471.18	1498.43	651.84	2330.50	529.44	136.50	2330.50	287.67	18.94	871.02
	insoluble	181.18	117.47	233.07	168.60	138.25	211.35	130.64	51.17	172.25	165.06	51.17	233.07	130.43	76.86	207.38
Ca ²⁺ (μ eqv./lit)	soluble	1440.27	763.00	1858.00	2887.21	729.50	5074.00	9889.47	2637.00	20528.50	3880.57	729.50	20528.50	1639.61	214.00	4248.00
	insoluble	259.10	78.00	950.50	376.55	121.50	874.00	164.06	87.50	482.00	283.65	78.00	874.00	126.68	124.00	345.00
Mg ²⁺ (μ eq./lit)	soluble	181.62	80.38	251.64	384.34	107.97	565.88	1568.10	761.42	2954.02	568.56	80.38	251.64	213.96	12.33	643.79
	insoluble	134.38	4.92	261.65	129.19	62.24	212.18	124.42	11.85	230.98	130.15	4.92	261.65	91.30	13.85	241.61
Cu ²⁺ (μ eq./lit)	soluble	22.77	13.54	38.43	74.50	18.90	117.64	172.28	103.62	329.13	76.11	13.54	329.13	2.17	1.42	9.45
	insoluble	18.00	11.97	29.29	21.01	9.45	30.55	10.55	1.26	16.38	17.52	1.26	30.55	3.34	0.94	11.02
Pb ²⁺ (μ eq./lit)	Soluble*	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	insoluble	4.29	2.93	5.85	4.91	1.10	9.88	4.02	3.11	5.31	4.47	1.10	9.88	2.38	2.01	2.93

* Below detection limit.

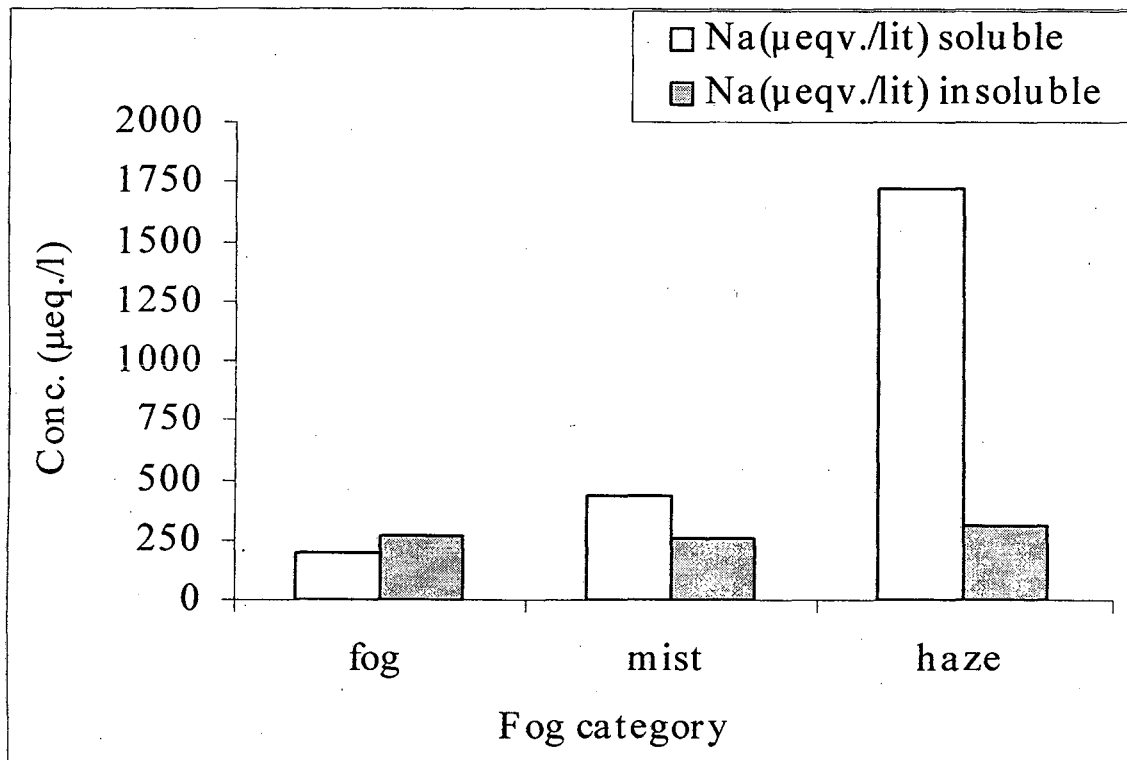


Figure 3.11: Concentrations of Na⁺ metal ion in soluble and insoluble fraction of fog water among various fog categories.

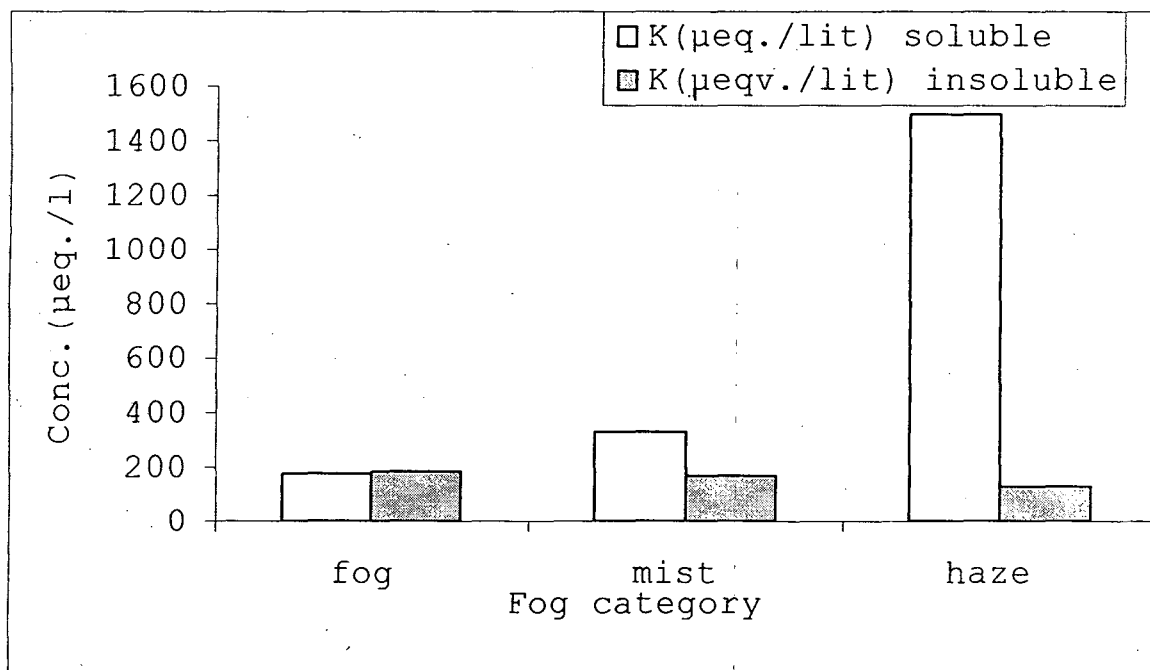


Figure 3.12: Concentrations of K⁺ metal ion in soluble and insoluble fraction of fog water among various fog categories.

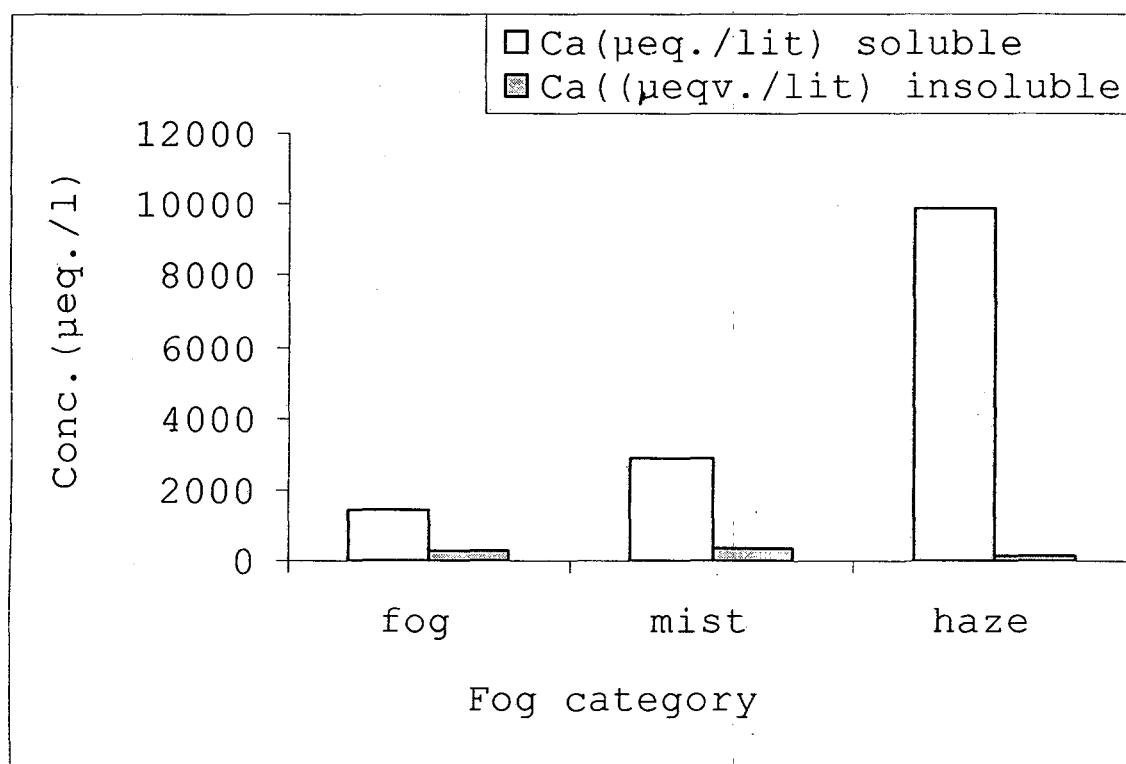


Fig 3.13: Concentrations of Ca^{2+} metal ion in soluble and insoluble fraction of fog water among various fog categories.

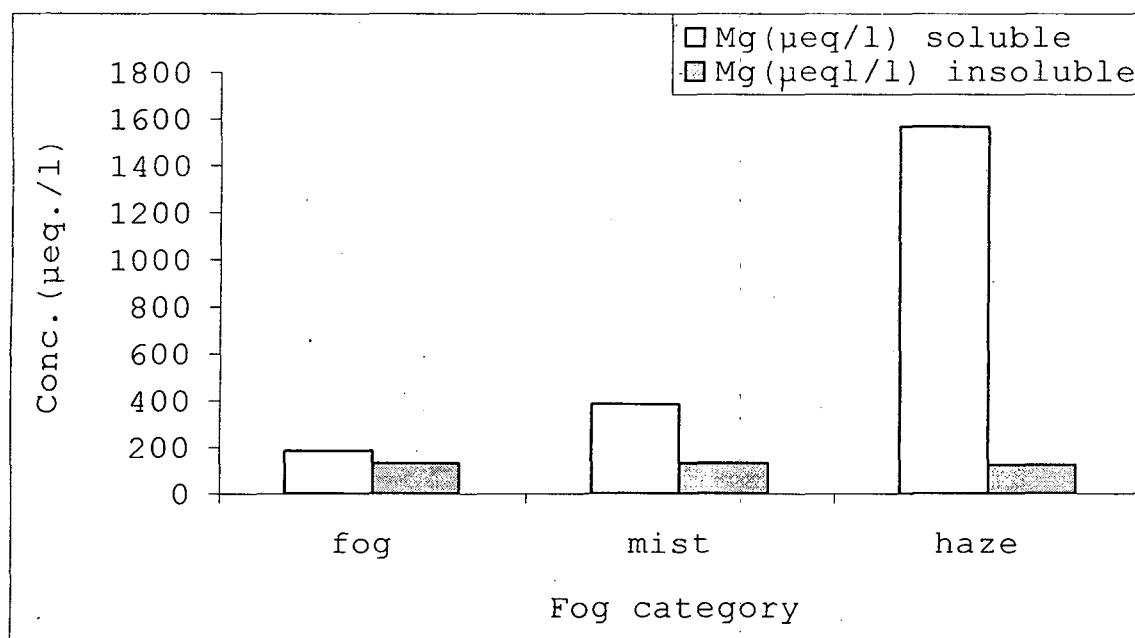


Figure 3.14: Concentrations of Mg^{2+} metal ion in soluble and insoluble fraction of fog water among various fog categories.

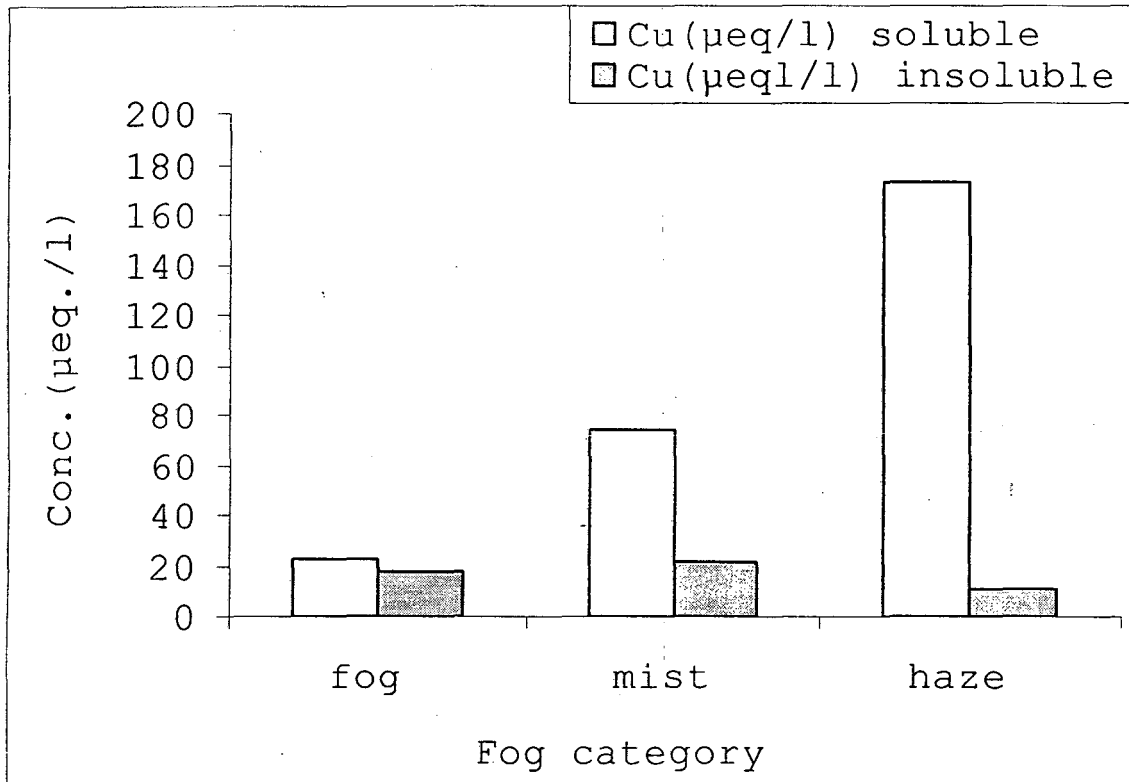


Figure 3.15: Concentrations of Cu^{2+} metal ion in soluble and insoluble fraction of fog water among various fog categories.

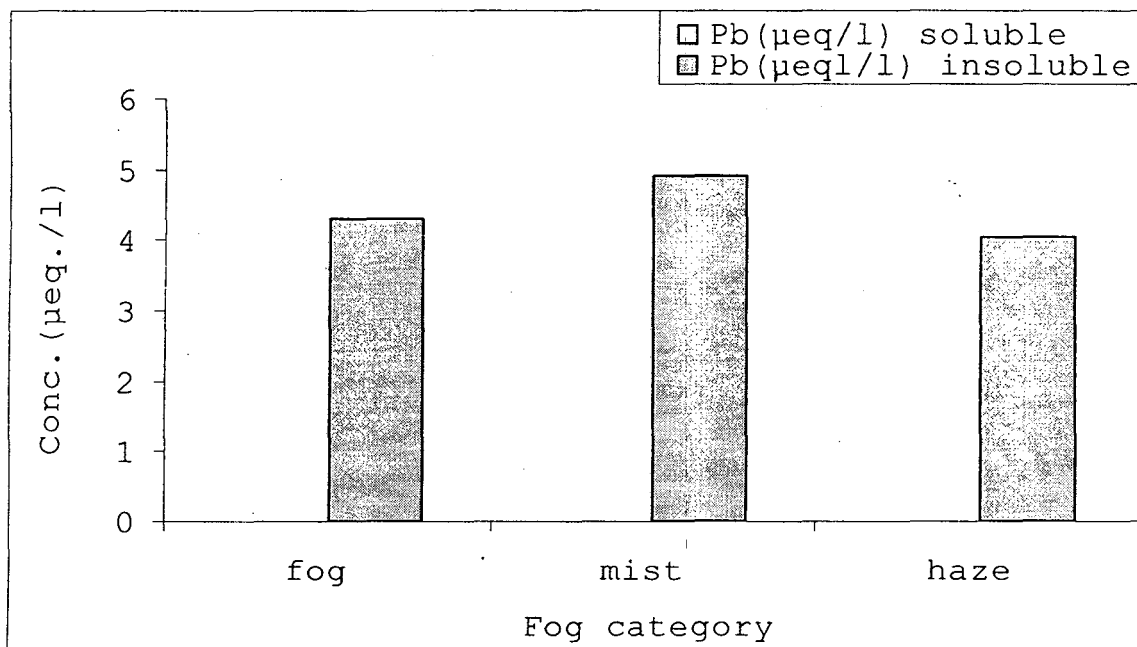


Figure 3.16: Concentrations of Pb^{2+} metal ion in soluble and insoluble fraction of fog water among various fog conditions.

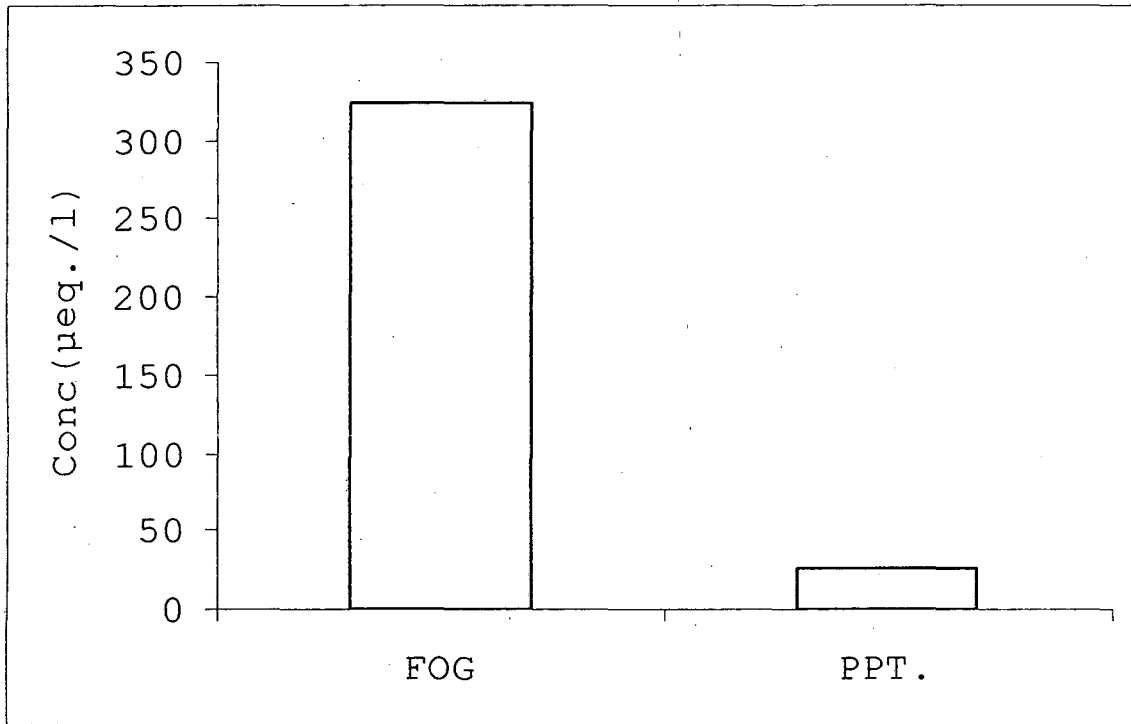


Figure 3.17: Concentration of Cl⁻ ions in fog and precipitation.

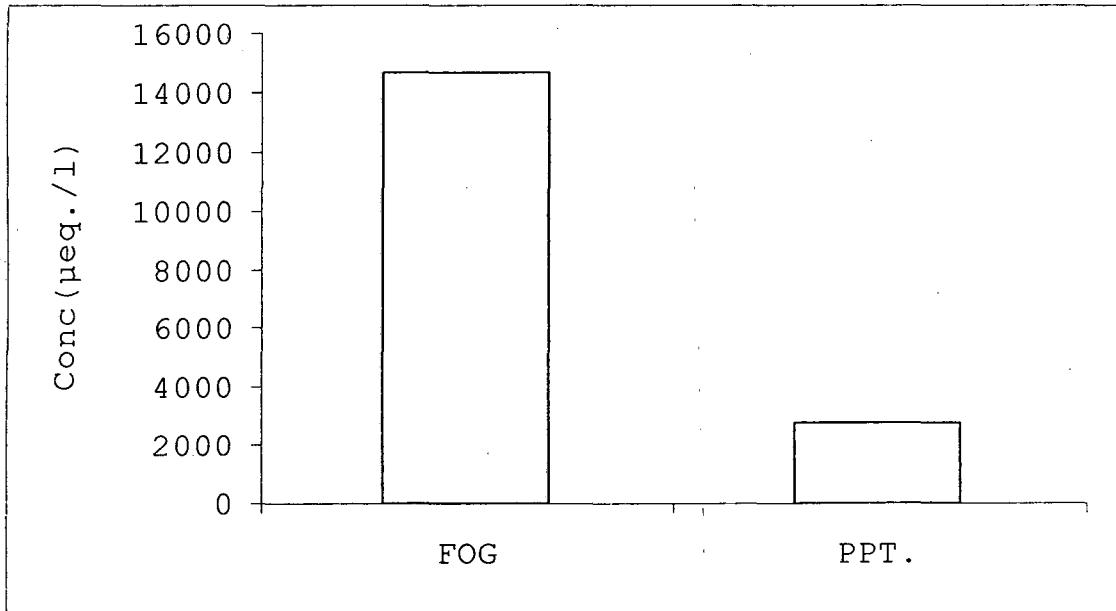


Figure 3.18: Concentration of SO₄²⁻ ions in fog and precipitation.

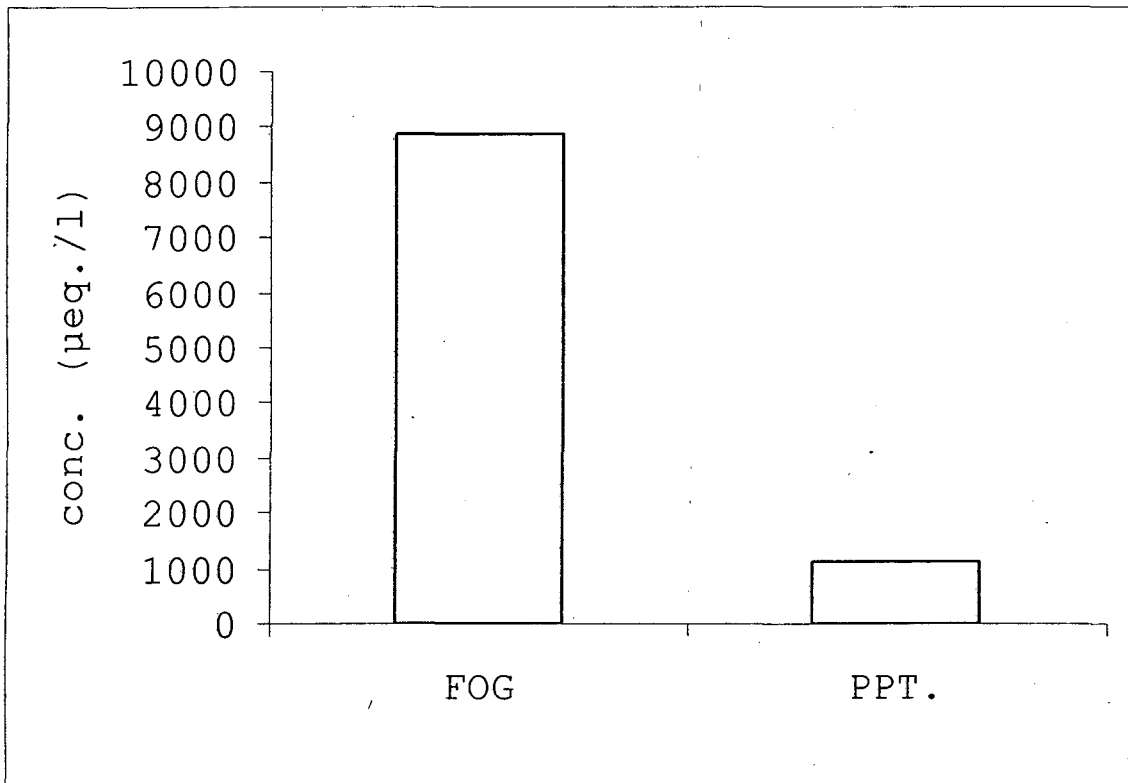


Figure 3.19: Concentration of NO_3^- ions in fog and precipitation.

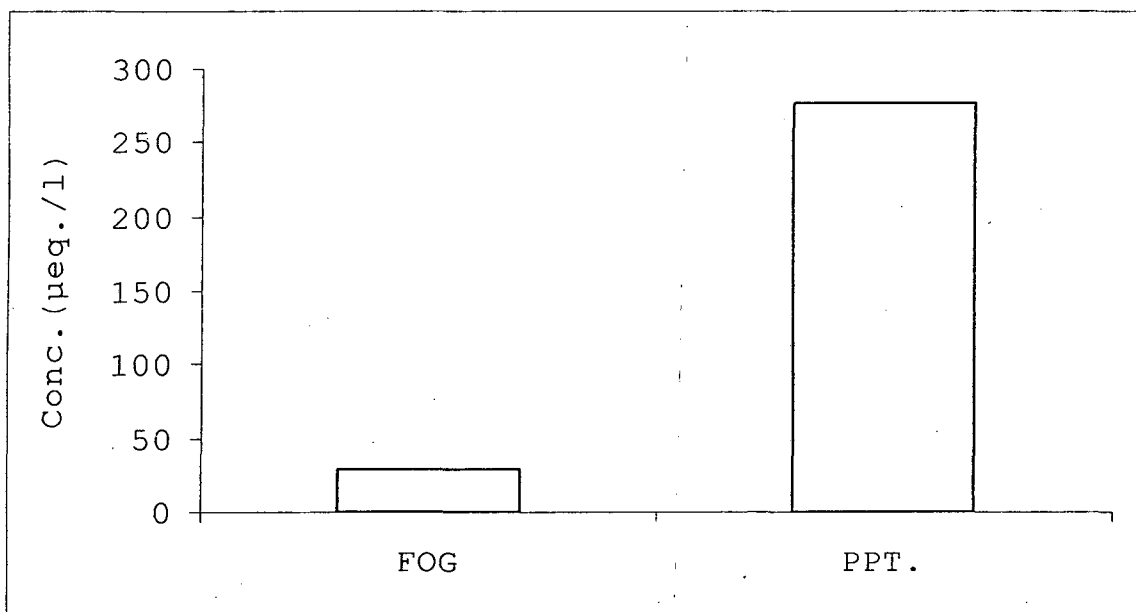


Figure 3.20: Concentration of NH_4^+ ions in fog and precipitation.

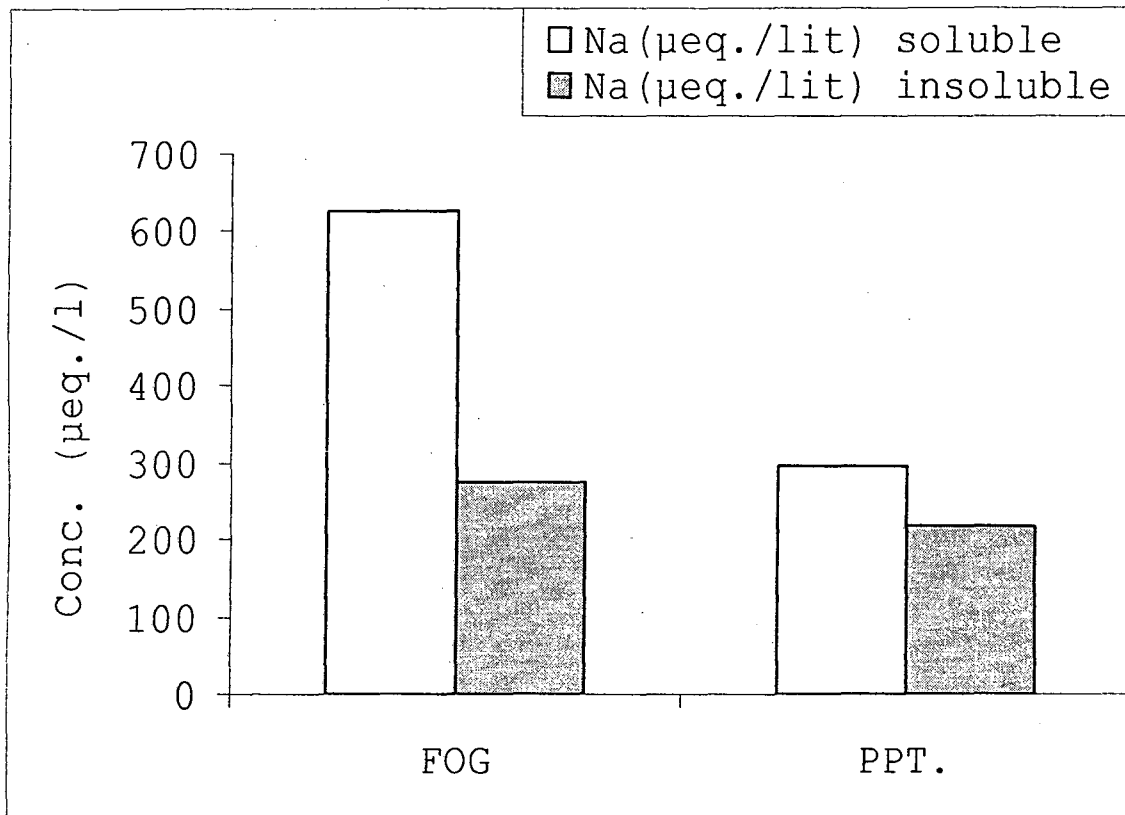


Figure 3.21: Concentrations of Na⁺ metal ions in soluble and insoluble fraction of fog water and precipitation.

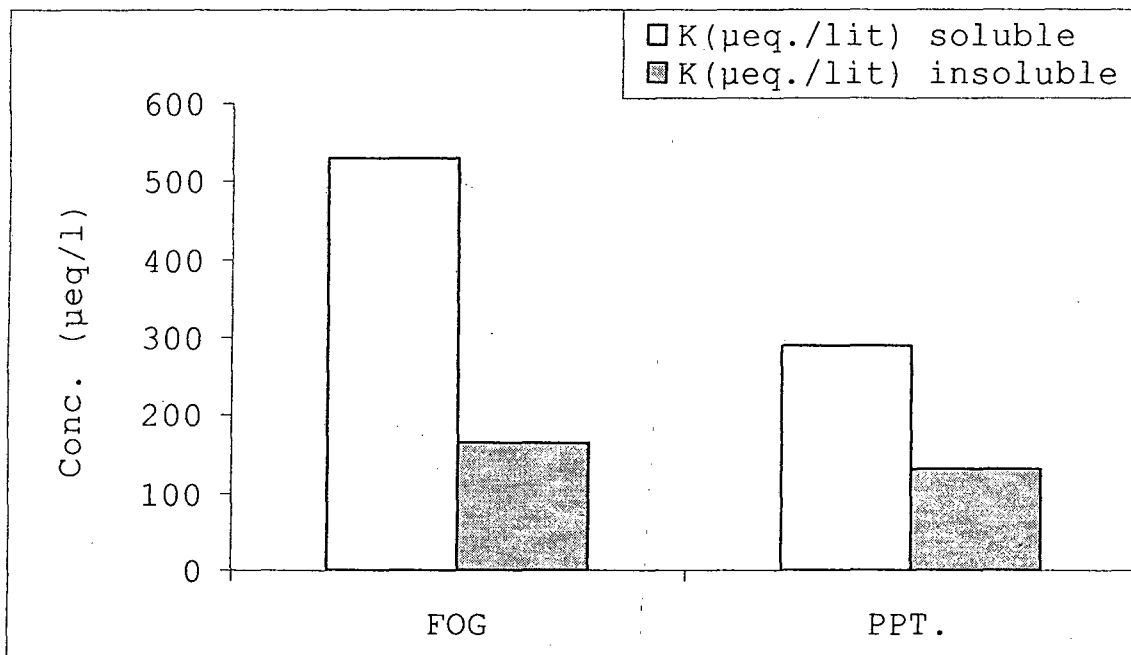


Figure 3.22: Concentrations of K⁺ metal ions in soluble and insoluble fraction of fog water and precipitation.

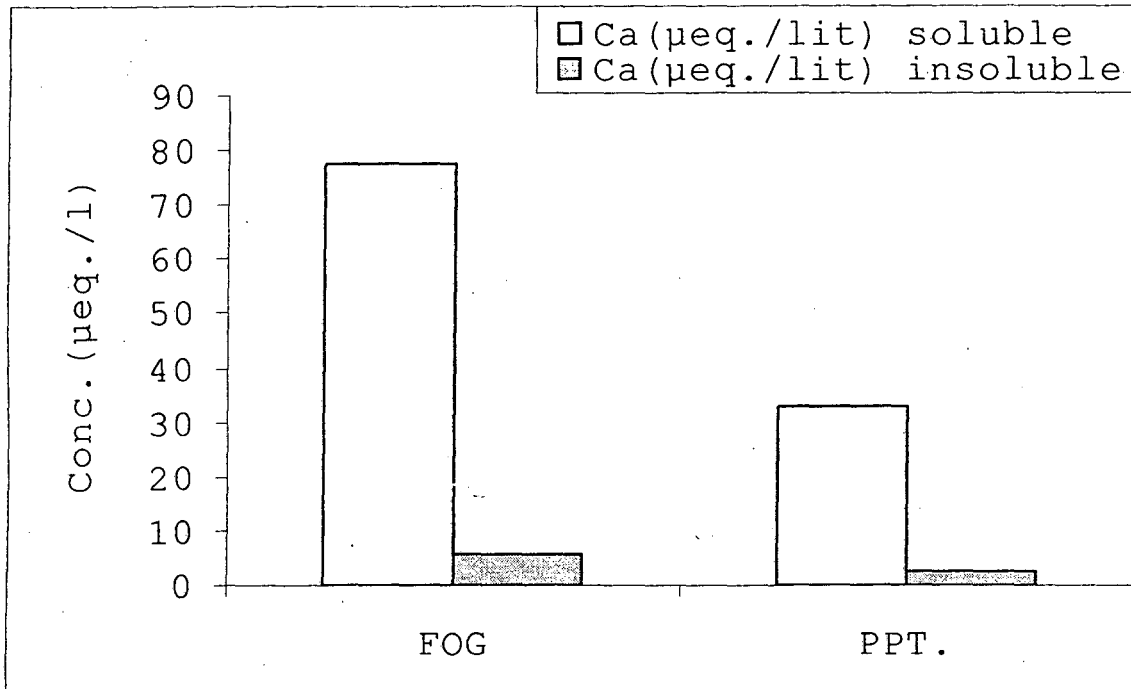


Figure 3.23: Concentrations of Ca^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation.

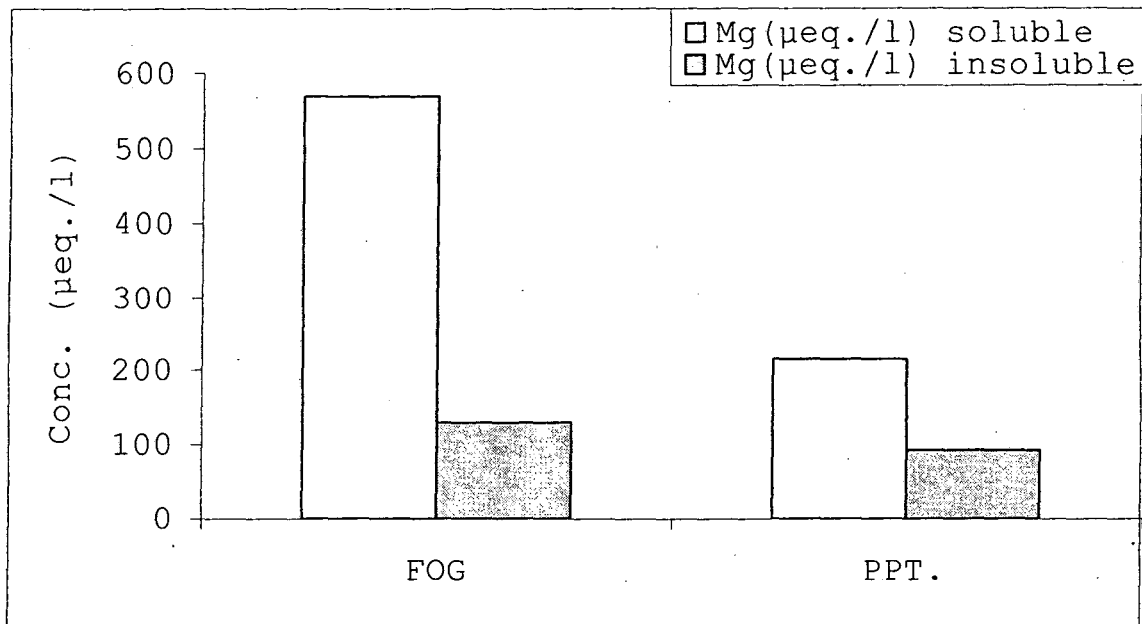


Figure 3.24: Concentrations of Mg^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation.

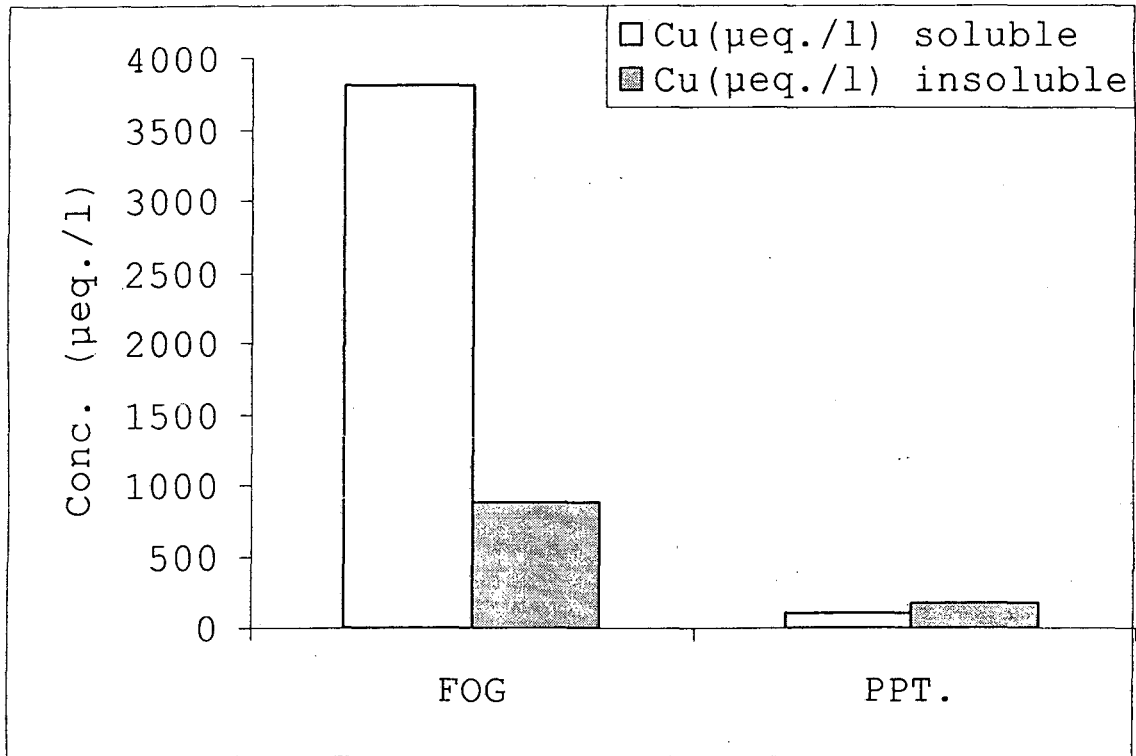


Figure 3.25: Concentrations of Cu^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation.

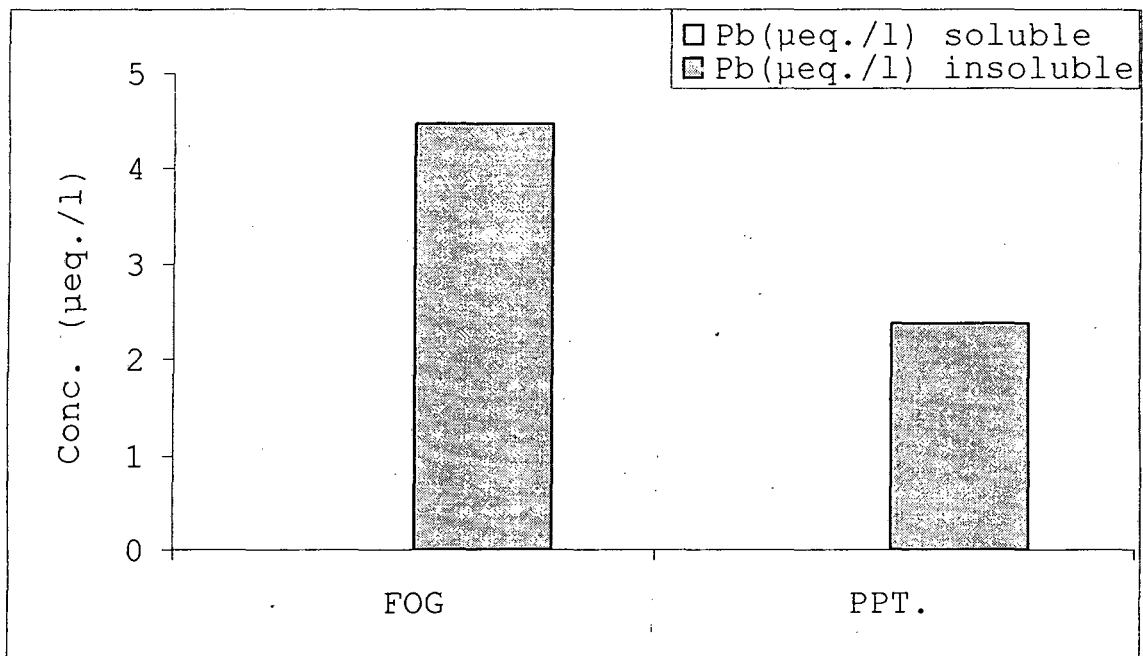


Figure 3.26:- Concentrations of Pb^{2+} metal ions in soluble and insoluble fraction of fog water and precipitation.

An examination of table 3.3 where the results of ionic concentrations are summarized, reveals that Ca^{2+} is the most prominent cation followed by Na^+ and Mg^{2+} in fog water and SO_4^{2-} is the most prominent anion followed by NO_3^- . In case of precipitation also, Ca^{2+} and SO_4^{2-} are the most prominent cation and anion, respectively. However, NH_4^+ concentration is also significant in precipitation sample, as is evident from table 3.3.

Table 3.3: Concentration ratios of different ions.

Ions	Fog	Precipitation
$\text{SO}_4^{2-}/\text{NO}_3^-$	1.65	2.48
Σ cations ($\mu\text{eq./lit.}$)	5711.76	2715.33
Σ anions ($\mu\text{eq./lit.}$)	23854.54	3897.72
cations/anions	0.24	0.57
$\text{Ca}^{2+}/\text{cation}$	0.68	0.60
$\text{Na}^+/\text{cation}$	0.11	0.11
K^+/cation	0.09	0.11
$\text{nh}_4^+/\text{cation}$	0.01	0.10
$\text{Mg}^{2+}/\text{cation}$	0.10	0.08
$\text{so}_4^{2-}/\text{anion}$	0.61	0.71
$\text{no}_3^-/\text{anion}$	0.37	0.29
$\text{so}_4^{2-}/\text{Na}^+$	3.78	1.68
Cl^-/Na^+	0.52	0.09

The results also reveal that almost all of the ions (cations and anions) are present in higher concentrations in fog water than the precipitation, except for the NH_4^+ ion concentration,

which shows reverse trend, i.e. NH_4^+ concentration is higher in precipitation samples than in the fog water sample. It contributes $\sim 10\%$ of the total cation concentrations in precipitation water, whereas in fog samples, it contributes a meagre 1% only. In general, ionic concentrations are found to be higher during haze and lower during foggy conditions except NH_4^+ ions, which are non-existent in haze. With the exception of Cu^{2+} and Pb^{2+} , rest of the cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) have higher concentrations in soluble fraction of the fog water in comparison to the insoluble fraction. In case of Cu^{2+} in precipitation sample (fig 3.25), the metal concentration in insoluble fraction far exceeded the concentration in soluble fraction.

In case of Pb^{2+} (fig 3.26), it is found below detection limit in soluble fraction of all of the fog samples as well as in precipitation samples where as, insoluble fraction has significant concentration of Pb^{2+} .

Figures (3.27 - 3.36) show the changes in ionic concentrations with the amount of water collected during fog. The result indicates that the concentration of all the ions decreases with increase in water content. Here also, NH_4^+ shows the opposite trend. Its concentration increases with the quantity of water. However, Pb^{2+} concentration shows no direct relation with the water content.

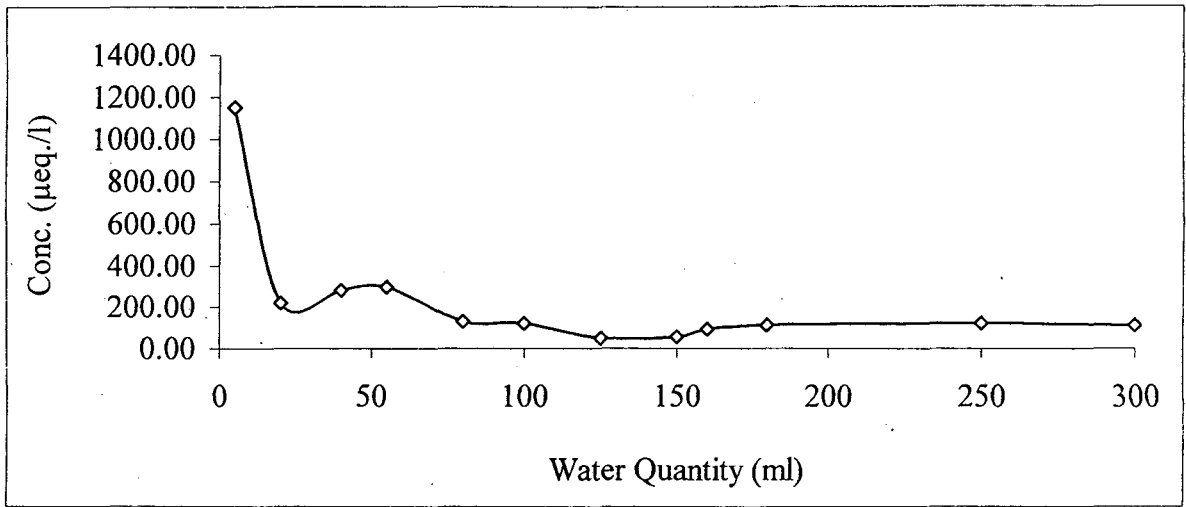


Figure 3.27: Variation in Cl⁻ ion concentration with water content in fog

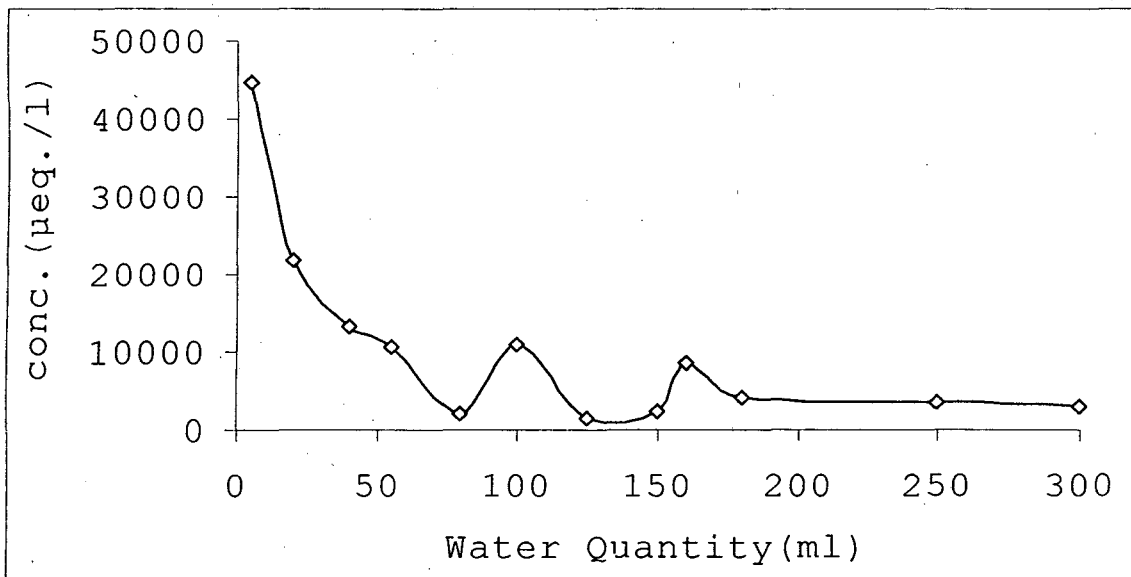


Figure 3.28: Variation in SO₄²⁻ ion concentration with water content in fog

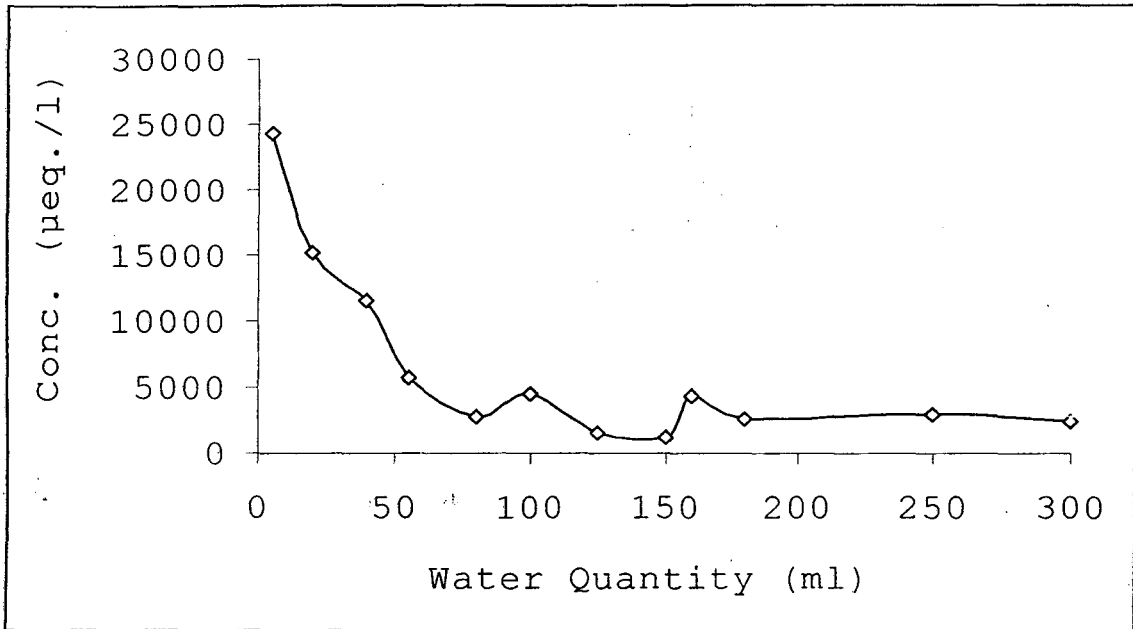


Figure 3.29: Variation in NO_3^- ion concentration with water content in fog.

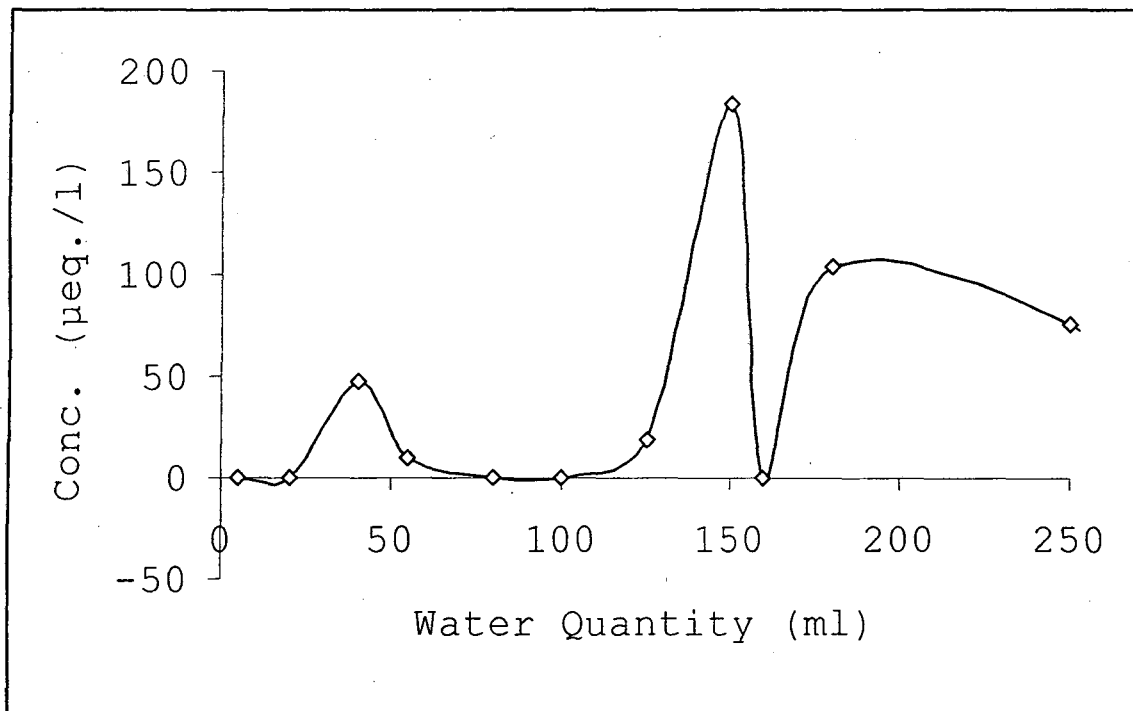


Figure 3.30: Variation in NH_4^+ ion concentration with water content in fog.

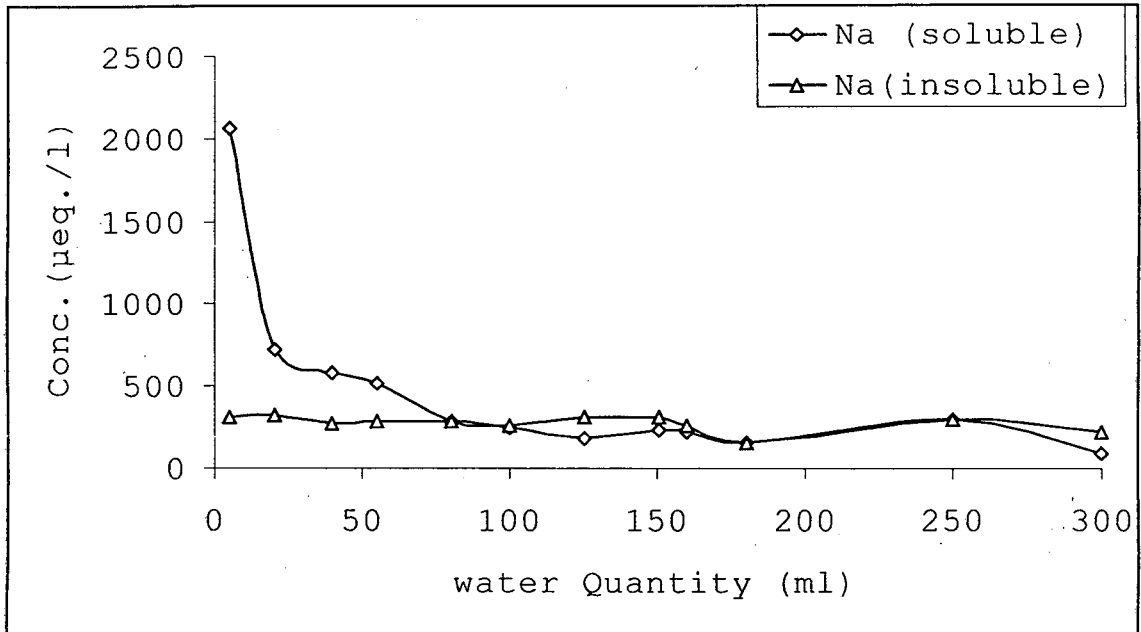


Figure 3.31: Variation in Na⁺ metal ion concentration in soluble and insoluble fraction with water content in fog

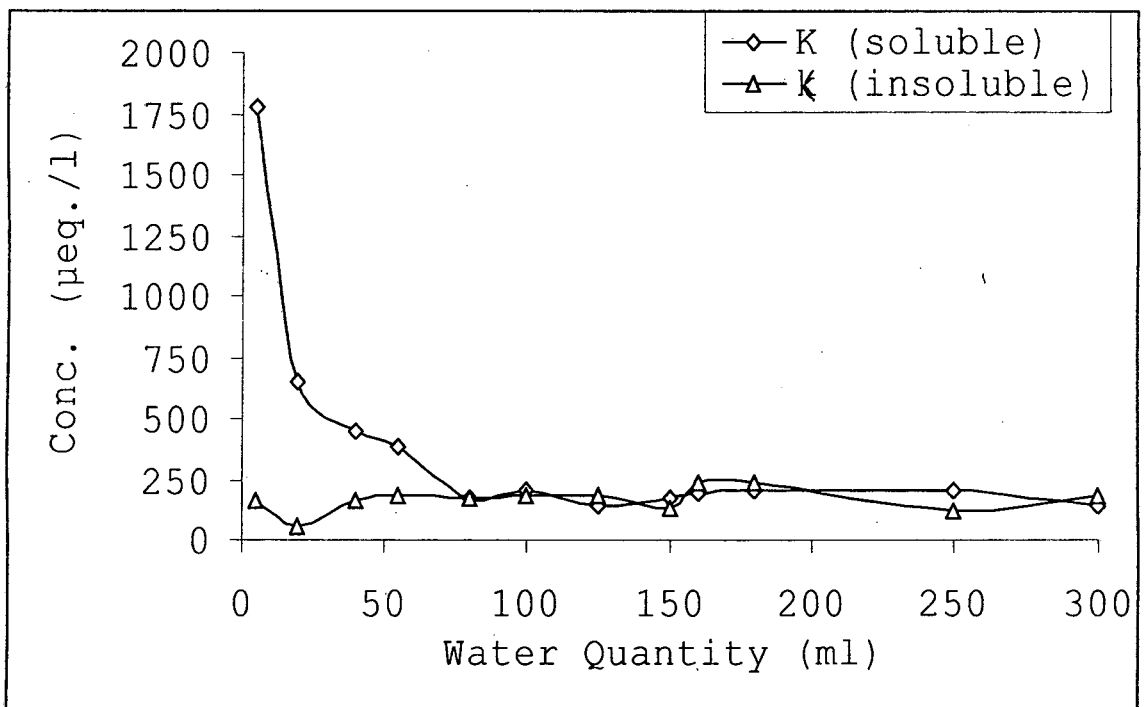


Figure 3.32: Variation in K⁺ metal ion concentration in soluble and insoluble fraction with water content in fog.

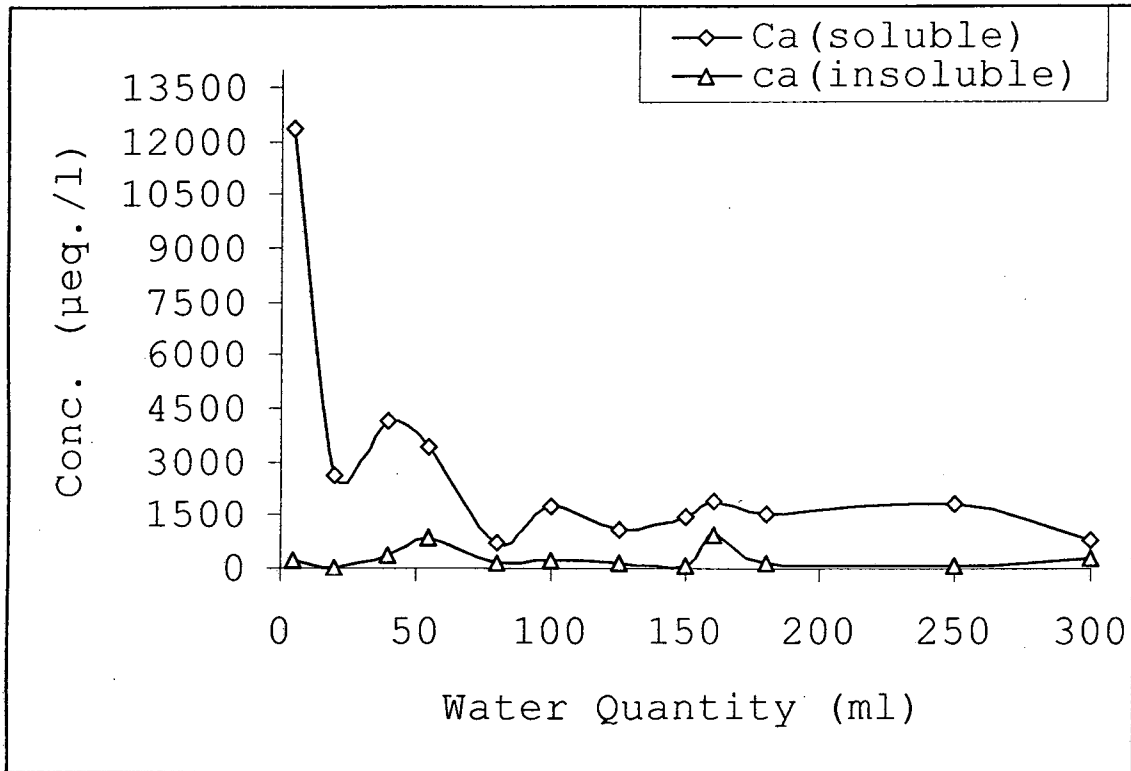


Figure 3.33: Variation in Ca²⁺ metal ion concentration in soluble and insoluble fraction with water content in fog.

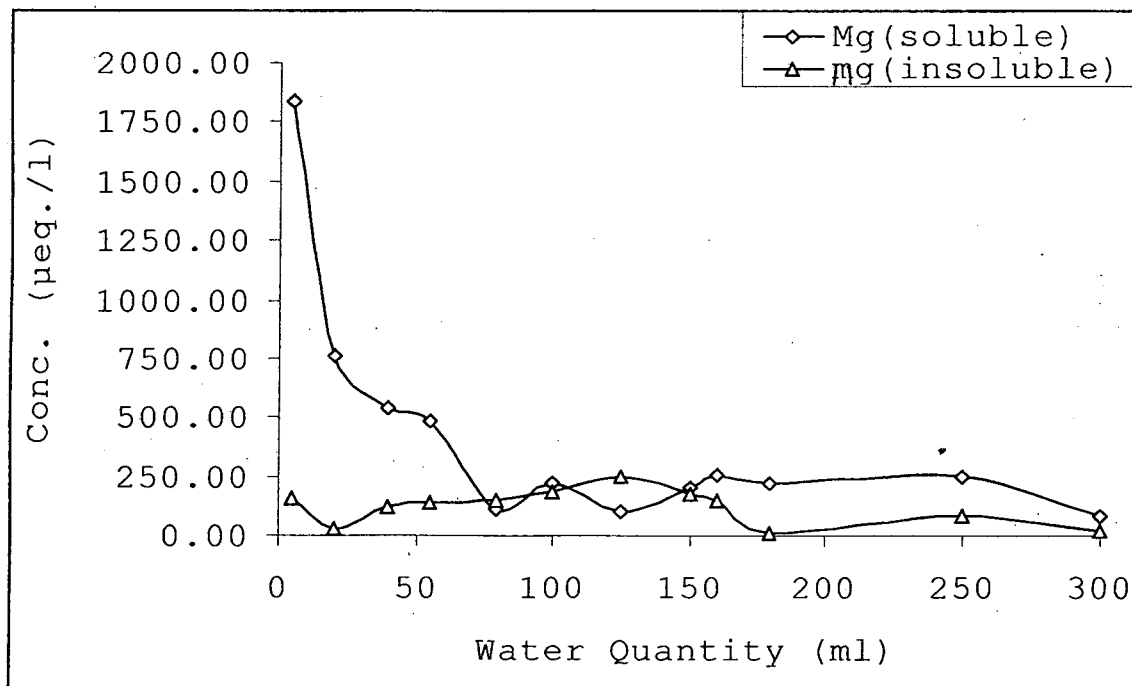


Figure 3.34: Variation in Mg²⁺ metal ion concentration in soluble and insoluble fraction with water content in fog.

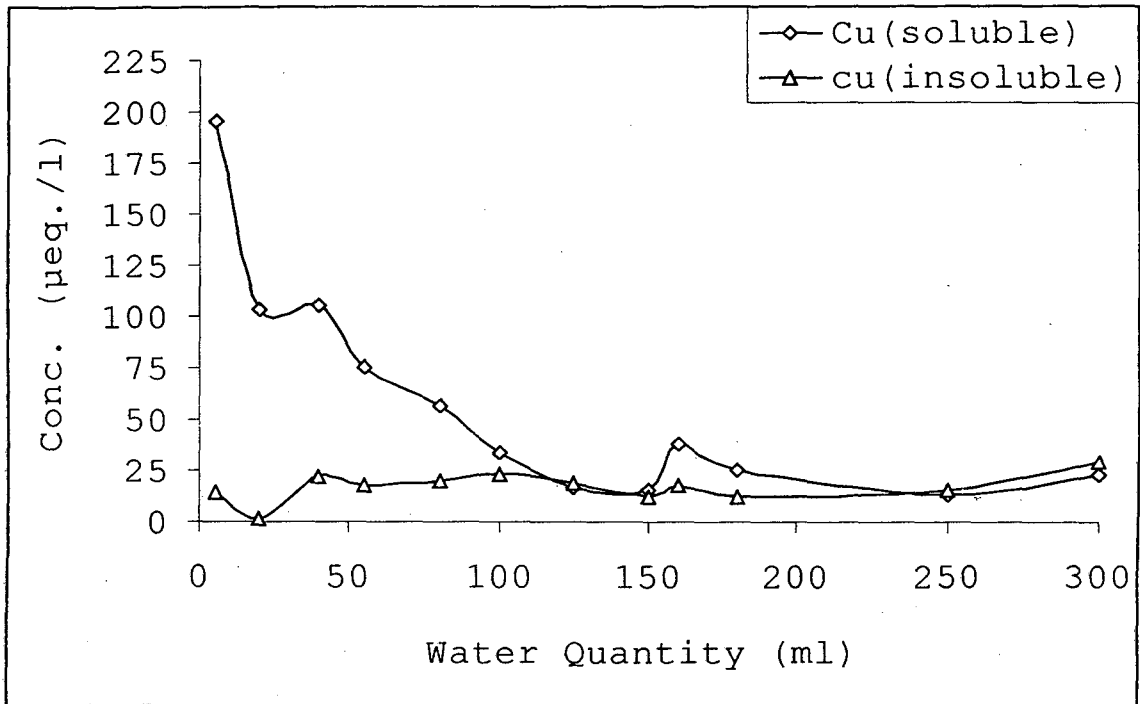


Figure 3.35: Variation in Cu²⁺ metal ion concentration in soluble and insoluble fraction with water content in fog.

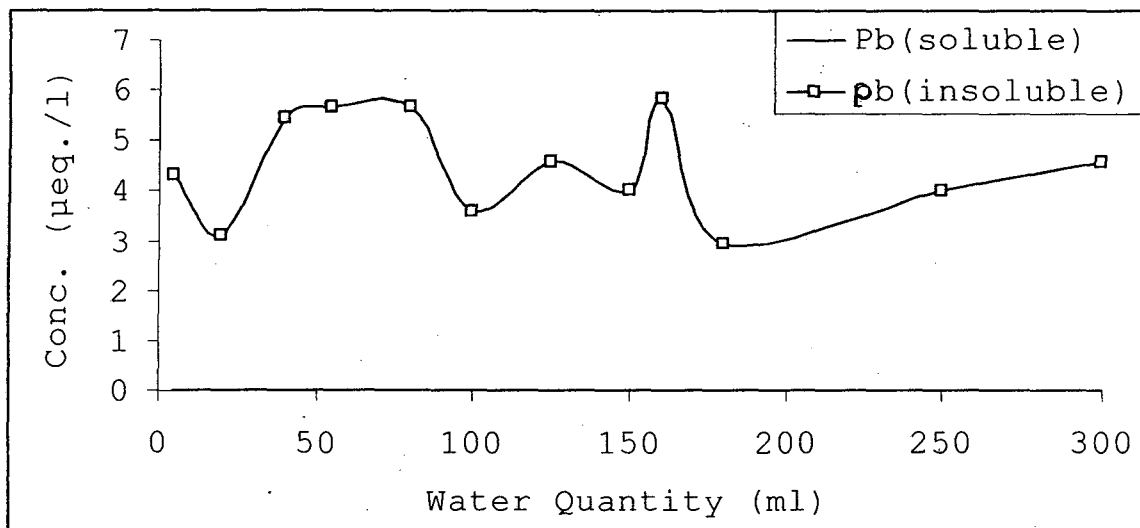


Figure 3.36: Variation in Pb²⁺ metal ion concentration in soluble and insoluble fraction with water content in fog.

The sulphate and nitrate concentrations need special mention as both these anions constitute 97% of the total anion concentration in fog samples and ~99% in precipitation samples. The fog nitrate can be derived from both scavenging of aerosol nitrate and uptake of gaseous nitric acid. It is found to vary considerably over different fog conditions (fig 3.9). Similarly, fog sulphate concentration also varies significantly over fog conditions (fig 3.8). The fog sulphate are thought to be derived from aerosol scavenging or in-situ oxidation of dissolved sulphur dioxide. When sulphate and nitrate concentrations are compared, it becomes evident that overall fog composition is typically sulphate dominated. The mean sulphate to nitrate ratio is found to be 1.65 in fog water and 2.48 in precipitation samples, which shows the dominance of sulphate. The concentrations of sulphate and nitrate found in fog are depicted in fig 3.37. Fig. 3.38 shows the ratio of concentration of sulphate to nitrate found in fog on each sampling days.

Figure 3.39 shows the ratio of total cations and total anions for each of the sampling events. The mean cation to anion ratio was found to be 0.24 in fog samples and 0.57 in precipitation samples (table 3.3). It reveals that the total anion concentration far exceeds the total cation concentration. Fig 3.40 shows the total cation and anion concentrations over different fog categories. The concentrations of sodium and chloride ions in fog samples for each fog event are represented in fig 3.41. The average Chloride to Sodium ratio in fog water was found to be 0.52 whereas in precipitation sample it was 0.09. This ratio is rather lower than the ratio typically found in seawater (1.17). This is not unexpected as the aerosols of sea water are ruled out in the urban environment of Delhi.

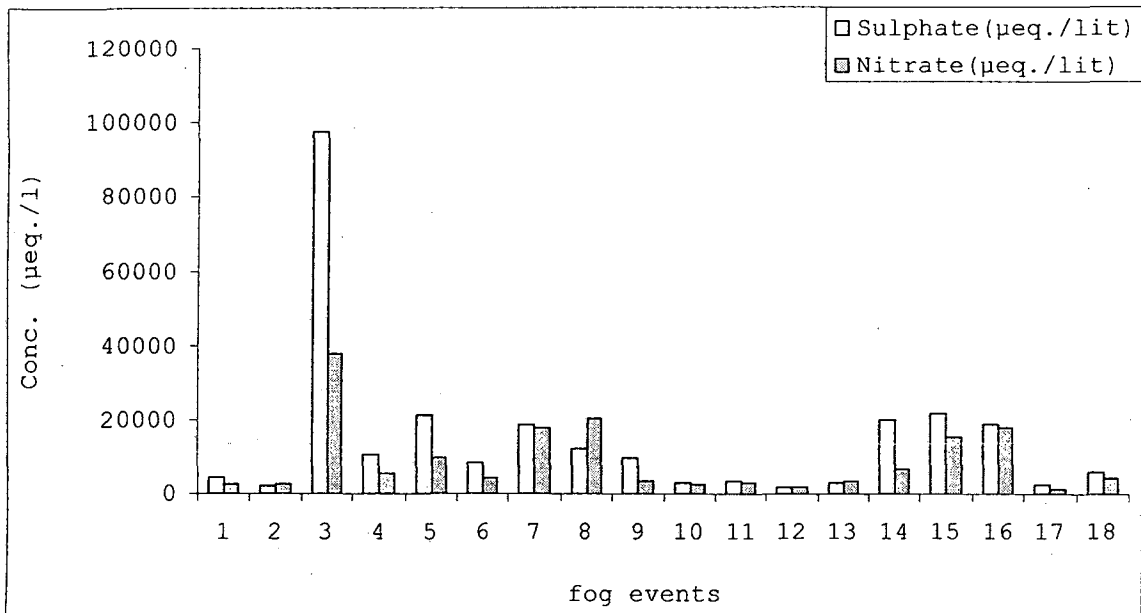


Figure 3.37: Fog sulphate and nitrate concentrations observed at each sampling events .

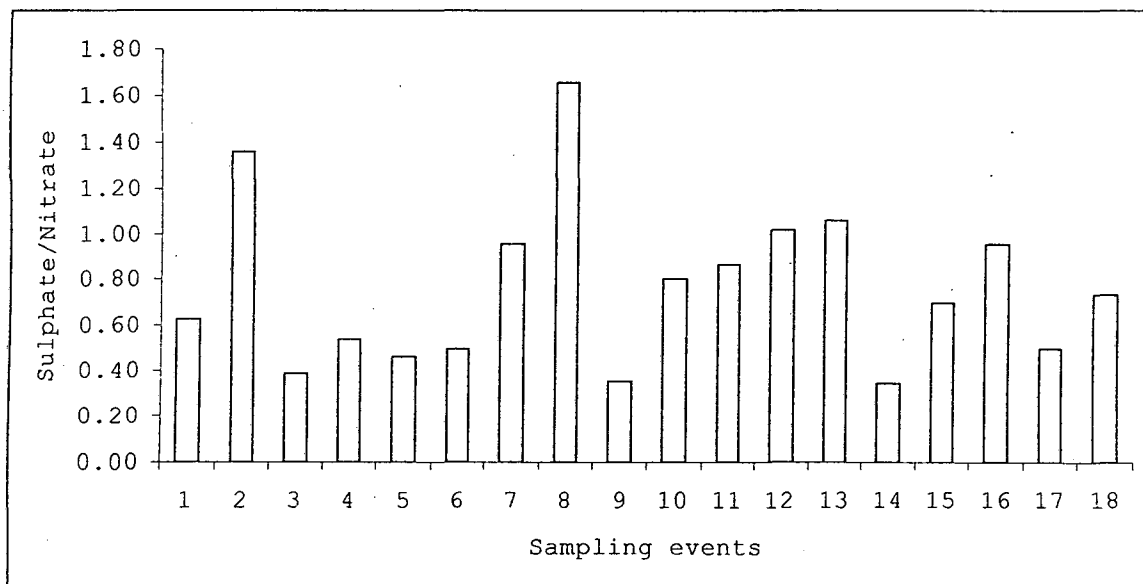


Figure 3.38: Sulphate /Nitrate concentration ratio (equivalent/ equivalent) observed in fog on each sampling events .

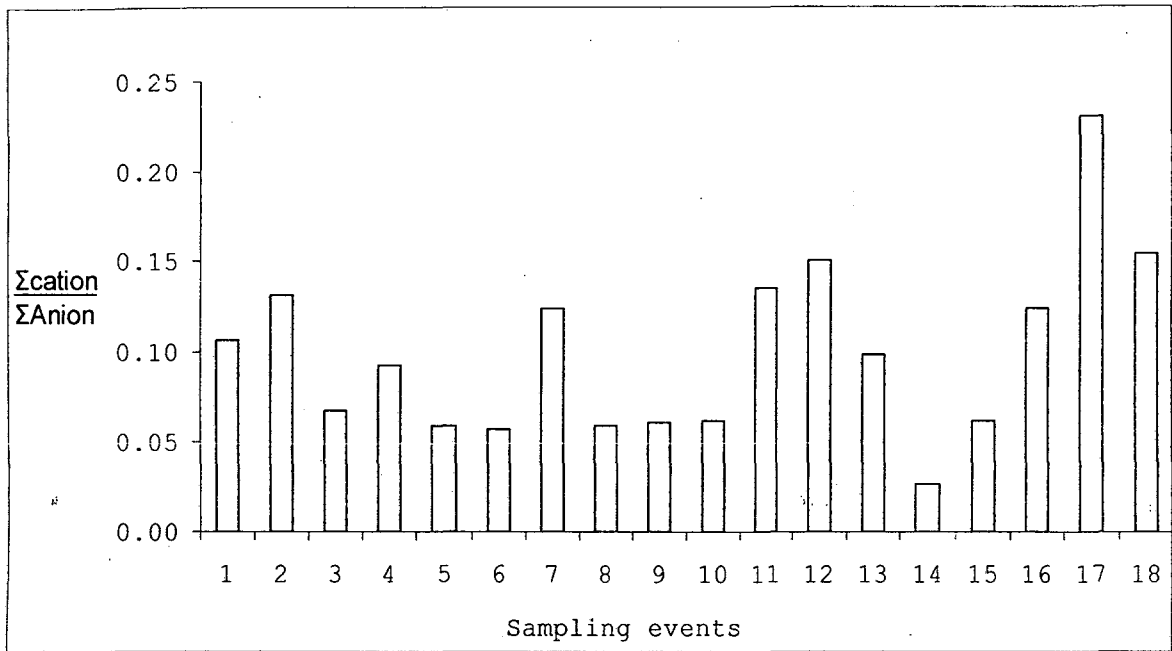


Figure 3.39: $\Sigma\text{cation} / \Sigma\text{Anion}$ ratio observed on each sampling events

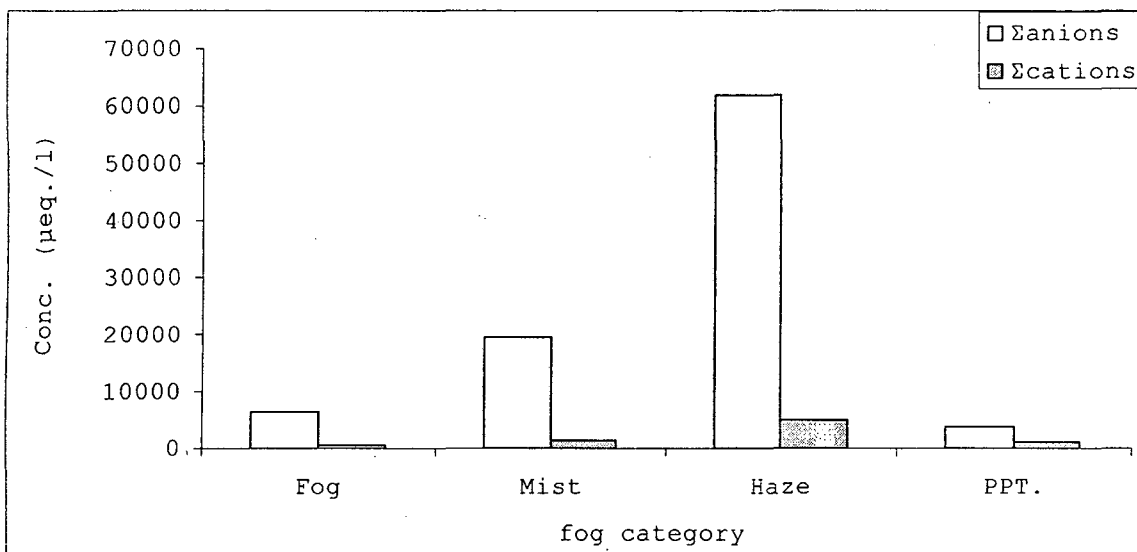
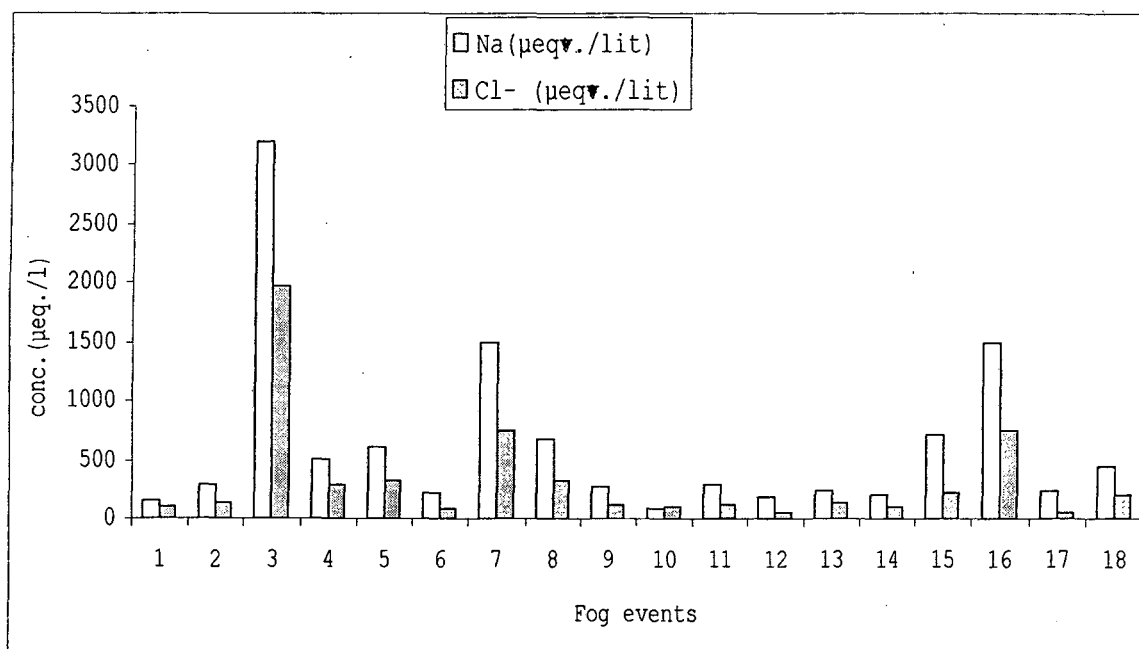


Figure 3.40: $\Sigma\text{Cations}$ and ΣAnions in different fog categories

Table 3.4: Ionic concentrations of fog water in Delhi; A comparison with previous studies.

		Present study	Kapoor et al, (1993)	Khameni et al, (1989)	Khameni et al, (1987)
component		2003-2004	1989-1990	1985-1986	1984-1985
pH		6.35	6.55	7.20	7.20
conductivity($\mu\text{s./cm}$)		2.32	-	-	-
TDS (mg/l)		1.32	-	-	-
Cl^- ($\mu\text{eq./lit}$)		324.28	300.00	203.00	203.00
SO_4^{2-} ($\mu\text{eq./lit}$)		14663.07	69.00	138.00	114.00
NO_3^- ($\mu\text{eq./lit}$)		8867.18	345.00	80.00	115.00
total anion ($\mu\text{eq./l}$)		23854.54	714.00	421.00	432.00
$\text{NO}_3^-/\text{SO}_4^{2-}$		0.77	5.00	0.58	1.01
NH_4^+ ($\mu\text{eq./lit}$)		29.57	77.00	147.00	99.00
Na^+ ($\mu\text{eq./lit}$)	soluble	627.51	494.00	227.00	484.00
	insoluble	273.24	-	-	-
K^+ ($\mu\text{eq./lit}$)	soluble	529.44	215.00	169.00	203.00
	insoluble	165.06	-	-	-
Ca^{2+} ($\mu\text{eq./lit}$)	soluble	3880.57	1588.00	327.00	575.00
	insoluble	283.65	-	-	-
Mg^{2+} ($\mu\text{eq./lit}$)	soluble	568.56	269.00	127.00	259.00
	insoluble	130.15	-	-	-
Cu^{2+} ($\mu\text{eq./lit}$)	soluble	76.11	--	--	--
	insoluble	17.52	-	-	-
Pb^{2+} ($\mu\text{eq./lit}$)	soluble	0.00	-	-	-
	insoluble	4.47	-	-	-
Total Cation ($\mu\text{eq./lit}$)	soluble	5711.76	2643	997	1620

Figure 3.41: Fog Na⁺ and Cl⁻ concentrations on each sampling events.

The comparison of ionic concentrations and pH of fog water in Delhi with the earlier studies reported by Khameni et al, (1987), Khameni et al, (1989) and Kapoor et al, 1993 is presented in table 3.4. A declining trend in the pH values of fog is seen. However, the rate of decline is not that sharp during last fourteen years (1989–1990 to 2003-2004) as compared to the previous five years (1984-1985 to 1989-1990). Hence, it can be inferred that fog in Delhi is tending to be more acidic in nature. Concentration of all the ions has enhanced significantly. Sulphate and Nitrate concentrations show excessive enhancements. In earlier studies, total cationic concentrations far exceeded the anionic concentrations but our study shows just the reverse trend, with the exception of Ammonium ion, which shows a declining trend.

CHAPTER -IV

CONCLUSION

The results show an average pH value of fog 6.35, that indicates slightly acidic fog. This slight acidic character was also observed in an earlier study carried out in Delhi (Kapoor et al, 1993). The reason for decline in pH value may be attributed to the presence of excess sulphate and nitrate ions in the fog water, which point towards the presence of anthropogenic sources. The presence of Ca^{2+} and Mg^{2+} ions, which dominate the particulate concentration in air as well as in fog droplets, can neutralize the acidic effect of Sulphate and Nitrate ions.

The concentration of ammonium ion was much less which is not unexpected, since there is hardly any agricultural activity in the proximity of the study area. It is worth mentioning that relatively high concentration of ammonium ion, observed in earlier studies compared to the present, could be attributed to the agricultural activities on the experimental farms near the sampling locations at Indian Agricultural Research Institute (IARI), Pusa, New Delhi.

The ion concentration in fog water is found to be far in excess as compared to the precipitation water. This feature could be attributed to the following: (i) fogs being located closer to the ground are generally exposed to higher ambient pollutant concentrations; (ii) the smaller fog and mist droplets saturate more rapidly, allowing a longer time interval for the aqueous phase production of secondary species (e.g. sulphate); (iii) owing to their smaller diameter, fog and mist droplets have a far greater combined surface area, again permitting an enhanced diffusion of ions or gases and therefore a higher final concentration of these components or their reaction products.

FOR FUTURE:

- (I) We would like to extend the scope of the present work to include some more sampling sites in peri-urban and rural areas. This would help in ascertaining the contributions arising out of aerosols from anthropogenic activities and from natural sources.

- (II) It could also be interesting to examine the impact of application of external fields (Acoustic, DC, RF and Microwave) on the collection efficiency of fog water.

- (III) Further attempts should be made to develop forecasting models to predict the onset and dispersal of fog.

- (IV) The exact duration of fog (in hours) i.e. from the onset of the fog to its disappearance will be determined by using an appropriately designed and fabricated instrument. This data would be useful in the development of forecasting models.

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