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Chemical Composition and Ionic Variability of Wet and Bulk Precipitation in Urban Environment of Karnataka State, India

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KEYWORDS

Wet and bulk precipitation,
acid rain,
urban activities,
neutralizing factors

A B S T R A C T

A comprehensive study on the chemical composition and ionic variability of wet & bulk precipitation were carried out in urban areas during 2005–07. During study period, total 520 (268 wet and 252 bulk) precipitation samples were collected from four pre-determined urban areas of Karnataka State, India, and analyzed them for various parameters such as pH, electrical conductivity (µS/cm), cations, and anions (µeq ℓ-1). The ionic composition shows that Ca2+ and SO42- are the dominant ions in urban areas in both wet and bulk precipitation. A high percentage of SO42- was observed at Hebbal (Bangalore North), however low percentage at Jayanagar (Bangalore South), Mandya and Mysore urban areas.The ionic composition shows higher concentration of cations and anions, except H+, in bulk precipitation, when compared to wet precipitation, mainly due to dry deposition. The smaller concentration and deposition of H+ in the bulk precipitation were because of reduction of acidity by dry-deposited calcium species, possibly CaCO3 being washed in by subsequent precipitation events. The annual volume weighted mean (VWM) pH of Hebbal area is 4.59 for wet precipitation, and 4.70 for bulk precipitation, which is less than the threshold point for neutrality (5.60). The present study shows acid precipitation (acid rain) in Hebbal urban area. In Jayanagar urban area, it is slightly, and at Mysore and Mandya, totally alkaline. The analysis has revealed that annual VWM pH of the bulk precipitation of Bangalore urban (both Hebbal and Jayanagar areas) was 5.22 during study period. The pH of bulk precipitation in Bangalore decreased from an average of 6.61 (1974–84) to 5.22 (2005–07) over the last three decades indicating that the alkaline nature of Bangalore urban precipitation has turned acidic. This is mainly due to high concentrations of SO42- and NO3- of local emission of SO2 and NOx from industries, urban activities and increase in automobiles. The neutralizing factor (NF) shows washouts of ions are more in bulk precipitation than in wet precipitation and clearly establishes that in urban wet and bulk precipitation, Ca2+ was the major neutralizing ion followed by NH4+, K+ and Mg2+; dry precipitation plays a major role in neutralizing acidic species of precipitation.

Introduction

Rainfall is an effective mechanism of the atmosphere purging of its pollutants. Its chemical composition reflects the quality of the air through which it falls, and consequently, changes in precipitation chemistry which is useful indicators of

trends in air chemistry. For these reasons, measurements of precipitation chemistry have been a standard feature of many national monitoring programs. It is well documented that precipitation in coastal areas is strongly affected by sea salt, while in inland areas it contains proportionately larger share of substances originating from the soil [1]. Past studies have shown very high concentration of anthropogenic substances like NO_3^- and SO_4^{2-} in urban or industrial areas compared to non-urban areas. Europe and North America have been adversely affected by acidic deposition [2], [3]. Air pollutants are increasing rapidly in many southeastern Asian countries [4] and China [2] due to fast population growth and the consequent upward trend in agricultural production, industrialization, energy consumption, transport, housing, etc. Systematic observations on the chemical composition of precipitation have been carried out for several years in Europe and North America (Rodhe *et al*., 2002) [2]; however, such studies are limited in the rest of the world, especially under non-urban conditions in the tropical region [4], [5], [6], [2].

During the last decade, studies on the chemical composition of precipitation conducted in India [7] [8] [9] [10] [11] [12] have highlighted the alkaline nature of rain water due to the contribution of soil-derived particles in the atmosphere, which buffer its acidity during below-cloud scavenging process. Rain water composition plays an important role in scavenging soluble components from the atmosphere and helps in understanding the relative contribution of different sources of atmospheric pollutants. The chemical composition of rain water varies from site to site and region to region due to the influence of local sources [12]. In India, wet removal process is effective only during the monsoon period (June – September) when around 90% of rainfall occurs. During the rest of the period, dry conditions prevail, which determine the atmospheric deposition chemistry. Ambient concentrations and atmospheric reactions are controlled during dry weather conditions by continuous input of suspended dust particles from soil suspension. Hence, dust fall deposition is a significant removal mechanism in India as it provides a very good sink for acidic gaseous pollutants covering atmosphere.

Recently, problems of acid rain have extended to Asia, because of significant increase in atmospheric emissions resulting from industries, automobiles, and human activities. In addition, industrialization and urbanization are polluting major metropolitan cities in Asia resulting in acid rainfall. Such local effects should not be ignored since they will have a major impact on local ecology. Therefore, it is important that rain chemistry is monitored in urban areas. Data from such monitoring activities are essential for determining temporal and spatial deposition trends to predict ecological effects, modeling atmospheric processes, or plan future control strategies.

The study of chemical composition of wet and bulk precipitation will help in understanding the geochemical cycles of various elements and in assessing the pollution status of different areas of sources or regions. In India, a number of studies have been carried out on the chemical composition of precipitation in urban locations [13, 14, 15]. Precipitation composition thus is an integral measurement and helps to understand the relative importance of different sources of these materials (gases and particles). Because of this concern, wet and bulk precipitation chemistry of urban areas has

been the subject of intense research in the last two decades [16], [17], [8]. Chemical composition and variability of wet and bulk precipitations in urban areas are very essential to determine deposition trends, modeling atmospheric process as well as plan future emission control strategies. Hence, the present work was carried out to investigate the chemical composition of wet and bulk precipitation at urban environments in Karnataka State during 2005–07. To begin with, a network was established at four stations in urban (Hebbal and Jayanagar- Bangalore, Mandya and Mysore) areas to monitor precipitation chemistry to understand the presence of acidic and alkaline species in it and the geochemical cycles of various elements. It helps in assessing the pollution status of different area sources.

Location of measurements

Karnataka State is situated between 11° 40' and 18° 27' north latitude and 74° 5' and 78° 33' east longitude in the centre of western peninsular India, covering an area of 19.1 M.ha and accounts for 5.8% of the country's total geographic area. It has a 350-km-long coastline, which forms the western boundary. According to the 2001 provisional census, the population of the state is 52,733,958 (26,856,343 males and 25,877,615 females), with a rural population of 66.02% and an urban population of 33.98%. The urban population is above the national average of 27.78 per cent. Karnataka is thus one of the more urbanized states of India [18] and is the eighth largest state in India both in area and population. Being the most industrialized state, it has the credit of being the first state to step into the industrial dawn. Bangalore urban area (120 581 N, 770 351 E, 921 m above the M.S.L) is thickly populated and industrialized and also there is a high density of automobiles. The study area includes: i) Bangalore south and (ii) Bangalore north. The Bangalore south (Jaya Nagar, 12^{0} 551 N77^{0} 341 E) bounded by residential and commercial activities and Bangalore north, (Hebbal, $13^{0}1'$ N 77^{0} 17.51 E) bounded by residential and commercial area, also close to national highway and number of small, medium and large scale industries exist in and around the area. These industries include engineering, chemical, pharmaceutical, food, brewery and distillery, textile, steel and metal smelting. Bangalore north has more number of industries as compared to the Bangalore south area. Mandya city (12033'N, 76039'E) is a major residential area consisting of agricultural land and is connected by state highway. Mysore city (12055' N, 76039'E) is a large city and is one of the historical places of India Fig 1 shows location of sampling in urban area.

Experimental set-up

In present study, we have used manual wet and bulk precipitation collectors which were placed on the terrace of the buildings to collect wet and bulk precipitation samples. Wet precipitation collector used for collection of wet precipitation (wet - only) and this collector minimizes the influence from local sources during dry periods and will therefore give more regionally representative samples, although influence from local sources during rain is, of course, not eliminated and collector consists of a polyethylene funnel (18cm dia) connected to 5 liters polyethylene reservoir. Wet precipitation is collected manually during the occurring of events on weekly/biweekly basis. The wet collectors were cleaned once every two weeks using demineralised water. A clean Teflon bag was inserted into the collection apparatus

when no rain events occurred within the week. Use of bulk precipitation (wet + dry) samples has been cited by Ramalingaiah (1985) [19] and Shivashankara, et al., (1998) [20]. The bulk collector consists of a polyethylene funnel (18cm diameter) connected to a five liter capacity polyethylene reservoir. The reservoir is attached to a vapor trap, and a vapor barrier using tygon tubing which is provided by a loop to prevent the gas exchange between the atmosphere and the sample and evaporation from the reservoir. A filter is used in the funnel to avoid contamination by insects and litter. The samples collected from were analyzed for pH, Electrical Conductivity (EC), cations cations ($Ca^{2+,}$ Mg^{2+}, Na^{+}, K^{+} and NH_4^{+}-N) and anions (Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}-N, NO_2^{-}N and PO_4^{3-}-P), using the standard methods (2005).

Data description and quality assessment

Ion balance, an important parameter for data quality, gives an assessment of the quality of analysis, and a hint of any missing parameter. The completeness of measured parameters of major ions in wet and bulk precipitation samples can be tested by calculating the charge balance. The concentration of cations and anions should balance, and the water must be electrically neutral. CB is expressed as a percentage of the sum of cations and anions and is an important parameter for data quality as it gives an indication of the quality of analysis assessment. Deviation from unity indicates that some of the ions are excluded [21] [1]. The test is based on the percentage difference defined as follows: % CB = ∑Cations– ∑Anions/∑Cations + ∑Anions) × 100 (the sums of anions and cations, expressed in $\mu eq\ell^{-1}$). The annual ratios of cations and anions in wet and bulk precipitation vary from 0.99 to 1.27 and 0.94 to 1.20 with average value of 1.13 and 1.07 (Table 1). The average annual concentration of total anions and total cations represents the values of total mineralization (anions and cations) and are expressed in $\mu eq\ell^{-1}$. As the measurements include major anions and cations, their ratio value should be 1.00 [22].The average values of the total anions are more than total cations in urban Bangalore (Hebbal and Jayanagar areas). Our study shows that the annual and seasonal CB% was ±10% in both wet and bulk precipitation. However, the annual ratio of anions and cations of 1.09 in wet precipitation and of 0.99 in bulk precipitation indicates that all the major cations and anions were considered in the analysis of the samples. The ratio of wet precipitation indicates greater than unity due to the presence of free anions responsible for rainwater acidity and bulk precipitation shows less than unity which indicates the alkaline nature of rain water due to dry deposition of major cations in bulk collectors.

Results and Discussion

Ionic composition of wet precipitation

The annual ionic composition of wet precipitation at Hebbal was estimated as: SO_4^{2-}, 25% of the total major ions, followed by Ca^{2+} (19%), HCO_3^{-} (13%), NO_3^{-} (8%); Na^{+} (8%), Cl^{-} (8%),NH_4^{+} (7%), H^{+} (6%), K^{+} (2%), Mg^{2+} (2%), PO_4^{3-} (1%) and NO_2^{-} (1%) (Tables 2 and Fig. 2). SO_4^{2-} and Ca^{2+} are the dominant anion and cation, respectively. The concentrations of cations and anions follows a general descending order as SO_4^{2} >Ca^{2+} >HCO_3^{-} > Na^{+} >NO_3^{-} >Cl- >NH_4^{+} >H^{+} >K^{+} >Mg^{2+} > PO_4^{3-} and >NO_2^{-}**,** whereas at Jayanagar it was Ca^{2+} (23% of total major ions) followed by SO_4^{2-} (114%), HCO_3^{-}(10%), NH_4^{+} (9%),

NO_3^- (10%), Na^+ (11%), Cl^- (10%), Mg^{2+} (2%), K^+ (2%), PO_4^{3-}(1%), H^+ (1%) and NO_2^-(1%) indicating that Ca^{2+} and SO_4^{2-} are once again the dominant cation and anion, respectively, here too. The concentration of cations and anions follows a general descending order as Ca^{2+} >HCO_3^- >SO_4^{2-} >Na^+ > NO_3^- >Cl- >NH_4^+ >K^+ >Mg^2 >PO_4^{3-} >H^+ and >NO_2^-. The study shows that Ca^{2+} and SO_4^{2-} are the dominant ions in the formation of alkaline and acid rain at Hebbal (Bangalore North) and Jayanagar (Bangalore South) areas, respectively. The contribution of SO_4^{2-} was almost the same in successive years at Hebbal.

The Mysore urban wet precipitation had 22% Ca^{2+} of the total major ions followed by HCO_3^- (16%), SO_4^{2-} (14%), NH_4^+ (12%), NO_3^- (9%), Cl^- (10%), Na^+ (9%), K^+ (3%), Mg^{2+} (2%), PO_4^{3-} (1%), NO_2^- (1%) and H^+ (1%) indicating that Ca^{2+} and NH_4^+ are the dominant cation and anion, respectively. The concentration of cations and anions follows a general descending order as Ca^{2+} >HCO_3^- >SO_4^{2-} >NH_4^+ >NO_3^- >Cl^- >Na^+ > K^+ >Mg^{2+} >PO_4^{3-} >NO_2^- >H^+. At Mandya, Ca^{2+} was 20% of the total major ions followed by HCO_3^- (15%), NH_4^+ (13%), SO_4^{2-} (11%), Na^+ (11%), NO_3^- (9%), Cl^- (9%), K^+ (4%), Mg^{2+} (3%), PO_4^{3-} (3%), NO_2^- (2%) and H^+ (0%). The concentrations of cations follows a general pattern in descending order as Ca^{2+} >NH_4^+ >Na^+ >K^+ >Mg2$^+$ >H^+, and of anions as HCO_3^- >SO_4^{2-} >NO_3^- >Cl^- >PO_4^{3-} >NO_2^- indicating that Ca^{2+} and SO_4^{2-} are the dominant cation and anion, respectively. The overall concentrations follows a general descending order as Ca^{2+} >HCO_3^- >NH_4^+ >SO_4^{2-} >Na^+ >Cl^- > NO_3^- >K^+ >Mg^{2+} > PO_4^{3-} >NO_2^- and >H^+. The study shows that Ca^{2+} and SO_4^{2-} are the dominant ions in urban area. A high percentage of SO_4^{2-} was observed at Hebbal (Bangalore North), and only a low percentage at Jayanagar (Bangalore South), Mandya and Mysore urban areas. Hebbal is surrounded by residential, commercial and industrial areas with very intensive road transport that throws up particulate matter into the atmosphere as well as great quantities of acidity-generating gases of SO_2 and NOx, which contribute to the generation of acid rain. These acidity-developing gases dissolve in the clouds, generating sulphuric and nitric acids. This is in agreement with Elba *et al*. (2008) [23]. On the average, NOx is responsible for generating 36% of the H^+ ions in rain water. NH_4^+ is the most important neutralizing substance. The probable source of Ca^{2+} ions is urban activities (with building construction) which generates aerosols in wet precipitation.

Ionic composition of bulk precipitation

The annual ionic composition of bulk precipitation at Hebbal (Table 2 and Fig 2) is estimated as follows: SO_4^{2-}, 24% of the total major ions, followed by Ca^{2+} (20%), HCO_3^- (12%), NO_3^- (9%); Na^+ (8%), Cl^- (8%), NH_4^+ (7%), H^+ (4%), Mg^{2+} (3%), K^+ (3%), PO_4^{3-} (1%) and NO_2^- (1%) with Ca^{2+} and SO_4^{2-} as the dominant cation and anion, respectively (Table 2 and Fig. 2). The concentrations of cations and anions follows a general descending order as SO_4^{2-} >Ca^{2+} >HCO_3^- >NO_3^- >Na^+ >Cl- > NH_4^+ >H^+ >Mg^{2+} >K^+ >PO_4^{3-} and NO_2^-, whereas at Jayanagar it was Ca^{2+} (25% of total major ions) followed by SO_4^{2-} (13%), HCO_3^-(12%), NH_4^+ (8%), NO_3^- (13%), Na^+ (10%), Cl^- (10%), Mg^{2+} (3%), K^+ (3%), PO_4^{3-}(2%), NO_2^-(1%) and H^+ (0%) indicating that Ca^{2+} and SO_4^{2-} are once again the dominant cation and anion, respectively. The concentrations of cations and anions follows a general descending order as: Ca^{2+} >SO_4^{2-} >HCO_3^- >NH_4^+ >NO_3^- >Na^+ >Cl- >Mg^{2+} >K^+ >PO_4^{3-}-

$>NO_2^-$ and $>H^+$. The study shows that Ca^{2+} and SO_4^{2-} are the dominant ions in the formation of alkaline and acid rains, respectively, at Hebbal and Jayanagar. The contribution of SO_4^{2-} was more at Hebbal area.

Ca^{2+} constituted 25% of the total of the major ions of the composition of bulk precipitation of Mysore followed by SO_4^{2-} (13%), HCO_3^- (12%), NH_4^+ (11%), SO_4^{2-} (11%), NO_3^- (11%), Na^+ (10%), Cl^- (9%), Mg^{2+} (3%), K^+ (3%), PO_4^{3-} (2%), NO_2^- (1%) and H^+ (0%) showing that Ca^{2+} and NH_4^+ are the dominant cation and anion, respectively. The concentration of cations and anions follows a general descending order as $Ca^{2+} > SO_4^{2-} > HCO_3^- > NH_4^+ > SO_4^{2-} > NO_3^- > Na^+ > Cl^- > Mg^{2+} > K^+ > PO_4^{3-} > NO_2^-$ and $>H^+$, and at Mandya Ca^{2+} constituted 24% of the total major ions followed by NH_4^+ (12%), SO_4^{2-} (13%), NO_3^- (11%), HCO_3^- (10%), Na^+ (10%), Cl^- (9%), Mg^{2+} (4%), K^+ (4%), PO_4^{3-} (3%), NO_2^- (2%) and H^+ (0%). The concentration of cations follows a general pattern in descending order as $Ca^{2+} > NH_4^+ > Na^+ > Mg^{2+} > K^+ > H^+$, while that of anions as $SO_4^{2-} > NO_3^- > HCO_3^- > Cl^- > PO_4^{3-} > NO_2^-$ indicating that $Ca^{2+}$and SO_4^{2-} are the dominant cation and anion, respectively. The overall concentration follows a general descending order as $Ca^{2+} > SO_4^{2} > HCO_3^- > NH_4^+ > NO_3^- > Na^+ > Cl^- > Mg^{2+} > K^+ > PO_4^{3-} > NO_2^- > H^+$.

The study shows that Ca^{2+} and SO_4^{2-} are the dominant ions in urban areas. A high percentage of SO_4^{2-} was observed at Hebbal, and only a small percentage at Mandya and Mysore. The pH of precipitation at Jayanagar, though in alkaline range, showed gradual decreasing trend, mainly due to the increasing acidic constituents, especially of SO_4^{2-} and NO_3^-, and simultaneously decreasing alkaline constituents, especially Ca^{2+}. NO_3^- contributed more than SO_4^{2-} towards acidification or rain, indicating the impact of vehicular emissions.

Several research workers have noted significantly greater concentrations of Ca^{2+} in precipitation, which are open (collectors) all the time [24] [25]. Hence, the major contribution of Ca^{2+} is from soil-derived particles. Based on the analysis of major ions of bulk precipitation in the study areas, it is assumed that the total major ions were Ca^{2+} and SO_4^{2-}. The possible source of Ca^{2+} ions is urban activities (building construction) which are the major sources of aerosols and soil-derived particulate matter in the urban areas of bulk precipitation, whereas SO_4^{2+} ions could be from the emission of SO_2 from industrial and urban activities. Table 5.2 shows the comparison of the relative magnitude of ionic species of wet and bulk precipitation with other sites. Ca^{2+} compounds are suggested as those which reduce the acidity of precipitation. The smaller concentration and deposition of H^+ in the bulk collector were because of reduction of acidity by dry-deposited calcium species, possibly $CaCO_3$ being washed in by subsequent precipitation events (David *et al*., 1992) [26]. Peter (1999) [27] had analyzed the Hong Kong daily wet and bulk deposition data from 1994 to 1995 and found that rain water acidity was greater for wet than bulk deposition, which is in agreement with the present study. An analysis of ionic composition showed higher concentrations of cations and anions (except H^+) in bulk precipitation compared to wet precipitation, mainly due to dry deposition.

pH of wet and bulk precipitation

Annual volume-weighted pH (Table 3 and Fig. 3& 4) shows that it was acidic at

Hebbal (4.59 in wet precipitation and 4.70 in bulk precipitation) and slightly alkaline at Jayanagar (5.65 in wet precipitation and 5.74 in bulk precipitation), followed by alkalinity at Mandya (5.85 in wet precipitation and 6.04 in bulk precipitation) and Mysore (5.93 in wet precipitation and 5.94 in bulk precipitation). The precipitation at Hebbal is considered acidic as the mean pH is 4.59 and 4.70, for wet and bulk precipitations, respectively, which is less than the threshold point for neutrality (5.60). Sequeira *et al.* [28] [29] have studied rain water samples over some parts of Mumbai's industrial areas of Chembur and Trombay and recorded pH as low as 4.85 and 4.45, respectively. Acid rain has been reported since 1974, at Chembur. Hence, the present study which confirms acid rain at Hebbal is in agreement with the study at Chembur. Hebbal is industrially mixed area located very close to Peenya Industrial area and National Highways. Acid rain at Hebbal is traceable to local emissions of SO_2 from industrial and urban activities, whereas the other urban areas received alkaline rain. Neutralization of acidity by ammonia and calcium occurred during the precipitation process.

Comparison of pH with earlier studied reported in India and present study of wet and bulk precipitation was presented in Table 4. The present study, annual mean pH for Bangalore urban area (Hebbal and Jayanagar) was 5.22, which is lower than the threshold limit for neutrality, indicating that all these areas were in an acidic range. The lower pH was due to the high concentration of SO_4^{2-}, (100.5µeqL^{-1} and 109.89 µeqL^{-1}) and NO_3^- (53.78 µeqL^{-1} and 54.40 µeqL^{-1}) that are attributable to local emissions of SO_2 and NO_x by industrial and urban activities and increase in the number of automobiles. Varma (1989a) [30] had reported an average of 6.61 pH for Bangalore region precipitation during 1974–1984, and compared with the present study's 5.22 (2005–07) it has decreased by a significant number, 1.4, and turned the city acidic in little over three decades. The pH of rain water at Agra and Delhi has decreased by 2.8 (9.1–6.3) and 0.9 (7.0–6.1), respectively, between 1960s and 1980s, due to industrialization and decrease in soil-oriented alkaline components in the rain water (Khemani *et al*., 1989a) [31]. The pH of rain water at New Delhi in 1996 was 5.70 (Kulshrestha *et al.,* 1996) [32], which in 1960s was 7.0 and in 1980s 6.1, clearly demonstrating a decreasing trend. The present study confirms the earlier findings of Khemani *et al*. (1989a) [31] and Kulshrestha *et al.* (1996) [32] establishing that the pH of bulk precipitation over Bangalore urban is moving towards acid precipitation (acid rain) owing to rapid industrialization, urbanization, and increase in the number of automobiles. Our study is in agreement with the earlier findings of Varma *et al*. (1989a) [30] and Shivashankara *et al*. (1998) [20] that the pH of bulk precipitation over Bangalore city is turning acidic (acidrain) as it has decreased by 1.4 over the past 25 years; if the trend continues it will further lower to 3.79 by 2030.

Neutralizing factors

Neutralizing factors (NF) provide a clue to neutralization of precipitation by different alkaline constituents and quantify their neutralizing effect. Kulshrestha *et al*. (1995a) [33] have developed an equation to calculate the role of alkaline species of Ca^{2+} and NH_4^+/Mg^{2+} in neutralizing acidity in precipitation, which they called as the neutralization factor (NF). Non-sea salt concentration of SO_4^{2-}, Ca^{2+}, Mg^{2+} and K^+ was used for calculating neutralizing factors.

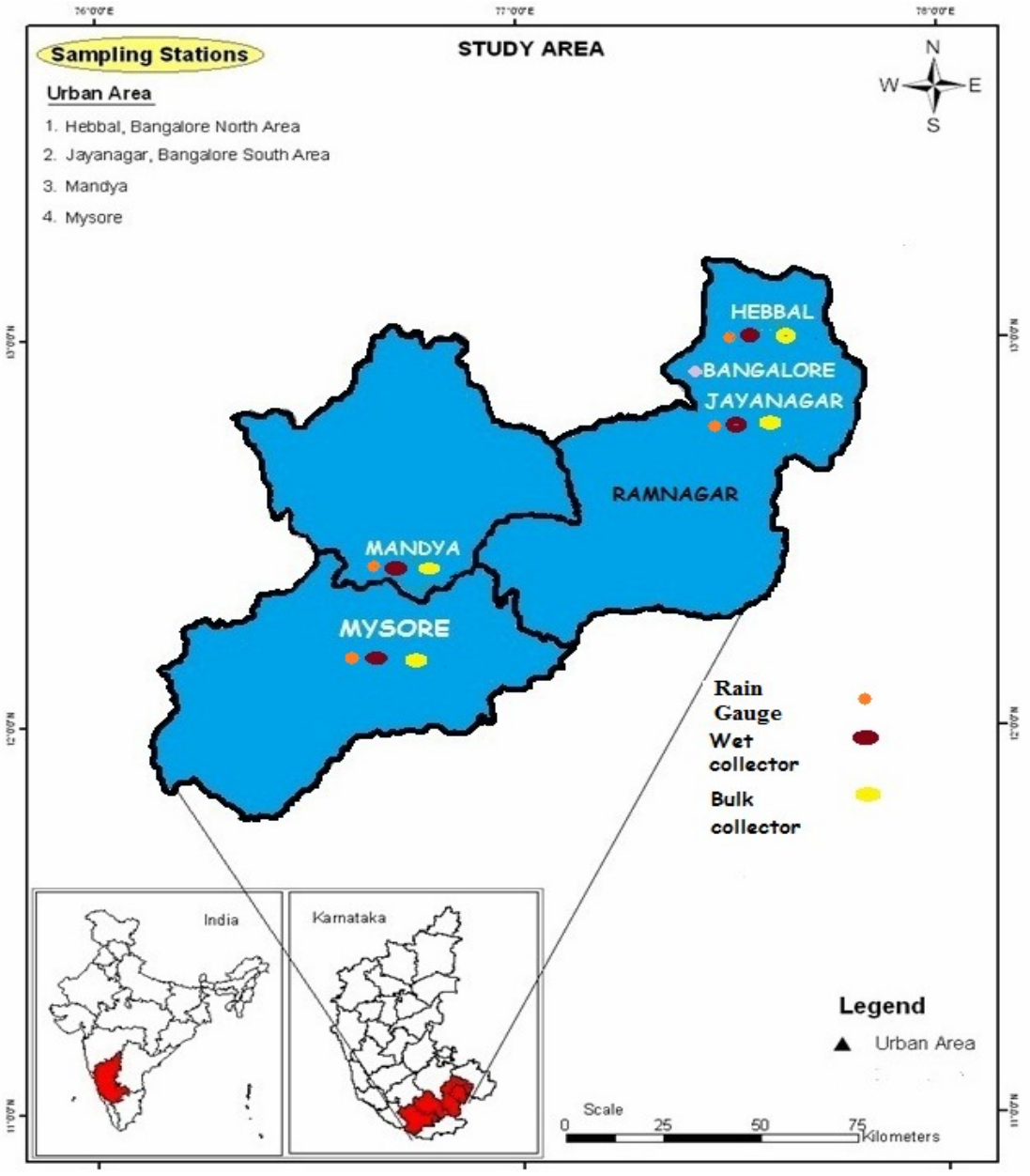
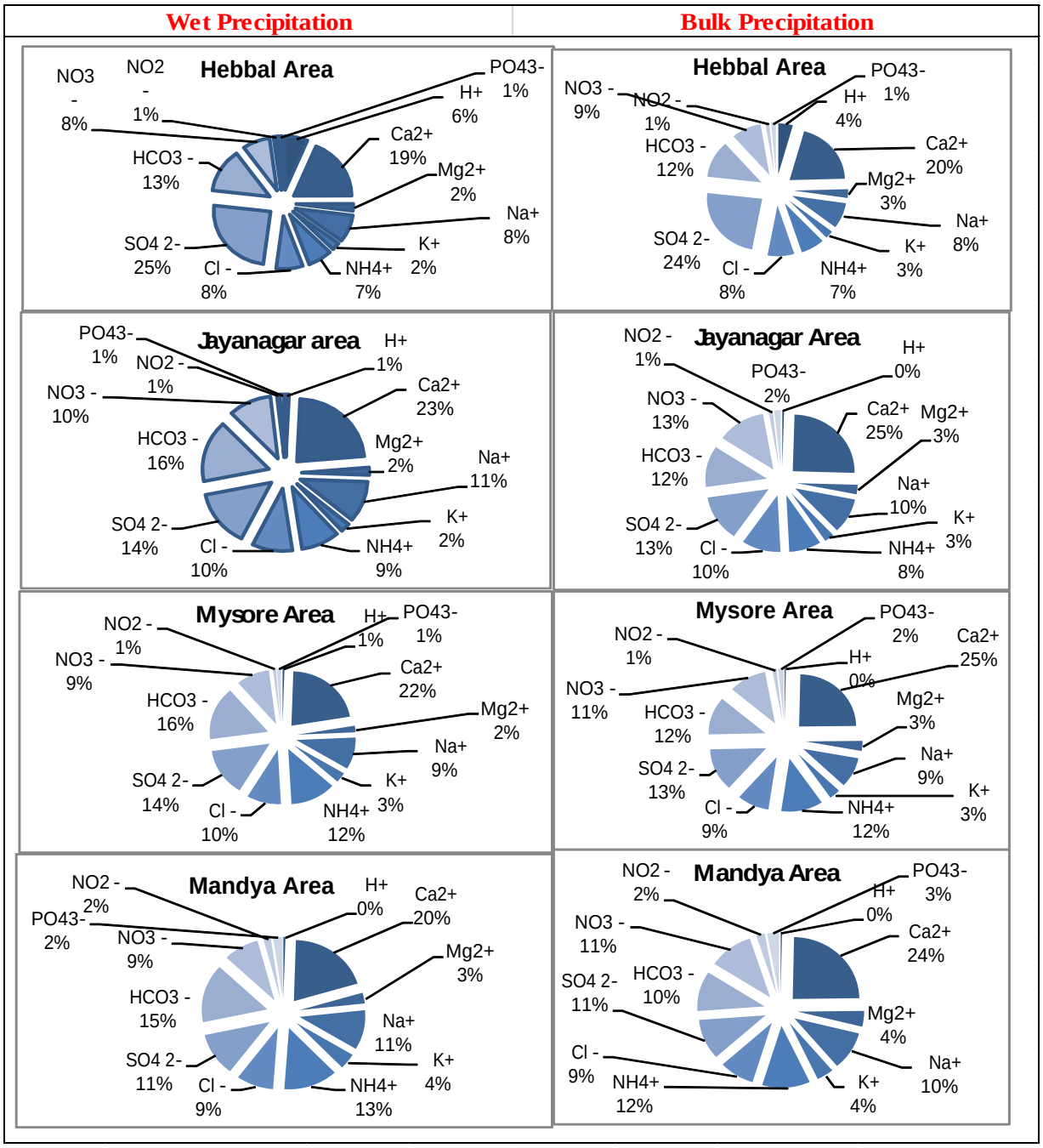


Fig.1 Sampling locations of urban areas in south Karnataka, India

Fig.2


Wet Precipitation
Bulk Precipitation
Hebbal Area
NO3 - 8%
NO2 - 1%
PO43- 1%
H+ 6%
Ca2+ 19%
HCO3 - 13%
Mg2+ 2%
Na+ 8%
SO4 2- 25%
K+ 2%
Cl - 8%
NH4+ 7%
Hebbal Area
NO3 - 9%
NO2 - 1%
PO43- 1%
H+ 4%
HCO3 - 12%
Ca2+ 20%
Mg2+ 3%
Na+ 8%
SO4 2- 24%
K+ 3%
Cl - 8%
NH4+ 7%
Jayanagar area
PO43- 1%
NO2 - 1%
H+ 1%
NO3 - 10%
Ca2+ 23%
HCO3 - 16%
Mg2+ 2%
Na+ 11%
SO4 2- 14%
K+ 2%
Cl - 10%
NH4+ 9%
Jayanagar Area
NO2 - 1%
H+ 0%
PO43- 2%
NO3 - 13%
Ca2+ 25%
Mg2+ 3%
HCO3 - 12%
Na+ 10%
SO4 2- 13%
K+ 3%
Cl - 10%
NH4+ 8%
Mysore Area
NO2 - 1%
H+ 1%
PO43- 1%
NO3 - 9%
Ca2+ 22%
HCO3 - 16%
Mg2+ 2%
Na+ 9%
SO4 2- 14%
K+ 3%
Cl - 10%
NH4+ 12%
Mysore Area
NO2 - 1%
PO43- 2%
Ca2+ 25%
H+ 0%
NO3 - 11%
HCO3 - 12%
Mg2+ 3%
Na+ 9%
SO4 2- 13%
K+ 3%
Cl - 9%
NH4+ 12%
Mandya Area
NO2 - 2%
H+ 0%
Ca2+ 20%
PO43- 2%
NO3 - 9%
Mg2+ 3%
HCO3 - 15%
Na+ 11%
SO4 2- 11%
K+ 4%
Cl - 9%
NH4+ 13%
Mandya Area
NO2 - 2%
PO43- 3%
H+ 0%
NO3 - 11%
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Mg2+ 4%
Cl - 9%
Na+ 10%
NH4+ 12%
K+ 4%

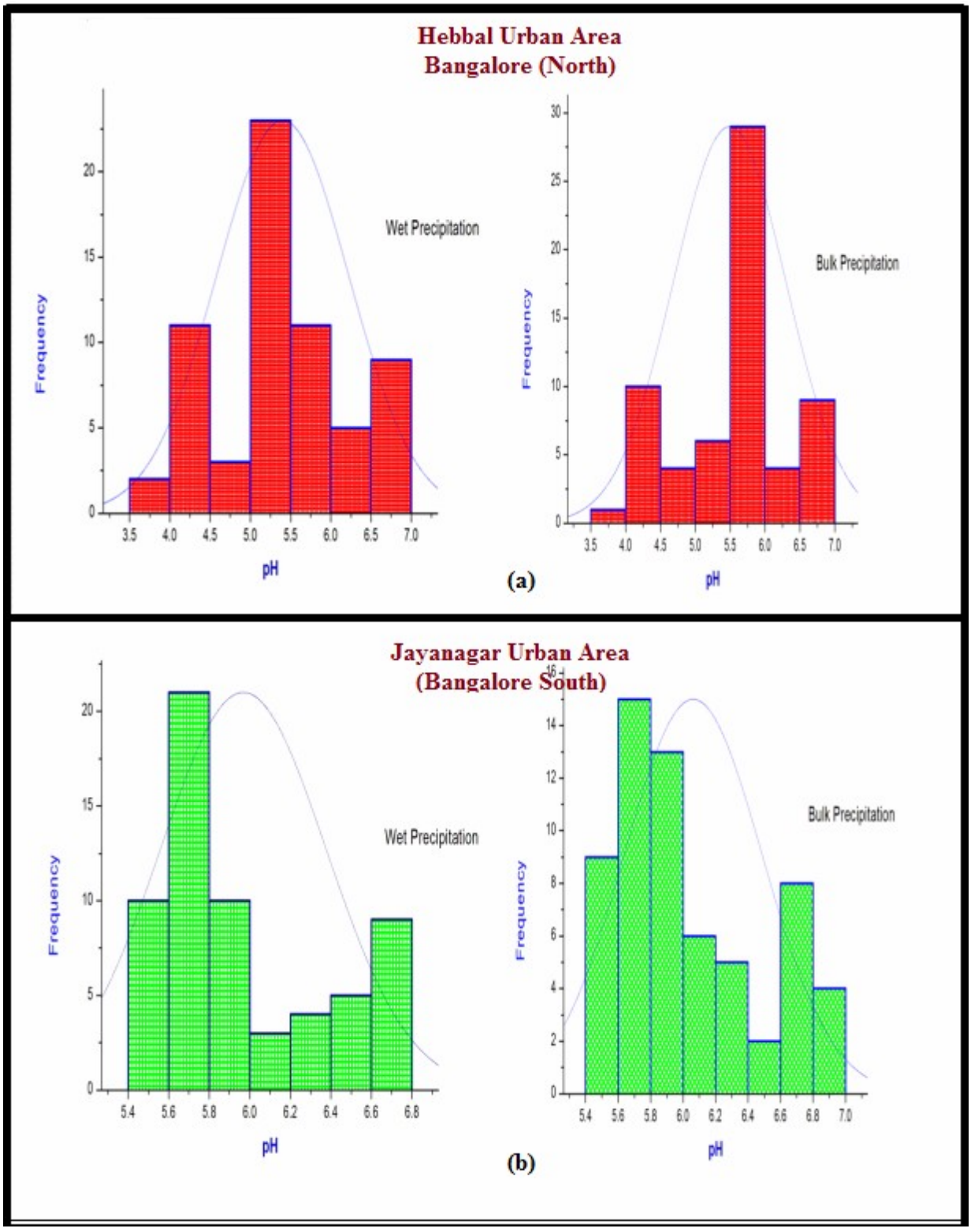

Fig. 3 (a) and (b) Frequency distribution of pH of wet and bulk precipitation at Hebbal (Bangalore North) and Jayanagar (Bangalore South) urban areas during 2005–07

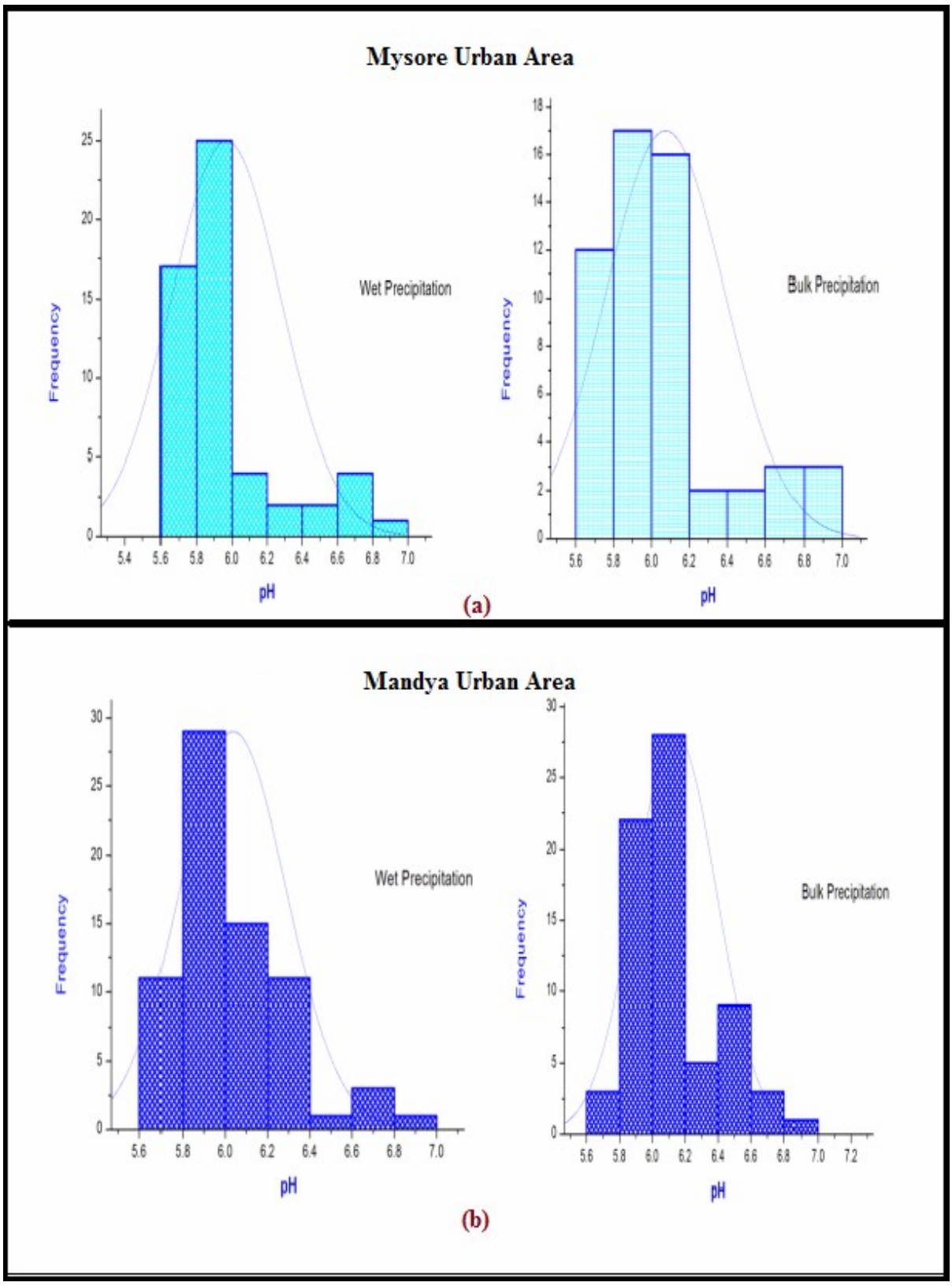

Fig. 4 (a) and (b) Frequency distribution of pH of wet and bulk precipitation at Mysore and Mandya urban areas during 2005–07

Table.1 Mean volume-weighted mean (VWM) concentrations of major ions (μeql^{-1}), electrical conductivity (μS/cm) and pH in wet and bulk precipitation samples from urban areas during 2005–2007

Urban Area	Precipitation (2005-07)	pH*	EC	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	NO_2^-	PO_4^{3-}	TA/ TC*	CB#
Hebbal (Bangalore North)	**Wet**	4.59	27.64	25.5	75.61	8.61	33.41	9.46	27.89	30.7	100.5	53.78	31.61	3.82	4.73		**-7.55**
Jayanagar (Bangalore North)		5.65	20.93	2.27	69.39	5.90	31.90	7.07	28.02	29.3	43.88	48.65	31.37	2.06	3.28	**1.20**	**-6.20**
Mysore		5.85	18.92	1.45	63.2	5.64	27.14	8.68	36.14	27.5	41.11	46.07	26.69	2.47	3.46	**1.03**	**5.35**
Mandya		5.93	15.56	1.19	47.17	6.78	24.85	9.81	31.54	21.6	26.98	36.70	20.77	4.29	5.50	**0.99**	**2.51**
Hebbal (Bangalore North)	**Bulk**	4.70	35.91	19.8	93.31	12.88	37.66	11.4	32.33	36.6	109.8	54.40	40.58	5.15	6.78	**1.20**	**-6.02**
Jayanagar (Bangalore North)		5.74	26.60	1.8	96.48	10.48	38.39	10.0	32.97	40.0	50.56	44.92	49.85	4.26	6.52	**1.14**	**-5.07**
Mysore		5.94	22.59	1.14	83.54	10.41	31.83	10.9	40.66	31.0	45.03	39.54	37.11	4.10	5.70	**0.96**	**1.95**
Mandya		6.05	19.33	0.90	73.87	12.39	30.24	12.4	35.16	25.8	31.81	31.08	32.79	6.34	8.72	**0.95**	**3.97**

VWM= $C_j = \left[\sum_{i=1}^{N} {}_{ij}\, V_i\right] \left[\sum_{i=1}^{N} V_i\right]$

Volume-weighted mean pH calculated by volume-weighted mean of H^+, TA/TC* = Ratio of total anions/total cations, CB = Charge balance

Table.2 Annual order of ionic species of wet and bulk precipitation of the study area during 2005–2007

LOCATION	Type	∑Cations	∑Anions	∑ Cations & ∑Anions
Hebbal	Wet	$Ca^{2+} > Na^{+} > NH_4^{+} > H^{+} > K^{+} > Mg^{2+}$	$SO_4^{2} > HCO_3^{-} > NO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2^{-}$	**$SO_4^{2} > Ca^{2+} > HCO_3^{-} > Na^{+} > NO_3^{-} > Cl^{-} > NH_4^{+} > H^{+} > K^{+} > Mg^{2+} > PO_4^{3-} > NO_2^{-}$**
Jayanagar	Wet	$Ca^{2+} > Na^{+} > NH_4^{+} > K^{+} > Mg^{+} > H^{+}$	$HCO_3^{-} > SO_4^{2} > NO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2^{-}$	**$Ca^{2+} > HCO_3^{-} > SO_4^{2-} > Na^{+} > NO_3^{-} > Cl^{-} > NH_4^{+} > K^{+} > Mg^{2} > PO_4^{3-} > H^{+} > NO_2^{-}$**
Mysore	Wet	$Ca^{2+} > NH_4^{+} > Na^{+} > K^{+} > Mg^{2} > H^{+}$	$HCO_3^{-} > SO_4^{2} > Cl^{-} > NO_3^{-} > PO_4^{3-} > NO_2^{-}$	**$Ca^{2+} > HCO_3^{-} > SO_4^{2-} > NH_4^{+} > Na^{+} > Cl^{-} > NO_3^{-} > K^{+} > Mg^{2} > PO_4^{3} > NO_2^{-} > H^{+}$**
Mandya	Wet	$Ca^{2+} > NH_4^{+} > Na^{+} > K^{+} > Mg^{2} > H^{+}$	$HCO_3^{-} > SO_4^{2} > Cl^{-} > NO_3^{-} > PO_4^{3-} > NO_2^{-}$	**$Ca^{2+} > HCO_3^{-} > NH_4^{+} > SO_4^{2-} > Na^{+} > Cl^{-} > NO_3^{-} > K^{+} > Mg^{2} > PO_4^{3} > NO_2^{-} > H^{+}$**
Hebbal	Bulk	$Ca^{2+} > Na^{+} > NH_4^{+} > H^{+} > Mg^{2+} > K^{+}$	$SO_4^{2} > HCO_3^{-} > NO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2^{-}$	**$SO_4^{2} > Ca^{2+} > HCO_3^{-} > Na^{+} > NO_3^{-} > Cl^{-} > NH_4^{+} > H^{+} > Mg^{2+} > K^{+} > PO_4^{3-} > NO_2^{-}$**
Jayanagar	Bulk	$Ca^{2+} > Na^{+} > NH_4^{+} > Mg^{2} > K^{+} > H^{+}$	$SO_4^{2-} > NO_3 > HCO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2$	**$Ca^{2+} > SO_4^{2-} > NO_3^{-} > HCO_3^{-} > Cl^{-} > Na^{+} > NH_4^{+} > Mg^{2+} > K^{+} > PO_4^{3-} > NO_2^{-} > H^{+}$**
Mysore	Bulk	$Ca^{2+} > NH_4^{+} > Na^{+} > K^{+} > Mg^{2} > H^{+}$	$SO_4^{2} > HCO_3^{-} > NO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2$	**$Ca^{2+} > SO_4^{2-} > NH_4^{+} > HCO_3^{-} > NO_3^{-} > Na^{+} > Cl^{-} > K^{+} > Mg^{2} > PO_4^{3} > NO_2^{-} > H^{+}$**
Mandya	Bulk	$Ca^{2+} > NH_4^{+} > Na^{+} > K^{+} > Mg^{2} > H^{+}$	$NO_3^{-} > SO_4^{2} > HCO_3^{-} > Cl^{-} > PO_4^{3-} > NO_2$	**$Ca^{2+} > NH_4^{+} > NO_3^{-} > SO_4^{2-} > HCO_3^{-} > Na^{+} > Cl^{-} > K^{+} > Mg^{2+} > PO_4^{3-} > NO_2^{-} > H^{+}$**

Table.3 Annual VWM pH range and number of acid rains

Station / Year		No. of events	Wet Precipitation			Bulk Precipitation		
			pH Range	pH Acidic range	No. of acid rains	pH Range	pH Acidic range	No. of acid rains
Hebbal	2005–06	39 (35)	4.02–6.67	4.02–5.47	20	4.06–6.77	4.06–5.59	18
	2006–07	32 (29)	3.65–6.67	3.65–5.49	17	3.75–6.77	3.75–5.59	16
	2005–07	71 (64)	3.65–6.67	3.65–5.49	37	3.75–6.77	3.75–5.59	34
Jayanagar	2005–06	38 (35)	5.50–6.78	5.50–5.59	5	5.58–6.88	5.58–5.59	4
	2006–07	28 (27)	5.51–6.77	5.51-–5.59	4	5.59–6.88	5.58–5.59	4
	2005–07	66 (62)	5.50–6.78	5.50–-5.59	9	5.58–6.88	5.58–5.59	8
Mysore	2005–06	31 (29)	5.69–6.36	-	Nil	5.80–6.48	-	Nil
	2006–07	27 (26)	5.62–6.83	-	Nil	5.66–6.95	-	Nil
	2005–07	58 (55)	5.69–6.83	-	Nil	5.66–6.95		Nil
Mandya	2005–06	35 (34)	5.79–6.85	-	Nil	5.86–6.52	-	Nil
	2006–07	38 (37)	5.66–6.87	-	Nil	5.71–6.97	-	Nil
	2005–07	73 (71)	5.66–6.87	-	Nil	5.71–6.97	-	Nil

Number in parenthesis is Number of Events of bulk precipitation

Table.4 Annual variation of VWM pH in wet and bulk precipitation at urban areas during 2005–07

Location/ Precipitation	2005–06		2006–07		2005–07	
	Wet	Bulk	Wet	Bulk	Wet	Bulk
***Hebbal (Bangalore North)**	4.57	4.68	4.62	4.73	4.59	4.70
***Jayanagar (Bangalore South)**	5.65	5.75	5.64	5.74	5.65	5.74
Mysore	5.84	5.94	5.85	5.95	5.85	5.94
Mandya	5.98	6.08	5.88	6.01	5.93	6.05

***The annual VWM pH of Bangalore urban areas for wet and bulk precipitation, respectively, is 5.11 and 5.22.**

Table.5 Neutralizing factors (NF) of wet and bulk precipitation during 2005–07

Station/NF	Precipitation	Hebbal	Jayanagar	Mysore	Mandya
Ca^{2+}	Wet	0.57	0.89	0.96	1.04
Ca^{2+}	Bulk	0.61	0.94	0.99	1.12
NH_4^+	Wet	0.12	0.2	0.39	0.42
NH_4^+	Bulk	0.21	0.33	0.49	0.54
K^+	Wet	0.03	0.05	0.09	0.12
K^+	Bulk	0.07	0.09	0.12	0.18
Mg^{2+}	Wet	0.02	0.01	0.03	0.05
Mg^{2+}	Bulk	0.03	0.02	0.04	0.09

The equation is $NF_X = X/NO_3^- + SO_4^{2-}$, where X may be Ca^{2+}, NH_4^+ or Mg^{2+} or K^+NO_3- and SO_4^{2-}. NF values can be calculated and shown in Table 5.

NF values for urban area are as follows: NF_{Ca2+} is maximum in both wet and bulk precipitation in the range 0.57–1.04 and 0.61–1.12, respectively, followed by NF_{NH4}^+ (0.12–0.42 and 0.21–0.54), NF_K^+ (0.03–0.12 and 0.071–0.18) and NF_{Mg}^{2+} (0.02–0.05 and 0.02–0.9). NF shows that washout of ions are more in bulk precipitation compared to wet precipitation and clearly establishes that in urban wet and bulk precipitation Ca^{2+} was the major neutralizing ion followed by NH_4^+, K^+ and Mg^{2+}. Dry precipitation plays a major role in neutralization of acidic species of precipitation. The study shows that the neutralization factor of Ca^{2+} was the maximum, and thus it plays a crucial role in neutralizing the acidic effect. Closely following Ca^{2+} in neutralizing factor is NH_4, which also neutralizes acidity in wet

and bulk precipitation and maintains alkalinity.

Kulshrestha *et al.* (1995a) [33] have studied the chemical composition of rain water at New Delhi and established the order of NF as : NH_4^+ (0.50), Ca^{2+} (0.19) and Mg^{2+} (0.02). Parashar *et al*. (1996) [34] reported that in both wet and bulk depositions, major neutralization happened with Ca^{2+} and Mg^{2+} at Goa and Pune, respectively. The pH is influenced by atmospheric concentrations of Ca^{2+}, which has been reported as a major component of soil in India. Ca^{2+} has been reported in coarse mode from Delhi, Agra and Pune indicating its origin from natural sources like soil. Kulshrestha *et al*. (1998) [35] and Khemani *et al* (1989b, 1993) [36], [37] have recorded the pH of the cloud base as 5.80 at Pune, and at the ground level, that of the rain water at 7.30. The concentration of Ca^{2+} in rain water was 40 times higher than that of the cloud base indicating that below-cloud scavenging of suspended dust affects the precipitation composition significantly. Saxena *et al*. (1996) [38] have reported that the acidity of precipitation at Agra was neutralized by Ca^{2+} derived from soil components. The present study found the NF values to be high for Ca^{2+}, followed by NH_4^+, and Mg^{2+} or K^+, which clearly establishes that the acidity of wet and bulk precipitation was mainly buffered by Ca^{2+} and NH_4^+ and it controlled faster reduction of pH which is in agreement with the earlier studies. A major portion of Ca^{2+} was probably from particulate fallout rather than from rainout or washout processes.

Conclusions

A comprehensive study of precipitation chemistry was conducted at four different urban environment of Karnataka State during 2005–07. The salient features were observed and given below:

Annual ionic ratio (sum of anions and sum of cations) for wet precipitation and bulk precipitation were 1.09 and 0.99 was respectively. A ratio of greater than unity in wet precipitation indicates the presence of free anions responsible for rain water acidity and less than unity in bulk precipitation shows the alkaline nature, which is due to dry deposition of major cations in bulk collectors. On a chemical equivalent basis, the ionic composition of major ions was Ca^{2+} and SO_4^{2-}. The possible source of Ca^{2+} ions is urban activities (building construction), particularly of soil-derived particulate matter of wet and bulk precipitation. Higher concentration of cations and anions (except H^+) was observed in bulk precipitation compared to wet precipitation, mainly due to dry deposition. At Hebbal, the VWM pH is 4.59 for wet and 4.70 for bulk precipitation, lower than the threshold point for neutrality. The pH was acidic there, while at Jayanagar it is slightly alkaline and at Mysore and Mandya, it is totally alkaline. The annual VWM pH of the bulk precipitation at Hebbal and Jayanagar was 5.22 during 2005–07, lower than the threshold point for neutrality, indicating that the annual mean was in acidic range resulting in acid rain. It decreased from an average of 6.61 (1974–84) to 5.22 (2005–07) over the last three decades indicating the turning of the alkaline nature of the precipitation to acidic nature. It is mainly due to high concentration of SO_4^{2-} and NO_3^- traceable to local emission of SO_2 and NOx from industrial and urban activities, and increase in automobiles. Neutralizing factor (NF) shows washouts of ions are more in bulk precipitation compared to wet precipitation establishing that in urban precipitation, Ca^{2+} was the major

neutralizing ion followed by NH_4^+, K^+ and Mg^{2+}. Dry precipitation also plays a major role in neutralization of acidic species of precipitation. Neutralizing potential (NP) to acidifying potential (AP) shows reduction in the neutralization potential of aerosols in wet precipitation in spite of increase in the concentrations of SO_4^{2-} and NO_3^-. Ca^{2+} was the main neutralizing constituent in both urban wet and bulk precipitation

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