

Wet and Bulk Precipitation Chemistry at Urban Area in Karnataka, India

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Abstract. Precipitation is the main process by which trace gases and aerosols are scavenged from the atmosphere in temperate climate. Wet precipitation is defined as anything wet fallout from the atmosphere and bulk precipitation is the mixture of rain (wet) and the dry fallout Bulk and wet precipitation samples were collected at Bangalore north (Hebbal), Bangalore South (Jayanagar), Mandya and Mysore in Karnataka state, India by using bulk precipitation collectors, during the year 2005-2007. Concentrations of major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and $\text{NH}_4^+\text{-N}$) and anions (Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , NO_2^- , and $\text{PO}_4^{3-}\text{-P}$) were determined and predominant ions were identified. The VWM pH of wet precipitation of Bangalore (Hebbal and Jayanagar) precipitation was 5.12 which is acidic rain and in Mandya urban area was 5.93 and Mysore was 5.84, which is alkaline in nature. The annual VWM pH of the bulk precipitation at Bangalore urban area 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 and in Mandya and Mysore urban area it was 6.04 and 5.94, which is alkaline in nature. The study also reveals that pH of bulk samples is always higher than wet only sample, which indicates the influence of dry deposition. The decreasing of pH in the precipitation of Bangalore urban area could be because of SO_4^{2-} and NO_3^- ions. NH_4^+ and Ca^{2+} were acting as neutralizing ions or in the absence of these ions; the pH reduction of precipitation may be much faster towards acidic range. The difference between wet only and bulk components indicates the influence of dry deposition.

Keywords: Acid rain, Chemical composition, Urban area, Pollution.

1. Introduction

Atmospheric deposition is a cleansing process for removing the gases, as well as particles from the atmosphere. Thus, it is playing an important role in controlling the concentration of species in the atmosphere and providing essential nutrients to ecosystems. The chemistry of precipitation is an indication to the state of atmosphere at any location. So far, acid rain incidences have been very few from the Indian region, mainly due to the dominance of alkaline components like Ca^{2+} and NH_4^+ (Khemani, 1989). Varma (1989a) reported an average pH of 6.61 for Bangalore region precipitation, for the years 1974-1984. However, Shivashankara et al., (1998) reported pH of 5.20 in Bangalore which indicates to the acidic rain, with a decrease of about 1.4 units in pH after the period of 14 years. Earlier, Khemani, et al., (1989a) have also reported that pH values of rain water at Agra and Delhi have decreased by 2.8 (9.1-6.3) and 0.9 (7.0-6.1) units respectively, during the periods from 1960's to 1980's. Therefore, at any location, it is important to monitor continuously the composition of precipitation to assess the impact of changes in anthropogenic activities. With this aim, we have studied the chemical composition of wet and bulk precipitation at different locations in urban area of Karnataka State, South India.

2. Location, Sampling and Analysis

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2.1. Location of Sampling Sites

Greater Bangalore city ($12^{\circ} 58^1$ N, $77^{\circ} 35^1$ 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, $12^{\circ} 55^1$ N $77^{\circ} 34^1$ E) bounded by residential and commercial activities and Bangalore north, (Hebbal, $13^{\circ} 1'$ N $77^{\circ} 17.5^1$ 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 ($12^{\circ}33'$ N, $76^{\circ}39'$ E) is a major residential area consisting of agricultural land and is connected by state highway. Mysore city ($12^{\circ}55'$ N, $76^{\circ}39'$ E) is a large city and is one of the historical places of India (Fig 1).

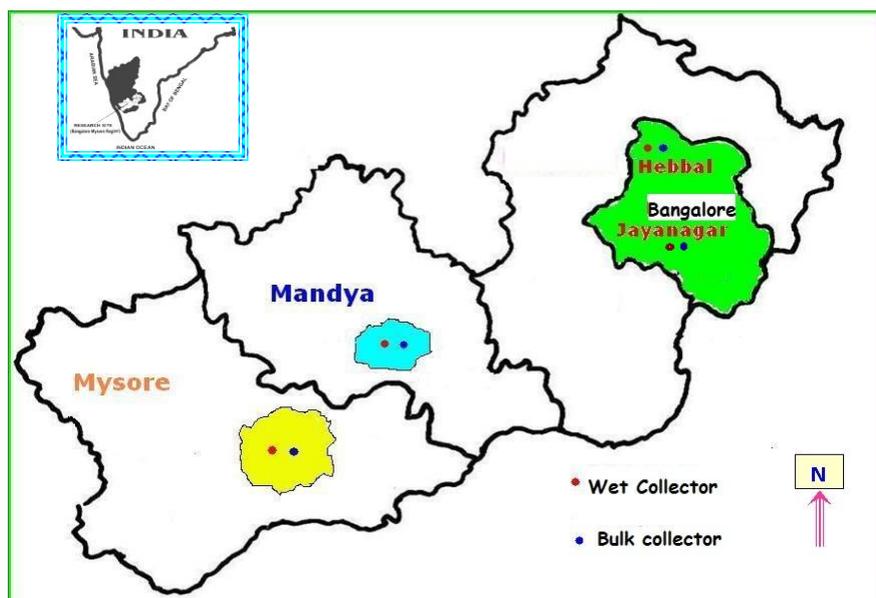


Fig 1: Map showing the location of sampling stations in urban area.

2.2. Sampling and Analysis

During the study period, 268 wet and 252 bulk precipitation samples were collected from all the four sampling stations in the study area during 2005-07. Wet 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 2 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 Likens (1967), Ramalingaih (1985) and Shivashankara, et al., (1998). 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 the four stations were analyzed for pH, cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and $\text{NH}_4^+\text{-N}$) and anions (Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , N , $\text{NO}_2\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$) using the standard methods(2005).

2.3. Results & Discussions

Annual volume weighted average concentrations (VWM) in μeqL^{-1} were calculated for all the chemical constituents of wet and bulk precipitation. The mean VWM of wet and bulk precipitation for all the four sampling stations i.e. Bangalore north (Hebbal), Bangalore south (Jayanagar), Mysore and Mandya is shown in Table 1.

Variations of pH

Review of Table 1 clearly observed that. the study period annual mean for Bangalore urban area (Hebbal and Jayanagar) was 5.22, which is lower than the threshold limit for neutrality (5.60) indicating that all these areas were in an acidic range. The lower pH was due to the high concentration of SO_4^{2-} , ($100.5 \mu\text{eqL}^{-1}$ and $109.89 \mu\text{eqL}^{-1}$) and NO_3^- ($53.78 \mu\text{eqL}^{-1}$ and $54.40 \mu\text{eqL}^{-1}$) 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) 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).

The pH of rain water at New Delhi in 1996 was 5.70 (Kulshrestha *et al.*, 1996), which in 1960s was 7.0 and in 1980s 6.10, clearly demonstrating a decreasing trend. The pH values at different locations in India vary from 5.30 to 6.44 (Pillai, 2001). The present study confirms the earlier findings of Khemani *et al.* (1989a), and Kulshrestha *et al.* (1996), 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.* (1989) and Shivashankara *et al.* (1999) that the pH of bulk precipitation over Bangalore city is turning acidic (acid rain) 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. The VWM pH of wet precipitation of Mandya urban area was 5.93 and Mysore was 5.84, and annual VWM pH of the bulk precipitation of Mandya and Mysore urban area was 6.04 and 5.94, which is alkaline in nature.

Table 1: Mean Volume Weighted Mean (VWM) concentrations of major ions (μeqL^{-1}), Electrical Conductivity($\mu\text{S/cm}$) and pH in wet and bulk precipitation samples in urban area during 2005 – 2007.

Urban Area	Type	pH	EC	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	NO ₂ ⁻	PO ₄ ³⁻
Hebbal	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
Jayanagar		5.64	20.93	2.27	69.39	5.90	31.9	7.07	28.02	29.3	43.88	48.65	31.37	2.06	3.28
Mysore		5.84	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
Mandya		5.93	15.56	1.19	47.17	6.78	24.85	9.81	31.54	21.6	26.98	36.7	20.77	4.29	5.50
Hebbal	Bulk	4.70	35.91	19.8	93.31	12.88	37.66	11.46	32.33	36.63	109.89	54.40	40.58	5.15	6.78
Jayanagar		5.74	26.60	1.8	96.48	10.48	38.39	10.04	32.97	40.03	50.56	44.92	49.85	4.26	6.52
Mysore		5.94	22.59	1.14	83.54	10.41	31.83	10.95	40.66	31.03	45.03	39.54	37.11	4.10	5.70
Mandya		6.05	19.33	0.90	73.87	12.39	30.24	12.43	35.16	25.83	31.81	31.08	32.79	6.34	8.72

Comparison between bulk precipitation and wet precipitation chemistry

The ratio of annual bulk and wet precipitation are calculated and represented in Table 2. The ratio of bulk and wet precipitation at Hebbal (Bangalore North) shows that major cations of Mg^{2+} , Ca^{2+} , K^+ , and NH_4^{2+} were higher by 61%, 31%, 30%, and 17% and major anions of SO_4^{2-} and NO_3^- by 11% and 44%, respectively. However, at Jayanagar (Bangalore South) major cations of Mg^{2+} , Ca^{2+} , K^+ , and NH_4^+ were higher by 58%, 49%, 40%, and 22%, respectively, and of SO_4^{2-} and NO_3^- by 26% and 42%. At Mysore, the ratios of major cations of Mg^{2+} , Ca^{2+} , K^+ , and NH_4^+ were higher by 87%, 35%, 23% and 15%, and major anions SO_4^{2-} and NO_3^- by 11% and 47%, respectively, and at Mandya, by 83%, 57%, 27%, and 11%, and of SO_4^{2-} and NO_3^- by 18% and 58%, respectively, in bulk samples than in wet-only samples. Ca^{2+} and NH_4^+ were acting as

neutralizing ions or in the absence of these ions; the pH reduction of precipitation may be much faster towards acidic range. The neutralizing effect was more in bulk precipitation when compared to wet precipitation due to dry deposition.

The ratio of H⁺ ions showed lower values in bulk samples than in wet samples at all four sampling sites. H⁺ ions of wet samples are generally always higher than the corresponding bulk samples. The remarkable higher concentration of Ca²⁺, Mg²⁺, and K⁺ in bulk precipitation seems to be due to the influence of dry deposition during long exposure of the bulk precipitation. The higher concentration of Ca²⁺, NH₄⁺, NO₃⁻ at lower heights seems to be due to their presence in coarse mode particles (Kulshrestha *et al.*, 1995).

Table 2: Comparison between the concentrations of annual bulk precipitation and wet-only precipitation during 2005-

07

Station Parameter	Hebbal	Jayanagar	Mysore	Mandya
	Bulk/Wet			
H ⁺	0.78	0.79	0.79	0.76
Ca ²⁺	1.23	1.39	1.32	1.57
Mg ²⁺	1.50	1.78	1.85	1.83
Na ⁺	1.13	1.20	1.17	1.22
K ⁺	1.21	1.42	1.26	1.27
NH ₄ ⁺	1.16	1.18	1.13	1.11
Cl ⁻	1.19	1.37	1.13	1.20
SO ₄ ²⁻	1.09	1.15	1.10	1.18
HCO ₃ ⁻	1.01	0.92	0.86	0.85
NO ₃ ⁻	1.28	1.59	1.39	1.58
NO ₂ ⁻	1.35	2.07	1.66	1.48
PO ₄ ³⁻	1.43	1.99	1.65	1.59
%	1.20	1.40	1.27	1.30

The contribution of fine-sized particles of SO₄²⁻ was more in the case of wet precipitation than in bulk precipitation as it undergoes nucleation scavenging (in-clouds). A reduction in acidity of dry-deposited calcium species, possibly CaCO₃, being washed in by subsequent precipitation events could be the reason for the smaller concentration and deposition of H⁺ in the bulk collector. The difference between wet-only and bulk components indicates the influence of dry deposition in the urban areas of Karnataka.

2.4. Conclusions

Annual mean pH of Bangalore urban area 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 SO₄²⁻ and NO₃⁻ traceable to local emission of SO₂ and NO_x from industrial and urban activities, and increase in automobiles. The pH of wet precipitation was higher compared to bulk precipitation, which may be due to the presence of acidic

species and lower dry deposition of cations. The difference between wet-only and bulk components indicates the influence of dry deposition in urban area of Karnataka.

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