"Temporal Variation and Sources of Rainwater Chemistry and Aerosol Trace Metals in Urban Environments: A Comprehensive Study in Bengaluru and Mysuru, Karnataka, India"

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Abstract: The research conducted in this study focused on analyzing the chemistry of rainwater through comprehensive field and laboratory tests, encompassing various water quality parameters such as pH, alkalinity, and trace metals. The study sites were strategically selected near pollution sources to maintain data integrity, aiming to establish correlations between pollutant emissions and precipitation acidity. A meticulous sampling program was implemented between June 2021 and May 2022, totaling 154 wet and 128 bulk precipitation samples, along with 45 aerosol samples. Sample preparation involved rigorous filtration, digestion, and instrumental analysis using techniques like Atomic Absorption Spectroscopy. Results revealed distinct seasonal variations in rainfall patterns, with the dominance of the south-west monsoon in Bengaluru and Mysuru regions. pH levels varied across locations, reflecting diverse environmental influences, while trace metal concentrations demonstrated consistent trends, with iron being the most abundant metal. Statistical analyses, including correlation tests and factor analysis, provided insights into the inter-relationships among physio-chemical parameters and the sources of trace metals. Overall, this study contributes valuable insights into the chemistry of rainwater and aerosols, highlighting the complex dynamics of environmental pollution and its impacts.

Keywords:

1. Introduction: Precipitation serves as a vital mechanism for purging pollutants from the atmosphere, with its chemical composition reflecting the quality of the air it traverses. Changes in precipitation chemistry offer valuable insights into trends in air chemistry, making measurements of precipitation chemistry a standard feature in many national monitoring programs [1]. Coastal areas typically exhibit high concentrations of sea salt in precipitation, while inland areas tend to have a larger proportion of substances originating from the soil [1]. Previous studies have highlighted elevated levels of anthropogenic substances like NO3- and SO42- in urban or industrial areas compared to non-urban regions [2], [3]. Regions such as Europe and North America have experienced adverse effects from acidic deposition due to air pollutants [2]. Rapidly increasing air pollution levels in southeastern Asian countries and China have been attributed to factors like population growth, agricultural production, industrialization, and transportation [4]. While systematic observations on precipitation chemistry have been conducted in Europe and North America, such studies are limited in other parts of the world, especially under non-urban conditions in tropical regions [4], [5], [6], [2].

Over the past decade, studies conducted in India have shed light on the alkaline nature of rainwater, attributed to the presence of soil-derived particles in the atmosphere, which act as buffers against acidity during below-cloud scavenging processes [7][8][9][10][11][12]. The chemical composition of rainwater plays a crucial role in scavenging soluble components from the atmosphere, offering insights into the relative contributions of various sources of atmospheric pollutants. This composition varies from site to site and region to region due to the influence of local sources [12]. In India, effective wet removal processes are observed primarily during the monsoon period (June-September), coinciding with approximately 90% of the annual rainfall. During the remaining period, characterized by dry conditions, atmospheric deposition chemistry is determined by suspended dust particles continuously input from soil suspension. Consequently, dust fall deposition serves as a significant removal mechanism in India, effectively sequestering acidic gaseous pollutants from the atmosphere.

In recent years, the issue of acid rain has expanded to Asia due to a significant rise in atmospheric emissions stemming from industrial activities, vehicular traffic, and other human endeavours. The process of industrialization and urbanization has particularly contributed to the pollution of major metropolitan areas in Asia, leading to acid rainfall. These local effects cannot be overlooked, as they pose significant threats to local ecology. Therefore, it is imperative to monitor rain chemistry in urban areas. Data collected from such monitoring efforts are vital for identifying temporal and spatial deposition trends, predicting ecological impacts, modelling atmospheric processes, and devising future control strategies.

The examination of the chemical composition of both wet and bulk precipitation is crucial for comprehending the geochemical cycles of various elements and evaluating the pollution status of different regions or sources. In India, numerous studies have delved into the chemical composition of precipitation in urban areas, highlighting its significance in discerning the relative contributions of different sources, be it gases or particles [13,14,15]. As a result of this concern, there has been a surge in research focused on the wet and bulk precipitation chemistry of urban areas over the past two decades [16],[17],[8]. Understanding the chemical composition and variability of wet and bulk precipitations in urban areas is vital for determining deposition trends, modelling atmospheric processes, and planning future emission control strategies. Hence, the present study was conducted to investigate the chemical composition of wet and bulk precipitation in urban environments in Karnataka State during the period of 2021 to 2022. Establishing a network at three stations in urban areas (Peenya and Vidyaranyapura in Bangalore, Hebbal in Mysore) was the initial step to monitor precipitation chemistry, aiming to comprehend the presence of acidic and alkaline species and the geochemical cycles of various elements, ultimately aiding in the assessment of pollution status from different area sources.

2. Methods

The rainwater chemistry was determined through comprehensive field and laboratory tests encompassing a range of water quality parameters, including pH, turbidity, alkalinity, hardness, major ions, and trace metals. Subsequently, the chemical composition of rainwater observed in the study area was juxtaposed with the established standards for drinking water quality parameters relevant to the region under investigation.

2.1 Study Sites for Analysis

Careful consideration has been given to the selection of sampling locations, emphasizing proximity to the pollution source to maintain the integrity of the collected data. The rationale behind this approach lies in the recognition that the concentration of air pollutants, such as SOx and NOx, tends to diminish with increasing distance from the emission source. By strategically siting the sampling stations close to the source area, the study aims to establish a clear correlation between the emission of pollutants in a given urban region and the resulting acidity of precipitation at the sampling sites. However, it's acknowledged that sampling too close to the source may introduce complications due to the influence of dust particles in emissions, impacting both wet and bulk precipitation samples. As depicted in Figure 1, the sampling stations for wet and bulk precipitation, as well as aerosols, are strategically positioned in the urban area, seeking a balance between proximity to the source and minimizing the effects of dust contamination. Table 1 provides detailed coordinates, land-use types, roof heights for collector placement, and approximate longitudes for each station, ensuring a systematic and comprehensive approach to the study. Additionally, Figure 2 offers a visual representation of the study area, providing context for the sampling station locations.

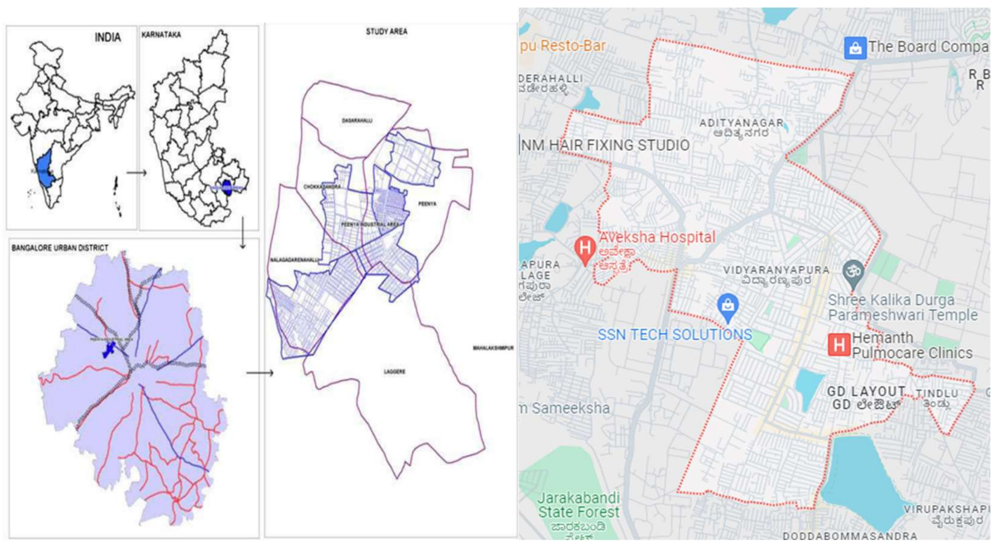

Fig 1: Location maps for Peenya and Vidyaranyapura (Bangalore)

Geographical coordinates: Latitude N 13° 51', Longitude E 77° 26'

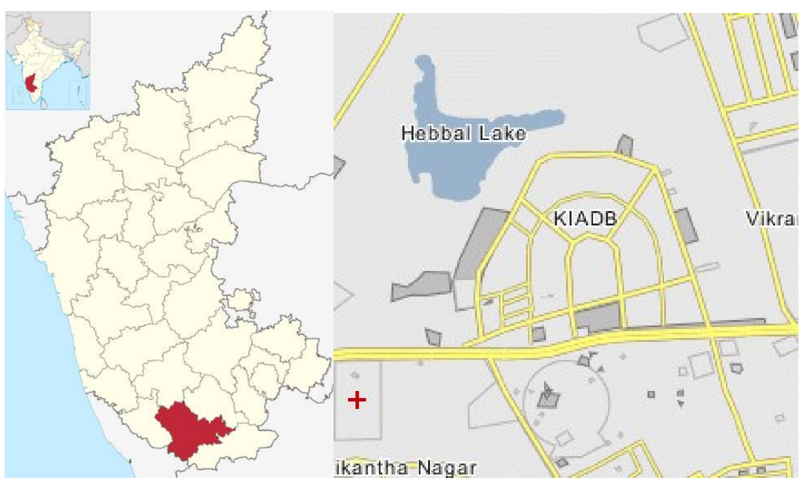

Fig 2: Location maps for Hebbal (Mysuru)

Geographical Coordinates: Latitude N 12° 21', Longitude E 76° 36'

Table 1: Coordinates, land-use types, roof heights for collector placement, and approximate longitudes for each station

SI NO	Sampling Site Location	Elevation (mts)	Land form type	Installation of Collectotrs and samplers	Altitude (mts)	Funnel Size (Cm)	Site Description
1	Peenya Bengaluru	945	Flat	Wet Collector, Bulk Collector High Volume Sampler	12.0	18.0	Surrounding by large no of Industries
2	Vidyaranyapura Bengaluru	945	Flat	Wet Collector, Bulk Collector High Volume Sampler	12.0	18.0	Surrounding by residential area with intensive road transport
3	Hebbal Mysuru	770	Flat	Wet Collector, Bulk Collector High Volume Sampler	12.0	18.0	Surrounding by large no of Industries

2.2 Sampling Program

Between June 2021 and May 2022, a rigorous data collection program was implemented, encompassing meticulous procedures to gather wet and bulk precipitation samples, as well as aerosols, from four designated sampling stations. These stations were strategically chosen to ensure representation across the study area, with details illustrated in Figure 1 and 2. Given the region's climatic classification, characterized by distinct seasons, ranging from summer to south-west monsoon and north-east monsoon, the sampling timeframe was crucial for capturing seasonal variations in precipitation patterns. Employing a manual sampling approach, samples were collected weekly or biweekly throughout the study period, totalling 154 wet and 128 bulk precipitation samples. Each sample underwent visual inspection to eliminate contamination, with 12 bulk precipitation samples discarded for this reason. Additionally, 45 aerosol samples were collected biweekly using a high-volume air collection system. Stringent rinsing and inspection protocols were followed to maintain data integrity, ensuring the reliability of the collected dataset. Furthermore, aerosol samples were transported to KSPCB for chemical analysis, enhancing the comprehensiveness of the study's findings.

2.3 Sample Collection

2.3.1 Wet and Bulk Precipitation Samples

In this study, a meticulous sampling program was developed to collect wet and bulk precipitation samples from specified locations, ensuring accuracy and representativeness in assessing air pollution status. Wet precipitation samples were collected biweekly using collectors designed to isolate wet precipitations and minimize contamination from dust fall and gas absorption during dry periods. Aerosol samples were collected monthly to provide insights into atmospheric particulate matter composition. The wet precipitation collector, featuring an 18-cm polyethylene funnel connected to a 5-liter reservoir, excluded dry period influences and contributed to regionally representative sampling. Bulk precipitation, comprising both wet and dry components, was collected using purpose-designed collectors equipped with vapor traps and vapor barrier tubing to prevent gas exchange and evaporation, ensuring sample integrity. This meticulous sampling methodology facilitated a robust assessment of air and precipitation quality, crucial for understanding trace metal dynamics in the urban setting.

Fig 3: Wet and bulk precipitation collectors and installation at the sites

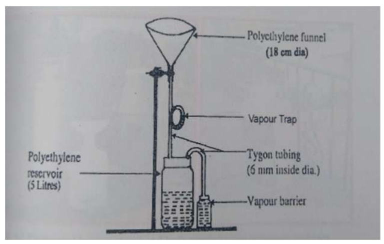

Fig 4: Bulk precipitation collector overview

2.3.2 Aerosols Samples

In air quality assessment, the Envirotech APM 415 high-volume air sampler is a key tool designed specifically for Total Suspended Particles (TSP) sampling. With features like removable roofs, a filter holder, and a motor, it offers efficiency and portability. Its compact design allows for easy transportation and setup at various sampling locations. The APM 415, known as the "DWARF" version of the APM 410, is lighter and more compact, fitting into a car dickey for convenient field use. Constructed with anodized aluminium body and framework, it ensures durability against environmental conditions. Its innovative design allows for easy separation of the gable roof for enhanced ruggedness and compactness during transportation. Equipped with a voltage stabilizer, it ensures a steady flow rate for reliable operation. Additionally, its unique cabinet design enables quick brush replacement without dismantling the blower assembly, streamlining maintenance efforts. Overall, the APM 415 demonstrates Envirotech's commitment to practical and efficient air quality monitoring solutions.

Fig 5: High Volume air sampler

2.4 Sample Preparation

2.4.1 Wet and Bulk Precipitation Samples

The wet and bulk precipitation samples were filtered using a vacuum filtration system equipped with Buchner funnels to separate the liquid phase from particulate matter. Nitric acid (HNO_3) was added to acidify the filtered samples to maintain sample integrity, enhance metal solubility, and preserve them for analysis. Acidified samples underwent digestion using a controlled heating process with a microwave digestion system to break down organic and inorganic compounds, ensuring the conversion of metals into an analysable form for total trace metal analysis. Instrumental analysis was conducted using Atomic Absorption Spectroscopy (AAS) to analyse the digested samples. The AAS system employed in this study is a fully automated, True double beam PC controlled system with a wavelength range of 185-900 nm and a sensitivity of 0.9 Absorbance for 5 mg/L Cu. Calibration standards were prepared using certified reference materials (CRMs) to establish a calibration curve for converting absorbance values into quantitative concentrations of trace elements. The pH determination of samples was performed using a WTW 2001 pH meter, adhering to standardized procedures outlined in the APHA 1995 guidelines. This meticulous approach ensures accurate data on the chemical composition of the samples, vital for understanding environmental or water quality conditions at the collection sites.

Fig 6: (a) Vacuum filtration system (b) Nitric acid (c) Atomic absorption spectrometer (d) WTW bench top pH meter

2.4.2 Aerosols Samples

The aerosol sampling process utilized the Envirotech APM 415 high-volume air sampler, renowned for its portability and precise sampling capabilities. This instrument, controlled by a PC and equipped with absorption and emission capabilities, efficiently collected suspended particles onto filters for subsequent analysis. The sampler's durable construction and modular design facilitated easy transportation and rugged operation. After collection, aerosol samples underwent digestion to prepare them for trace metal analysis using Atomic Absorption Spectroscopy (AAS). Calibration standards ensured accurate quantification of trace metal concentrations. Quality control measures, including procedural blanks and periodic analysis of certified reference materials, were implemented to ensure reliable results. Overall, this comprehensive methodology provided valuable insights into the trace metal composition of ambient air in the study area.

3. Results and Discussion:

3.1 Rainfall Data for the Sampling Period

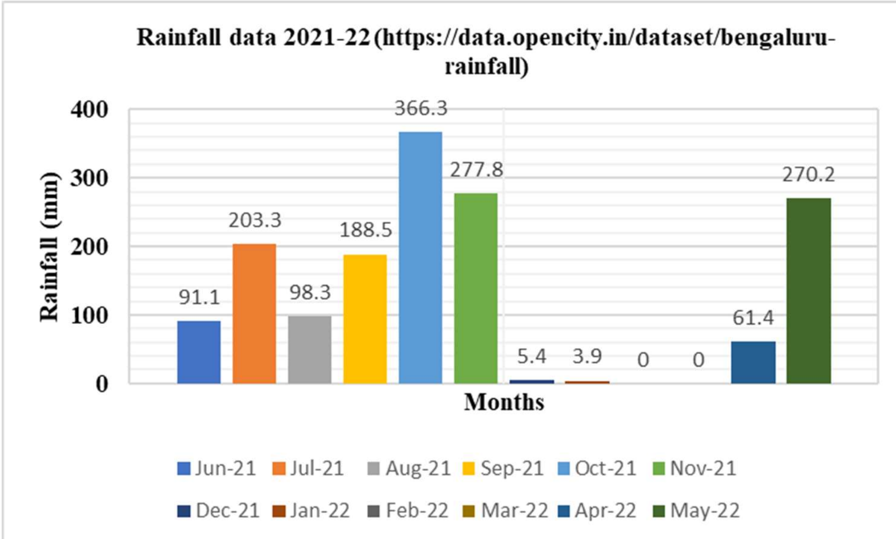

Fig 7: Rainfall data for Bengaluru for the year 2021-2022 (https://data.opencity.in/dataset/bengaluru-rainfall)

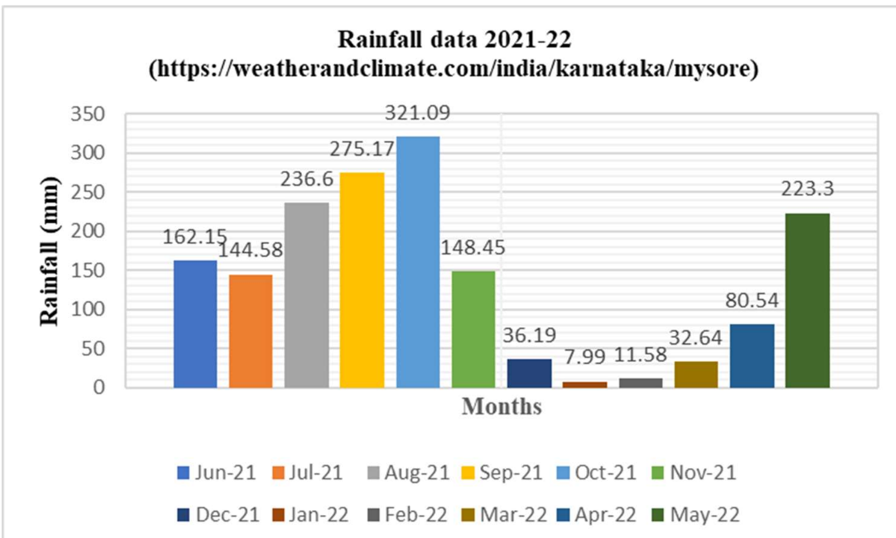

Fig 7: Rainfall data for Mysuru for the year 2021-2022 (https://weatherandclimate.com/india/karnataka/mysore)

The first two considered sample stations lie in Bengaluru (Capital city of Karnataka). Peenya is an Industrial area, established in the late 1970s by the Karnataka Small Industries Development Corporation, Bengaluru's Peenya industrial area is one of Southeast Asia's oldest and largest industrial zones. With over 2,000 industries, it is considered severely polluted, ranking 32nd with a Comprehensive Environmental Pollution Index (CEPI) score of 65.11 (50-70 indicates severe pollution) and an air pollution score of 56. Among the 2,101 industries, 334 are classified as red-category, indicating significant pollution contributors, while 473 fall under the orange category. Major polluting industries include engineering with surface treatment, spray painting, pharmaceutical R&D, service stations, electroplating, garment washing, and dyeing and printing. On the other hand, Vidyaranyapura, located in the north-west of Bangalore at 13°05' N and 77°33' E, sits at an altitude of approximately 3,050 ft

(930 m) above sea level. It is surrounded by areas such as Yelahanka, Thindlu, Kodigehalli, Doddabommasandra, Jalahalli, MS Palya, and Sahakara Nagar. The locality comprises several sub-blocks and layouts, including AMS, Ganesha, Balaji, Defence Colony, Nanjappa, Chamundeshwari, Srinidhi, BEL, HMT, and NTI layouts. Close proximity to government sector factories like BEL and HMT characterizes Vidyaranyapura. It also boasts premier educational institutions like the Centre for Liquid Crystal Research, University of Agricultural Sciences, Indian Institute of Science, National Centre for Biological Sciences, Jawaharlal Nehru Centre for Advanced Scientific Research, and TIFR Centre for Applicable Mathematics. The other station, Hebbal is an industrial area and suburb of Mysore city in India.

From figure 8, the rainfall data for Bengaluru, Karnataka for the year 2021-22 highlights distinct seasonal variations. From March to May, minimal precipitation is observed, characteristic of the summer season. Subsequently, the onset of the south-west monsoon in June brings a significant increase in rainfall, peaking in July and tapering off towards September. Transitioning into the north-east monsoon, October and November experience considerable rainfall, followed by a gradual decrease in precipitation in December and January. Overall, this data underscores the influence of the monsoon seasons on Bengaluru's climate, with the south-west monsoon dominating from June to September and the north-east monsoon bringing variable rainfall from October to January/February. From figure 9, in Mysuru, Karnataka, the 2021-22 rainfall data illustrates clear seasonal variations. During the summer season from March to May, minimal precipitation is recorded, aligning with the region's typically dry conditions. The onset of the south-west monsoon in June brings a significant increase in rainfall, with June to September experiencing the highest precipitation levels. This reflects the influence of the south-west monsoon on Mysuru's climate. Following the south-west monsoon, the transition to the north-east monsoon occurs from October to January/February. This period shows variable rainfall, with a gradual decrease towards the end of the year and the beginning of the new year. Overall, the data highlights distinct seasonal patterns, with the south-west monsoon dominating from June to September and the transition to the north-east monsoon characterized by variable rainfall from October to January/February.

3.2 pH and Trace metal concentrations

3.1 Rain water characteristics (Physical)

The figure 8 illustrates the temporal distribution of pH levels in rainwater samples collected from Peenya Bengaluru, Vidyaranyapura Bengaluru, and Hebbal Mysuru over the sampling period. Each location possesses unique characteristics, with Peenya Bengaluru surrounded by numerous industries, Vidyaranyapura Bengaluru located in a residential area with heavy road traffic, and Hebbal Mysuru also surrounded by industrial activity. Analysis of the pH values reveals notable variations across different months and locations.

In Peenya Bengaluru, pH levels exhibit a considerable range, with Wet Precipitation pH ranging from 3.95 to 5.11, Bulk Precipitation pH from 3.7 to 5.14, and Aerosols pH from 4.25 to 4.94. The maximum pH is observed in December 2021 for Wet Precipitation, contrasting with the minimum pH noted in November 2021 for Bulk Precipitation. On average, the pH across all columns in Peenya Bengaluru approximates 4.6. Vidyaranyapura Bengaluru showcases a narrower pH range compared to Peenya. Wet Precipitation pH spans from 5.21 to 5.61, Bulk Precipitation from 5.2 to 5.79, and Aerosols from 5.3 to 5.82. Notably, the maximum pH values occur in December 2021 for both Wet and Bulk Precipitation, while the minimum is recorded in July 2021 for Bulk Precipitation. The average pH across all columns in Vidyaranyapura Bengaluru is approximately 5.5. Hebbal Mysuru demonstrates consistency in pH levels, with Wet Precipitation consistently exhibiting the highest pH values across all months, ranging from 5.2 to 5.36. Bulk Precipitation and Aerosols pH ranges from 4.67 to 5.36. Interestingly, the minimum pH value is observed in Aerosols for November 2021. On average, the pH across all columns in Hebbal Mysuru is approximately 5.4. These variations in pH values reflect the diverse environmental influences present in each location, including industrial emissions, vehicular pollution, and atmospheric processes. Understanding pH variations in rainwater samples is crucial for assessing environmental impacts and potential risks to ecosystems and human health, offering valuable insights into the acidity or alkalinity of the precipitation.

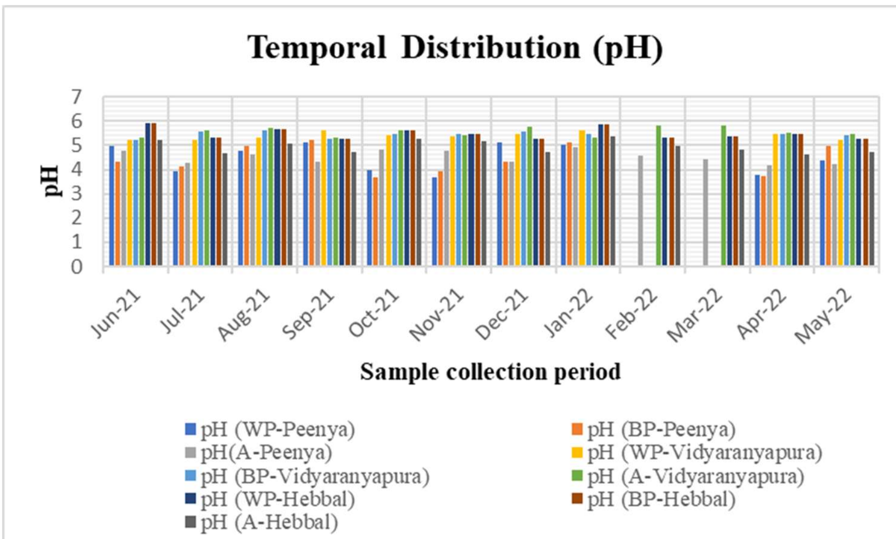

Fig 8: Temporal distribution of pH measured using rain water samples during sampling period

3.2 Trace Metal Concentrations

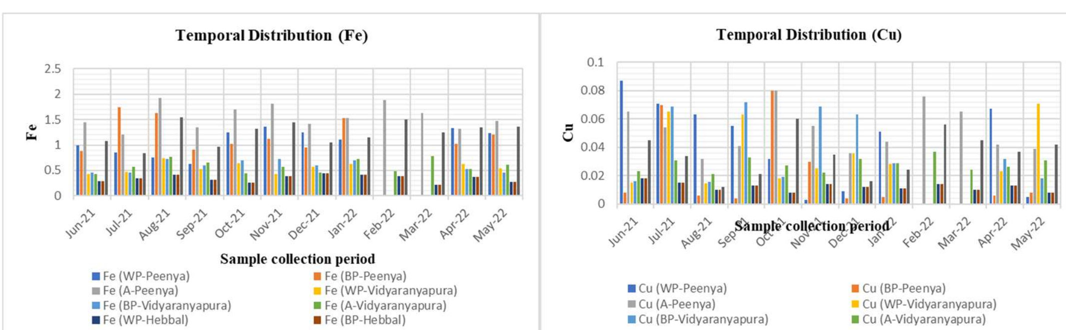

Fig 9: Temporal distribution of Trace metal concentrations measured using rain water samples (Wet precipitation – WP, Bulk precipitation – BP) and Aerosol samples during sampling period

The temporal distribution of trace metal concentrations in rainwater samples collected from various sampling locations reveals interesting insights into the variation and abundance of these metals across different seasons. Analysis of Rainwater Samples: Wet Precipitation (WP) and Bulk Precipitation (BP) Sampling Locations: Peenya: Summer (March to May): The mean concentrations of trace metals in Peenya during this period show variation, with Fe exhibiting the highest concentration followed by Cu, Zn, Ni, Pb, Cd, Cr, and Mn. South-West Monsoon (June to September): Fe remains the predominant trace metal, followed by Cu, Ni, Zn, Pb, Cd, Cr, and Mn. North-East Monsoon (October to January/February): Similar trends persist with Fe being the highest, followed by Cu, Ni, Zn, Pb, Cd, Cr, and Mn. Vidyaranyapura: Summer: Fe dominates the trace metal concentrations, followed by Cu, Zn, Ni, Pb, Cd, Cr, and Mn. South-West Monsoon: Fe continues to be the most abundant, followed by Cu, Zn, Ni, Pb, Cd, Cr, and Mn. North-East Monsoon: Fe remains the highest, followed by Cu, Zn, Ni, Pb, Cd, Cr, and Mn. Hebbal: Summer: Fe exhibits the highest concentration, followed by Cu, Zn, Ni, Pb, Cd, Cr, and Mn. South-West Monsoon: Fe remains the predominant trace metal, followed by Cu, Ni, Zn, Pb, Cd, Cr, and Mn. North-

East Monsoon: Fe still shows the highest concentration, followed by Cu, Ni, Zn, Pb, Cd, Cr, and Mn. Decreasing Order of Trace Metal Concentrations: Peenya: Fe > Cu > Zn > Ni > Pb > Cd > Cr > Mn Vidyaranyapura: Fe > Cu > Zn > Ni > Pb > Cd > Cr > Mn Hebbal: Fe > Cu > Zn > Ni > Pb > Cd > Cr > Mn. The dominant trace metal in rainwater across all locations and seasons is iron (Fe). Variability in concentration is observed among different metals and sampling locations. The north-east monsoon season generally exhibits similar trends to the south-west monsoon season. Sources of trace metals include natural processes like forest fires, as well as anthropogenic activities such as industrial emissions and vehicular pollution. The order of trace metal concentrations can vary slightly between locations, possibly due to different local sources of pollution and atmospheric dynamics.

The analysis of trace metal concentrations in aerosol samples collected from various sampling locations during different monsoon periods provides valuable insights into seasonal variations. In Peenya, during the summer season (March to May), iron (Fe) exhibits the highest concentration, followed by copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), and manganese (Mn). This pattern remains consistent during the south-west monsoon (June to September) and the north-east monsoon (October to January/February) periods. Similar trends are observed in Vidyaranyapura and Hebbal, with Fe consistently dominating the trace metal concentrations across all seasons. The decreasing order of trace metal concentrations remains unchanged across all locations and seasons: Fe > Cu > Zn > Ni > Pb > Cd > Cr > Mn. These variations in trace metal concentrations can be attributed to both natural processes, such as forest fires, and anthropogenic activities, including industrial emissions and vehicular pollution. Overall, these findings highlight the complex interplay of factors influencing trace metal levels in aerosol samples across different seasons and locations.

3.3 Statistical Analysis

3.3.1 Correlation

Table 1: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (wet precipitation) collected from Peenya.

	pH	Fe	Cu	Zn	Ni	Pb	Cd	Cr
Fe	0.764							
Cu	0.553	0.230						
Zn	0.774	0.753	0.400					
Ni	0.707	0.457	0.556	0.477				
Pb	0.813	0.558	0.474	0.560	0.357			
Cd	0.652	0.430	-0.054	0.369	0.376	0.438		
Cr	0.618	0.686	0.446	0.582	0.726	0.326	0.051	
Mn	0.438	0.428	0.005	0.444	0.519	0.387	0.151	0.639

Table 2: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (Bulk precipitation) collected from Peenya.

	pH	Fe	Cu	Zn	Ni	Pb	Cd	Cr
Fe	0.858							
Cu	0.139	0.381						
Zn	0.876	0.713	0.323					
Ni	0.667	0.821	0.743	0.732				
Pb	0.568	0.428	0.256	0.805	0.453			

Cd	0.863	0.745	0.118	0.670	0.498	0.264		
Cr	0.757	0.506	0.237	0.871	0.511	0.697	0.662	
Mn	0.884	0.769	0.288	0.782	0.635	0.521	0.796	0.774

Table 3: Pearson's correlations matrix for the physico-chemical parameters in Aerosol samples collected from Peenya.

	pH	**Fe**	**Cu**	**Zn**	**Ni**	**Pb**	**Cd**	**Cr**
Fe	0.570							
Cu	0.404	0.304						
Zn	0.599	0.014	0.065					
Ni	0.395	0.469	-0.126	-0.047				
Pb	0.286	0.455	0.279	0.053	0.353			
Cd	-0.480	-0.242	-0.281	-0.472	-0.363	-0.765		
Cr	0.004	0.369	0.355	-0.327	0.355	0.629	-0.195	
Mn	0.057	0.596	0.480	-0.286	0.166	0.147	-0.044	0.347

Table 4: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (wet precipitation) collected from Vidyaranyapura.

	pH	**Fe**	**Cu**	**Zn**	**Ni**	**Pb**	**Cd**	**Cr**
Fe	0.930							
Cu	0.567	0.418						
Zn	0.879	0.786	0.542					
Ni	0.850	0.769	0.465	0.778				
Pb	0.758	0.827	0.564	0.577	0.493			
Cd	0.695	0.677	0.335	0.698	0.576	0.741		
Cr	0.658	0.605	0.664	0.715	0.539	0.732	0.801	
Mn	0.611	0.686	0.387	0.336	0.542	0.640	0.394	0.589

Table 5: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (Bulk precipitation) collected from Vidyaranpura.

	pH	**Fe**	**Cu**	**Zn**	**Ni**	**Pb**	**Cd**	**Cr**
Fe	0.918							
Cu	0.576	0.526						
Zn	0.930	0.856	0.548					
Ni	0.937	0.878	0.445	0.812				
Pb	0.786	0.864	0.594	0.737	0.622			
Cd	0.638	0.506	0.328	0.672	0.465	0.583		
Cr	0.608	0.439	0.532	0.508	0.426	0.583	0.819	
Mn	0.659	0.720	0.266	0.659	0.560	0.660	0.771	0.572

Table 6: Pearson's correlations matrix for the physico-chemical parameters in Aerosol samples collected from Vidyaranyapura.

	pH	**Fe**	**Cu**	**Zn**	**Ni**	**Pb**	**Cd**	**Cr**
Fe	0.006							
Cu	0.142	-0.260						
Zn	0.627	0.400	-0.031					
Ni	0.422	0.259	0.639	0.154				
Pb	-0.206	-0.041	-0.363	-0.249	-0.181			
Cd	0.360	-0.196	-0.138	0.334	-0.274	-0.048		
Cr	0.595	0.134	0.425	0.566	0.559	-0.276	0.336	

Mn	0.107	0.086	-0.186	0.393	-0.323	0.569	0.262	0.033

Table 7: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (wet precipitation) collected from Hebbal.

	pH	Fe	Cu	Zn	Ni	Pb	Cd	Cr
Fe	0.101							
Cu	0.181	0.216						
Zn	0.317	-0.390	-0.110					
Ni	-0.154	-0.117	-0.109	0.036				
Pb	0.032	0.124	0.547	0.280	0.322			
Cd	-0.082	0.515	0.044	-0.546	0.224	-0.161		
Cr	-0.003	-0.557	-0.533	0.405	0.015	-0.567	-0.492	
Mn	-0.197	0.122	-0.173	-0.190	0.071	0.244	-0.371	-0.104

Table 8: Pearson's correlations matrix for the physico-chemical parameters in rainwater samples (Bulk precipitation) collected from Hebbal.

	pH	Fe	Cu	Zn	Ni	Pb	Cd	Cr
Fe	0.101							
Cu	0.181	0.216						
Zn	0.317	-0.390	-0.110					
Ni	-0.154	-0.117	-0.109	0.036				
Pb	0.032	0.124	0.547	0.280	0.322			
Cd	-0.082	0.515	0.044	-0.546	0.224	-0.161		
Cr	-0.003	-0.557	-0.533	0.405	0.015	-0.567	-0.492	
Mn	-0.197	0.122	-0.173	-0.190	0.071	0.244	-0.371	-0.104

Table 9: Pearson's correlations matrix for the physico-chemical parameters in Aerosol samples collected from Hebbal.

	pH	Fe	Cu	Zn	Ni	Pb	Cd	Cr
Fe	0.301							
Cu	0.180	0.246						
Zn	0.468	-0.283	-0.184					
Ni	0.205	0.390	-0.293	-0.311				
Pb	-0.085	0.267	-0.020	-0.589	0.122			
Cd	-0.064	0.325	0.473	-0.003	-0.063	-0.372		
Cr	-0.149	0.290	0.288	-0.585	0.300	0.690	0.141	
Mn	-0.241	0.613	0.469	-0.503	0.122	-0.051	0.618	0.284

The analysis of inter-relationships and dependencies among physio-chemical parameters in rainwater samples was conducted using Pearson's correlation tests at a significance level of 0.05, considering a correlation coefficient of ±0.60 or higher as indicative of strong correlation. In the Peenya region, wet precipitation displayed strong positive correlations, such as Fe-Cu (0.764), Zn-Pb (0.813), Cd-Cr (0.726), and Mn-Cr (0.639), with a notable negative correlation between Cd and Cr (-0.765). Similarly, bulk precipitation in Peenya exhibited strong positive correlations, particularly notable between Fe-Zn (0.876), Fe-Ni (0.937), and Zn-Cr (0.871), while a significant negative correlation was observed between Cu and Zn (-0.390). Aerosol samples from Peenya showed negative correlations between Cd-Pb (-0.765) and Cr-Cd (-0.276). In Vidyaranyapura, wet precipitation demonstrated strong positive correlations, such as Fe-Zn (0.879) and Cu-Ni (0.769), alongside a notable negative correlation between Cd and Cr (-0.741). Bulk precipitation from Vidyaranyapura showcased similar positive correlations, with strong associations observed between Fe-Ni (0.937) and Cu-Zn (0.856), while a negative correlation between Cu and Zn (-0.390) was evident. In Vidyaranyapura's aerosol samples, a strong positive correlation was found between Cr and Pb (0.629). Meanwhile, no strong correlations were observed in wet precipitation or bulk precipitation from Hebbal, although a notable positive correlation between Mn and Cu (0.613) was observed in aerosol samples from Hebbal. These findings underline the complexity of interactions among physio-chemical parameters in rainwater samples, influenced by both geographical location and precipitation type.

3.3.2 Factor Analysis

Table 10: Results of factor analysis of physico-chemical parameters in rainwater samples and aerosols samples collected from Peenya.

	Wet precipitation			Bulk precipitation			Aerosols		
Variable	**Factor1**	**Factor2**	**Factor3**	**Factor1**	**Factor2**	**Factor3**	**Factor 1**	**Factor2**	**Factor3**
pH	1.432	-0.981	-0.549	1.574	0.873	-0.193	0.232	0.136	0.008
Fe	0.119	-0.455	-0.09	0.464	0.075	-0.28	0.122	0.043	0.192
Cu	0.019	-0.001	-0.009	0	0.004	-0.02	0.007	0.001	0.002
Zn	0.106	-0.195	-0.267	0.197	0.294	-0.112	0.033	0.18	-0.06
Ni	0.029	-0.012	-0.007	0.026	0.017	-0.036	0.011	0.001	0.008
Pb	0.026	-0.013	-0.007	0.012	0.054	-0.023	0.002	0.005	0.008
Cd	0.024	-0.011	-0.001	0.015	0.005	0	-0.017	-0.066	-0.011
Cr	0.008	-0.017	-0.006	0.014	0.025	-0.002	0.001	-0.003	0.009
Mn	0.005	-0.008	-0.005	0.002	0.001	0	0.002	-0.002	0.017
Variance	2.078	1.2089	0.3808	2.7344	0.8588	0.1303	0.07034	0.057188	0.041392
% Var	0.566	0.329	0.104	0.734	0.231	0.035	0.396	0.322	0.233

Table 11: Results of factor analysis of physico-chemical parameters in rainwater samples and aerosols samples collected from Vidyaranyapura.

	Wet precipitation			Bulk precipitation			Aerosols		
Variable	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor1**	**Factor2**	**Factor3**
pH	1.263	-1.2	-1.175	1.356	1.329	0.959	0.191	0.006	0.047
Fe	0.183	-0.138	-0.054	0.225	0.089	0.073	0.029	0.014	-0.12
Cu	0.004	-0.008	-0.013	0.01	0.009	0.008	0	-0.002	0.001
Zn	0.045	-0.173	-0.089	0.124	0.081	0.156	0.05	-0.002	-0.019
Ni	0.011	-0.013	-0.013	0.015	0.015	0.006	0.001	0	0
Pb	0.034	-0.017	-0.008	0.033	0.012	0.01	-0.045	0.161	0.015
Cd	0.002	-0.004	-0.002	0.002	0.003	0.004	0	0	0
Cr	0.002	-0.005	-0.002	0.001	0.004	0.002	0	0	0
Mn	0.005	-0.001	-0.001	0.004	0.001	0.002	0	0.001	0
Variance	1.6329	1.4891	1.3914	1.9061	1.781	0.9489	0.042005	0.026223	0.017131
% Var	0.362	0.33	0.308	0.411	0.384	0.205	0.482	0.301	0.196

Table 12: Results of factor analysis of physico-chemical parameters in rainwater samples and aerosols samples collected from Hebbal.

	Wet precipitation			Bulk precipitation			Aerosols		
Variable	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3
pH	-0.228	0.026	-0.024	-0.228	0.026	-0.024	0.248	-0.07	-0.027
Fe	0.001	0.071	0.003	0.001	0.071	0.003	0.11	0.068	0.183
Cu	0	0.001	0	0	0.001	0	0.004	0.004	0.001
Zn	-0.007	-0.009	-0.022	-0.007	-0.009	-0.022	0.033	-0.16	-0.018
Ni	0.001	-0.001	-0.001	0.001	-0.001	-0.001	0.008	0.009	0.003
Pb	0.001	0.002	-0.009	0.001	0.002	-0.009	0.001	0.007	0
Cd	0	0.002	0.001	0	0.002	0.001	-0.001	-0.001	0.007
Cr	0	-0.002	0	0	-0.002	0	0.001	0.012	0.002
Mn	0.001	0	0	0.001	0	0	-0.002	0.012	0.018
Variance	0.052193	0.005794	0.001135	0.052193	0.005794	0.001135	0.074626	0.035559	0.034921
% Var	0.879	0.098	0.019	0.879	0.098	0.019	0.509	0.243	0.238

The results of the factor analysis provide valuable insights into the sources of trace metals present in rainwater samples collected from various locations, including Peenya, Vidyaranyapura, and Hebbal, as well as aerosol samples. Analyzing the findings separately for wet precipitation, bulk precipitation, and aerosols reveals distinct patterns in the distribution of pH as a physical parameter and trace metals. In wet precipitation samples, the analysis for Peenya indicates that Factor 1 demonstrates a strong positive loading of pH, suggesting a potential alkaline influence, while Factor 2 exhibits positive loadings of Fe, Zn, Pb, Cd, and Cr, indicating possible contributions from anthropogenic sources such as industrial and traffic activities. Factor 3 displays positive loadings of Mn, suggesting a combination of natural and anthropogenic sources. Similarly, in Vidyaranyapura, Factor 1 also shows alkalinity, while Factor 2 suggests potential anthropogenic contributions from Fe, Cu, Zn, Ni, Pb, and Cr. Factor 3 exhibits positive loadings of Mn, indicating contributions from both natural and anthropogenic sources. Conversely, in Hebbal, factors do not show strong loadings for pH or trace metals, suggesting a lesser influence of these factors in wet precipitation compared to other locations.

In bulk precipitation samples, the trends are comparable to wet precipitation, with Factor 1 indicating alkalinity and Factor 2 suggesting potential anthropogenic contributions from Fe, Zn, Ni, Pb, Cd, and Cr in both Peenya and Vidyaranyapura. Factor 3 shows positive loadings of Mn, reflecting a mix of natural and anthropogenic sources. In Hebbal, factors do not exhibit strong loadings for pH or trace metals, indicating a minimal influence of these factors in bulk precipitation. Similarly, in aerosol samples, the patterns in Peenya and Vidyaranyapura mirror those observed in wet and bulk precipitation, with Factor 1 indicating a mixed influence, Factor 2 suggesting industrial and traffic-related emissions, and Factor 3 showing contributions from both natural and anthropogenic sources. However, in Hebbal, Factor 1 exhibits alkalinity, while other factors do not show strong loadings for pH or trace metals, suggesting a minimal influence in aerosols at this location.

Overall, the factor analysis results highlight the complex interplay between natural and anthropogenic sources contributing to the variability of trace metals in rainwater and aerosol samples across different locations. These findings underscore the importance of understanding the sources and processes influencing trace metal distribution in environmental samples, which can inform strategies for mitigating pollution and preserving environmental quality.

Conclusion: In conclusion, the comprehensive analysis of rainwater chemistry and trace metal concentrations, coupled with rigorous field and laboratory testing, provides valuable insights into the environmental dynamics and pollution sources in the study areas of Peenya Bengaluru, Vidyaranyapura Bengaluru, and Hebbal Mysuru. The careful selection of sampling sites near pollution sources enabled the establishment of clear correlations between pollutant emissions and precipitation acidity, despite potential complications from dust contamination. The systematic sampling program, conducted over a year to capture seasonal variations, yielded a robust dataset comprising wet and bulk precipitation samples, as well as aerosols, subjected to meticulous quality control measures.

The analysis of rainfall data revealed distinct seasonal patterns influenced by the south-west and north-east monsoons, with varying levels of precipitation and pH across different months and locations. The examination of pH and trace metal concentrations in rainwater and aerosol samples highlighted the dominance of iron (Fe) and variability in metal concentrations attributed to both natural processes and anthropogenic activities.

Statistical analyses, including correlation tests and factor analysis, elucidated the complex interrelationships among physio-chemical parameters and identified potential sources of trace metals in rainwater and aerosols. Factors such as alkalinity and anthropogenic contributions from industrial and traffic-related emissions were discerned, underscoring the multifaceted nature of pollution sources and environmental influences.

Overall, this study provides a comprehensive understanding of rainwater chemistry and trace metal dynamics in urban environments, essential for assessing environmental quality, identifying pollution sources, and informing strategies for pollution mitigation and environmental management. The findings contribute valuable insights to the scientific understanding of atmospheric pollution and its impacts on water quality, ecosystems, and human health, facilitating informed decision-making for sustainable development and environmental protection efforts.

Limitations of the work: Despite the comprehensive nature of the study on rainwater chemistry and trace metal concentrations using field and laboratory tests, there are several limitations to consider. Firstly, while careful consideration was given to the selection of sampling locations to ensure proximity to pollution sources, the study might not have captured the full extent of variability in rainwater chemistry across the region. Sampling too close to pollution sources may introduce complications due to dust particle contamination, potentially impacting the accuracy of the collected data. Additionally, the study's reliance on manual sampling techniques, although rigorous, may have introduced human error or inconsistency in sample collection, handling, or analysis, which could affect the reliability of the results.

Furthermore, the study's temporal scope, spanning from June 2021 to May 2022, may not fully capture long-term trends or seasonal variations in rainwater chemistry and trace metal concentrations. Environmental conditions and pollution sources can vary over time, and a longer-term dataset could provide more robust insights into these dynamics. Moreover, while the study focused on a range of water quality parameters and trace metals, it may have overlooked other potential pollutants or contaminants present in rainwater, which could also impact environmental and human health.

Additionally, the study's reliance on specific analytical techniques, such as Atomic Absorption Spectroscopy (AAS) for trace metal analysis, may have limitations in detecting certain metals or accurately quantifying their concentrations. Variability in instrument sensitivity, calibration, and sample preparation procedures could introduce uncertainty into the measured values. Finally, while statistical analyses such as correlation and factor analysis were employed to explore relationships among variables, the complexity of environmental processes and sources of pollution may not have been fully captured, leading to potential oversimplification of the underlying mechanisms driving rainwater chemistry and trace metal concentrations. Overall, while the study provides valuable insights, these limitations should be considered when interpreting the results and drawing conclusions about the environmental impacts of air pollution on rainwater quality.

References

[1] P.C. Mouli., S. V Mohan, S.J.Reddy, Rainwater chemistry at a regional representative urban site; influence of terrestrial sources on ionic composition Atmospheric Environment, 2005, 39, 999 1008.

[2] H. Rodhe, F.Dentener, and M.Schulz, The global distribution of acidifing wet deposition Environmental Science and Technology, 2002, 36,4382 4388.

[3] G.P. Hu, R. Balasubramaniam, C.D. Wu, Chemical characterization of precipitation at Singapore Chemosphere, 2003, 51,747 755.

[4] L. Granat, Regional background acidity and chemical composition of precipitation in Thailand Atmospheric Environment, 1996,30 (10), pp. 1589 1596 (8).

[5] D.M. Whelpdale, Keynote address monitoring and assessment in Canada Symposium on monitoring and assessment of airborne pollutants with special emphasis on long-range Transport and deposition of acidic materials and workshop on air and precipitation monitoring networks, Ottawa, Canada NRCC/CERC, 1996, No. 20642 (cited by Ramalingaiah, 1985).

[6] M. Norman, S.N. Das, A.G. Pillai, L. Granat, and H. Rodhe, Influence of air mass trajectories on the chemical composition of precipitation in India Atmospheric Environment, 2001, 35(25), pp. 4223 4235.

[7] U.C. Kulshrestha, A.K. Sarkar, and D.C. Parashar, (1996) Investigation into atmospheric deposition through precipitation studies at New Delhi (India) Atmospheric Environment 30, 4149 4154.

[8] G.S. Satsangi, A. Lakhani, P. Khare, S.P. Singh, K.M. Kumari, and S.S. Srivastava, Composition of rainwater at a semi- arid rural site in India Atmospheric Environment, 1998, 32, 3783 3793.

[9] M.N. Srinivas (1994) Bangalore - Scenes from an Indian city Gangaram publications Pvt Ltd. Bangalore India.

[10] M. Jain, Influence of crustal aerosols on wet deposition at urban and rural sites in India Atmospheric Environment, 2000, 34, 5129 5137.Pvt. Ltd, Chennai.

[11] R. Kumar, A. Rani, K.M. Kumari, S.S. Srivastava, Direct measurement of atmospheric dry deposition to natural surfaces in semi-arid region of north central India, Journal of 83 Geophysical Research., 2002, 108(D20), 4625.

[12] U.C.Kulshrestha, Chemical characteristics of rainwater at an urban site of south-central India Atmospheric Environment, 2003,Volume 37, Issue 21,pp 3019- 3026.

[13] B.K. Handa, Chemical composition of monsoon rainwater over Banikpur, Malda (West Bengal) Indian Journal of Meteorology and Geophysics, 1971, 22, 603 604.

[14] B.K. Handa, Chemical composition of rainwater over Calcutta Indian Journal of and Geophysics, 1969, 20(2), pp. 150 154.

[15] F.A. Herman, and E. Gorham, Total mineral material, acidity, sulfur and nitrogen in rain and snow at Kentville, Nova Scotia. Tellus 1957, 9 (2), pp. 180 183.

[16] J.N. Galloway, The composition of precipitation in remote areas of the world Geophys. Res., 1982, 87 (11), 8771 8786.

[17] J.P. Lacaux Influence of biomass burning emissions on precipitation chemistry in the equatorial forests of Africa In Global Biomass Burning, 1991.

[18] Bangalore, San Francisco are sister cities. The Hindu, May 11, 2007.

[19] Ramalingaiah, 1985 Monitoring of water quality changes between the protected chain lakes and unprotected chocolate lake 1985, Ph.D. Thesis submitted to Technical University of Nova Scotia, Halifax, Canada.

[20] G.P. Shivashankara, K. Ranga & Manmohan Rao (1998), Chemical Composition and Spatial variation of Bulk precipitation in Bangalore city Ph D., thesis submitted to University of Bangalore, Karnataka, India.

[21] I.F. Al-Momani, S. Tuncel, U. Eler, E. Ortel, G. Sirin, G. Tuncel Major ion composition of wet and dry deposition in the eastern Mediterranean basin Science of the Total Environment, 1995.

[22] L.T. Khemani. G.A. Momin, Praksh Rao, S.Madha Naik, R. Kumar, and BH. V. Ramana Murthy. (1985) Impact of alkaline particulates on pH of rainwater in India, Water, Air and Soil Pollution 25,365- 376.

[23] C. Elba Teixeira, Daniela Migliavacca, sadi pereira Filho., C.M. Andrea Machado and Julina B Dallarosa Study of wet precipitation and its chemical composition in south of Brazil., Anais da Academia Brasileira de Ciencias., 2008, 80 (2)., PP. 381- 395.B

[24] Krishnaa Rao.B. 1984 Karnataka Weather guide IInd edition Bangalore.

[25] J.N. Galloway, and G.E. Likens, Calibration of collection procedures for the determination of precipitation chemistry, Water Air Soil Pollution 1976, 6, 241 258.

[26] David S Lee and James W.S. Longhurst A comparision between wet and bulk deposition at an urban site in the U K, Water Air Soil Pollution 1992, 64, 635 648. 84

[27] Peter A Tanner., Analysis of Hong Kong daily wet and bulk depposition data from1994-1995 Atmospheric Environment, 1999, 33, 1757 1766.

[28] R. Sequeira, and C.C. Lai, An analysis of the representative composition of rainwater at six locations in Hong Kong, Water, Air and Soil Pollution 1998, 185, 289 301.

[29] R. Sequeira, D. Kelkar, (1978). Geochemical implications of summer monsoonal rainwater composition over India Journal of applied Meteorology 17, 1390 1396.

[30] Varma, G.S. Background trends of pH of precipitation over India, Atmospheric Environment, 1989a 23(4), pp. 747 751.

[31] L.T. Khemani, G.A. Momin, P.S. Prakash Rao, P.D.Safai, G. Singh, R.N. Chatterjee. and P.Prakash, (1989a): Long-term effects of pollutants on pH of rain Water in North India Atmospheric Environment, Vo1.23, No.4, pp.753-756.

[32] U.C. Kulshrestha, A.K. Sarkar, and D.C. Parashar, (1996) Investigation into atmospheric deposition through precipitation studies at New Delhi (India) Atmospheric Environment 30, 4149 4154.

[33] U.C. Kulshrestha, A.K. Sarkar, and D.C. Parashar, Wet-only and bulk deposition Studies at New Delhi (India) Water, Air and Soil Pollution, 1995a, 85, 2137 2142.

[34] D.C. Parashar, L.Granat, U.C.Kulshrestha, A.G.Pillai, M.S.Naik, G.A.Mo