Tellus SERIES B CHEMICAL AND PHYSICAL METEOROLOGY
PUBLISHED BY THE INTERNATIONAL METEOROLOGICAL INSTITUTE IN STOCKHOLM

Tellus (2010), 62B, 172–180
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Neutralization of rainwater acidity at Kanpur, India

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(Manuscript received 12 May 2010; in final form 4 March 2010)

ABSTRACT

Particulate matter (PM) levels show significant seasonal variability and this can influence the neutralization of rainwater acidity. Months were grouped in two periods: monsoon (July to October) and non-monsoon (November to June) for studying the seasonal variability in PM and rainwater composition. To clearly establish the cause effect relationship of acid rain neutralization, a two tier model was proposed involving source apportionment of particulates at two levels: (i) ambient air and (ii) rainwater particulate interaction. For modelling purpose, PM_{10} ($n = 100$), soil ($n = 4$) and rainwater ($n = 83$) samples were collected at Kanpur, India during 2000–2002. The collected samples were analysed for metals and water soluble ion composition to employ factor analysis for source identification. Knowledge of statistical correlation and chemistry fundamentals were combined to estimate the sources for acid rain neutralization. NH_4^+ was a dominating ion responsible for neutralizing the acidity of rainwater in monsoon period and Ca^{2+} was dominating in non-monsoon period. Components of secondary particles (SO_4^{2-} and NO_3^-) showed affinity with NH_4^+, signifying the major role that ammonia can play if present in excess of stoichiometric requirements.

1. Introduction

Historically, scientists (e.g. Hegg and Hobbs, 1982; Richards et al., 1983) have shown influence of acidic gases (e.g. SO_2 and NO_x) and acidic aerosols on pH of cloud and rainwater. However, the problems of acid rain have not yet been widely faced in India. In the context of Indian subcontinent, it is important to understand interaction of SO_2/NO_x with other atmospheric constituents to determine the extent of acid neutralization. The complexity in understanding the acid-particle interaction (a neutralization mechanism) arises because of the monsoon type climate, where 80% of annual rain is received in about 3 months and high levels of particulate matter (PM) concentration (Shukla and Sharma, 2008).

Over the last few decades, rainwater in India has been reported to be alkaline. Acid rain neutralization by soil-derived Ca^{2+} and Mg^{2+} present in PM has been reported by several researchers (Khemani et al., 1987; Das et al., 1994; Saxena et al., 1996; Satsangi et al., 1998; Kulshrestha et al., 2005). In general, the above references indicate that pH of rainwater was quite high at locations where concentration of basic soil derived PM, rich in Ca^{2+} and Mg^{2+}, was also high. In a recent research, Das et al. (2005) reported that Ca^{2+} and NH_3 are the primary neutralizing agents of rainwater acidity in Bhubaneswar, India. Rodhe et al. (2002) through global atmospheric distribution models showed that acid-base status of precipitation is a result of a balance between acidifying and alkaline compounds including NH_3. In summary, the gases like SO_2 and NO_X translate into acids, which are neutralized by cationic constituents present in the airborne particles.

To observe the variability in PM concentrations, data of past 5 yr from the study area, Kanpur (longitude 80°14′E and latitude 26°30′N) were analysed. It was established that in monsoon period (July to October) and non-monsoon period (November to June), PM concentrations and meteorology (temperature, wind speed, mixing height, etc.) were different in a statistical sense (at 5% level of significance). Therefore, two partitions of the year (i) monsoon (July to October) and (ii) non-monsoon (November to June) were considered for the purpose of analysing the variation in characteristics of rainwater and PM_{10} (particles of size less than 10 μm). In this paper, an attempt has been made to apportion the sources of PM_{10}, which are responsible for acid rain neutralization. The role of particles is critical in neutralizing the acidic nature of rainwater; however, the particulate concentration has shown significant seasonal variability in North India (Shukla and Sharma, 2008). It can be argued that to understand the issue of acid rain and rainwater chemistry including acid neutralization, it is of great significance that seasonal variability of particulate concentration, their characterization, their sources and seasonal rain events must be studied together.

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DOI: 10.1111/j.1600-0889.2010.00454.x

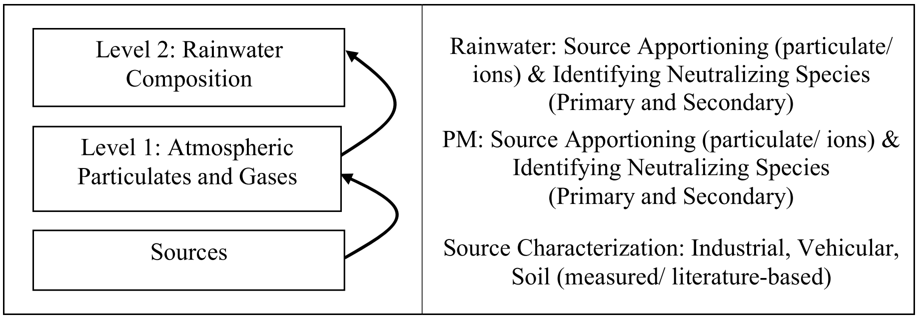


Fig. 1. Two level modelling approach.

The objective of present study is to understand the seasonal variability in terms of characteristics and concentrations of: (i) PM and (ii) rainwater. The gained knowledge can help in identifying the sources of PM responsible for neutralizing acid in rainwater. For this purpose, a study was designed and carried out during June 2000 to February 2002 in Kanpur.

1.1. *Apportionment of PM and rainwater neutralization factors*

Although there have been several studies for PM source apportionment in air (e.g. Saxena et al., 1996), the application of receptor modelling for PM interacting with rainwater is not straightforward. It may be noted that PM in atmosphere, may bear signatures of their sources, but these signatures may be lost when the PM interact physically or chemically with rainwater (due to non-linearity in system of particulate-water interaction). For example, some components of PM may selectively get removed or get enriched while interacting with rainwater. To describe this interaction and to identify the sources of PM for acid rain neutralization, a two level modelling approach has been adopted (Fig. 1).

To be able to implement the above scheme, the overall study comprised: (i) selection of sampling site and parameters, (ii) laboratory analysis of the samples and (iii) interpretation of results. The choice of sampling site was aimed to select a relatively clean site in the city of Kanpur.

Details of PM sampling, gaseous concentration, meteorological parameters, and PM source apportionment have been described in Shukla and Sharma (2008). Here, we are describing sampling and characteristics of soil and rainwater.

2. Study design and materials and methods

2.1. *Study area*

The study area of Kanpur is centrally located in the Ganga basin and is a representative site of atmospheric environment in terms of the weather conditions and atmospheric seasonal variability prevailing in the basin.

IIT Kanpur (IITK), an educational institute with no commercial or industrial activities in its campus was taken as the sampling site (Fig. 2). The campus lies at about 15 km north of city downtown area. Within the campus, vehicular population mainly comprises motorcycles and cars. During peak hours (9.00 a.m. to 10.00 a.m.), the traffic count was: 141 motorcycles, 02 three-wheelers, 37 cars, 05 buses/trucks and 03 tractors. For most part of the year, campus lies on the upwind of Kanpur City. In the upwind of sampling site, there are villages having extensive agricultural activities.

2.2. *Sampling and quality control*

A total number of 100 PM$_{10}$ samples were collected and analysed. PM$_{10}$ measurements were carried at a height of about 10 m. The frequency of sampling was two 24-h (6 a.m.–6 a.m.) samples in a week. All weightings of filter papers were done with Mettler Balance (Model 440 with sensitivity 0.00001*g*) in humidity-controlled room and filters were conditioned in desiccators for 24 h before and after the sampling. High volume sampler (APM 450 Envirotech, New Delhi) was used for sampling PM$_{10}$ on Whatman GF/A $8'' \times 10''$ size filter paper at a flow rate of 1 m^3 min^{-1}. Rainwater samples were collected starting from June 2000 to February 2002 (Table 1).

Efforts were made to collect samples from all rain events. Manual collectors were used for collecting the rainwater samples. Samples were collected at height of 1.5 m above the roof of environmental engineering laboratory of IITK (at a height of about 10 m above the ground) on an event basis. Polyethylene bottles and funnels, previously rinsed with wash water (milli-Q) (pH: 6.9–7.1, EC < 0.055 μS cm^{-1}) were used for rainwater collection as described by Khemani *et al.* (1989). The pH of the blank water after washing the funnel and bottle was in the range of 7.0 to 7.1 and EC was <0.055 μS cm^{-1}. The collectors were deployed as soon as rain began and retrieved immediately after the rain stopped. The efficiency of collection (percentage of rainwater samples collected to number of rainfall events occurred during the study period) was 96.5%. The covers of samplers were removed as soon as the rain began and were replaced immediately after the rain stopped. The collected rainwater was

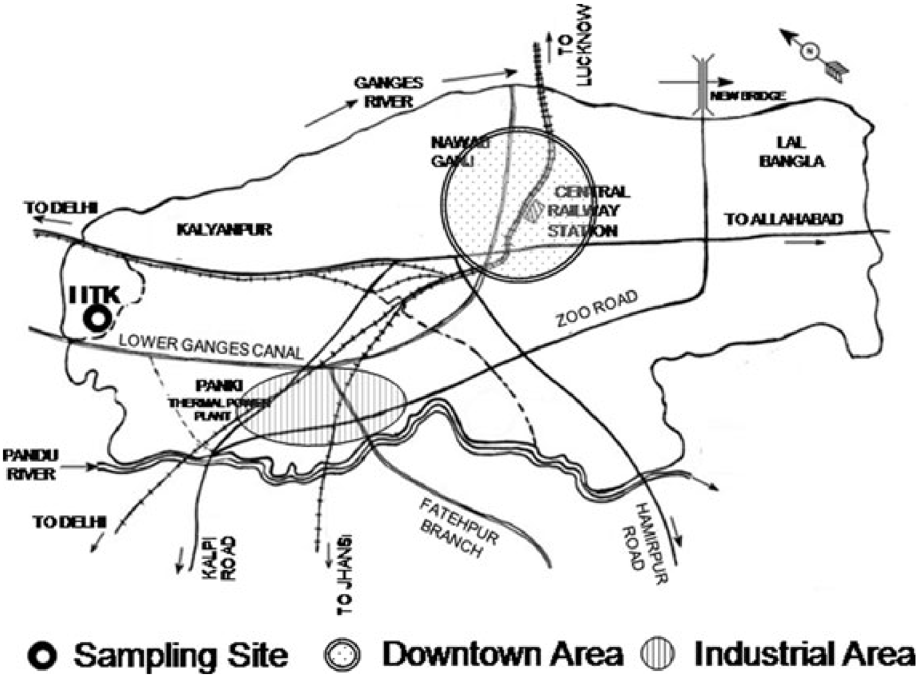


Fig. 2. Map of Kanpur showing the location of the sampling site.

Table 1. Details of rainwater samples

Sampling periods	Sampling months	Parameters measured	Number of samples
Monsoon	July–October, 2000 July–October, 2001	pH, conductivity, alkalinity, Al, Fe, Mn, Pb, Na^+, $NH_4{}^+$, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, $NO_3{}^-$ & $SO_4{}^{2-}$.	56
Non-monsoon	June, 2000 November, 2000–June, 2001 November, 2001–February, 2002		27

transferred into sample containers, which were pre-washed with detergents, acids, and Milli-Q water. pH and EC of the rainwater samples were determined immediately after the collection. The samples were then filtered into two clean polyethylene bottles. One part was stored under refrigeration and used for ion analyses and the other part was acidified with HNO_3 and used for metal analyses. Ion balance in rainwater samples was performed and is discussed later.

Soil samples, uncontaminated from any local source, were collected from the open grounds of IITK campus. The top surface was cleaned to remove garbage from the top of soil. Then the soil up to 1cm depth was collected in plastic bags from three marked points on the ground and a composite sample was prepared. Total four soil samples were collected during the study period. Soil samples were immediately crushed in mortar and pestle and sieved through 25 μ sieve. Thereafter moisture content, pH and EC of soil samples were determined. Remaining portion of soil samples was sealed in plastic bags and stored in freezer until further chemical analysis for metals (Al, Ba, Fe, Mn and Pb) and ions (Na^+, $NH_4{}^+$, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, $NO_3{}^-$ and $SO_4{}^{2-}$) was undertaken.

Standard operating procedures (SOPs) of the laboratory practices, previously reviewed and approved have been followed for weighing, sampling and analysis (e.g. SOP for PM sampling: IITK-AHM Lab-102, version 2). High purity analytical grade reagents (Merck) and milli-Q water were used for preparation of standard solutions for analysis.

2.3. *Estimation of heavy metals*

2.3.1. *PM_{10}*. The extraction and analysis of metals in PM_{10} samples was carried out as per the USEPA Method IO-3.2 (USEPA, 1999). Al, As, Ba, Ca, Fe, K, Mg, Mn and Pb were analysed in acid digested samples.

2.3.2. *Rainwater*. The filtered rainwater samples were analysed for metals using a graphite furnace of atomic absorption spectrophotometer (AAS) (Model GBC Avanta Σ, Australia).

2.3.3. Soil. Soil samples were digested as per the procedure of USEPA Method 3050B (USEPA, 1996) for analysis of metals (Al, Ba, Fe, Mn, Pb and Se) on AAS.

2.4. Estimation of ions

2.4.1. PM$_{10}$. Half portion of PM$_{10}$ filter papers were analysed for water soluble ions (Shukla and Sharma, 2008).

2.4.2. Rainwater. Filtered rainwater samples were analysed for water soluble ions. The samples were filtered through 0.22 μm Whatman membrane filter paper to remove insoluble matter. The water soluble cations Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} and anions F^-, Cl^-, NO_3^- and SO_4^{2-} were analysed by ion chromatograph (IC) (model: Metrohm 761 compact).

2.4.3. Soil. 0.5 g dry sieved soil was shaken with 100 ml of Milli-Q water for 2 h. The suspension so obtained was filtered through 0.22 μm filter paper to remove insoluble matter (Satsangi et al., 1998). Water soluble cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) were analysed by IC.

2.5. Factor analysis

Factor Analysis Multiple-Regression (FA-MR) is a receptor modelling technique employed to apportion the contributing sources to ambient pollution. One such technique of factor analysis is the principal component analysis (PCA). The objective of applying PCA is to derive a small number of components, which explain a maximum of the variance in the data. Initially, the PCA results in as many PCs as there are original variables. Usually, however, only a limited number of these uncorrelated PCs are required to explain virtually all of the variance in a data set of fifteen or more original (intercorrelated) variables. For this reduction in the dimensionality to be useful, the newly obtained components (or factors) must have simple substantive interpretations (Thurston and Spengler, 1985). To be able to interpret the component in terms of physical meaning, loadings of variables on the component are estimated. Loading represents the degree and direction of relationship of the variables with a factor. An examination of the PC loadings on the original variables allowed the identification of the PCs as pollution sources affecting the data. Varimax rotated PCA was employed to apportion sources using a statistical package, SYSTAT (2004).

Back trajectory analysis using NOAA HYSPLIT MODEL using FNL meteorological data (http://ready.arl.noaa.gov/HYSPLIT.php) was also carried for the days of rainfall events. This analysis traced the wind trajectory indicating that most of the rains in Kanpur came from north and northwest in non-monsoon period and from east and southeast in monsoon period. An attempt is made to link the impact of sources to rain water constituents. There are large emission sources in north and northwest (large city like New Delhi, Agra and 4000 MW of coal-based power plants) and in east and southeast, there are power plants of capacity more than 15 000 MW. Estimated SO_2 emissions (from 80 km wide corridor) were 0.42 Tg yr^{-1} from north and northwest and 0.51 Tg yr^{-1} from east and southeast (Bhatt, 2009). PM$_{10}$ and pollution levels in rain continue to be high regardless of direction of wind trajectory. Further source apportionment could not be done due to unavailability of source specific tracer species.

3. Result and discussion

3.1. PM$_{10}$

PM$_{10}$ concentrations were lowest in monsoon period and highest (with higher variability) in non-monsoon period due to high-speed winds prevalent in non-monsoon period. Table 2 presents mean ambient air (24-h) concentration of various species of PM$_{10}$. Local soil and road dust (15–47%) and secondary particles like $(NH_4)_2SO_4$ and NH_4NO_3 (21–26%) were the key sources contributing towards PM$_{10}$ in monsoon and non-monsoon periods.

3.2. Soil

Table 3 presents the average concentration of various species in soil. pH of soil was in the range 7.6–8.3 indicating its alkaline nature. Concentration of Al, Ca^{2+}, Fe, Na^+, Mg^{2+} was higher than the concentration of NH_4^+, SO_4^{2-} and NO_3^-. The soil analysis signifies two points: (i) presence of Ca^{2+}, Mg^{2+}, Al can be taken as markers for soil contribution to PM and (ii) contribution of NH_4^+, SO_4^{2-} and NO_3^- in the atmosphere from soil is not expected to be significant (Shukla and Sharma, 2008).

3.3. Rainwater

The number of sampled rainwater events was limited to 83 (56 in monsoon period and 27 in non-monsoon period). Table 4 presents rainwater characteristics along with *t*-test analysis. Purpose of this analysis was to determine if concentration of rainwater components differ in monsoon and non-monsoon period. Concentrations of soil-derived particles and components generated by anthropogenic activities were higher during the non-monsoon period. This could be because of large quantity of soil dust, which gets airborne due to high wind speeds and dry conditions prevalent in the non-monsoon period.

Figures 3a and b show the frequency distribution (in number as well as in percentage) of rainwater samples against pH during monsoon and non-monsoon periods, respectively. The pH of rainwater samples during monsoon and non-monsoon periods were observed to be different. During monsoon period, due to frequent rain events the airborne alkaline soil derived particles and acid aerosols are washed out resulting in lower pH range. During non-monsoon period, alkaline soil derived particles and

Table 2. Mean ambient air (24 h) concentration of various PM_{10} species

Species	Monsoon (μg m^{-3})	Non-Monsoon (μg m^{-3})	
	July-October ($n = 41$)	November-February ($n = 33$)	March-June ($n = 26$)
Al	5.89 ± 2.20	14.67 ± 5.08	22.15 ± 7.23
As	0.69 ± 0.59	0.37 ± 0.29	0.54 ± 0.44
Ba	4.02 ± 1.69	3.24 ± 1.26	9.10 ± 4.85
Ca	6.45 ± 2.25	14.15 ± 3.79	21.33 ± 8.65
Fe	1.16 ± 0.57	1.15 ± 0.45	2.08 ± 0.87
K	0.60 ± 0.38	1.08 ± 1.89	0.62 ± 0.18
Mg	3.60 ± 0.88	2.78 ± 0.91	5.19 ± 1.81
Mn	0.08 ± 0.03	0.09 ± 0.03	0.16 ± 0.05
Pb	0.22 ± 0.10	0.32 ± 0.13	0.22 ± 0.11
NH_4^+	0.87 ± 0.65	5.52 ± 1.90	1.76 ± 0.83
F^-	0.26 ± 0.17	0.30 ± 0.09	0.76 ± 0.32
Cl^-	1.12 ± 0.59	1.33 ± 0.49	2.06 ± 1.26
NO_3^-	4.50 ± 2.03	18.02 ± 5.91	7.52 ± 2.64
SO_4^{2-}	7.07 ± 2.18	10.10 ± 2.74	10.25 ± 2.54

Note: '*n*' denotes number of samples.

Table 3. Average concentration of various components in soil

Parameters	Values
pH	8.1 ± 0.2
EC	410 ± 140
Na^+	750 ± 130
NH_4^+	110 ± 40
K^+	310 ± 180
Ca^{2+}	3100 ± 500
Mg^{2+}	640 ± 120
F^-	8 ± 5
Cl^-	220 ± 220
NO_3^-	24 ± 7
SO_4^{2-}	190 ± 180
Al	15000 ± 2000
Ba	590 ± 60
Fe	1300 ± 100
Mn	290 ± 30
Pb	14 ± 2

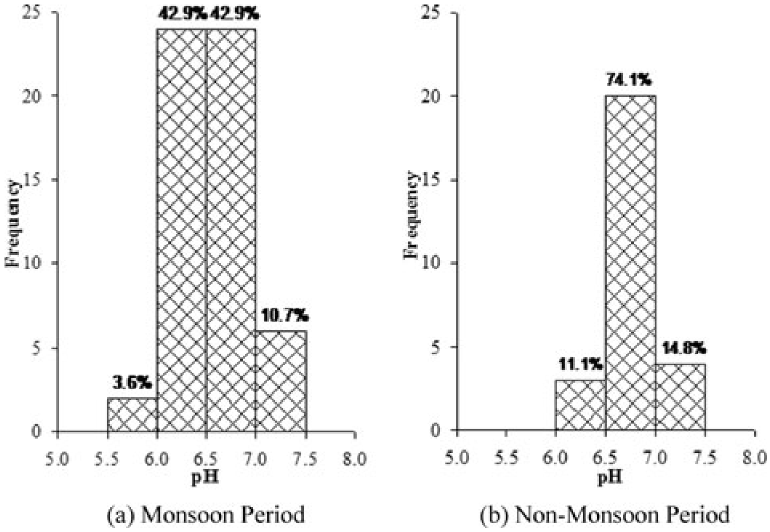
Note: All values are in μg g^{-1} except for pH and EC. Values of EC are in μS cm^{-1}.

acid aerosols are not removed due to few sporadic rain events resulting in higher pH range. The high pH range, possibly suggests role of soil-derived alkaline particles (e.g. Ca^{2+}, Mg^{2+}) and gases like NH_3.

pH was generally in alkaline range (5.8–7.1) (i.e. more than 5.6, pH of CO_2 equilibrium in rainwater). In India, pH has been reported between 6.0 and 7.75 in rural (Satsangi et al., 1998; Norman et al., 2001) and urban areas (Khemani et al., 1989; Mouli et al., 2005; Kulshrestha et al., 2005).

Ion balance in rainwater was examined. The average cation excess of 51.45 μeq L^{-1} (30.3%) and 161.52 μeq L^{-1} (37.6%) during monsoon and non-monsoon periods was observed. This ionic imbalance is similar to several other studies at Agra (Satsangi et al., 1998), Alibag, Colaba, Pune and Kalyan (Khemani et al., 1985), and Tirupati (Mouli et al., 2005), which reported average cation excess between 29 and 197 μeq L^{-1}. Cation and anion difference found in this study is somewhat higher than the acceptable USEPA range of ion difference in rainwater samples (15–30%) for samples having ion sum >100 μeq L^{-1} (Jain et al., 2000). Possible reasons for the poor ion balance may be due to the exclusion of some anions (organic ions, NO_2^-, PO_4^{2-} and Br^-). The concentration of HCO_3^- ions would be significant at high pH encountered in these rainwater samples, which was only estimated and not measured.

Figures 4a and b show the percentage contribution of various cations and anions in rainwater during monsoon and non-monsoon periods, respectively. The alkaline components (Ca^{2+}, Mg^{2+}, Na^+ and K^+) contribute 38%, NH_4^+ contributes 22% and the contribution from the acidic components is 41% (F^-, Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-) during monsoon period (Fig. 4a) to ionic composition of rainwater. During non-monsoon period, the alkaline components (Ca^{2+}, Mg^{2+}, Na^+ and K^+) contribute 58%, NH_4^+ contributes 4%, whereas the contribution from the acidic components is 38% (Fig. 4b). The concentration of major ionic species in μeq L^{-1} has the following order: $NH_4^+ > Ca^{2+} > SO_4^{2-} > HCO_3^- > NO_3^- > Mg^{2+} > Cl^- > Na^+ > K^+ > F^-$ during monsoon period and $Ca^{2+} > SO_4^{2-} > Mg^{2+} > Cl^- > Na^+ > HCO_3^- > NO_3^- > NH_4^+ > K^+ > F^-$ during non-monsoon period, respectively. The analysis of results establishes that abundance of cationic species varies from one period to another and so will be their role in acid neutralization.



(a) Monsoon Period

(b) Non-Monsoon Period

Fig. 3. Frequency distribution of pH of rainwater samples. Left-hand panel: monsoon period, right-hand panel; non-monsoon period.

Table 4. Average concentration of various species in rainwater

Components	Monsoon ($n = 56$)	Non-monsoon ($n = 27$)
pH	6.55 ± 0.30	6.78 ± 0.22[a]
HCO_3^-	1709 ± 1168	2593 ± 1111[a]
EC	30 ± 24	93 ± 64[a]
Alk	7821 ± 5260	13280 ± 11909[a]
Al	146 ± 117	105 ± 58[b]
Fe	35 ± 27	28 ± 14[c]
Mn	37 ± 18	102 ± 72[a]
Pb	13 ± 11	4 ± 3[b]
Na^+	448 ± 284	1285 ± 549[a]
NH_4^+	1056 ± 791	504 ± 173[b]
K^+	240 ± 156	1052 ± 771[a]
Ca^{2+}	1107 ± 770	4333 ± 1665[a]
Mg^{2+}	268 ± 213	1020 ± 476[a]
F^-	27 ± 21	159 ± 120[a]
Cl^-	729 ± 506	2172 ± 1082[a]
NO_3^-	1714 ± 1616	2607 ± 934[a]
SO_4^{2-}	1557 ± 1081	4576 ± 1832[a]

Note: All values are in $\mu g\ L^{-1}$ except for pH and EC. Values of EC are in $\mu S\ cm^{-1}$.

[a] Statistically higher.

[b] Statistically lower.

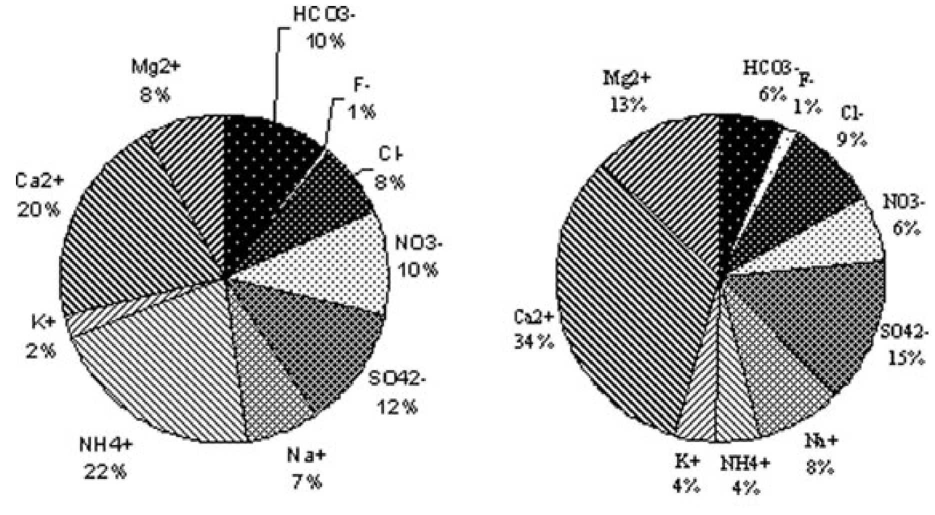
[c] Statistically no difference.

Chemistry of neutralization is similar during monsoon and non-monsoon periods as acidity and alkalinity causing ions are the same. The difference is in the quantity of acidity and alkalinity causing ions in these two periods. During non-monsoon period, dry conditions prevail resulting in suspension of dust and other particles during dust storms resulting in higher concentration of alkaline soil based cations.

3.3.1. Ionic correlation. Correlation between elements/ions of rainwater suggests the likely sources of pollutants and it indicates 'particulate-rainwater' and 'gas-rainwater' interactions. Correlation matrices of main components of rainwater are presented in Tables 5 and 6.

NO_3^- and SO_4^{2-} show good correlation ($r = 0.97$ and 0.94 during monsoon and non-monsoon periods, respectively) in rainwater samples indicating their origin from similar sources (mostly combustion and formation in atmosphere). It is possible that fraction of NO_3^- and SO_4^{2-} may be derived from soil as primary pollutant, or may be associated with Ca^{2+} and Mg^{2+} after the neutralization process; this hypothesis has been examined below. Ca^{2+} and Mg^{2+}, which are essential components of soil have good correlation with each other ($r = 0.97$ and 0.93 during monsoon and non-monsoon, respectively) implying common origin. As the ratios of SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} in rainwater (1.41 and 1.55, respectively, during monsoon and 1.05 and 0.60, respectively, during non-monsoon) is much higher than the ratios of SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} in soil (0.06 and 0.01, respectively), it suggests that atmosphere is enriched with SO_4^{2-} and NO_3^- formed in the atmosphere as secondary particles. Hence, it can be said that most of the SO_4^{2-} and NO_3^- in the atmosphere are from combustion or other anthropogenic sources as opposed to the contribution from soil.

As the ratio of NH_4^+/Ca^{2+} in rainwater (0.95 and 0.12 during monsoon and non-monsoon, respectively) is high compared to the ratio of NH_4^+/Ca^{2+} in soil (0.03), origin of NH_4^+ from the soil is ruled out and it can be concluded that NH_4^+ is being contributed by other sources. NH_3 is also released due to the agricultural activities carried out in the vicinity of the sampling site (Saylor et al., 1992). In the atmosphere, ammonia generally occurs as $(NH_4)_2SO_4$ and NH_4NO_3 suggesting association of NH_4^+ with SO_4^{2-} and NO_3^- after the neutralization process. This is supported by the fact that NH_4^+ has good correlation with NO_3^- ($r = 0.97$ and 0.93 during monsoon and non-monsoon, respectively) as well as with SO_4^{2-} ($r = 0.94$ and 0.88 during monsoon and non-monsoon, respectively).



(a) Monsoon Period (b) Non-Monsoon Period

Fig. 4. Percentage contribution of each ion in rainwater. Left-hand panel: monsoon period, right-hand panel: non-monsoon period.

Table 5. Correlation matrix of important parameters in rainwater during monsoon

	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
NO_3^-	1					
SO_4^{2-}	0.97	1				
NH_4^+	0.97	0.94	1			
K^+	0.73	0.72	0.69	1		
Ca^{2+}	0.74	0.74	0.74	0.77	1	
Mg^{2+}	0.77	0.77	0.78	0.78	0.97	1

Note: All correlation coefficients were statistically significant at 0.05 level of significance.

Table 6. Correlation matrix of important parameters in rainwater during non-monsoon

	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
NO_3^-	1					
SO_4^{2-}	0.94	1				
NH_4^+	0.93	0.88	1			
K^+	0.50	0.52	0.51	1		
Ca^{2+}	0.62	0.60	0.59	0.50	1	
Mg^{2+}	0.66	0.63	0.62	0.64	0.93	1

Note: All correlation coefficients were statistically significant at 0.05 level of significance.

It is interesting to note is that SO_4^{2-} and NO_3^- correlate much better with NH_4^+ than with Ca^{2+} and Mg^{2+}. The preliminary finding that NH_4^+ appears to play a vital role in acid rain neutralization needs further analysis through source apportionment studies.

3.4. *Quantification of sources contributing to acid rain neutralization*

The objective of this research was to quantitatively apportion the sources responsible for acid rain neutralization. One can think of FA-MR technique for rainwater constituents. The second approach may be to estimate neutralization factors (NF) (Parashar et al., 1996). We have tried both the approaches.

3.4.1. PCA/FA for rainwater constituents. Table 7 presents factor loadings of dissolved components for rainwater during monsoon period. Varimax rotated PCA (Principal Component Analysis) suggested three sources in monsoon period based on ions present in the rainwater.

During monsoon period, the first factor was strongly loaded with soil derived cations (Ca^{2+}, Mg^{2+}) and secondary particles produced in atmosphere (NH_4^+, NO_3^- and SO_4^{2-}). Second factor was strongly loaded with Pb and Al. The plausible reason for Al being loaded on Factor 2 is that Al did not take part in acid neutralization like Ca^{2+}, Mg^{2+}. Third factor was strongly loaded with Fe and weakly loaded with Mn. Based on justifications given in case of PM_{10} (Shukla and Sharma, 2008), factor 1 is heavily loaded with components of soil but unlike PM_{10}, the secondary particles have got lumped to this factor. Factor 2 can be attributed towards vehicular emission and road dust. Factor 3 can be attributed towards industrial and metal processing. Similar results were obtained for non-monsoon period (not shown here). During monsoon period, major portion of the percentage variance (56.40%) was explained by factors associated with soil origin and secondary particles. Although PCA has identified the factors to summarize the data, this appears of little use as PCA has essentially lumped two sources of PM_{10} (soil and secondary particles) into one and more specific information is lost. Probably the chemical reaction in the atmosphere between cations

Table 7. Varimax rotated PC matrix for rainwater during monsoon period

Species	Possible emission sources		
	Soil and secondary particles	Vehicular emission and road dust	Industrial and metal processing
Al	0.22	**0.78**	0.37
Fe	−0.06	0.08	**0.94**
Mn	0.57	−0.43	0.35
Pb	0.06	**0.89**	−0.09
Na^+	**0.92**	0.06	0.09
$NH_4{}^+$	**0.91**	0.07	−0.06
K^+	**0.84**	0.07	0.22
Ca^{2+}	**0.90**	0.14	0.09
Mg^{2+}	**0.92**	0.19	0.10
F^-	0.69	−0.03	−0.14
Cl^-	**0.88**	0.09	0.01
$NO_3{}^-$	**0.93**	0.02	−0.07
$SO_4{}^{2-}$	**0.90**	−0.01	0.01
Eigenvalue	7.33	1.62	1.25
%Variance	56.40	12.49	9.61
Cumulative% variance	56.40	68.89	78.50

Note: Values in bold indicate strong loadings.

of soil origin and secondary particles reach to some chemical equilibrium in atmosphere and mix with rainwater as a whole. Although initially cations of soil origin and secondary particles are being contributed from different sources, atmospheric chemistry has brought them in one group. Therefore, there is still a need to separate out roles of secondary precursor pollutant NH_3 (or $NH_4{}^+$ ions) and soil derived Ca^{2+} and Mg^{2+}.

3.4.2. *Neutralization factor*. For all further analyses on rainwater constituents, their concentrations were converted to μeq L^{-1}. The protons from sulfuric and nitric acids are taken up by bases such as NH_3 and anions (oxides, carbonates, or bicarbonates, etc.) of base cations like Ca^{2+}, Mg^{2+}, K^+, etc. Neutralization of the acids (H_2SO_4 and HNO_3) by these base cations ($NH_4{}^+$, Ca^{2+}, K^+ and Mg^{2+}) was obtained by calculating the NFs using

$$NF_{NH4} = NH_4^+ / \left(NO_3^- + SO_4^{2-}\right)$$

$$NF_{Ca} = Ca^{2+} / \left(NO_3^- + SO_4^{2-}\right)$$

$$NF_K = K^+ / \left(NO_3^- + SO_4^{2-}\right)$$

$$NF_{Mg} = Mg^{2+} / \left(NO_3^- + SO_4^{2-}\right)$$

The values of NF for $NH_4{}^+$, Ca^{2+}, K^+ and Mg^{2+} were 0.97, 0.92, 0.10, and 0.37 respectively during monsoon period, whereas the values during non-monsoon period were 0.20, 1.57, 0.19 and 0.61 respectively. This analysis suggests that major neutralization has occurred due to $NH_4{}^+$ in monsoon and due to Ca^{2+} in non-monsoon.

It is felt that the knowledge of statistics and chemistry fundamentals needs to be combined to determine which sources are important in neutralization. The first step is to understand association or affinity of $[SO_4{}^{2-} + NO_3{}^-]$ towards specific cation(s) through correlation study. The second step is to determine whether associated cations are present in enough quantity to neutralize $[SO_4{}^{2-} + NO_3{}^-]$. If the sufficient quantity of correlating cation is present then it will neutralize the atmospheric acidity fully or to a large extent. If the quantity of associated/correlated cation is not enough (to neutralize) then the other cations depending on their association/affinity towards $SO_4{}^{2-}$ and $NO_3{}^-$ will play a role to neutralize remaining $[SO_4{}^{2-} + NO_3{}^-]$.

In the present study, it is $NH_4{}^+$, which is highly correlated with $SO_4{}^{2-}$ and $NO_3{}^-$ could play a substantial role both in monsoon and non-monsoon periods (see Tables 5 and 6). However, one needs to see if enough quantity of $NH_4{}^+$ is present in rainwater. For monsoon period sufficient amount of $NH_4{}^+$ (one can see by converting the data in Table 4 to μeq L^{-1}) is present to fully neutralize $[SO_4{}^{2-} + NO_3{}^-]$. However, in non-monsoon period the quantity of $NH_4{}^+$ is not sufficient to neutralize the $[SO_4{}^{2-} + NO_3{}^-]$. Therefore, in non-monsoon period, other cations should additionally neutralize $[SO_4{}^{2-} + NO_3{}^-]$ and that role could be played by Mg^{2+} and Ca^{2+}.

Seinfeld and Pandis (1998) have explained in details the vital role that NH_3 plays in neutralizing acidic substances such as H_2SO_4 and HNO_3, mostly as a sole gaseous neutralizer of acidic species. It is also reported that available NH_3 will be first taken up by H_2SO_4 and then the remaining NH_3 will be available to react with HNO_3 to produce ammonium nitrate.

It may, therefore, be concluded that $NH_4{}^+$ plays a significant role in neutralization of rainwater acidity in monsoon period. Gaseous NH_3 emissions are the major source of $NH_4{}^+$ in the atmosphere. A recent study at IITK (Sharma et al., 2007) found significant correlation of NH_4^+ with SO_4^{2-} ($r = 0.75$) and NO_3^- ($r = 0.63$) in PM_{10} and high levels of ammonia in ambient air (19 μg m^{-3}). The major sources responsible for NH_3 emission are the agricultural (urea application) activities and intensive animal production facilities in India (http://dahd.nic.in/stat.htm).

4. Conclusions

This study is an attempt to establish the role of alkaline soil constituents (e.g. Ca^{2+}) and NH_3 in neutralization of rainwater acidity over Kanpur in Ganga basin. The values of NF (neutralizing factor) for NH_4^+, Ca^{2+} and Mg^{2+} were 0.97, 0.92 and 0.37 during monsoon and 0.20, 1.57 and 0.61 in non-monsoon periods, respectively. It can be concluded that predominantly neutralization occurs due to NH_4^+ during monsoon and due to Ca^{2+} during non-monsoon periods. Secondary particle components, SO_4^{2-} and NO_3^- showed affinity with NH_4^+, signifying the major role that ammonia can play if present in excess of stoichiometric requirements.

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