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Chemical characterization of rain water in a seasonally dry tropical region (Varanasi), India

Author Details

Jitendra Pandey (*Corresponding author*)
Environmental Science Division, Department of Botany, Banaras Hindu University, Varanasi - 221 005, India
e-mail: jiten_pandey@rediffmail.com

Ashima Singh
Environmental Science Division, Department of Botany, Banaras Hindu University, Varanasi - 221 005, India

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Abstract

Rain water samples, covering 44 rain events of 2008 and 52 rain events of 2009, were collected at urban and suburban locations of Varanasi and analyzed for pH, conductivity and for metal and nutrient ions. The pH of rainwater varied between 6.3 and 7.9, with over 70% of samples having alkaline range. Volume weighed mean concentration of ions indicated Ca^{2+} (11.62 - 41.60 μeq l^{-1}) to be the most dominant species followed by SO_4^{2-} (4.7 - 25.2 μeq l^{-1}), Na^+ (1.60 – 10.25 μeq l^{-1}), Mg^{2+} (0.22 – 7.21 μeq l^{-1}), (NO_3^- (0.73 – 4.02 μeq l^{-1}), K^+ (0.50 – 3.70 μeq l^{-1}) and PO_4^{3-} (0.02 – 0.97 μeq l^{-1}) respectively. Among the heavy metals, Cr (12.60 to 44.60 μg l^{-1}), Zn (4.25 to 34.55 μg l^{-1}) and Mn (10.62 to 28.40 μg l^{-1}) were found to be the dominant component of rain water. The varimax rotation of PCA results extracted four major factors namely urban-industrial emission, crustal aerosols, wind transport and biomass burning accounting for 80% of the total variance. The study has relevance in establishing cause-effect relationships for terrestrial as well as for aquatic ecosystems.

Key words

Rain water, Heavy metal, Nutrient ions, Crustal aerosols, Atmospheric deposition

Introduction

Atmospheric emission and scavenging process cycles play important role regulating cross-domain transfer mechanisms (Pandey and Pandey, 2009a). Atmospheric aerosols emitted from natural and anthropogenic sources are transported, diluted and scavenged by dry and wet removal processes or by complex biogeochemical mechanisms (Saad *et al.,* 2005). Rainfall, dew, fog, hail and snow are the important wet removal processes. Chemical composition of rain water reflects the quantity and quality of air emissions added to the atmosphere from natural and anthropogenic sources (Obaidy and Joshi, 2006). Analysis of rain water composition helps in evaluating the relative importance of different sources and estimating future possible acidification or buffering (Khanh *et al.,* 2000; Choi *et al.,* 2008). Both anionic and cationic components are considered for evaluating rain water quality (Kulshrestha *et al*., 2003). Although inconsistency exists, studies conducted in our country indicate that atmospheric particulates contain significant amount of base cations (Agrawal *et al*., 2001) which often buffer the acidifying influences during below cloud scavenging process.

Atmospheric aerosols contain a variety of nutrient ions and metal particulates. Nutrient ions such as NO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, NH_4^+, Cl^- are commonly associated with acidity or alkalinity of rain water. Long term depositions of nutrient ions, in addition to their effects on terrestrial ecosystems including agriculture, are important modifier of surface water quality (Pandey and Pandey, 2009a). Rain water, rich in metal particulates, affects soil physico-chemical properties and soil microbial interactions (Pandey, 2008). Atmospherically deposited metal particulates may enter in our body through dietary intake (Pandey and Pandey, 2009 b,c) and cause adverse health effects including carcinogenesis-induced tumor promotion (Jarup, 2003). Atmospheric deposition is increasingly becoming an important source of heavy metal addition to natural and derived ecosystems even to those situated away from the emission sources (Sharma *et al*., 2007; Bajpai *et al.,* 2011). Recent studies conducted in our laboratory have indicated that atmospheric deposition adds sizably high amount of heavy metals into river Ganga (Pandey *et al*., 2009).

The present study was an effort to investigate the composition of rainwater in terms of nutrient ions and heavy metal and to explore

their possible emission sources and magnitude of acidification in urban and sub-urban areas of Varanasi, India.

Materials and Methods

Study area: The present study was conducted at selected urban and sub-urban sites of Varanasi (latitude 25° 18' N, longitude 83° 01' E and 76.19 m a msl). The climate of the region is dry tropical with three distinct seasons, a hot and dry summer (March - June) followed by a humid monsoon season (July - October) and a moderately cool winter season (November - February). Rainy season starts with onset of heavy monsoon towards the end of June and continue till mid October, ending up with 90% of annual rainfall within 4 months. The wind direction shifts from predominantly westerly and northwesterly in October through April and easterly and north westerly in the remaining months. The five sites selected for the present study were BHU campus (mostly residential), Lanka and Cantonment area (highly commercial), Sunderpur (residential and shopping) and Ramnagar (residential and industrial).

Sampling and analysis: The rain water samples were collected during two consecutive monsoon seasons. Of the 96 rain events considered in this study, 44 were sampled during 2008 and 52 during 2009. Of the total 160, 90 samples were collected from Sunderpur, Cantt and Ramnagar (30 sample from each site) and 35 each from BHU and Lanka site. The containers were washed with distilled water and were fixed at about 3 m above the ground level to avoid surface contamination. To avoid dry deposition, the containers were deployed for sampling at the onset of rain and retrieved soon after the rain. Immediately after collection, the pH and conductivity of rain water samples were measured using portable pH and conductivity meter (Milwaukee C62, Portugal). Thereafter, the rain water samples were filtered and divided into two halves. The first half was preserved in chloroform and used to determine nutrient ions (potassium, sodium, calcium, magnesium, nitrate, sulfate, phosphate) and the second half was preserved in nitric acid (HNO_3) and analyzed for heavy metals (copper, manganese, cadmium, lead, chromium, nickel, zinc). Concentrations of SO_4^{2-} and NO_3^- were measured by turbidimetric method (Tabatabai, 1974) and phenol di-sulphonic acid method (Jackson, 1958), respectively. Concentration of PO_4^{3-} was determined following stannous chloride method (Mackereth, 1963). Base cations such as K^+, Na^+, Ca^{2+}, Mg^{2+} and heavy metals were analyzed using atomic absorption spectrophotometer (Perkin-Elmer, Model 2380, USA). The limits of detection (µg ml^{-1}) of heavy metals were 0.0005 (cadmium); 0.001 (copper); 0.002 (chromium); 0.001 (manganese); 0.004 (nickel); 0.01 (lead) and 0.0008 (zinc). A quality control was performed using acidified water blanks for checking the contamination during field collection and during sample treatment in the laboratory. Blank and standards were run after five determinations to calibrate the instrument. The analytical variances of the data obtained remained below 10% for all metals.

Statistical analysis: For test of significance two-way analysis of variance (ANOVA) was used. Principal component analysis was carried out to extract major factors explaining variances (SPSS version 16.0).

Results and Discussion

The pH of rain water varied between 6.3 and 7.9 (Fig. 1), the values being highest at Ramnagar (7.6) and lowest at Sunderpur site (6.4). The frequency distribution of pH measured in 160 samples indicated that over 70% of the total samples had pH above neutral (7.1-7.9). About 16% of the rain water samples showed pH between 6.0 and 6.5. However, none of the rain water sample of this region showed pH close to the reference pH (5.6) of acid rain (Charlson and Rodhe, 1982). A major fraction of the pH records could be explained by the presence of carbonate and bicarbonates rich Ca^{2+} with high buffering potential (Kulshrestha *et al*., 2003).

In addition to the particulates added from agricultural, commercial and urban-industrial activities, the entire north central India is under the influence of dust blown- up from the arid soils of continental Asia (Shukla and Sharma, 2010). These together probably account for relatively high pH of rainwater. In particular, the Indian soils are rich in Ca^{2+} (Kulshrestha *et al.,* 1995). Such

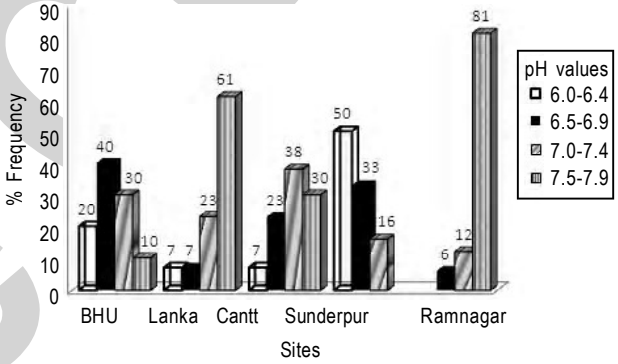

Fig. 1: Frequency distribution (%) of pH of rainwater at Varanasi

Table 1 : Results of two way analysis of variance (ANOVA) for nutrients and heavy metals in rain water

Variable	Sampling location (A)	Month (B)	A x B
Conductivity	3.299[a]	2.291[a]	6.154[a]
Na^+	24.552[a]	31.805[a]	13.882[a]
K^+	60.089[a]	8.759[a]	6.384[a]
Ca^{2+}	255.689[a]	22.274[a]	11.021[a]
Mg^{2+}	140.309[a]	126.669[a]	11.000[a]
PO_4^{3-}	187.241[a]	17.595[a]	4.007[a]
NO_3	5.658[a]	4.245[a]	0.671[ns]
SO_4^{2-}	377.386[a]	40.861[a]	1.822[ns]
Cr	1022.800[a]	22.270[a]	3.490[a]
Cu	12.410[a]	16.770[a]	1.750[ns]
Cd	81.630[a]	33.780[a]	6.690[a]
Zn	144.854[a]	17.000[a]	2.410[a]
Mn	24.400[a]	45.140[a]	6.470[a]
Pb	1142.110[a]	32.880[a]	3.250[a]
Ni	650.422[a]	45.560[a]	1.770[ns]

Significant at a = p<0.001; ns = not significant

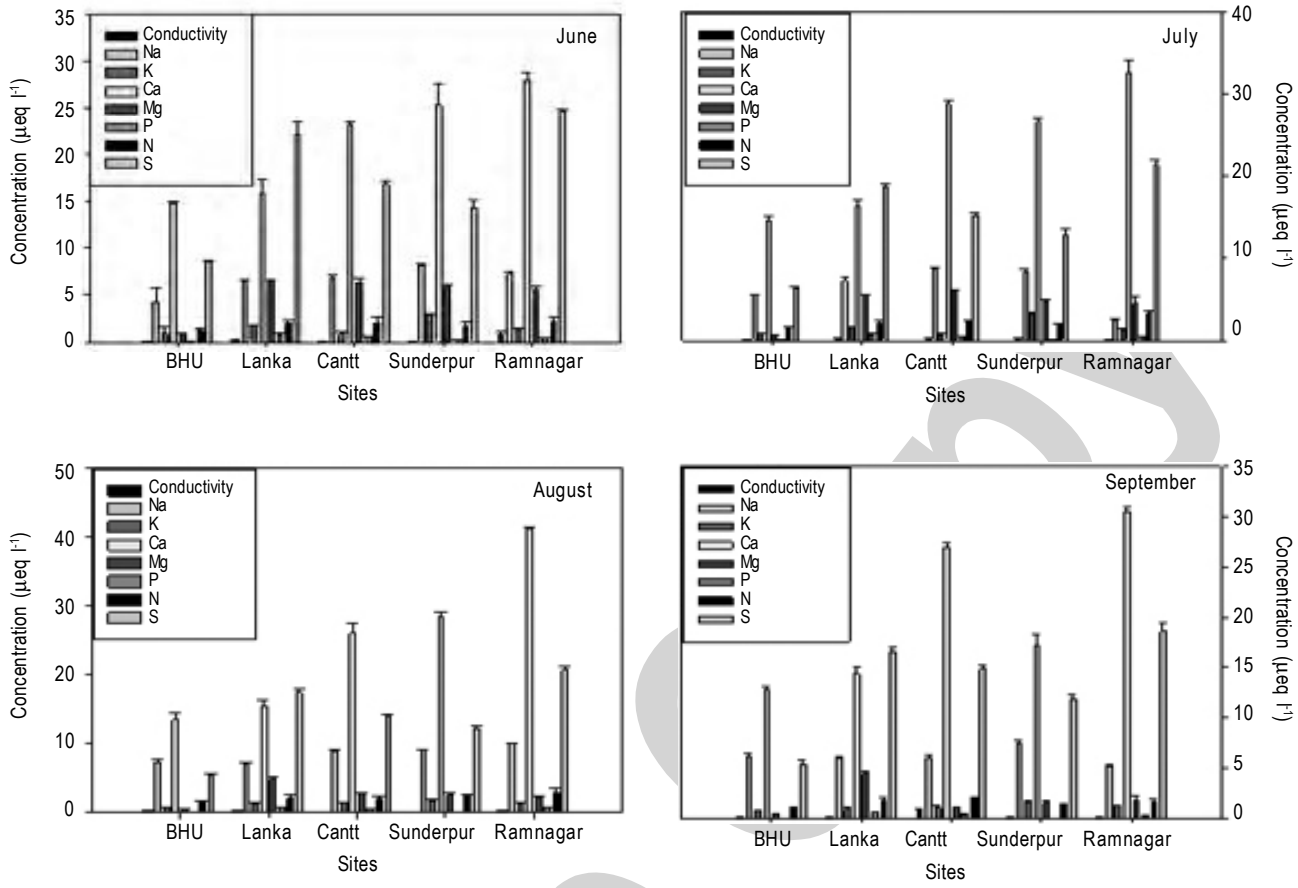

Fig. 2: Nutrient concentration in rainwater in different months (June-September) of monsoon season at Varanasi. (Error bars represent SE)

particulates when transported with air could buffer the acidifying influences during below cloud scavenging process. The rainwater pH at Varanasi although appeared similar in range recorded for some other urban areas (Das *et al.,* 2005), remained higher than those recorded at Delhi (Kulshrestha *et al.,* 1996) and Brazil (Teixeira *et al.,* 2008).

Concentrations of anions and cations indicated significant negative correlation with the amount of rainfall. For conductivity, which remained lower at BHU site, no specific temporal and spatial patterns were observed. Among nutrients, Ca^{2+} contributed maximum (48%) followed by SO_4^{2-} (22%), Na^+ (20%), NO_3^- (5%) and K^+ (3%). On spatial scale, no definite trend in distribution of ions was observed. For instance, SO_4^{2-} (4.7 - 25.2 µeq l^{-1}), NO_3^- (0.73 - 4.02 µeq l^{-1}) and Ca^{2+} (11.62 - 41.60 µeq l^{-1}) were found maximum at Ramnagar, while PO_4^{3-} (0.02 - 0.97 µeq l^{-1}) and Mg^{2+} (0.22 – 7.21 µeq l^{-1}) appeared maximum at Lanka. Concentrations of all the cations and anions were recorded minimum at BHU site (Fig. 2). On temporal scale also, concentration varied with ionic species. Significant positive correlations between Na^+ - K^+ (r = 0.435); NO_3^- - Ca^{2+} (r = 0.584); Mg^{2+} - PO_4^{3-} (r = 0.658); SO_4^{2-} - Mg^{2+} (r = 0.681) and SO_4^{2-} - PO_4^{3-} (r = 0.738) indicated common sources of their origin. Two-way analysis of variance (ANOVA) indicated significant effects ($p<0.001$) of site and month on concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+ and PO_4^{3-} (Table 1).

Increased concentrations of NO_3^- in rain water could be due to emission of N oxides from the combustion of fossil fuel and biomass burning (Pandey *et al.,* 1992; Ceron *et al.,* 2008). Nitrate in rain water although appeared lower, Ca^{2+} remained higher at Varanasi than those reported at some other urban areas (Das *et al.,* 2005; Teixeira *et al.,* 2008). Increased amount of Ca^{2+} and Mg^{2+} in precipitation may be attributed to the influence of crustal aerosols coupled with anthropogenic emissions (Kulshrestha *et al.,* 1995). Rainwater PO_4^{3-} measured in this study appeared substantially higher than those reported at some other locations of India (Das *et al.,* 2005; Pandey and Pandey, 2009a). This merits attention since PO_4^{3-} is the most limiting nutrient for plant and microbial growth in terrestrial as well as in aquatic ecosystems. High concentration of PO_4^{3-} may be attributed to industrial sources, biomass burning and soil-borne dust from agricultural activities. Tsukuda *et al.* (2006) reported that about 47% of P in atmosphere was contributed by biogenic particles including those from biomass burning and 39% by combustion of fossil fuels. Biomass burning

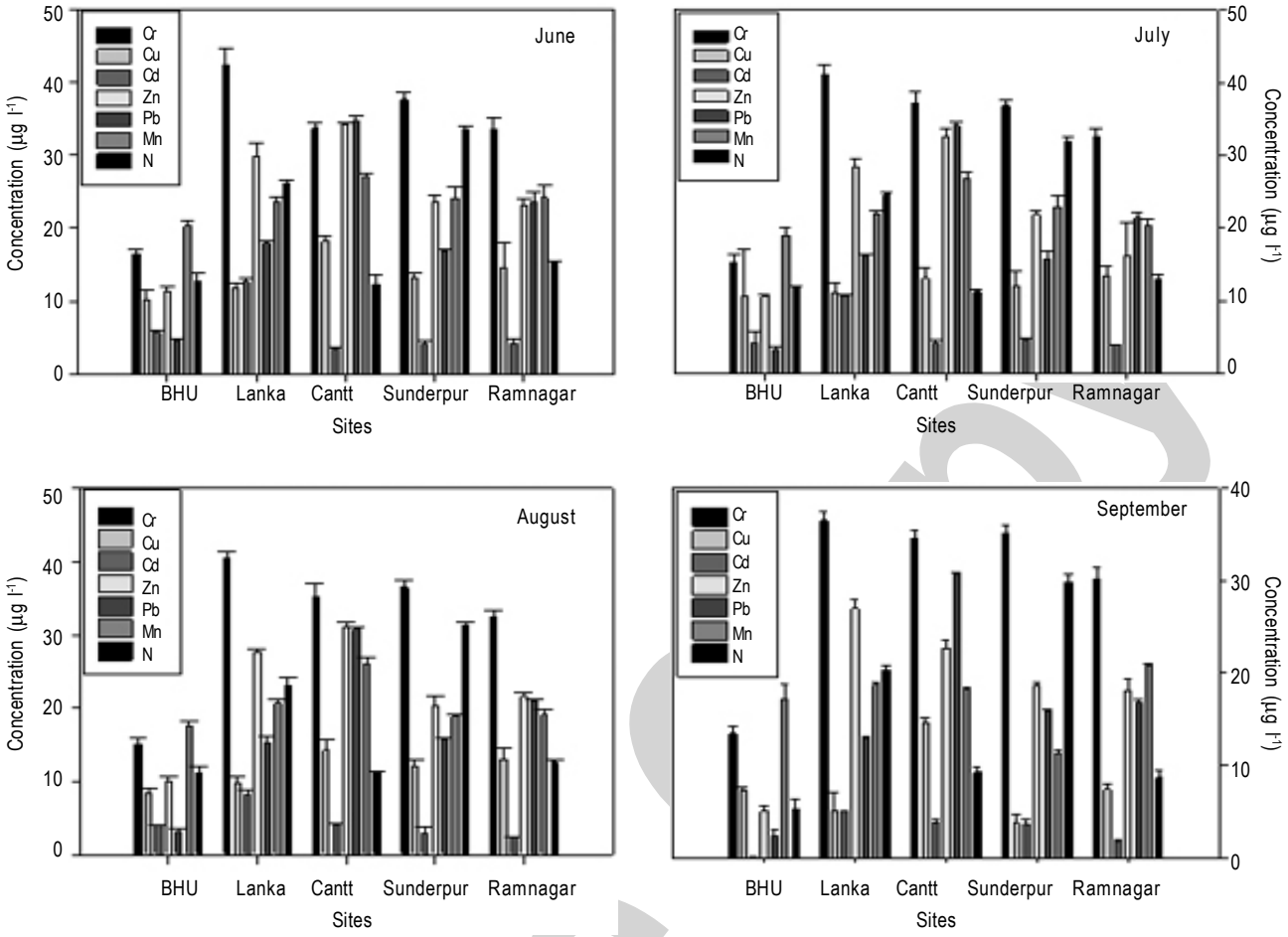

Fig. 3: Heavy metal concentration in rainwater in different months (June-September) of monsoon season at Varanasi. Values are mean of replicates ±SE.

during dead body cremation at Varanasi could be an important source of PO_4^{3-} and K^+ in the atmosphere. High concentrations of Na^+ and K^+ at Varanasi along with local sources, could at least partly be explained by Ganga river evaporation-linked wind transport and trapping mechanisms.

For the heavy metals in rain water, the trend appeared as Cr > Zn > Mn > Ni > Pb > Cu > Cd. Heavy metal concentrations in rainwater ranged from 0.19 to 13.31 µg l^{-1} for Cd; 0.89 to 19.63 µg l^{-1} for Cu; 12.60 to 44.60 µg l^{-1} for Cr; 10.62 to 28.40 µg l^{-1} for Mn; 3.38 to 34.20 µg l^{-1} for Ni; 0.82 to 35.9 µg l^{-1} for Pb and 4.25 to 34.55 µg l^{-1} for Zn, respectively (Fig. 3). Concentrations of Zn, Cu, Mn, and Pb were found to be maximum at Cantonment site and that of Cr and Cd at Lanka site. Concentrations of all the metals appeared minimum at BHU. Variations in heavy metal concentrations were significant ($p<0.001$) with respect to site and month. (Table 1).

Significant positive correlations between Zn – Cr (r = 0.821); Mn – Cu (r = 0.596); Mn – Zn (r = 0.607); Pb – Cu (r = 0.562) and Pb – Zn (r = 0.775) indicated common sources of their emission. On the other hand, metal pairs such as Ni – Cu, Ni – Mn and Ni – Pb showed negative correlations indicating their independent and site specific origin. Highest concentration of Zn at Cantonment site could be attributed to high frequency of automobiles coupled with other sources including rubber, lubricating oils and corrosion of galvanized parts (Conko *et al.,* 2004). Despite the use of lead free petrol, high concentration of Pb at Cantonment site could be due to Pb particles in street dust accumulated for a long time. An inverse relationship between rainfall and metal concentration indicated cleansing action of rainfall on atmospheric particulates (Wedyan *et al.,* 2009). Heavy metal concentration in rainwater at Varanasi appeared lower than those recorded at some other urban sites (Patel, 2001). However, except for Zn and Cu, concentrations recorded in this study remained higher than those reported from Virginia (Conko *et al.,* 2004).

The results of principal component analysis PCA showed that only four eigenvalues were >1 which explains over 80% of variance (Table 2). Studies have indicated that principal component analysis can effectively be used in interpretation of rain water composition data (Zhang *et al*., 1992; Shukla and Sharma, 2010). In the present study, the results in rotated component matrix (Table

Table 2 : Results of principal component analysis (PCA) showing initial eigenvalues and % of variance explain by PCs with eigenvalues >1

Component	Initial Eigenvalues[a]			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative Variance	Total	% of Variance	Cumulative Variance	Total	% of Variance	Cumulative Variance
1	5.967	42.620	42.620	5.967	42.620	42.620	3.302	23.588	23.588
2	2.264	16.171	58.791	2.264	16.171	58.791	3.047	21.762	45.350
3	1.803	12.875	71.666	1.803	12.875	71.666	2.468	17.625	62.975
4	1.192	8.512	80.178	1.192	8.512	80.178	2.408	17.203	80.178
5	0.864	6.174	86.351						
6	0.614	4.388	90.740						
7	0.423	3.025	93.765						
8	0.295	2.108	95.873						
9	0.208	1.486	97.359						
10	0.150	1.069	98.484						
11	0.095	0.676	99.1049						
12	0.051	0.365	9.4699						
13	0.047	0.335	9.804						
14	0.027	0.196	100.000						

[a] Extraction method: Principal component analysis

Table 3 : Varimax rotation of PCA results showing loadings of 14 variables with 4 independents varimax factors (VF)

Variables	Component			
	VF1	VF2	VF3	VF4
Cd	0.872	0.055	-0.205	0.130
Cr	0.609	0.331	0.363	0.503
Mn	0.304	0.796	0.003	-0.014
Pb	0.563	0.763	0.428	0.018
Cu	0.039	0.719	0.238	-0.062
Zn	0.603	0.647	0.168	0.247
Ni	0.619	-0.169	0.040	0.691
NO_x	0.748	0.075	0.834	0.087
PO_4^{3-}	0.767	0.340	0.351	0.753
SO_4^{2-}	0.582	0.238	0.683	0.046
Ca^{2+}	-0.281	0.410	0.805	0.138
Mg^{2+}	0.701	0.427	0.224	0.309
Na^+	-0.187	0.474	0.623	0.607
K^+	0.074	-0.035	0.600	0.874

Extraction method: Principal component analysis. Rotation: Varimax with Kaiser Normalization. Rotation converged in eight interactions

3) showed that all the 14 ion species analyzed are explained by four factors (varimax factors 1, 2, 3 and 4). The first factor (VF 1), which explained over 23% variance, showed high loading of most of the heavy metals and nutrient ions such as Mg^{2+}, PO_4^{3-}, NO_3^-, and SO_4^{2-} indicating the influence of local anthropogenic activities such as urban-industrial emissions. Similar observations have been made by Zhang *et al*. (1992). VF 2 that accounted for 22% of the layout variance showed high loading of Cu, Zn, Mn and Pb. Infact, Factor 1 and 2 (overall contribution 45%) indicate cumulative influence of their origin from anthropogenic sources coupled with wind transport. Factor 3 and 4 each explained about 17% of variance (overall contribution about 34%) and had significant loading of Ca^{2+}, Na^+, K^+, NO_3^- and SO_4^{2-} (VF3) and PO_4^{3-}, K^+, Ni and Na^+ (VF4) indicating the influence of crustal aerosols and biomass burning, respectively. Shukla and Sharma (2010) observed significant effect of crustal aerosols in neutralizing rain water acidity at Kanpur. PO_4^{3-} and K^+ are sizably emitted from biomass burning (Tsukuda *et al.,* 2006). This has relevance since PO_4^{3-} is the most critical nutrient for productivity of both terrestrial and aquatic ecosystems. K^+ is considered as chemical signature of wood burning. Coupling of soil-derived Ca^{2+} with SO_4^{2-} and NO_3^- suggests their neutralization reaction in atmosphere prior to precipitation (Shukla and Sharma, 2010). Precursors of acidic components (SO_4^{2-} and NO_x) are largely emitted from automobiles and industrial sources and significant amount may be contributed by long range transport.

The present study indicated that the nutrient ions such as Na^+, Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} were found to be the dominant species in rainwater at Varanasi. The PO_4^{3-} appeared substantially higher than those reported at some other locations of India. Among the heavy metals, Cr appeared to be the most dominant constituent followed by Zn, Mn, Ni, Pb, Cu and Cd. The varimax rotation of PCA results identified four separate factors including urban-industrial emission, biomass burning, crustal aerosols and wind transport to explain over 80% of variance. Although no acidic event was found, our study indicated that anthropogenic emissions along with soil re-suspension and wind transport have significantly altered the rain water quality at Varanasi with increased fractions of base cations and toxic metals.

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