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

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, 2009b,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.m.s.l). 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 (HNO₃) and analyzed for heavy metals (copper, manganese, cadmium, lead, chromium, nickel, zinc). Concentrations of SO₄²⁻ and NO₃⁻ were measured by turbidimetric method (Tabatabai, 1974) and phenol di-sulphonic acid method (Jackson, 1958), respectively. Concentration of PO₄³⁻ 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 Ca²⁺ 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
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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...
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
most of the heavy metals and nutrient ions such as Mg, which explained over 23% variance, showed high loading of four factors (varimax factors 1, 2, 3 and 4). The first factor (VF1), included K, Mg, Ca, SO\textsubscript{4}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, Na, Cd, Pb, Cu, Zn, Mn, Ni, Cr, and NO\textsubscript{3}\textsuperscript{-}, and NO\textsubscript{2}\textsuperscript{-} indicating the influence of local anthropogenic activities such as urban-industrial emission, biomass burning, crustal aerosols and wind transport. Factor 3 and 4 each explained cumulative influence of their origin from anthropogenic sources coupled with wind transport. Factor 3 and 4 each explained cumulative influence of their origin from anthropogenic sources coupled with wind transport.

The present study indicated that the nutrient ions such as Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, K\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} are largely emitted from automobiles and industrial sources and significant amount may be contributed by long range transport.

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**References**


