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Characterization and Source Identification of Major Inorganic Ions in Precipitation of Nagpur, India

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The chemical composition of precipitation provides important information from which the deposition to the earth's surface of water soluble gases and aerosol bound constituents can be estimated. Such estimates of deposition are fundamental in many studies of terrestrial and marine ecology. They also provide data for testing of regional and global traces transport models. Wet deposition constitutes an important natural pathway for the removal of atmospheric pollutants. However, contamination of rainwater by atmospheric pollutants is of growing concern on both regional and global scales. Determination of chemical composition of rainwater, provides an understanding of the source types that contribute to rainwater chemistry, and enhances the understanding of the local and regional dispersion of pollutants and their potential impacts on ecosystems through deposition processes. Thus, precipitation chemistry has been the subject of intense research since the last two decades (Galpin and Turner, 1999; Lee et al. 2000; Marquardt et al. 2001).

In India, soil has been considered as a major contributor of particulates in the atmosphere, due to its dusty nature (Khemani et al. 1985; Mahadevan et al. 1989). In India, both rainwater and aerosols are mostly alkaline, which is due to low contribution of secondary aerosols (SO_4 and NO_3) from anthropogenic sources and high contribution of primary aerosols (Ca, K and Mg) from soil (Khemani et al. 1985; Mahadevan et al. 1989; Kulshrestha et al. 1999; Saxena et al. 1996; Satsangi et al. 1998; Balachandran and Khillare, 2001; Thakre and Joshi, 2001; Singh et al. 2001). Knowledge about ion composition of rainwater can provide information on the prevailing state of the atmospheric environment of that area.

MATERIALS AND METHODS

Nagpur is known as Orange city and is situated in the central part of India. It is located between $21^0 45$ N to $20^0 30$ N and $78^0 15$ E to $79^0 45$ E, in the Deccan Plateau, covers an area of 9,931.00 Sq. km, and has a dry tropical weather. The rainwater samples were collected on event basis during monsoon season (2005),at National Environmental Engineering Research Institute (NEERI) campus bearing lat: $21^O 07'20.6''$N, long: $79^O 04'15.5''$E, alt: 310m located almost in the centre part of the study area. The site is surrounded uniformly by almost all activities

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that exist in the study area. A national highway lies about 0.5km from the sampling site. Samples were collected on the roof of the NEERI building about 10m from ground level. The sampler was placed 1m from the floor of the roof. Sampling was done manually on an event basis, using only wet collectors, which were fitted with a 2 l polypropylene bottle and a polypropylene funnel 22 cm in diameter. Sample collection equipment used on an event basis were washed with 10% HCl and then rinsed with double distilled water (DDW).

The collectors were deployed as soon as the rain began and were withdrawn immediately after they were filled up or when the rain ceased. A total of 34 samples had sufficient volume for chemical analysis, which represented all of the rain events during the study period. Upon arrival at the laboratory, the pH was measured in an aliquot of the sample. The pH meter was calibrated before and after each measurement. After pH measurements, the remaining sample was filtered through a prewashed Whatman filter No. 41 (Balachandran and Khillare, 2001; Singh et al. 2001) into precleaned polypropylene bottles, after preconditioning the filter and filter device by rinsing with 20 ml DDW. In order to remove the inorganic contaminants, filters were prewashed with 200 ml DDW and dried at 100^0C, and the filter blanks showed no contamination. All the filtered samples were preserved at 4^0C in a refrigerator until subjected to major inorganic ion analysis by ion chromatograph.

The major inorganic anions and cations were quantitatively determined by Dionex ion chromatograph, a Dionex IonPac AS11 for anions and CS12A for cations, a self-regenerating suppressed conductivity detector and gradient pump. The gradient weak base eluent (1.7 mM sodium carbonate or 1.8 mM sodium bicarbonate) was used for anion detection, while weak acid eluent (2 mM MSA) for cation detection at a flow of 1 ml/min. and air pressure 10 kg/cc. The cation and anion standards were procured from Dionex for calibration purpose. This provides a simple, cost-effective, fast, accurate and highly sensitive method for determination of micro level ions present in environmental samples.

RESULTS AND DISCUSSION

The ratio of total cations to that of anions (cations/anions) is an indicator for the completeness of measured parameters. The difference between the sum of cations (Na, K, Ca, Mg and NH_4) and anions (Cl, NO_3 and SO_4) and the ratio was 124.21 μeql^{-1} and 1.54, respectively. The observed anion deficiency is more likely to be due to the exclusion of the $HCOO^-$, CH_3COO^- and HCO_3^- from the measurements, which can greatly alter the cation/anion ratio. Previous studies on precipitation in India have also reported a cation excess ranging between 29 and 197 μeq^{-1} with a ratio greater than unity (Khemani et al. 1985; Mahadevan et al. 1989; Saxena et al. 1996; Satsangi et al. 1998; Singh et al. 2001). The main source of organic acids in the atmosphere is either the oxidation of hydrocarbons emitted by vegetation or the direct emission from the industrial sources. Since the site is encompassed by forest along with agricultural fields and the soil is calcareous, both organic and bicarbonate ions might have contributed in an appreciable quantity.

Rainwater samples collected during the monsoon season were analyzed for major cations and anions namely Cl, NO_3, SO_4, Na, K, Ca, Mg and NH_4 by employing the ion chromatography technique. The average and standard deviation of ions was found to be 581.63± 181μeql^{-1}. The ionic composition of rainwater is presented in Table 1. Among the ionic constituents calcium contributed maximum (32.87%) followed by sulfate (22.53%), magnesium (11.24%), chloride (10.44%), nitrate (6.33%), sodium (6.09%), potassium(5.92%) and ammonium(4.54%).The ionic balance of rainwater samples showed a trend as SO_4>Cl>NO_3 for anions and Ca>Mg>Na>K>NH_4 for cations. The total anions contribute 39.32% and cations 60.67 %, respectively to rainwater.

Table 1. Ionic composition of rainwater (μeql^{-1}).

Component	Min	Max	Mean	SD	%
pH	6.14	7.04	6.59	0.29	-
Cl	40.25	99.28	60.78	20.07	10.44
NO_3	20.69	61.24	36.85	12.17	6.33
SO_4	28.51	288.14	131.09	78.06	22.53
Na	14.24	84.25	35.43	15.84	6.09
Ca	40.15	391.24	191.21	133.28	32.87
K	11.24	81.14	34.47	25.82	5.92
Mg	21.47	174.25	65.39	45.89	11.24
NH_4	18.01	45.61	26.41	9.48	4.54

The average pH value was found to be 6.59 which is alkaline in nature. The pH of individual precipitation events ranged from 6.14 to 7.04 showing alkalinity during the study period. The pH was alkaline in all the samples as compared to the reference level, 5.6 (Charlson and Rodhe, 1982). Earlier studies in different parts of India also reported the alkaline pH ranging between 6.0 and 7.5, (Khemani et al. 1985; Mahadevan et al. 1989; Saxena et al. 1996; Satsangi et al. 1998). The mean pH of 6.57 during the study period reflects a strong impact of alkaline soil dust on rainwater quality, pH values of less than 4.8 suggests the influence of anthropogenic sources.

The relatively high average pH values measured in this region are not due to the lack of acidity in precipitation, but rather due to the neutralization of acidity. Neutralization was further confirmed by a good correlation between the acidic ions SO_4 and NO_3 with major cations Ca, Mg, K and NH_4 Table 2. A good correlation was seen between SO_4 and Ca, SO_4 and Mg, NO_3 and Ca, and NO_3 and Mg. These correlations, therefore, indicate the significance of these ions in acid neutralization. Neutralization factors (NF) were also used to evaluate the neutralization of precipitation by crustal components and NH_4, which were calculated by the following equation (Possanzini et al. 1988):

$$NF_{xi} = [X_i]/[SO_4]+[NO_3]$$

where Xi is the chemical component of interest, with all the ions expressed in μeql^{-1}. The NF_{NH4} was less than both NF_{Ca} and NF_{Mg}, the factors being 0.15 for

NH_4, 0.38 for Mg and 1.1 for Ca, revealing that the crustal components neutralize a larger fraction of the available acid.

Table 2. Correlation coefficient of ionic species of rainwater at the probability of 95% in all the samples.

	Cl	NO_3	SO_4	Na	Ca	K	Mg	NH_4
Cl	1.00	0.89	0.85	0.92	0.84	0.71	0.77	0.88
NO_3		1.00	0.84	0.91	0.86	0.69	0.76	0.89
SO_4			1.00	0.96	0.88	0.72	0.81	0.90
Na				1.00	0.86	0.67	0.78	0.91
Ca					1.00	0.51	0.82	0.92
K						1.00	0.52	0.56
Mg							1.00	0.71
NH_4								1.00

In order to find possible association between ions in precipitation, and consequently, the likely sources of pollutants, correlation between ions in precipitation was calculated and is presented in Table 2. The acidic ions SO_4 and NO_3 correlated well (r=0.83) indicating their origin from similar sources, because of the similarity in their behavior in precipitation and the co-emissions of their precursors SO_2 and NO_X. Similarly, a good correlation was seen between Ca and Mg (r = 0.82); suggesting the common occurrence of these ions from crustal origin. Other relatively good correlations were observed between Ca and SO_4 (r = 0.88), Mg and SO_4 (r = 0.81), Ca and NO_3 (r = 0.86), Mg and NO_3 (r =0.76), Ca and Cl (r =0.84) and Mg and Cl (r = 0.77) Table 3. Most of these well-correlated pairs have common sources or occur in precipitation as a result of atmospheric chemical reactions probably from the reaction of acids H_2SO_4, HNO_3 and HCl with alkaline compounds rich in Ca and Mg carried into the atmosphere by wind blown dust. This suggests that wind carried dust and soil play an important role in precipitation chemistry (Khemani et al. 1985; Varma, 1989). Ammonium compounds generally occurs in the atmosphere as $(NH_4)_2SO_4$ and NH_4NO_3 (Seinfeld, 1986), which is supported by the significant correlation between NH_4 and SO_4 (r = 0.90) and NH_4 and NO_3 (r = 0.89). The good correlation of NH_4 with NO_3 might reflect agricultural activity such as fertilizer use whereas presence of high concentration of both NH_4 and NO_3 ions might be due to the use of ammonium nitrate fertilizers to fertile the gardening area in the vicinity of the sampling site apart from the very little contribution of anthropogenic sources.

The major inorganic ions in rainwater samples collected at Nagpur together with those reported in other selected areas of Indian cities are presented in Table 3. The data compared with that of other areas reveals that concentration of both Ca and SO_4 is higher than those reported for other sites close to that in Delhi. The high concentration of both the ions is due to the large contribution of soil dust, which was further confirmed by the mineralogy of the dust material collected during rain sampling. The dissolution of minerals ($CaCO_3$, $MgCO_3$ and $CaSO_42H_2O$) accounts for the high concentrations of Ca and SO_4. The high concentration of K is due to the dense vegetation in the vicinity of the study area. Concentrations of ions of marine origin in rainwater are less because the site is about 834 km away from coast.

Table 3. Ionic composition (μeql^{-1}) of rainwater at different sites in India.

Site	Cl	NO_3	SO_4	Na	Ca	K	Mg	NH_4	References
Chembur	164.5	29.5	70.4	168.2	89.5	6.9	36.5	41.1	Khemani et al. (1994)
Silent Valley	43.0	21.0	20.0	46.0	43.0	4.0	14.0	3.0	Rao et al. (1995)
Dayalbagh	23.7	17.6	28.4	54.8	83.9	7.7	26.4	12.7	Saxena et al. (1996)
Gopalpura	30.6	42.6	15.4	19.4	134.3	2.5	78.4	43.4	Satsangi 1998
Delhi	43.2	109.02	131.31	44.04	180.64	20.17	44.39	82.2	Balachandran and Khillare 2001
Tirupati	33.91	40.84	127.96	33.08	150.66	33.89	50.51	20.37	Mouli et al. 2005
Nagpur	60.78	36.85	131.09	35.43	191.21	34.47	65.39	26.41	Present study

Table 4. Ratio values of the major of components of rainwater and the corresponding values for sea water.

	Cl/Na	K/Na	Mg/Na	Ca/Na	SO_4/Na
Rainwater	1.71	0.93	1.84	5.39	3.70
Sea water	1.8	0.037	0.038	0.12	0.25

In order to determine the marine contribution in rainwater composition, sea salt ratios were calculated considering Na as sea salt tracer, assuming all the Na to be of marine origin. The calculated ratios for rainwater deviated considerably from the seawater ratios Table 4, indicating a modification of the sea salt constituents along the trajectory of the air masses.

The observed Cl/Na ratio (1.71) is closer to that of seawater ratio (1.8) indicates fractionation of sea-salt and modifications by non-marine constituents. It was noticed that insignificant contribution of sea-salt in precipitation which is away from the coastal region. The elevated K/Na, Mg/Na, Ca/Na and SO_4/Na ratios indicate the possible contribution of other components, probably the soil. To discriminate the marine influence, excess concentration of SO_4 was calculated using Na and Cl as tracers. It was found that about 93% with respect to Na and 95% with respect to Cl was contributed from sources other than sea salt, whereas 82% of SO_4 is contributed from terrestrial origin. The rest may be attributed to heterogeneous reactions of SO_2 with soil particles. The rainwater composition at Nagpur is predominantly influenced by the local terrestrial sources. Since the study area is surrounded by dense vegetation and anthropogenic activity. SO_4 may originate from soil particles and the possible mechanism could be the aqueous-phase oxidation of SO_2 in cloud droplets (Hegg and Hobbs, 1982; Pandis et al. 1992) while the NO_3 may be formed by homogeneous gas-phase transformation of NO_X to HNO_3, followed by the reaction with NH_3 to form NH_4NO_3. Apart from these, the industrial and urban activities may also play little role in the contribution of acidic ions. Careful observation of correlation coefficients among the ionic components Table 3 suggests that NaCl, $CaSO_4$, $MgSO_4$, $MgCl_2$, HNO_3, NH_4NO_3, NH_4SO_4 and $(NH_4)_2SO_4$ are predominant species combinations.

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