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Characterization of Major Inorganic Ions in Precipitation in Area of Hisar, India

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Abstract : *The rainwater samples were collected on event basis during June-July-August-2012 and were analyzed for pH, major anions (Cl, NO_3, SO_4) and cations (Ca, Mg, Na, K, NH_4). The pH value varied from 6.0 to 7.2 indicating alkaline nature of rainwater. The pH of the rainwater was found well above the reference pH (5.6), showing alkalinity during the monsoon season. The average and standard deviation of ionic composition was found to be 98.1 ± 9.8 l eq L-1. The total anions contribute 48 % and cations 52 %, respectively to rainwater. Neutralization factors (NF) followed a sequence of NFCaNFMg ($NFNH_4$) with factors of 1.1, 0.36 and 0.16 indicating the crystal components are responsible for neutralization of anions. The average ratio of (NO_3 + Cl)/SO_4 observed as 1.2 indicates that nitric and hydrochloric acid influences the acidity of rainwater. The ratio of NH_4/NO_3 and NH_4/SO_4 was observed as 0.7 and 0.3 thus indicates that the possible compounds which may predominate in the atmosphere are NH_4NO_3 and $(NH_4)_2SO_4$. Ionic correlation was established to identify sources of origin. A good correlation was seen between Ca and Mg (r = 0.98); suggesting the common occurrence of these ions from crustal origin. Similarly, the acidic ions SO_4 and NO_3 correlated well (r = 70) indicating their origin from similar sources. Other relatively significant correlations were observed between Ca and SO_4 (r = 0.93), Mg and SO_4 (r = 0.76), Ca and NO_3 (r = 0.07), Ca and Cl (r = 0.28) and Mg and Cl (r = 0.32), and Mg and NO_3 (r = 0.69). The observed rainwater ratio of Cl/Na (1.4) is closer to that of seawater ratio (1.18) indicates fractionation of sea-salt and modifications by non-marine constituents as the site is 2040 km away from the sea coast. The nss-Ca contribution was observed as 95.7% suggesting their crustal origin whereas nss-Mg and nss-K shows their contribution as 86.8% and 83.9% indicating influence of soil sources. The nss-SO_4 contributed as 86.7% shows anthropogenic origin.*

Keywords: Anthropogenic, Sea water, Anion, Cation, pH, Rainwater, Fractionation.

Introduction

Rainwater composition plays an important role in scavenging soluble components from the atmosphere and helps us to understand the relative contribution of different sources of atmospheric pollutants (Malik *et al.,* 2007; Tham and Sakugawa, 2007). The chemical composition of rainwater varies from site to site and region to region due to influence of local sources. Rainwater is an efficient pathway for removing the gases and particles from the atmosphere. Therefore, rainwater chemistry measurements play a critical role in defining both the level of acid deposition, the state of important biogeochemical cycles of the earth atmosphere system and to understand the relative importance of the different sources (Moody *et al.,* 1991; Galloway *et al.,* 1984; Salve *et al.,* 2006). The chemistry of rainwater provides its compositions largely by dissolving particulate materials in the atmosphere when droplets of water nucleate on atmospheric particulates, and secondarily by dissolving gasses from the atmosphere. Rainwater compositions vary geographically. In open ocean and coastal areas they have a salt content essentially like that of sea water plus CO_2 as bicarbonate anion. Terrestrial rain compositions vary significantly from place to place because the regional geology can greatly

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affect the types of particulates that get added to the atmosphere. Likewise, sources of gaseous acids (SO_3, NO_2) and bases (NH_3) vary as a function of biome factors and anthropogenic land use practices. Each of these gasses can be added in varying proportions from natural and non natural input sources. Particulate load to the atmosphere can also be greatly affected by human activities. Finally, local climate especially the amount of precipitation in one area compared to another will affect the solute concentrations in terrestrial rainwater. The result is highly variable compositions, so there isn't one simple formula. In India, the reported pH values of rainwater varies from 6.4 to 7.2, which is higher as compared to reference pH of rainwater (5.6) (Mouli *et al.,* 2005; Kulshrestha *et al.,* 2005). The acid rain events are also reported in Delhi (Balachandran and Khilare, 2001), Dhanbad (Singh *et al.,* 2007). Literature suggests that if the source is influenced by anthropogenic activities, the nature of rainwater becomes acidic because anthropogenic activities contribute acidic gases like SO_2 and NOx and a basic gas like NH_3. When these acidic gases are dissolved in clouds, sulphuric and nitric acids are formed, respectively. The study area fall under residential area and has narrow roads on which vehicular traffic activity takes place. A national highway lies about 0.7 km from the sampling site. There is thermal power plant and small scales industries which is 10 km away from it. The air pollutants encountered in the region are of both particulate and gaseous in nature, which is coming out as vehicular emission, thermal power plant and small scale industries. The thermal power plant emit particulate matters and various gaseous pollutants in to the atmosphere; causing the deterioration of air quality. An attempt has been made to investigate the chemical composition of major ions, understand rainwater chemistry, and generate data on rainwater composition at an urban environment.

Materials and Methods

The rainwater samples were collected on event basis during monsoon season (June-July-August, 2012), at Hisar. Samples were collected on the roof of the building about 5 m from ground level. The sampler was placed 1 m 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 24 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 20 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. All the filtered samples were preserved at 4°C 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 Ion Pac AS11 for anions and CS12A for cations, a selfregenerating 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 is highly sensitive method for determination of micro level ions present in environmental samples. The limits of detection for cations and anions were 1 ppb in Dionex ion chromatograph. The analytical precision was maintained through running of known standards. The analytical precision was between 5% and 10% for different anions and cations measurements. The statistical analysis, One way ANOVA was applied to estimate the measurement uncertainty in analysis. The analytical variance for the data should comprise not more than 20% of the total variance. The statistics was performed within and between batches using SPSS software and F test results are presented in Table 1. The F test statistic was applied to test the null hypothesis and is true for cations and anions. The calculated F value were observed in the range of 0.014-0.520 which is less than F critical of 2.0 for a stated level of confidence (typically 95%) means that the difference being tested is statistically significant at 95% confidence level (Ramsey *et al.*, 1992).

Table 1 One way ANOVA test for cations and anions.

Ions	Variation	Sum of squares	Df	Mean Square	F
SO_4	Bet. groups Within groups total	0.792 109.02 109.8	1 40 41	0.792 27.15	0.029
NO_3	Bet. groups Within groups total	0.198 105.51 105.71	1 40 41	0.198 2.563	0.074
Na	Bet. groups Within groups total	0.006 193.7 193.7	1 40 41	0.006 4.88	0.014
K	Bet. groups Within groups total	0.229 41.67 41.901	1 40 41	0.229 1.066	0.214
Ca	Bet. groups Within groups total	17.1 1214.52 1231.6	1 40 41	17.1 32.86	0.520
Mg	Bet. groups Within groups total	0.007 44.7 45.82	1 40 41	0.006 1.168	0.066
NH4	Bet. groups Within groups total	0.935 181.9 182.88	1 40 41	0.945 4.522	0.209

Table 2 Major ions composition of rainwater (µeql^{1}).

Component n = 20 no. of samples	Min	Max	Average	SD	%
pH	6.0	7.3	6.3	0.3	-
Cl	8.9	21.2	13.3	2.6	13.6
NO3	8.1	14.8	10.3	1.7	10.5
SO4	9.8	32.8	20.7	5.4	21.1
Ca	22.5	42.5	29.1	5.9	29.7
K	1.1	4.9	2.3	1.0	2.3
Mg	1.8	7.1	3.3	1.2	3.3
NH4	3.2	12.4	7.0	2.2	7.2

Results and Discussion

The major ions in rainwater are presented in Table 2. The pH of rainwater is generally affected by acidic and alkaline ions in the rainwater. The average pH of rainwater is found to be alkaline (value 6.3 ± 0.3). The pH of individual rainwater events ranged from 6.0 to 7.3 thus showing higher alkalinity which may be due to suspension of particles in the atmosphere which is rich in carbonates and bicarbonates of calcium buffers, the acidity generated by mineral acid. The pH was alkaline in all the samples as compared to the reference level, 5.6 (Charlson and Rodhe, 1982). Acidic pH reveals the presence of strong acids in rainwater while neutral or alkaline pH indicates neutralization of acids by wind blown soil dust and ammonia. Rainwater quality is a function of its contents of both acid and alkaline. The average and standard deviation of ionic composition was found to be 98.1 ± 10.6 l eqL-1. The ionic balance of rainwater samples showed a trend as SO$_4$|Cl|NO$_3$ for anions and Ca|Na|NH$_4$|Mg|K for cations. Among the ionic constituents calcium contributed maximum (29.7%) followed by sulfate (21.1%), chloride (13.6%), sodium (12.4%), nitrate (10.5%), ammonium (7.2%), magnesium (3.3%) and potassium (2.3%). The total anions contribute 45.1% and cations 54.9%, respectively to rainwater. The slight cationic excess is probably due to some excluded anions. According to literature, acidity originates primarily from sulfuric acid and nitric acid and neutralization by Ca and Mg, so the ratios of SO$_4$ + NO$_3$/Ca + Mg (anions/cations) can be considered as indicator for acidity, if anions/cation is less than one it indicates alkaline nature of rainwater and the ratios greater than unity indicates the presence of free anions which is responsible for precipitation acidity (Kumar *et al.,* 2002). The ratio of sum of SO$_4$ and NO$_3$ and sum of Ca and Mg was observed as 0.95 which NO$_3$ lower than one indicating alkaline nature of rainwater. Neutralization factors (NF) were also used to evaluate the neutralization of ions by crustal components and ammonia. The NFNH$_4$ was less than both NFCa and NFMg, the factors being 0.15 for NH$_4$, 0.38 for Mg and 1.1 for Ca, revealing that the crustal components are responsible for neutralization of anions. Studies reported on rainwater at Ahmedabad, and Pune reported NF of 0.73, 0.66 0.45 for NH$_4$, 1.77, 1.64, 1.25 for Ca and 0.11, 0.43 and 0.23 for Mg, respectively suggesting main neutralization occurred due to Ca followed by Mg and then ammonium (Rastogi and Sarin, 2005; Kulshrestha *et al.,* 2005, Mouli *et al.,* 2005). The ratio of different species is presented in Table 3. The average ratio of $(NO_3 + Cl)/SO_4$ observed as 1.1 indicates that nitric and hydrochloric acid influences the acidity of rainwater whereas ratio below one indicates the influence of sulphuric acid (Khemani *et al.,* 1994). The ratio of $(Ca + NH_4)/(NO_3 + SO_4)$ is 1.2 indicates that Ca and NH_4 ions plays an important role in neutralization of acidic ions in rainwater. The NO_3/SO_4 was observed as 0.56 which indicates that about 46% of sulphuric acid and 54% of nitric acid contributes to the acidity in rainwater. The ratio of $(SO_4 + NO_3)/(Ca + Mg)$ was observed as 0.95 which is below one indicating the alkaline nature of rainwater. The ratio of NH_4/NO_3 and NH_4/SO_4 was observed as 0.68 and 0.34 indicates that the possible compounds which may predominate in the atmosphere are NH_4NO_3 and $(NH_4)_2SO_4$ (Seinfield, 1986). Moreover ammonium nitrate dominates over ammonium sulphate compound (Parmar *et al.,* 2000) whereas ammonium sulphate dominates over ammonium nitrate (Khare *et al.,* 2004). A correlation between ions in rainwater is presented in Table 4. A significant correlation was seen between Ca and Mg (r = 0.95); suggesting the occurrence from crustal origin. Similarly, the acidic ions SO_4 and NO_3 correlated well (r = 0.60) 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. Other relatively significant correlations were observed between Ca and SO_4 (r = 0.92), Mg and SO_4 (r = 0.83), Ca and NO_3 (r = 0.09), Ca and Cl (r = 0.34) and Mg and Cl (r = 0.31), and Mg and NO_3 (r = 0.71). Most of these well-correlated pairs have common sources or occurance in rainwater 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 rainwater chemistry (Mouli *et al.,* 2005).

Table 3 Ratio of different ionic species.

Ratio	Values
NO_3/SO_4	0.56
NH_4/NO_3	0.68
NH_4/SO_4	0.34
$(Ca + NH_4)/(NO_3 + SO_4)$	1.2
$(NO_3 + Cl)/SO_4$	1.1
$(SO_4 + NO_3)/(Ca + Mg)$	0.95

Table 4 Ionic correlation of rainwater.

Cl	NO_3	SO_4	Na	Ca	K	Mg	NH_4	Cl
Cl	1.00	0.82	0.22	0.00	0.34	0.50	0.31	0.11
NO_3		1.00	0.60	0.88	0.09	0.78	0.71	0.73
SO_4			1.00	0.54	0.92	0.67	0.83	0.67
Na				1.00	0.45	0.90	0.13	0.33
Ca					1.00	0.21	0.95	0.56
K						1.00	0.71	0.06
Mg							1.00	0.05
NH_4								1.00

Table 5 Ratio values of ions, EF, SS and NSS in rainwater.

	Cl	K	Mg	Ca	SO_4	NO_3
Sea water	1.16	0.037	0.038	0.12	0.25	0.00002
Rainwater	1.1	0.2	0.3	2.4	1.7	0.00021
EF		0.95	5.09	7.08	20.0	6.2
SS (%)		48.6	16.8	12.1	4.3	12.6
NSS (%)		51.4	83.2	87.9	95.7	87.4

EF = Enrichment factor; SS = Sea-salt fraction; NSS = Nonsea-salt fraction.

Ammonium compounds generally occurs in the atmosphere as $(NH_4)_2SO_4$ and NH_4NO_3 (Seinfield, 1986), which is supported by the significant correlation between NH_4 and NO_3 (r = 0.73) followed by NH_4 and SO_4 (r = 0.67). An attempt has been made to distribute the ratio values with respect to sea salt are presented in Table 5. The enrichment factor of Mg, Ca, Mg and SO_4 was higher than one whereas Cl has value almost equivalent to one indicating significance influence of local sources. The observed rainwater ratio of Cl/Na (1.1) is closer to that of seawater ratio (1.16) indicating fractionation of sea-salt and modifications by non-marine constituents. The elevated K/Na, Mg/Na, Ca/Na SO_4/Na and NO_3/Na ratios indicate the possible contribution of other components, probably the soil. The observation of relative ratios among the ionic species suggests that the possible combinations are NaCl, $CaSO_4$, $MgSO_4$, $MgCl_2$, HNO_3, NH_4NO_3, NH_4SO_4 and $(NH_4)_2SO_4$. The nonsea-salt (nss) contributions of ionic constituent, nss-Ca contribution was observed as 95.7% suggesting their crustal origin whereas nss-Mg and nss-K shows their contribution as 87.9% and 83.2%

indicating influence of soil sources. The nss-SO_4 contributed as 87.4% shows crustal and anthropogenic origin. Studies carried out by other researchers in India shows similar pattern (Rastogi and Sarin, 2005; Das *et al.,* 2005). The nss-NO_3 shows 99.998% indicating influence of non-marine sources in the region. This was supported by other study conducted at northern region of India (Hameed *et al.,* 2006).

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