Precipitation chemistry and occurrence of acid rain over Dhanbad, coal city of India

Abhay Kr. Singh · G.C. Mondal · Suresh Kumar · K.K. Singh · K.P. Kamal · A. Sinha

Abstract The present study investigated the chemical composition of wet atmospheric precipitation over Dhanbad, coal city of India. The precipitation samples were collected on event basis for three years (July 2003 to October 2005) at Central Mining Research Institute. The precipitation samples were analyzed for pH, conductivity, major anions (F, Cl, NO_3, SO_4) and cations (Ca, Mg, Na, K, NH_4). The pH value varied from 4.01 to 6.92 (avg. 5.37) indicating acidic to alkaline nature of rainwater. The pH of the rainwater was found well above the reference pH (5.6), showing alkalinity during the non-monsoon and early phase of monsoon, but during the late phase of monsoon, pH tendency was towards acidity (<5.6 pH) indicating the non-availability of proper neutralizer for acidic ions. The observed acidic events at this site were 91, ($n = 162$) accounting 56% for the entire monitoring months. The $(NO_3 + Cl)/SO_4$ ratio in majority of samples was found below 1.0, indicating that the acidity is greatly influenced by SO_4. The calculated ratio of $(Ca + NH_4)/(NO_3 + SO_4)$ ranges between 0.42–5.13 (average 1.14), however in most of the samples, the ratio is greater than unity (>1.0) indicating that Ca and NH_4 play an important role in neutralization of acidic ions in rainwater. Ca and SO_4 dominate the bulk ionic deposition and these two ions along with NH_4 accounts 63% of the annual ionic deposition.

1 Introduction

Deposition of atmospheric pollutants is a serious threat to human environment, such as vegetation, soil, water, forestry etc. and therefore, the research on deposition monitoring and its effects on human environment are going on extensively in many countries of the world. Emission of sulphur and nitrogen oxides into the atmosphere in Asia, Europe and North America have resulted in wide spread environmental effects including acidification of soils, surface waters, ground waters, injury to vegetation, corrosion of building materials and decreased in visibility (Fujita *et al.*, 2000; Tsuruta, 1989; Weng, 1993; Ayers *et al.*, 2002; Hooper and Peters, 1989). Atmospheric deposition is not just a domestic concern; it is also a regional environmental problem that transcends national boundaries. As emphasized in Chapter 9 on Agenda-21 (on transboundary atmospheric pollution) adopted at the 1992 United Nations Conference on Environment and Development

A. Kr. Singh (✉) · G.C. Mondal · S. Kumar · K.K. Singh
Environmental Management Group, Central Mining Research Institute, (Council of Scientific & Industrial Research), Dhanbad-826001, India
e-mail: singhak@yahoo.com

K.P. Kamal · A. Sinha
Department of Chemistry, V.B. University, Hazaribag-825 003, India

(UNCED) in Rio de Janeiro, acid deposition is a problem that requires international cooperative efforts for its solution. Acidic rain mainly results from the oxidation of sulphur dioxide and nitrogen oxides almost exclusively from anthropogenic sources and the main contributor to precipitation acidity are sulphuric acid and nitric acid. Ammonia and alkaline dust are able to neutralized acidic components and thus influence the extent of acidic precipitation. The occurrence of acid rain has been documented by an ever-increasing number of studies around the world including India and the published data have been useful in evaluating atmospheric pollution localities.

During the last two decades, a number of studies have been carried out on the chemical composition of precipitation in India (Mahadevan *et al.*, 1984; Naik *et al.*, 1988; Mukhopadhyay *et al.*, 1992; Kulshrestha *et al.*, 1995; Saxena *et al.*, 1991, 1996; Rao *et al.*, 1992, 1995). These studies revealed the pH of rainwater between 6 and 7 in India, which is higher as compared to values of natural rainwater (5.6) and those reported from other locations of the world. Elevated pH values might be due to interference by dust particles, rich in buffering species like Ca and Mg, leading to the neutralisation of acidity of rainwater (Khemani *et al.*, 1985; Kumar *et al.*, 2002). It has been observed that the buffering influence of dust particulates is more significant at rural sites than that at urban sites. It may be due to the fact that the suspended particulates of rural areas are almost free from anthropogenic components (Mahadevan *et al.*, 1989). Although studies suggest that under the prevailing situation of emissions, there is no threat of acid rain in most part of the Indian subcontinent, however, there are reports of acid rain events over some parts of the country like Delhi (Ravichandran and Padmanabhamurty, 1994; Balachandran and Khilare, 2001), Bangalore (Shivashankara *et al.*, 1999) Korba (Chndravanshi *et al.*, 1997) and Bombay (Sequeria, 1976; Khemani *et al.*, 1989, 1994) in recent past. The occurrence of acidic rains at these sites is attributed to the industrial and vehicular emission of the gaseous pollutants.

Dhanbad, known as coal city of India, are actively associated in mining activities for more than a century. It lies in the eastern part of the Jharkhand state and is bounded by the latitude of $86°07'$ and $86°50'$E and longitude of $24°37'$ and $24°02'$N (Fig. 1). The district has a total area of 2041.62 km^2 and population of 1.9 million. Jharia, Bhagmara, Katras, Bhowrah, Bhagatdih, Govindpur and Nirsa are the major coal-mining townships and important business center of this district. The area lies in the tropical region where climate is characterized by very hot summer ($15–46°$C) and cold winters ($5–31°$C). The climate of Dhanbad may be broadly devised into three seasons: winter (November–February), summer (March–June) and monsoon (July–October). The average annual rainfall of 1280 mm is recorded for the Dhanbad district. The south-west monsoon lasts from July to October and the area gets more than 85% of the annual rainfall during these four monsoon months (Fig. 2).

There are many working and abandoned coalmines in and around Dhanbad city. About two hundreds coal mines of Jharia coalfield are located 6 km south of the Dhanbad town. The air pollutants encountered in this coal-mining region are both particulate and gaseous in nature, which is coming out as emission from different industrial and mining processes. The region is characterised by high value of suspended particulate matter (SPM). The principal causes of high SPM are vehicular emission, emission from different industrial and mining processes and loading and unloading of coal at various depots (Jain and Saxena 2002, Varma *et al.*, 1994). Major air polluting industries in the study area include thermal power plants, steel plants, beehive coke ovens, hard coke oven plants, fertilizer plants, cement plants, refractories and miscellaneous other industries. These industries emit particulate matters and various gaseous pollutants in to the atmosphere; causing the deterioration of air quality and increase the potential for acid rains. Besides, industrial and mining operations, mine fire are the other major source of emission of gaseous pollutants in the region. Considering the importance of acid rain and greater concern over the particulate and gaseous emission of pollutants in this India's richest coal mining belt, rainwater study has been carried at Central Mining Research Institute. This study reports the chemical composition of individual precipitation events collected on seasonal basis for three years from July 2003 to October 2005. The major objectives of the study are to (i) characterise the chemical composition of precipitation events, (ii) decipher the possible source of the ions and (iii) assessing the wet deposition of the chemical constituents.
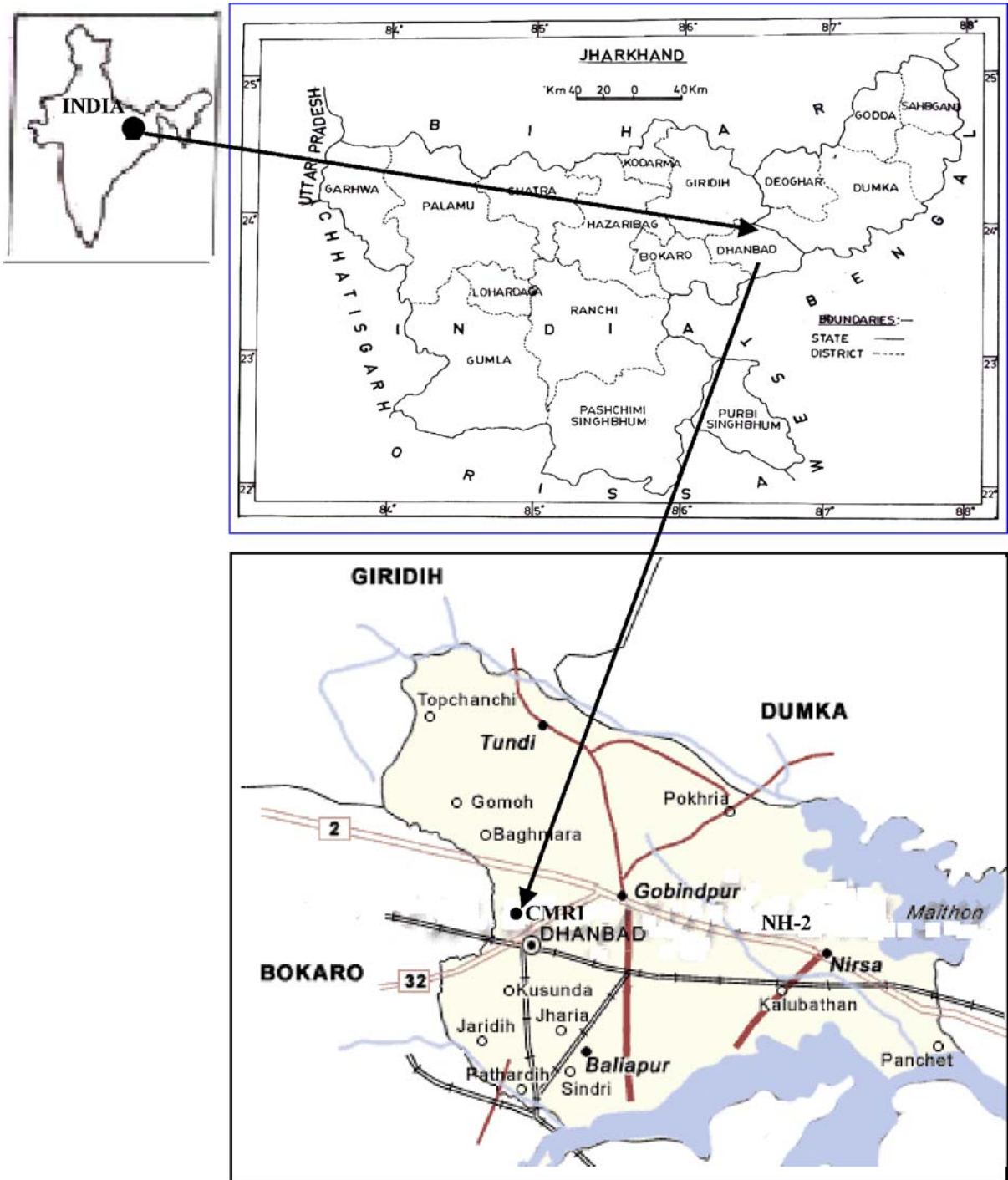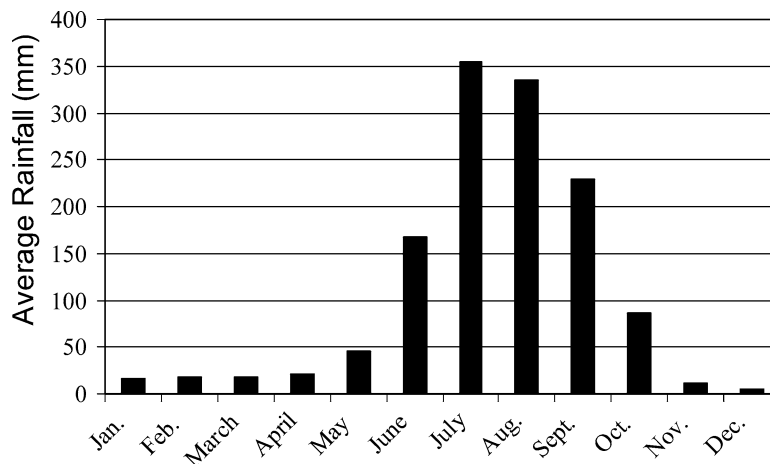
Fig. 1 Map showing location of sampling site

2 Materials and methodology

Rainwater samples (wet deposition) were collected by using a high density polypropylene funnel of 30 m diameter fitted on a 5-litre polyethylene bottle mounted on iron stands (1 meter high) on the roof of institute building (6 m above the ground). The CMRI is residential institute having dense vegetation cover, however the area is surrounded by coal mines and coal based industries like beehive coke ovens, hard coke oven plants

Fig. 2 Monthly variation in rainfall over Dhanbad (Fifty years average)

3 Results and discussion

Mean concentration of major ionic components, electrical conductivity (EC), total dissolved solids (TDS) and pH along with their minimum, maximum values and standard deviation for three monitoring years 2003, 2004 and 2005 are given in Table 1. During the study period, a total 162 event samples were collected and analysed for major ion chemistry. The samples has been further separated in to three seasons: monsoon (July–October), post-monsoon (November–February) and pre-monsoon (March–June).

3.1 pH and acidity

The analytical results show that pH of rainwater ranged between 4.01 and 6.92 indicating acidic to alkaline nature of rainwater as compared to the reference level of 5.6 (Charlson and Rodhe, 1982). The mean pH of the entire monitoring period was 5.37. Investigation of pH of each collected shower sample shows that, monitoring site experiences 91 events ($n = 162$) of the acidic precipitation (<5.6 pH), accounting 56% of the rainfall events (Fig. 3). The pH was found to be more than 5.6 (alkaline) during the non-monsoon and early phase of the monsoon period, but during the late monsoon phase (mid-July to early October), pH tendency was towards the acidity. This may be due to the removal of suspended particulate matter (SPM) containing Ca, Mg, Na and K and lake of proper neutralization of acidic ions in the late monsoon period. In the late monsoon, the concentration of cations gets reduced because of heavy rainfall and removal of atmospheric dust from the

etc. in the vicinity of 10–15 km. The site is 500–600 m away from the road having mixed vehicular traffic of 1500–2000 vehicles per day and about 10 km south of National Highway (NH-II) having dense vehicular traffic of 25,000–35,000 per day. Residential colonies, commercial complexes, coal mines and coal depots lies in the area immediately surrounding the site. The famous Jharia coal filed situated at about 10–12 km south of this site (Fig. 1).

The duration of each sampling was 24 h. To avoid the dry deposition, the collector was opened only during the period of precipitation and it was washed by distilled water in every 24 h interval. The samples were transferred into 1-liter high density polypropylene bottle and brought to the laboratory immediately after collection. pH and conductivity were determined with the help of bench-top pH and conductivity meter. The samples were filtered through 0.45 μm Millipore filter paper and refrigerated for further analysis. Concentration of major anions (Cl, F, NO_3, SO_4) and cations (Ca, Mg, Na, K and NH_4) were determined by Ion Chromatograph (Dionex-120), using anion and cation columns respectively. The analytical precision was maintained through running of known standards. The analytical precision was between 5–10% for different anions and cations measurements. The abundance of total dissolved solids (TDS) in the samples was calculated by adding the measured concentrations (mg $^{-1}$) of all ions. The abundance of individual ions, interelemental correlations and the ratios of different ions i.e. $(NO_3 + Cl)/SO_4$, $(Ca + NH_4)/(NO_3 + SO_4)$ were calculated in micro-equivalent (μeq) unit.

Table 1 Statistical summary of the chemical composition of rainwater over Dhanbad during 2003–2005

Parameters	2003 ($n = 37$)				2004 ($n = 68$)				2005 ($n = 57$)				3 years average ($n = 162$)			
	Min.	Max.	Avg.	Std.Dev.	Min.	Max.	Avg.	Std.Dev.	Min.	Max.	Avg.	Std.Dev.	Min.	Max.	Avg.	Std.Dev.
pH	4.41	6.85	5.30	0.59	4.01	6.92	5.64	0.84	4.10	6.47	5.08	0.70	4.01	6.92	5.37	0.78
EC	4.6	91.6	19.3	19.3	4.0	97.2	22.6	22.5	4.7	178.0	29.6	31.4	4.0	178.0	26.5	25.5
TDS	1.7	29.9	6.3	6.4	1.74	32.7	10.4	8.4	1.57	77.7	11.5	12.6	1.6	77.7	9.8	9.9
F	8.6	36.3	14.6	6.6	6.3	52.2	21.4	10.5	8.9	62.1	16.6	9.9	6.3	62.1	18.2	9.8
Cl	7.1	113.1	23.1	25.2	7.3	168.1	33.5	30.7	3.7	191.8	35.8	45.7	3.7	191.9	31.9	35.9
NO_3	BDL	34.8	7.4	0.48	BDL	92.3	12.9	17.4	BDL	129.0	17.2	21.6	BDL	129.0	12.6	17.9
SO_4	15.4	203.0	53.3	40.3	11.9	229.0	76.8	54.1	8.5	709.9	87.3	107.2	8.5	709.9	74.6	75.2
Ca	5.5	250.5	37.9	52.0	3.5	461.1	100.2	116.8	12.5	603.8	102.4	119.4	3.5	603.8	86.5	108.8
Mg	BDL	65.8	11.4	14.5	BDL	81.4	19.8	18.3	1.7	204.8	24.2	33.5	BDL	204.8	19.4	24.3
Na	1.74	85.3	15.8	19.3	2.2	154.9	27.7	31.2	3.5	141.4	18.9	23.9	1.7	154.8	21.9	26.7
K	BDL	151.9	13.8	31.6	1.28	54.3	13.8	16.4	BDL	270.3	27.0	53.2	BDL	270.3	18.3	36.8
NH_4	1.67	143.3	30.4	29.1	3.9	173.3	48.1	40.3	BDL	300.4	46.4	56.6	BDL	300.4	43.4	44.8
H^+	0.14	38.9	9.2	8.8	0.12	61.7	10.5	15.9	0.34	79.4	20.9	23.1	0.12	79.4	13.8	18.3

Units: Concentration in $\mu eq\ l^{-1}$, except EC ($\mu S\ cm^{-1}$), TDS (mg l^{-1} and pH), BDL = below detection limit.

atmosphere. The occurrence of acidic rains at this site is related to the site-specific activities, predominately by coal mining, mine fire and coal based industries. More that three hundreds medium to large sized coke, coal beneficiation plants and other coal based industries are located in the Dhanbad district.

The pH of natural precipitation is controlled by the dissolved CO_2 and it is greatly influenced by the addition of acidic components (SO_2 & NOx) generated by civil and industrial activities (Primerano *et al.*, 1998). In the atmosphere, both SO_2 and NOx ($NO + NO_2$) are subjected to chemical transformation by oxidants such as H_2O_2, O_3 and OH radicals, which lead to the formation of H_2SO_4 containing aerosols and gaseous HNO_3 (Seinfeld and Pandis, 1998). These two products could then react further under typical condition with NH_3, so that both SO_4 and NO_3 are in the aerosol phase as ammonium sulphate and ammonium nitrate, or may be deposited to the earth's surface by either dry or wet deposition process (Finlayson and Pitts, 1986). The study area is experiencing rapid changes in land-use pattern because of expanding mining activities, reducing vegetation cover and accelerated industrialization, resulted in rapid increase in SO_2 and NOx concentration in the atmosphere (CMRI, 1999). Surface and subsurface coal fire burning throughout the Jharia coalfield (JCF), gives rise to continuous and uncontrolled emission of green house gases like CO_2, NOx, SO_2, CO, CH_4 (methane), C_2H_6 (ethylene), C_3H_6 (propane) etc. Jharia mine fire is one of the largest coalmine fire complexes in the world (Gupta and Prakash, 1998). Today, about seventy coalmine fires are reported from the Jharia coalfield, covering 17.32 km^2 of the area (BCCL, 2003). Atmospheric pollution in China primarily from coal combustion is among the highest in the world (Johnson *et al.*, 1997). Acid rain from SO_2 and NOx is problem in 88 major Chinese cities and the problem has spilled over the Taiwan, Japan, Korea and Philippines (World Resource Institute, 1999). As in the China, JCF fires are responsible for environmental degradation and human suffering including the acid rain events.

3.2 Major ion chemistry

Precipitation quality is a function of its contents of both acids and bases (alkaline) and any attempts to understand the processes causing acid precipitation must deal with the potential acid neutralizing capacity of alkaline materials such as Ca, Mg, Na, K and NH_4. The chemical

Fig. 3 Variation of pH values in different rainfall events during 2003–2005
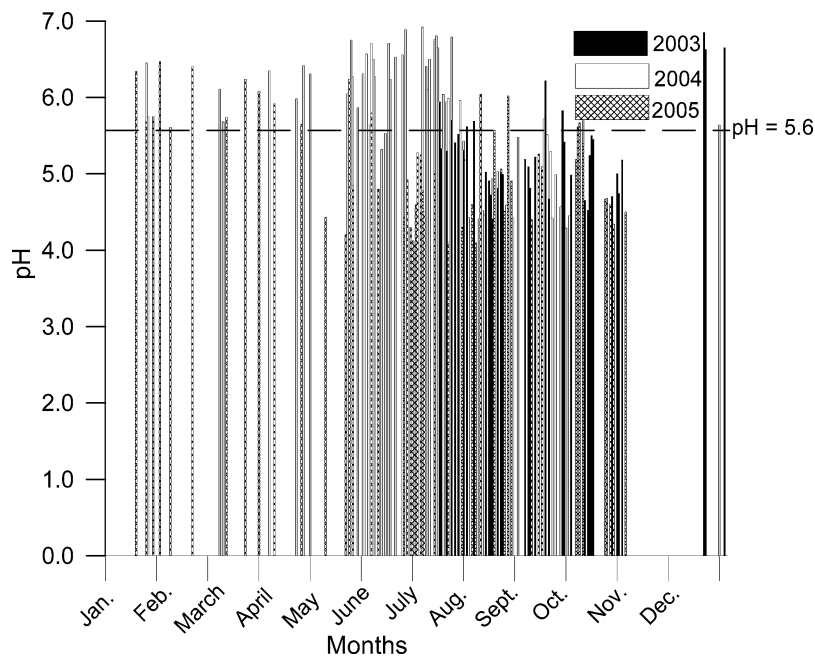
composition of precipitation data of Dhanbad follows a general pattern of $SO_4 > Ca > NH_4 > Cl > F > Na > Mg > K > NO_3$ (Fig. 4a). The contribution of individual cations and anions to the total cationic and anionic mass balance is given in Fig. 4 b&c. Ca and NH_4 are the dominant cations, contributing 40% and 29% of the total cations respectively. It follows by Na (12%) and Mg (11%) and K is the least dominating cation (8%). Among anions, SO_4 is the predominant anion contributing 53% of the total anionic mass balance followed by Cl (21%), F (18%) and NO_3 (8%).

The monthly variation in the concentration of measured cations and anions are illustrated in Fig. 5 a&b. It shows a sharp increase in concentration of Ca, Mg, Na and K during the dry months of pre-monsoon (March–June) and post-monsoon (December–February) and low concentration in wet months (July–October). Seasonal concentrations of major anions (SO_4, Cl, F and NO_3) are also characterized by monsoon minima and non-monsoon maxima. Such seasonal pattern might be caused by the least mean precipitation and enhanced suspended particulates in the lower atmosphere during the dry periods. The higher residence period of particulates favor the reactions with the acids in rainwater and causing the increase of concentration of ionic species especially the dust derived components like Ca, Mg, Na and K during non-monsoon months. The removal of particulates in late monsoon phase cause the de-

crease in concentration of dissolved ions and increase the acidity of rainwater.

The acidic/alkaline nature of the rainwater is the result of balance between acidic and alkaline species. The ratio of $(Ca + NH_4)/(NO_3 + SO_4)$ has been calculated to know the relative significance of these ions to the acidity and alkalinity of the rainwater in the study area. The ratio of $(Ca + NH_4)/(SO_4 + NO_3)$ varies between 0.42 to 5.13 in the analysed rainwater samples and bivariate plot between $(Ca + NH_4)$ and $(SO_4 + NO_3)$ shows that most of the plotted points fall above the equiline, indicating that Ca and NH_4 play an important role in neutralization of acidic ions in rainwater. However, at lower concentration, some plotted points fall below the equiline indicating that Ca and NH_4 alone do not neutralize the acidic ions ($SO_4 + NO_3$), and possibly some other cations are also contributing in this process (Fig. 6a).

The ratio of $(NO_3 + Cl)/SO_4$ indicates the relative importance of these ions in acidification, a ratio of above 1.0 indicates that HNO_3 and HCl influences acidity and the ratio below 1.0 indicates the influence of H_2SO_4 is more (Khemani *et al.*, 1994). The variation diagram between $(NO_3 + Cl)$ vs SO_4 shows that majority of the plotted points fall well below the equiline and average $(NO_3 + Cl)/SO_4$ ratio of 0.60 indicates that the acidity in the study area is greatly influenced by SO_4 (Fig. 6b). The high contribution of SO_4 to the

Fig. 4 Contribution of
different ionic species
towards (a) total ionic mass
(b) total cationic and
(c) anionic mass balance

(a)

(b)

(c)
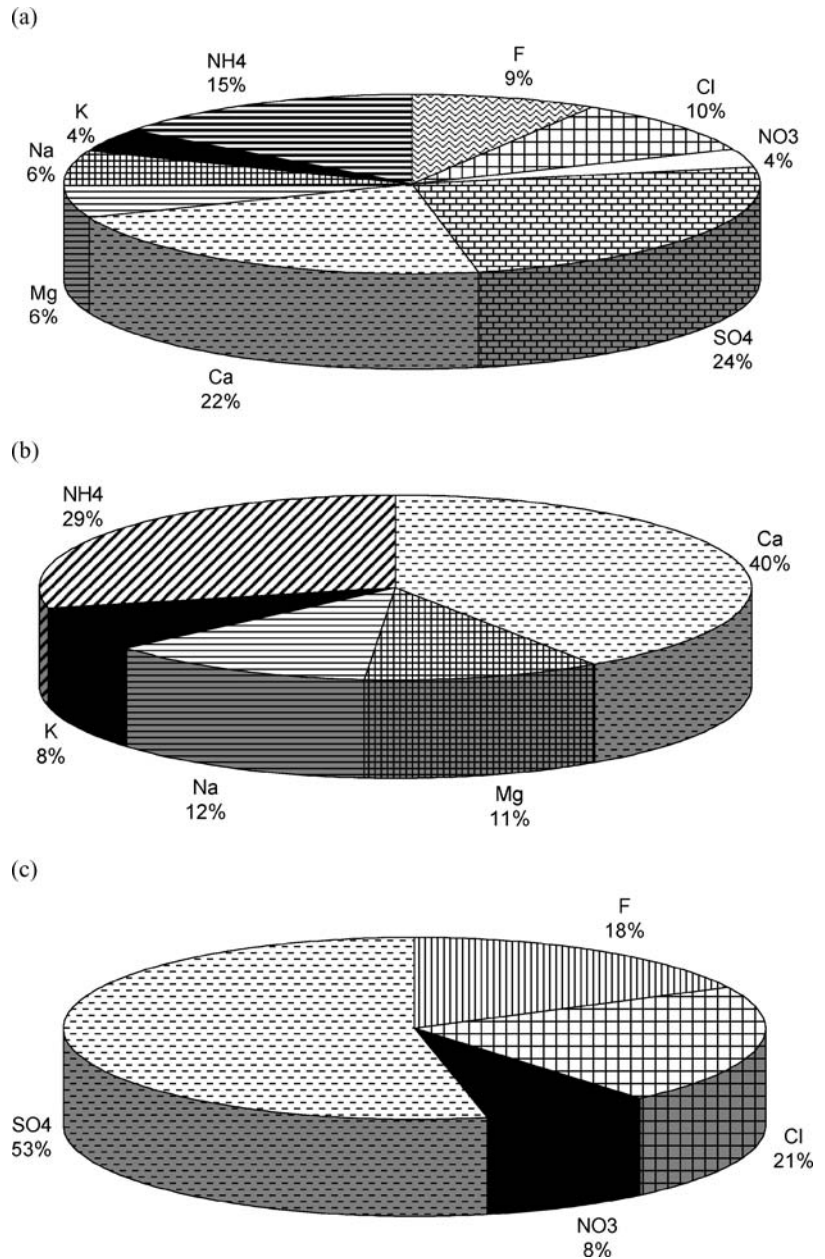
anionic mass (53%) and quite good correlation of SO_4 and NO_3 with Ca (0.80 & 0.72), Mg (0.89 & 0.75), Na (0.70 & 0.68) and K (0.78 & 0.60) suggests that SO_4 and NO_3 in precipitation originate from ionisation of sulphate and nitrate salts, which are produced in the atmosphere from the neutralization of acids by alkaline dusts (Samara *et al.*, 1992).

The contribution of sea salts to ion concentrations in precipitation may be evaluated by comparing the Na/Cl ratio in rain to the seawater. Sea is considered to be the major source of both ions, although they may also be emitted from other industrial or natural sources (Ranor and Hayes, 1982). Table 2 presents the equivalent ionic ratios and estimated non-seas salt (nss) fraction of different ions in Dhanbad rainwater in comparison to the seawater ratios. Mean Cl/Na ratio is higher than the seawater by a percentage of 20–25% indicating that part of the rain chemistry is influenced by the marine

(a)

(b)
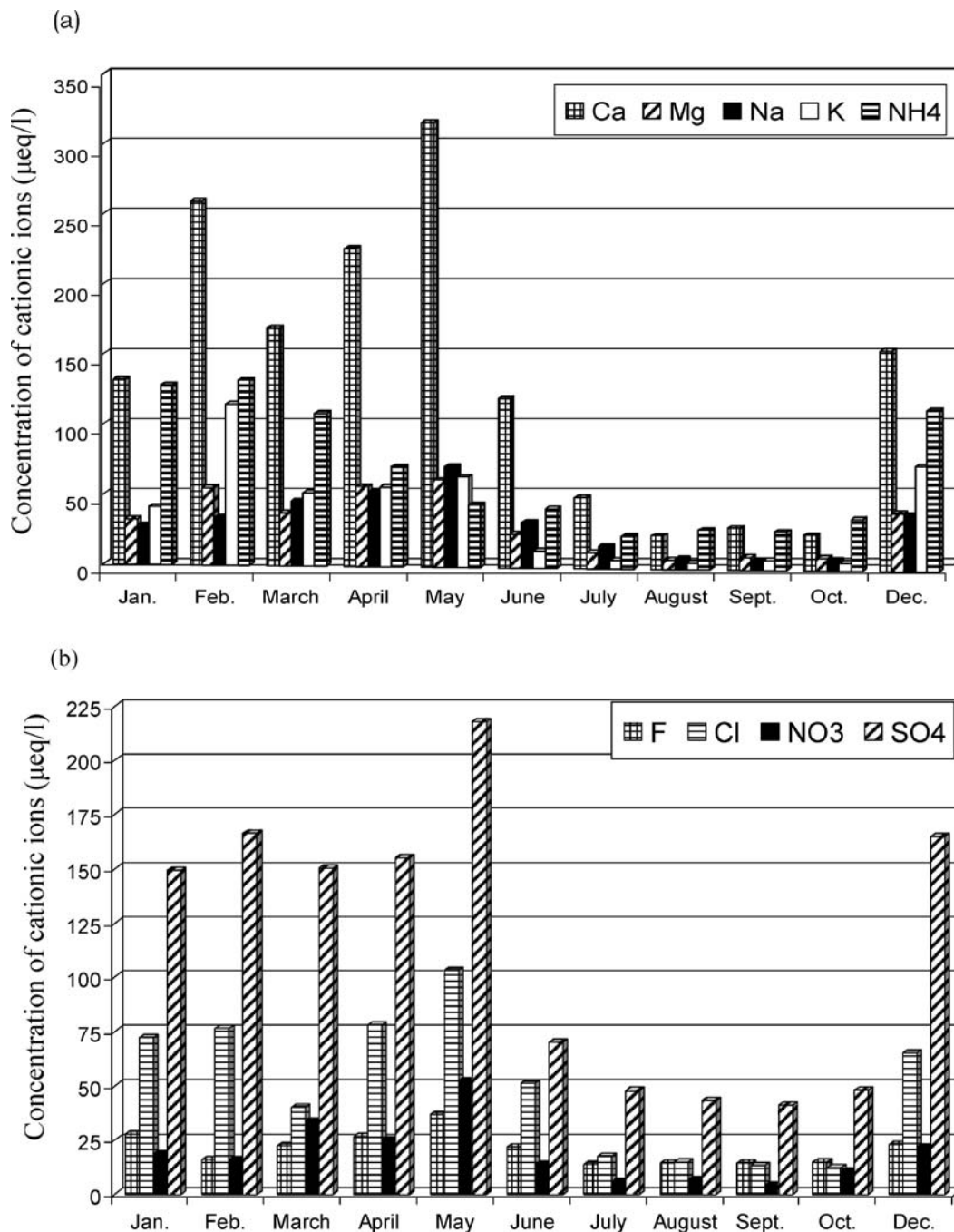
Fig. 5 Monthly variation in mean concentration of measured (a) cations and (b) anions

sprays coming from Bay of Bengal, when winds are favorable, but there must be some other non-marine sources for major ions. Assuming that all Na in rainwater originates from sea salts, the contribution of marine sources was calculated to 4% of SO_4 and 80% of Cl. High nss SO_4 (96%) at Dhanbad shows the anthropogenic influence. The high percentage of non seas salt fractions of Ca (99%) and Mg (95%) indicate the non-marine origin and probably derived from the crustal sources.

Fig. 6 Scattered plot between (a) $(NO_3 + Cl)$ vs SO_4 and (b) $(NH_4 + Ca)$ vs $(NO_3 + SO_4)$

Table 3 compared the chemical composition rainwater of the Dhanbad to some other selected Indian sites. The pH of the present study area is lower than the Indian average (6.5) and the other Indian cities like Agra, Goa, Sinhagad, Pune, Ahmedabad, Lucknow, Hyderabad and Bhubaneswar and is higher than the reported pH of Bangalore, Kalyan, Korba and Chembur. The higher pH of rainwater at Delhi, Agra and other parts of India are due to high loading of alkaline rich atmospheric suspended particulate. The observed low pH of rain water at Dhanbad may be attributed to results of anthropogenic SO_2 and NOx emission from thermal power plants, steel plants, beehive coke ovens, hard coke oven plants besides fuel burning and mine fire around the city. The concentrations of Cl and Na are high at the coastal sites i.e. – Chembur, Goa, Kalyan Colaba, Alibag, Thumba, Bombay and low at the present and other inland sites i.e. – Hyderabad, Delhi, Korba, Pune, Agra etc. The Na and Cl are mostly derived from the oceanic circulation; therefore contribution of sea decreases with increasing distance from the seacoast. The concentration of SO_4 is high at Chembur, Kalyan, Delhi and Bangalore, high industrialized and heavy vehicular locations and at Korba and at present study site, locations with huge deposits of fossil fuels. The higher SO_4 concentration signifies the anthropogenic contribution from the fossil fuel burning, industrial and vehicular emission at these places. The relatively high concentration of NO_3 at Delhi, Kalyan and Bangalore may be attributed to the heavy vehicular traffic in these metro cities.

3.3 Wet deposition of ions

Monthly and total annual bulk deposition levels (meq m^{-2}) of major anions and cations were calculated and given in Table 4. Table shows that the bulk ionic

Table 2 Equivalent ratios of various species to Na and estimated non sea salt (nss) fraction in rain water samples and the corresponding values for sea water

Ion Ratio	Rain Samples	Sea Water	nss fraction %
Cl/Na	1.45	1.17	20.1
K/Na	0.83	0.021	72.4
Ca/Na	3.94	0.044	99.4
Mg/Na	0.88	0.23	95.0
SO$_4$/Na	3.41	0.125	96.3
SO$_4$/NO$_3$	13.51	—	—
(Ca + NH$_4$)/(NO$_3$ + SO$_4$)	1.41	—	—
(NO$_3$ + Cl)/SO$_4$	0.60	—	—

Table 3 Major ion chemistry (volume weighted) of rainwater over Dhanbad and comparison with some other selected sites of India

Locations	pH	F	Cl	NO_3	SO_4	Ca	Mg	Na	K	NH_4	Reference
Present Study	5.3	16.6	27.4	10.2	62.8	70.0	15.6	17.8	13.1	35.3	Present Study
Delhi	5.7	—	140.1	66.8	89.7	133.7	69.6	81.7	44.3	25.8	Ravichandran and Padmanamurty (1994)
Ahmedabad	6.7	—	50	13	37	78	15	41	3.4	30	Rastogi and Sarin (2005)
Dyalbagh (Agra)	7.01	17.6	31.8	22.8	36.4	56.1	45.6	18.4	7.6	40.1	Kumar et al. (2002)
Gopalpura (Agra)	6.5	24.6	31	43	15	134	78	19	3	43	Satsangi et al. (1998)
Lucknow	6.5	4.6	9.9	7.7	9.3	14.9	4.4	8.5	2.4	10.2	Khare et al. (2004)
Korba	4.8	12.2	31.8	25.1	213.0	182.9	42.8	20.7	3.7	15.3	Chandravanshi et al. (1997)
Pune	6.1	—	44	18	23	68	17	39	3	26	Pillai et al. 2001
Hyderabad	6.1	—	46.8	10.3	32.4	119.2	20.4	40.2	35.9	12.8	Kulshrestha et al. (2003)
Bangalore	4.82	—	59.2	26.5	88.8	89.6	12.9	54.9	15	28.8	Shivashankara et al. (1999)
Bhubaneswar	6.2	0.3	18.0	10.0	19.1	20.2	5.2	15.0	1.9	18.7	Das et al. (2005)
Goa	6.3		113.4	5.5	27.4	41.5	24.5	97.2	2.5	5.5	Parashar et al. (2001)
Chembur	4.8	—	140.1	—	421	175	57	96	28	117	Khemani et al. (1989)
Kalyan	5.7	6	112	31	108	93	39	103	26	21	Khemani et al. (1989)
Kalyan	5.28	—	134	66	110	130	48	147	6	14	Naik et al. (2002)
Colaba	6.4	—	171	34	52	155	59	179	6	12	Naik et al. (2002)
Alibag	6.74	—	236	9	36	133	64	220	5	8	Naik et al. (2002)
Thumba	—	—	228	—	14	46	38	207	5.6	—	Sequeria (1976)
Bombay	—	—	138	—	10	36	24	115	3.6	—	Sequeria (1976)
Nilgiris (South India)		—	43	21	20	43	14	46	4	3	Rao et al. (1995)

Units: $\mu eq\ l^{-1}$, except pH.

deposition was dominated by Ca ($89.6\ meq\ m^{-2}$) and SO_4 ($80.4\ meq\ m^{-2}$) and these two ions together with NH_4 ($45.2\ meq\ m^{-2}$) account for about 63% of the total annual ionic mass deposition. The monthly variation in ionic deposition rate is influenced by two processes, firstly the variation in rainfall and secondly by the variation in ionic concentration. No, specific trend in the ionic deposition rate has been observed, however, in general, rainfall amount is negatively correlated with ionic concentration and positively with the ionic deposition rate. The deposition rate of the most of the ions is lower during the non-monsoon months and higher during the peak monsoon months (July–September). On an average, four months i.e. June, July, August and September accounts 82% of the total rainfall and about 63% of the total ionic deposition.

Table 4 Monthly variation in rainfall (mm) and deposition of major ions (in $meq\ m^{-2}$)

	Rainfall (mm)	F	Cl	NO_3	SO_4	Ca	Mg	Na	K	NH_4	Total
January	12.5	0.34	0.90	0.23	1.86	1.64	0.41	0.35	0.51	1.60	7.85
February	24.7	0.40	1.88	0.39	4.11	6.41	1.35	0.84	2.83	3.26	21.47
March	19.6	0.44	0.79	0.65	2.94	3.33	0.73	0.90	1.02	2.13	12.93
April	19.2	0.51	1.50	0.48	2.97	4.35	1.09	1.02	1.08	1.37	14.38
May	54.8	2.02	5.64	2.88	11.93	17.42	3.41	3.92	3.53	2.45	53.21
June	191.5	4.14	9.77	2.66	13.42	23.17	4.56	6.15	2.32	8.12	74.30
July	326.7	4.41	5.68	1.80	15.58	16.47	3.63	5.10	1.89	7.61	62.17
August	311.7	4.39	4.68	2.06	13.47	7.39	2.09	2.21	1.37	8.76	46.41
September	217.9	3.07	2.83	0.87	8.89	6.45	1.92	1.48	1.46	5.97	32.95
October	97.7	1.47	1.18	1.02	4.67	2.46	0.84	0.74	0.50	3.60	16.47
December	3.0	0.07	0.19	0.06	0.49	0.47	0.12	0.12	0.23	0.35	2.11
Total	**1279.3**	**21.2**	**35.1**	**13.1**	**80.4**	**89.6**	**20.1**	**22.8**	**16.7**	**45.2**	**344.3**

4 Conclusions

The chemical composition of precipitation in Dhanbad was analysed to evaluate the temporal variations and the influence of natural and anthropogenic sources. The rain showed acidic to alkaline pH and 56% of the rain events having pH lower than the reference value (5.6). The acidity of precipitation increased in late monsoon months and related to site specific activities. Ca and NH_4 dominate the major ion chemistry in cationic balance and SO_4 in anionic budget. The low ratio of $(NO_3 + Cl)/SO_4$ suggest that acidity is greatly influenced by H_2SO_4 rather than HNO_3. The average $(Ca + NH_4)/(NO_3 + SO_4)$ ratio of 1.4 indicates that Ca and NH_4 play major role in neutralization of acidic ions in rainwater. The dominance of non-sea salt fractions (nss) of majority of the ions and good correlation of SO_4 and NO_3 with the Ca, Mg, Na and K indicated that atmospheric dust and soil play a significant role in precipitation chemistry of Dhanbad city. Ca, SO_4 and NH_4 dominate the bulk ionic deposition and the monthly variation in ionic deposition rate is influenced by rainfall and concentration of ionic species.

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