

## Studies on rainwater and dry depositions at Jaipur, India

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**Abstract :** The rainwater samples were collected at and around Rajasthan University Campus in Jaipur and analyzed for pH, conductance, concentration of ions, viz. bicarbonate, chloride, nitrate, sulfate, calcium, magnesium, sodium and potassium. In addition, heavy metals, viz. iron, copper, lead, zinc, manganese, cobalt and nickel were also determined. The pH of rainwater lied in the range, 6.82–8.45. The ratios of the concentrations of ions relative to sodium ion concentration were determined in both rainwater and soil samples and were found to fit the eq. (A).

$$\{[X]/[Na]\}_{\text{rain}} = 0.96 + 0.95\{[X]/[Na]\}_{\text{soil}} \quad (\text{A})$$

The slope of nearly  $\sim 1$  indicates the soil to be major source of ions in water. The results of ion balance analysis between total concentrations of anions,  $\Sigma[A^{n-}]$ , and total concentrations of cations,  $\Sigma[M^{n+}]$  were in agreement with eq. (B) showing good correlation.

$$\Sigma[A^{n-}] = 0.034 + 0.97\Sigma[M^{n+}] \quad (\text{B})$$

There was a good linear correlation between observed,  $\Lambda_{\text{obs}}$ , and calculated,  $\Lambda_{\text{cal}}$ , conductivities in rainwater as defined by eq. (C).

$$\Lambda_{\text{cal}} = 0.98 + 1.02\Lambda_{\text{obs}} \quad (\text{C})$$

The ion balance analysis, and correlation analysis between observed and calculated conductivities were also done.

Atmospheric dry deposition samples were collected from two sites and analyzed for pH, conductivity and concentrations of major ions. The deposition flux of each ion has been calculated. There was good correlation between  $\Sigma[A^{n-}]$  and  $[M^{n+}]$  and between  $\Lambda_{\text{cal}}$  and  $\Lambda_{\text{obs}}$ . A comparison of pH values of rainwater, dry depositions, soil and groundwater at Jaipur showed these to be generally  $\sim 7$  or more indicating the alkaline nature of all these.

**Keywords :** Dry deposition, wet deposition, rainwater, pH, heavy metals, cations, anions.

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### Introduction

The removal of particulates and gaseous substances from the atmosphere is accomplished by dry and wet deposition processes leading to their deposition on the surface of vegetation, soil, water, buildings etc. The wet deposition is responsible for several chemical reactions within atmospheric aqueous systems<sup>1</sup>. The trace metal ions like iron, manganese, copper etc. catalyze the oxidation of dissolved  $\text{SO}_2$  and increase rainwater acidity. On the other hand, incorporation of alkali and alkaline earth materials, composed of  $\text{Na}^+$  and  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , is able to neutralize hydrogen ions and increase pH.

There are several studies in the area of wet and dry

depositions related to Indian sub-continent<sup>2-16</sup>. Even then, such studies for the State of Rajasthan, which comprises about 10% of the India, are scarce, and only one study, limited to transition metal ions, on the rainwater analysis of Jaipur<sup>8</sup>, which is the State capital of Rajasthan, has been published. In the area of dry depositions, no such study appears to have been undertaken. Keeping this in view, we in this paper report the results of our studies on Jaipur covering 1998-2006 for rainwater and 1998-2004 for dry depositions. An important part of this study is the measurement of heavy metal ions, viz. iron, manganese, cobalt, nickel, lead and zinc, which have largely been ignored in the studies on rainwater from Indian Sub-continent.

A comparison of pH values of rainwater, dry depositions, soil and groundwater has been done.

### Experimental

*Sampling site and collection of rainwater/dry deposition samples :*

Jaipur (26°50'N-75°52'E) lies in a semi-arid zone adjacent to the Thar Desert in the North-Western part of India. It is a fast growing city with a population of about 2.5 million. The average annual long term rain fall is about 64 cm mostly by South-West monsoon.

A total of 120 rainwater samples were collected on event basis mostly in the monsoon season (June-September) beginning the year 1998 and up to 2006 at different locations in and around Rajasthan University Campus, which is situated within the city, surrounded by residential colonies and has heavy traffic around it. The samples were collected by using polyethylene funnels of 30 cm diameter fitted on 10 L capacity polyethylene bottles. The funnels and bottles were cleaned thoroughly every day before the sample collection in order to reduce the effect of dry deposition. The rainwater samples were filtered through Whatman No. 41 filter paper (pore size, 20–25 μm) and were kept at 6 °C in the refrigerator until the metal ion analysis was complete.

Dry deposition samples were collected at two sites, namely, Malviyanagar, a residential colony situated in the South-Eastern part of the city during 1998-2000, and Banipark, again a residential colony situated in the North-Western part of the city, during 2001-2004. The samples were collected on the roofs of the houses situated in two sites. To collect the dry deposition samples, passive polythene funnel facing upward was fitted on to a plastic bottle and kept on the roofs of the houses with the help of iron stand. After exposure for 48 h, dry deposition samples were extracted with 200 ml of distilled water and after shaking kept in refrigerator overnight to allow the particulate material to settle down. Then it was decanted to obtain soluble fractions.

*Analysis of rainwater and aqueous dry deposition extract :*

pH in each case was measured using digital pH meter (Systronics) and conductance was measured using conductivity meter (Systronics). Then the samples were ana-

lyzed for bicarbonate, chloride, nitrate, sulfate, calcium and magnesium. The remaining rainwater/soluble extract was acidified with nitric acid and kept in refrigerator until analysis of sodium and potassium was completed. Sodium and potassium were analyzed by using flame photometer. Sulfate was determined by turbidity method and other cations and anions were determined by titrimetric method.

Bicarbonate was determined by acid-base titrimetry using bromocresol green as indicator. Whereas chloride was determined using argentometric method,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by EDTA-complexometry. The concentrations of transition metal ions were determined with the help of atomic absorption spectrophotometer.  $\text{Na}^+$  and  $\text{K}^+$  were determined using flame photometer. While sulfate and nitrate were determined spectrophotometrically, pH and conductance were determined using usual methods.

*Sampling and analysis of soil :*

In all four soil samples from four different points in Malviyanagar, selected randomly in the vicinity of the site chosen for collection of dry depositions, were lifted. For chemical analysis the known amount of soil was leached in the distilled water. In the leachate, the concentrations of the ions, pH, and electrical conductivity were determined as described.

### Results and discussion

*Soil analysis :*

Since the results of soil analysis are used subsequently for comparison with rainwater and dry deposition results, these are being presented first. The values of conductivity and pH lied in the range :  $91.75 \pm 26.1 \mu\text{S cm}^{-1}$  and  $7.72 \pm 2.0$ , respectively. The concentrations of ions in  $\text{meq L}^{-1}$  were :  $[\text{HCO}_3^-] = 24.6 \pm 1.35$ ;  $[\text{Cl}^-] = 12.86 \pm 4.04$ ;  $[\text{NO}_3^-] = 1.01 \pm 0.41$ ;  $[\text{SO}_4^{2-}] = 2.86 \pm 1.56$ ;  $[\text{Ca}^{2+}] = 21.96 \pm 3.65$ ;  $[\text{Na}^+] = 2.88 \pm 0.52$ ;  $[\text{Mg}^{2+}] = 22.77 \pm 3.82$  and  $[\text{K}^+] = 1.33 \pm 0.25$ . The pH value range 7.45 to 7.85 shows the nature of soil to be alkaline. Incidentally, in the dry deposition studies too, the pH of the extract was almost in the same range.

*Wet deposition studies :*

*Trend in pH :*

The rainwater pH values, which are given in Table 1, lie in the range 6.8–8.47, showing the rainwater to be

Table 1. The concentrations ( $\mu\text{eq L}^{-1}$ ) of anions and alkali and alkaline earth metal ions, and pH and conductivity values in rainwater

Species	1998	1999	2000	2001	2002	2003	2004	2005	2006
[HCO <sub>3</sub> <sup>-</sup> ]	Max.	315	270	315	143	417	261	-	-
	Min.	52	54.2	52.4	11	21	20	-	-
Av.	155.02 ± 57.13	155.58 ± 6.95	150.49 ± 62.32	83.31 ± 32.45	154.92 ± 81.06	144.84 ± 63.99	92.33 ± 47.47	-	-
[Cl <sup>-</sup> ]	Max.	217	282	327.1	281	507	331.6	-	-
	Min.	93	93	93	63	10.4	20	-	-
Av.	132.15 ± 34.80	175.75 ± 60.15	135.07 ± 45.9	164.09 ± 62.10	158.78 ± 87.87	139.26 ± 71.27	100.92 ± 54.12	-	-
[NO <sub>3</sub> <sup>-</sup> ]	Max.	48.4	56.4	32.2	24.2	62	48	-	-
	Min.	8.1	8.1	8.1	5.2	0.5	0.8	-	-
Av.	14.53 ± 8.22	22.16 ± 12.08	16.10 ± 5.85	15.21 ± 4.83	13.08 ± 9.80	16.42 ± 10.53	9.41 ± 7.55	-	-
[SO <sub>4</sub> <sup>2-</sup> ]	Max.	104	83.2	83.2	83	156	80.1	-	-
	Min.	32.2	12.5	20.8	10.5	3.5	1.5	-	-
Av.	55.4 ± 19.86	48.36 ± 15.72	48.53 ± 13.86	48.05 ± 18.11	32.87 ± 19.19	44.21 ± 24.14	24.83 ± 18.60	-	-
[Ca <sup>2+</sup> ]	Max.	319	259.5	379.2	400	469	356.2	-	-
	Min.	39.9	59.3	39.9	80	25	39	-	-
Av.	141.84 ± 61.48	145.24 ± 62.41	97.44 ± 58.70	173.81 ± 71.36	150.13 ± 99.50	170.66 ± 80.44	120.48 ± 60.56	-	-
[Mg <sup>2+</sup> ]	Max.	178.2	149.9	202.4	118.2	345	241	-	-
	Min.	80.6	39.9	19.9	10	21	15.7	-	-
Av.	124.28 ± 29.89	84.22 ± 38.88	56.6 ± 30.9	67.34 ± 26.93	109.82 ± 50.52	101.94 ± 37.37	77.68 ± 38.01	-	-
[Na <sup>+</sup> ]	Max.	152.2	165.3	64.2	87	61	78.5	-	-
	Min.	4.3	17.4	2.1	2.5	2	1.5	-	-
Av.	42.97 ± 30.19	44.28 ± 31.35	19.41 ± 15.17	20.50 ± 16.31	17.27 ± 16.41	40.11 ± 30.20	15.72 ± 15.11	-	-
[K <sup>+</sup> ]	Max.	20.5	48.6	23	33	25	34.1	-	-
	Min.	1.54	1	1	1.5	1.5	1	-	-
Av.	7.7 ± 5.11	14.07 ± 11.63	7.56 ± 5.7	8.29 ± 5.93	5.57 ± 5.55	9.52 ± 11.12	7.95 ± 6.90	-	-
pH	Max.	7.5	7.6	7.6	7.6	7.52	7.71	8.47	8.33
	Min.	7.0	7.0	6.9	6.8	6.95	6.98	7.3	6.78
Av.	7.2 ± 0.21	7.2 ± 0.20	7.1 ± 0.21	7.0 ± 0.20	7.1 ± 0.18	7.1 ± 0.22	7.1 ± 0.19	7.7 ± 0.32	7.6 ± 0.55
Conductivity ( $\mu\text{S cm}^{-1}$ )	Max.	71	38	51	40	38	85	-	-
	Min.	14	15	20	19	11	11	-	-
	Av.	39 ± 18.5	27.3 ± 7.9	37 ± 10.9	28.8 ± 10.2	25.8 ± 10.1	32.9 ± 15.8	30.1 ± 19.7	-

alkaline as compared to the reference<sup>1,10</sup> pH of 5.6. Somewhat lower pH values have been reported for neighbouring cities of Agra and New Delhi<sup>6,7,18</sup>. The temporal variation in pH for study period is shown in Fig. 1. The pH data for 11 years including 1996-1997 data published earlier for Jaipur city<sup>8</sup> are available for discerning the trend in pH variation. The temporal variation in average annual pH is shown in Fig. 2, which passes through a minimum around 2001. The decrease in pH may be linked to spurt in anthropogenic sources and human activities. The increase in pH since 2004 is probably due to massive construction boom that started around 2003 and still continues resulting in the increased release of alkaline material to the atmosphere. On the whole, trend line in Fig. 2 indicates only a slight decrease ( $\sim 3\%$ ) in pH.

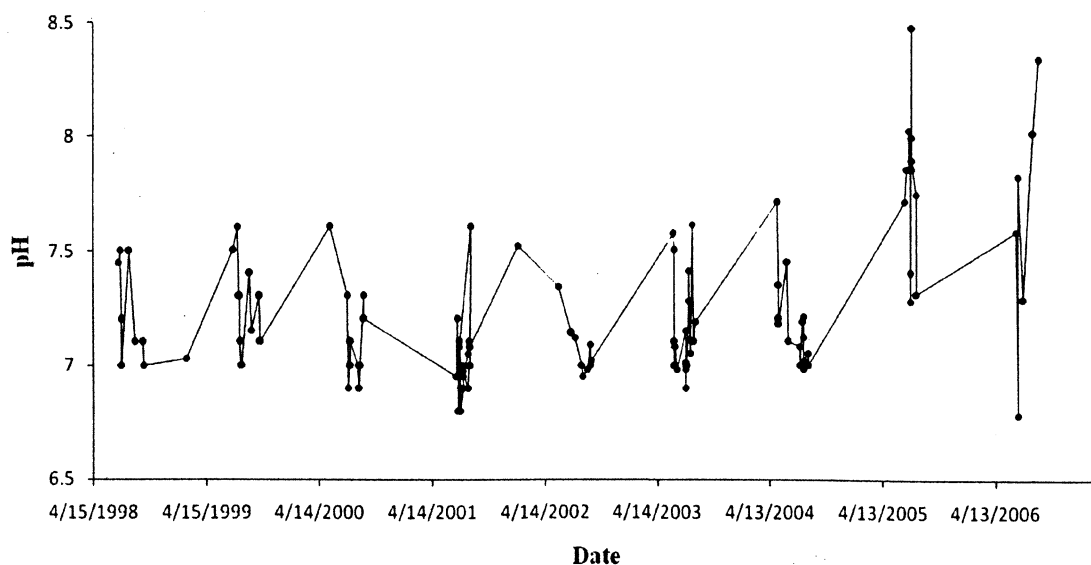


Fig. 1. The temporal variation of pH during 1998-2006.

The average rainfall in the region is low, generally scattered and scanty. Many a time, it may rain in one part of city leaving the other part completely dry. So only on few occasions sequential samples from a particular rainfall event could be collected. We got such opportunities in the 2002-2004, and the analytical data for these samples are presented in Table 2. An examination of the results shows the pH, conductance, individual and total ion concentrations in sequential rainwater samples, pertaining to a particular continuous rain event, to decrease in general. Similar results have been reported previously<sup>20</sup>. This can be explained as follows. Composition of initial part of

rain fall is largely controlled by wash-out process through scavenging of suspended particulate matter (SPM), which is largely alkaline, and gaseous constituents. As the rainfall progressed, the amount of SPM available for wash out decreased and hence the pH also decreased.

#### Major ions :

The average concentrations of major ions, pH and electrical conductivity along with their minimum and maximum values and standard deviations are given in Table 1. The concentrations of trace heavy metals, viz. Cu, Pb, Zn, Ni, Co, Fe and Mn, which act as catalyst in several aqueous phase atmospheric oxidation reactions of sulfur dioxide<sup>1,19,21</sup>, were also determined and are collected in Table 3.

The average values of ion concentrations in meq L<sup>-1</sup> together with their relative contribution in parenthesis, pertaining to the entire study period, were : [HCO<sub>3</sub><sup>-</sup>] = 124.4 ± 79.7 (21%); [Cl<sup>-</sup>] = 142.01 ± 87.7 (24%); [NO<sub>3</sub><sup>-</sup>] = 14.97 ± 12.3 (2.5%); [SO<sub>4</sub><sup>2-</sup>] = 41.38 ± 27.6 (7%); [Ca<sup>2+</sup>] = 144.56 ± 99.5 (24.5%); [Mg<sup>2+</sup>] = 86.83 ± 55.9 (14.7%); [Na<sup>+</sup>] = 27.4 ± 32.5 (4.6%) and [K<sup>+</sup>] = 8.78 ± 10.2 (1.5%). The relative average ionic concentrations are in the order : Ca<sup>2+</sup> > Cl<sup>-</sup> > HCO<sub>3</sub><sup>-</sup> > Mg<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> > Na<sup>+</sup> > NO<sub>3</sub><sup>-</sup> > K<sup>+</sup>.

For estimating contribution of sea salt fraction (SSF) and non-sea salt fraction (nSSF) to the rainwater, usu-

**Table 2.** Results of chemical analysis of sequential rainwater samples (2002-2004)

Event	Date	pH	Cond.	Ionic concentrations ( $\mu\text{eq L}^{-1}$ )							
			( $\mu\text{S cm}^{-1}$ )	[HCO <sub>3</sub> <sup>-</sup> ]	[Cl <sup>-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[Ca <sup>2+</sup> ]	[Mg <sup>2+</sup> ]	[Na <sup>+</sup> ]	[K <sup>+</sup> ]
1	08-Sep-02 A	7.09	38.00	130.00	124.80	5.50	34.00	125.00	118.10	31.00	5.00
	08-Sep-02 B	7.00	20.00	ND	ND	ND	ND	50.50	62.00	2.00	1.50
2	08-Jun-03 A	7.10	55.00	144.00	78.00	32.00	40.00	74.00	65.00	ND	ND
	08-Jun-03 B	7.00	19.00	80.00	56.00	5.00	20.00	69.00	74.00	41.00	2.00
3	11-Jun-03 A	7.08	28.00	90.00	141.00	8.00	20.00	149.00	82.00	4.00	0.20
	11-Jun-03 B	7.02	20.00	ND	ND	ND	ND	ND	ND	ND	ND
4	13-Jul-03 A	7.15	63.00	180.00	183.00	32.00	156.00	309.00	156.00	95.00	38.00
	13-Jul-03 B	6.90	31.00	96.00	112.00	8.00	40.00	94.00	65.00	ND	ND
5	06-Aug-03 A	7.61	60.00	213.00	239.00	14.00	48.00	239.00	123.00	126.00	30.00
	06-Aug-03 B	7.10	39.00	ND	ND	ND	ND	ND	ND	ND	ND
6	11-May-04 A	7.35	55.00	185.00	171.00	10.20	40.00	211.00	123.00	50.00	10.00
	11-May-04 B	7.20	31.00	90.00	90.00	14.60	18.00	109.00	79.00	12.30	1.00
	11-May-04 C	7.18	12.00	20.00	52.00	2.00	8.50	39.00	29.00	3.50	1.00
7	18-July-04 A	7.08	42.00	100.00	145.00	8.00	5.00	110.00	125.00	12.00	8.00
	18-July-04 B	7.00	14.00	40.00	20.00	0.80	1.50	39.00	18.00	2.00	4.10
8	30-July-04 A	7.12	35.00	131.00	124.00	8.00	29.00	148.00	129.60	4.90	1.50
	30-July-04 B	6.80	23.00	54.90	71.00	3.00	30.00	93.00	60.70	3.10	2.00
	30-July-04 C	6.98	15.00	60.00	75.90	1.50	10.80	69.00	65.00	7.50	5.00
9	16-Aug-04 A	7.05	24.00	110.00	63.00	8.00	40.00	127.00	77.00	10.00	16.00
	16-Aug-04 B	7.00	15.00	25.00	60.00	3.00	11.60	50.00	37.00	4.50	3.00
	16-Aug-04 C	7.00	11.00	31.00	51.00	5.10	10.60	53.00	33.00	8.10	3.00

**Table 3.** Average concentrations (mg L<sup>-1</sup>) of heavy trace metal ions in rainwater of Jaipur city during 1998-2006

Year	Cu	Pb	Zn	Ni	Co	Fe	Mn
1998	0.016 ± 0.008	0.01 ± 0.0	0.018 ± 0.002	0.005 ± 0.002	Bdl	-	0.004 ± 0.002
1999	0.04 ± 0.015	0.01 ± 0.0	0.015 ± 0.005	0.005 ± 0.0	0.0015 ± 0.007	0.015 ± 0.005	0.0015 ± 0.0005
2000	0.011 ± 0.05	0.01 ± 0.0	0.014 ± 0.033	0.009 ± 0.004	0.001 ± 0.0	0.12 ± 0.04	0.0028 ± 0.0008
2001	0.014 ± 0.004	0.01 ± 0.0	0.022 ± 0.008	0.038 ± 0.022	0.032 ± 0.012	0.13 ± 0.056	0.0034 ± 0.0012
2002	0.0198 ± 0.002	0.007 ± 0.003	0.0126 ± 0.001	0.0074 ± 0.003	0.0064 ± 0.002	-	0.0015 ± 0.0008
2003	0.0125 ± 0.005	0.0045 ± 0.002	0.0122 ± 0.006	0.005 ± 0.004	0.0045 ± 0.002	-	0.003 ± 0.0008
2004	0.0093 ± 0.004	0.0072 ± 0.003	0.018 ± 0.004	0.006 ± 0.004	0.0053 ± 0.003	-	0.0021 ± 0.001
2005	0.02 ± 0.013	<0.1	0.031 ± 0.012	0.01 ± 0.0	0.01 ± 0.003	0.15 ± 0.05	0.004 ± 0.001
2006	0.0096 ± 0.002	<0.05	0.05 ± 0.02	Bdl	Bdl	0.13 ± 0.04	0.0028 ± 0.0007

Bdl = Below detection limit.

ally, the ratios, [Ion]/[Na<sup>+</sup>] in rainwater are calculated and compared with corresponding values for sea water<sup>3,15,20</sup>. A comparison of these ratios shows (Table 4) these ratios to be relatively very high in rainwater as compared to sea water<sup>3,22</sup>. For example, compared to the recommended [Cl<sup>-</sup>]/[Na<sup>+</sup>] ratio of 1.17 in sea water, the value of this ratio in rainwater lies in the range 3.07–9.19. Likewise, [Ca<sup>2+</sup>]/[Na<sup>+</sup>] ratio in rainwater is also very high. The rainwater ratios compare favorably with

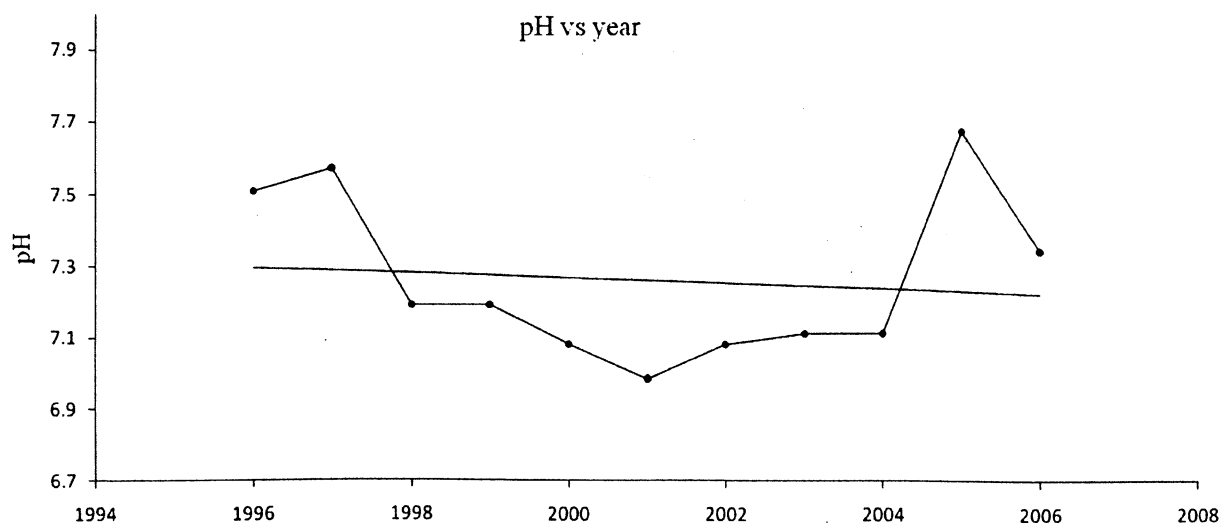
these ratios for soil (Table 4), indicating the contribution of anthropogenic or crystal sources to be the main cause for such high ratios. Indeed, the values of SSF and nSSF support this (Table 4). Expectedly, the plot of the {[Ion]/[Na<sup>+</sup>]}<sub>rain</sub> versus {[Ion]/[Na<sup>+</sup>]}<sub>soil</sub> (Fig. 2) is almost linear defined by eq. (1).

$$\{[X]/[Na]\}_{\text{rain}} = 0.96 + 0.95\{[X]/[Na]\}_{\text{soil}} \quad (1)$$

Among cations, the concentration of Ca<sup>2+</sup> is seen to be

**Table 4.** [X]/[Na<sup>+</sup>] ratios ions in rainwater, sea water and soil and non sea salt fraction (nSSF) and sea salt fraction (SSF) in percent

	Sea water	Rainwater								Average rainwater	Soil	nSSF (%)	SSF (%)
		1998	1999	2000	2001	2002	2003	2004	2004				
K/Na	0.021	0.179	0.323	0.389	0.478	0.32	0.23	0.5	0.35	2.05	94	6	
Ca/Na	0.044	3.35	3.28	5.02	9.8	8.68	4.25	7.66	6.005	5.3	99	1	
SO <sub>4</sub> /Na	0.125	1.34	1.09	2.46	2.67	1.9	1.1	1.57	1.73	2.08	92	8	
NO <sub>3</sub> /Na	0.00002	0.34	0.5	0.87	0.74	0.75	0.41	0.59	0.6	0.94	99.9	0.1	
Mg/Na	0.23	2.89	1.9	2.92	3.02	6.35	2.54	4.94	3.51	6.42	93	7	
Cl/Na	1.17	3.07	4.16	6.96	8.66	9.19	3.47	6.41	5.99	6.9	80	20	

**Fig. 2.** The temporal variation of average annual pH during 1996-2006.

very high (24.5%). Excess Ca<sup>2+</sup> appears to be a general feature of monsoon precipitation in India<sup>25,26</sup>. Indeed, the major contribution of Ca<sup>2+</sup> originates from soil, which is major contributor to aerosols in India. The soil analysis data presented earlier confirm this. It is seen that Ca<sup>2+</sup> together with Mg<sup>2+</sup> contribute the most to the ionic concentration of soil.

Recently, Obaidy and Joshi<sup>3</sup> for Roorkee – North Indian city in Uttarakhand – suggested the rainwater acidity to originate primarily from sulphuric and nitric acids and its neutralisation by Ca<sup>2+</sup> and Mg<sup>2+</sup>. On this basis, they considered the ratio,  $\frac{[SO_4^{2-}] + [NO_3^-]}{[Ca^{2+}] + [Mg^{2+}]}$  or {TA/TC} to be an indicator of alkaline or acidic nature of rainwater. If this ratio is greater than unity, it indicates the rainwater to be acidic. On the other hand, if this ratio is less than one, the rainwater should be alkaline. The value of {TA/TC} in our case is 0.24,

which indicates the rainwater to be alkaline as found experimentally. The values of {TA/TC} followed by pH for some Indian cities are : 0.24, 7.17 (Jaipur, 1998-2006); 0.34, 7.02 (Roorkee)<sup>3</sup>; 0.24, 7.06 (Agra, 1991)<sup>13</sup>; 0.42, 7.00 (Agra, 1991)<sup>16</sup>; 0.29, 7.03 (Agra, 1995)<sup>13</sup>; 0.54, 7.07 (Agra, 1996)<sup>13</sup>; 2.99, 4.42 (Delhi, 1994); 3.95, 5.7 (Delhi, 1996)<sup>18</sup>; 4.04, 6.7 (Delhi, 1996); 0.32, 6.3 (Pune, 1989)<sup>26</sup>; 0.45, 6.50 (Pune, 1996)<sup>18</sup>; 1.05, 5.70 (Kalyan, 1989)<sup>26</sup>; 0.79, 6.44 (Chembur, 1994)<sup>24</sup> and 0.50, 6.30 (Goa, 1996)<sup>18</sup>. These data show that in all those cases, where {TA/TC} ratio is low, the rainwater is alkaline.

For an ion balance analysis, the relationship between  $\Sigma[M^{n+}]$  and  $\Sigma[A^{n-}]$ , where  $\Sigma[M^{n+}]$  and  $\Sigma[A^{n-}]$  represent total concentrations of cations and anions, respectively, was examined. The least square plot of  $\Sigma[A^{n-}]$  versus  $\Sigma[M^{n+}]$  (Fig. 3) was linear (correlation coefficient = 0.99) and defined by eq. (2).

$$\Sigma[A^{n-}] = 0.034 + 0.97\Sigma[M^{n+}] \quad (2)$$

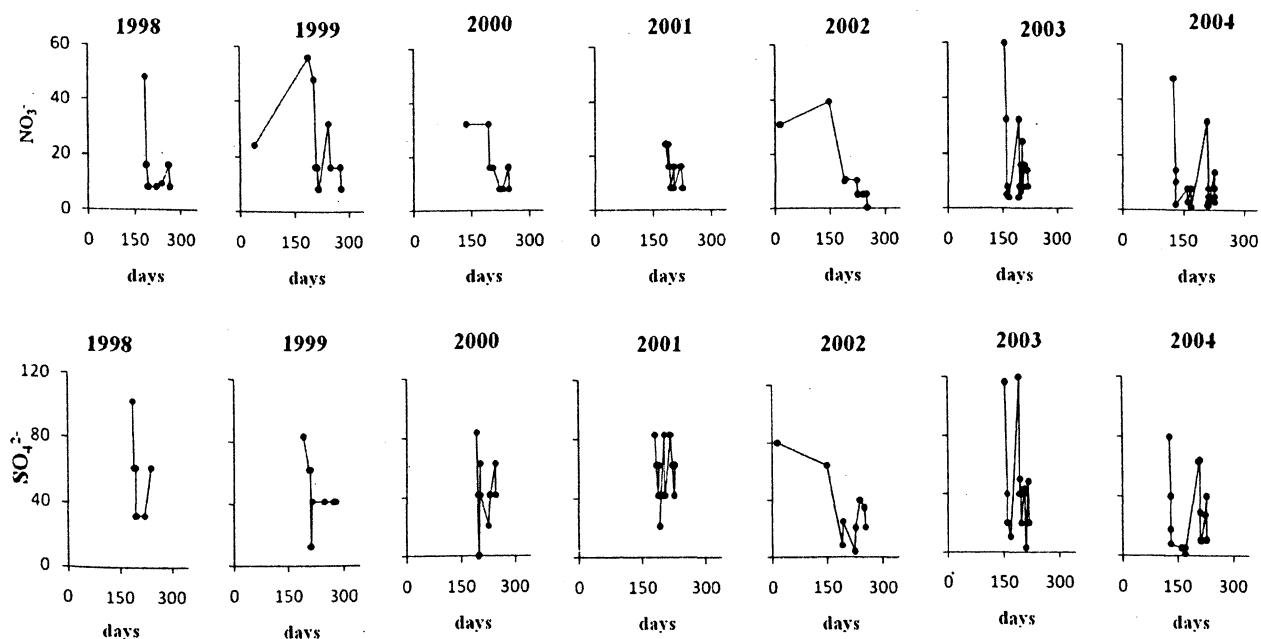


Fig. 3. The temporal variation in concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  during 1998-2004.

Similar results of ion balance analysis have been reported by Rastogi and Sarin<sup>5</sup> for Ahmedabad situated in Gujarat state, which is contiguous to Rajasthan state. The values of slope and correlation coefficient of eq. (2) indicate the excellent correlation. Harrison *et al.*<sup>27</sup> have suggested that values of ion balance,  $R = \Sigma[\text{M}^{n+}]/\Sigma[\text{A}^{n-}]$ , should be considered consistent, if  $0.95 < R < 1.05$  and questionable, if  $0.85 > R > 1.05$ , where  $R$  is correlation coefficient. Incidentally, in most cases  $\Sigma[\text{A}^{n-}]$  was higher than  $[\text{M}^{n+}]$ . This could be due to non-determination of ammonium ion concentration.

Subsequently, the relation between calculated conductivity,  $\Lambda_{\text{cal}}$ , and observed conductivity,  $\Lambda_{\text{obs}}$ , was examined. And the plot of  $\Lambda_{\text{cal}}$  and  $\Lambda_{\text{obs}}$  was linear (Fig. 4) defined by eq. (3).

$$\Lambda_{\text{cal}} = 0.98 + 1.02\Lambda_{\text{obs}} \quad (3)$$

The values of  $\Lambda_{\text{cal}}$  were calculated using eq. :  $\Lambda_{\text{cal}} = \Sigma \lambda_i^{\circ} C_i$ , where  $\lambda_i^{\circ}$  is the equivalent conductance at infinite dilution of the ion, and  $C_i$  is the concentration of that ion in eq  $\text{L}^{-1}$ . The value of the slope is 1.02 (eq. (3)), which is almost the same as ideal value of unity. The values of  $\Lambda_{\text{cal}}$  are in general, 15% higher than  $\Lambda_{\text{obs}}$  values. This is probably due to the use of  $\lambda_i^{\circ}$  values<sup>5</sup>, which are always higher than the  $\lambda_i$  values of solutions of finite ionic con-

centration. Keeping this in view, the agreement in  $\Lambda_{\text{obs}}$  and  $\Lambda_{\text{cal}}$  is considered good and this testifies the accuracy of present measurements.

#### Trace heavy metal ions :

In this study, the trace heavy metals namely Cu, Zn, Ni, Co, Fe, Mn and Pb have also been determined in rainwater samples and the values are given in Table 4. It must be pointed out that the transition metals play an important role in the oxidation of  $\text{SO}_2$  dissolved in atmospheric water as catalysts<sup>1,19,21</sup>. The concentrations of iron, copper, cobalt and manganese are seen to be significant and sufficient to catalyze aqueous  $\text{SO}_2$  autoxidation<sup>19</sup> in atmospheric waters.

#### Dry deposition studies :

##### pH of dry deposition extracts :

The year wise maximum, minimum and average pH values (in that order) at two sites were : {Malviyanagar (1999) 7.80, 6.95,  $7.48 \pm 0.25$ ; (2000) 7.60, 7.00,  $7.23 \pm 0.14$ ; (2001) 7.42, 6.90,  $7.15 \pm 0.12$ }; {Banipark (2002) 7.50, 7.00,  $7.22 \pm 0.17$ ; (2003) 7.67, 6.94,  $7.28 \pm 0.25$ ; (2004) 7.60, 6.90,  $7.24 \pm 0.25$ }. In all cases, the pH of dry depositions is  $\sim 7.0$  or more. The temporal variation in pH is shown in Fig. 5. The observed pH values indicate the dry depositions to be alkaline, owing

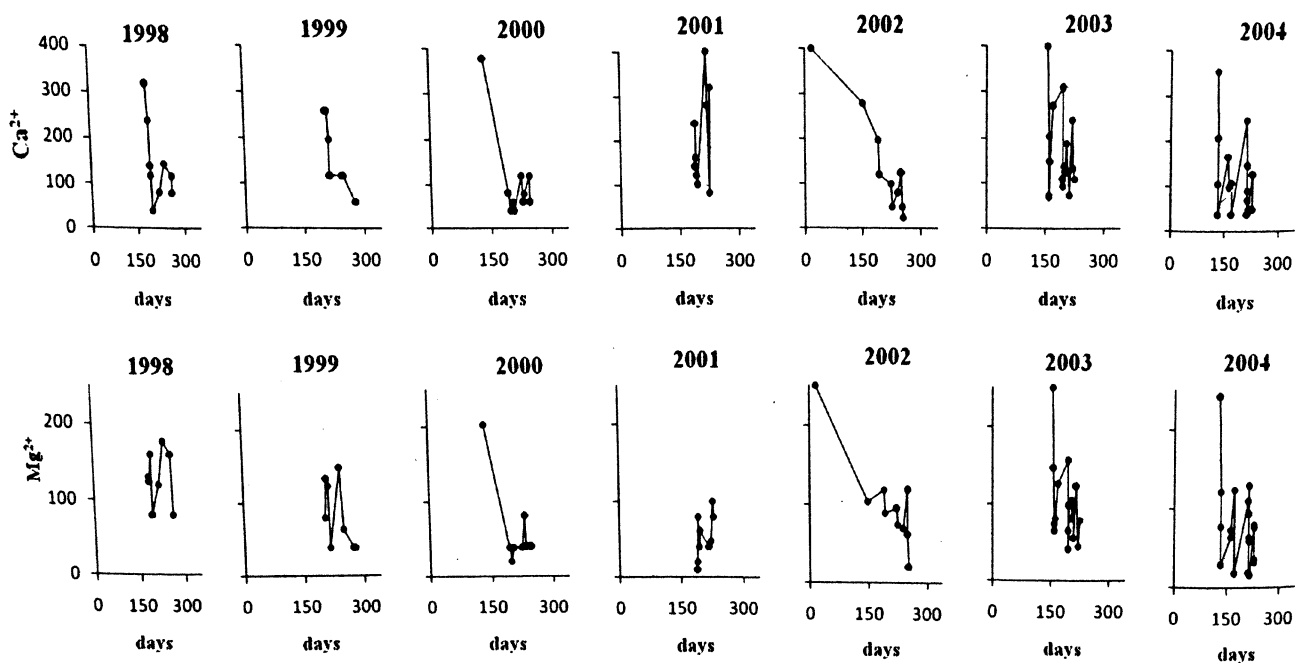


Fig. 4. The temporal variation in concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  during 1998-2004.

$$\{[X]/[Na]\}_{\text{rain}} = 0.96 + 0.95\{[X]/[Na]\}_{\text{soil}}$$

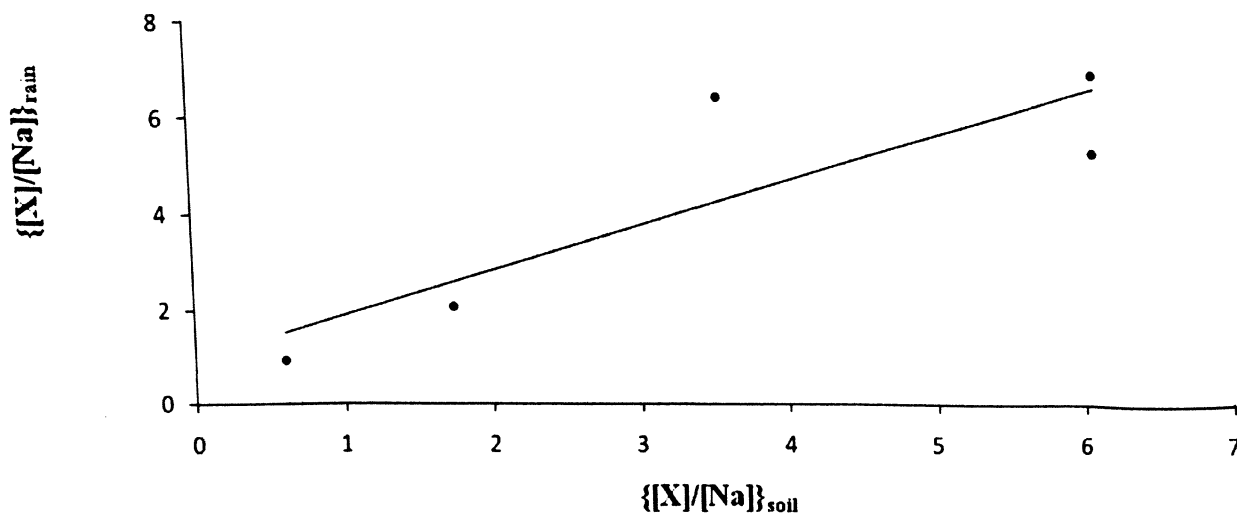


Fig. 5. The plot of  $\{[X]/[Na]\}_{\text{rain}}$  versus  $\{[X]/[Na]\}_{\text{soil}}$

to the neutralization of acid by alkaline materials such as  $\text{CaCO}_3$  and  $\text{MgCO}_3$  present in soil dust<sup>6</sup>. The high pH values observed are in agreement with the high concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{HCO}_3^-$  ions. This is the reason for alkaline nature of rainwater as discussed

earlier. In general, the values of pH are low in the month of July to October, i.e. monsoon season. And except few exceptions, the pH values are high in the summer (March-June).

The results of  $\Sigma[\text{A}^n]$  and  $\Sigma[\text{M}^n]$  and  $\Lambda_{\text{cal}}$  and  $\Lambda_{\text{obs}}$



correlations were defined by eqs. (4–7) at two sites :

Malviyanagar (1999-2001) :

$$\Sigma[A^{n-}] = 0.018 + 0.97\Sigma[M^{n+}]$$

(Correlation coefficient = 0.98) (4)

$$\Lambda_{cal} = -1.78 + 1.28\Lambda_{obs}$$

(Correlation coefficient = 0.98) (5)

Banipark (2001-2004) :

$$\Sigma[A^{n-}] = 0.025 + 0.99\Sigma[M^{n+}]$$

(Correlation coefficient = 0.89) (6)

$$\Lambda_{cal} = 14.9 + 0.89\Lambda_{obs}$$

(Correlation coefficient = 0.85) (7)

There is good correlation between  $\Sigma[A^{n-}]$  and  $\Sigma[M^{n+}]$ . The values of  $\Lambda_{cal}$  calculated are higher, in general, than  $\Lambda_{obs}$ , which appears to be due to use of  $\lambda_i^0$  values as explained earlier.

*Deposition fluxes :*

The average deposition fluxes for measured ions are given in Table 5 along with maximum and minimum val-

ues and standard deviations. The overall average deposition fluxes are : ( $[HCO_3^-] = 23.2 \pm 5.36$  (Malviyanagar),  $15.7 \pm 4.99$  (Banipark);  $[Cl^-] = 18.66 \pm 5.37$  (Malviyanagar),  $19.49 \pm 3.5$  (Banipark);  $[NO_3^-] = 1.19 \pm 0.72$  (Malviyanagar),  $1.42 \pm 0.58$  (Banipark);  $[SO_4^{2-}] = 3.79 \pm 0.95$  (Malviyanagar),  $3.22 \pm 1.1$  (Banipark);  $[Ca^{2+}] = 10.78 \pm 3.66$  (Malviyanagar),  $8.57 \pm 1.8$  (Banipark);  $[Mg^{2+}] = 3.09 \pm 1.38$  (Malviyanagar),  $2.49 \pm 0.9$  (Banipark);  $[Na^+] = 3.21 \pm 1.98$  (Malviyanagar),  $2.68 \pm 1.3$  (Banipark) and  $[K^+] = 2.06 \pm 1.07$  (Malviyanagar),  $1.66 \pm 0.87$  (Banipark). Their comparison shows these to follows the order :  $HCO_3^- > Cl^- > Ca^{2+} > SO_4^{2-} > Na^+ > Mg^{2+} > K^+ > NO_3^-$  at Malviyanagar. On the other hand, at Banipark the order of deposition fluxes to be  $Cl^- > HCO_3^- > Ca^{2+} > SO_4^{2-} > Na^+ > Mg^{2+} > K^+ > NO_3^-$ . There is little difference in the deposition fluxes of ions other than bicarbonate at the two sites except the bicarbonate, which is about 50% higher at Malviyanagar then at Banipark. It indicates the decline in bicarbonate source during 2001-2004 as compared to 1999-2000.

Table 5. The values of dry deposition fluxes ( $mg\ m^{-2}\ d^{-1}$ )

Species	Malviyanagar			Banipark			
	1999	2000	2001	2002	2003	2004	
[HCO <sub>3</sub> <sup>-</sup> ]	Max.	26.32	31.36	46.66	23.62	24.06	28.02
	Min.	15.32	14.69	14.68	8.90	8.90	8.81
	Av.	22.4 ± 2.83	22.97 ± 3.28	25.68 ± 7.63	15.82 ± 2.67	17.34 ± 4.7	14.88 ± 5.49
[Cl <sup>-</sup> ]	Max.	25.40	29.07	27.08	21.66	24.58	22.73
	Min.	12.70	10.01	12.67	9.52	9.73	10.76
	Av.	18.98 ± 3.41	18.83 ± 5.68	17.53 ± 4.79	16.82 ± 2.21	17.24 ± 3.13	16.54 ± 3.17
[NO <sub>3</sub> <sup>-</sup> ]	Max.	4.59	4.59	1.53	2.69	3.13	2.33
	Min.	0.76	0.76	0.76	0.72	0.98	0.90
	Av.	1.32 ± 0.56	1.18 ± 0.51	0.95 ± 0.29	1.46 ± 0.56	1.54 ± 0.57	1.28 ± 0.40
[SO <sub>4</sub> <sup>2-</sup> ]	Max.	4.59	6.12	4.59	4.65	6.10	3.61
	Min.	1.53	3.06	3.06	1.94	1.25	0.83
	Av.	3.49 ± 0.73	3.98 ± 0.89	4.01 ± 0.43	3.22 ± 0.69	3.67 ± 1.13	2.72 ± 0.82
[Ca <sup>2+</sup> ]	Max.	23.2	20.81	17.14	11.69	11.58	9.64
	Min.	5.6	6.12	7.34	4.34	4.89	5.53
	Av.	10.64 ± 2.41	10.52 ± 2.39	11.74 ± 2.62	8.78 ± 1.29	9.51 ± 1.54	7.93 ± 1.23
[Mg <sup>2+</sup> ]	Max.	4.44	4.44	3.71	3.21	5.25	3.51
	Min.	0.80	0.80	0.73	1.40	1.56	0.88
	Av.	3.17 ± 0.93	3.41 ± 1.26	2.13 ± 1.01	2.56 ± 0.59	2.59 ± 1.00	1.96 ± 0.77
[Na <sup>+</sup> ]	Max.	5.81	9.18	1.07	5.01	5.01	6.31
	Min.	1.07	1.07	8.57	1.46	1.63	1.23
	Av.	3.32 ± 1.4	3.09 ± 1.61	3.27 ± 1.71	2.57 ± 0.82	2.12 ± 0.83	3.04 ± 1.37
[K <sup>+</sup> ]	Max.	3.06	4.13	5.79	2.49	2.32	2.32
	Min.	0.76	0.76	1.07	0.56	0.51	0.51
	Av.	2.05 ± 0.68	1.92 ± 0.77	2.45 ± 1.45	1.34 ± 0.57	1.68 ± 0.64	1.93 ± 0.56

It is interesting to compare the values of our dry deposition fluxes with those of Saxena *et al.*<sup>23</sup> for Agra, which is about 225 km from Jaipur in the neighboring State of Uttar Pradesh. In our study, the deposition fluxes are much higher than for Agra<sup>23</sup>. Secondly, while the deposition flux of nitrate was higher than sulfate in Agra, it is just the opposite in Jaipur at both sites. In general, the deposition flux values are higher in winter than in summer.

The pH values of rainwater, dry depositions, soil and groundwater<sup>17</sup> for Jaipur are : 6.8–8.47 (rainwater); 6.9–7.8 (dry depositions); 6.45–7.85 (soil) and 7.30–7.85 (groundwater). Interestingly, in all cases, the pH values fall in the same range indicating their alkaline nature.

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#### References

1. C. Brandt and R. van Eldik, *Chem. Rev.*, 1995, **95**, 119.
2. P. R. Salve, A. Maurya, S. R. Wate and S. Devotta, *Bull. Environ. Contam. Toxicol.*, 2008, **80**, 242.
3. A. H. M. Jawad Al Obaidy and H. Joshi, *Atmospheric Environment*, 2006, **40**, 6886.
4. S. Tiwari, A. Ranade and D. Singh, *Indian J. Rad. Space Phys.*, 2006, **35**, 35.
5. N. Rastogi and M. M. Sarin, *Atmospheric Environment*, 2005, **39**, 3313.
6. G. S. Satsangi, A. Lakhani, P. Khare, S. P. Singh, K. M. Kumari and S. S. Srivastava, *Atmospheric Environment*, 1998, **32**, 3783.
7. S. Sharma, U. C. Kulshrestha, A. Saxena and S. S. Srivastava, *Indian Journal of Environmental Protection*, 1990, **10**, 677.
8. S. V. Manoj, C. D. Mishra, M. Sharma, A. Rani, R. Jain, S. P. Bansal and K. S. Gupta, *Atmospheric Environment*, 2000, **34**, 4479.
9. P. D. Safai, P. S. P. Rao, G. A. Momin, K. Ali, D. M. Chate and P. S. Praveen, *Atmospheric Environment*, 2004, **38**, 1705.
10. L. T. Khemani, *Indian J. Radio Space Phys.*, 1993, **22**, 207.
11. P. S. P. Rao, G. A. Momin, P. D. Safai, A. G. Pillai and L. T. Khemani, *Atmospheric Environment*, 1995, **29**, 2025.
12. U. C. Kulshrestha, A. K. Sarkar, S. S. Srivastava and D. C. Parashar, *Water Air Soil Poll.*, 1995, **85**, 2142.
13. R. Kumar, A. Rani, S. P. Singh, K. M. Kumari and S. S. Srivastava, *J. Atmos. Chem.*, 2002, **41**, 265.
14. R. Mandal, PhD Thesis, University of Calcutta, Kolkata, 2001.
15. U. C. Kulshrestha, A. K. Sarkar, S. S. Srivastava and D. C. Parashar, *Atmospheric Environment*, 1996, **30**, 4149.
16. A. Saxena, S. Sharma, U. C. Kulshrestha and S. S. Srivastava, *Environmental Pollution*, 1991, **74**, 129.
17. C. D. Mishra, S. P. Bansal and K. S. Gupta, *J. Indian Chem. Soc.*, 2006, **83**, 210.
18. D. C. Parashar, L. Granat, U. C. Kulshrestha, A. G. Pillai, M. S. Naik, G. A. Momin, P. S. Prakasa Rao, P. D. Safai, L. T. Khemani, S. W. A. Naqvi, P. V. Narverkar, K. B. Thapa and H. Rodhe, 'Chemical composition of precipitation in India and Nepal. A Preliminary Report on an Indo-Swedish Project on Atmospheric Chemistry', Department of Meteorology, Stockholm University and International Meteorological Institute, Stockholm, Report CM-90, 1996.
19. P. K. Mudgal, A. K. Sharma, C. D. Mishra, S. P. Bansal and K. S. Gupta, *J. Atmos. Chem.*, 2008, **61**, 31.
20. M. S. Naik, L. T. Khemani, G. A. Momin, P. S. P. Rao, A. G. Pillai and P. D. Safai, *Tellus*, 1994, **46B**, 68.
21. K. S. Gupta, R. K. Mehta, A. K. Sharma, P. K. Mudgal and S. P. Bansal, *Trans. Met. Chem.*, 2008, **33**, 809.
22. A. K. Singh, G. C. Mondal, S. Kumar, K. K. Singh, K. P. Kamal and A. Sinha, *Environ. Monit. Assess.*, 2007, **125**, 99.
23. A. Saxena, U. C. Kulshrestha, N. Kumari, K. M. Kumari, S. Prakash and S. S. Srivastava, *Atmospheric Environment*, 1997, **31**, 2361.
24. L. T. Khemani, G. A. Momin, P. S. P. Rao, A. G. Pillai, P. D. Safai, K. Mohan and M. G. Rao, *Atmospheric Environment*, 1994, **28**, 3145.
25. L. T. Khemani, G. A. Momin, M. S. Naik, P. S. P. Rao, P. D. Safai and A. S. R. Murty, *Atmospheric Environment*, 1987, **21**, 1137.
26. L. T. Khemani, G. A. Momin, P. S. P. Rao, P. D. Safai, G. Singh and R. K. Kapoor, *Atmospheric Environment*, 1989, **23**, 757.
27. R. M. Harrison and R. Perry, "Handbook of Air Pollution Analysis", Chapman and Hall, London, 1986.