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Studies on Temporal Variation of Acid Precipitation in Delhi

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Precipitation samples were collected as wet-fall only and primarily on event basis in Delhi (capital of India) during the monsoon period of 2005. Concentration of major anions (SO_4^{2-}, NO_3^- and Cl^-) and cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were determined. The pH of the rain water was found to be more than 5.6, showing acidity during the early phase of monsoon, but during the late phase of monsoon pH tendency was towards alkalinity at some locations and acidity at other locations due to lack of proper neutralization of acidic ions. Neutralization is not only due to the local process but also due to the pre-monsoon wind which brings suspended particulate matter (SPM) containing Ca^{2+}, Mg^{2+}, Na^+ and K^+ as well as the local emission of NH_3. In the late mansoon, the concentration of the cations gets reduced because of heavy rainfall and relatively unfavourable condition for their transport from the adjoining areas, where as the anion concentration remains unchanged owing to their continuous emission.

Key Words: Rain water chemistry, Delhi, pH, Electrical conductivity.

INTRODUCTION

Water sources all over the world including India are under stress due to pollution from various sources. Year 2007 was celebrated by Government of India as "Year of Water". Rain water is the primary source for the recharge of the ground water as well as flow in the surface water. Therefore, any change in the chemistry of rain water is bound to have impact on ground water as well as surface water quality. Therefore, the present study tries to find out the temporal variation in rain water chemistry in Delhi in India.

Acidity of precipitation especially for industrialized and developing countries has been a subject of concern and research in recent times. The problem of acidity has not been widely addressed in India, but studies show that there is a decreasing trend in the pH of rain water.

Delhi, the capital city, is often categorized as a service town with government office complexes and medical, agricultural, educational and industrial institutions. From the air pollution point of view Delhi ranks 4th in the world and first in India for its suspended particulate matter concentration level, 27th in the world and second in India for its SO_2 level[1].

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Major sources of air pollution in Delhi are vehicles, thermal power plants and industrial and domestic coal burning. An estimated 2000 metric tonnes of pollutants are emitted into the atmosphere of Delhi everyday[2]. Vehicular sources contributes to about 64 % of the total pollutants emitted followed by coal fired thermal power plants 16 %, industries 12 % and domestic sector 7 %. In addition to man-made sources, climate and natural sources also play an important role in the pollution level of Delhi. The region has regular pre-monsoon features of dust storm westerly winds from the Great Indian Desert resulted a large amount of SPM, as high as 500-800 tonnes miles^{-2}. Ground based temperature inversions are a regular features in winters, which restricts the mixing height to low levels, limiting the pollutant dispersal.

The soil of Delhi is alluvial in nature. It is rich in minerals like calcium, magnesium and potassium. The monsoon season lasts for about 3 months from July to September showing an average annual rainfall[3] of 666 mm. The heavy rains of monsoon acts as a 'Scrubber'. The winter rains are scanty and uncertain. In Delhi mostly North west wind prevails, except during monsoon where south east winds are predominant.

In the present work, Delhi has been choosen as the study area because of excessive concentration of gases and total suspended particulate matter in the ambient air of Delhi, thus increasing the potential for acidic precipitation.

EXPERIMENTAL

Precipitation samples collected from 5 sites in Delhi during the monsoon months of 2005 (July to Sept) were assessed to evaluate the relation between the rain water quality and existing source of pollution and the influence of various pollutants on rain water quality. The study permits the explanation of various components, which affects the rain water quality (pH).

Ambient air quality monitoring: Central Pollution Control Board (C.P.C.B.) has been conducting ambient air quality monitoring at 7 locations in Delhi. The locations have been categorized based on land use, *i.e.*, residential, industrial and traffic intersections. The comparison of air quality data (average annual mean values) from the year 2000 to 2005 has been shown in Fig. 1.

Location sampling and analysis: Rain water samples from 11 different sites in Delhi were collected on event basis, which includes almost every shown during monsoon season in Delhi. These sites are located at (1) Jawaharlal Nehru University (JNU), (2) All India Institute of Medical Sciences (AIIMS), (3) Badarpur, (4) Okhla, (5) Laxmi Nagar, (6) Shahdara, (7) Paharganj, (8) Mukherjee Nagar, (9) Rohini (10) Rajendra Nagar and (11) Dwarka.

For collecting the precipitation samples, wet-only samples were used[4,5]. Care was taken that the collection procedure results in sampling of wet deposition only and not bulk samples. To achieve this the collction was opened only during the period of precipitation and closed tightly at other times.

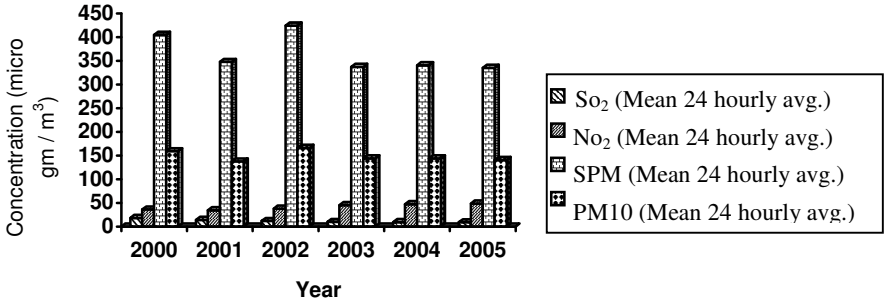

Fig. 1. Variation of air quality parameters in Delhi (Source C.P.C.B.)

Precipitation samples were collected on volume basis. The collector consists of conical flask (1000 mL) funnel (18 cm dia) and a mesh to prevent the insects from falling inside. These components were assembled as single unit. The whole assembly was kept one meter above the ground level to prevent the splashing of the rain water from the ground. During dry spell, the funnel was covered to avoid dry deposition.

Rain water was brought to the laboratory immediately after collection and pH was determined with digital pH meter using an ingold electrode standardized with pH 4.0 and 7.0 buffers. Conductivity of the samples were also measured immediately. The samples were filtered by Whatmann filter paper No. 14 and stored in a cold room at 4 ºC. Major anion concentrations like SO_4^{2-}, NO_3^-, Cl^- and cations NH_4^+ were analyzed as early as possible. HCl was added to reduce the pH below 2.0 and the samples were stored in a dark room at 4 ºC for further analysis of metals[6-9].

RESULTS AND DISCUSSION

Chemical composition of rain water: The measured concentration of major zones in rain water at various location in Delhi are given in Table-1.

Variation of average pH, EC and TDS at different locations figures in Delhi has been shown in Figs. 2 and 3, respectively.

Variation of total cation total anion and ratio of anion/cation ($NO_3^- + SO_4^{2-}$) and ($Ca^{2+} + NH_4^+$) is shown in Table-2. Mean values of different chemical constituents in Delhi rain water is shown in Table-3.

The pH of rain water at Delhi changed between 4.88 and 7.38. The minimum pH was recorded at Paharganj while maximum pH was recorded at Mukherjee Nagar. The lowest volume weighted mean was at (6.05) and highest was at Rohini (6.45). From the data it is apparent that Shahdara was the most polluted area since the mean pH value is 6.06. This value is higher than the lowest mean pH of 6.03 that was found by Balachandran and Khillare[3] in Okhla. The increase in vehicular traffic combined with industrial output of pollutants is the main reason for low pH observed at Shahdara.

TABLE-1
MAXIMUM, MINIMUM AND AVERAGE VALUES (IN μ eq/L, EXCEPT pH, EC AND TDS) AT DIFFERENT PLACES DURING JUNE-SEPT 2005

	pH	E.C. (μS/cm)	T.D.S. (ppm)	HCO_3	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	Na^+	K^+
J.N.U.												
Max	7.16	105.2	54.2	95.08	145.3	304.5	250	813	144	191.1	119.1	52.1
Min	5.51	12.0	8.9	9.18	13.5	28.3	23.2	102	29.5	11.6	13.9	4.1
Avg.	6.44	54.037	31.632	40.97	60.96	135.1	114	309	79.54	89.56	61.32	23.76
AIIMS												
Max	6.89	150.0	81.2	172.1	160.5	347	458	834	183.9	215.3	144.8	112.9
Min	5.25	18.5	10.3	7.37	11.2	31.5	29	11.5	16.8	8.1	10.8	5.7
Avg.	6.11	68.365	37.493	70.34	53.35	126.3	152	203	97.11	75.47	63.22	32.57
Badarpur												
Max	6.9	172.2	105.6	204.9	160.9	216.2	311	1416	1025	586.7	227	159
Min	4.93	28.0	15.85	5.74	25.35	41.8	43.5	86.7	17.4	21.2	23.3	9.5
Avg.	6.1	65.677	38.958	72.43	74.88	125.6	146	299	120.3	114.7	69.79	37.45
Okhla												
Max	6.89	103.5	73.5	139.3	161	341.2	337	700	209.7	255.8	174.7	69.2
Min	4.9	21	12.56	4.1	23.66	38.8	40.6	31.1	25.8	10	6.8	8.7
Avg.	6.08	64.435	36.278	65.95	84.85	121.6	162	198	79.58	71.7	61.31	33.9
Laxmi Nagar												
Max	6.92	135.23	77	249.2	159.3	386.6	325	435	219	208.8	189.5	66.1
Min	4.98	12.36	7.12	0.82	6.7	14.16	12.7	64.2	11.7	8.5	11.8	2.26
Avg.	6.26	61.186	33.766	71.23	80.03	114.9	147	193	86.65	69.11	65.86	27.78
Shahdara												
Max	6.98	121.21	63.23	259	150.7	187.7	293	413	185.8	263.6	125.2	61.7
Min	4.95	15.2	10.25	8.2	16.9	35.4	34.9	28.7	19.3	28.8	24.7	5.7
Avg.	6.06	58.578	32.552	54.39	68.41	117	140	184	84.58	68.73	60.19	26.22
Paharganj												
Max	7.08	140.6	75.65	121.3	148.5	325.8	393	515	122.7	234.7	108.6	60.7
Min	4.88	7.6	4.85	3.27	6.8	13.2	11.6	41.6	12.5	11.4	8.2	1.4
Avg.	6.14	55.835	32.307	45.42	62.49	132.4	137	193	64.12	71.22	57.85	20.8
Mukherjee Nagar												
Max	7.38	138	76.99	221.3	157.4	371.8	305	982	293.5	358.3	192.4	60.7
Min	5.65	14.6	10.36	0.65	15.2	29.8	26.1	98.5	33.2	56.1	18.2	5.8
Avg.	6.39	58.057	34.607	46.16	46.95	125.9	117	298	137.5	188.1	68.75	24.11
Rohini												
Max	7.35	217.2	112.6	254	169.3	396.6	325	1203	303.8	408.3	167.8	66.1
Min	5.82	7	4.85	0.82	6.81	14.2	11.6	51.2	12.3	28.8	10	2.1
Avg.	6.45	68.755	37.681	74.16	57.85	111.6	141	297	143.1	151.1	89.64	29.72
Rajendra Nagar												
Max	6.85	179.2	96.18	327.8	169.3	396.6	317	1099	305.8	308.8	196.5	66.2
Min	5.45	22	12.01	4.26	11.5	51	44	54.1	13.6	8.3	17.4	4.6
Avg.	6.23	61.961	33.92	79.76	48	109	150	212	76.49	79.42	62.71	23.84
Dwarka												
Max	7.32	170.5	101	191.6	164.5	408.5	351	1240	308.7	473.8	302.8	83
Min	5.75	21.22	9.87	8.2	10.5	25.3	24.2	91.9	12.5	50.5	13.2	5.1
Avg.	6.34	67.988	38.218	59.86	52.37	110.9	152	350	100.8	131.8	63.54	33.62

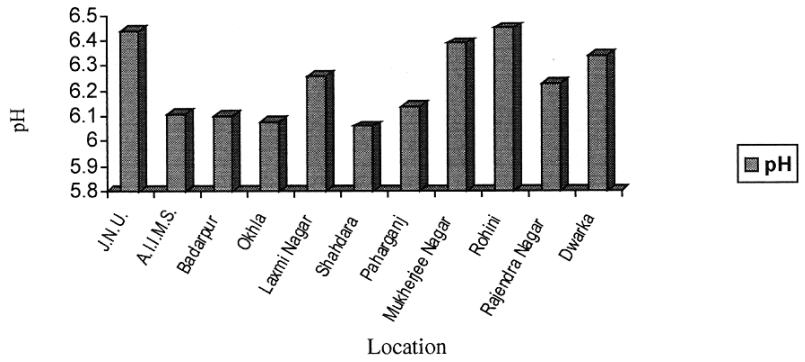

Fig. 2. Variation of average pH at different locations in Delhi

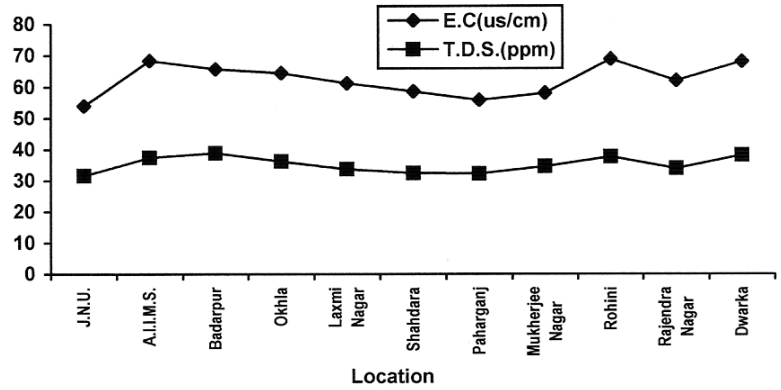

Fig. 3. Variation of average EC and TDS at different locations in Delhi

TABLE-2
SHOWING THE VARIATION OF TOTAL CATION TOTAL ANION AND RATIO OF ANION/CATION, NO_3^-/SO_4^{2-} $(Ca^{2+}+NH_4^+)/(NO_3^- + SO_4^{2-})$

Location	Total cation	Total anion	Anion/Cation	NO_3/SO_4^{2-}	$(Ca^{2+}+NH_4^+)/(NO_3^- + SO_4^{2-})$
J.N.U	563.66	350.72	0.62	0.841	1.60
A.I.I.M.S.	472.24	402.13	0.85	1.200	0.99
Badarpur	643.50	471.01	0.65	1.160	1.52
Okhla	446.24	434.49	0.97	1.330	0.94
Laxmi Nagar	443.28	413.30	0.93	1.280	0.99
Shahdara	426.02	379.95	0.89	1.190	0.98
Paharganj	408.18	377.23	0.92	1.030	0.97
Mukherjee Nagar	717.27	337.11	0.47	0.930	2.00
Rohini	711.09	385.01	0.54	1.260	2.81
Rajendra Nagar	455.81	386.75	0.85	1.370	1.12
Dwarka	680.63	374.34	0.55	1.370	1.83

TABLE-3
MEAN VALUES (IN μ eq/L, EXCEPT pH E.C. AND T.D.S.) OF DIFFERENT CHEMICAL CONSTITUENTS IN DELHI RAINWATER

	pH	EC (μS/cm)	TDS (ppm)	HCO_3	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	Na^+	K^+
Avg.	6.2	62.3	35.2	61.9	62.7	120.9	141.7	248.7	97.3	101.0	65.8	28.5

During the monsoon period of 2005, the average pH of rain water was 6.20. The no. of acidic events in JNU, AIIMS, Badarpur, Okhla, Laxmi Nagar, Shahdara, Paharganj, Mukherjee Nagar, Rajinder Nagar 1, 2, 3, 2, 1, 5, 3, 1, 4 out of 19 samples on each location and accounted for 5, 11, 16, 5, 26, 16, 5 and 21 % acidic events while such events were not observed at all at Dwarka and Rohini. The acidic events at the 9 sites except Dwarka and Rohini can be related to the specific gravity of these areas, which are predominantly commercial cum industrial sites with heavy vehicular traffic. When compared with the report of Kapoor *et al.*[10] and Subramanium and Saxena[11], the values are less alkaline.

SO_4^{2-} and NO_3^- are conventional acidic ions in precipitation. The relative contribution by these ions to the acidity remaining 30 % being accounted forms by HNO_3. However, the contribution of H_2SO_4 to the acidity of the perecipitation has decreased recently and that of HNO_3 has increased owing to reduction in SO_2 emissions and less stringent controls on NO_x emission, particularly in the U.S. and Europe and in India at Delhi.

The average ratio of NO_3^-/SO_4^{2-} in the rain at Delhi was 1.18 which indicates that the contribution of HNO_3 to the acidity of precipitation is more than 50 %. This is particulalrly due to the reduction in SO_2 emission in Delhi as a result of CNG implementation. The concentration of NO_2 in ambient air of Delhi has increased by 1.36 times since the year 2000 as a result the contribution of HNO_3 in acidity, which was less than 50 % in 1995 has now became more than 50 % and the acidity is now no longer influenced more by SO_4^{2-}. This trend was observed at AIIMS, Badarpur, Okhla, Laxmi Nagar, Sahdara, Paharganj, Rohini and Dwarka. The NO_3^-/SO_4^{2-} was less than 1.0 at J.N.U. and Mukherjee Nagar.

Ratio's of $(NH_4^+ + Ca^{2+})$ to $(NO_3^- + SO_4^{2-})$ were also calculated in order to know if acidic components like NO_3^- and SO_4^{2-} were neutralized basically by NH_4^+ and Ca^{2+}. If the ratio is greater than one, it indicate NH_4^+ and Ca^{2+} have neutralized SO_4^{2-} and NO_3^-. The average ratio of (NH_4^+ and Ca^{2+})/$(NO_3^- + SO_4^{2-})$ in the present study varied between 0.94 and 2.81 for the whole delhi and it was greater than 1.0 in J.N.U., Badarpur, Mukherjee Nagar, Rohini, Rajinder Nagar and Dwarka. At Okhla, Laxmi Nagar, Shahdara, Paharganj and AIIMS the ratio was below 1.0 indicating that NO_3^- and SO_4^{2-} were not neutralized by NH_4^+ and Ca^+ alone but possibly by other cations.

When anions to cations ratio were calculated, the values were always below 1.0 which shows that there is a deficit in anionic concentrations like weak organic acids, fluoride and phosphate which contribute to electroneutrality.

From the figures show the variation of different chemical constituents with days at various location in Delhi. It is clear that Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, NH_4^{+}, NO_3^{-}, Mg^{2+} and K^{+} concentration decreased with rain duration. From the historical perspective of acid rain studies the most well known, rain water acidification mechanism is SO_2 and NO_x entitled into the atmosphere being oxidized to H_2SO_4 and HNO_3 through both gas and resource phrase processes. HCl also play a role in contribute to rain water acidity. In addition, weak acids such as H_2CO_3 from dissolved atmospheric CO_2 in rainwater and organic acid) (formic acids, acetic acid, *etc.*) contribute to rain water acidity.

Conclusion

The average pH of all the eleven sites was 6.20 which is taken as alkaline for rain water. Out of the 209 samples of rain water collected, 22 times pH was found to be below 5.67 which is about 11 % of the collected samples. The average ratio of NO_3^{-}/SO_4^{2-} was 1.18 which indicates that SO_4^{2-} was no longer the predominant ion and acidity is more dominantly caused by NO_3^{-}. The $(NH_4^{+} + Ca^{2+})/(NO_3^{-} + SO_4^{2-})$ ratio was 1.43 which indicates that NH_4^{+} and Ca^{2+} play an important role in neutralization of acidic ions in rainwater. For almost all the locations the concentration of chemical species Cl^{-}, NO_3^{-}, SO_4^{2-}, Na^{+}, NH_4^{+}, K^{+}, Ca^{2+} and Mg^{2+} decreased with days as monsoon progressed from July to Sept. It is evident from the result that NO_3^{-} concentration are higher. This also corresponds well with NO_x concentration in the ambient air quality data which shows an increase of 1.36 times between the years 2000 and 2005 *i.e.* after the CNG implementation in Delhi. This may be due to the fact that the number of CNG vehicles was increasing more over, CNG has a higher flash point of 540 ºC than diesels which has a flash point of (232-282) ºC. At such high temperatures, more nitrogen from the air compresses and reacts with oxygen in the combination chamber of CNG driven vehicle in comparison to petrol driven vehicle and thus produces more NO_2^{-}. At the same time there are other reasons also for increasing NO_3^{-} concentrated in rain water and NO_x in air and we can't put the blame only the CNG which can only be one of the reason. However, there are many sources of nitrogen dioxide. The capitals 4.87 million strong fleet of vehicle's which is even increasing can't be underestimated. The annual 5 % increase in the no. of vehicles on Delhi roads is another major reason. These are some of the issues which need to be further investigated and can be apart of any future research on rain water chemistry.

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