551.578.11 : 541.41 (548.8) "1981"

CHEMICAL COMPOSITION OF RAIN WATER WITH SPECIAL REFERENCE TO HEAVY METALS OVER LUCKNOW, UTTAR PRADESH IN 1981

Rain water samples were collected in 1981 and analysed for various constituents, including trace elements by standard methods described in literature (Handa 1976).

The data given in Table 1 is in conformity with the findings reported earlier (Handa *et al.* 1982) that there is no incidence of 'acid' rain over Lucknow; the mean pH value being 7.45 with standard deviation of 0.45 pH units. The EC of rain water, however, showed considerable variations and ranged between 3 & 118 microsiemens/cm with mean average of 30.8 microsiemens/cm and standard deviation of 27.5 microsiemens/cm. However, in qualitative terms, the EC value is inversely proportional to the 'total rainfall' in any particular event, but here too exceptions were noted. It is interesting to record that the PO_4 and NH_4 concentrations in rain water ranged around 0.28 mg/l and 0.66 mg/l respectively. These values may be compared with the average value of 0.016 mg/1 and 0.5 mg/1 of PO_4 and NH_4 ions respectively, reported by Leonard *et al.* (1981). This fact shows that the NH_4-ion concentrations are more or less similar (apparently being more of global origin), but the PO_4 ion concentrations differ markedly, being mainly of local origin. The average value for NO_3 at Davis and Lake Tahoo (Leonard *et al.* 1981) was 1.07 mg/1 (as NO_3), which value compares favourably with the average value of 1.26 mg/l NO_3 recorded at Lucknow.

2. *Trace elements* — Most of the trace elements in the atmosphere owe their origin to anthropogenic activities and are likely to be both of global and local origins. The most important sources are:

(a) mining activities ;

(b) industrial waste emanations;

(c) incineration of sludge and waste;

(d) fossil fuel combustion, including automobile engine exhausts;

(e) soil dust etc.

From the data given in Table 2, it is obvious that in Lucknow, the concentrations of trace elements vary considerably. Here too, no direct relationship between quantity of rainfall and trace element concentration is observed. Iron was the most abundant trace element (mean 30.9 mg/l), followed by copper, zinc, strontium and manganese in that order. The concentrations of Cs, Rb, Ag, Co & Li were found to be quite low, while Cd and Mo could not be detected. Table 3 gives a comparison of the trace element content in Lucknow and that reported from other parts of the world (Jefferies and Snyder 1981).

TABLE 1
Chemical composition of rain water samples collected in Lucknow in 1981

S. No.	Date	Rainfall	pH	EC	CO₃	HCO₃	Cl	NO₃	NH₄	F	PO₄	Ca	Mg	Na	K
1	23 June	19.5	7.40	16	nd	5.2	0.53	1.45	1.08	0.14	0.18	2.00	nd	1.1	0.7
2	27 ,,	12.1	7.40	29	nd	9.5	1.49	3.45	0.42	0.08	0.22	2.10	nd	0.32	0.58
3	28 ,,	7.0	7.65	40	nd	9.8	0.67	4.00	—	—	0.28	2.20	nd	0.38	0.55
4	28–29 ,,	56.8	6.95	11	nd	4.6	1.42	1.05	1.30	0.04	0.20	nd	nd	0.27	0.15
5	29 ,,	39.0	7.25	8.5	nd	7.3	0.85	1.80	0.17	0.03	0.14	1.60	nd	0.11	0.08
6	30 ,,	5.0	7.70	48	nd	5.5	1.28	3.50	—	—	0.43	4.40	0.24	1.91	0.64
7	1 July	24.4	7.50	22	nd	11.6	0.99	0.25	1.11	0.08	0.16	2.80	nd	0.38	0.09
8	2 ,,	4.0	7.20	90	nd	29	3.30	3.60	—	—	0.10	13.0	0.61	2.65	1.22
9	5 ,,	28.4	7.60	54	nd	14.3	3.12	2.55	0.19	0.08	0.39	5.00	nd	1.54	0.28
10	7 ,,	tr	7.90	118	nd	—	1.60	3.35	—	—	2.45	5.40	nd	1.45	1.92
11	10 ,,	5.2	7.35	35	nd	23	0.67	0.40	—	—	0.14	4.00	1.09	0.81	0.82
12	12 ,,	40.6	8.10	22	nd	7.6	0.92	0.10	0.86	0.02	0.02	2.00	nd	0.22	0.07
13	14 ,,	6.5	7.75	21	nd	4.9	1.84	0.20	—	0.02	0.06	2.50	nd	0.94	0.22
14	18 ,,	tr	7.65	54	nd	9.2	1.52	3.80	—	—	1.14	6.20	0.49	1.88	0.58
15	18 ,,	33.4	7.75	8.0	nd	1.53	0.11	0.35	0.34	nd	0.15	nd	nd	0.12	0.16
16	19 ,,	6.5	7.60	37	nd	24	0.50	nd	1.08	nd	0.14	2.90	nd	0.44	0.28
17	20 ,,	4.5	7.65	43	nd	29	1.00	0.50	—	—	0.08	6.00	nd	1.96	0.22
18	22 ,,	5.0	7.75	66	nd	13	1.88	3.70	—	—	0.17	7.20	0.24	2.42	1.80
19	26–27 ,,	83.4	7.40	23	nd	9.8	0.53	nd	0.57	0.04	nd	2.90	nd	0.51	0.07
20	27 ,,	8.3	5.90	10	nd	4.9	0.50	0.80	—	—	0.18	1.00	nd	0.36	0.33
21	28 ,,	13.5	7.15	24	nd	7.6	0.32	nd	0.20	0.04	nd	2.00	nd	0.30	0.08
22	1 Aug	61.0	7.00	22	nd	9.8	0.855	nd	0.37	0.02	0.03	2.20	nd	0.40	0.22
23	2 ,,	11.0	6.95	28	nd	14	0.57	0.35	—	—	0.07	3.40	nd	0.60	0.22
24	13 ,,	12.4	8.00	25	nd	14	0.46	0.10	—	—	0.17	3.20	nd	0.50	1.08
25	22 ,,	26.8	7.60	32	nd	15	0.82	1.45	0.92	nd	0.17	3.50	nd	0.70	0.30
26	22–23 ,,	24.3	7.55	25	nd	5.8	0.71	—	—	0.8	—	3.50	nd	0.61	0.90
27	6 Sep	6.0	8.10	105	nd	63	2.10	1.90	—	—	0.22	21.60	2.2	3.40	1.40
28	7–8 ,,	36.5	7.80	20	nd	9.8	0.50	—	—	nd	—	2.80	nd	0.21	0.07
29	8–9 ,,	56.5	7.75	3	nd	1.83	0.21	nd	—	nd	—	nd	nd	0.21	0.05
30	9 ,,	34.1	7.25	4	nd	2.44	0.28	nd	—	nd	—	nd	nd	0.06	0.02
31	27 ,,	17.0	7.95	12	nd	6.41	0.28	—	—	nd	—	1.40	0.12	0.12	0.09
32	28 ,,	11.4	7.95	10	nd	4.30	0.32	—	—	0.02	—	nd	nd	0.12	0.02
33	28 ,,	40.6	6.65	8	nd	4.60	0.28	—	—	nd	—	nd	nd	0.06	0.02
34	14–15 ,,	37.5	7.70	6	nd	4.20	0.28	nd	0.66	0.04	0.12	0.70	nd	0.18	0.02
35	28–29 ,,	56.8	6.85	3.5	nd	1.83	0.28	—	—	nd	—	nd	nd	0.16	0.03
36	1 Nov	10.0	7.45	20	nd	9.80	0.57	0.54	—	0.02	0.37	2.80	0.12	0.53	0.32
	Mean		7.48	30.6		11.26	0.93	1.26	0.66	0.031	0.28	3.34	0.14	0.78	0.41
	Standard dev :		.45	27.5		11.3	0.77	1.45	0.39	0.037	0.48	4.05	0.42	0.83	0.50

EC in microsiemens/cm at 25° C ; Concentrations in mg/l ; TH=total hardness as $CaCO_3$; nd=not detected ; Rainfall in mm

TABLE 2

Trace element content of rain water samples collected in Lucknow in 1981
(Rainfall in mm ; nd=not detected ; Concentrations in micrograms/l)

S. No.	Date sampled	Rainfall (mm)	Fe	Mn	Ag	Cu	Zn	Co	Mo	Cd	Sr	Li	Rb	Cs
R-1	3 Jun	19.5	15.0	4.75	1.13	4.00	15.00	0.05	nd	nd	6.25	nd	0.50	2.25
R-3	28 Jun	56.8	21.5	1.31	0.59	1.50	5.90	0.013	nd	nd	1.13	0.29	0.13	0.63
R-4	29 Jun	39.0	21.2	0.66	1.58	20	6.60	nd	nd	nd	3.30	nd	0.25	0.75
R-6	5 Jul	28.4	37.5	0.31	2.00	32.5	—	0.25	nd	nd	22.5	—	1.25	3.00
R-7	12 Jul	40.6	30.9	0.94	1.25	15	1.87	nd	nd	nd	2.81	0.13	nd	0.06
R-9	14-15 Jul	37.6	26.3	2.25	nd	16.5	13.75	0.06	nd	nd	3.75	0.13	nd	0.12
R-10	18 Jul	33.4	35.0	2.33	nd	2.7	9.16	0.13	nd	nd	nd	0.17	nd	0.16
R-12	26-27 Jul	83.4	16.8	3.75	0.38	33	19.4	0.17	nd	nd	2.50	0.25	nd	0.12
R-13	28 Jul	13.5	11.3	2.75	0.63	13.5	27.5	0.25	nd	nd	3.75	0.25	nd	nd
R-14	1 Aug	61.0	52.5	2.75	nd	34.5	13.8	0.25	nd	nd	5.00	0.25	nd	0.24
R-15	22 Aug	26.8	56.3	3.75	0.50	41.0	12.5	0.25	nd	nd	10.0	0.50	nd	0.73
R-16	23, 24 Aug	24.3	85.0	4.75	nd	20.7	10.0	0.50	nd	nd	5.00	0.25	nd	nd
R-17	7 & 8 Sep	36.5	81.3	3.00	0.63	39.5	5.0	0.25	nd	nd	6.25	0.25	nd	nd
R-18	8 & 10 Sep	56.5	39.4	1.88	1.50	20.5	31.3	0.25	nd	nd	3.13	0.13	nd	nd
R-19	9 &10 Sep	34.1	nd	1.25	0.60	8.30	1.25	0.25	nd	nd	2.50	0.25	nd	nd
R-20	27 & 28 Sep	17.0	nd	1.00	nd	2.00	nd	0.35	nd	nd	0.25	0.25	nd	nd
R-21	28 Sep	11.4	nd	0.75	nd	2.00	1.25	0.50	nd	nd	2.50	0.~5	nd	0.24
R-22	29 Sep	40.6	16.3	2.50	nd	11.0	5.00	0.50	nd	nd	2.50	0.25	nd	nd
R-23	30 Sep	56.8	26.5	2.16	nd	24.5	10.00	0.17	nd	nd	2.50	0.17	nd	nd
R-24	1 Nov	10.0	45.0	6.00	nd	46.0	7.50	0.50	nd	nd	7.50	0.50	nd	0.49
	Mean		30.89	2.44	0.53	19.44	10.36	0.23			4.83	0.22	0.11	0.94
	Standard dev.		24.77	1.54	0.63	14.31	8.53	0.17			4.74	0.13	0.30	0.80

TABLE 3

Comparative statement of trace elements in rain water over Lucknow and other parts of the world (Concentrations in micrograms/l)

S. No.	Parameter	Remarks	Europe Range	Europe Mean	N. America Range	N. America Mean	Lucknow Range	Lucknow Mean
1	Copper	Urban	16-60	40	6.4-49.6	30.4	1.5-46	19.49
		Rural	1.4-27	16	2.0-30	8	—	—
2	Zinc	Urban	71-221	136	16-840	557	nil-31.3	10.36
		Rural	5.3-370	62	22-760	30.8	—	—
3	Manganese	Urban	19-43	28	—	—	0.31-6.0	2.44
		Rural	3.5-30	9.8	2.3-38	17	—	—
4	Iron	Urban	29.9-1750	768	14-878	160	0.0-850	30.9
		Rural	135-1900	192	34-890	45	—	—

TABLE 4

Relative proportion of trace constituents with respect to iron, present in rain water over Lucknow and some natural sources

S. No.	Ratio	Soil	Fossil fuel	Industrial waste emanations	Rain water Lucknow 1981
1	Ag/Fe	2.63×10^{-6}	3.1×10^{-4}	4.0×10^{-2}	1.72×10^{-2}
2	Mn/Fe	2.24×10^{-2}	4.96×10^{-3}	3.2×10^{-4}	7.9×10^{-1}
3	Cu/Fe	5.26×10^{-1}	1.33×10^{-2}	2.93×10^{-2}	6.29×10^{-1}
4	Zn/Fe	1.32×10^{-3}	4.34×10^{-2}	9.3×10^{-3}	3.35×10^{-1}
5	Co/Fe	2.10×10^{-4}	7.45×10^{-3}	6.2×10^{-4}	5.3×10^{-4}

The data shows that the ranges and mean concentration values of the trace elements in Lucknow are much lower than those found in the move industrialized countries of Europe and N. America.

3. *Origin of various constituents in rain water* — It has already been indicated that there are several sources for the constituents present in rain water. These sources include *interalia* sea salt nuclei, volatile constituents from stagnant water bodies, mining activities, waste incineration, agricultural activities which include aerial spraying of insecticides etc, forest fires. fossil fuel burning. automobile emissions, soil dust particles, exudation of heavy metals by vegetation etc (Beuford et al. 1975, 1977). Table 4 gives the ratio of the various constituents present in rain water and various

TABLE 5

Correlation coefficient and regression coefficient values between some parameters present in rain water over Lucknow

Parameter	EC		HCO₃		Cl		Ca		Na		K	
	r	b	r	b	r	b	r	b	r	b	r	b
EC	1	—	0.81	0.397	0.710	0.029	0.93	.165	.923	.033	.835	.015
HCO₃	—	—	1	—	0.474	0.032	.904	.328	.730	.051	.575	.022
Cl	—	—	—	—	1	—	.660	.529	.750	.816	ᵖ.53	.347
Ca	.929	.124	.904	2.50	0.664	0.126	1	—	.839	.184	.65	.08
Na	.925	25.9	.722	9.86	0.750	0.696	.893	4.34	1	—	.72	.43
K	.836	45.9	.575	15.1	0.524	0.814	.649	5.25	.721	1.201	1	—

r = correlation coefficient ;   b = regression coefficient

natural sources with respect to iron. Iron has been chosen as it is present in a very large concentrations relative to the other trace elements.

The data seems to indicate that silver content could possibly owe its origin to industrial activity, while copper could be more from soil. Similary for zinc and cobalt the main sources could be the industrial activity, while for Mn the most important contribution may be made by soil.

For the major constituents statistical methods were employed and the coefficient correlation values obtained are tabulated (Table 5).

The data shows that all the major ions have a positive correlation with electrical conductivity. Amongst the various ions the highest values for correlation were found for Ca and Na. Interestingly with the anions, the correlation coefficients had somewhat low values indicating that, perhaps, the presence if anomalous values of NO₃ and PO₄ ions was affecting the relationship considerably. Amongst the ions themselves, the correlation coefficient between HCO₃ and Ca ions had a good value (0.90) but the value was lower for the ion pair Cl : Na. Similarly the correlation coefficient had a high value for the ion pair Ca : Na, indicating that they have a similar origin, viz., soil dust.

4. The studies reported here indicate that the various constituents present in rain water owe their origin to a multitude of sources, both natural and anthropogenic. Further, the data confirms the earlier findings that there is no incidence of acid rain over Lucknow. The concentrations of trace elements present in rain water are normally much below those present in rains over industrialized countries of W. Europe and N. America; the present data serving as 'background or baseline data' to monitor future pollution studies.

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