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Rainfall composition in Lucknow in 1982 and its significance to man

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सार — 1982 के दौरान लखनऊ में वर्षा संयोजन के अध्ययन से यह पता चलता है कि लगभग 4.1 कि. ग्रा./हे. पोटाशियम, 3.6 कि. ग्रा/ हे. केल्शियम और 7.8 कि. ग्रा./हे. ना. आ. आयन वर्षा के साथ धरती पर आए हैं। इसके अतिरिक्त 0.29 कि. ग्रा./हे.लोहय, 0.11 कि. ग्रा./हे। जस्ता और 0.03 कि. ग्रा./हे. मैन्गनिज आयन भी वर्षा के साथ नीचे आये हैं। हालांकि इनकी मात्रा पौधों की सम्पूर्ण पोषक आवश्यकताओं को देखते हुए कम है किन्तु फिर भी ये निरर्थक नहीं है। इन आयनों के अतिरिक्त, अन्य आयन/स्पीशीज भी वर्षा के साथ नीचे गिर जाती है, तथापि, रजत आयनों के अलावा अन्य घटको की सांद्रता सामान्यतः ताजे जल के लिए या पेय जल की निर्धारित सीमा से कम थी ।

ABSTRACT. The study of rainfall composition in Lucknow during 1982, has shown that around 4.1 kg/ha K, 13.6 kg/ha Ca & 7.8 kg/ha NO_3 ions were brought down. Apart from these 0.29 kg/ha of iron, 0.11 kg/ha Zn and 0.03 kg/ha Mn ions were also brought down. Although these amounts are still small in relation to the overall nutrient requirements of plants, these are by no means insignificant. Apart from these ions, other ions/species were also brought down by rain. However, except for Ag ions, the concentrations of other constituents were normally lower than the limits prescribed for potable waters or for fresh water biota.

1. Introduction

The atmosphere is a significant pathway for the movement and redistribution of several metals in the eco-system. Both natural and anthropogenic activities contribute to the cycling of metallic and non-metallic elements (Handa 1978, 1983; Handa *et al.* 1982, 1984; Khemani 1974; Sadasivan 1973; Sequeria 1976 & Zutshi *et al.* 1978). The occurrence of various trace metals in the atmosphere is of considerable significance to man and aquatic biota. Trace metals present in the atmosphere may be health hazards to humans & even animals; they may act as catalysts in atmospheric reactions, some of which may cause production of acids; they may promote corrossion of materials; they may cause far reaching changes in the receiving eco-system and in association with suspended particulate matter may induce changes in climate at micro and even at macro levels.

Similarly, the occurrence of some plant nutrients like nitrogen, potassium and calcium species may provide nutrients to plants either directly by foliar absorption or indirectly by deposition on soil. The paper emphasizes the significance of rainfall composition for humans and fresh water aquatic life and also reports *Pb, Cr & Ni contents in rain water over* Lucknow, not reported before.

2. Experimental

Rainwater samples were collected in polyethylene bottles fitted with larger diameter polyethylene funnels. To minimize changes in composition of rain water, analysis of collected samples was conducted with the minimum loss of time except in those cases where the rainfall occurred on weekends or on holidays. A portion of the sample was analysed for pH, EC, CO_3, HCO_3, C1, NO_3, Ca, Mg, Na, K & SiO_2 by standard methods described in literature (Handa 1976), while the remaining sample was acidified with reagent grade HNO_3, concentrated at low heat and analysed for trace elements, using atomic absorption spectrophotometer.

3. Results

The chemical composition of rain water samples is given in Tables 1 & 5, while statistical data is given in Tables 2, 4 & 7.

4. Discussion of results

Various natural and anthropogenic activities like (a) release of gaseous & particulate matter by volcanic activity; (b) reduction of sulphur, nitrogen & other species in stagnant water bodies with concomitant production of volatile compounds; volatalization of

TABLE 1

Chemical composition of rain water at Lucknow in 1982

Date of collect. (1982)	Rain-fall (mm)	pH	EC	CO_3	HCO_3	Cl	F	NO_3	Ca	Mg	Na	K	SiO_2
25 Jan	3.2	6.45	70	nd	24	9	0.61	3.0	6.6	0.12	2.24	8.5	1.1
25 Jan	16.2	6.90	22	nd	7.9	0.7	0.39	0.52	2.6	0.12	0.22	0.12	0.06
27 Jan	0.9	6.65	23	nd	10	0.53	0.33	0.44	2.2	nd	0.61	0.36	0.06
12 Feb	6.6	7.40	48	nd	29	2.23	0.57	2.1	—	—	1.42	0.92	0.09
15 Feb	tr	6.40	147	nd	—	5.3	—	0.26	—	—	—	—	—
1 Mar	8.5	7.60	35	nd	18	1.24	0.76	2.90	2.1	0.88	0.68	1.84	1.10
6 Mar	2.2	7.80	176	nd	83	2.30	0.33	4.10	30.3	nd	1.32	0.72	1.40
24 Mar	15.8	7.80	49	nd	21	1.24	0.33	2.10	7.3	nd	0.34	0.61	0.09
12 May	tr	7.70	206	nd	—	11	1.10	4.50	—	—	—	—	1.90
15 May	3.95	7.10	93	nd	—	3.9	0.71	4.90	9.50	0.73	3.10	1.22	0.09
4 Jun	22.1	7.10	25	nd	8.8	1.77	0.57	1.85	2.24	—	1.00	0.82	0.06
5 Jun	9.5	6.70	16	nd	1.7	1.06	0.33	1.80	0.64	nd	0.39	1.04	nd
5 Jun*	30.5	6.30	8	nd	4.4	0.53	0.26	0.39	—	—	0.28	0.54	0.09
13 Jun	26.8	7.50	31	nd	11	1.60	0.15	0.80	2.08	0.20	0.54	0.54	0.04
14 Jun	15.8	7.20	31	nd	10	1.06	0.18	0.70	3.05	0.20	0.76	0.58	1.10
17 Jun	14.2	7.40	27	nd	12	2.66	0.23	0.64	—	—	0.39	0.24	0.09
13 Jul	78.9	7.15	11	nd	4.4	1.24	0.04	0.34	—	—	0.20	0.16	0.06
13 Jul**	1.6	6.75	127	nd	38	6.21	0.39	1.96	11	1.36	5.80	2.30	1.40
23 Jul	14.2	7.10	32	nd	16	2.31	0.01	0.52	4.17	6.8	0.97	1.18	1.14
24 Jul	2.5	6.80	14	nd	3.9	0.89	0.01	0.50	—	—	0.30	0.16	0.06
24 Jul	6.3	6.80	12	nd	4.3	0.89	0.05	0.25	nd	nd	0.34	0.18	0.09
25 Jul	25.3	6.45	18	nd	6 7	0.89	0.04	0.25	—	—	0.34	0.38	0.06
27 Jul	23.7	7.20	13	nd	7.3	0.71	0.01	0.50	—	—	0.28	0.08	0.09
30 Jul	3.8	7.60	37	nd	15	2.13	0.23	0.70	—	—	1.72	1.90	1.10
3 Aug	44.2	7.40	10	nd	6.4	0.35	0.05	0.75	—	—	0.34	0.45	0.06
4 Aug	4.7	7.10	24	nd	7.3	1.95	0.05	0.58	—	—	0.32	1.07	0.06
8 Aug	7.9	7.75	39	nd	17	2.31	0.05	0.20	3.69	0.10	2.18	0.79	1.90
12 Aug	12.6	7.60	48	nd	12	0.89	0.11	0.74	3.12	0.08	1.40	1.92	1.65
14 Aug	3.8	7.80	43	nd	18	1.24	0.01	0.58	2.81	0.29	0.54	0.74	1.90
18 Aug	31.8	6.70	18	nd	4.9	0.71	0.01	0.58	nd	0.91	0.37	0.04	0.09
20 Aug	34.7	7.10	7	nd	3.4	0.36	nd	nd	nd	0.85	0.28	nd	0.09
22 Aug	22.1	7.25	10	nd	4.9	0.71	nd	0.20	—	—	0.29	0.06	0.09
24 Aug	6.3	7.80	26	nd	4.9	1.60	nd	3.14	0.50	0.43	1.24	2.34	0.09
24 Aug	6.3	7.80	26	nd	4.9	0.53	0.29	—	0.50	0.43	0.54	0.52	0.09
26 Aug	15.0	7.78	7.7	nd	4.6	—	0.04	—	nd	nd	0.28	0.08	0.06
27 Aug	26.8	7.55	10	nd	4.3	—	—	—	nd	nd	0.20	0.05	—
30 Aug	4.7	7.50	24	nd	17	—	—	—	1.90	nd	0.50	nd	—
30 Aug	13.4	8.20	19	nd	4.3	—	—	—	nd	nd	0.30	0.20	—
31 Aug	102.6	7.40	8	nd	4.9	—	—	—	nd	nd	0.20	0.16	—
5 Sep	2.5	7.20	62	nd	24	—	—	—	6.80	nd	1.40	2.00	—
7 Sep	12.6	8.20	21	nd	16	—	—	—	1.48	nd	0.61	0.16	—
10 Sep	2.3	7.60	31	nd	15	—	—	—	4.20	nd	0.76	0.80	—
10 Sep	15.8	6.70	12	nd	9.8	—	—	—	nd	nd	0.28	0.04	—
11 Sep	44.0	7.65	11	nd	8.6	—	—	—	nd	nd	0.20	nd	—
12 Sep	37.9	6.00	11	nd	5.5	—	—	—	nd	nd	0.28	nd	—
13 Sep	11.8	8.60	32	3	14.6	—	—	—	2.80	nd	1.24	0.27	—
8 Oct	3.2	7.75	52	nd	29.3	—	—	—	8.40	1.09	—	—	—
22 Oct	1.6	7.80	44	nd	22	—	—	—	5.20	nd	—	—	—
10 Nov	9.5	8.60	20	4.2	25	—	—	—	9.60	nd	—	—	—

Note : EC is in microsiemens/cm at 25° C : Concentrations are in mg/1; nd=not detected; *=second sampling site; **First shower

TABLE 2

Statistical relationship between rainfall (mm) & other parameters

X	Y									
Rainfall (mm)	EC (μs/cm)	HCO_3	Cl	F	NO_3 (mg/l)	Ca	Mg	Na	K	SiO_2
r	−.41	−.38	−.36	−.38	−.38	−.41	−.04	−.36	−.30	−.16
n	50	47	35	35	34	36	35	45	45	35
(x)	38.1	13.4	2.14	0.24	1.29	2.91	0.42	0.83	0.85	0.58
Weighted x	19.4	8.2	1.2	0.15	0.78	1.36	0.36	0.45	0.41	0.47
s	42.2	13.3	2.37	0.27	1.33	3.18	1.17	0.99	1.36	0.67
$s/\sqrt{n}$	6.16	1.94	0.40	0.05	0.23	0.53	0.20	0.15	0.20	0.10

Note : r=Correlation coefficient; n=number of observations; (x)=mean average values; Weighted x=Weighted average value; s=Estimate of standard deviation; $s/\sqrt{n}$=Standard error of mean

TABLE 3

Total amounts of various plant nutrients etc brought down by rain (1982)

Unit	HCO_3	Cl	F	NO_3	Ca	Mg	Na	K	SiO_2
Kg/hect.	82	12	1.5	7.8	13.6	3.6	4.5	4.1	4.7
Kg/sq km	8.2×10^3	1200	150	780	1360	360	450	410	470

metallic elements like Hg, Se, Pb etc as methyl derivatives; forest fires, soil dust, sea salt nuclei generated by strong cyclonic and/or monsoon winds; (c) mining activities; (d) release of gaseous & particulate matter by smelters, blast furnaces, foundaries; (e) incineration of garbage; (f) emissions from cement industries, chemical industries; (g) burning of fossil fuel (including emissions from automobiles); (h) aerial spraying of insecticides etc affect the chemical composition of the atmospheric constituents. Numerous factors like wind velocity, wind direction, height of emitter, topographical conditions, aerodynamic properties of the particulate matter emitted, cloud formation and rainfall, atmospheric photoelectric reaction etc affect the transport of these aerosol to long distances. Although eventually all particulate matter is deposited on the surface of the earth as 'dry fall-out' or in rain, due to varying contribution from these sources and due to varying influences, the composition of rain water shows considerable variations. Other factors like frequency of rain, intensity of rain, height of cloud base etc also affect the chemical composition of rain water (Table 1).

In cases, where rainfall is preceded by heavy dust storms, the total dissolved solids content in the rain water may be quite high, *viz.*, on 15 Feb, 12 May, 15 May, 13 July etc (Table 1). Similarly if the interval between two succeeding rainfall events be high, the salinity of the rainwater may be quite high, as seems to be indicated by the data for 25 Jan & 8 Oct rainfall events. Similarly several other factors, *viz.*, quantity and intensity of rainfall also affect the solute concentration in rain water as would be evident from two observations (Table 2).

(a) there is a negative correlation between total rainfall and the concentration of ionic constituents;

(b) the weighted average values ($\sum_{i}^{n}$rainfall $\times$ conc. of ion/total rainfall) is normally lower than the mean average values.

These constituents are likely to be present in ionic form in rain water (except for silica) and as such can be taken up by the plants directly (foliar absorption) or by the plant roots from the soil, in so far as these are not lost by runoff. It would be apparent from data (Table 3) that 13.6 kg/ha of Ca, 7.8 kg/ha NO_3 & 4.1 kg/ha K ions were brought down by rains.

The examination of data given in Table 1 also shows that unlike some other places like Calcutta & Bombay (Handa 1983), there was no incident of acid rain over Lucknow in 1982.

4.1. *Sources of various constituents* — The exact identification of any specific emitter contributing to the various constituents present in atmosphere or in rainfall is somewhat easy in areas, where the sampling site is near the emitting sources. In Lucknow,

TABLE 4

Correlation coefficients between various constituents present in rain water over Lucknow in 1982

Parameter (X)	Parameter (Y)									
	EC	HCO_3	Cl	F	NO_3	Ca	Mg	Na	K	SiO_2
EC	1	.760	.666	.600	.726	.793	.088	.829	.575	.393
HCO_3		1	.543	.520	.449	.911	.089	.659	.444	.498
Cl			1	.459	.533	.607	.091	.658	.887	.077
F				1	.729	.521	—.172	.471	.420	—.169
NO_3					1	.579	—.120	—.014	.489	—.036
Ca						1	.121	.546	.479	.275
Mg							1	.099	.050	.225
Na								1	.569	.466
K									1	.375

TABLE 5

Trace elements in rain water samples collected at Lucknow in 1982

Date of collection (1982)	Fe	Mn	Ag	Cu	Zn	Co	Mo	Cd (micrograms/l)	Sr	Li	Rb	Cs	Cr	Pb	Ni
25 Jan	25	4	nd	31	12	nd	nd	nd	5	nd	nd	nd	2	3	5
1 Mar	120	21	2	14	25	1	nd	nd	18	nd	2	nd	3	5	8
4-5 Jun	23	8	4	5	13	.75	nd	nd	5	nd	1	nd	nd	2	2
14 ,,	32	11	8	3	20	nd	nd	nd	7	nd	.66	nd	nd	6	3
5-6 ,,	24	.8	11	5	22	.25	nd	nd	3	nd	nd	nd	nd	3	2
17 ,,	40	7	nd	nd	18	nd	nd	nd	5	nd	nd	nd	nd	3	3
13 Jul	30	5	.6	3	5	nd	nd	nd	2	.2	.5	nd	nd	nd	2
23 ,,	37	3	2	6	7	nd	nd	.3	7	.8	2	.3	nd	nd	6
25 ,,	16	1	nd	3	5	nd	nd	nd	1	.3	.4	nd	nd	nd	3
27 ,,	25	3	nd	2	5	nd	nd	nd	2	.3	.4	nd	.6	nd	1
3 Aug	23	2	.8	4	6	nd	nd	nd	2	.4	.6	nd	nd	nd	2
3 ,,	83	2	nd	6	14	nd	nd	nd	2	.8	2	nd	3	nd	6
8 ,,	45	4	8	8	19	2	nd	nd	9	2	2	.5	nd	nd	16
12 ,,	40	2	nd	10	29	nd	nd	nd	7	2	3	1	nd	nd	4
19 ,,	26	2	.8	3	14	nd	nd	nd	2	.3	.5	nd	nd	nd	3
20 ,,	39	2	3	1	9	nd	nd	.1	1	.3	.4	nd	nd	nd	5
21-22 ,,	16	2	.8	2	7	nd	nd	nd	2	.4	.6	.2	nd	nd	5
26 ,,	77	2	1	6	29	1	nd	.5	nd	.8	.6	nd	nd	nd	6
27 ,,	40	2	nd	2	9	.5	nd	nd	2	.4	.3	nd	nd	nd	4
30-31 ,,	35	3	2	6	29	nd	nd	nd	4	.8	.8	nd	nd	nd	4
1 Sep	18	1	.4	1	9	nd	nd	nd	1	.4	.4	.2	nd	nd	3
10 ,,	21	2	nd	2	9	nd	nd	nd	nd	nd	.9	nd	nd	nd	nd
11 ,,	2	.8	nd	nd	3	nd	nd	nd	nd	nd	.19	nd	nd	nd	.6
12 ,,	13	nd	nd	1	6	nd	nd	nd	nd	nd	.13	nd	nd	nd	nd
13 ,,	13	nd	nd	3	16	nd	nd	nd	nd	2	.4	nd	nd	nd	nd
10 Nov	23	nd	nd	nd	9	nd	nd	nd	9	nd	4	6	nd	nd	2
28 Dec	166	25	nd	22	43	nd	nd	nd	nd	nd	8	nd	nd	8	25
28 ,,	133	20	nd	6	17	nd	nd	nd	nd	nd	5	nd	nd	11	7
Average	41.8	4.8	1.6	5.5	14.6	.2	nd	.03	3.4	.46	1.31	0.29	0.31	1.46	4.49
Weight av.	28.7	2.8	1.3	2.9	10.6	.1	nd	.02	2.2	.35	.65	.15	0.12	0.53	2.91
s	38.7	6.6	2.9	6.8	9.6	.46	nd	.11	4.0	.62	1.80	1.1	0.85	2.83	5.13
$s/\sqrt{n}$	7.3	1.2	0.5	1.3	1.8	.09	nd	.21	.76	.12	.34	.22	0.16	0.53	0.97

nd=not detected; *s*=estimate of standard deviation

TABLE 6

Trace elements (Kg/ha) brought down by rainfall in Lucknow in 1982

Unit	Pb	Fe	Mn	Ag	Cu	Zn	Co	Cd	Ni	Li	Rb	Cs	Cr
Kg/ha	.005	.287	.028	.013	.029	.106	.001	.0002	.029	.0035	.0065	.0015	.001

TABLE 7

Reccommended limits & ranges in trace element concentrations

	Cd	Cr	Pb	Ni	Ag
Recommended limits μg/l	.2	40	5-20	30	0.1
Lucknow rains (1982) (μg/l)	nd-0.5	nd-3	nd-11	nd-25	nd-11

Recommended limits are for fresh water bodies (biota); nd=not detected

TABLE 8

Correlation coefficient (r) between trace elements in rain water, Lucknow (1982)

Parameter (X)	Parameter (Y) Fe	Mn	Ag	Cu	Zn	Co	Cd	Sr	Li	Rb	Cs	Cr	Pb	Ni
Fe	1	.87	—.07	.48	.67	.22	.13	.17	—.10	.78	.11	.34	.73	.75
Mn		1	.03	.48	.57	.14	—.12	.30	—.30	.68	—.17	.25	.88	.65
Ag			1	—.02	.22	.45	—.003	.31	.06	.14	—0.19	—.12	.16	.12
Cu				1	.50	.14	—.004	.26	.005	.39	—.14	.48	.42	.57
Zn					1	.26	.15	.22	.23	.55	—.07	.08	.49	.64
Co						1	.24	.45	.34	.01	—.04	.12	—.02	.39
Cd							1	—.08	.15	—.05	—.05	—.11	—.16	.08
Sr								1	.08	.12	.33	.45	.13	.16
Li									1	.02	—.01	—.07	—.38	.14
Rb										1	.33	—.02	.59	.74
Cs											1	—.10	—.14	—.06
Cr												1	.13	.11
Pb													1	.46
Ni														1

however, there is no predominant emitting source and as such only a very tentative approximation about the various sources contributing the various constituents to rain water can be made.

The data given in Table 4 shows that there is very good correlation between Ca & HCO_3 ion pairs as also between C1 & K ion pair. It is suggested that calcareous aerosol particles which owe their origin to soil dust react with aq. CO_2 to form Ca $(HCO_3)_2$. Further, the high correlation coefficient value between C1 & K ions would seem to indicate that the influence of marine salt nuclei is not significant over Lucknow.

4.2. *Trace elements* — The examination of trace elements in rain water (Table 5) shows that the concentrations of various trace elements vary considerably from shower to shower. Further since the weighted average values are lower than the mean average values, it is obvious that the concentration of trace elements decreases with increase in quantum of rainfall. As a corollary to this, the trace element concentrations during monsoon season in rain water are normally lower than during the non-monsoon seasons, although exceptions may occur.

Assuming 1000 mm as the total rainfall in Lucknow in 1982, it would be observed that around 0.287 kg/ha of Fe were brought down by rain (Table 6). The significant point is the very low concentration of Pb and Cd ions, which are toxic to humans and other forms of life.

4.3. *Water quality for aquatic biota* — Fish and some other forms of aquatic life are quite sensitive to some elements (Table 7). An examination of the data shows that at times the Cd, Ag and Pb content exceed the limits given for aquatic biota.

4.4. *Sources of trace elements* — As with the major constituents, the trace elements too owe their origin to both natural & anthropogenic sources. Due to non-occurrence of any specific emitter like blast furnace or a smelter in the vicinity of the sampling site, only generalized conclusions can be drawn. An examination of the correlation coefficient values between various ion pairs (Table 8) it is observed that their is fairly good correlation between the following ion pairs; indicating that they may have a common source :

Fe : Mn ; Fe : Zn ; Fe : Rb; Fe : Pb; Fe : Ni;

Mn : Rb ; Mn : Pb; Mn : Ni; Zn : Ni ; Rb : Ni

On the other hand there are certain ion pairs, which have little or even the correlation coefficient is —ve, indicating that these come from diverse sources, *viz.*,

Fe : Ag; Fe : Cd; Fe : Li ; Fe : Cs; Ag : Cu;
Ag : Cd ; Ag : Li; Ag : Cs; Ag : Cr ; Mn : Ag;
Mn : Cd ; Mn : Li; Mn : Cs; Ag : Pb; Ag : Ni;
Cd : Sr; Cd : Rb; Cd : Cs

Since there is little information about the contributions from various sources contributing these trace elements to the atmosphere, except in the most qualitative terms, it is difficult to pinpoint the contributions from the various sources, except that the high concentration of Fe, would seem to indicate soil dust as an important source.

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