

## CHEMICAL COMPOSITION OF RAIN WATER OVER CALCUTTA

Although scattered references on the chemical composition of rain water in some parts of India occur in literature (Leather 1906, Hayman 1906, Holland and Christie 1908; Dhar and Ram 1933, Das, Sen and Pal 1933, Ram 1934, Narayanaswamy 1939, Mukherji 1958 and Banerji *et al.* 1967), a detailed analysis of the various constituents present in rainwater has been lacking. Due to the significance of these constituents in supplying ions to inland water supply (Eriksson 1958, Gorham 1961, Junge 1958 and others) a detailed study of the chemical composition of rainwater over Calcutta for the period June 1967 to June 1968 was made. Discussion of some of the main results and conclusions drawn are briefly outlined below.

The data given in Table 1 shows clearly that the

chemical composition of rain water varies considerably from month to month with maximum values lying around April and May. This is quite in contrast with the findings of the European investigators (Eriksson 1952), who report a winter maxima. The explanation seems to lie in the fact that during these months there are considerable dust storms and part of this dust is likely to be washed down during the rains; the soluble portion of the dust contributing to high values for the dissolved mineral content in rain water. This hypothesis seems to get confirmation from the fact that the concentration of bicarbonate ions in rain water is extremely high. Since bicarbonate ions are likely to be primarily of local origin, this explanation does not seem to be illogical.

The calculation of the coefficient of variation values (Table 2) and the plot of the 'integral frequency' curve shows interesting light on the variations of the various constituents in rain water

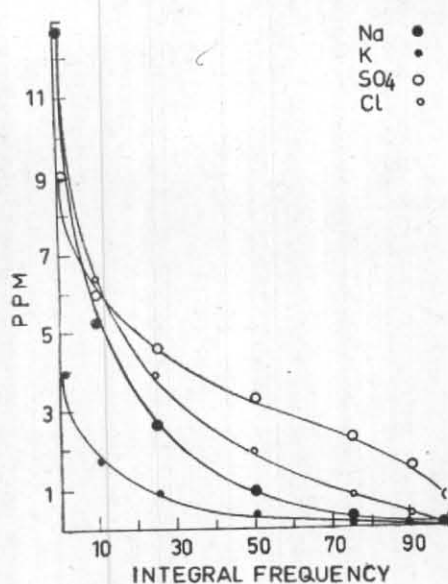


Fig. 1

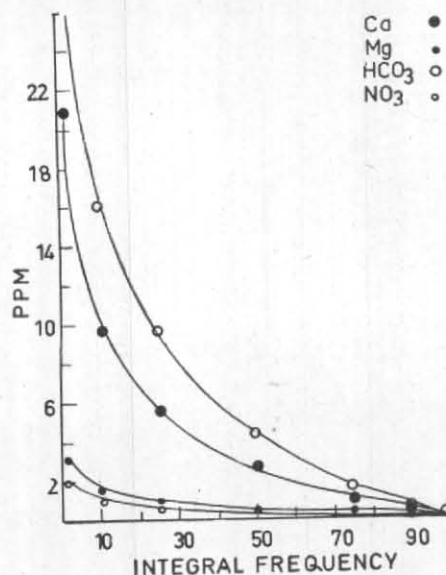


Fig. 2

Integral frequency values for Na, K, SO<sub>4</sub>, Cl; Ca, Mg, HCO<sub>3</sub> and NO<sub>3</sub> ions present in rain water over Calcutta

TABLE 1

Monthly average chemical composition of rain water over Calcutta (1967 to 1968)

Constituents	1967					1968					
	Jun	Jul	Aug	Sep	Nov	Jan	Feb	Mar	Apr	May	Jun
HCO <sub>3</sub>	14.4	7.16	5.65	1.19	8.00	4.00	7.00	6.00	12.70	16.80	4.80
Cl	4.42	3.13	2.24	1.04	3.00	2.50	2.00	2.00	6.10	9.80	2.59
SO <sub>4</sub>	5.14	5.54	3.16	2.59	—	9.66	4.50	4.90	5.20	5.69	.98
NO <sub>3</sub>	.10	.22	.28	.32	1.60	—	.06	.11	1.57	.67	.51
Fe	—	.02	.016	.005	—	—	—	—	—	—	—
B	—	.002	.025	.011	—	—	—	—	—	—	—
Ca	5.94	3.76	3.44	.81	11.60	8.00	3.60	3.20	8.88	7.29	2.29
Mg	1.08	.43	.57	.09	tr	.12	tr	tr	1.02	1.61	.69
Na	1.32	1.66	.87	1.13	1.30	.30	1.32	1.70	3.54	7.09	1.17
K	.38	.49	.43	.14	3.10	.10	.90	.50	1.38	1.87	.61
SiO <sub>2</sub>	—	—	2.27	1.37	—	—	—	—	2.07	0.85	1.20
pH	6.20	6.05	6.13	5.11	6.10	6.10	6.05	7.15	6.35	6.68	6.80
F	—	—	—	.07	—	—	—	—	—	.12	.02

TABLE 2

Mean average, standard deviation and coefficient of variation values for various constituents present in rain water over Calcutta

	N	K	Ca	Mg	SO <sub>4</sub>	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	pH
Mean average (ppm)	1.96	.64	3.93	.60	3.62	6.88	2.80	.37	5.97
Std. deviation	2.75	.86	4.54	.68	1.84	7.41	2.78	.42	.68
Coeff. of var. (Cv)	1.40	1.34	1.15	1.12	.50	1.10	1.00	1.13	.11

If it be assumed that the values of  $C_v$  (coefficient of variation) 0.5 or lower, represent low variations and values above 1.0 as high variations, it is apparent that the majority of the ions reported in Table 2 show high variations in their absolute values in rain water, with the alkali metals leading in this respect. Only  $\text{SO}_4$  and hydrogen ions concentrations show reasonably low variations (Figs. 1 and 3).

Calcutta is only 50 km from the mouth of the *Ganga* and 150 km from the sea proper. Since the topography of the land from Calcutta to the mouth of the *Ganga* is flat one would expect considerable contribution of the sea salt nuclei (Leefflang 1938). An examination of the ratios of various constituents present in rain water, however, shows that in the case of Calcutta, at least this seems to be far from true (Table 5, Fig. 4). An examination of the ratios of Na/K, Na/Ca, Ca/Mg, Na/Mg, Na/Cl and Cl/ $\text{SO}_4$  shows that these values are vastly different from that prevalent in sea water. The ratio Na/K (calculated on the basis of their concentrations expressed in mg/l or parts per million) in sea water is around 28, while in rain water over Calcutta, values varying from 0.4 to 12.9 have been encountered, indicating considerable addition of potassium ions from local sources. The same is true for other ratios, excepting for the ratio Na/Cl, which except for the one sample analysed in January 1968, seems to vary within reasonable limits.

An examination of the values of the coefficient of variation as well as that of the integral frequency curves (Fig. 4), shows that the ratio  $\text{SO}_4/\text{NO}_3$  shows only small variations, while the ratios Ca/Mg, Na/Cl and Cl/ $\text{SO}_4$  show only moderate variations. One explanation for this low variation could be that the major portions of these ion pairs have a more or less the same source. This explanation seems to be quite plausible for the ion pair  $\text{SO}_4$  and  $\text{NO}_3$ , both owing their origin to a great extent—in rain water over Calcutta—to the combustion of the fossil fuel, although it is possible that part of the sulphate ions are likely to be of marine origin, while part of the nitrate ions are likely to be produced through electric discharges in the atmosphere or photochemical oxidation processes.

An investigation of the chloride concentration is of special interest as it is generally assumed that all of the chloride derived in rain water is of marine origin (Eriksson 1958). Conway (1942) and Leefflang (1938), have given equations to describe the variations in chloride concentration in rain water with distance from the sea. These equations are

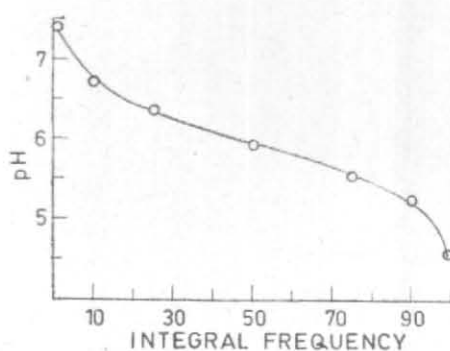


Fig. 3. Integral frequency values for hydrogen ion concentrations (pH) in rain water over Calcutta

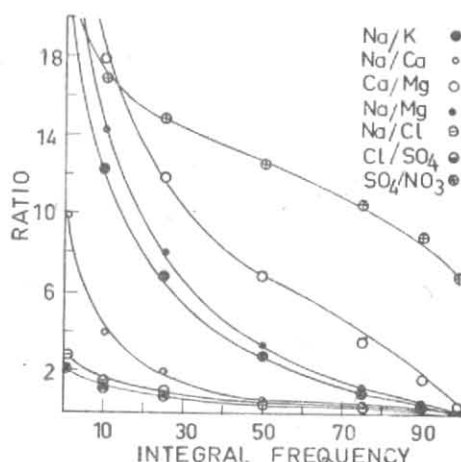


Fig. 4. Integral frequency values for the ratios between various ions present in rain water over Calcutta

as follows—

$$\text{Cl} = 5.7e^{-0.0367x} + 0.55e^{-0.00242x} \quad (\text{After Conway})$$

$$\text{Cl} = 11.7e^{-0.525x} + 3e^{-0.0230x} + 3.0 \quad (\text{After Leefflang})$$

where  $x$  represents the distance in kilometres from the sea. Both these equations consist of two terms with the difference that the equation due to Leefflang contains a third term—a constant—which according to Eriksson (1952) seems to be quite reasonable, as there is always chloride in rain water even very far from the sea. If it be assumed that Calcutta is around 150 kilometres from the sea, the expected values for chloride concentrations in rain water over Calcutta are 0.41 (Conway's equation) and 3.1 ppm (Leefflang's equation) respectively (the corresponding values assuming a distance of 50 km from the sea are 1.41 and 3.9 ppm respectively). The data given in Table 2

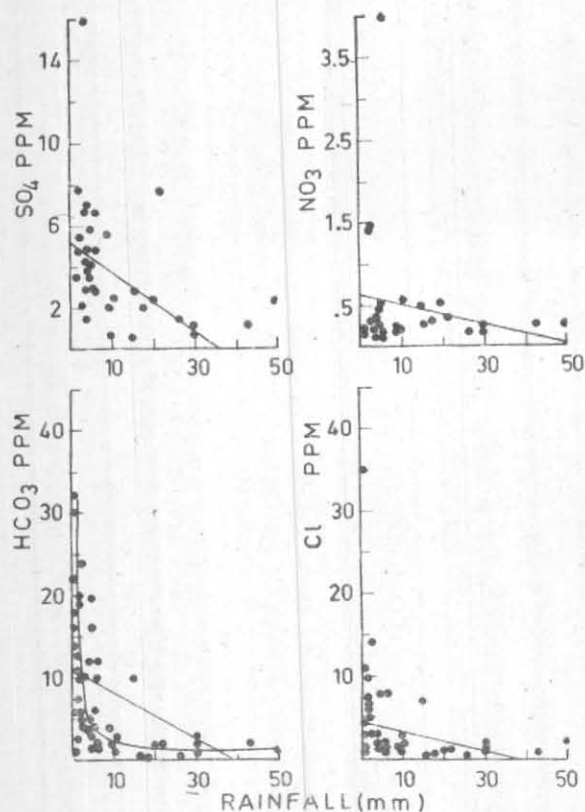


Fig. 5. Variations in the concentrations of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4$  and  $\text{NO}_3^-$  as a function of total rainfall

shows that the mean average value for chloride concentration is quite close to that obtained by Leeflang's equation, but the data given in Table 1 and Fig. 1, shows clearly that the actual chloride concentration in rain water fluctuates considerably.

The same is true for the other constituents.

From the preceding paragraphs it is quite obvious that the chemical composition of rain water is likely to be affected by several factors like distance from the sea, local contribution (as dust and/or products of combustion of fossil fuels etc (and even to the differential washing down of various salts during the transport of the salts from the sea (Sugawara 1949), as well as during the occurrence of rainfall. However, it seems reasonable to expect that the first few showers will carry

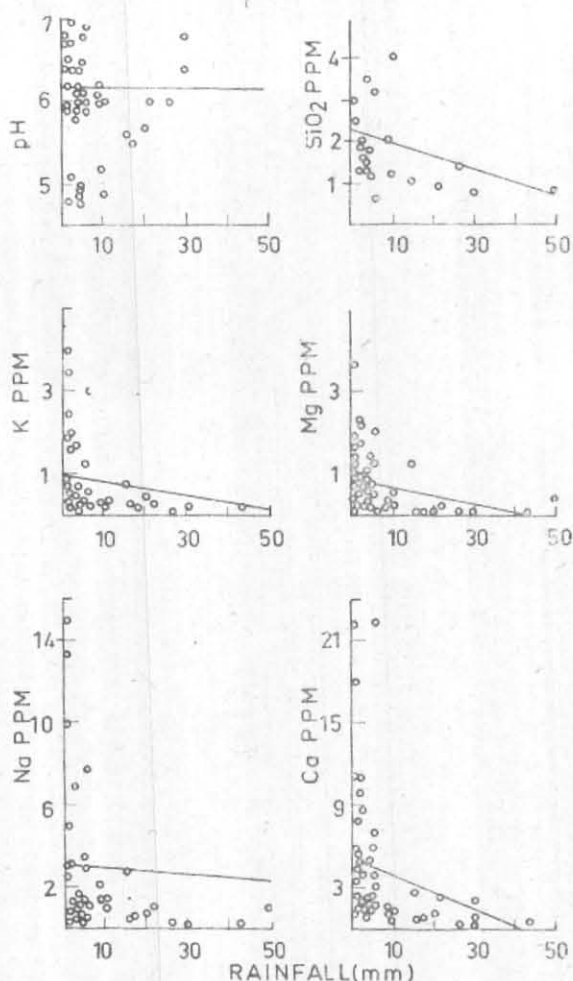


Fig. 6. Inter relation between quantity of rainfall and concentration of various constituents present in rain water, viz., Na, Ca, K, Mg, pH and  $\text{SiO}_2$

down the major portion of the dust particles as well as soluble gases present in the atmosphere, so that the subsequent showers are relatively poor in dissolved mineral content (although it may be pointed out that investigations carried out by Handa (1969) have shown conclusively that the chemical composition of the subsequent showers vary quite irregularly). Under these circumstances, there should be a negative correlation between the total quantity of rainfall and the concentrations of the various ions present in rain water. Calculation of the sample regression coefficients between the total quantity of rainfall and the concentrations of various ions show that this coefficient has negative values in all the cases, although the coefficient of correlation values fall short of the ideal values of unity (Figs. 5 and 6).

It is interesting to record that a 'hyperbolic curve' seems to fit into the data quite appropriately in

most of the cases, although it has been drawn only in the case of bicarbonate ions alone.

*Soil Research Laboratory,  
Model Town, Amritsar  
August 24, 1968*

B. K. HANDA

REFERENCES

- |  |      |  |
|--|------|--|
| Banerji, Partha, Mukhopadhyay, P. K.,<br>Handa, B. K. and Chatterji, S. D. | 1967 | <i>Indian J. Met. Geophys.</i> , <b>18</b> , p. 291.                             |
| Chebotaiev, I. I.  | 1951 | <i>Wat. &amp; Wat. Engng.</i> , <b>21</b> , pp. 121-129.                         |
| Conway, E. J.  | 1942 | <i>Proc. roy. Irish, Acad.</i> , <b>48</b> , pp. 119-159.                        |
| Das, A. K., Sen, G. C. and Pal, C. K.                                      | 1933 | <i>Indian J. agric. Sci.</i> , <b>3</b> , pp. 353-359.                           |
| Dhar, N. R. and Ram, A.  | 1933 | <i>J. Indian chem. Soc.</i> , <b>10</b> , pp. 125-133.                           |
| Eriksson, E.   | 1952 | <i>Tellus</i> , <b>4</b> , pp. 215-232 and 280-303.                              |
|  | 1958 | <i>Climatology</i> , Rev. Res. UNESCO, Paris, pp. 147-180.                       |
| Handa, B. K.   | 1969 | <i>Tellus</i> , <b>21</b> , 2, pp. 95-106.                                       |
| Gorham, E.   | 1961 | <i>Bull. geol. Soc. Amer.</i> <b>72</b> , pp. 795-840.                           |
| Hayman, J. M.  | 1906 | <i>Rep. Cawnpore India Agric. Stn.</i> , pp. 23-29.                              |
| Holland, T. H. and Christie, W. A. K.                                      | 1908 | <i>Rec. geol. Surv. India</i> , <b>38</b> , Pt. 2.                               |
| Junge, C. E.   | 1958 | <i>Advances in Geophys.</i> , <b>4</b> , pp. 1-108, Acad. Press, Inc., New York. |
| Leather, J. W.   | 1906 | <i>Mem. Dep. Agric. India</i> , Chem. Ser. 1, No. 1, pp. 1-11.                   |
| Leefflang, K. W. H.  | 1938 | <i>Chem. Weekbl.</i> , <b>35</b> , pp. 658-664.                                  |
| Mukherji, A. K.  | 1958 | <i>Indian J. Met. Geophys.</i> , <b>9</b> , pp. 67-71.                           |
| Narayanaswamy, R.  | 1939 | <i>Proc. Indian Acad. Sci.</i> , <b>9A</b> , pp. 515-525.                        |
| Ram, A.  | 1934 | <i>Proc. Acad. Sci. (U.P. Agric. Oudh)</i> , <b>4</b> , pp. 147-158.             |
| Sugawara, K., Oana, S. and Kayama, T.                                      | 1949 | <i>Bull. Chem. Soc., Japan</i> , <b>22</b> , pp. 47-52.                          |