Chemical composition of monsoon rains over Calcutta. Part I

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ABSTRACT

Monsoon rainwater over Calcutta was analysed for Na, K, Ca, Mg, Cl, SO_4, HCO_3, NO_3, pH, SiO_2, B and Fe. The data shows that the dissolved mineral content is greatly affected by meteorological conditions viz. intensity, quantity and interval between various showers as well as wind velocity (cyclonic weather). Amongst the ions bicarbonate ions are quite prominent, particularly when rainfall is low. The sulphate ions generally exceed the chloride ions. The origin of the various constituents is also discussed.

Introduction

Although considerable data on the chemical composition of rainwater in Europe, Australia and U.S.A. is available (Eriksson, 1959, 1960; Junge and Werby, 1958; Carroll, 1962; Hutton & Leslie 1958) little systematic studies have been reported from India, although the significance of some constituents present in rainwater to agriculture had long been recognised. Naraynaswamy (1939), for example, quotes values for Cl and NO_3 from Calcutta and Kanpur respectively, determined by early workers, while he himself analysed the NO_3, NO_2 and Cl content of monsoon rains over Bombay. Partial analysis of rainwater samples over Calcutta (in press), was also undertaken by Prof. Chatterji of Jadavpur University, at the suggestion of the author (1966). In the current season, a more systematic study of the chemical composition of rainwater was undertaken by the author. In part I of this paper, a general idea of the chemical composition of rainwater and sources for dissolved constituents in rainwater is outlined. In part II the composition of various fractions is described.

Experimental

The water samples were collected in polyethylene containers fitted with polyethylene funnels. They were placed on a raised platform (about 0.7 m high), on the top of the roof (around 30 m from ground level). No attempt was made to separate the suspended matter.

The analytical methods employed for analysis are briefly outlined below:

(i) pH: The pH was determined with the help of Cambridge pH-meter, using glass electrode and calomel electrode.

(ii) SiO_2: Around 250–500 ml of rainwater sample was acidified and evaporated to dryness. The SiO_2 was determined by the conventional gravimetric method.

(iii) Na, K: A measured quantity (50 or 100 ml) was concentrated slowly at low heat to around 10 ml. The volume was then made exactly 10 ml and Na and K determined flame photometrically.

(iv) Ca & Mg: These were determined complexometrically using murexide and Eriochrome Black T as indicators respectively.

(v) HCO_3: Acidometric titration using methyl orange-bromocresol green mixed indicator.

(vi) Cl: A suitable aliquot (25–200 ml) was made alkaline with the addition of 0.5 ml standard N/40 NaOH and concentrated to around 10 ml at low heat. The alkali was then neutralised by the addition of an equivalent amount of standard HNO_3, followed by addition of a few crystals of $CaCO_3$. Chloride was then determined by the conventional method viz. titration with standard $AgNO_3$, using K_2CrO_4 (saturated with Ag_2CrO_4) as indicator.

(vii) SO_4: 250–1000 ml of water sample was made alkaline with NaOH and concentrated down to around 10–20 ml at low heat. The solution was then filtered off and residue washed

Table 1. *Chemical composition of monsoon rainwater over Calcutta (1967)*

Sl. No.	Date of coll.	Rain-fall mm	Constituents (p.p.m)											
			HCO_3	Cl	SO_4	NO_3	Fe	B	Ca	Mg	Na	K	SiO_2	pH
1a	19.6.67	0.1	18.0	4.50	—	—	—	—	4.00	1.95	—	—	—	6.5
2b	19.6.67	0.1	22.0	4.50	—	—	—	—	4.00	1.22	—	—	—	6.2
3a	21.6.67	4.0	5.00	2.00	2.90	0.10	—	—	1.00	0.85	1.34	0.30	—	6.1
4b	21.6.67	3.0	5.00	3.00	—	—	—	—	2.00	1.10	—	—	—	—
5	23.6.67	tr	16.00	4.95	—	—	—	—	12.80	0.39	—	—	—	6.0
6a	28.6.67	2.0	19.00	9.95	4.80	—	—	—	11.20	0.97	1.2	0.24	—	5.9
7b	28.6.67	6.0	12.00	1.97	—	—	—	—	3.10	1.30	—	—	—	—
8c	28.6.67	4.0	12.00	2.95	—	—	—	—	5.20	1.10	—	—	—	6.2
9	30.6.67	2.0	20.00	5.98	7.72	—	—	—	10.20	0.85	1.42	0.61	—	6.4
10	2.7.67	5.1	19.80	1.98	5.83	—	0.02	—	6.90	0.73	1.56	0.30	—	6.5
11a	3.7.67	3.9	2.90	1.94	7.02	—	0.01	—	1.90	0.59	1.34	0.27	—	6.1
12b	3.7.67	6.0	1.50	1.48	4.80	0.11	—	—	1.72	0.12	1.18	0.30	—	5.9
13	6.7.67	tr	13.90	10.9	—	—	—	—	10.20	1.60	2.60	0.13	—	6.2
14	14.7.67	6.0	1.96	1.49	2.82	0.15	0.02	—	1.62	0.19	0.74	0.33	—	6.0
15a	18.7.67	4.0	3.95	1.25	3.80	0.35	0.02	—	2.38	0.24	0.78	0.37	—	5.9
16b	18.7.67	1.0	7.35	1.00	—	—	—	—	2.40	0.48	—	—	—	—
17a	19.7.67	3.6	5.95	2.97	6.70	—	—	—	2.38	0.73	1.18	0.76	—	5.8
18b	19.7.67	1.8	7.45	2.50	—	—	—	—	4.75	0.48	—	—	—	5.9
19c	19.7.67	9.0	4.00	1.50	4.80	0.26	—	0.002	1.60	0.24	2.26	0.36	—	6.1
20	21.7.67	1.7	9.95	7.45	—	—	—	—	5.50	0.30	3.26	1.62	—	6.2
21	3.8.67	5.7	10.00	2.25	2.90	0.21	0.04	0.020	4.00	0.49	0.67	0.60	—	6.0
22π	6.8.67	15.6	0.50	0.48	2.43	0.24	0.02	0.031	0.70	0.05	0.59	0.36	—	5.6
23λ	6.8.67	17.3	tr	0.88	2.00	0.31	0.01	0.032	0.60	tr	0.71	0.28	—	5.5
24	7.8.67	0.1	5.95	2.95	—	—	—	—	—	—	—	—	—	6.5
25	10.8.67	42.8	2.60	0.75	—	0.32	0.03	0.021	—	—	0.37	0.27	—	—
26	11.8.67	19.8	2.00	0.97	2.40	0.52	0.02	—	1.24	0.10	0.81	0.47	—	5.7
27	13.8.67	0.1	14.95	7.45	—	—	—	—	6.00	1.20	—	—	—	6.7
28a	16.8.67	0.5	5.85	2.90	—	—	—	—	4.00	1.11	—	—	—	—
29b	16.8.67	1.5	4.95	1.50	3.50	0.21	0.02	0.005	2.00	0.24	0.45	0.36	—	6.3
30π	17.8.67	4.4	1.50	1.00	3.82	0.31	0.03	0.004	1.40	0.36	0.35	0.27	1.5	6.4
31λ	17.8.67	0.3	1.25	0.95	—	—	—	—	1.20	0.28	—	—	—	6.2
32	19.8.67	0.1	31.95	9.98	—	—	—	0.050	22.1	1.44	3.18	1.96	—	6.8
33a	20.8.67	1.0	11.20	3.76	—	—	—	—	8.00	1.93	—	—	—	—
34b	20.8.67	1.4	10.00	2.86	—	—	—	—	4.40	0.24	—	—	—	—
35	21.8.67	21.6	2.00	1.30	7.68	0.32	0.01	0.008	2.40	0.24	2.16	0.34	0.9	6.0
36a	24.8.67	10.6	2.95	1.97	2.48	0.58	—	0.010	1.20	0.60	1.02	0.39	4.0	6.0
37b	25.8.67	9.5	3.87	1.00	2.05	0.19	0.02	0.005	1.20	0.24	1.52	0.32	2.0	6.2
38	24.8.67	26.3	0.50	0.50	1.48	0.18	0.01	0.065	0.44	0.18	0.32	0.11	1.4	6.0
39	28.8.67	4.0	—	—	4.25	0.32	—	0.016	—	—	0.40	0.34	3.5	6.0
40a	29.8.67	0.5	1.00	0.98	2.00	0.23	0.007	0.024	1.00	0.12	0.40	0.29	3.0	5.95
41b	29.8.67	3.0	2.50	0.89	2.11	0.16	0.009	0.058	1.60	0.24	0.36	0.16	2.0	5.95
42	30.8.67	1.2	2.00	0.98	3.01	0.18	0.012	0.029	1.80	0.12	0.59	0.35	2.5	6.30
43	31.8.67	2.5	3.78	2.87	5.36	0.20	—	0.026	3.60	0.49	0.82	0.45	1.9	6.40
44	2.9.67	4.4	2.50	1.00	3.50	0.29	0.008	0.062	1.80	0.19	0.61	0.26	1.3	6.10
45π	4.9.67	10.0	1.00	2.89	0.73	0.20	0.003	0.027	0.60	0.29	1.45	0.34	1.2	6.00
46λ	4.9.67	3.6	3.87	2.95	1.52	0.20	0.005	0.015	2.20	0.24	1.86	0.32	1.6	6.00

a, b, c indicate showers occurring during different times of the same day.
π, λ represent different fractions collected during one continuous shower.

thoroughly with hot water thrice; the total volume of the filtrate being kept around 50–60 ml. Sulphate was then determined gravimetrically (after acidification of the filtrate) by the conventional method as $BaSO_4$.

(viii) NO_3: A measured quantity (50 or 100 ml) water sample was made alkaline and then allowed to evaporate to almost complete dryness on water bath. A drop of dilute sulphuric acid was then added to neutralise the alkali and the

Table 2. *Average chemical composition of rainwater in Calcutta and other places*

Constituent p.p.m.	Calcutta			Bombay			N. Europe			Australia (S.E.)		
	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
HCO_3	31.95	tr	7.50	—	—	—	—	—	—	—	—	—
Cl	10.92	0.50	2.87	26.5	2.7	13.6	64.0	0.06	3.47	138.5	–.0	4.43
SO_4	7.72	0.73	3.73	—	—	—	6.52	0.18	2.19	tr	tr	—
NO_3	0.58	0.10	0.26	0.2	0.08	0.13	1.6	0	0.27	—	—	—
Fe	0.04	0.01	0.016	—	—	—	—	—	—	—	—	—
B	0.065	0.002	0.025	—	—	—	—	—	—	—	—	—
Ca	11.20	0.30	3.83	—	—	—	25.5	0.20	1.42	20.0	0	1.20
M	1.95	tr	0.58	—	—	—	2.93	0.12	0.39	27.6	0	0.50
Na	3.26	0.32	1.17	—	—	—	63.20	0.60	2.05	82.8	0	2.46
K	1.96	tr	0.43	—	—	—	11.20	0.00	0.35	6.6	0.04	0.37
SiO_2	4.00	0.90	2.23	—	—	—	—	—	—	—	—	—
pH	6.80	5.50	6.13	—	—	—	7.7	3.9	5.47	—	—	—

Data from Bombay from Narayanaswamy (1939) and data from Europe and Australia quoted by Carrol (1962).

basin allowed to dry completely at room temperature. The NO_3 was then determined by the phenol-disulphonic acid method.

(ix) Iron: After concentration of an aliquot of the sample, the thioglycollic acid method was used for colorimetric determination of iron.

(x) Boron: A measured quantity (50 or 100 ml) were made weakly alkaline and allowed to evaporate in an oven at 90°C to around 1–2 ml. One ml of turmeric-oxalic acid mixture in alcohol was then added the mixture allowed to dry at 50 ± 3°C. The scarlet coloured residue was then extracted with methyl alcohol and the absorbance determined spectrophotometrically.

Results

The chemical analysis data, together, with the approximate quantity of rainfall have been given in Table I. Following generalised conclusions may be drawn from the data given there:

(i) At the beginning of the monsoon season the bicarbonate ions are very prominent, but later on they become relatively less significant.

(ii) The concentration of dissolved salts seems to be greatly affected by the intensity and total quantity of rainfall. The salinity generally seems to be highest in rainwater samples, when the total rainfall is less than 1–2 mm and when it occurs as a fine drizzle. The interval between different showers also plays an important role.

(iii) The relative proportion of various ions present in rainwater is also affected by other meteorological conditions. Viz. during cyclonic weather e.g. on (3.9.1967 and) 4.9.67, the values for the ratio Na/Ca and Cl/SO_4 exceed unity, where as on the average reverse seems to occur during normal conditions.

(iv) Silica and boron seem to be universally present in rainwater samples although their concentrations vary considerably. Nitrate ions also are present universally, at least as judged from the limited number of samples analysed for this constituent.

(v) The rainwater samples are generally mildly acidic in reaction, the average pH value being around 6.13 (Table II).

(vi) The sulphate concentration generally exceeds the chloride ions, except when the weather is cyclonic in nature. The average sulphate value given in Table II is somewhat misleading not as in cases of low rainfall, sulphate ions could be determined due to shortage of sample. While on the other hand these very samples have high values for chloride ions.

(viii) Amongst the cations, the calcium ions are generally the most prominent although sometimes e.g. during cyclonic weather the sodium ions also become dominating. The magnesium and potassium ions play a subordinate role to these ions.

Discussion of results

Calcutta is situated on the left bank of the river Hooghly, whose active delta begins just

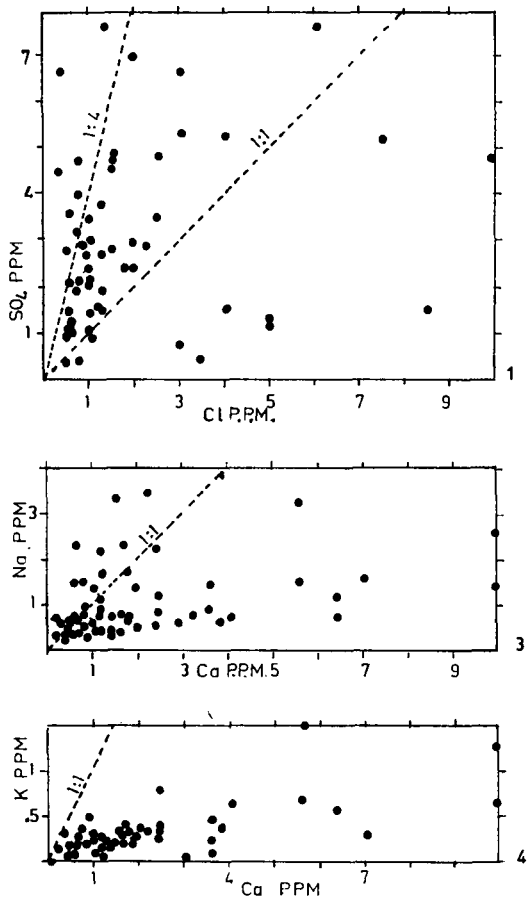

Fig. 1. Plot of SO_4 vs. Cl in rainwater samples.

Fig. 2. Inter-relation between Ca + Mg (expressed as Ca) and HCO_3 ions in rainwater over Calcutta.

Fig. 3. Plot of Na against Ca conc. in rainwater samples.

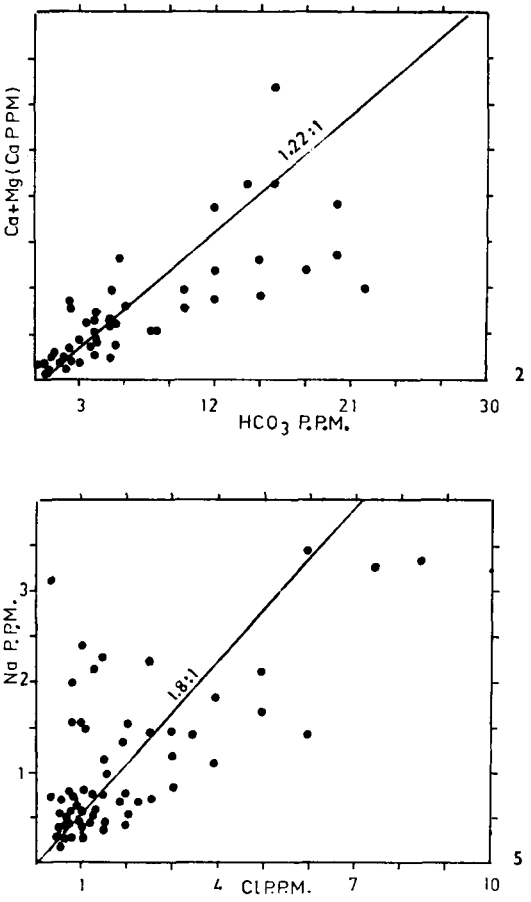

Fig. 4. Plot of K vs. Ca in rainwater samples.

Fig. 5. Variation in conc. of Na ions as a function of Cl-ion conc. in rainwater samples.

south of the city. It is an industrial town, about 50 km from the sea, and has a population of around 8 millions. Although little data on the composition of the suspended matter in the atmosphere is known, it may be assumed that the atmosphere is quite polluted and must have composition, more or less similar to that of the other big cities of the west. The combustion of coal, petroleum, coal, gas, cow dung etc. are likely to release considerable quantities of H_2S, HCl, NH_3, carbonaceous material to the atmosphere. Similarly dust storms, which precede the monsoons, or strong dust raising winds which sometimes occur during the rain pause or sometimes just before the rain actually starts can also contribute dissolved constituents to rainwater. The low level flat topography of the land and its short distance from the sea indicates that sea can also be an important source of salts, particularly when cyclonic conditions prevail.

It is a well known fact that rain brings down particulate matter from the atmosphere, removing matter from the whole depth of the cloud, provided it is below the rainforming layer. During their fall the rain drops collect air borne particles. It is obvious that the dissolved salt content of rain will be affected by all the factors mentioned above. The extent to which, however, each will affect the salinity should broadly be affected by:

(i) The intensity, quantity and time interval

between various showers: factors whose role has already been indicated earlier.

(ii) Quantum of dust in the atmosphere, which will be considerably affected by the meteorological conditions.

(iii) The combustion products or volatile products from fuel etc. The role of these factors in affecting the concentrations of various constituents dissolved in rain is briefly outlined below:

(a) HCO_3-ions: The bicarbonate ions are produced through reaction of the carbon dioxide with calcium carbonate, apparently present in the soil dust. This assumption seems to get confirmation if the conc. of alkaline earths (calculated in terms of Ca p.p.m.) is plotted against the HCO_3-ion conc. The fact that some rainwater samples plot to the left of the 1.22:1 (or 1:1 in terms of equivalent) line indicates (Fig. 2) that some of the magnesium ions may be of marine origin, where as the rainwater samples that plot to the right of this line, indicate the presence of part of the alkali metals as bicarbonate in the atmosphere.

(b) Ca-ions: As already pointed out in the preceding paragraph, soil dust seems to be an important source of calcium ions in rainwater in Calcutta. This non-marine origin of calcium ions is further confirmed if the conc. of calcium ions be plotted as a function of the sodium ions in rainwater (Fig. 3). In sea water, the ratio Na:Ca is around 26:1, however, from Fig. 3 it appears that in majority of the rainwater samples the calcium ions exceed the sodium ions and lie to the right of the 1:1 line.

Similarly the plot of Ca vs K also confirms this assumption (Fig. 4). In sea water the ratio Ca:K is around 1:.95, however, from Fig. 4 it is obvious that except in a few cases the calcium ions far exceed the potassium ions. It may be pointed out, here, that the fact that part of the sodium and potassium ions are likely to be of nonmarine origin does not invalidate this assumption.

(c) Sulphate ions: The main source of sulphur or H_2S in Calcutta is likely to be the combustion of coal, petroleum, cow dung, wood etc. The organic decomposition may also be of some significance in Calcutta area, as considerable amount of land around Calcutta gets waterlogged resulting in the formation of stagnant pools of water e.g. under rice cultivation, which can release H_2S into the atmosphere, which subsequently gets oxidised to SO_2 and then finally into H_2SO_4. The tides occurring in the Hooghly river, or near the mouth of the sea, where the river enters the sea can also help in release of H_2S produced in the relatively shallow basins to diffuse into the atmosphere. While in these preliminary investigations it is not possible to assess the contribution from these factors individually, the results do indicate that the sulphate ions generally exceed the chloride ions in rainwater in Calcutta. However, the relative proportion of $Cl:SO_4$ ions is greatly affected by the meteorological conditions. During cyclonic weather, the chloride ions may exceed the sulphate ions, as due to the relatively short distance and flat topography of the land, the sea salt nuclei can travel farther inwards (Samples dated 4.9.1967), (Fig. 1).

(d) Mg-ions: The conc. of magnesium ions is much less than that of calcium ions (Tables I and II), although it can partly be of marine and partly of non-marine origin. The fact that in the plot of Ca+Mg (calculated in terms of Ca p.p.m.) against HCO_3 (Fig. 2), many rainwater samples plot to the left of the 1.22:1 line, indicates that part of the magnesium ions (and probably also calcium ions) may originally be present in combination with sulphate or even with chloride ions, which fact would then indicate them to be of marine origin. However, magnesium sulphate can also be produced through action of sulphuric acid on soil dust. Similarly $MgCl_2$ may be produced through the action of HCl on soil dust particles.

(e) Na-ions: The sodium ions can be of marine as well as of nonmarine origin. The fact that several rainwater samples plot to the right of the 1.22:1 line (Fig. 2), indicates the presence of sodium bicarbonate (the potassium conc. being very small). However, it is interesting to record that many rainwater samples plot near about the 1.8:1 (Cl:Na) line, the proportion in which these ions are present in sea water. However, the fact that several rainwater samples plot to the left of this line, indicate that in some cases non-marine sources may also be quite significant.

(f) Cl-ions: Of all the trace substances in the air, the chloride ions are the only ones whose major source is geographically well defined. Due to the flat topography of the land and the fact that Calcutta is only around 50 km from the sea, shows that the sea is likely to be an im-

portant source of chloride ions in rainwater in Calcutta area. This is particularly true during cyclonic weather when mechanical carry over of sea salt nuclei (as well as their production in the sea) farther inland (Sl. No. 45, 46, Table I). However, the fact that many rainwater samples plot to the right of the 1.8:1 (Cl:Na) line indicate that in the case of Calcutta, areas, local sources can also be of considerable significance in contributing chloride ions to rainwater.

(g) NO_3-ions: According to Hutchinson (1958), the basic source of nitrate ions is likely to be the soil. Eriksson (1952), however, considers the fuel consumption to be the main source of ammonia-nitrate ions. Larson and Hettick (1956) even report a correlation between NO_3 + NH_3 and sulphate ions since they have a common source-soil and fuel. The data in Table I, however, does not show any such correlation although it must be pointed out that no determinations for NH_3 could be carried out, but the conc. of ammonia is likely to be a fraction of that of the NO_3 ions. This indicates the atmosphere to be an important source for these ions (thunder-lightning).

(h) Silica and Iron: The presence of both these constituents is to be expected and they are more or less entirely of terrestrial non-marine origin.

(I) Boron: All samples which were analysed for this constituent were found to contain this element, although its concentration varies considerably. In the absence of any known volcanic source in the neighbourhood, it may be assumed that boron ions are of terrestrial non-marine origin.

(J) pH: The pH of the rainwater samples varies from 5.5 to 6.8, with average around 6.13 (Table I & II). The acidic reaction is to be expected due to the presence of large amounts of sulphate ions (produced from sulphuric acid), while the relatively high salinity acts as a buffering agent to maintain the pH around 6.1.

In Table II, the maximum, minimum and average values of various constituents have been compared with those of other countries (Carroll, 1962), and those obtained by Narayanaswamy (1939).

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ХИМИЧЕСКИЙ СОСТАВ МУССОННЫХ ДОЖДЕЙ НАД КАЛЬКУТТОЙ. Часть I

Вода муссонных дождей над Калькуттой была проанализирована на Na, K, Ca, Mg, Cl, SO_4, HCO_3, NO_3, pH, SiO_2, B и Fe. Результаты показывают, что концентрация растворенных веществ сильно зависит от метеорологических условий, а именно, от интенсивности, количества и интервала между различными ливнями, так же, как и от скорости ветра (циклонической погоды). Среди ионов большое количество приходится на ионы бикарбонатов, особенно, в случае низких дождей. Количество ионов сульфатов обычно превосходит количество ионов хлоридов. Обсуждается также происхождение различных химических компонент.