Chemical composition of monsoon rains over Calcutta. Part II

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(Manuscript received October 10, 1967)

ABSTRACT

Various fractions of rainwater were collected and analysed for various constituents viz. HCO_3, Cl, SO_4, Ca, Mg, Na and K. In some cases B, NO_3, Fe and pH values were also determined. It was found that although the initial showers are generally more saline than the subsequent ones (with some exceptions), the ratios between various constituents vary quite irregularly. An attempt has been made to account for this irregularity, by discussing the sources of the various constituents.

Introduction

A decrease in salinity of rainwater with time during precipitation has been noted by several observers (Junge, 1958), indicating that major part of the trace substance is collected by falling raindrops. Further a depletion of the trace substances also occurs within the cloud itself. It is obvious, therefore, that there should be a continuous decrease in salinity of rainwater with time. Further it gives an inverse relationship between the dissolved mineral content in rainwater and the quantity of rainfall. This fact frequently observed has sometimes led to the conclusion that the first portion of the rainfall removes nearly all the chemical compounds from the air, the remainder of the rain merely diluting the first portion. However, according to Eriksson (1958), the conc. of chemical compounds in rainwater varies quite irregularly.

In the present paper an attempt has been made to analyse the various fractions generally collected during any one continuous shower and account for the variations in dissolved mineral content. It may be observed here, that although the shower was a continuous one, the intensity of the rainfall varied considerably-sometimes from a heavy shower to a mere fine drizzle.

Experimental

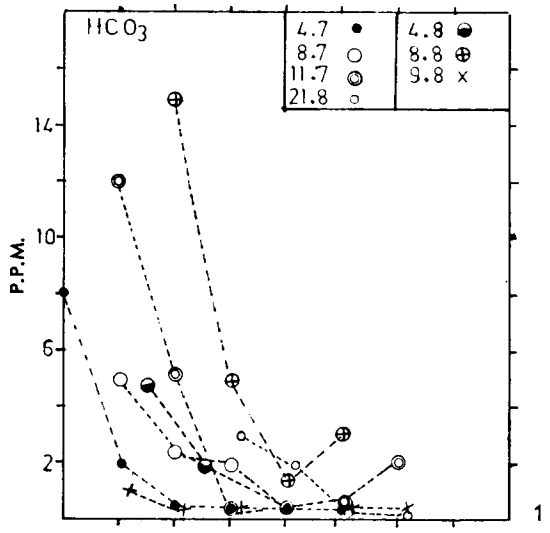
The rainwater samples were collected and analysed in the same manner as described in part I of the paper, except that different fractions were collected.

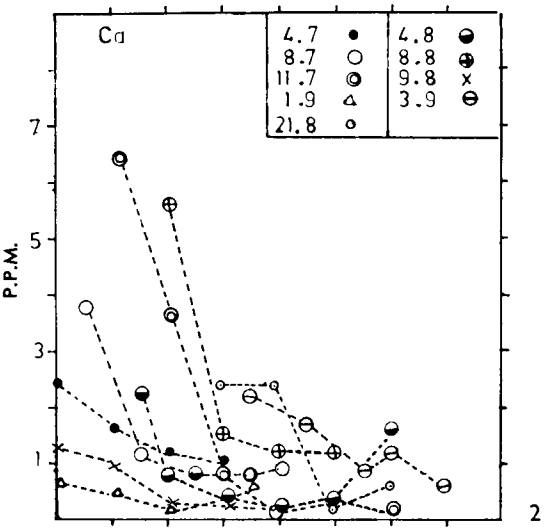
Results

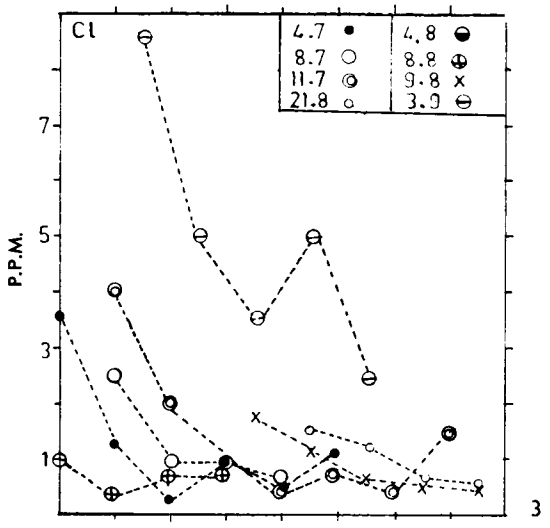
The concentrations of various constituents in the different fractions have been plotted in Fig. 1 to Fig. 11. Broadly speaking one observes a steep fall in the concentration of the various constituents in rainwater with time, although some interesting exceptions are also noticeable; the last fraction frequently having higher dissolved mineral matter than the previous fraction. The fluctuations in the concentrations of various constituents are briefly described below.

(a) HCO_3-ions: The bicarbonate ions are produced by reaction of the carbon dioxide present in the atmosphere, with the calcium or even magnesium carbonate that may be present in the soil dust or otherwise present in the atmosphere as particulate matter. As has already been pointed out in part I of this paper, presence of sodium or potassium bicarbonate is also indicated. Since these ions are primarily of local origin, they are likely to be washed down in the first shower, particularly because the bicarbonates are quite soluble. The precipitate decrease in bicarbonate concentration (Fig. 1), seems to confirm this assumption. The slight increase in bicarbonate conc. in the last fraction is to be attributed to the lowering of intensity of rainfall, with consequent greater evaporation loss as the droplets fall through the atmosphere, with consequent increase in concentration of the dissolved constituent.

(b) Ca-ions: The calcium ions follow the same







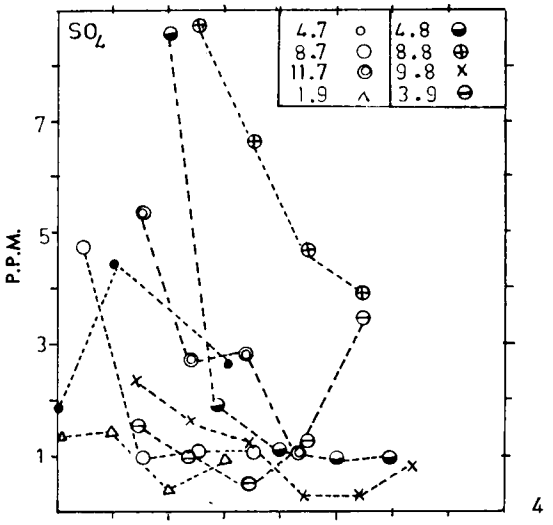


Fig. 1. Variations in HCO_3 conc. in rainwater with time of rainfall.

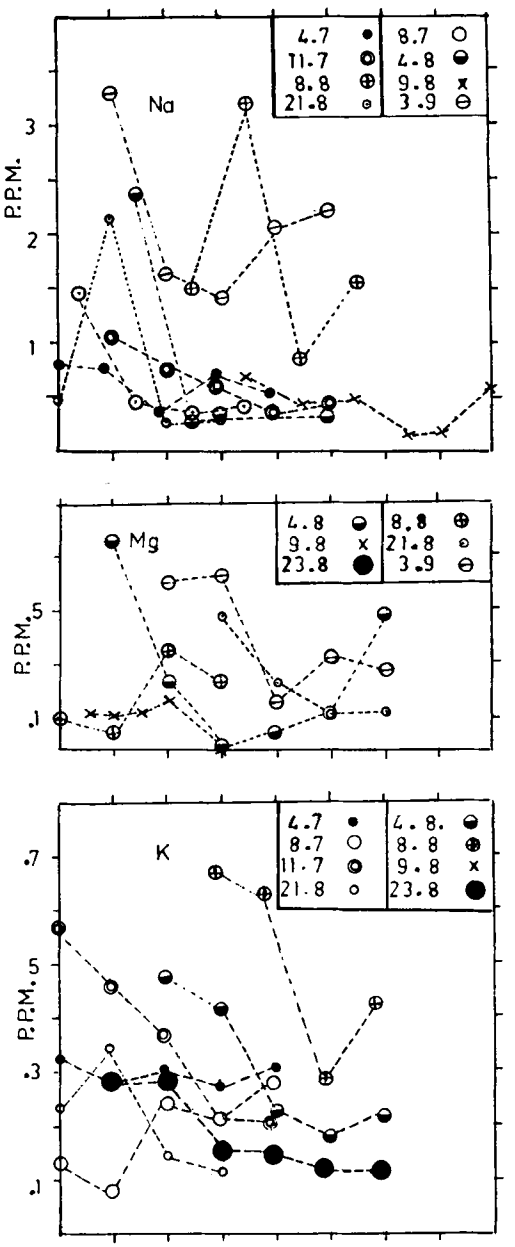
Fig. 2. Changes in conc. of Ca-ions in different fractions.

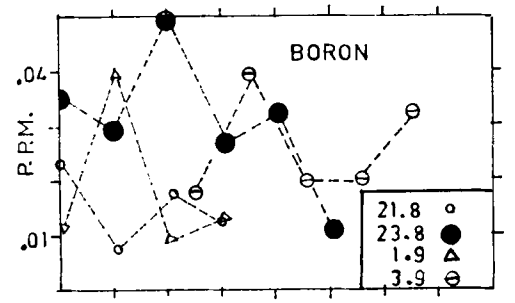
Fig. 3. Variations in Cl-ion conc. in rainwater with time.

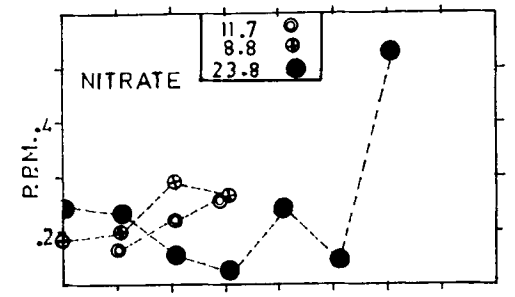
Fig. 4. Changes in SO_4-ion conc. in different fractions of rainwater.

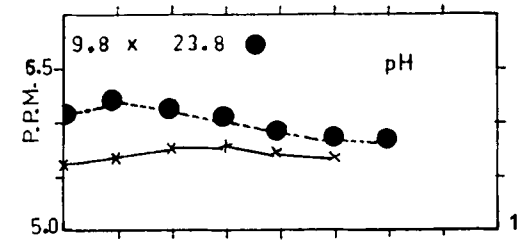
pattern as that of the bicarbonate ions, although some minor differences are noticeable (Fig. 2). This is to be expected as not all of the bicarbonate ions are combined with calcium ions as some calcium ions may also be associated with sulphate ions.

(c) Cl-ions: The study of chloride ions is quite interesting, as they are supposed to be primarily of marine origin (Eriksson, 1954; Leeflang, 1938 & Facy 1931). The chlorine ions also like the bicarbonate and calcium ions generally show a decrease with the progress of the rain, with notable exception on 3.9.1967. However, on 3.9.1967, cyclonic conditions had prevailed, the fluctuations in the conc. of chloride ions are to be expected. The interesting feature, however, is that the ratio of Cl/Na (Fig. 12) differ appreciably from the ideal value of 1.8;









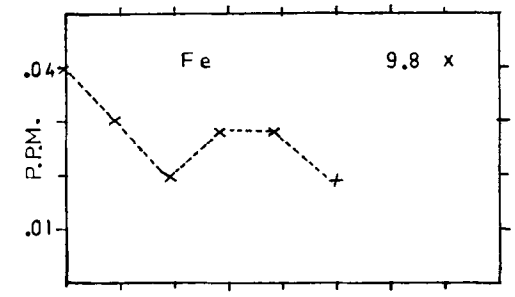


Fig. 5. Variations in Na-ion conc. with time.
Fig. 6. Changes in Mg conc. with time.
Fig. 7. Variations in K-ion conc. with time.
Fig. 8. Changes in boron conc. with time.
Fig. 9. Effect of time on NO_3-conc. in rainwater.
Fig. 10. Variations in pH values of rainwater with time.
Fig. 11. Iron content of various fractions of rainwater.

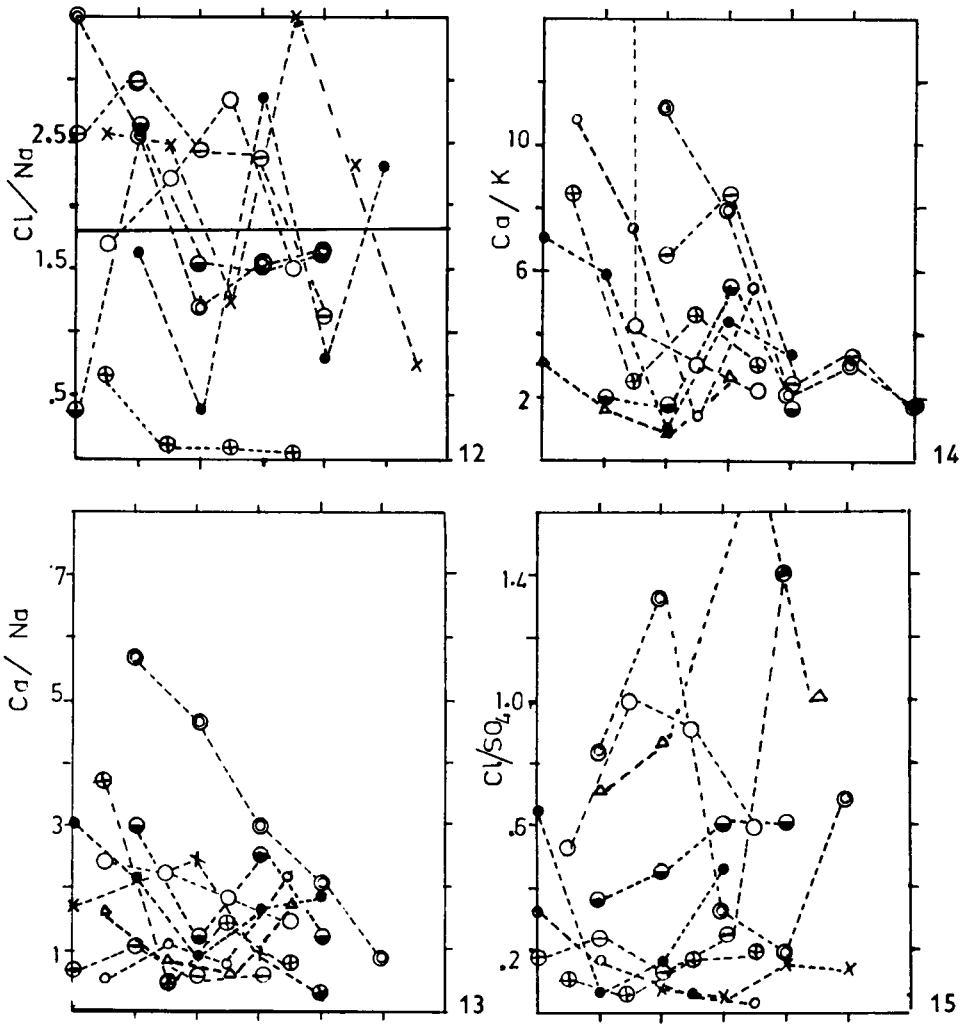


Fig. 12. Cl/Na ratio of different fractions of rainwater. ●, 4.7; ○, 8.7; ◎, 11.7; ◒, 4.8; ⊕, 8.8; ×, 9.8; ○, 21.8; △, 1.9; ⊖, 3.9.

Fig. 13. Changes in Ca/Na ratio with time. (Symbols as in Fig. 12.)

Fig. 14. Variations in Ca/K ratio with time. (Symbols as in Fig. 12.)

Fig. 15. Effect of time on Cl/SO_4 in rainwater samples. (Symbols as in Fig. 12.)

the ratio in which they are present in sea water. The ratio Cl/Na sometimes is as high as 3.0 and varies quite erratically in rainwater with the progress of time. In consideration of this ratio following factors have also to be taken into consideration:

(i) Loss of chloride ions by oxidation and diffusion into the upper layers of the atmosphere.

(ii) Supplemental sources of chloride ions present on the land.

(iii) Supplemental sources of sodium ions viz. particulate mineral matter of terrestrial origin, which may be present in the atmosphere and which is attacked by sulphuric acid (produced through oxidation of H_2S).

While the first mechanism may not play any significant role, the last two may play the most important roles in affecting the ratio of Cl/Na. It is interesting to record that at some stage or other, the rainwater has the same ratio of Cl/Na as in sea water (except for rainfall on 8.8.1967).

It may be mentioned that values for the ratio Cl:Na differing from the ratio in sea water of 1.8:1 has been reported by several authors. Rossby and Egnér (1955) showed that the ratio Cl:Na undergoes large fluctuations over Scandinavia. Eriksson (1958) has suggested losses of chloride ions by vertical separation. However, from Fig. 2 and Fig. 12, it is obvious that the ratio over Calcutta is affected to a considerable extent by local contribution.

(d) Na-ions: The concentration of sodium ions with time also follows the same pattern viz. precipitate decrease with time, but some notable exceptions are observed. While a continuous decrease of sodium ions with time is to be expected, the sudden increase in sodium conc. in the second fraction on 8.8.67 and 12.8.1967 can only be explained on differential removal of sodium ions from the condensation nuclei, because all the other major ions viz. calcium, chloride, sulphate show a decrease.

The study of the ratio of Ca/Na with time is quite revealing. If both calcium and sodium ions were to be entirely of terrestrial origin, one would expect a constant ratio value—except for some differential removal of one or the other cation. The ratio Ca/Na, however, generally shows a sharp decrease (Fig. 13) indicating that calcium ions are removed relatively more than the sodium ions. This fact can be explained from the fact that the sodium ions owe their origin both to the terrestrial particulate matter as well as to the sea salt nuclei. While depletion in the latter also occurs as rainfall progresses, the removal of the former is relatively more rapid, resulting in a decrease of the Ca/Na ratio.

(e) SO_4-ions: The sulphate ions also show a gradual decrease with time of the same order as the other ions mentioned above (Fig. 4). The ratio Cl/SO_4 follows more or less a similar pattern as the ratio Ca/Na, showing, however, much greater fluctuations than obtained for the latter ratio. The occasional rise in the ratio SO_4/Cl (sometimes, although less often, it also decreases), may again be explained by the removal of the sulphate ions of terrestrial origin by raindrops during their downward passage. However, unlike calcium ions, the sulphate ions are also partly of marine origin. The rapid decrease in Cl/SO_4 ratio may also be due to relatively more efficient washing down of sulphate particulate matter, although it must be added a more thorough investigation is needed to establish these points. It is, however, interesting to record that during cyclonic weather, the ratio Cl/SO_4 shows a sharp rise in the last fraction (Fig. 15).

(f) Mg-ions: The ratio Cl:Mg in sea water is around 15:1 and if it be assumed that the major part of chloride is of marine origin around .1–.2 ppm of magnesium ions (on the average) are to be of marine origin (Part I, Table II), but the major part is likely to be of terrestrial origin. The concentration of magnesium ions also decreases with the passage of time, although some exceptions are also observed (Fig. 6).

(g) K-ions: Potassium ions like calcium ions are primarily of non-marine origin and show a decrease with the passage of time, although here too some exceptions are noticeable. These probably can be attributed to the intensity and quantity of rainfall (Fig. 7). The plot of the ratio Ca/K (Fig. 14), also shows an erratic trend, with the general tendency towards decrease of this ratio, more or less on the lines similar to that of the ratio Ca/Na. Since unlike Na-ions, K-ions are primarily of non-marine origin, it appears that some differential removal of Ca and K ions occurs during rain.

(h) Boron: Data on boron is quite scanty. Carroll (1962) has reported that Odum and Parrish found 0.009–0.015 ppm boron in rain at Gainesville, Fla. Values considerably higher than these have been found in rainwater over Calcutta (Fig. 8, also Part I, Tables I & II). It is interesting to record that the boron values fluctuate considerably, the highest values generally exceeding 0.03 ppm. It is possible that these ions are of terrestrial origin. Since no quantitative study of the intensity of rainfall was undertaken, it is difficult to attribute the variation in boron concentration except perhaps very broadly to the variations in the intensity of rainfall.

(i) NO_3: In part I of this paper it was pointed out that there being little correlation between SO_4 and NO_3, it was possible that the nitrate ions also owe their origin to thunder activity. The fact that in the last fraction the conc. of nitrate ions on 23.8.1967 showed a sharp rise, may be attributed to the thunder activity (Fig. 9).

(j) pH: The systematic study of the pH of the various fractions could only be carried out

in two cases. The results indicate that the hydrogen ion conc. varies quite erratically (Fig. 10).

(k) Fe: The iron conc. also varies quite irregularly and does not show a continuous decrease (Fig. 11), which fact may be attributed to the variations in the intensity of the rainfall.

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ХИМИЧЕСКИЙ СОСТАВ МУССОННЫХ ДОЖДЕЙ НАД КАЛЬКУТТОЙ. Часть II

Различные пробы дождевой воды были проанализированы на различные компоненты, именно, HCO_3, Cl, SO_4, Ca, Mg, Na и K. В некоторых случаях были определены также концентрации B, NO_3, Fe и pH. Было найдено, что хотя начальные ливни являются, вообще говоря, более солеными, чем последующие ливни (с некоторыми исключениями), отношения между различными компонентами меняются совершенно нерегулярно. Была сделана попытка объяснить эти нерегулярности путем обсуждения источников происхождения различных компонент.