Chemical composition of rain water in some parts of northern India — Preliminary studies

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ABSTRACT. A systematic study of the chemical composition of rain water from different parts of northern India, reveals that their composition is greatly affected by several factors like distance from the sea, topography and geology of the area, intensity, duration and interval of rain. The dissolved constituents accordingly owe their origin to both marine and non-marine sources, although except in the case of chloride, and to some extent for Na and Mg, the influence of non-marine factors far outweighs the contribution from marine sources.

1. Introduction

In view of the great significance of the chemical composition of rain water in geochemistry, agriculture etc a network of stations has been set up in Europe, U.S.A. etc to collect and analyse rain water samples. The data about the chemical composition of rain water from India is, however, scanty and incomplete. In the present paper an attempt has been made to fill this gap, by collecting and analysing water samples from different parts of the country.

2. Experimental

The rain water samples were collected in polyethylene containers, fitted with large polyethylene funnels from the following localities — Dehra Dun, Sahasradhara (about 7 miles from Dehra Dun), Hardwar, Laksar, Diamond Harbour, Calcutta, Bhasha (Diamond harbour road), Sonarpur and Sangrampur (24 Parganas, West Bengal).

The Ca and Mg ions were determined complexometrically with EDTA, using murexide and Eriochrome Black T as indicators. The Na and K were determined after concentration, by Beckman Flame Photometer. Nitrate, boron and iron were determined colorimetrically using phenol disulphonic acid, turmeric and thioglycollic acid reagents respectively. Bicarbonate ions were determined by titration with standard acid using methyl orange—bromo cresol green indicator. For chloride, the water sample was made alkaline by adding known amount of standard NaOH (Ca $N/40$), and concentrating it to a small volume (Ca 10 ml). The alkali was then completely neutralized by addition of an equivalent amount of acid (determined earlier by a separate titration). Chloride was then determined by titration with standard Ag NO_3 solution using K_2CrO_4 as indicator. Sulphate was determined gravimetrically, after initial concentration of the sample in the same manner as that of chloride. The pH was determined by Cambridge pH-meter.

3. Results

The chemical analysis data of water samples from different localities is given in Tables 1 to 3. Due to shortage of the water samples, it was not possible to determine always all the constituents, and these have been mentioned as n.d. (not determined). The date of collection of the samples is also given with each water sample analysed.

4. Discussion of Results

Since the cloud droplets, from which practically all precipitation is derived are formed around condensation nuclei, rain water always contains some dissolved salts, acting thereby as a mixed electrolyte. Further since gaseous compounds always tend to attain equilibrium with the liquid phase (the cloud droplets in the present case), rain water will also absorb gases from the atmosphere. According to Hutchinson (1957), rain water is likely to contain the following constituents —

Major ions : Na, K, Ca, Mg, Cl, HCO_3, SO_4, NO_3

Minor ions : NO_2, NH_3 and other nitrogen compounds, B, Al, SiO_2, Fe, Br, I etc

While some of these constituents are of marine origin, significant contributions may also be made through other factors, *viz.*, fresh water and saline lakes, land masses, vegetation, man made industries, reactions occurring in the atmosphere, volcanoes etc. A brief discussion of the sources of various constituents reported in this paper is given below.

(a) *Bicarbonate ions* — Bicarbonate ions seem to be more or less universally present in rain water in India, although their concentration varies considerably. The bicarbonate ions apparently are produced through reaction of H_2CO_3 (produced

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TABLE 1

Chemical composition of rain water samples from different areas Dehra Dun (Winter 1966-67)

Date	Constituents (parts per million)								Remarks
	HCO_3	Cl	SO_4	Ca	Mg	Na	K	pH	
22-3-67	12·8	0·24	n.d.	3·2	·72	n.d.	n.d.	6·2	Strong drizzle
23-3-67	7·6	0·30	n.d.	2·2	·30	n.d.	n.d.	6·1	Do.
24-3-67*	7·6	0·40	n.d.	1·6	·48	n.d.	n.d.	6·0	1st fraction
24-3-67**	5·1	0·30	1·59	1·6	·24	·46	·077	6·0	2nd fraction
24-3-67†	4·5	0·23	1·0.	1·0	·22	·35	·198	5·9	3rd fraction
25-3-67*	10·2	0·51	n.d.	2·4	·48	n.d.	n.d.	6·3	Hailstorm
25-3-67**	10·0	0·28	1·06	2·3	·41	n.d.	n.d.	6·2	Rain water
25-3-67†	10·8	0·28	1·76	2·5	·44	0·90	·20	6·1	Hailstorm
25-3-67††	12·8	0·45	2·30	4·0	·59	0·41	·03	6·0	Hailstorm
23-4-67	31·0	0·28	1·54	5·6	2·89	0·51	·15	5·9	Fine drizzle
25-4-67	36·0	1·56	2·15	9·6	1·45	0·90	·21	6·1	Do

*First fraction **Second fraction †Third fraction ††Fourth fraction

n.d. — not determined due to shortage of sample

TABLE 2

Chemical composition of rain water samples from Dehra Dun during July 1967

Date	Constituents (parts per million)									
	HCO_3	Cl	SO_4	NO_3	Ca	Mg	Na	K	pH	Fe
28-7-67	3·0	·25	·96	·17	·80	·24	·26	·18	5·4	·02*
28-7-67	1·4	·50	2·90	·18	·40	·10	1·82	·39	5·6	·03**
29-7-67	38·0	·41	2·88	·34	12·80	·24	1·07	·37	5·9	·04*
29-7-67	5·0	·49	2·40	·20	·85	·80	·71	·28	5·9	·02**

*First fraction ** Second fraction

TABLE 3

Chemical composition of rain water samples from different parts of northern India during summer 1967

Sample	Date	Constituents in parts per million										
		HCO_3	Cl	SO_4	NO_3	Ca	Mg	Na	K	pH	Fe	B
(1)	26-7-67	2·5	1·5	n.d.	n.d.	0·8	0·12	n.d.	n.d.	5·9	n.d.	n.d.
(2)	26-7-67	2·0	0·85	2·90	·21	0·8	0·24	0·97	0·47	6·1	·02	n.d.
(3)	28-7-67	6·9	1·95	4·67	·11	3·0	0·85	0·81	0·59	6·2	·03*	n.d.
(4)	28-7-67	3·9	0·98	2·85	·17	2·0	0·24	0·65	0·41	6·0	·01**	n.d.
(5)	31-7-67	1·9	0·97	7·16	·15	1·2	0·24	3·16	0·59	5·8	·01	0·1*
(6)	31-7-67	1·9	0·95	8·35	·32	1·2	0·21	3·91	0·33	5·8	·00	·005**
(7)	1-8-67	4·9	1·90	8·20	·32	1·9	0·27	2·45	0·35	5·9	·00	·003
(8)	2-8-67	9·9	2·75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
(9)	6-8-67	9·9	3·95	1·44	n.d.	3·2	0·25	1·86	1·41	5·7	n.d.	0·05
(10)	6-8-67	1·0	0·50	0·96	n.d.	0·4	0·12	0·28	0·22	6·0	n.d.	0·01
(11)	6-8-67	0·5	0·97	0·66	n.d.	0·6	tr.	0·70	0·33	6·0	n.d.	0·04
(12)	11-8-67	1·9	0·98	2·40	·52	1·24	0·10	0·82	0·48	5·7	·02	0·02
(13)	12-8-67	1·9	2·97	n.d.	n.d.	1·92	0·29	n.d.	n.d.	5·8	n.d.	n.d.*
(14)	12-8-67	1·0	1·30	0·96	·30	0·40	0·39	0·43	0·28	5·6	·016	0·02**
(15)	16-8-67	3·9	2·45	3·72	n.d.	3·02	0·59	0·91	0·08	5·9	n.d.	n.d.

Location of samples — Laksar (1) ; Hardwar (2); Sahasradhara (3, 4); Asansol (5, 6, 7 and 8); Diamond Harbour (9); Sonarpur (10, 11); Calcutta (12); Bhasha (13, 14); Sangrampur (15)

*First fraction   **Second fraction

through dissolution of atmospheric CO_2 in water), with the $CaCO_3$ and even $MgCO_3$ that may be present in the atmosphere as dust. The origin of the calcareous dust may either be the land mass or the burning kilns for limestones (*e.g.* in Dehra Dun). The fact that there exists an almost linear relationship between alkaline earths and the bicarbonate ions (Fig. 1) seems to support this hypothesis.

It is interesting to record in the rainfall data reported by Carroll (1962), and Gorham (1961), about rain water analysis from Europe and United States, no mention is made of the presence of bicarbonate ions in rain water.

(b) *Ca and Mg ions* — It is apparent that in the rain water calcium ions exceed the magnesium ions (Tables 1 to 3), which fact again indicates the non-marine origin of the calcium ions (in sea water the ratio Ca: Mg is around 1: 3). A part of the magnesium ions, however, are likely to be of marine origin. Although an approximate idea of the relative contribution of magnesium ions from marine and non-marine sources can be computed by assuming that all the chlorine is of marine origin (which is not entirely true) and dividing this by 16 (the ratio Cl : Mg in sea water is 16 : 1), there are several other factors, *e.g.*, loss of chlorine through diffusion into the upper atmospheres, differential removal of
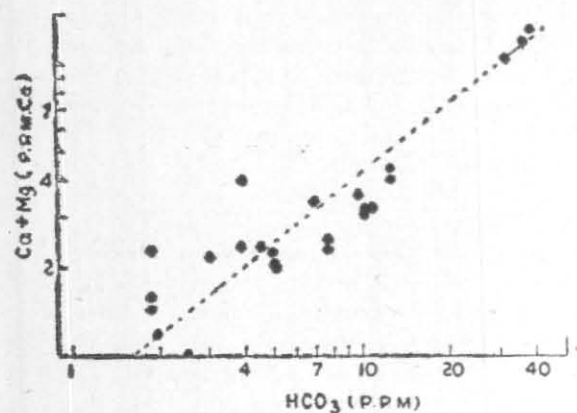
Fig. 1. Variation in concentration of alkaline earths (calculated in terms of ppm Ca) as a function of bicarbonate content
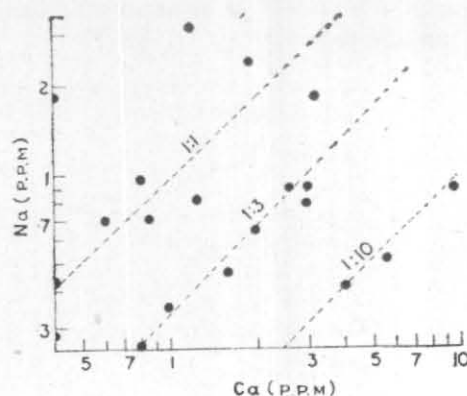

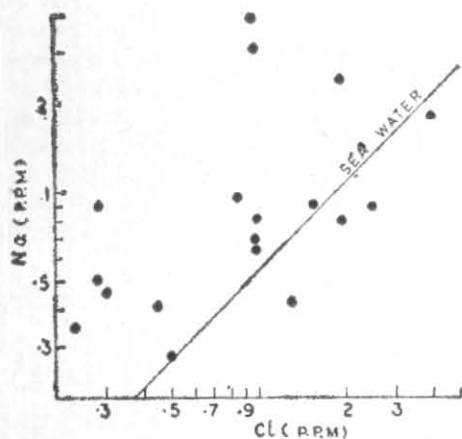Fig. 2. Plot of Na *vs* Ca concentration in rain water samples
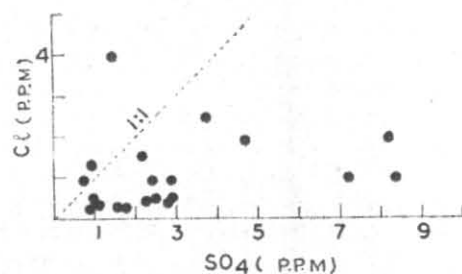

Fig. 3. Plot of Na *vs* Cl in rain water samples

Fig. 4. Inter-relation between Cl and SO_4 ions in rain water samples

magnesium ions and sodium ions in precipitation because of differences in the hydroscopicity of their chloride salts ($MgCl_2$. NaCl), such a calculation would be of little value.

The fact that calcium ions are primarily of non-marine origin is further evident when the concentration of Na ions is plotted as a function of the calcium ions. In sea water the ratio Na : Ca is around 27 : 1 (calculated in terms of p.p.m.); whereas in rain water the calcium ions generally exceed the sodium ions, the ratio in some cases being as high as 1: 10 (Fig. 2).

(c) *Chloride ions* — The major source of chloride ions in rain water is likely to be the sea. During the monsoon the sea surface is churned by strong winds resulting in the formation of minute droplets or the sea salt nuclei, some of which may be carried upwards through convection. Although some of these return to the sea either mechanically or through rainfall, others are carried inland and act as condensation nuclei, coming down with precipitation. The rather high values at Diamond Harbour for chloride as compared to stations inland seems to lend some support to this view. The rainfall data from Asansol area, however, seems to indicate, that even here, local factors can play significant role. A plot of Na conc. *vs* Cl (Fig. 3) seems to indicate that only a few rain water samples had the same ratio as in sea water, the

majority of the samples, however, deviating considerably from this ideal value. The deviation may be caused by —

(*i*) Loss of chlorine through diffusion into the upper atmosphere.

(*ii*) Gain of chlorine through local factors—combustion of fuel etc.

(*iii*) Gain of Na ions from local factors, *viz.*, dust etc.

(d) *Sodium ions* — The concentration of sodium ions like that of chloride ions varies considerably. However, as would be apparent from the preceding, besides the sea, local factors are also likely to be of considerable significance in this case.

(e) *Sulphate ions* — The fact that the concentration of chloride ions is generally less than that of sulphate ions (Tables 1 to 3 and Fig. 4) shows that in the case of sulphate ions the non-marine sources are of considerable significance. In Asansol area (a coal mining area), the burning of coal will release considerable quantities of H_2S into the atmosphere, which on oxidation would form SO_2, SO_3 and eventually H_2SO_4. In Dehra Dun area, the sedimentary rocks-Krol limestones etc contain pyrite quite often, which again seems to be an important source of sulphate ions, through a similar mechanism. It is interesting to record that even at Diamond Harbour, where the sulphate concentration is lower than that of chloride ions, the ratio SO_4: Cl in rain water is higher than that of sea water.

(f) *Potassium ions* — Since the ratio K : Na is generally much higher than that of sea water (Tables 1 to 3), it is obvious that contributions from non-marine sources is not inconsiderable. The atmospheric dust—very fine soil dust particles—is apparently attacked by mineral acids present in the atmosphere (*e.g.*, H_2SO_4, HCl etc), resulting in release of potassium ions. The presence of iron in rain water is also indicative of the importance of this source in supplying dissolved constituents to rain water.

(g) *Boron* — It is interesting to record that boron was found to be present in almost all the samples analysed for this constituent, although its concentration varies considerably. The main source of boron is likely to be the volcanic emanation or may be the dust particles. In the absence of any specific volcanic source, one is induced to believe that the latter may be the predominant source for these ions.

(h) *Nitrate ions* — Considerable controversy seems to exist about the origin of these ions, as to whether atmospheric reactions, landmass or fuel are the main sources for these ions. The data here is too scanty to permit any specific opinion about the significance of these sources. Nitrate ions were found to be present more or less in all the samples analysed for this constituent, although their concentration vary considerably.

General — The chemical composition of rain water is affected by several factors like (1) distance from the sea, (2) topography of the land, (3) local factors like geology of the area etc, (4) intensity and duration of rainfall, (5) interval between various showers etc. In view of these it is difficult to draw any conclusion on the basis of only a few observations. However, data reported in Tables 1 to 3 seem to indicate the following features —

(*i*) If the rainfall occurs as a fine drizzle, the salinity is higher (Table 1).

(*ii*) The concentration of dissolved salts in rain water varies from place to place and even at the same place. Even the concentration of the dissolved constituents may vary from shower to shower; the first fraction being generally more saline than the subsequent fractions, although here too some exceptions may be noted.

5. Summary

Preliminary studies were carried out to find out the chemical composition of rain water in different parts of northern India. The results indicate that the chemical composition varies considerably from place to place and even from shower to shower at the same place. Local factors like geology of the area, fuel consumption etc also play a significant role in affecting the chemical composition of the precipitation.

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