Cosmogenic ^{39}Cl and ^{38}Cl as tracers for cloud condensation mechanism

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सार – अनेक वर्षों की मानसूनी वर्षा में अन्तरिक्ष किरणों से उत्पन्न समास्थानिकों ^{39}Cl एवं ^{38}Cl को व्यापक रूप से मापा गया है । क्रियाशीलता के साथ साथ उनके अनुपात में काफी अन्तर पाया गया है । वर्षा के बाद के चरण में इनमें परमसांद्रण की ओर बढ़ती हुई स्पष्ट प्रवृत्ति कुछ ज्यादा ही रही । इसमें सामान्यतः निम्नवर्षण दरें है । नाभिकण और वर्षण (मेघों के समय में) के मध्य अन्तराल की ^{39}Cl/^{38}Cl के अनुपात से गणना की गई—इसके मानों में कुछ मिनटों से कुछ घंटों तक का परिवर्तन हुआ है ।

ABSTRACT. Extensive measurements of cosmic-ray-produced isotopes, ^{39}Cl and ^{38}Cl have been made in monsoon rains for several years. The activities as well as their ratios vary widely. There is a clear tendency for the absolute concentrations to be somewhat higher in the later phase of a rain, which usually also have lower precipitation rates. Time intervals between nucleation and precipitation (in-cloud time) have been calculated from ^{39}Cl/^{38}Cl ratio. The values vary from a few minutes to a few hours.

1. Introduction

Spallation of atmospheric argon by cosmic radiation produces a spectrum of radionuclides with halflives ranging from a few minutes to a million year (Lal and Peters 1967). The radionuclides with short halflives (less than a day) have been recognized as useful tracers to study such short term atmospheric phenomena as mechanism of cloud condensation and height of cloud formation etc.

Among the nuclides of this group, the first to be detected was ^{39}Cl by Winsberg (1956) in rain water. Perkins *et al.* (1965) measured ^{38}S and ^{38}Cl which were also independently studied by Bhandari *et al.* (1966). The isotopic pair ^{39}Cl (55.7 min) and ^{38}Cl (37 min) has the advantage that their relative concentrations in a geochemical reservoir change only due to radioactive decay and are unaffected by any chemical differentiation. Recently Rowland (1978) has proposed some differentiation effect due to various chemical forms of chlorines. However in the lower atmosphere such an effect would not be significant. Perkins and coworkers (1970 a, b) attempted to use ^{39}Cl and ^{38}Cl data to understand some aspects of cloud physics. We undertook the present measurement of ^{39}Cl and ^{38}Cl to understand some aspects of precipitation mechanism in monsoon rains.

2. Experimental

Rain water was collected at Kanpur over a $4m \times 4 m$ polythene (pvc) sheet which had been washed just before collection with 1:10 dilute HNO_3. At the end of collection, the sheet was washed with dilute HNO_3 for complete desorption of the nuclides. Since the rain water contained very small amount of chlorine (about 0.0014 g AgCl per litre, determined colorimetrically), NaCl carrier equivalent to 1g of AgCl was added. Fe^{3+} and holdback carriers of La^{2+} Bi^{2+}, and pb^{2+} were added. After acidifying with HNO_3, AgCl was precipitated in acid medium with $AgNO_3$. Ammonium hydroxide was added to bring the pH to 7-8 which precipitated $Fe(OH)_3$ leaving the bulk of AgCl undissolved, which was subsequently dissolved in a minimal amount of NH_4OH and filtered. The filtrate was diluted and passed through a Dowex-50 ion exchange column in the NH_4+ form. The effluent was generally free of metalcations. AgCl was precipitated in presence of 10 ml, 10 per cent EDTA solution. The precipitate was filtered, washed, dried, powdered and mounted for counting. The interval between the collection of rain water and final counting was around one hour.

TABLE 1

Concentration of ^{39}Cl and ^{38}Cl in monsoon rain

S. No.	Date	Volume of rain water (lit.)	Time of collection (min)	ppt. rate (mm/min)	^{38}Cl (dpm/l)	^{39}Cl (dpm/l)	^{39}Cl/^{38}Cl	In-cloud time (min)
1	3 Jul 72	35	10	0.22	3.3±3.0	6.2±2.2	—	—
2	6 Jul 72	30	10	0.19	3.1±1.4	1.6±1.0	—	—
3	10 Jul 72	35	9	0.24	2.1±1.0	2.6±0.7	1.20	93-172
4*	10 Jul 72	30	15	0.13	7.7±2.1	6.8±1.4	0.88	54-77
5	11 Jul 72	24	7	0.21	—	3.9±1.0	—	—
6	5 Aug 72	30	5	0.38	—	3.2±1.2	—	—
7	7 Aug 72	25	10	0.21	2.6±1.1	2.2±0.8	0.85	49-72
8	7 Aug 72	25	10	0.16	—	5.7±2.7	—	—
9*	12 Sep 73	14	10	0.075	6.4±4.9	15.6±3.2	—	—
10*	12 Sep 73	27	10	0.14	—	18.0±6.9	—	—
11*	12 Sep 73	12	15	0.05	—	33.1±5.4	—	—
12	15 Jul 74	26	6	0.27	8.1±7.0	10.9±3.0	—	—
13	9 Aug 74	24	4	0.54	2.9±1.6	7.8±1.0	—	—
14	13 Aug 74	20	12	0.11	—	4.9±1.0	—	—
15	16 Aug 74	30	6	0.31	2.4±2.0	8.5±1.2	—	—
16	19 Aug 74	27	4.5	0.38	2.5±1.2	2.0±0.9	0.80	44-56
17	21 Jun 75	35	6	0.38	2.5±1.7	5.2±1.3	—	—
18	9 Jul 75	30	4	0.47	9.4±4.7	8.6±3.3	0.92	56-103
19*	11 Jul 75	30	7	0.27	5.5±1.8	2.3±1.2	0.42	00-00
20*	14 Jul 75	30	8	0.24	7.4±2.3	10.2±1.6	1.4	115-168
21	15 Jul 75	30	7	0.27	1.2±1.1	2.6±0.8	—	—
22	17 Jul 75	27	14	0.12	5.8±1.9	4.4±1.3	0.76	34-46
23*	26 Jul 75	10	18	0.04	13.6±5.7	23.0±3.4	1.7	134-231
24	30 Jul 75	25	5	0.31	6.4±4.2	4.8±20.0	—	—
25*	3 Aug 75	30	8	0.24	3.6±1.8	8.2±1.3	2.28	175-302
26	22 Aug 75	21	9	0.14	3.5±1.9	2.6±1.4	0.61	00-00
27	23 Aug 75	10	2	0.05	—	9.8±2.9	—	—
28	6 Sep 75	30	4	0.70	—	3.1±0.8	—	—
29*	8 Sep 75	30	33	0.06	20.9±3.7	17.5±2.1	0.85	46-65
30	11 Sep 75	10	3	0.21	—	3.9±1.0	—	—
31*	8 Jul 76	30	13	0.16	4.1±3.1	10.21±.9	—	—
32*	8 Jul 76	10	14	0.04	13.5±8.8	30.4±5.8	—	—

TABLE 1 (*contd*)

S. No.	Date	Volume of rain water (lit)	Time of collection (min)	ppt. rate (mm/min)	^{38}Cl (dpm/1)	^{39}Cl (dpm/1)	$^{39}Cl/$ ^{38}Cl	In-cloud time (min)
33*	8 Jul 76	9	32	0.02	9.1±6.4	12.2±4.4	—	—
34	11 Jul 76	15	15	0.06	—	11.9±2.5	—	—
35*	13 Jul 76	9.5	53	0.01	39.3±9.6	20.9±4.6	0.53	00-00
36*	13 Jul 76	10	40	0.02	33.8±8.7	21.4±5.0	0.63	6-14
37	15 Jul 76	25	15	0.11	5.5±2.3	5.5±1.3	1.0	61-128
38	25 Jul 76	26	3	0.54	—	2.0±1.0	—	—
39	27 Jul 76	27	3	0.56	2.7±1.2	2.1±0.8	0.78	35-60
40*	8 Aug 76	25	21	0.075	16.3±3.2	19.2±2.0	1.18	97-128
41	21 Aug 76	27	22	0.075	6.3±2.4	5.3±1.7	0.84	48-70
42	26 Aug 76	25	4	0.39	—	5.9±1.8	—	—
43*	29 Aug 76	27	25	0.07	3.8±2.1	15.1±1.3	—	—
44*	29 Aug 76	24	4	0.38	13.1±3.7	9.1±1.9	0.70	14-40
45	10 Sep 76	25	10	0.16	—	2.5±1.0	—	—
46	13 Jul 77	23	6	0.24	5.3±3.0	—	—	—
47	16 Jul 77	24	11	0.14	2.9±2.1	5.6±1.3	—	—
48	25 Jul 77	30	3	0.63	3.3±2.4	—	—	—
49	6 Aug 77	30	16	0.12	10.0±5.8	8.7±2.7	—	—
50	8 Aug 77	35	4	0.55	1.6±0.9	—	—	—
51	9 Aug 77	35	9	0.24	7.2±2.3	3.9±1.1	0.54	00-00
52	10 Aug 77	35	5	0.41	—	7.3±1.3	—	—
53	22 Aug 77	23	2	0.72	5.1±1.7	2.5±1.1	0.49	00-00
54	22 Aug 77	23	10	0.14	6.3±2.4	6.3±1.6	1.00	68-114
55	25 Aug 77	23	15	0.09	10.0±1.9	3.9±1.3	0.39	00-00
56	29 Aug 77	23	23	0.06	4.3±3.7	25.8±2.3	—	—
57	10 Sep 77	23	5.25	0.28	5.2±1.9	—	—	—
58	2 Jul 78	40	10	0.13	1.9±1.0	0.69±0.59	—	—
59	6 Jul 78	24	3	0.25	1.9±1.7	1.6±1.0	—	—
60	17 Jul 78	12	11	0.04	4.8±4.4	25.7±2.8	—	—
61	20 Jul 78	60	8	0.24	1.3±0.7	1.3±0.4	—	—
62	20 Jul 78	300	12	0.78	0.9±0.6	0.6±0.3	—	—
63	21 Jul 78	85	23.25	0.11	5.0±1.5	1.2±0.7	—	—
64	21 Jul 78	30	19	0.05	2.3±1.3	—	—	—
65	1 Aug 78	42	18	0.14	4.1±1.7	5.1±1.0	1.24	91-170
66	4 Aug 78	43	14	0.19	1.7±0.8	1.5±0.5	0.88	47-100
67	9 Aug 78	32	9	0.23	7.7±2.4	6.4±1.6	0.83	45-67
68	9 Aug 78	31	15.25	0.13	13.7±4.1	2.8±2.2	—	—
69	10 Aug 78	137	21	0.41	2.3±1.6	1.0±0.8	—	—
70	19 Aug 78	26	13	0.13	3.6±2.6	6.5±1.5	—	—
71	19 Aug 78	156	20	0.49	4.5±1.7	1.4±0.7	—	—
72	19 Aug 78	86	20	0.28	—	4.1±1.0	—	—
73	11 Sep 78	113	83	0.12	3.1±0.7	0.7±0.4	—	—
74	11 Sep 78	44	23	0.09	—	2.9±0.9	—	—
75	19 Sep 78	77	17	0.28	3.3±1.8	3.5±0.9	—	—

*Rain II all other are Rain I.

During 1978 the following procedure was followed. Sodium chloride carrier (0.2g AgCl) was added to rain water and stirred well. This was passed through anion exchange resin (Dowex 1×-8). The chloride retained in the resin bed was eluted with 2 litres of dilute HNO_3. AgCl was precipitated from the effluent and was purified by distilling with H_2SO_4 in a vacuum system. HCl was absorbed in a solution of NaOH. Radiochemically pure AgCl was recovered from this solution by adding HNO_3 followed by $AgNO_3$.

Beta counting was done on a low background counting equipment supplied by Sharp/Beckman (Low Beta). The background of the detectors was about 0.4 cpm. The counting efficiency of the detectors was determined by counting several standard beta sources of various energies. Successive counts were collected for 10 minutes duration. Each sample was counted for more than two hours to follow the decay. The sample was again counted after 5-6 hours, for a longer period, for background determination. This provided an additional check on the purity of the sample from any long-lived contamination.

The individual activities of the two isotopes were obtained by Biller's plot. The least square fitted line was obtained by giving proper weightage to the statistical errors. The specific activity of some of the heavy rains was so low that it was difficult to resolve the activities of ^{39}Cl and ^{38}Cl. These, as well as the cases where Biller's plot gave an apparently negative value for one nuclide, were rejected.

3. Results

The measured specific activity of rain water in dmp/l is given in Table 1. Values having errors greater than 100 per cent are discarded. Various factors that might give such large errors are: (*i*) small size of the sample collected, (*ii*) low chemical recovery, (*iii*) long processing time, (*iv*) low nuclide concentrations, (*v*) low $^{38}Cl/^{39}Cl$ ratio, and (*vi*) possible contamination. Such a rejection generates a bias against samples having long in-cloud scavenging time. Our data may not give the most appropriate average value of the in-cloud scavenging time. However, we do get meaningful ranges for this, meteorologically interesting, parameter.

The reported specific activity represents the activity of rain water at the time the rain first hits the ground. No correction for the decay during its travel from cloud base to the ground has been applied, since the time taken by a drop to reach the ground is not known. If the minimum terminal velocity of smallest rain drop (diameter 1 mm) is considered (Beard 1976) the duration to reach the ground from a 1 km cloud base is less than 5 minutes. The decay correction can be neglected. Specific activities of both ^{39}Cl and ^{38}Cl show very large variations. The $^{39}Cl/^{38}Cl$ ratio does not vary much. The observed variation in activities of the two radionuclides is greater in case of drizzle (*i.e.*, rains with precipitation rates less than 0.1 mm/min). The rains with low precipitation rates are usually associated with higher specific activities while heavy rains give low activity.

The variation of ^{38}Cl activity in rain samples with the precipitation rate is shown in Fig. 1. Precipitation rate was determined by two methods, *viz.*, from a raingauge type arrangement, and by dividing the total volume of rain water collected by the duration of collection. As the rainfall rate might fluctuate during collection, an uncertainty is introduced which was kept low by keeping the collection periods generally short.

From Fig. 1 an inverse relationship is seen between the ^{39}Cl activity of rain water and its precipitation rate. The decrease in specific activity with increasing precipitation rate shows that low specific activity is due to dilution as a result of condensational growth. This trend of increase in activity with decrease in precipitation rate has been noticed by several other workers in the case of cosmogenic radionuclides (Engelmann and Perkins 1971 ; Lal *et al.* 1979), radon-genic ^{214}Bi (Bhandari *et al.* 1970) and artificial radionuclides (Avramenko and Makhon'ko 1970; Noyce *et al.* 1971). Similar observations have been made for stable trace elements (Junge 1963; Handa 1968; Georgii and Wotzel 1970; Tsunogai *et al.* 1975).

Several workers have studied temporal variations of the activity of rain water during the course of rainfall (Perkins *et al.* 1970 a, b; Gavini *et al.* 1974 ; 1976). The change is attributed to the parameters like size of drops (Avramenko and Makhon'ko 1970), evaporation, cloud altitude and nature of scavenged air mass (Gavini *et al.* 1974; 1976). It was not possible to determine systematically the temporal variation of activity in all the rains. More than two runs could be made only for three rains. But in several rains it was possible to collect two samples. The first sample (R-I) was collected at the beginning of the rain while the second sample (R-II) was either from the middle or towards the end of the rain. It is noted from the data that there is a clear tendency of the activity to increase as the time passes. Moreover, as stated earlier, the increase is usually associated with a decrease in precipitation rate. Ground level air mass of the updraft with low specific activity and high humidity in the beginning of rain may result in low activity and high precipitation rates while the higher altitude air mass in the downdraft with low humidity, appearing in the later phases of rain may cause high activity and low precipitation rate.
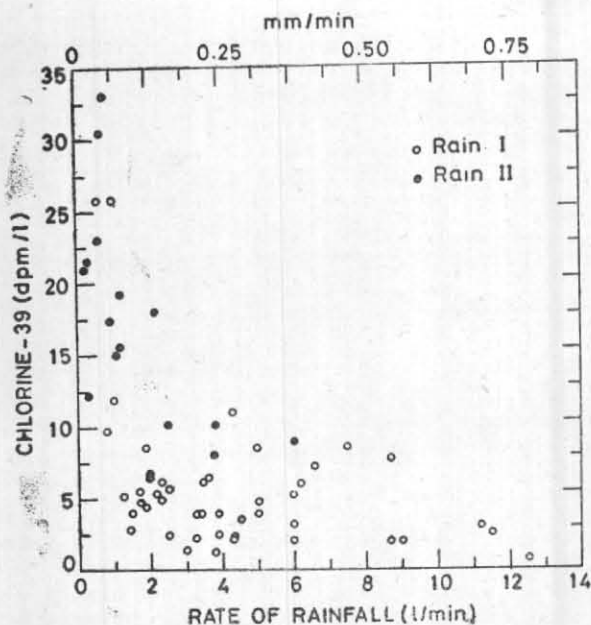
Fig. 1. Variation of ^{39}Cl activity with precipitation rate

Fig. 2. Histogram showing in-cloud time (min) with frequency of rains

The time interval between the nucleation of cloud droplets and the commencement of precipitation can be calculated from the measured $^{39}Cl/^{38}Cl$ ratio in the rain water (Perkins et al. 1970 a). Considering a hypothetical air mass devoid of radioactivity (scavenged by previous rain), one would expect the activity ratio $^{39}Cl/^{38}Cl$ to be equal to the relative production rate multiplied by (37/55). This will, after sometime, approach the secular equilibrium value of production rate ratio. If now the nucleation of a droplet occurs and there is no further addition of radionuclides (i.e., post-nucleation scavenging is negligible), the $^{39}Cl/^{38}Cl$ ratio will continue to increase with the delay in its precipitation as a result of the faster decay of the shortlived ^{38}Cl.

The value of in-cloud time thus obtained will be lower than the true-in-cloud time if post-nucleation scavenging is significant. When a cloud is condensed out of an air mass which has just been completely washed of its radioactivity so that secular equilibria had not been achieved, the $^{39}Cl/^{38}Cl$ activity would be lower than the production rate ratio. This case of 'unsaturation' may also result when ground level air mass with low specific activity moves to the higher level without mixing with the surrounding air. The true in-cloud period may be higher than estimated by this method. On the other hand the calculated time period of in-cloud may be too high if an air mass of higher altitude which has reached the equilibrium value of $^{39}Cl/^{38}Cl$ ratio, descends slowly to a lower altitude just before the nucleation of cloud droplets. In this situation $^{39}Cl/^{38}Cl$ ratio will be high even with an insignificant in-cloud time. Downward movement of high altitude air mass prior to the nucleation will be reflected in high specific activities (decay corrected) of
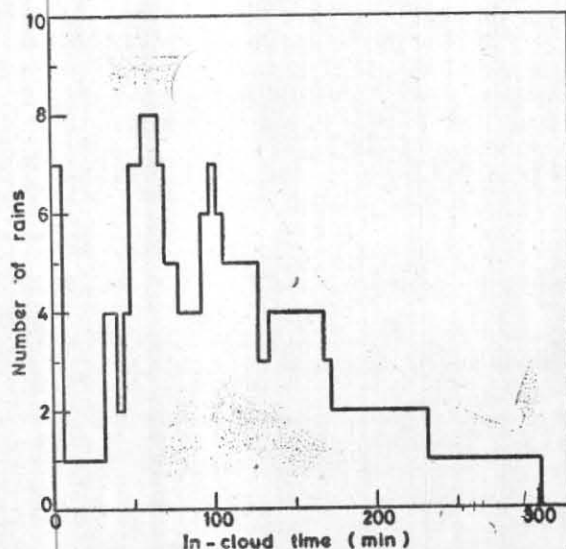
^{39}Cl and ^{38}Cl along with high $^{39}Cl/^{38}Cl$ ratio. The contribution of ^{38}Cl by the decay of ^{38}S can also alter the $^{39}Cl/^{38}Cl$ ratio but it is negligible since its production cross section is about one twentieth than that of ^{38}Cl (Lal and Suess 1968; Goel and Prem Sagar 1981).

Fig. 2 represents the histogram showing in-cloud time with frequency of rains. Our calculated in-cloud times range from a few minutes to about 200 minutes (Prem Sagar 1977). The value of in-cloud times are given in Table 1. In five cases condensation took place before secular equilibrium was reached (which are in case of rains having serial No. 19, 35, 51, 53 & 55) and in two cases secular equilibrium value is obtained which shows very fast precipitation (e.g., in case 26 and 36). It may be remarked that in rains having large in-cloud time and originating from low altitude, the absolute activities of ^{38}Cl will be rather low making its unambiguous resolution difficult. A bias in the calculated values is thus introduced.

Our results of ^{39}Cl and ^{38}Cl concentration and the ratio of $^{39}Cl/^{38}Cl$ are compared in Table 2 with the literature data. The average values given by Bhandari et al. (1966) are based on 12 measurements for ^{39}Cl and one for ^{38}Cl. The values of Perkins et al. (1970 a, b) are based on several observations of about 8 rain storms. In general our values are lower than those of Perkins et al. The higher values of Perkins et al. can neither be a result of lower dilution due to difference in precipitation rate as cited by Wogman et al. (1968) nor due to the latitude effect, which can at most account for a factor of 2. The differences must be ascribed to variable meteorological conditions at the two places, viz., moisture

TABLE 2

Minimum, average and the maximum values of ^{39}Cl, ^{38}Cl and the ratio $^{39}Cl/^{38}Cl$

^{39}Cl (dpm/l)			^{38}Cl (dpm/l)			$^{39}Cl/^{38}Cl$			References
min.	avg.	max.	min.	avg.	max.	min.	avg.	max.	
2.1	8.2	15.7	—	13.3	—	0.40	0.60	0.80	Bhandari *et al.* (1966)
4.2	74.0	162.0	2.16	40.0	60.4	1.29	2.09	3.06	Perkins *et al.* (1970)
0.6	6.9	33.1	1.70	5.3	39.3	0.39	0.96	2.18	This work

contents, altitudes of cloud base and cloud top, and difference in micro-structure of rain formation. Such climatological differences have been found to influence the mechanism of precipitation formation (Knight *et al.* 1974). This has been seen by Perkins *et al.* (1970 b) to result in the differences of specific activity of rain water at Quillayute and Richland in USA. Good agreement with the values of Bhandari *et al.* (1966) for the Bombay (India) rains is well understood.

Our value of in-cloud time varies from few minutes to around 200 minutes. The in-cloud time obtained by Perkins *et al.* (1970 a) ranges from 30 minutes to 130 minutes. One of the reasons for discrepancy may be that our calculations are based on equilibrium value of $^{39}Cl/^{38}Cl$ ratio to be 0.6 (Lal and Suess 1968; Goel and Prem Sagar 1981), whereas the calculation of Perkins *et al.* (1970 a) is based on the value taken to be 1.5 which would give a shorter in-cloud time.

4. Summary

In heavy rains as well as during the initial phase of a rain condensation is the main mode of growth of the rain drops. Either post-nucleation scavenging is significant or in-cloud time is short giving $^{39}Cl/^{38}Cl$ ratio a near equilibrium value. Severe updraft with high moisture and low altitude condensation may be controlling the initial condensation. On the other hand the trailing phase of rain is usually of low precipitation rate (drizzle), high activity and high $^{39}Cl/^{38}Cl$ ratio suggesting a larger number of activated cloud condensation nuclei. The higher in-cloud time for the smaller drops is apparently due to colloidal stability (Twomey and Squres 1959 ; Simpson 1976). The mode of droplet growth is by collision-coalescence. The post-nucleation scavenging in this case seems to be insignificant; otherwise the $^{39}Cl/^{38}Cl$ ratio should have been close to the secular equilibrium value. Thus in the later phase of the rain either the cloud deck moves upward or an entrainment of high altitude air mass takes place, due to downdraft appearing in the later phase of rain.

Acknowledgement

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