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Chlorine, bromine and iodine in monsoon rains in India

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ABSTRACT

The mean concentrations of the halogens chlorine, bromine and iodine in a large number of rain-water samples collected in India during the south-west moonsoon at the west coast and at two sites on the hill range near the west coast are presented and discussed. The concentration and ratios of these halogens in the rain-water samples compare very well with those previously observed in marine precipitations. There is no change in the Cl/Na ratios with collection altitude. Br shows a slight enrichment relative to Na at most of the sampling locations and a nominal depletion at one of the sites on the hills. Iodine enrichment is high at all sampling sites and the samples from the higher altitude station on the hills show the maximum enrichment. The study confirms that large deposition of sea-salt occurs along the west coast of India due to the monsoonal flow.

1. Introduction

Halogens in the atmosphere are primarily from sea-water and are known to be conserved in it. Atmospheric Cl has been studied over the last decades, while detailed investigations of atmospheric Br and I have been reported only in the last 15 years though there are a few earlier measurements (Duce et al., 1965 and earlier references therein). The measurement of these halogens in atmospheric aerosols and precipitations provides useful information on sea–air exchange processes, chemistry of marine atmosphere and geochemical cycling of halogens (e.g. Working symposium on sea–air chemistry, Fort Lauderdale 1972; International symposium on the chemistry of sea/air particulate exchange processes, Nice, 1973). The study of halogens in atmospheric samples also finds application in cloud physics (Woodcock et al., 1971). The halogen concentrations in aerosol and precipitation are not in the same relative proportions as in the sea-water. In bulk marine aerosols and precipitation, generally, the Cl/Na ratio is nearly equal to the sea-water value of 1.8. However, values both above and below 1.8 for Cl/Na in precipitation samples are reported in literature (Eriksson, 1960; Junge, 1963). In the small size particles, this ratio tends to be less than 1.8 due to loss of Cl. In marine atmospheric samples, iodine is enriched relative to Na or Cl by orders of magnitude, while the Br/Cl ratio lies around the sea-water value (Duce et al., 1965). Both Br and I are present in gaseous and particulate forms in marine atmosphere and the gaseous concentrations are 4–10 times and 2–4 times higher than particulate concentrations, respectively (Moyers and Duce, 1972a, b). Marine aerosol size distributions for the halogens are different from each other, due to loss of particulate halogen to the gas phase or vice versa and fractionated transfer from sea-water to air.

Chloride concentrations in rain-water in India have been reported in a few papers (Narayanaswami, 1939; Kundra et al., 1962; Handa, 1968 and 1969; Khemani and Ramana Murty, 1968) but there are no published measurements on bromide and iodide. We have measured the haolgen concentrations in a large number of rain-water samples along the west coast of India with a view to investigate the variation with sampling altitude of the halogen enrichment in rain-water as compared to sea-water and to study the halogen depositions due to the monsoonal flow. The results of our investigations are presented in this paper.

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2. Sampling and analysis methods

Rain-water samples were collected during the south-west monsoon at two sampling sites, Lonavala and Mahabaleshwar, on the hill range near the west coast of India. These two sampling sites are respectively 625 m and 1380 m high, are approximately 60 and 65 km from the west coast and lie ESE and SE of Bombay on the coast. During the monsoon period, June to September, the west coast and the adjoining hills receive 200–300 cm of rainfall. The winds are mainly westerly and orographic rainfall predominates. A large number of rain-water samples were collected at three sites at Bombay. The three sites are (1) inside this research centre (BARC), (2) on top of the 305 m high Trombay hill adjoining this Centre and (3) on the terrace of Colaba Observatory near the southern tip of the Bombay island. The hill top site is 2 km north of the sampling site inside BARC while Colaba Observatory is south-west of BARC at a distance of 15 km. Petroleum and fertilizer industries are located on the other side of the Trombay hill. Rain-water samples were collected during 1971 and 1975 at Lonavala and Mahabaleshwar, respectively. At Bombay a large number of samples were collected at the three sites during 1973 and a few samples were collected during 1971 and 1975 at the BARC site. Five samples were collected from a ship on the Arabian Sea during the Indo-Soviet Monsoon Experiment of 1973. Rain-water sample collection procedures are described elsewhere (Sadasivan et al., 1974). The concentrations of chlorine, bromine and iodine were measured by neutron activation analysis. The concentration of the sea-water reference element sodium in samples collected during 1971 was estimated by neutron activation analysis, while this concentration in all the later samples was measured by both neutron activation and atomic absorption or flame photometry. The overall errors for the determination of these elements in the samples were around 15%. In all over 180 samples were collected and analysed.

3. Results and discussion

3.1. *Results*

The mean concentrations of the halogens and sodium for various sampling sites are presented in Table 1. Mean concentrations of these elements at Colaba were higher than those at the other sites. It is likely that due to its location near the southern tip of the island the concentration at this site was influenced by direct sea-spray contamination and washout of giant sea-salt particles. The mean concentrations in samples collected at this research centre (BARC) are taken to represent the coastal values. In Table 1, the concentration in reference sea-water (Mason, 1966) and results for marine precipitation samples collected at Hawaii (Duce et al., 1965) are also included. The results for Hawaiian rain samples taken at altitudes of 610 m and 1372 m are taken from the figures in reference (Duce et al., 1965) since these are approximately the altitudes of Lonavala and Mahabaleshwar, respectively, and the concentration and composition are known to change with altitude. The higher concentrations in samples taken while at sea

Table 1. *Halogen and sodium concentrations in rain-water*

Element/Ratio	Sea-water (Mason, 1966)	At sea*	Coast, BARC*	Lonavala*	Duce† et al. (1965)	Mahabaleshwar*	Duce‡ et al. (1965)
Na§	—	4.6 ± 3.9	3.7 ± 4.2	2.2 ± 1.4	—	0.28 ± 0.18	—
Cl	—	6.8 ± 2.8	7.1 ± 6.7	4.4 ± 2.5	3.1	0.56 ± 0.32	1.0
Br	—	33.6 ± 33.2	34.9 ± 24.2	11.4 ± 7.0	15	5.01 ± 1.97	8.0
I	—	13.3 ± 4.7	15.7 ± 9.4	6.6 ± 3.0	6.4	2.57 ± 1.17	3.3
Cl/Na	1.8	1.82 ± 0.54	2.05 ± 0.57	2.00 ± 0.26	—	2.07 ± 0.34	—
Br/Cl ($\times 10^3$)	3.42	4.59 ± 3.74	6.37 ± 3.77	2.80 ± 0.87	4.8	10.9 ± 5.1	8.0
I/Cl ($\times 10^3$)	2.63×10^{-3}	2.19 ± 1.03	2.97 ± 1.72	1.66 ± 0.6	2	5.36 ± 3.24	3.3
I/Br	0.77×10^{-3}	0.70 ± 0.52	0.56 ± 0.39	0.63 ± 0.29	0.43	0.59 ± 0.39	0.41

* This work.

† Values read from Figures 4–8 of the reference, from the least squares line, for 610 m altitude.

‡ Values read from the same figures but for 1372 m altitude.

§ Na and Cl are in μg/ml; Br and I are in ng/ml. The ratio values are the average of individual ratios.

Table 2. *Br and I enrichment in rain-water samples*

Element	Enrichment in samples collected at				
	Sea	Coast BARC	Coast Trombay hill top	Lonavala	Mahabaleshwar
Br	0.1 ± 0.03	0.9 ± 0.4	0.58 ± 0.32	−(0.1 ± 0.03)	2.6 ± 1.2
I	800 ± 360	1230 ± 730	1720 ± 1250	690 ± 210	2410 ± 1600

and on the coast are the results of higher air concentrations. It is seen that the mean concentrations for sampling sites on the hills agree very well with those for the Hawaiian marine precipitation samples.

3.2. *Variation of halogen enrichment in rain-water with sampling altitude*

Chlorine and sodium in the rain-water samples show good correlation and no change is detected in the Cl/Na ratios with collection altitude within experimental errors. Seto et al. (1969) found that the Cl/Na value remained nearly the same as that of sea-water in a number of rain-water samples collected at varying altitudes and distances from shore in Hawaii. In cloud-water samples collected at Mahabaleshwar (Sadasivan, 1977) this ratio was 1.79 ± 0.02, very close to that of the sea-water value. The mean ratio value for the three sites on land is slightly higher than the sea-water ratio of 1.8, though within errors they bracket the sea-water ratio.

Bromine enrichment in rain-water samples collected at sea and on the coast are indicated by the Br/Na and Br/Cl values. The enrichment of any sea-water derived element is calculated with reference to sodium. The enrichment E is defined as (Duce et al., 1972),

$$E = [(X/Na)_{atm}/(X/Na)_{sea\text{-}water}] - 1$$

where $(X/Na)_{atm}$ is the weight ratio of any element X to the reference sodium in an atmospheric sample and $(X/Na)_{sea\text{-}water}$ is the same element weight ratio in sea-water. The calculated Br and I enrichment in the rain-water samples is given in Table 2. Bromine enrichment is more in samples from the higher altitude station on the hills and the rain-water samples from Lonavala at a lower altitude show a nominal depletion. The iodine enrichment in the samples is very high in agreement with the many earlier observations. Maximum enrichment of iodine is observed in samples from the higher altitude station on the hills. In marine aerosols a small depletion of Br and high enrichment of iodine has been observed and is explained to be due to the loss of Br from sea-salt particles and conversion of gaseous iodine to particulate form (Moyers and Duce, 1972a, 1972b). Increase in Br/Cl and I/Cl values in rain-water as compared to aerosol has been measured and interpreted (Moyers and Duce, 1972a; Martens and Harriss, 1973) as being due to the dissolution of gaseous Br and I in raindrops. However, our measurements on aerosol and rain-water composition indicate that there is no significant dissolution of gaseous Br and I in raindrops and that the aerosol composition adequately explains the rain-water composition (Sadasivan et al., 1974; Sadasivan, 1977). The increase in Br/Cl and I/Cl ratios that is observed in rain-water samples from Mahabaleshwar is also observed in aerosol collections. The Br/Cl ratios in aerosols larger than 0.1 μm radius at coast and at Mahabaleshwar are 0.003 and 0.008 respectively, while the I/Cl values for these two sites are 0.001 and 0.003 respectively.

Table 3. *Average Cl, Br and I concentrations in rain-water*

Element	Global average (Bewers, 1972)	Bombay	Lonavala	Mahabaleshwar
Cl (μg/g)	1.8–3.6	7.1	4.4	0.6
Br (ng/g)	4.3	34.9	11.4	5.0
I (ng/g)	0.6	15.7	6.6	2.6

3.3. *Mean concentration of halogens in rain-water for halogen geochemistry*

The mean concentration of the halogens in global precipitation as calculated by Bewers (1972) from his halogen circulation model and the mean concentration of these elements in our samples is given in Table 3. Although Bewers (1972) finds general agreement between his estimated concentrations and experimental measurements at a few sites, our results show that these concentrations in precipitation over large areas with high rainfall amounts differ considerably from the global average. Yearly averaged data of concentration in precipitation over vast areas including ocean regions and involving large precipitation amounts will therefore be necessary for a comparison with model calculations and for a proper evaluation of halogen deposition on a global scale.

The reported iodide concentrations in precipitation all over are certainly higher than the model predicted global average value. The model calculation assumes that the amount of a halogen injected into the air from sea-water is related to the total dissolved halogens in sea-water and is also related to the water transfer. However it is now well known that in the transfer across sea–air interface the concentrations in the top microlayer rather than total dissolved amounts determine the quantity injected into the atmosphere, and in the case of iodine there is also the possibility of its transfer from sea-water to air unrelated to water transfer. These may explain the lower value predicted by the model.

3.4. *Monsoonal transport of sea-salt*

Eriksson (1960) had predicted, based on the monsoonal transport of sea-salt into U.S.A., that India should also receive an abundant supply of the sea-salt. Average chloride concentration in precipitation over the U.S.A. as given by Junge (1963) shows a value of 8.0 μg/g near the east coast with the concentrations falling rapidly inland. In the present measurements also a similar trend is obtained though the concentrations are somewhat higher. Increased sea-salt deposition inland due to monsoonal flow has also been observed by Tsunogai (1975) in Japan who found the deposition on the Japan sea side region to be more than that on the Pacific ocean side region by a factor of 3 or more, due to the northwest monsoon in winter. Tsunogai (1975) measured a mean deposition of 6.45 g/m^2 for this period at a site 20 km inland. The precipitation averaged (from 1-week measurements) Cl concentration in rain-water at Lonavala (625 m high, 60 km inland) is calculated to be 4.9 μg/ml and this gives, for the average monsoon rainfall of 4100 mm a deposition of 20 g/m^2. The actual value will, however, be somewhat less than this estimate since the measurements were made in July when specific concentrations and rainfall are high. At the coast, the deposition values are very much higher. The sea-water-derived chloride in precipitation over Calcutta, approximately 50 km inland in eastern India, during the monsoon has been estimated to be 2.9 μg/ml (Handa, 1969). The chloride concentration in rain-water at Delhi, during the monsoon, has been found to be 0.4 μg/ml (Khemani, 1974) and this value is already low and comparable to values obtained inland in U.S.A. by Junge (1963). During the monsoon high rainfall occurs along the west coast and parts of east coast and the rainfall decreases rapidly inland. The average rainfall for the monsoon period is 115 cm at Calcutta while it is 60 cm at Delhi. Poona, which is about 150 km from Bombay but on the lee side of the hills, has an average monsoon rainfall of 52 cm. Hence the fairly high sea-salt deposition due to the monsoon current should be restricted from coast line to certain distances inland on the west coast side as well as parts of the east coast where the bay branch of the monsoon reaches.

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ХЛОР, БРОМ И ИОД В МУССОННЫХ ДОЖДЯХ В ИНДИИ

Описываются и обсуждаются результаты измерений средних концентраций галогенов-хлора, брома и иода в большом количестве проб дождевой воды, собранных на западном берегу Индии в период югозападного муссона и на двух станциях на невысоком горном хребте вблизи западного побережья. Концентрации и отношения этих галогенов в пробах дождевой воды очень хорошо сопоставимы с таковыми, ранее наблюдавшимися в морских осадках. Среднее отношение Cl/Na проявляет небольшое увеличение с высотой сбора проб. Бром выявляет небольшое обогащение по отношению к Na в большинстве мест и номинальное обеднение на одном из горных мест. Обогащение иода в пробах увеличивается с высотой места сбора. Это исследование подтверждает, что благодаря муссонному потоку вдоль западного побережья Индии происходит осаждение морской соли в больших количествах.