Difference in chemical composition of atmospheric sea salt particles produced in the surf zone and on the open sea in Hawaii

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ABSTRACT

Cascade impactor samples of atmospheric sea salt particles have been collected at a tower site on the east coast of Hawaii. In an-attempt to differentiate between surf-produced particles and particles produced by bubble bursting on the open sea, samples were collected simultaneously near the tower base and at the top of the tower, 24 meters above sea level. Analyses of the samples by neutron activation for iodine, bromine, and chlorine showed that the total bromine and chlorine concentration was 20–50 times higher at the tower base than at the tower top, whereas total iodine was only twice as high. The I/Cl ratio was a factor of 3–30 higher for samples collected at the tower top. Concentration per cubic meter vs particle size curves for all three halogens were considerably different for samples collected at the two elevations. This vertical gradient shows the large differences between spray particles from waves breaking on the shore and spray particles from waves breaking at sea. Great care must be exercized in selecting coastal sampling sites for the collection of atmospheric sea salt particles which are intended to be representative of particles present in the atmosphere over the open ocean.

Introduction

When marine winds pass over coastal regions and blow inland they carry salt spray particles from the open sea as well as spray added during passage over the shore-line surf. The purpose of this paper is to compare and contrast certain physical-chemical characteristics of the open-sea spray particles and the particles present after the air passes over the local surf. The study should prove useful in planning coastal observations aimed at understanding airborne particles from the open sea and in evaluating earlier coastal observations of this nature. Unfortunately, very little attention has been given in the past to the possibility that particles collected behind the surf zone may be chemically different from particles formed on the open sea.

In experimental studies of breaking waves, Boyce (1951) showed that relatively few salt particles were produced by the mechanical disintegration of the water but that a much greater number of particles were produced a few seconds later when the air bubbles resulting from the wave action burst at the sea surface. Jacobs (1937) had suggested earlier that bursting bubbles were the source of the airborne salt particles he found over the coast of southern California.

High speed photography, by Kientzler et al. (1954), has shown that bubbles bursting at a sea water surface form jets which eject droplets into the air. Droplet size was found to be a function of bubble size. Blanchard & Woodcock (1957) investigated various processes of bubble formation in the sea and concluded that most bubbles were probably formed by breaking waves but that bubbles formed in the sea by falling rain or snow could also be significant.

Several complicating factors arise when particulate matter is produced in a heavy surf zone near shore. Waves breaking on a rocky and irregular shoreline may undergo considerable mechanical disintegration. It is probable that a significant fraction of the mass of sea salt

particles in the air immediately downwind from the heavy surf are formed by this process as well as by normal bubble breaking. In addition, along coastlines with onshore winds, organic films of surface-active materials, both of naural and pollution origin, can be blown into the shore area and may pile up several molecular layers thick. This abnormal amount of organic material may alter the chemistry and the mechanical bubble-fractionation processes of the local surface sea water significantly (Blanchard, 1963) and effect the relative amounts of trace elements present in the sea salt particles formed in the surf zone.

River, stream, and seepage effluents, ship operations, and sewerage outfalls may all combine to make the chemical composition of near shore waters considerably different from that on the open ocean, especially among trace elements. Thus the trace element chemical composition of sea salt particles collected at ground level near the surf zone may be different from particles produced on the open sea, due to different particle production mechanisms as well as to changes in the trace element composition of the near shore bulk and surface water.

It has been known for a number of years that the I/CI ratio in sea salt particles and rain collected from marine air at various locations is 10 to 1 000 times that in sea water (Duce et al., 1963; Miyake and Tsunogai, 1963; Dean, 1963; Duce et al., 1965; Duce et al., 1967). Since both the iodine and chlorine in these samples are almost certainly from the sea, some chemical fractionation process must be taking place at the air–sea interface. The possible processes responsible for the iodine enrichment are discussed in the papers above. Since the enrichment of iodine in the atmospheric particles has been found to be so large in many cases previously, it was believed that a simultaneous study of the I/CI ratio in particles produced by bubbles breaking on the open sea as well as particles produced in the surf zone would be most likely to show any effect of the different production mechanisms or different chemical composition of the sea water on this ratio. At the same time, a study of the Br/Cl ratio on the particles would indicate the effect of the different source areas on an element which is apparently not normally enriched in sea salt particles. Previous studies of the Br/Cl ratio on bubble-produced particles formed on the open ocean have shown Br/Cl ratios only slightly less than those found in sea water (Duce et al., 1965; Duce et al., 1967).

Sampling location and methods

In order to avoid locally-surf-produced particles, a walk-up aluminum tower was constructed on the windward coast of Hawaii approximately 9 km east of Hilo during the fall of 1967. The tower location has been described previously (Duce et al., 1967). The present tower was approximately 20 meters high and was located on the end of a lava headland which was itself about 4 meters above mean sea level. At a height of 24 meters above the sea, no spray particles from the waves breaking against the headland reached the top of the tower under normal sea and tradewind conditions. On the other hand, the base of the tower was intermittently bathed in sea spray particles produced by waves breaking against the lava headland.

Particulate samples were collected using two six-stage in-line cascade impactors manufactured by Scientific Advances Co., Columbus, Ohio. One impactor was located at the top of the tower and the other was on the ground approximately 4 meters shoreward from the base of the tower, partially shielded by the lava headland. This type of cascade impactor has been described by Mitchell & Pilcher (1959) and problems relating to its use in the marine environment have been discussed by Duce et al. (1967), especially with regard to changes in collection efficiencies for various impactor stages with change in ambient relative humidity. The first stage slide (slide A) collects sea salt particles with a radius ≥ 10 μm at a relative humidity of 90% with an efficiency of approximately 100%. The radius of particles which are collected with 100% efficiency (r_{100}) decreases by a factor of 2 on each succeeding stage. Thus r_{100} for stages B, C, D, E, and F are approximately 5 μm, 2.5 μm, 1.2 μm, 0.6 μm, and 0.3 μm, respectively.

When in use, the intake orifice of the impactor opened vertically upward. Isokinetic sampling was not attempted, since the elemental ratios were of primary interest. Thus there was undoubtedly some discrimination by the impactor against the largest particles, as shown earlier by May (1945). In addition, the impactor at ground level was shielded from direct fallout of the largest of the surf spray droplets by

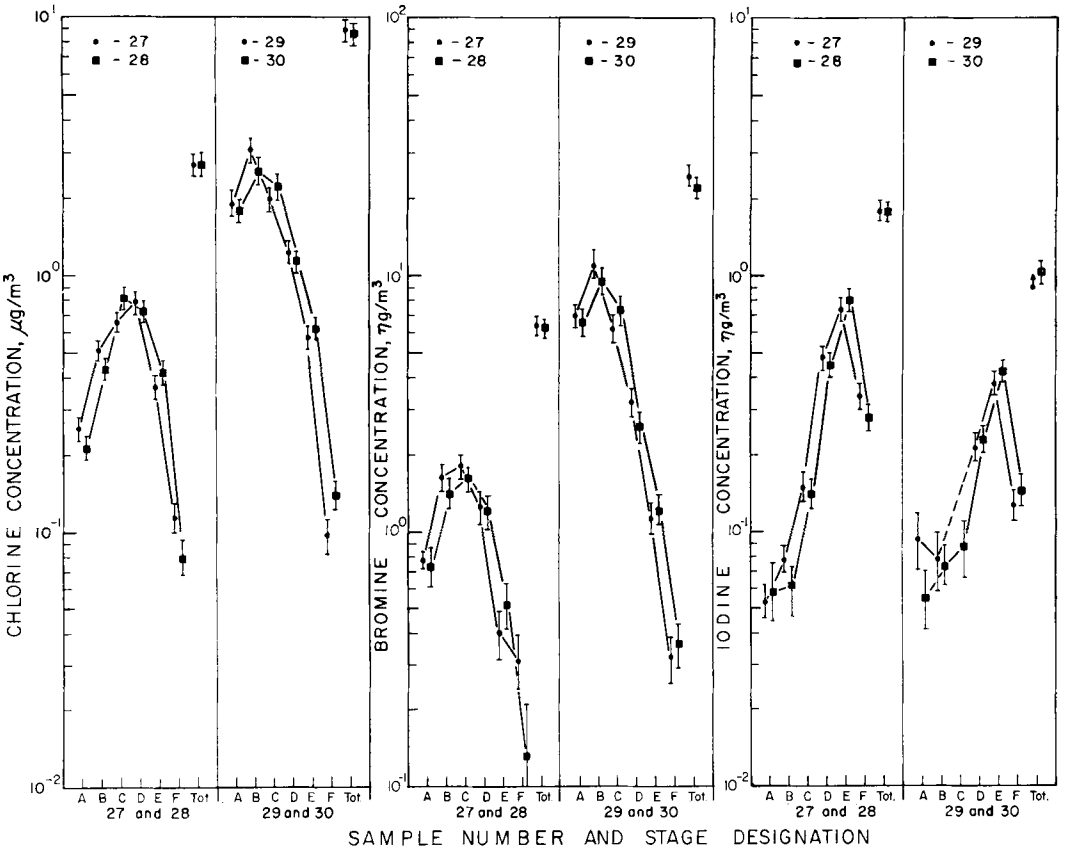

Fig. 1. Chlorine, bromine, and iodine concentrations for two sets of cascade impactor samples collected simultaneously at the top of the tower.

placing it under a 30 × 50 cm shelter. No shelter was required for the impactor at the top of the tower.

Air was drawn through the impactors at a rate of 0.75 m³/hr using vacuum pumps powered by a gasoline motor-generator located approximately 20 meters downwind from the base of the tower. For samples collected near the base of the tower, the sampling duration was generally 1–2 hours, whereas sampling at the top of the tower took 4–6 hours.

Care was taken to sample only when the trade winds were blowing from the sea. Under normal wind conditions the movement of surface air on the east side of Hawaii shifts from generally easterly during the day to westerly at night. This wind shift is caused by the cooling and sinking of air during the evening hours on the upper slopes of the volcanoes Mauna Kea and Mauna Loa, located in the center of the island (Mendonca, 1969). Usually by mid-morning solar heating of the land allows the trade wind regime to again be dominant along the east coast of the island. The downslope winds, which are rather shallow (see ESSA Weather Bureau noon GMT soundings, Lyman Field, Hilo, Hawaii) often extend as far as 15 miles to sea off the east coast of Hawaii (Woodcock, 1969). As the air passes out to sea it carries with it particulate matter from the land, and when the wind reverses direction the next morning some of the particulate matter is brought back to the island for a brief time prior to the arrival of the unmodified oceanic air (Blanchard, 1968). We did not begin collecting sea salt particles in this work until the condensation nucleus count at the top of the tower dropped to 100–300 particles/cc, its usual level in uncontaminated marine air (Blanchard, 1969).

The sea salt was removed from the impactor

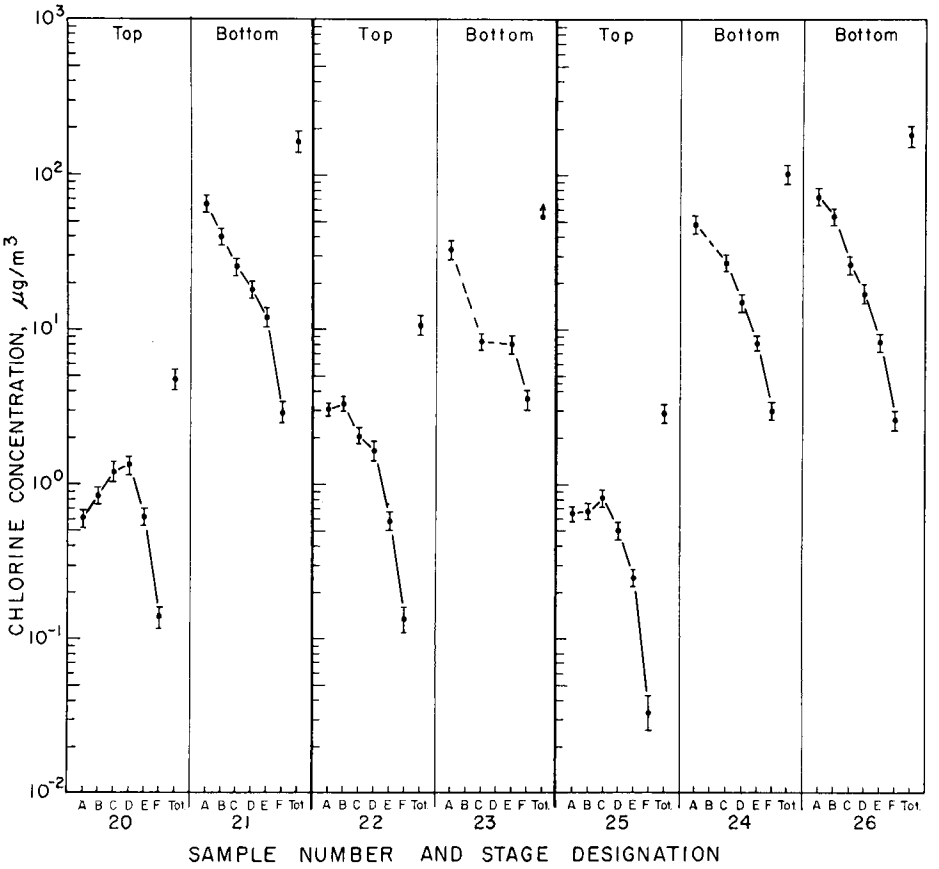

Fig. 2. Chlorine concentration for cascade impactor samples collected at the top and near the bottom of the tower.

slides in the same manner as that described by Duce et al. (1967). The samples were analyzed for iodine, bromine, and chlorine by neutron activation analysis using the procedure of Duce & Winchester (1965). The nuclear reactor and laboratory facilities at the Massachusetts Institute of Technology, Cambridge, Mass. were used.

Results and Discussion

Sixteen impactor samples were collected during November, 1967. Five of these samples were taken with only a single impactor operating at the top of the tower. They show halogen concentrations and ratios similar to the samples reported by Duce et al., (1967) and are not reported here to conserve space. These data will, however, be supplied to any interested reader on request. On two different days, two impactors were operated side by side at the top of the tower in an attempt to assess the reproducibility of the entire sampling and analytical procedure. The results of the analyses of the samples, Nos. 27–30, are presented in Fig. 1. The uncertainty bars in this figure represent the analytical precision of the analyses. Both the shapes of the concentration vs particle size curves and the concentrations themselves are remarkably similar in all cases. Occasional discrepanicies in the concentration (i.e., no overlap of the analytical uncertainty bars) occur only on slide F, where the concentration of all these elements is very low.

Since the atmospheric concentration of sea salt particles was much higher at the base than at the top of the tower, simultaneous sampling throughout the duration of a sample collection

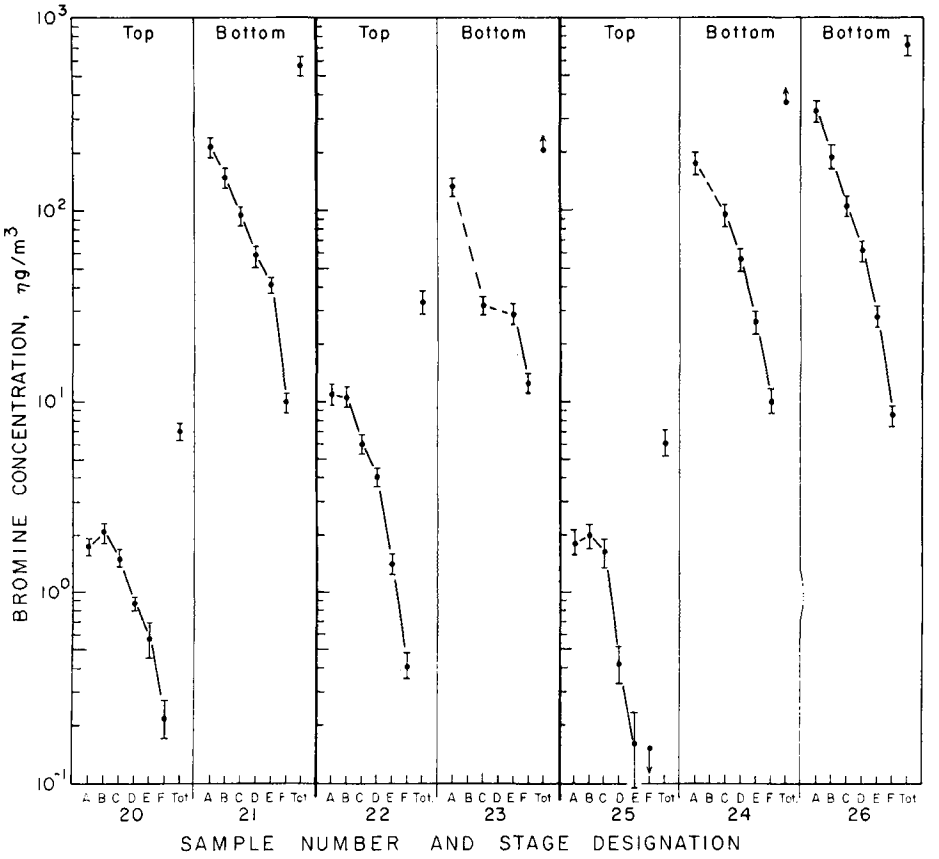

Fig. 3. Bromine concentrations for cascade impactor samples collected at the top and near the bottom of the tower.

at both locations was not possible. A minimum of 4 hours was required for adequate sample collection at the top of the tower, but after approximately 2 hours of collection at the tower base, the slides would become practically saturated with sea salt and there was danger of salt blow-off from the glass slides. Thus bottom samples were collected at some 1–2 hour interval during the longer collection period for samples collected at the tower top. Sample 25, collected at the top of the tower, was collected over a 2 day period due to interruption of collection by rain during the first day. Bottom sample 24 was collected on the first and bottom sample 26 was collected on the second of the 2 days.

The results of the Cl, Br, and I analyses for these top and bottom samples are presented in Figs. 2, 3, and 4 respectively. The effect of the different sampling location is immediately evident. The total Br and Cl concentration is a factor of 20–50 lower on the tower top than at the bottom. More important, however, since the bottom samples were shielded, is the shape of the concentration vs particle size plots. The typical shape of the Cl and Br plots for samples collected at the tower top indicates a low concentration of each element on the largest and smallest particles with a maximum generally on particles in the intermediate range. This can be seen in the data of Duce et al. (1967), and in Fig. 1, and has been generally noted in the concentration of salt particles in the lower air over the open sea near Hawaii (Woodcock, 1953, Fig. 1). It is also apparent in sample 20 and, to a certain extent 22 and 25 in Figs. 2 and 3. However, all the samples collected at the base of the tower show the highest concentration for the largest particles, with regularly decreasing concentra-

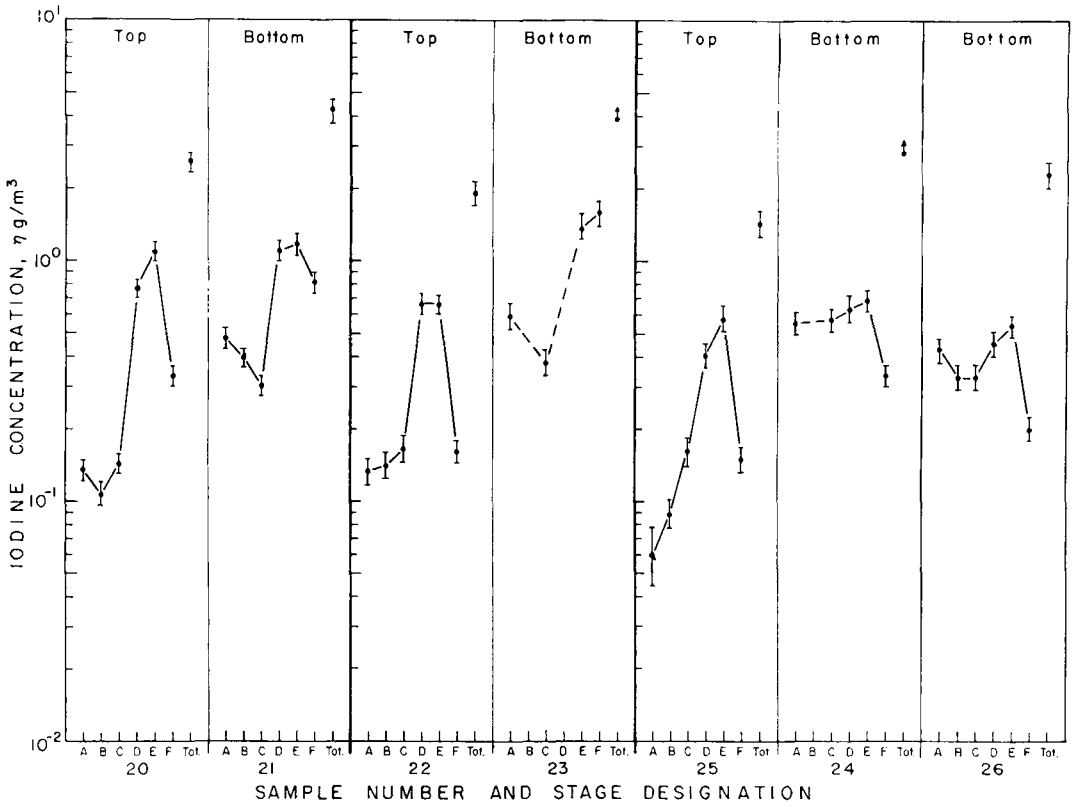

Fig. 4. Iodine concentrations for cascade impactor samples collected at the top and near the bottom of the tower.

tions for decreasing particle size. In terms of mass, it is apparent that the particles produced in the surf zone far surpass particles already present in the air blowing in over the surf zone from the open sea, in all size ranges. It is quite apparent that collection of particles behind a surf zone of this type could give no information on the number or size distribution of sea salt particles over the open sea.

For iodine (Fig. 4) the situation is considerably different. The concentration of the total iodine at the top and bottom of the tower is practically the same, with the iodine collected at the bottom only a factor of approximately 2 greater than at the top. It appears that the major portion of the increase in iodine at the bottom of the tower comes on the largest particles, although there are not sufficient samples to be certain of this.

The variation of the I/Cl ratio with particle size at the top and bottom of the tower is shown in Fig. 5. The I/Cl ratio is generally a factor of 3–40 greater on the top than at the bottom, reflecting the large production of Cl and small production of I in the surf-zone. The general shape of the I/Cl ratios vs particle size at the top and bottom of the tower are similar, largely due to the very great production of the largest particles high in Cl in the surf zone. The sea water I/Cl ratio varying from 3 to 6×10^{-6} is also indicated on Fig. 5 (Duce et al., 1965). The largest particles collected at the bottom of the tower have I/Cl ratios very close to bulk sea water, perhaps indicating that these giant particles may be largely the result of mechanical tearing of the waves striking the lava headland. Blanchard (1968) has shown that mechanical disintegration (atomization) of coastal waters fails to transfer organic materials in the quantities to be found in the particles naturally present in the air over the sea.

The shape of the Br/Cl ratio curves, presented

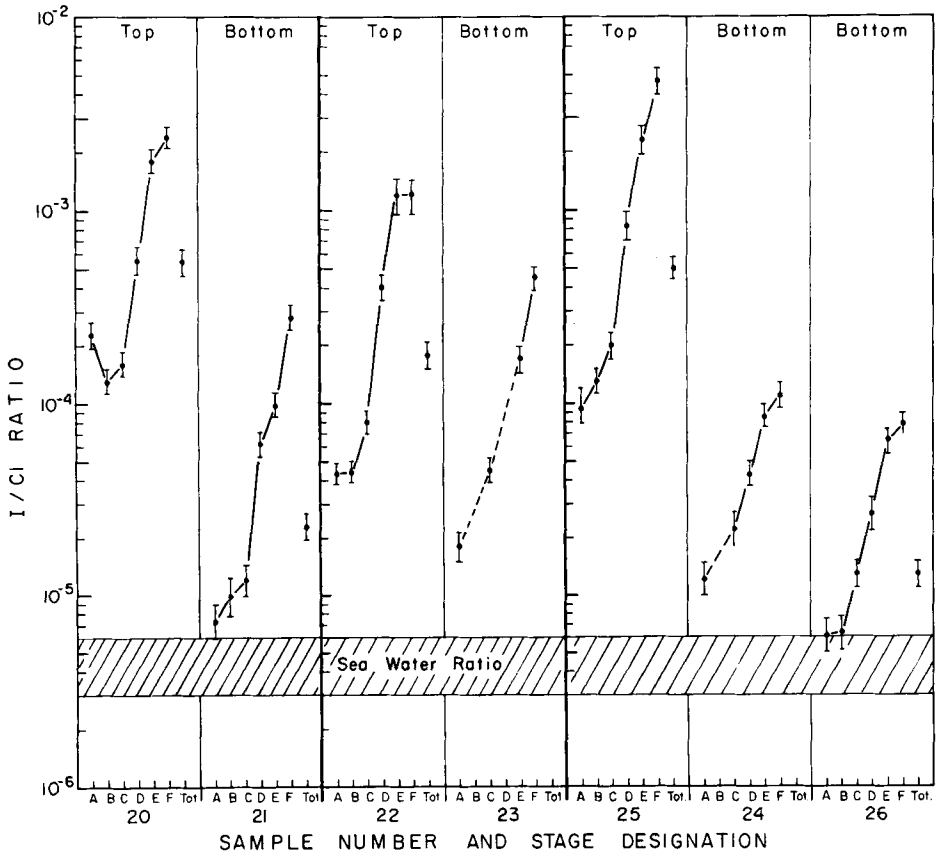

Fig. 5. I/Cl ratios for cascade impactor samples collected at the top and near the bottom of the tower.

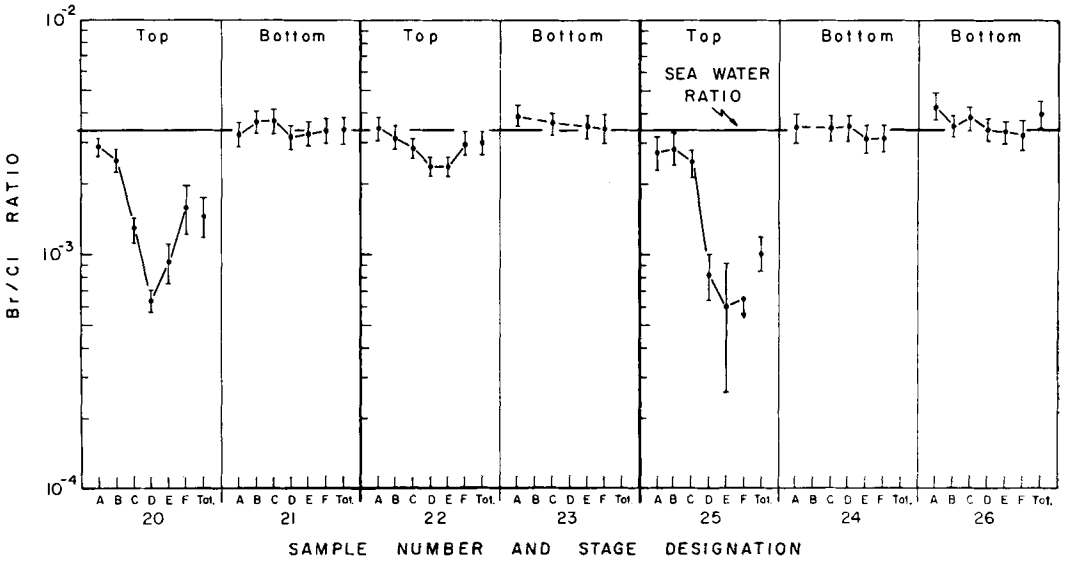

Fig. 6. Br/Cl ratios for cascade impactor samples collected at the top and near the bottom of the tower.

in Fig. 6, is different for samples taken at the top and bottom of the tower. At the top, the characteristic U shaped curve for this ratio is observed and the ratio is somewhat lower than the sea water ratio. This has been discussed by Duce et al. (1967). At the bottom, however, there is no significant variation of the ratio with particle size and the Br/Cl ratio has essentially the same value as in sea water.

Conclusions

It is quite apparent that, at least for the halogens, there is considerable variation in the relative chemical composition of sea salt particles produced on the open sea and those produced in this surf zone. In addition, the number and size distribution of particles produced in these two areas are significantly different. It seems quite likely that relative concentration differences for other trace elements, which may undergo chemical fractionation during the normal bubble bursting process, may be found on sea salt particles produced in these two different areas. Certainly great care must be taken in selecting coastal sampling sites for the collection of atmospheric sea salt particles in any subsequent study attempting to investigate the possible chemical fractionation effects during bubble bursting on the open sea. In addition, only enrichment values obtained from such carefully selected sites should be used in any calculations attempting to determine atmospheric or total geochemical cycles for any of the enriched trace elements on a global basis.

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РАЗНИЦА В ХИМИЧЕСКОМ СОСТАВЕ ЧАСТИЦ СОЛИ В ВОЗДУХЕ В ЗОНЕ ПРИБОЯ И В ОТКРЫТОМ МОРЕ НА ГАВАЙЯХ

На башне на восточном берегу Гавайских островов с помощью каскадных заборных датчиков были собраны частички морской соли в воздухе. В попытке различить частички, порождённые в зоне прибоя, и частички, порождённые при разрушении пузырей в открытом море, пробы брались одновременно вблизи основания мачты и на её верху на высоте 24 *м* над уровнем моря. Нейтронный активационный анализ на иод, бром и хлор показал, что полное содержание брома и хлора было в 20–50 раз выше у основания мачты, чем наверху, в то время как содержание иода было лишь вдвое больше. Отношение I/Cl было в 3–30 раз больше для проб, взятых наверху. Зависимости концентрации на $м^3$ от размера частиц для всех трёх галогенов, значительно различались для проб с разных уровней. Эти вертикальные градиенты указывают на большую разницу между частицами пены от обрушения волн на берег и от обрушения волн в открытом море. К выбору мест для сбора на берегу частиц морской соли, которые по предположению должны представлять частицы, порождённые в открытом море, надо подходить с большой осторожностью.