Variation of ion ratios with size among particles in tropical oceanic air[1]

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ABSTRACT

During the summer of 1966, size fractions of sea-salt particles were collected in the marine atmosphere using a six-stage cascade impactor mounted on a tower 14 meters above the windward shoreline near Hilo, Hawaii. The particle sizes collected varied from essentially all particles of unit density with radii greater than 10 microns on the first stage to all particles with radii of approximately 0.3 microns on the sixth stage. The use of the tower assured that no local surf spray would be collected by the impactor while sampling during onshore trade wind flow. Iodine, bromine, and chlorine analyses were performed on eight sets of samples by neutron activation. The I/Cl ratio showed a regular increase by a factor of 50 to 100 from the largest to the smallest particles. On the smallest particles this ratio was approximately a thousand times that in sea water. The Br/Cl ratio showed a minimum at intermediate particle sizes, with a majority of the values below the sea water ratio. Most of the iodine mass was found on particles with radii of approximately 0.6 microns, whereas the majority of the chlorine and bromine was on particles with radii between 1.25 and 2.5 microns.

This information provides a possible method for tracing the role of sea-salt nuclei in precipitation processes, and may be used to gain new insight into the cycle of the halogens between the atmosphere and the sea.

Introduction

The world oceans are a significant source of atmospheric particles (Eriksson, 1960, and Blanchard, 1963), and there is evidence that these particles are not simply sea salt (Blanchard, 1964, and Duce *et al.*, 1965). A study of ion ratio differences among particles in marine air can expand this evidence and aid us in tracing the roles of these particles in precipitation and other atmospheric processes. This study may also add to our comprehension of exchange mechanisms occurring at the air–sea interface.

Recent efforts to use the salt content of rain water to further our understanding of the role of sea-produced particles in raindrop formation have been handicapped by problems concerning the effects of evaporation and of drop coalescence.

Turner (1955) found a potentially useful inverse relationship of raindrop size and raindrop sodium concentration in the warm rains of Hawaii. This relationship could be regarded as confirmation of the hypothesis (Woodcock, 1952) that the salt in rain waters might result from the formation of individual raindrops on individual sea-salt nuclei of various sizes. It was not clear, however, that the higher concentration found by Turner in the smaller drops might not result simply from a differential evaporation among the drops falling through unsaturated air.

Later Woodcock & Blanchard (1955) discovered experimentally that all of the salt found in individual raindrops might indeed result from initial drop formation on individual salt particles present in the air. In this second investigation, however, an alternative explanation of the presence of a given weight of salt in a raindrop is that it represents the sum of the weights of salt in the droplets which have coalesced to form the raindrop, and is not simply the weight of the salt in the nucleus on which the drop initially formed.

It will be noted in the discussion above concerning the work of Turner (1955) and Wood-

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cock & Blanchard (1955) that in both cases the concentration of sodium or chloride was used in an effort to trace the role of sea salt in raindrop formation. If it could be shown that there were regular variations of certain elemental ion ratios on salt particles with changing particle size, it might be possible to eliminate in large measure the above problems concerning the salts in solution in raindrops. For instance, evaporation of water changes only the amount of water and not the mass ratios of the various ions present in the droplets. On the other hand, if coalescence among the particles of the different size ranges or among the droplets formed on these particles occurs, marked changes in the ion ratios will result.

It has been known for a number of years that the I/Cl ratio in salt particles and precipitation samples collected in maritime air is in general a hundred to a thousand times greater than the same ratio in sea water (Heymann, 1927; Komabayasi, 1962; Duce *et al.*, 1963; Miyake & Tsunogai, 1963; Dean, 1963; Duce *et al.*, 1965). The cause of these high ratios in the atmosphere is still unknown. However, the source of both the I and Cl is almost certainly the sea, and there are undoubtedly some interesting processes involving chemical exchange across the air–sea interface at work here. A further study of the chemistry of the sea salt particles may well shed some light on the chemical exchange processes themselves.

As a possible explanation for the high I content of the air, Miyake & Tsunogai (1963) suggested that photochemical oxidation of I^- to I_2 occurs in sea water near the sea–air interface, with the subsequent escape of I_2 into the atmosphere. This I_2 then presumably makes its way by diffusion to the sea-salt particles suspended in the air and is adsorbed on their surfaces. A second explanation suggests the presence of organically bound iodine in a surface-active film on the sea surface. If there is selective enrichment of film material on the sea-salt droplets formed when bubbles break through the film, there may also be selective enrichment of iodine on these particles (Bolin, 1959; Dean, 1963). Blanchard (1964) has shown that compressed films of surface active material are present on the sea-salt particles collected in the surf zone in Hawaii. Similar films are thought to be present on atmospheric particles produced on the open sea (Wilson, 1959).

Previous attempts have been made in Hawaii to determine the cycle of the halogens between the sea and the atmosphere. Duce *et al.* (1965) showed that a considerable portion of each of the halogens I, Br, and Cl was apparently present as a gas, although quantitative values were quite uncertain. This had previously been shown for Cl by Junge (1957). A study of the variation of halogen ratios on sea-salt particles during the investigation reported by Duce *et al.* (1965) indicated a tendency for the I/Cl ratio to be greatest on the smallest particles. Variations in this ratio were, however, generally less than an order of magnitude and often not particularly regular. This was due in part to chemical blank problems and to mechanical problems with the old four-stage cascade impactor used to collect the particles.

A third and very critical factor in this earlier sampling was the location of the sampling sites. It was realized that the land itself might have some effect on the ion ratios, either through man's alteration of the chemical composition of the air or by some natural process. Thus particle samples were collected near the windward shore with the impactor about one meter above ground level at the 1963 site (see Fig. 1). Our effort then was to determine the variation of the halogen ratios with the size of particles which had not yet passed over land and which should have been representative of the chemical exchange processes occurring over the open ocean. Unfortunately this type of sampling did not allow a representative collection of "open sea" particles due to the production of large numbers of particles by the surf breaking against the lava headlands. Because of the nature and the nearness of the surf, these local particles are thought to be chemically different from the particles produced on the open sea, thus perhaps masking and confusing the effects that were being investigated.

Sampling location and methods

In the present work these locally produced particles were avoided by sampling at the top of a tower. This tower was so close to the shore line that the surf-produced particles could not reach the top of the tower before being carried inland by the prevailing trade winds. In this way it was expected that sea-salt particle samples could be collected which would be truly

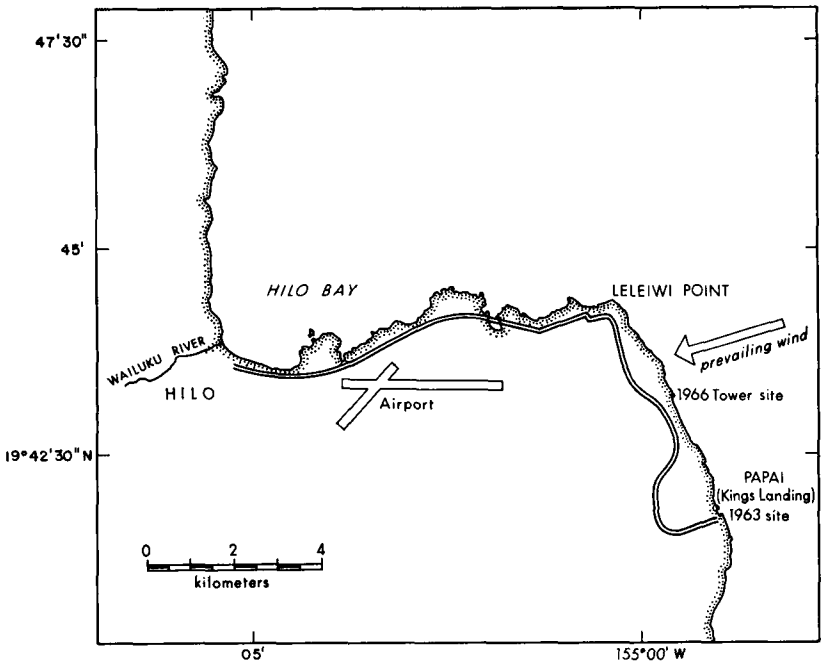


Fig. 1. Sampling locations during 1963 and 1966 on the island of Hawaii.

representative of the air–sea interaction processes on the open sea. The 10-meter-high scaffolding tower was built near the King's Landing road, approximately 9 km east of Hilo, Hawaii on the end of a lava headland which was itself about 4 meters above sea level. It was found that under usual trade wind conditions no spray particles from the waves breaking against the headland reached the top of the tower. Figure 1 shows sampling site locations and prevailing wind direction during the 1963 and 1966 sampling periods.

A modern six-stage in-line cascade impactor, manufactured by Scientific Advances Co., Columbus, Ohio, was mounted on the tower in order to sample airborne particles. A description of this instrument is given by Mitchell & Pilcher (1959), and Figure 2 shows the range of particle size deposited on each stage for particles of unit density. We have used this instrument, however, for sampling particles whose density varied with time due to differences in atmospheric relative humidity. It is necessary therefore to discuss the effect of this density change upon the collection efficiency of the device. If we define r_{100} as the particle radius which is collected with 100% efficiency on any given impactor stage then, according to Ranz & Wong (1952), r_{100} is inversely proportional to the square root of the impacting particle density, ϱp. At relative humidities of approximately 90% (the highest expected under the sampling conditions) the density of the sea-salt droplets is between 1.0 and 1.1 g/cc. Below a

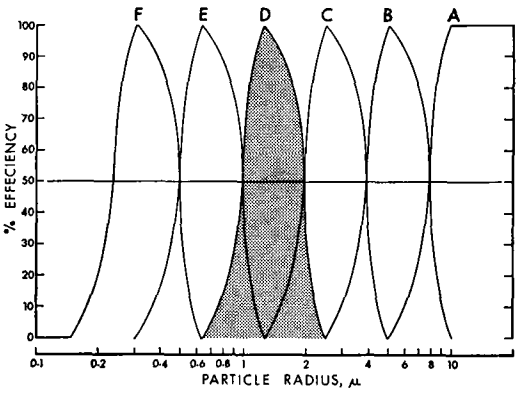
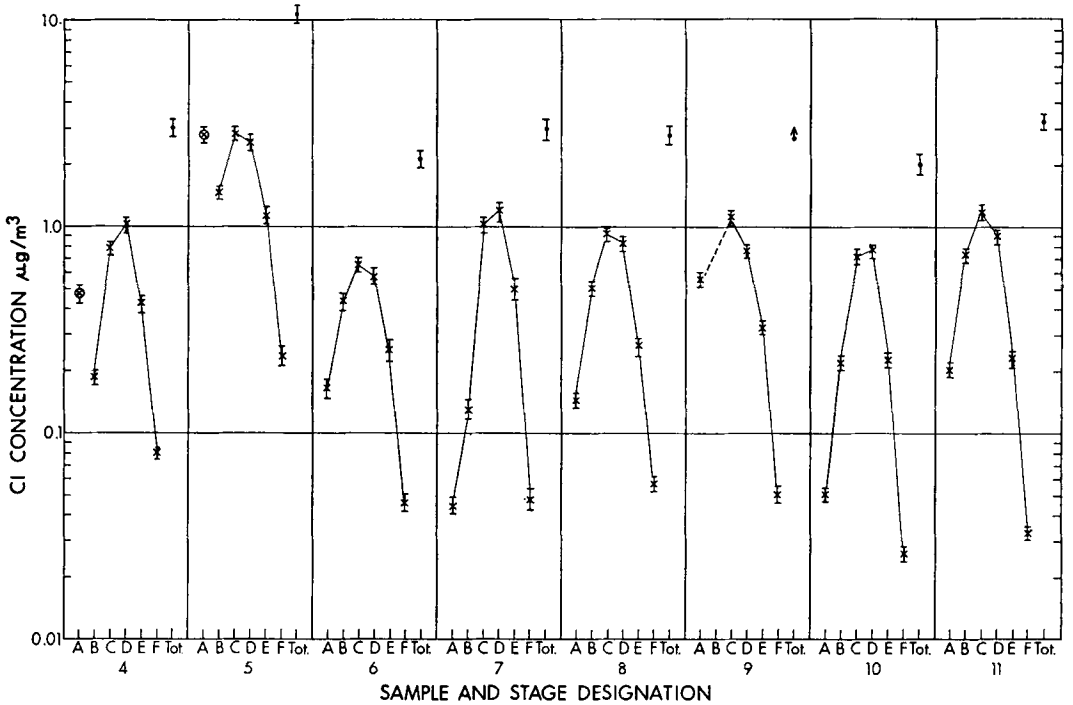


Fig. 2. Collection efficiencies for unit density particles on stages A through F of the six-stage impactor used during the summer of 1966. The shaded area illustrates the spectrum of sizes collected on one of the stages (D).

relative humidity of about 70% (the phase-change point for sodium chloride) the density of the particles increases to approximately 2.2 g/cc. Thus it is possible that the particle density could have varied by up to a factor of approximately two during any sampling period, indicating that r_{100} values for any stage could range from the radius values given in Figure 2 to approximately 0.7 times these values. However, with a relative humidity change from 90% to 70% the particle radius itself will decrease by a factor of approximately 2.3 (Woodcock, 1952). Thus the actual particles collected on any stage, normalized to unit density (90% relative humidity) will have radii varying from the values indicated in Figure 2 to $0.7 \times 2.3 = 1.6$ times these values.

As an example consider stage D in Figure 2. The r_{100} value for particles of unit density is 1.25 μ. If the relative humidity dropped to 70% during the collection period, the r_{100} value for stage D would be 1.25×0.7 or 0.88 μ. However, the 0.88 μ particles collected at 70% relative humidity would correspond to $0.88 \times 2.3 = 2.0$ μ particles at 90% relative humidity. Thus if we normalize all our calibration figures to a unit density condition, it is obvious that the r_{100} values for stage D vary from 1.25 to 2.0 μ, assuming the ambient relative humidity varies from 70% to 90%. This argument would apply to the r_{75}, r_{50}, etc. values, as well as the corresponding values for any other stage. Subsequent reference to particle size will assume r_{100} values at unit density as given in Figure 2.

When in use, the intake orifice of the impactor opened vertically upward. No attempt was made to make the sampling isokinetic, 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). Air was drawn through the instrument at a rate of 0.75 m³/hr, using a vacuum pump powered by a gasoline generator located approximately 20 meters downwind from the base of the tower. The sampling duration was approximately eight hours. Great care was taken to sample only when the trade winds were blowing, the sea was not



Figs. 3–5. Halogen concentrations for each stage of the eight samples collected and total halogen concentrations for each complete sample. Fig. 3: Cl concentration.

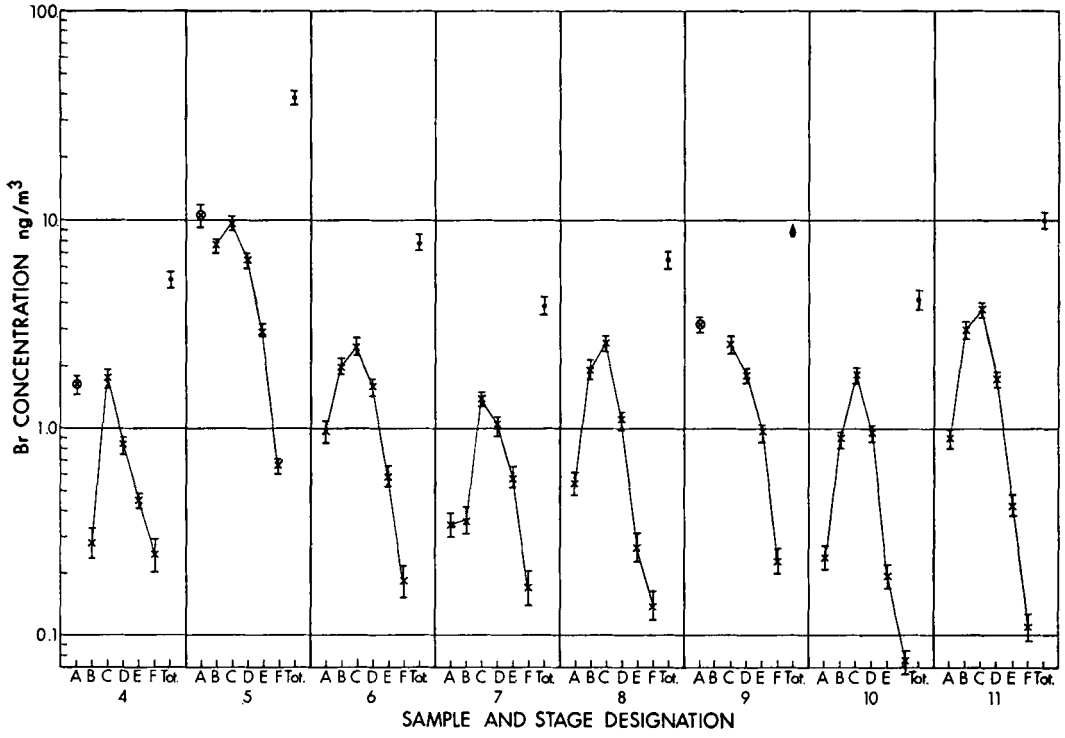


Fig. 4. Br concentration.

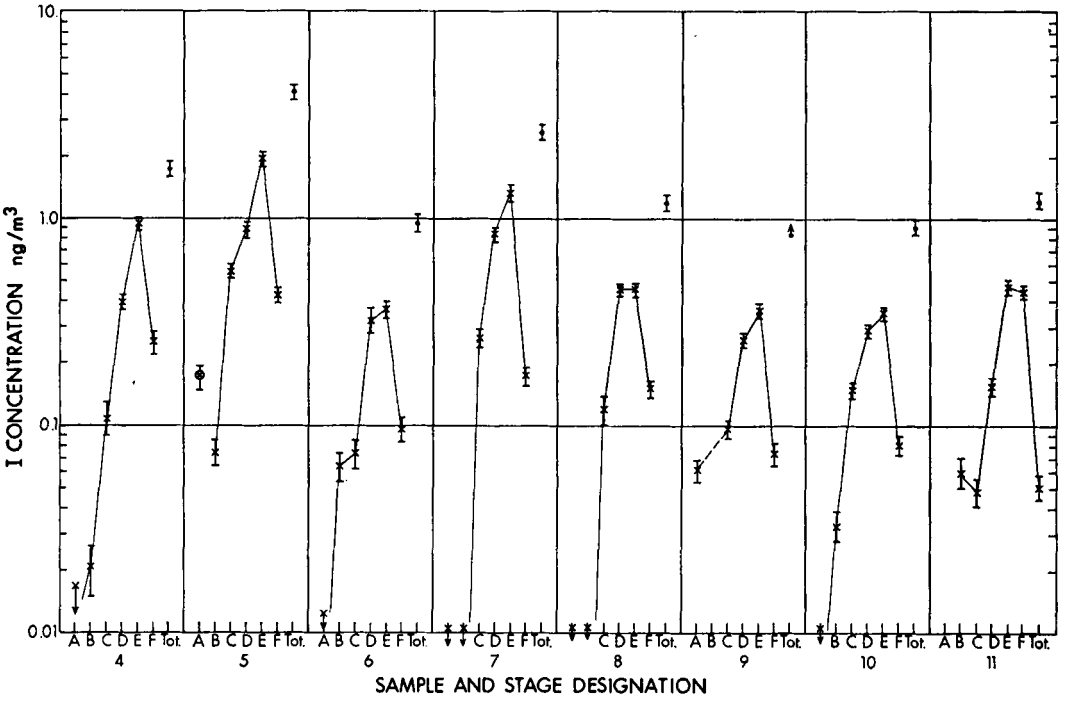


Fig. 5. I concentration.

too rough, and no rain was falling. However, there is some evidence that the latter two conditions were not always met. Sampling hours were generally between 0900 and 1700 LST, for it was during this interval that the winds were mostly easterly and on-shore.

The salt particles were deposited according to their size on clean glass slides in the six stages of the impactor. These slides were removed from the impactor in the laboratory and the salt was dissolved in 0.1 to 0.3 ml of ultra-pure distilled water. This aqueous salt solution was then packaged in small vials (made from polyethylene tubing) for later analysis. A Millipore filter was placed behind the sixth stage to collect the smallest particles, but due to high blank corrections from the filter itself no useful analytical results were obtained from these samples.

The analytical procedure used was neutron activation analysis, which is extremely sensitive for the halogens. Analytical sensitivities for I, Br, and Cl under the conditions used for these analyses were approximately as follows:

I—0.025×10^{-9} *g*,
Br—0.020×10^{-9} *g*,
Cl—0.50×10^{-9} *g*.

The procedure used has been described in detail by Duce & Winchester (1965). For this work the nuclear reactor and laboratory facilities at the Massachusetts Institute of Technology, Cambridge, Massachusetts, were used.

Results

Eight sets of sea-salt particle samples were collected at the Hilo coastal tower site and analyzed for I, Br, and Cl during the summer of 1966. The results of the analyses of these samples are shown graphically in Figures 3 through 8. The uncertainty bars in these figures refer to precision values and have a confidence level of 67%. Concentrations and concentration ratios which appear to be anomalously high on stage A for several samples are indicated by crossed circles. For samples below the limit of detection (after correction for blanks) appropriate upper or lower limits to the concentrations and ratios are indicated with arrows. Stage B in sample 9 was not analyzed due to leakage in the reactor. In addition to the individual values for each stage, the total concentration and concentration ratio for each complete impactor sample is given in Figures 3 through 8.

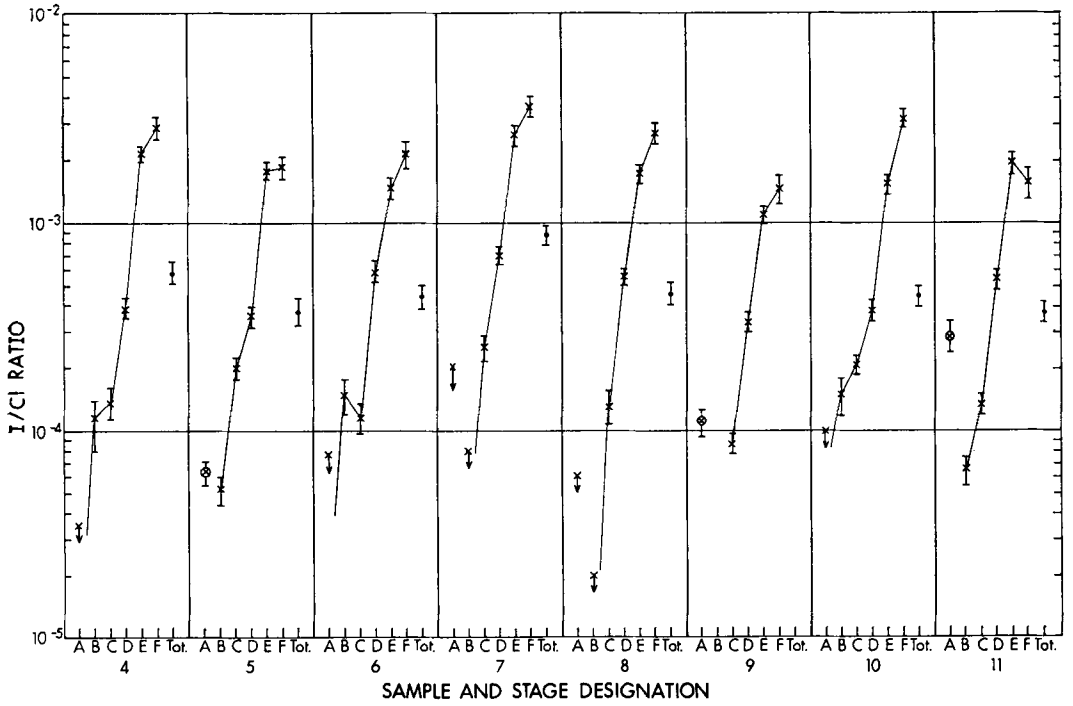
Table 1. *Halogen ratios in sea water*

I/Cl	Br/Cl	I/Br
$\sim 3 \times 10^{-6}$	3.4×10^{-3}	$\sim 0.9 \times 10^{-3}$

Certain definite trends can be seen in the concentration values for the various particle size ranges. Both Br and Cl have a maximum concentration in the intermediate size ranges collected by the impactor. For Cl the maximum is split between stages C and D ($r = 1.25$ to $2.5\ \mu$). For Br the maximum is on stage C ($r = 2.5\ \mu$) in every case, indicating that the maximum Cl concentration appears to be on slightly smaller particles than the maximum Br concentration. The maximum I concentration is generally on stage E ($r = 0.62\ \mu$). Thus the major portion of the I is distributed on much smaller particles than either Br or Cl. The uniformity of the total concentrations, with the exception of sample 5 which was collected on a windier day than the others, is also quite striking. The total respective halogen concentrations differed by less than a factor of two on most of the sampling days. These totals are much like those found earlier in this area for chloride by Junge (1957).

Samples 4, 5, and 9 show higher concentration values on the first stage for some of the elements than the general trend of concentration versus particle size would indicate. Since stage A, the first stage, is directly exposed to any fallout from the atmosphere, it would be expected to collect raindrops, local spray, or any other large particles whose source may not be the sea (e.g., particles from the clothing of individuals working on the tower, etc.). Although efforts were made to protect the collector from rain, it would have taken only one or two 1-mm raindrops to change the iodine concentration on the first stage by a factor of 2 or 3, and some rain occurred on each of the days in which spurious iodine values were found.

Regularities also appear in the halogen ratios shown in Figures 6, 7, and 8. For comparison, the sea-water ratios are given in Table 1, and the Br/Cl ratio is shown in Figure 7 as the heavy horizontal line. The I/Cl ratio in Figure 6 shows a very regular increase with decreasing particle



Figs. 6–8. Halogen weight ratios for each stage of the eight samples collected and total halogen weight ratios for each complete sample. Fig. 6: I/Cl ratio.

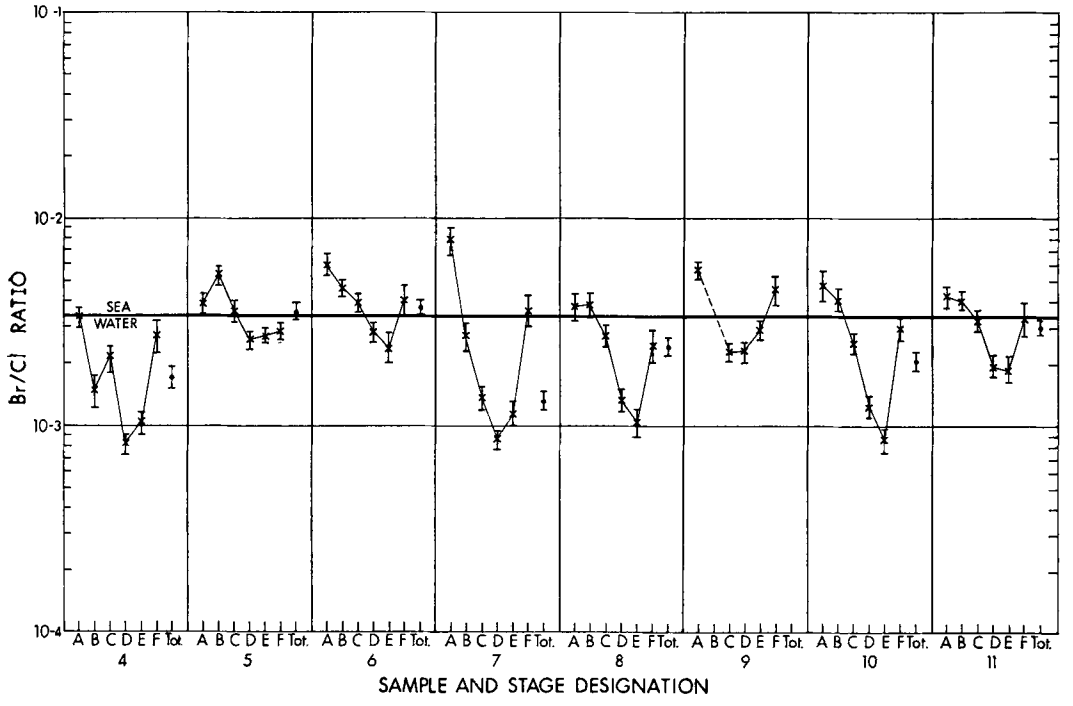


Fig. 7. Br/Cl ratio.

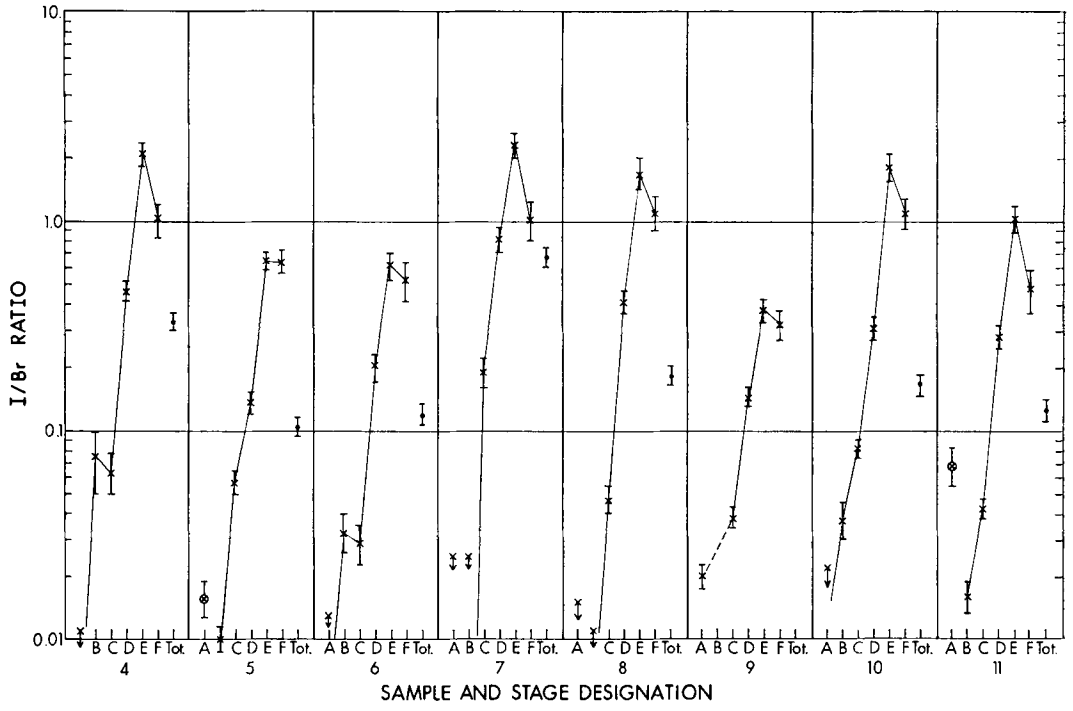


Fig. 8. I/Br ratio.

size, with a few exceptions between stages A and B. The magnitude of the increase is greater than a factor of 100 in several cases. It is also observed that even on the largest particles the I/Cl ratio is considerably greater than the sea-water value.

The Br/Cl ratios in Figure 7 appear to show interesting and rather surprising variations with particle size. While not as clear-cut as the I/Cl case, the Br/Cl ratios appear to show a minimum value at particle sizes between approximately $r = 0.62\ \mu$ and $r = 1.25\ \mu$ (stages D and E). This is also borne out by the plot of the average values of the Br/Cl ratio for each stage (Figure 9). These particular results have been checked very carefully to determine whether or not the Br/Cl trends could be explained by some systematic error such as improper blank values. It is certain that these results could not be due to such factors and that these trends are real. The majority of the individual values of the Br/Cl ratio on the particles are below the sea water ratio, which agrees with results found previously (Duce *et al.*, 1963; Duce *et al.*, 1965) when sampling sea-water nuclei over the sea from an aircraft. However, Duce *et al.*, (1965) found at sampling locations in the surf zone or on the ground at various distances inland that all particulate samples showed Br/Cl ratios equal to or above that of sea water. Thus the effect of the land or the surf on the relative composition of Br and Cl in the particles is quite significant.

The I/Br ratio also shows regular trends with changing particle size, beginning with very low values on the largest particles, reaching a maximum on stage E ($r = 0.62\ \mu$), and then dropping off on stage F.

Discussion

It is of interest to speculate on how these results correlate with the two predominant theories which attempt to explain the high iodine concentration in the marine atmosphere. As pointed out by Duce *et al.* (1965), if a vapor phase of I_2 were present in the atmosphere and it diffused to the surface of the particles, the overall effect of the addition of I_2 to the chemical composition of the particles would be in-

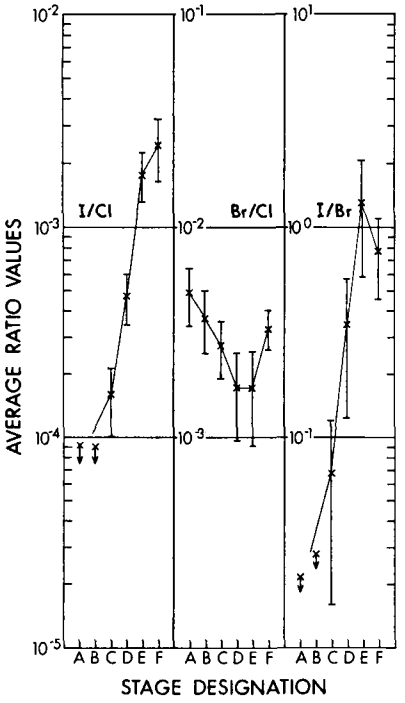


Fig. 9. Average ratio values for all samples in the same size range (i.e. all stages A, all stages B, etc.).

versely proportional to the radius of the particle, since it is a surface effect. Thus the smaller particles would have the greater I/Cl ratios, as is found experimentally in this investigation. If we ignore the particles collected on stage A (since it is impossible to determine an "average" radius for them) and consider only those on stages B through F, we can see from Figure 2 that the radii of particles on stage B are 16 times greater than the radii of particles on stage F. Thus if I_2 diffusion were the primary source of I on the sea–salt nuclei, particles on stage F should have an I/Cl ratio approximately 16 times greater than that for particles on stage B. In Figure 9 we can see from the average values of the I/Cl ratio for all eight sets of samples that the actual increase is approximately a factor of 20 or greater. Thus, while the actual ratio increase appears to be somewhat greater than expected if only I_2 adsorption is occurring, the agreement is reasonably satisfactory.

There is also evidence, however, that a similar sort of particle-size dependence could occur for the proposed surface-active film mechanism. Baylor, Sutcliffe & Hirschfeld (1962) show evidence that dissolved surface-active compounds are adsorbed on the skin of bubbles beneath the sea surface. Those bubbles which dissolve before reaching the sea surface leave behind colloidal micelles of organic material. Bubbles that do not dissolve will burst and spread part of the bubble skin as a monomolecular film on the sea surface.

Blanchard (1963) showed in laboratory studies that jet drops from bursting bubbles carry off surface-active materials from a liquid surface only if the bubble which produces the jet drops has a diameter greater than 1.0 to 1.4 mm. If this laboratory information can be extended to the open sea, where the majority of the bubbles have a diameter of less than 1.0 mm, it would appear that jet drops would not carry a significant amount of the surface-active material which is present on the sea surface itself. However, as mentioned above, bubbles themselves would be expected to pick up surface-active material on their skin as they pass through bulk sea water on their way to the sea surface. It is possible that part of this bubble skin is carried off with the jet drops.

Another source of particles when a bubble bursts at a liquid surface is the shattering bubble skin itself. Blanchard (1963) has pointed out that a large number of these skin or film droplets are produced when an individual bubble breaks at a clean water surface, but that no film droplets are observed when a single bubble bursts at an organically contaminated water surface. Blanchard also pointed out, however, that when bubble clusters break at an organically contaminated water surface, film droplets are observed, and he concluded that "the bubble clusters that form in the first few seconds after a wave breaks at sea might produce film nuclei independent of the effects of organic surface films, while the film nuclei of the more numerous bubbles that subsequently rise and break at the surface may be very much a function of the presence or absence of this contamination". Since any bubble or bubble cluster must break through any surface active film already present on the sea surface before it can burst, it is obvious that the bubble skin and the surface-active film already present on the sea surface become closely interrelated. It would thus be very reasonable to assume that when the bubble bursts the film drop particles will contain material from the sea surface film as well as

from the bubble skin. MacIntyre (1965) has shown laboratory evidence that inorganic phosphate, which presumably becomes attached to dissolved surface-active molecules, is enriched in film droplets, and that the enrichment is dependent upon particle size. Sea water as well as various surface-active materials in distilled water were used. Particle-size dependence of the fractionation was observed in every case, although the maximum enrichment shifted to different particle sizes as the surface-active material was changed. While it would be difficult to extrapolate these laboratory experiments concerning PO_4^{---} enrichment to the problem of iodine enrichment on the open sea, it is at least apparent that there can be particle-size-dependent enrichment effects from the film drop production mechanism and that these effects may be contributing to the iodine enrichment. Thus, unfortunately, we can only say that both the free iodine and organic film mechanisms still appear as valid possibilities, and indeed both may be occurring.

It is also of interest to examine the variation of the Br/Cl ratio with particle size. The results in Figure 7 and 9 may indicate two different types of particles containing Br in the marine atmosphere. This was also suggested by Duce *et al.* (1966) in an investigation of atmospheric particles at Pt. Barrow, Alaska, during the winter of 1964–65. In the present work the general decrease in the Br/Cl ratio with decreasing particle size could be explained by a selective loss of Br either by direct volatilization (e.g., as HBr) or by oxidation and subsequent volatilization (e.g., as Br_2 from O_3 oxidation). The loss of Br could be interpreted as either a strictly time-dependent effect or an effect of the size of the particles themselves. The former interpretation is based on the fact that the average residence time in the atmosphere is less for large than for small particles, so the process of Br loss would not have been occurring as long on the large as on the small particles. This interpretation implicitly assumes that the attainment of bromine equilibrium between the particulate and gas phase is a slow process—an assumption that may not be valid. The latter interpretation would suggest that the rate of loss of Br per unit volume of particle would be greater on the smaller particles due to their larger surface areas.

Apparently at particle sizes of approximately $r = 1\ \mu$, where the decreasing Br/Cl ratio starts leveling off, a second type of particle becomes significant for Br. The rise in the Br/Cl ratio on particles particles with radii $< 1\ \mu$ indicates that this second type of particle apparently becomes the predominant source of Br in the smaller size ranges. This information would suggest that either this high-bromine-content particle has a source other than the sea or that for some reason the bromine on these smaller particles is chemically different (perhaps organically bound as suggested concerning the iodine) from that on the larger particles. A combination of these two explanations is also possible.

Conclusions

The most obvious conclusion to be drawn from this investigation is that a regular variation of the I/Cl ratio with changing particle size definitely exists. These ratio changes are so large that they may prove useful in studying processes of droplet coalescence in rain formation. Since raindrops are thought to form on the sea-salt particles, a study of the variation of the I/Cl ratio on raindrops of various sizes could give valuable information concerning the raindrop formation mechanisms. A raindrop spectrometer has been constructed which will separate and collect raindrops according to their size, and an investigation of the chemical composition of these raindrops is underway.

Differences in the I/Cl ratio may also enable us to trace temporal, geographical, and other changes in the microphysics of droplet formation in the air-sea boundary layer.

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ВАРИАЦИИ В ОТНОШЕНИЯХ СОДЕРЖАНИЙ ИОНОВ ПО РАЗМЕРАМ СРЕДИ ЧАСТИЦ ТРОПИЧЕСКОГО ВОЗДУХА НАД ОКЕАНОМ

В течение лета 1966 года провидился сбор частиц морской соли разных размеров в атмосфере над морем с помощью шестиступенчатого каскадного приемника, смонтированного на вышке высотой 14 м, расположенной на подветренном берегу вблизи Хило на Гавайях. Размеры собираемых частиц изменялись от всех частиц с единичной плотностью с радиусом более 10 микрон на первом каскаде до всех частиц с радиусом, примерно, в 0,3 микрона на шестом каскаде. Использование вышки гарантировало то, что приемником не собирались водяные брызги местного прибоя в то время, когда направление пассатов было с моря на берег. На восьми сериях отборов проб был проведен нейтронно-активационный анализ на содержание йода, хлора и брома. Отношение I/Cl показывает регулярное увеличение с коэффициентом от 50 до 100 при переходе от больших частиц к меньшим. Для самых малых частиц это отношение примерно в 1000 раз больше, чем в морской воде. Отношение Br/Cl имеет минимум для частиц промежуточных размеров, причем большая часть значений этого отношения ниже соответствующего значения для морской воды. Основная масса йода найдена у частиц с радиусом примерно 0,6 микрон, тогда как главная часть хлора и брома обнаружена на частицах с радиусом в интервале 1,25 + 2,5 микрон.

Эти сведения дают возможный метод прослеживания роли ядер морской соли для изучения процессов выпадения осадков и могут быть использованы с целью добиться лучшего понимания цикла обмена галогенами между атмосферой и морем.