

Variation of Sodium and Chloride Concentrations with Rainfall Intensity in Hawaiian Trade Wind Showers¹

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ABSTRACT: The variation of sodium and chloride concentrations with rainfall intensity in Hawaii was investigated in 13 trade wind showers. The variation was found to be inversely dependent on rainfall intensity, although the ratio of Na to Cl appeared to be independent of the intensity. Several factors which may affect the dependence of concentration on rainfall intensity are discussed, and it is concluded that: (1) washout and evaporation, more than any process which may occur within the cloud, are the dominant factors in increasing the salinity of the small raindrops collected below the cloud base, and (2) exchange of gaseous and dissolved chlorine is a minor factor affecting the variation of chloride concentration with rainfall intensity.

IT IS WELL ESTABLISHED that the concentration of various soluble substances in rain depends upon total rainfall amount.³ In general, concentration of such species as NO_3^- , SO_4^{2-} , Na^+ , and Cl^- , and radioactivity, etc., decrease with increasing amount of rainfall, both for widespread rain systems and for thundershowers. An extensive review of the dependence of concentration on rainfall amount is given by Junge (1963).

Woodcock and Blanchard (1955) have shown that an inverse dependence of chlorine concentration in rain on rainfall intensity occurs in Hawaiian trade wind showers. This relationship was corroborated for sodium (and from this, for total salt) by Eriksson (1957) and Georgii and Weber (1961), and for total dissolved nitrogen (ammonia and nitrate) by Mordy (1953). In none of these investigations

was an attempt made to collect numerous samples in a short time period so that the detailed variations which possibly occur in the chemical composition with rainfall intensity could be investigated within an individual rain shower. In fact, very few studies of this sort have ever been attempted, and in those only one or two showers were examined with generally a maximum of 5 or 6 samples collected in each shower (Gorham, 1958; Turner, 1955). Perhaps the most detailed study of the dependence of concentration on rainfall intensity was that of Gatz and Dingle (1966), who investigated the variation of radioactivity and pollen in the rain associated with two squall lines in Oklahoma.

The purpose of our study was to investigate in detail the variation of the sodium and chloride concentrations with rainfall intensity in Hawaiian trade wind showers in order to evaluate some of the major factors which influence these concentration variations. In addition, it was hoped, by studying changes in the Na/Cl ratio with varying rainfall intensity, that information could be obtained on the exchange of gaseous chlorine with dissolved chloride in the rain.

METHODS

Thirteen trade wind showers were sampled at various locations on the islands of Oahu and Hawaii. As many as 28 samples were collected

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³ There is confusion in the literature concerning the meaning of "amount" and "intensity" when applied to rainfall. In general, "amount" has referred to the volume of rain collected, with no reference to the length of the collection period, whereas "intensity" has referred to the amount collected per unit time. These terms have been erroneously used interchangeably on many occasions. There is no necessary relation between rainfall "amount" and rainfall "intensity" as defined above.

from an individual shower as it passed over a sampling site. The samples were collected in a conical stainless steel collector, with a base diameter of 80 cm, equipped with wiper blades which could be moved over the steel surface to assure complete drainage after each sample was collected. A wooden cover (120 cm \times 120 cm) prevented any rain from falling into the funnel between sample collections. Shortly before each shower began, the collector was thoroughly cleaned with distilled water. Rain intensities were calculated by measuring the volume of the rain collected in known time intervals.

The samples were analyzed for chloride using a modification of the photometric method of Zall et al. (1956), and for sodium by flame photometry. Details of the collection and analytical procedures are given by Seto (1967).

RESULTS

Figures 1 through 7 show the variation of the sodium and chloride concentration and that of the Na/Cl ratio with rainfall intensity at various times in 7 representative showers of the 13 investigated. Analytical uncertainties are generally less than 5 percent for the Na and Cl analyses. The Na/Cl ratio in sea water is also indicated on these figures. Figures 1 through 5 represent collections well below the cloud base of the showers, and Figures 6 and 7 represent collections within the rain cloud. All concentrations and ratios are reported for the midpoint of the sampling interval. Approximately 15 to 30 seconds elapsed between the end of one sampling interval and the start of the next.

The data on Figures 1 and 2 appear to be representative of single-cell showers which passed over the sampling site. Both showers were at or near sea level, one on Oahu and one on Hawaii. In both cases, the concentrations were quite high around the perimeter of the shower, where the rainfall intensity was low, but dropped off very rapidly as the intensity increased near the center of the shower. As the intensity decreased toward the trailing edge of the shower, the concentration increased again, although it did not return to its initial value.

Figures 3 and 4 also represent showers sampled near sea level. In both cases, the shower had two apparent cells which caused fairly

large intensity changes as the shower passed over the sampling site. It can be seen that the inverse relationship between the Na and Cl concentration and rainfall intensity holds even when a decrease in intensity occurs in regions not near the edge of the shower. Figure 5 represents a shower with quite erratic rain intensities; again, the inverse dependence of concentration on rainfall intensity can be seen.

Figures 6 and 7 represent two sets of samples collected in cloud at approximately 800 meters elevation on Hawaii. The long rainfall duration (40 to 50 minutes) for these two sets of samples indicates that several individual showers were probably being sampled. On both sample collection days, the upper-level soundings for Hilo show large direction and speed shear in the wind field with increasing altitude. Blanchard (1957) has pointed out that wind shear such as this can cause the various size raindrops to be spread out not only in the direction of motion of the shower but also at right angles to that direction, with the smallest drops being deflected the most. It is thus possible that a sampling site on the ground would collect rain from several different showers simultaneously due to overlapping of different raindrop size distributions. Even though there may have been simultaneous collections from several showers, however, the inverse dependence of sodium and chloride concentration on rainfall intensity is still apparent.

It should be noted that there is no regular variation in the Na/Cl ratio in any of these seven showers; the ratio is generally quite close to that of sea water (0.56).

Woodcock and Blanchard (1955) have shown that there is a direct relationship between rainfall intensity and raindrop size in Hawaiian trade wind showers, the higher intensities being associated with the larger drops. In subsequent discussions in this paper, we will assume that the highest intensity portions of a shower have the largest raindrops and the lowest intensity portions, the smallest raindrops.

DISCUSSION AND CONCLUSIONS

Woodcock (1952) suggested that the presence of salt in rain from trade wind showers results from the formation of individual rain-

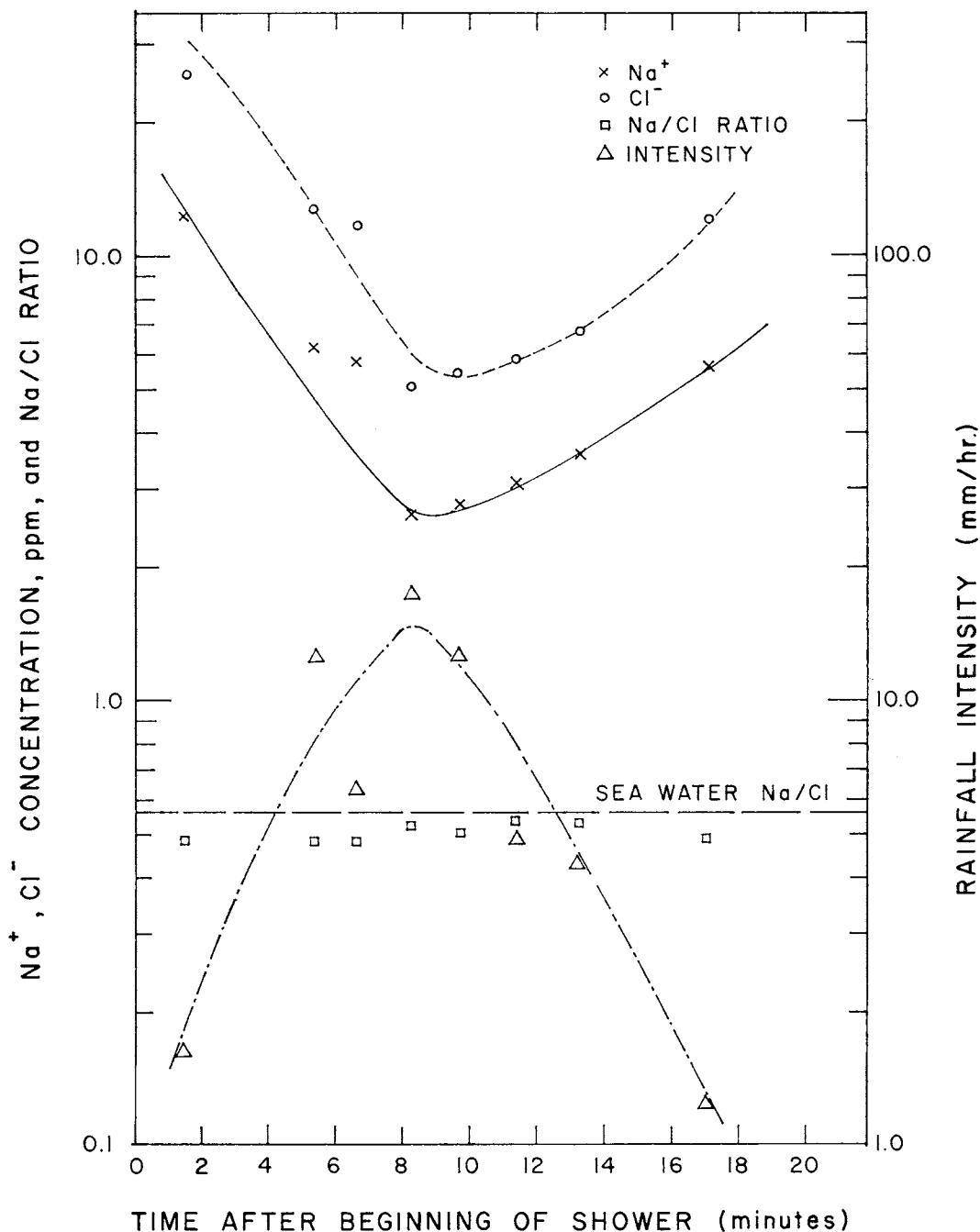


FIG. 1. Data from rain shower collected June 24, 1967 below cloud at Hilo, Hawaii. Elevation 80 meters.

drops on individual salt particles of different sizes present in the marine atmosphere. In the presence of the high relative humidity in a developing cumulus, the salt nuclei would grow

initially due to condensation of water vapor on their surfaces. As the growing saline droplets became larger, they would begin to fall, relative to the cloud droplets, and subsequent

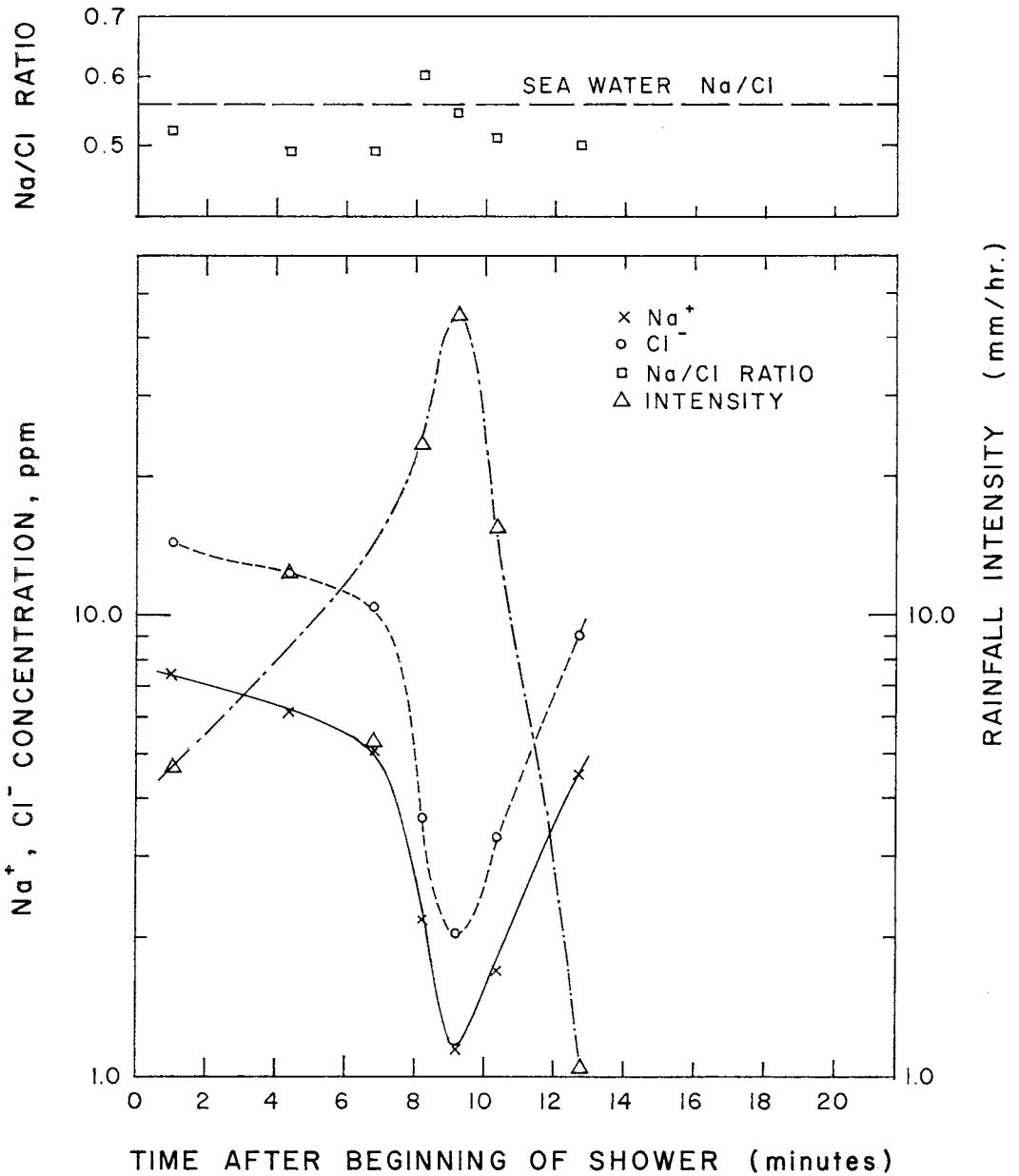


FIG. 2. Data from rain shower collected March 31, 1967 below cloud on the windward side of Oahu at sea level.

growth would be due largely to droplet coalescence until they fell from the cloud as raindrops.

At least five factors must be considered in attempting to explain the variation of the concentration of soluble sea salt in rain with rainfall

intensity: (a) raindrop-cloud drop coalescence, (b) raindrop-raindrop coalescence, (c) washout, (d) evaporation, and (e) incorporation of trace gases in raindrops and cloud drops. Raindrop-cloud drop and raindrop-raindrop coalescence processes in rain showers are extremely com-

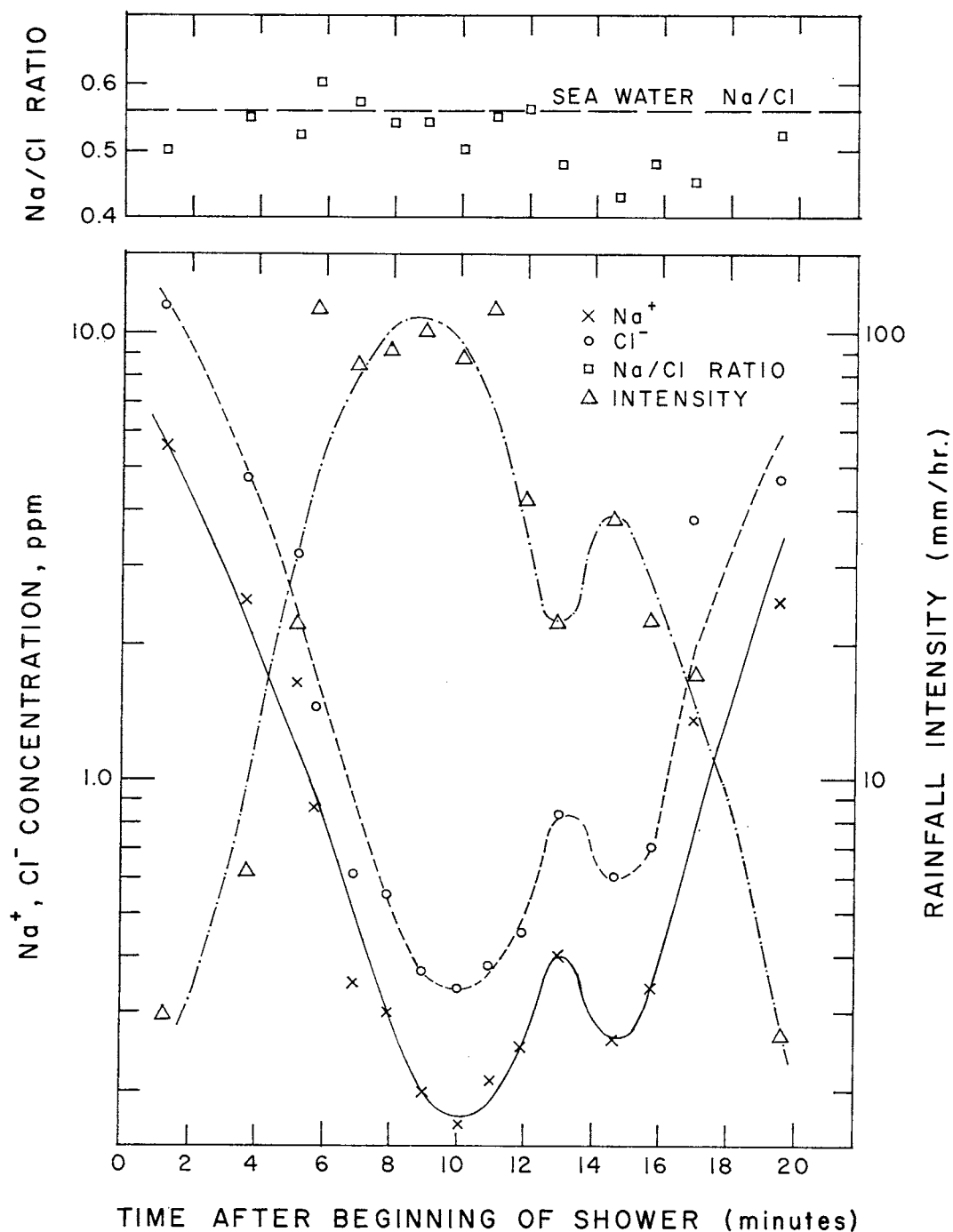


FIG. 3. Data from rain shower collected July 7, 1967 below cloud at Hilo, Hawaii. Elevation 80 meters.

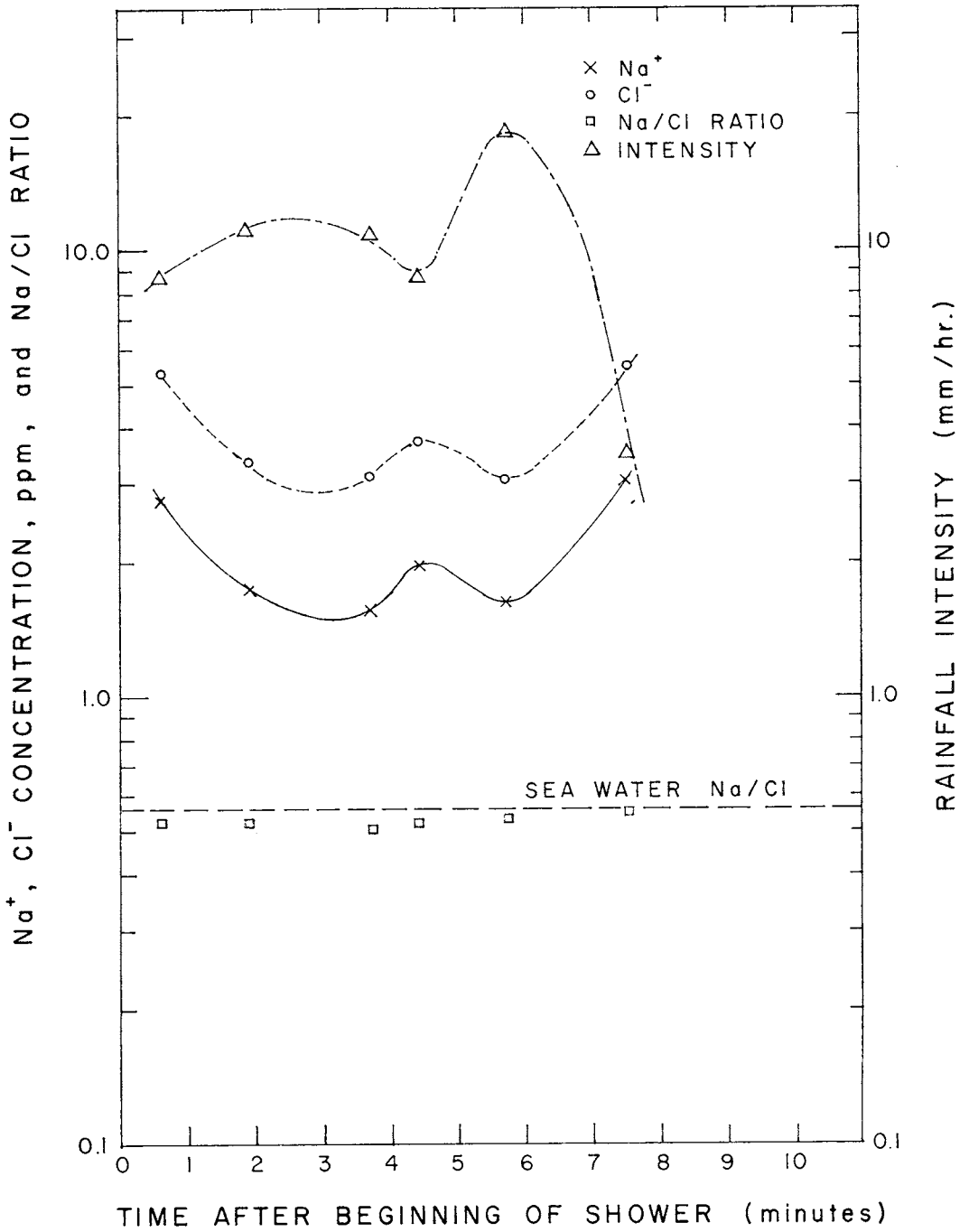


FIG. 4. Data from rain shower collected July 3, 1967 below cloud at Hilo, Hawaii. Elevation 20 meters.

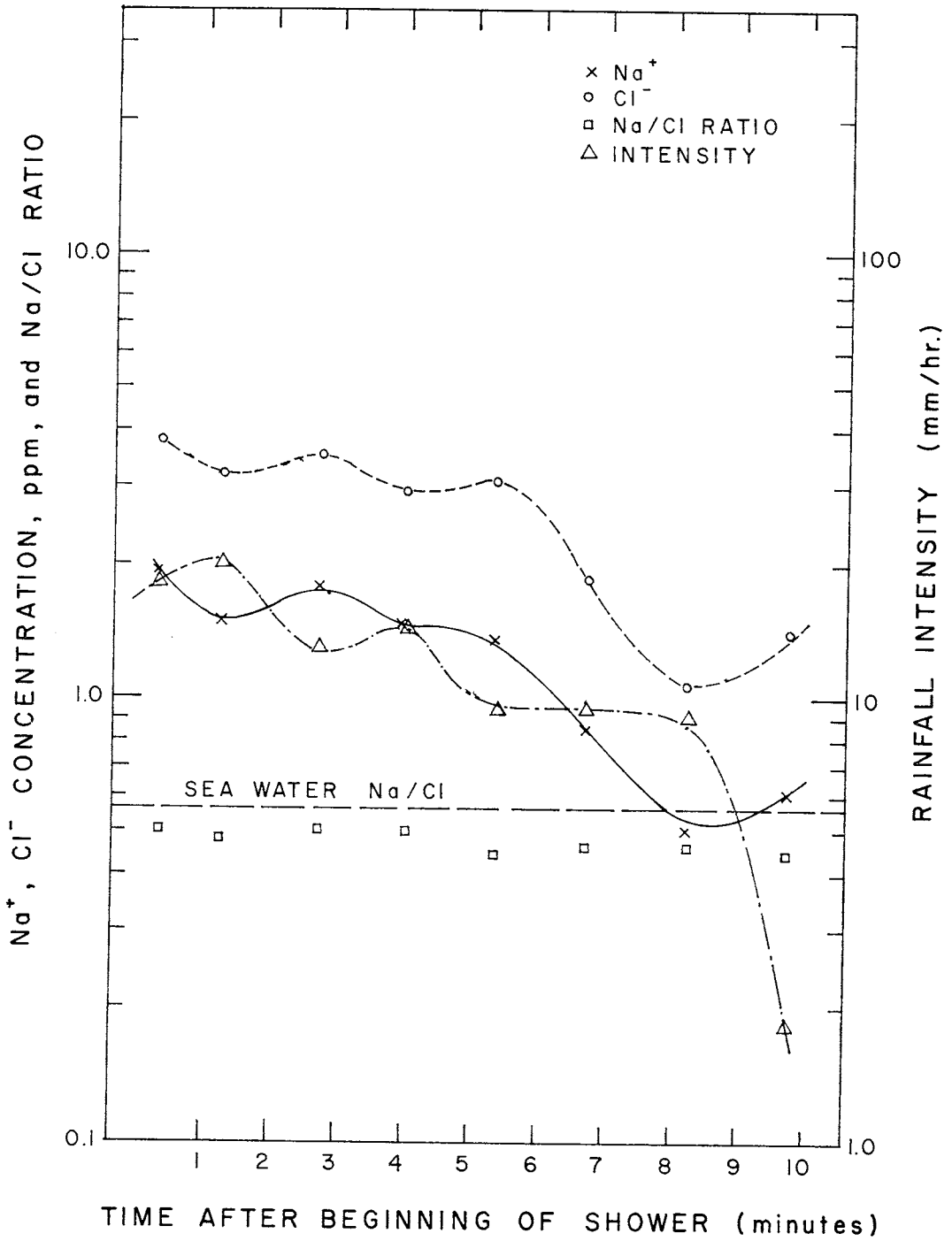


FIG. 5. Data from rain shower collected June 26, 1967 below cloud at Hilo, Hawaii. Elevation 100 meters.

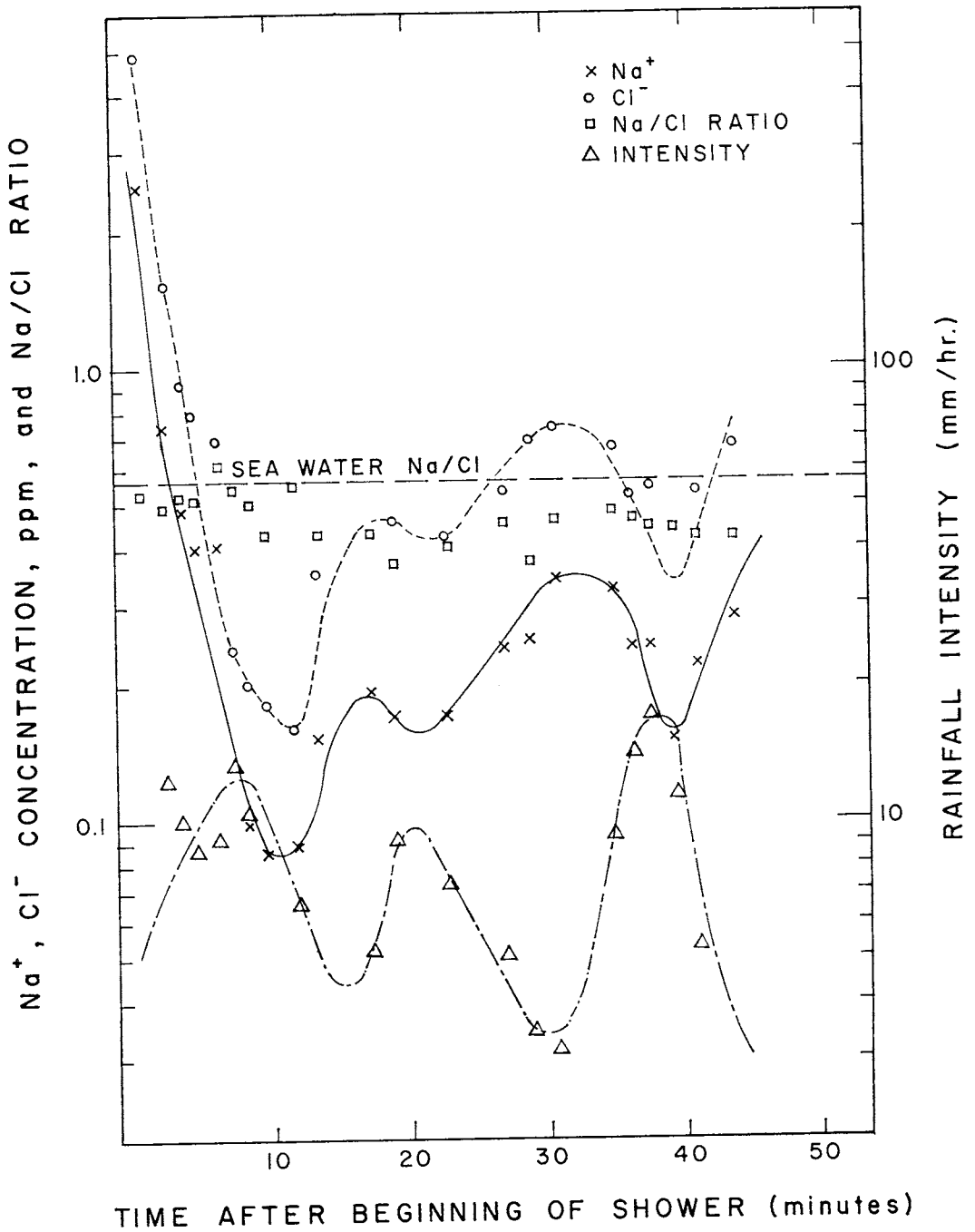


FIG. 6. Data from rain shower collected June 27, 1967 in cloud on the Saddle Road, Hawaii. Elevation 850 meters.

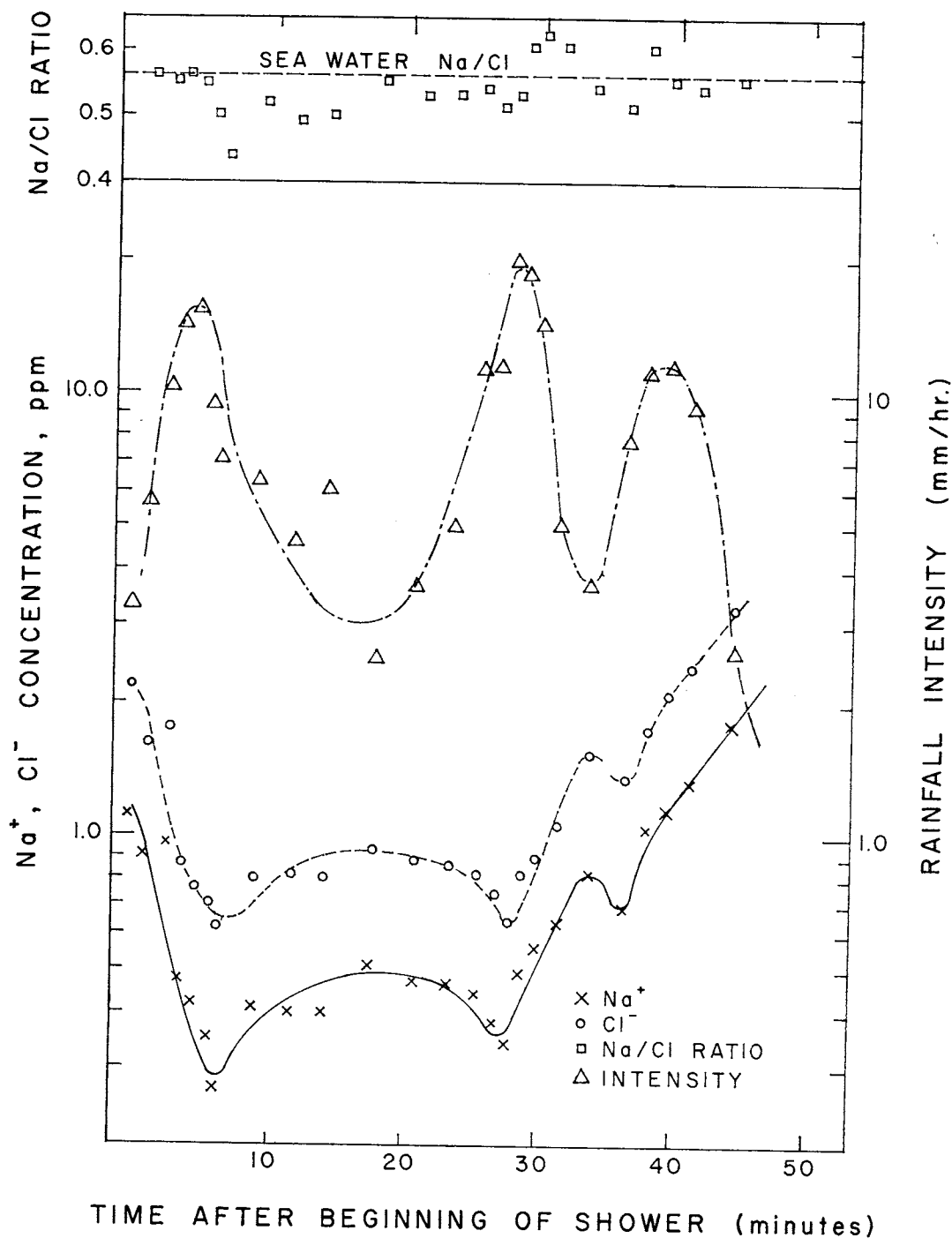


FIG. 7. Data from rain shower collected June 30, 1967 in cloud on the Saddle Road, Hawaii. Elevation 850 meters.

plex, and the detailed growth mechanism of raindrops by coalescence is poorly understood. Prediction of the dependence of sea-salt concentration on raindrop size due to coalescence processes must therefore await more reliable models of rain shower formation. The other three factors affecting the variation of soluble sea-salt concentration with rainfall intensity will be considered separately.

Washout of Salt Particles Below the Cloud

As the rain falls below the base of the cloud it may pick up particulate matter suspended in the air before striking the ground. The mass of sea salt collected by a raindrop falling through air containing sea-salt particles will depend upon the volume of air swept out by the falling drop. This volume is proportional to the cross-sectional area, or r^2 , of the raindrop, where r is the radius of the raindrop. This is only an approximation since one must also consider the collection efficiency, E , of the various size raindrops for salt particles. If we assume that the shape of salt particles suspended in the air is spherical, the collection efficiency, E , for a $10\text{-}\mu$ radius salt particle will vary from 0.66 for a 0.10-mm radius raindrop to 0.89 for a 1.0-mm radius raindrop (Langmuir, 1948). However, this correction is generally small compared with the cross-sectional area change, and the assumption that the collection of particles is dependent upon r^2 of the raindrop is satisfactory for present considerations. Since the concentration of a given amount of dissolved salt in the raindrop is inversely proportional to the volume of the raindrop, or $1/r^3$, the net salinity change for raindrops falling through sea-salt particles suspended in the air will be proportional to $1/r$. Thus the larger raindrops associated with the higher intensity rains should have the lowest salinities, due to washout.

Another factor to be considered at this point is the relative movement of the shower with respect to the surface air. If a shower is moving more rapidly than the air at the land surface, the leading edge of the shower will be raining through air which is "unwashed." Hence, the light rain on the leading edge of the shower will fall through such "unwashed" air and, after picking up salt particles, will contain higher

concentrations of Na and Cl. Subsequent portions of the shower passing over the collection site will then fall through much cleaner air, washout will be less, and the concentrations will be lower. When this sort of situation prevails, the concentrations in the trailing edge of the shower as it passes over the collection site will not be as high as they were in the leading edge, even if the shower intensities are the same. This appears to be the case for most of the below-cloud showers investigated here, since almost all had higher salinities on the leading edge than on the trailing edge of the shower.

Evaporation

This factor is of primary importance for samples collected below cloud base, but can also sometimes be important for samples collected near cloud base or even in cloud, especially near the perimeter of a shower. For droplets greater than 0.1μ radius, the amount of evaporation will be proportional to the surface area of the drop, and therefore to r^2 . Concentration will again be inversely proportional to the volume of the drop, or $1/r^3$ and, thus, concentration changes caused by evaporation will be proportional to $1/r$. The smaller the raindrop radius the greater the effect of evaporation on raindrop concentration; that is, the smaller raindrops (characteristic of low intensity rains) will be the most concentrated by this mechanism.

We separated the 13 showers sampled into two groups—those (4) collected within cloud or very near cloud base ("in cloud") and those (9) near sea level, approximately 600 meters below cloud base ("below cloud")—and made plots of rainfall intensity versus chlorine concentration for all samples collected in the two groups (Fig. 8). It is apparent from Figure 8 that the average concentration of "below-cloud" rains is approximately 10 times that of "in-cloud" rains.

Straight lines have been fitted to the in-cloud and below-cloud samples by the method of least squares; they are shown in Figure 8. There appears to be very little dependence of salinity on rainfall intensity for the in-cloud samples. In fact, the tendency, if any, is for higher rainfall rate to be associated with higher rainfall salinity. As was seen previously, this is just the

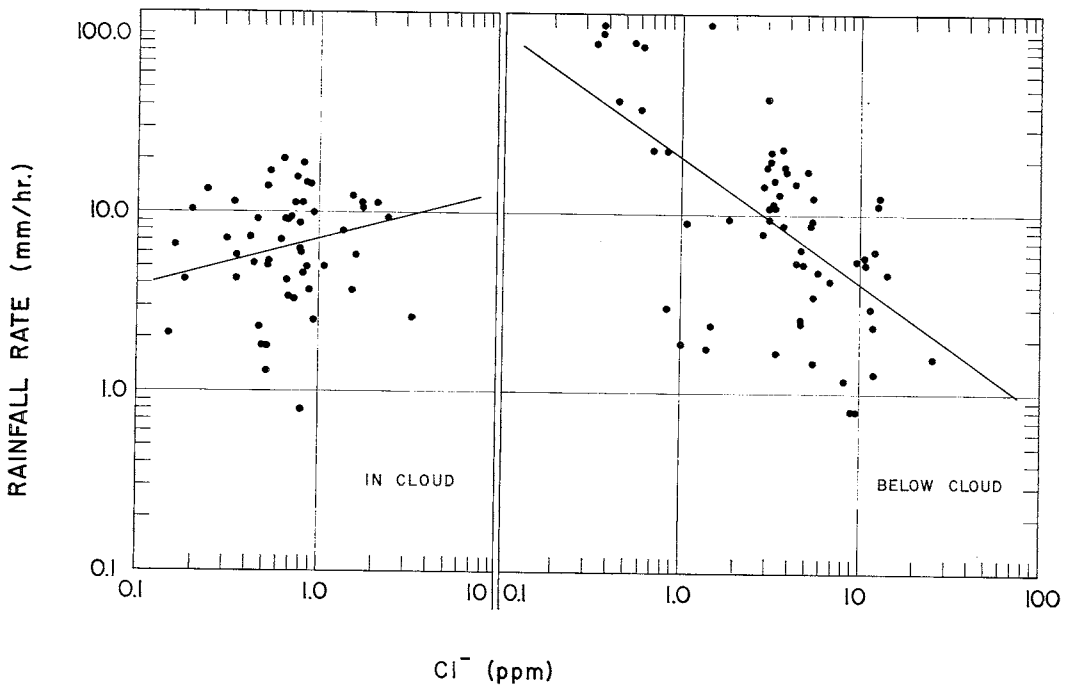


FIG. 8. Chloride concentration vs. rainfall intensity for all samples collected in cloud and below cloud on Oahu and Hawaii.

opposite of the situation observed for the individual showers. This is not too surprising, however, since in many cases the relative concentration changes with varying rainfall intensity in in-cloud samples collected in an individual rain shower were rather small. However, the concentration of salt in rain showers collected at different locations and at different times may vary a great deal and are dependent on wind force, the number of salt nuclei and their size distribution, and the drop sizes which are developed in a shower, all of which vary considerably from day to day. This illustrates clearly the danger of drawing generalizations from plots of rainfall rate versus concentration for a number of different rainfall situations unless individual shower data are also available.

The below-cloud samples show a rather clear-cut inverse dependence of salinity on rainfall rate, although this is partly due to very high intensity rains (above 30 mm/hr) which are rarely observed in in-cloud samples and were not observed in any samples collected in cloud in this investigation. The inverse dependence of salinity on rainfall rate for all the below-

cloud samples agrees with the results given previously for the individual showers. In these cases, the changes of salinity with changing rainfall intensity in individual showers are so great that the effect is also observed when all the shower data are combined.

Since the concentration changes with varying rainfall intensity are considerably greater for below-cloud than for in-cloud samples, it is apparent that the mechanisms of washout and evaporation, both effective primarily below cloud, are more important in increasing the salinity of the small raindrops collected about 600 meters below cloud base than any processes occurring within the cloud.

Incorporation of Trace Gases in Cloud Droplets and Raindrops

For elements which have volatile species possible at ambient temperatures and pressures, the incorporation of the gaseous species in the water droplets (or escape of the gaseous species from the droplets) can be a significant factor in the chemical composition of the droplet. Assuming that the dissolved species is not

initially in equilibrium with the gas phase and the attainment of equilibrium is neither extremely slow nor extremely fast, the concentration of the dissolved species in solution may vary for different droplet sizes. If the rate of attainment of equilibrium is more rapid than the growth rate of the raindrops in cloud, no difference would result in the chemical composition of different drop sizes. However, if the rate of equilibrium attainment is somewhat slower than the droplet growth rate, the larger drops will require longer equilibration times, after the drops cease growing, because of their smaller surface area to volume ratio. In the latter case, if there were not time for complete equilibration of all drop sizes before sample collection on the ground, and if equilibrium between the gaseous and aqueous phases of a chemical species involved a net absorption of the gas phase into the droplets, the concentration of the dissolved species would be greater in the smaller droplets. If, however, the attainment of equilibrium meant a net loss of the species from the droplet, the concentration of the dissolved species would be less in the smaller droplets.

Since there apparently is considerable gaseous chlorine ($0.1\text{--}10\ \mu\text{g}/\text{m}^3$) of undetermined chemical species in the marine atmosphere (Junge, 1957; Duce et al., 1965) this gaseous phase could be a significant factor in affecting the concentration of chlorine in the rain at various rainfall intensities. The Na/Cl ratios in the showers reported here do not appear to vary with intensity and have essentially the same value as that for sea water, indicating that the attainment of equilibrium of gaseous with dissolved chlorine is either very fast or very slow. Duce (1969) has shown that if the gaseous chlorine is HCl, which seems most likely, it is not in equilibrium with chloride concentrations commonly found in Hawaiian rains, indicating that the rate of equilibrium attainment is apparently very slow. Seto et al. (1969) have also shown that the Na/Cl ratio is independent of altitude and distance from the sea in Hawaiian rains. Thus the exchange of gaseous and dissolved chlorine is probably a minor factor affecting the variation of chloride concentration with rainfall intensity in Hawaiian trade wind showers.

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