Chemical Analysis of Aerosol Particles and of Gas Traces on the Island of Hawaii

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Abstract

Aerosols of two different size ranges with radii between $0.08 < r < 0.8\,\mu$ (large particles) and $0.8 < r < 8\,\mu$ (giant particles) were analyzed for NH_4^+, Cl^-, SO_4^{--} and NO_3^-. Parallel with this, the concentration of corresponding gas traces, that is of NH_3, chlorine components, SO_2 and nitrogen dioxide was measured.

The results show that the *giant* particles consisted almost entirely of sea spray. Their content of NO_3^- was small compared to the data from the East Coast of the United States (Round Hill, Massachusetts and Homestead, Florida).

The Cl^- content of the *large* particles was less than 1.5 % of that of the giant particles, confirming previous data which showed that the sea spray is almost completely restricted to particles larger than $0.8\,\mu$ radius. The large particles contained NH_4 in amounts comparable with the other components, indicating the presence of other than sea spray nuclei in this size range. The NH_4 is probably present in the form of $(NH_4)_2SO_4$.

Both particle sizes were completely missing in the raining orographic clouds.

All *gas components* were found to be present and the concentrations did not fluctuate very much. They were washed out, to a small degree, if at all, by rain.

1. Introduction

A previous paper (Junge 1954) gives results on the chemical composition of natural aerosols which were obtained in the coastal region between Boston and New York. Air masses of this area, even with onshore winds are almost always subject to continental influences such as industry and densely populated areas. In order to find out what substances are due to this continental influence, a location had to be selected where this influence is negligible. Measurements were, therefore, made in connection with Project "Shower" on the Island of Hawaii during October and November 1954. Here on the east coast in the onshore winds, the influence of any continents should have been reduced to a minimum. Furthermore, the high mountains of this island presented the opportunity for measurements at different altitudes with respect to the cloud level.

Besides the chemical composition of the nuclei, certain gas traces were measured. The results of previous research seemed to indicate the presence of gas traces in our atmosphere, in concentration comparable to those of the particulate matter. Departures from the ratio of Na^+ to Cl^- in rain water, e.g., necessitate some such assumption with respect to Cl. However, this question, which is of interest in cloud and fog chemistry, had never been tested by direct measurements.

Measurements of the gaseous components had been made previously only in studies of air pollution. The concentrations present in polluted air are greater by two or three orders

of magnitude, and conclusions from these data can hardly be drawn for uncontaminated natural conditions. In the chemistry of unpolluted air no attempt was made to separate gases and aerosols to the knowledge of the author. Almost always, the air was bubbled through an absorption solution, which retained both aerosols and gases, but with different efficiencies. Progress in this field could only be obtained by separating the gaseous components from the aerosols.

The following analytical program was therefore planned:

1. Aerosols: Separate collection and analysis of two size ranges, large particles with radii between 0.08 and 0.8 μ and giant particles with radii between 0.8 and 8 μ. Analysis for the ions Cl^-, SO_4^{--}, NO_3^- and NH_4^+.

2. Gas traces: Analysis for gaseous chlorine components, SO_2, nitrogen oxides and NH_3.

Similar measurements were performed in July—August 1954 on the east coast of Florida; the results of these measurements are discussed at another place (Junge 1956).

2. Methods

Aerosols. The method for sampling and analyzing aerosols is discussed in detail in (1). By further refinements of the spot tests and by greater personal experience, the limit of detection could be lowered for a number of components. The old (I) and new (II) limits in microgram γ are:

	Cl^-	SO_4^-	NH_4^+	NO_3^-
I	0.2	1.0	0.1	0.1
II	0.05	0.5	0.05	0.05

The limit of detection in terms of the *concentration* is obtained by dividing these figures by the volume of the air sampled. Since most of the samples were taken from two or more cubic meters of air, these concentration limits in γ/m^3 are still lower.

Gas traces.[1] The gas traces were collected by bubbling the air through an absorbent in a wash tube at a flow rate of 200—300 cm^3/sec. In order to obtain a concentration as high as possible, a special form of wash bottle was developed which contained only 25 ml of absorption solution, but worked with high efficiency. A cone of fritted glass was mounted at the end of the inside glass tube (Fig. 1) and was covered with the absorption solution. Several polyethylene baffles were attached to the glass tube to collect droplets and a final spray trap was fixed to the outlet. The evaporated water was replaced during the run from a storage bottle on the top of the apparatus at intervals of about half an hour. At the end of the run the solution was drained through the bottom stopcock.

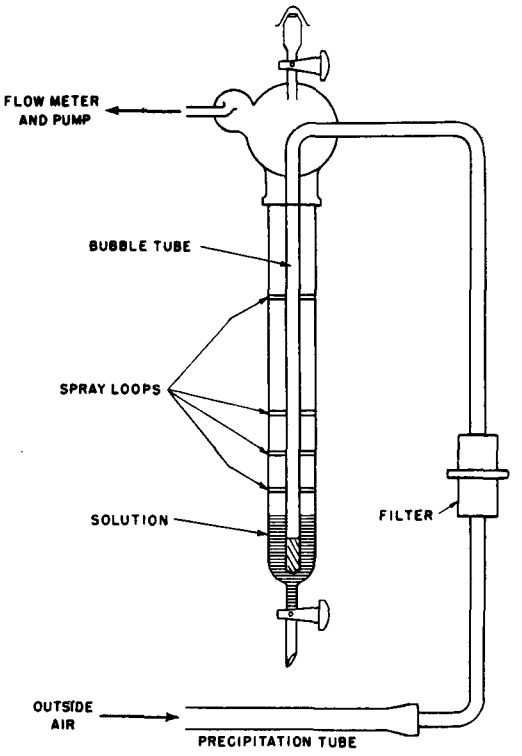

Fig. 1.

The loss by spray during a three-hour run was found to be only 3 percent of the absorbing reagent in the 25 cm^3 solution. Checks on the efficiency of the gas traps by using two traps in tandem showed that more than 90 percent of all the gases investigated were absorbed.

All aerosols were carefully removed from the air stream before entering the wash tube. At first the air passed through the same rectangular tube used with the impactors, in order to eliminate particles with radii larger than 8 μ. This was a protection against fog

[1] These methods were partly developed under Contract No. AF 19 (604)-1022 of the Air Force Cambridge Research Center by Dr. D. P. Norman, Skinner and Sherman, Inc.

droplets and other coarse contaminants of the air that may harm the subsequent millipore filter. These millipore filters have a very homogeneous pore size, low flow resistance, and a high collection efficiency. They were carefully checked for efficiency under field conditions, since the presence of gas traces could only be detected with certainty if no significant amount of aerosol material passed the filter. The following checks were made:

a. One of the impactors, which collects particles down to a radius of 0.08 μ was placed behind the millipore filter and run for two hours. The number of particles found on the plates of this impactor was smaller than that found on the plates of another impactor run at the *same* time for *one* minute *without* a millipore filter. The collection efficiency of the filter is thus greater than 99 percent for particles larger than 0.08 μ radius.

b. Particles below this size, i.e. Aitken nuclei, can be counted by the Aitken counter. Counts taken in the air stream before and after the filter indicated that less than 1.0 percent of the particles passed through the filter. With this figure the possible error in the gas analysis due to the particles that pass the filter can be estimated. For this estimation the chloride value will be used because this aerosol component predominated by far. If 1,000 Aitken nuclei per cm^3 (the number was even less in maritime air) with an average radius of 0.05 μ and consisting of dry NaCl are assumed, then the values of Table 1 are obtained. The figures show that the amount of aerosols that can pass the filter is negligible, compared to the amount of gas found in the bubble tubes. It must, therefore, be concluded that the chloride found in the absorption solution is a *gaseous* chlorine component of the air.

c. A further check was made with respect to chlorine. Two parallel runs were made with one bubble tube filled (as usual) with 25 cm^3 of 0.01 normal KOH and the other with 0.01 normal H_2SO_4 solution. If the chloride stems from particulate matter, both bubble tubes should show the same amount of chloride. But the tube with H_2SO_4 showed no chloride, as must be expected with a gaseous chlorine component.

This conclusion drawn for the Cl-component is even more valid for the other gas components, since the corresponding aerosol concentrations were even less and could in no way be the source of the quantity of substance trapped in the bubble tubes. A more serious problem was the absorption or adsorption of gas traces by the filter. Repeated checks under field conditions indicated that the filter trapped a portion of the gases. This effect decreased with continued use of the filter. New filters reduced the ammonium and the chloride value up to 50 percent, the sulfur-dioxide and the nitrogen-oxide components less. Since unnecessary filter changes were avoided, the actual values are most likely not more than 10 or 20 percent higher than the measured ones.

All the physical errors, loss of spray, incomplete gas absorption and filter retention cause a reduction in the measured gas concentration. But the measured values were not corrected, because the primary interest was in demonstrating the presence of these gas traces and the fact that their concentrations are of importance compared with those of the aerosols.

The analytical procedures for the gas traces were the following:

NH_3. Originally, Nessler's reagent was added to the 25 cm^3 0.01-normal H_2SO_4 absorption solution and the resultant color compared in a Leitz-Rouy photometer with those of standards prepared under the same conditions. The limit of detection was 0.5 γ. But after a few tests it was noticed that the

Table 1. Estimation of chloride passed through the filters and comparison with the chlorine gas component.

Observed concentrations of Cl^- in the size range of the large and giant particles with radii between 0.08 and 8 μ. Average of the Hawaii data from Table 2	5.05	γ/m^3
Maximum possible concentration of Cl^- represented in the Aitken particles with radius <0.1 μ	0.3	»
Total possible concentration of Cl^- in *aerosol*	5.35	»
Concentration of aerosols which can pass the filter (≤ 1 %)	0.05	»
Concentration of the chlorine gas component observed. Average of the Hawaii d ata from Table 2	1.92	»

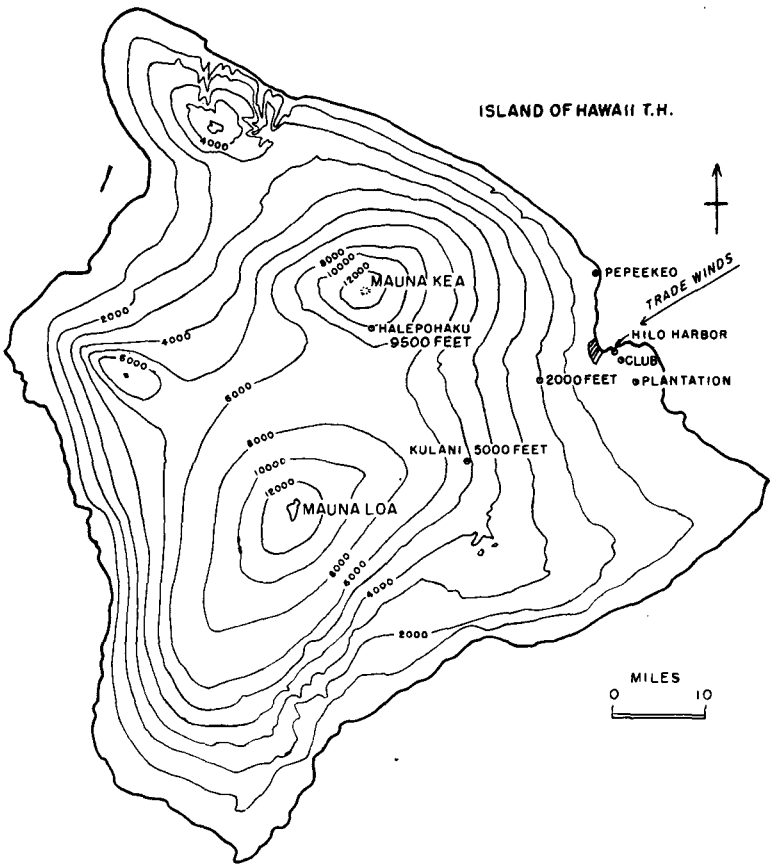

Fig. 2.

normally clear yellow developed by the Nessler reaction was turbid. To eliminate any interference of other components, the NH_4 sample was treated with alkali and distilled prior to adding Nessler's reagent.

SO_2. The 25 cm³ 0.01-KOH absorption solution was treated with fuchsin and formaldehyde. In the presence of SO_2 a purple color formed which was compared in the photometer with standards. The limit of detection was about 0.5 γ. For better comparison with the aerosols the SO_2 concentrations are converted to equivalent SO_4^{--} concentration throughout the paper.

Cl component. The 25 cm³ 0.01-KOH absorption solution was treated with $AgNO_3$ and the turbidity compared in Nessler tubes with standards prepared under the same condition. The limit of detection was 0.4 γ. This analysis yields amounts of Cl^- ions only. Since nothing is known about the chemical constitution of the clorine component, the degree of dissociation remains unknown too. The values of the gaseous chloride component presented here are, therefore, considered to be minimums.

Nitrogen oxides. The 25 cm³ 0.01 normal KOH solution was treated with sulfuric acid and a chloroform solution of brucin alkaloid. The yellow color produced in the presence of nitrate was compared in the photometer with standards. The limit of detection was 0.5 γ. It is assumed that the main constituent of the nitrogen oxides is NO_2, but no attempt was made to identify this component more precisely.

3. Results

Fig. 2 shows the sites of the sampling stations in Hawaii. In the normal northeasterly trade winds, an orographic cloud is formed below the inversion layer at about 6,000 feet on the eastern slopes of the two big volcanoes,

Table 2. Average values of the Hawaii coastal analyses. The figures in parentheses are the average limits of detection. All values in μ/m^3.

	NH_4^+			NO_3^-			Cl^-			SO_4^{--}		
	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas
Average values and average limits of detection	0.026 (0.021)	< 0.021 (0.021)	2.45 (0.3)	0.026 (0.022)	0.064 (0.022)	3.90 (0.3)	0.093 (0.038)	4.96 (0.038)	1.92 (0.3)	< 0.31 (0.31)	0.79 (0.31)	1.10 (0.3)
Number of values	14	14	14	14	14	14	10	10	14	10	10	14

Mauna Loa and Mauna Kea. These slopes are easily accessible by roads and ideal for the investigation of the chemical composition of aerosols and gas traces at different altitudes with respect to the inversion layer, and also for a study of the washout effects in and below raining clouds. An important part of the program was to obtain data at sea level in the trade winds under conditions which excluded all interference of land in order to compare them with our former results at other places, and to study the influence of land.

To cover this program in the time available, five groups of measurements were made which are discussed briefly below. The author is well aware that, especially with the measurements on the slopes of the mountains, the number of observations is too small to draw definite conclusions. But the little knowledge about the composition of aerosols and gas traces will certainly justify their publication.

a. Measurements at sea level in the trade winds, with particular exclusion of any land influence (Table 2).

The initial measurements were made in a lighthouse at Pepeekeo; however, the tremendous production of sea spray in the surf on the rocky beach made it impossible to get representative samples. After a few days the sampling station was moved to a Coast Guard station on the eastern shore of the harbor of Hilo, which was protected against the surf by a breakwater. However, smoke contamination from the harbor and the town occurred during calm and shifting winds as well as during rainy weather. Thus, a third location on a nut plantation was selected for the last few days.

With the exception of the Cl-content (sea spray) the fluctuations of the various components were relatively small. Therefore, only the average values are presented. They were obtained by excluding some data, which were obviously contaminated by local sources, such as heavy sea spray by the surf in Pepeekeo and smoke due to winds from the town. The number of values is, therefore, different for the different components in Table 2.

For a number of components the observed values were close to the limit of detection. For this reason, the average values in Table 2 were calculated in such a way that this limit of detection was used in those cases where nothing could be found above it. The average limit of detection was also calculated separately in the table. If the average value equals this average limit of detection, then this limit was not surpassed in any of the individual observations.

Table 2 shows the following results: The predominant component of the aerosols is Cl, found almost exclusively in the giant particles. The concentration of the other components is small or below the limit of detection. NH_4 is almost completely concentrated in the large particles and NO_3 in the giant ones. This is in good agreement with our findings on the coast of Massachusetts and Florida. However, the NH_4 and NO_3 concentrations in Hawaii are much lower, indicating their continental origin. The NH_4 content of the large particles is so small that it was impossible to detect the corresponding amount of SO_4 if the NH_4 were present as $(NH_4)_2SO_4$. The SO_4 concentration which would correspond to the NH_4 value of 0.026 is 0.070, which is far below the limit of detection of 0.31 γ/m^3.

The actual SO_4 content of the giant par-

Table 3. Comparison of the coastal values (harbor) and the values some miles down wind inland (club), Hawaii. Values in γ/m^3.

Date	Location	NH_4^+			NO_3^-			Cl^-	SO_4^{--}	Weather
		Large P.	Giant P.	Gas	Large P.	Giant P.	Gas	Gas	Gas	
Oct. 13	Harbor	0.017 lim.	< 0.017	3.26	<0.017	0.052±0.01	4.72	1.66	1.20	fair, cu, good
	Club	0.033 lim.	< 0.033	3.91	0.033 lim.	0.10 ±0.02	4.35	2.66	2.50	sea breeze
Oct. 14	Harbor	<0.020	< 0.020	2.22	<0.040	0.09 ±0.016	4.16	2.22	0.88	fair, cu, good
	Club	0.052±0.017	< 0.017	3.88	<0.034	0.12 ±0.017	4.00	3.88	2.90	sea breeze
Oct. 15	Harbor	<0.016	< 0.016	1.66	< 0.016	0.09 ±0.016	6.20	1.60	0.75	fair,cu,mostly
	Club	0.016 lim.	< 0.017	1.66	< 0.017	0.12 ±0.02	5.60	3.88	1.24	sea breeze

<0.017—means smaller than the actual limit of detection.
0.033 lim.—means value on or about the actual limit of detection.

Table 4. Comparison of the coastal values (harbor) and the value at 2,000 feet, Hawaii. Values in γ/m^3.

Date	Location	NH_4^+			NO_3^-		
		Large P.	Giant P.	Gas	Large P.	Giant P.	Gas
Oct. 19	Harbor	<0.017	<0.017	2.66	0.017 lim.	0.13±0.017	4.40
	2,000 feet	0.034 lim.	<0.034	2.11	<0.034	0.19±0.035	2.30
Oct. 20	Harbor	0.49±0.1	0.35 lim.	2.16	<0.017	0.28±0.05	3.88
	2,000 feet	<0.068	<0.068	1.90	no sample		2.66
Oct. 21	Harbor	0.55±0.14	0.07±0.035	2.23	0.017 lim.	0.45±0.1	4.10
	2,000 feet	0.17±0.035	<0.035	2.14	0.07±0.035	0.28±0.07	4.20
Oct. 24	Harbor	0.02 lim.	<0.020	2.04	<0.017	0.017 lim.	4.70
	2,000 feet	0.02 lim.	<0.020	1.15	<0.035	<0.035	3.60

Cl			SO_4			Weather	
Large P.	Giant P.	Gas	Large P.	Giant P.	Gas		
0.31+0.07	12.0±1.7	2.50	<0.35	1.2 ±0.27	0.60	Harbor:	mostly sea breeze
0.05	1.7±0.35	6.10	<0.35	0.34 lim	0.55	2,000 ft:	increasing cloudiness, rain with the gases
0.035	3.5±0.7	2.50	0.62±0.1	0.80±0.17	1.00	Harbor:	Few showers, mostly land wind, smoke!
0.035	0.27±0.1	2.20	no sample		< 0.5	2,000 ft:	Almost continuous rain, cloud base lightly above station
0.035	2.5±0.35	3.40	1.1 ±0.17	1.0±0.17	0.8	Harbor	Few showers, sometimes land wind, smoke!
0.035	0.35±0.2	4.40	0.28±0.14	<0.28	0.8	2,000 ft:	Almost continuous rain, cloud base above station
0.035	5.1 ±1.4	2.50	<0.17	0.7±0.17	1.4	Harbor:	mostly sea breeze
0.035 lim	3.1 ±0.7	5.90	<0.35	0.35 lim	2.0	2,000 ft:	fair weather

ticles must be between 0.79 and 0.79—0.31 = = 0.48 γ/m^3, corresponding to 16 percent and 10 percent of the Cl value. This is in good agreement with the value of 14 percent for sea water, indicating the maritime origin of the sulfate.

Table 5. Comparison of the coastal values (harbor and plantation) and the values at 5,000 feet, Hawaii. Values in γ/m^3.

Date	Location	NH_4			NO_3		
		Large P.	Giant P.	Gas	Large P.	Giant P.	Gas
Oct. 25	Harbor	<0.017	<0.017	1.44	<0.035	0.10±0.035	3.40
	5,000 feet	0.14±0.035	<0.035	1.55	<0.035	0.20±0.035	2.95
Oct. 26	Harbor	0.14±0.05	0.017 lim	1.30	<0.035	0.20±0.035	3.00
	5,000 feet	<0.035	<0.035	1.05	<0.035	<0.35	1.27
Oct. 27	Plantation	<0.017	<0.017	1.11	<0.017	0.05±0.01	3.88
	5,000 feet	0.035 lim	<0.035	2.30	<0.035	0.12±0.02	2.10
Oct. 28	Plantation	<0.017	<0.017	1.33	0.017 lim	0.07±0.017	2.77
	5,000 feet	<0.017	<0.017	2.17	<0.035	<0.035	1.55

Cl			SO_4			Weather
Large P.	Giant P.	Gas	Large P.	Giant P.	Gas	
0.20±0.05	7.0±1.0	1.95	<0.17	1.4±0.35	0.55	Harbor: Good sea breeze
0.035	1.0±0.2	3.61	<0.35	0.5±0.2	0.44	5,000 ft: Fair weather
0.035	2.8±0.5	2.77	0.5±0.14	0.5±0.14	0.66	Harbor: Showers, mostly sea breeze
0.035	<0.035	1.66	<0.35	<0.35	0.50	5,000 ft: In clouds, drizzle
0.035	2.8±0.35	1.0	<0.35	<0.35	< 0.25	Plantation: Good sea breeze
0.035	0.35±0.14	1.8	<0.35	<0.35	< 0.40	5,000 ft: Fair weather
0.035	4.8±0.7	2.22	<0.35	<0.35	< 0.50	Plantation: Few showers, mostly sea breeze
0.035	<0.14	2.60	< 0.35	<0.35	< 0.60	5,000 ft: In clouds, drizzle

In confirmation of our former results, the Cl-content of the large particles was very small and the sea spray almost completely confined to the giant particles.

The *gas traces* were much higher than the corresponding aerosol components, with the exception of the Cl. This is an interesting result, indicating that for the chemistry of the air and probably of the rain water too, the gaseous components are important in the Hawaii area.

The fluctuations of the gas traces from day to day were rather small and no correlation with weather phenomena could be detected.

b. Measurements at sea level on the coast and inland (Table 3).

In order to evaluate the influence of the land on the composition of the aerosols and gas traces in the trade wind-air, concurrent measurements were made during a few days in the harbor and at a site marked club (fig. 2) which is located on the windward side of Hilo in a sparsely populated area.

Table 3 shows a very slight increase of NH_4 in the large and of NO_3 in the giant particles, again confirming the land origin of these components.

The gas concentration of SO_2 and Cl increased markedly over land, that of NH_3 only slightly, while that of the nitrogen oxides stayed constant. This shows that the gases were sensitive to a short contact with the land and probably with human activity.

c. Measurements at 2,000 feet and sea level (Table 4).

A few measurements at 2,000 feet, parallel with such in Hilo were made to find out how the various components were influenced by falling rain. Unfortunately, the samples in Hilo Harbor on the 20th and 21st of October were contaminated by local sources.

Table 4 shows that the *aerosols* suffered a definite decrease of the Cl and SO_4 content

of the giant particles, which may be a little more pronounced on rainy days. The other aerosol components show no important changes.

The gas measurements showed an increase of Cl, especially during fair weather, while the other gaseous components do not differ very much with respect to the limits of accuracy.

d. Measurement at 5,000 feet and sea level (Table 5).

A few measurements at 5,000 feet, in the orographic clouds, were made to learn how condensation processes affect aerosols and gas traces. The prison camp Kulani is ideally located in the broad fern-tree woods which cover the entire slope of Mauna Loa. Under normal trade-wind circulation the air is not contaminated by any populated areas.

The results are quite interesting. The weather conditions were very favorable, two days fair with a few scattered clouds over land and sea, and two days with pronounced orographic rainfall with a maximum below 5,000 feet and Kulani in clouds with constant drizzle.

Table 5 shows that on the rainy days all components of the *aerosols* were below the limit of detection, and there was not the slightest visible precipitation on the impactor slides. The condensation process had removed almost completely all condensation nuclei. This was also confirmed by some measurements with an Aitken nucleus counter.

For fair weather a slight increase of NH_4 with the large particles and of NO_3 with the giant particles can be noticed, similar to Table 3.

From the gas measurements, NH_3 shows, in general, a slight increase (decomposition from the fern-woods?), nitrogen oxides a decrease, while SO_2 was on or below the limit of detection.

Cl again shows clearly an increase during fair weather, but only a slight increase or even decrease during rain. This might indicate a wash out effect by cloud formation and rainfall, and may have a bearing on the sodium to chloride ratio of the rain water analyses. But compared to the Cl in the aerosols, the gaseous component is only affected to a small degree by clouds and rain.

e. Measurements above the inversion layer at 9,500 feet (Table 6).

These measurements are of particular interest with respect to the origin of the different components. Halepohaku, a rest house of the Forestry Department, is located on the upper slopes of Mauna Kea at 9,500 feet. To avoid contamination from lower levels due to warm air rising up the slopes during the day, measurements were made during the night when cooled air drifted down the slopes. These measurements are considered to be a representative sample of the air of that altitude. They were carried out over a period of five nights.

Some preliminary tests indicated that the concentration of *aerosols* present in the air at Halepohaku was very small. In order to get a sample large enough to be analyzed, it was decided to accumulate the material on the plates by sampling for a total of twenty-seven hours during four consecutive nights. Unfortunately, only two samples were obtained due to technical difficulties. We decided that analysis for Cl^- and NH_4^+ would be most fruitful. The results are:

	NH_4^+	Cl^-
Large Part.	0.003 ± 0.0008	$< 0.00062\ \gamma/m^3$
Giant Part.	0.00085 limit	$< 0.00062\ \gamma/m^3$

In any case, NH_4 predominates, if Cl is present at all. This indicates that the particles at this altitude are *not* of maritime origin. Probably they consist entirely of $(NH_4)_2SO_4$. It should be stressed that this analysis is considered to be of special importance since it is an average value over four nights obtained well above the inversion layer under very favorable and unique conditions in the center of the Pacific.

Table 6 lists the amounts of the *gas traces* found. Samples No. 1, 3, 6, and 8, obtained during the day, show higher values of NH_4^+ and NO_3^- components than do the night samples. This is the expected influence of the chimney-effect of the heated slopes, transporting air from lower levels up the mountain side. The average night values are given at the end of the table. For better comparison with the average values at sea level which are repeated from Table 3, they were reduced to pressure at sea level. The table indicates that the concentrations above the inversion layer

Table 6. Analyses of the gas components at 9,500 feet, Mauna Kea, Hawaii. Values in γ/m^3.

Date	NH_4^+	NO_3^-	Cl^-	SO_4^{--}
Nov. 2 12.00—13.00 No. 1	2.70 ± 0.26	—	—	—
Nov. 3 21.00—23.00 No. 2	0.63 ± 0.11	1.74 ± 0.26	0.57 ± 0.23	0.39
Nov. 4 8.30—9.30 No. 3	1.26 ± 0.19	4.10 ± 0.48	0.67 ± 0.19	0.79
Nov. 4 21.00—23.00 No. 4	0.66 ± 0.09	2.50 ± 0.41	0.72 ± 0.26	0.62 lim.
Nov. 5 21.00—23.00 No. 5	0.68 ± 0.09	1.72 ± 0.26	0.96 ± 0.26	0.35 lim.
Nov. 6 14.15—16.15 No. 6	1.60 ± 0.10	3.80 ± 0.26	0.72 ± 0.26	0.35 lim.
Nov. 6 21.00—23.00 No. 7	1.16 ± 0.10	2.20 ± 0.26	0.87 ± 0.26	0.35 lim.
Nov. 7 7.10—8.10 No. 8	1.70 ± 0.19	—	—	—
Average of No. 3, 4, 5, 7	0.79 ± 0.10	2.04 ± 0.3	0.78 ± 0.25	0.42 lim.
Average correct. for sea level pressure	1.08 ± 0.14	2.8 ± 0.41	1.06 ± 0.33	0.57 lim.
Average of Table 3 at sea level	2.45	3.90	1.92	1.10

were roughly half the surface values. The remarkable result is that even above the inversion layer the gaseous components were present, and their concentrations more than one order of magnitude higher than that of the aerosols.

f. The Cl content of the large particles.

Because of the higher amount of the sea-spray component in the surface values at Hawaii, a little more information can be obtained on the Cl content of the large particles in pure maritime air. This information is important with respect to the size distribution of the sea spray nuclei, because the direct information about this size distribution as primarily obtained in the well known investigations of Woodcock does not extend below 1 μ radius (see also Junge 1956).

The high sea-spray concentrations at Pepeekeo were especially favorable for this computation because the Cl-content of the large particles was well above the limit of detection for these samples. Together with other values, where the Cl^- amount of the large particles was also above the limit of detection, they are listed in the upper part of Table 7.

The average Cl^- concentration of the large particles is 2.23 percent of that of the giant particles and the individual values do not scatter too widely, indicating that this mass ratio seems to be always of the same order of magnitude, at least under trade-wind conditions. The value of 2.23 percent is, however, a kind of maximum value because of the manner in which the values were selected. Therefore, in the lower part of the table the rest of

Table 7. Cl^- content of the large and giant particles and the percentage fraction of the former.

Large P. γ/m^3	Giant P. γ/m^3	Percentage fraction of the Large P. %	Location
0.7	165	0.42	Pepeekeo
1.1	90	1.22	"
0.25	9.4	2.65	"
1.40	70	2.00	"
0.14	2.8	5.00	"
0.035	3.0	1.16	Hilo Harbor
0.31	12.0	2.60	" "
0.20	7.0	2.86	" "
		Average 2.23 %	
0.07	5.5	< 1.30	" "
0.035	3.5	< 1.00	" "
0.034	3.1	< 1.10	" "
0.035	3.5	< 1.00	" "
0.035	2.5	< 1.40	" "
0.035	8.3	< 0.42	" "
0.035	5.1	< 0.69	" "
0.035	2.8	< 1.25	" "
0.035	2.8	< 1.25	" "
0.035	4.8	< 0.73	" "
		Average < 1.01 %	
		Total Average ≤ 1.56 %	

the Hawaiian Cl^- measurements are listed in which the Cl^- content did not reach the limit of detection. According to these data, the Cl^- amount of the large particles is < 1.01 percent of the giant particles. The average based on the total data amounts to ≤ 1.56 percent.

This is an important result. It indicates that the mass of the particles with radii $\leq 0.8\,\mu$ is only about 1 percent of the total mass of sea spray produced under normal trade wind conditions. It is, however, believed that this value holds true also for other oceanic areas.

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