Recent Investigations in Air Chemistry

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Abstract

1. New results of chemical analyses of natural aerosol particles in Florida and in the Boston area are presented.

2. These data are compared with the results obtained earlier at various other locations. The continental and maritime components of NH_4, Na, Cl, SO_4, and NO_3 can be separated for two different size ranges, viz. large particles (radius 0.08 μ to 0.8 μ) and giant particles (radius 0.8 μ to 8 μ). It is found that the continental influence on aerosols extends far into the ocean.

3. The nitrate content of the particles presents an especially interesting problem, since it appears that the major part of NO_3 stems neither from a continental nor from a maritime source, but from a certain area along the coast.

4. A comparison is made of the total amounts of material found in the large and the giant particles of the various locations. Information gained from this comparison provides the basis for conclusions regarding the size distribution of aerosols. A pronounced difference between maritime and continental distributions becomes evident in this case.

5. The concentration of the corresponding gas traces of NH_3, SO_2, nitrogen oxides and chlorine components were measured in Florida and at other locations simultaneously with the chemical analysis of the aerosols. For most components the concentration of these gas traces is considerably higher than that for the corresponding substances in the aerosols. The importance of these findings for air chemistry is discussed.

Introduction

A series of investigations dealing with the chemistry of natural aerosols and gas traces has recently been made under widely varying geographical conditions. Detailed reports of early measurements have already been published (JUNGE 1953, 1954, 1955 a). This paper contains the results of measurements made in Florida and in the vicinity of Boston; its main concern, however, is to present a critical survey and general conclusions.

The investigation was concerned chiefly with the chemical analysis of two different particle size ranges of the natural aerosol for NH_4^+, Cl^-, SO_4^{--}, NO_2^-, NO_3^-, and Na^+ (JUNGE 1953, 1954).[1] Additional measurements of the traces of gases such as NH_3, SO_2, nitrogen oxides, and chlorine components were made in Florida, on the Island of Hawaii, and, to some extent, in the vicinity of Boston. The major effort was directed towards a better understanding of the relative importance of the continental and maritime sources of chemical trace substances. In some respects, the total number of observations is still small and insufficient; nevertheless, general and interesting features become evident in this special field of meteorology.

[1] The + and — symbols, indicating that we analyzed for the ions in aqueous solutions, are omitted later in this paper, for simplicity.

Methods

A detailed description of the methods used for the analysis of aerosols and of gas traces was given in (JUNGE 1954) and (JUNGE 1955a), respectively. Only a few important points essential for an understanding of the results and conclusions given below need be mentioned here.

The aerosols are sampled in a two-stage cascade impactor, which separates the two radius ranges 0.08—0.8 μ and 0.8—8 μ. According to the nomenclature generally accepted, particles with radii below 0.1 are called Aitken nuclei, those with radii between 0.1 and 1.0 μ, large nuclei, and those with radii above 1.0 μ, giant nuclei. Our impactor therefore covers rather closely the size range of large and giant nuclei.

The particles are precipitated on dry and clear plexiglass disks where they stick, since most of them are droplets at normal humidities. The soluble matter of these samples is removed with a droplet of distilled water and analyzed by spot tests. The amount of insoluble matter, which is considerable at some continental locations, could not be measured. The components NH_4, Cl, SO_4, NO_3, and Na represent a considerable fraction of the soluble materials in natural aerosols. Rain water analyses indicate that Ca, K, and Mg may also contribute to the soluble materials. In a few cases we analyzed for Mg; however, we did not try to analyze for Ca and K because of a lack of adequate spot tests.

The gas traces are sampled in special bubble tubes after removal of the aerosols by MILLIPORE[1] filters. The efficiency of these filters was carefully checked under field conditions (JUNGE 1955 a). It was shown that the small fraction (< 1 %) of particles from all size ranges that pass through the filters does not influence the measured values of the gas traces.

It takes several hours to obtain a set of adequate aerosol and gas samples, depending on their concentration. Several sets of pumps, impactors, and bubble tubes were used so as to obtain nearly simultaneous samples of the different components.

[1] Trade name for special cellulose ester filters, manufactured by Millipore Filter Corporation, Watertown 72, Massachusetts.

Results of Measurements Made in Florida and Hawaii

The detailed data of the measurements made on Hawaii will be published elsewhere (JUNGE 1955 a); however, they are so closely related to the Florida measurements that a joint discussion here is justified.

The measurements in Florida and on Hawaii were made during the trade wind season, July, August and October of 1954, respectively,

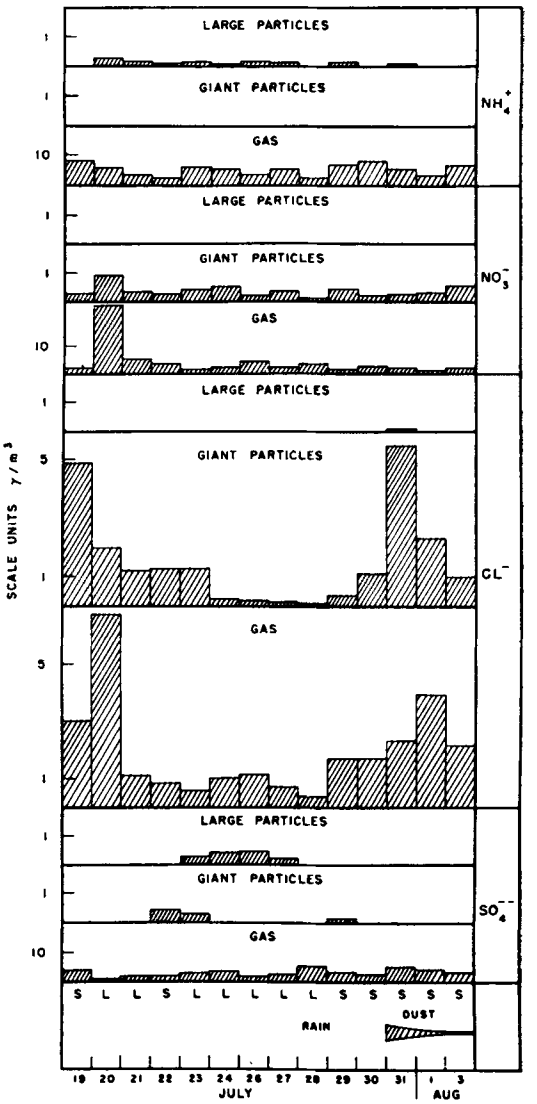

Fig. 1. Florida analyses. Note the different scales of gas traces for NH_4^+, NO_3^-, and SO_4^{--}. S and L denote sea and land air, respectively.

so as to obtain data in pure maritime air masses. At both places the samples were taken on the east coast in onshore trade winds. To minimize the influence of land, the sampling sites were located right on the coast, that is at Homestead, Florida (40 miles southwest of Miami), and at Hilo on the Island of Hawaii. The samples were collected at hours when the sea winds were most favorable. At both sites the trade winds were not always very pronounced, sometimes calm and even blowing offshore, so that the influence of the land could not be excluded completely. However, in most cases it was possible to satisfactorily separate these samples from the pure maritime samples.

Fig. 1 shows the results for Florida. One complete set of analyses was obtained each day. L (land) or S (sea) indicate the "origin" of the air, based on weather maps and the observation of local winds. The figures give the concentrations of the various components in micrograms ($\gamma = 10^{-6}$ gr) per m^3 of air. The gas traces will be discussed later.

The distribution of the various components is the same as in our previous measurements, especially those made at Round Hill: NH_4 is confined almost exclusively to large particles; NO_3, on the other hand, to giant particles. There was no exception to this rule during the fourteen-day period. The sulfate values lie at the limit of detection (the analysis of sulfate being the most insensitive) and are, therefore, not very reliable. Chloride was found to be concentrated almost completely in giant particles. A slight trace was found at the limit of detection for the large particles only on 31 July. An interesting finding is the observation that nitrates and chlorides are confined to the same particle size. This is in agreement with our findings at Round Hill.

It might be mentioned here as a matter of curiosity that during the last three days, beginning with 31 July, the aerosol samples of both sizes contained considerable, though decreasing amounts of reddish-yellow dust. Investigation of the weather maps ruled out the American continent as the source of this dust. Very steady easterly (trade) winds prevailed at all levels above the Atlantic Ocean during this period. It is very probable that this dust was carried across the Atlantic from West Africa, where several dust storms had occurred during the first half of July. It is a well-known

Table 1. Average concentrations for Florida. The figures in parentheses are the average limits of detection. All values in γ/m^3

Kind and number of data	NH_4			NO_3			Cl		
	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas
All values (13)	0.085 (0.036)	0.036 (0.036)	5.05 (0.3)	0.030 (0.030)	0.32 (0.030)	2.70 (0.3)	0.050 (0.048)	1.49 (0.048)	1.57 (0.3)
Values with sea breeze (7)	0.057 (0.034)	0.034 (0.034)	5.7 (0.3)	0.033 (0.033)	0.33 (0.033)	2.25 (0.3)	0.041 (0.38)	2.35 (0.038)	2.23 (0.25)
Values with land breeze (6)	0.12 (0.038)	0.038 (0.038)	4.2 (0.3)	0.026 (0.26	0.31 (0.026)	3.2 (0.3)	0.059 (0.058)	0.500 (0.059)	0.80 (0.35)

Kind and number of data	SO_4			Na		
	Large P.	Giant P.	Gas	Large P.	Giant P.	Gas
All values (13)	0.32 (0.29)	0.32 (0.29)	3.00 (0.3)	0.062 (0.046)	0.85 (0.046)	
Values with sea breeze (7)	0.32 (0.32)	0.37 (0.32)	3.35 (0.3)	0.074 (0.044)	1.26 (0.044)	
Values with land breeze (6)	0.33 (0.26)	0.27 (0.26)	2.63 (0.3)	0.048 (0.048)	0.34 (0.048)	

fact that dust from the Sahara desert, carried aloft by strong winds, can be transported to places such as Central Europe, the Azores, and the Cape Verde Islands. In this case, however, it must be assumed that the dust was carried all the way across the Atlantic Ocean *below* the inversion layer. It is surprising that it was not washed out by the trade-wind showers.

In table 1, average values are computed for all samples and for land and sea air, separately. The value of 20 July was excluded, because the exceptionally high concentration of nitrogen oxides suggested some local contamination, probably from Miami. The values of table 1, as well as those of the other tables, are computed in the following manner. When a component does not show up in the analysis, it may only be stated that it is not present *above* the limit of detection, which varies with every component and with the volume of air used in the sample. In the computation of the average values, this limit of detection is substituted for zero and the maximum values are thereby obtained. The average limits of detection are also computed and listed in parentheses. The difference between both values, therefore, is the minimum value. If both figures are equal, nothing is found above the limit of detection.

In table 1 the land winds show a little higher NH_4 content for large particles and a lower Cl content for giant particles. No difference is observed in the case of nitrate.

On five days the aerosols were checked for NO_2 and no trace was found above 0.03 μ/m^3, the limit of detection. This is in agreement with our results from Frankfurt and Round Hill. We believe it can be stated rather definitely that, under normal conditions, no NO_2 is present in natural aerosols. No further checks, though, were made on Hawaii.

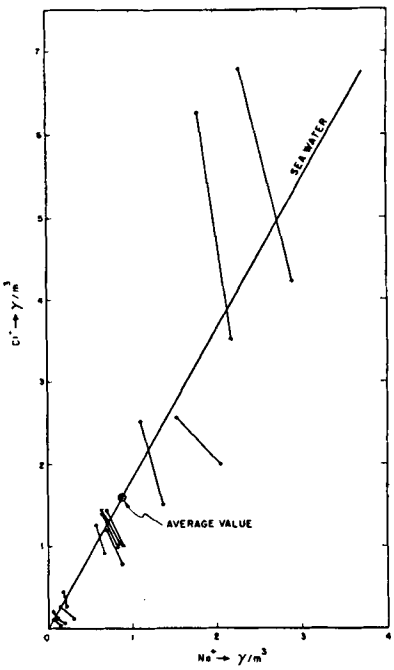

Fig. 2. The Cl and the Na contents of giant particles (Florida), plotted against the line of sea water. The limits of accuracy are indicated by a line for each pair of values.

In Fig. 2 the chloride values are plotted against the sodium values for giant particles. Each value is represented by a line, which indicates the limits of accuracy. Within these limits, the chloride-to-sodium ratio equals that of sea water. This agrees with other observations made near the ocean (TWOMEY, 1954) and shows that particles of this size do not decompose very rapidly. This result is of interest in view of the recent observations of strong deviations of the Cl/Na ratio in rain water over Scandinavia (ROSSBY, EGNER, 1955).

Table 2. Average concentrations for Hawaii. The figures in parentheses are the average limits of detection. All values in γ/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 value 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

It may be mentioned, however, that our Round Hill measurements indicated greater deviations of this ratio for giant particles. We believe that this departure from the sea water value is due mainly to independent sources of sodium or chloride over the continent, rather than to decomposition (KALLE, 1953/54). However, further observations are necessary to clarify this interesting question.

On the basis of the results of Fig. 2, sodium analyses on Hawaii were discontinued.

The presence of NH_4, SO_4, and NO_3 even in the maritime air of Florida, raised the question as to whether this still pointed to some continental influence. To investigate this further, measurements were made on the windward side of the Island of Hawaii. Here, in the center of the Pacific, any continental influence should be reduced to a minimum.

Table 2 gives the average values for Hawaii. Only those measurements which were representative of pure maritime air and not influenced either by the Island or by the heavy sea-spray production of the surf were selected (cf. JUNGE, 1955 a). Compared with table 1, the NH_4 content of large particles and the nitrate content of giant particles is further decreased. The data on the gas traces will be discussed later.

The measurements made on the slopes of Mauna Kea (Hawaii) at an altitude of 9,500 feet (i.e. well above the inversion layer, which is normally located at about 5,000 feet) are especially interesting. To avoid any contamination by convectively rising air streams along the slopes of this dead volcano, the samples were taken only during the night when well-developed downslope winds appeared; this guaranteed a sampling representative of the air masses at that level. The concentration of aerosols was so small that the material on the impactor plates had to be accumulated over a period of twenty-seven hours in the course of four consecutive nights. Because of technical difficulties, only two samples were obtained, which were analyzed for Cl and NH_4.

Table 3 shows that no Cl was found above the limit of detection, which was very low here because of the large air volume involved. In the size range of large particles, NH_4 clearly predominates and the Cl concentration can be no larger than 14 per cent of the NH_4 concentration. However, quite contrary to the results below the inversion layer, the giant particles also show a higher NH_4 concentration, although this value is already near the limits of detection. This analysis may be considered as fairly representative, inasmuch as it represents an average value over four nights; it indicates that nuclei other than sea-spray particles predominate in the subsiding air masses of these latitudes.

Table 3. Aerosol data of 9500-foot level (Hawaii)

	NH_4	Cl	
Large particles	0.003 ± 0.0008	< 0.00062	γ/m^3
Giant particles	0.00085 limit	< 0.00062	γ/m^3

Comparison of Data from Various Locations

We will now compare the results obtained in Florida and Hawaii with those of Frankfurt and Round Hill (JUNGE, 1953, 1954). Interesting features become visible when we arrange the data in the order of decreasing continental and increasing maritime influences, as done in Figs. 3 and 4.

The winter values obtained at the outskirts of Frankfurt under very stable weather conditions and with a pronounced inversion layer represent the measurements most subject to influences of industry and other human activity. Because of more intense mixing, horizontally and vertically, the summer values in Frankfurt are less contaminated. Round Hill is located on a fairly isolated section of the coast between Boston and New York; nevertheless, the air masses of this location are still influenced by the industrial and the populated areas of the northeastern U.S. The Island of Hawaii naturally has a more pronounced maritime character than Florida.

Due to the low concentration of some components, we have also plotted the average limits of detection; the differences between these limits and the actual values are set off by shaded areas. The NH_4 value at Mauna Kea was also included. No NO_3 data had been obtained at Frankfurt.

In Fig. 3, all components show a drop as one approaches more maritime areas. The slope of the SO_4 curve parallels that of NH_4 until one reaches the data for Florida. From there on

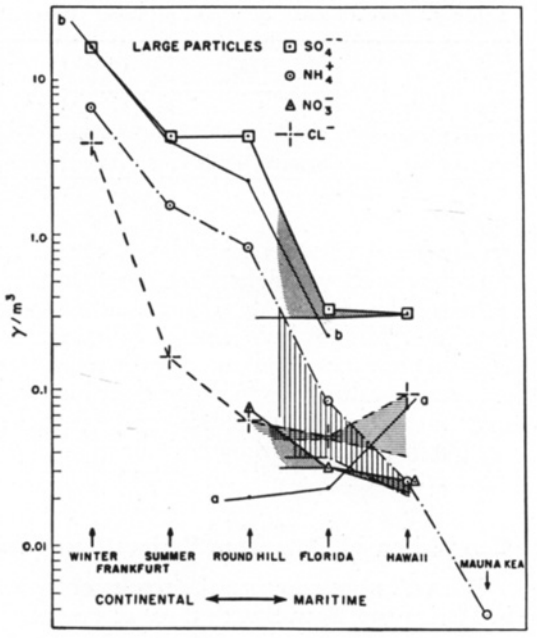

Fig. 3. Survey of the results of our chemical analyses of large particles. For the low values the difference with respect to the limit of detection is indicated by the shaded areas.

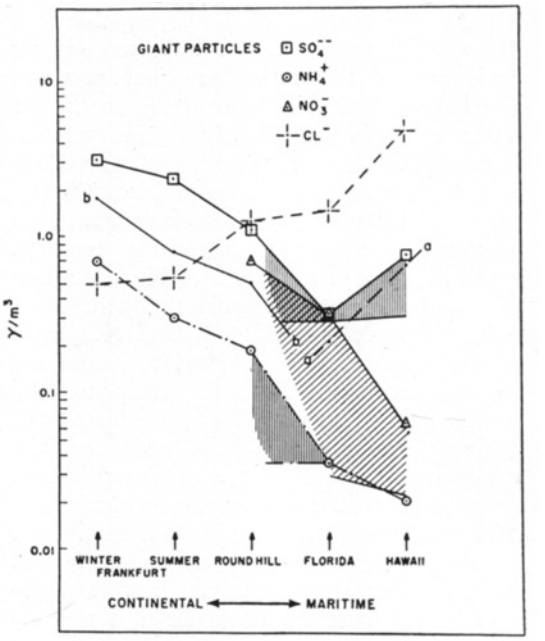

Fig. 4. Survey of the results of our chemical analyses of giant particles. For the low values, the difference with respect to the limit of detection is indicated by the shaded areas.

the relatively high limit of detection made successful SO_4 analyses difficult or impossible. Line b—b represents the SO_4 concentration, calculated under the assumption that all NH_4 would be present as $(NH_4)_2SO_4$. The actual SO_4 values are a little higher at most points, but generally the agreement is rather good, indicating that either $(NH_4)_2SO_4$, $NH_4H\ SO_4$, or a mixture of both is the predominant soluble substance of the large nuclei. We believe that the same result would have been found for Hawaii and Mauna Kea, too, had there been a better analytical method for SO_4 available.

The pronounced drop of Cl ceases in Florida and is reversed on Hawaii. It will become evident later that the maritime Cl concentration of the large nuclei is about 1.5 per cent or less than that of the giant particles. This figure applied to the Cl curve in Fig. 4 yielded the line a—a. This estimated value is much less than the observed Cl concentration over the continent; this leads one to conclude that the source of the large Cl nuclei over the continent cannot be maritime. This fact is important when conclusions about the origin of air masses are drawn from the presence of Cl particles. *The small maritime Cl in this size range first becomes predominant upon reaching such marked maritime places as Florida.*

We may summarize the results of Fig. 3 as follows. All components of the large nuclei, including Cl, are of a continental origin, with the exception of a small amount of sea spray, which is found only in places with very pure marine air masses. The major constituents in this size range are NH_4 and SO_4 which are present probably as a mixture of $(NH_4)_2SO_4$ and $NH_4H\ SO_4$. The curves show that the continental influence extends far into the oceans, so that some remnants can be distinguished, even on Hawaii.

Fig. 4 gives the data for the giant nuclei. NH_4 and NO_3 show a trend similar to Fig. 3; Cl, on the other hand, behaves quite differently, for it increases continuously with maritime influence, indicating its maritime origin. It is, of course, incidental that the value on Hawaii

is higher than that in Florida, a difference that depends on the average wind speed and probably on some influence of the surf.

The behavior of the SO_4 component is similar to that of Cl in Fig. 3. At first, the SO_4 drops roughly parallel to NH_4, though the ratio SO_4/NH_4 is higher than in Fig. 3. The rise in the Hawaiian value can be accounted for by the SO_4 content in sea water. The line a—a depicts the SO_4 content calculated from the Cl curve according to the composition of the sea water. It agrees satisfactorily with the observed SO_4 value from Hawaii, though it is already lower in such maritime regions as Florida.

The results of Fig. 4 may be summarized as follows. In places of a distinct continental nature, sulfate is the most important soluble component of the giant particles; however, as one approaches the coast, one finds that the sea spray becomes predominant.

We think that Figs. 3 and 4 give a fairly clear picture of the geographical distribution of the chemical composition of our natural aerosols. It becomes evident that the old controversy about the predominant role of the continental or maritime nature of the nuclei can be settled for *limited size ranges only*. Almost all the *large* particles are of a continental origin, even over the oceans. Near the coasts and over the oceans, the giant sea-spray particles become the predominant component.

The Origin of Nitrate

Figs. 3 and 4 show that NO_3 is concentrated predominantly in the giant particles. The similarity in size limitation to the sea spray suggests that it might come from a maritime source; on the other hand, the concentration decreased with increasing maritime influence. This points to a continental origin. For further study of this subject, a series of nitrate analyses was made near Boston under various weather conditions.

The measurements summarized in table 4 were made from February through May of 1954 in West Newton, a rural residential section twelve miles west of Boston. The air masses were defined according to the main air trajectories, viz. continental with winds SW through W to NNE, otherwise maritime. The continental air masses were transported almost exclusively by west-to-northwest winds, and were thus not influenced by local industrial sources. Southerly or southeasterly winds brought the maritime air masses; hence, in most cases, they had not passed over Boston. A few days with fair weather and calm winds were labeled indifferent.

Table 4. NO_3-concentration (in γ/m^3) in the aerosols for West Newton, Mass., U.S.A. Figures in parentheses are the average limits of detection

Air mass and number of values	Large particles	Giant particles
Continental 23	0.030 (0.030)	0.053 (0.030)
Maritime 27.....	0.038 (0.030)	0.690 (0.030)
Indifferent 12.....	0.110 (0.030)	0.320 (0.030)
All values 62.....	0.052 (0.030)	0.370 (0.030)

The results are rather striking. The average value of nitrate in the giant particles (0.37) for all cases is already lower than that found at Round Hill (cf. Fig. 4). The value for the continental air masses (0.053), however, is even lower than that of Hawaii (0.064) in the same figure. On the other hand, the maritime air masses have values (0.69) equal to the highest found at Round Hill (0.70).

These data show that the continent *cannot* be the source of the nitrate. It is possible that the nitrate is a product of the air pollution of large cities and industrial areas and thus shows up at Round Hill and West Newton in southerly air masses that may have passed over the New York or Boston areas on their way northward. Although this possibility was not very likely at either location, considering the trajectories of the air masses, we nevertheless investigated this point further. Over a period of fourteen days, we made simultaneous measurements at West Newton and in the center of the city of Boston (tables 5 and 6). Concurrent data on NH_4 were obtained to show the degree of pollution. The difference between the NO_3 in the giant particles of the two locations is small by comparison with the differences of the corresponding NH_4 values of the large particles. We must conclude that

Table 5. NO_3- and NH_4- concentration for Boston and West Newton. Average vaules of fourteen days in γ/m^3

	NO_3		NH_4	
	Large Particles	Giant Particles	Large Particles	Giant Particles
Boston	0.12 (0.03)	0.35 (0.03)	2.35 (0.04)	0.19 (0.04)
West Newton	0.086 (0.03)	0.30 (0.03)	0.79 (0.04)	0.07 (0.04)

Table 6. NO_3- and NH_4- concentration for Boston and West Newton with fair weather in γ/m^3

	NO_3		NH_4		
	Large Particles	Giant Particles	Large Particles	Giant Particles	
Boston	0.30 (0.03)	1.00 (0.03)	10.0 (0.04)	0.5 (0.04)	April 30 8—9
West Newton	0.10 (0.03)	0.70 (0.03)	1.00 (0.04)	0.05 (0.04)	
Boston	<0.03 (0.03)	0.90 (0.03)	9.00 (0.04)	0.50 (0.04)	May 14 8—9
West Newton	0.50 (0.03)	0.50 (0.03)	1.00 (0.04)	<0.04 (0.04)	

Boston, at least, represents no great source of NO_3. This is illustrated even better by table 6, where two days with very stable air and calm winds have been selected from the series. The samples were taken under the most favorable conditions, i.e. in the morning when the dust cloud had its greatest concentration prior to the onset of the daytime convection. In this case, the NO_3 concentration is a little higher in Boston; this points to some industrial sources. At the same time, however, the NH_4 content is about ten times higher, a phenomenon that indicates that the NO_3 source is fairly inefficient compared to the total pollution.

We may summarize the results for the NO_3 content as follows.

1. With but few exceptions, the nitrate in or near Boston was always concentrated in giant particles.

2. Lowest concentrations were found at the center of the ocean and in pure continental air masses.

3. The highest concentrations were found in maritime air masses on the east coast of the U.S.A.

4. Cities and industrial areas do not represent great sources of NO_3.

These observations are supported by a study of the aerosol composition of American cities carried out by the U.S. Public Health Service (CHAMBERS, FOTER and CHOLAK, 1955). The cities show only slightly higher NO_3 concentrations than do nonurban areas. Only two exceptions were found: Los Angeles and San Francisco, where the values departed considerably from the general level. Both places are located in coastal areas.

We believe that the nitrate is formed by oxidation of NO_2 to NO_3 when sea-spray aerosols mix with continental air masses in coastal areas. Although the nitrates are not a particularly important component in the composition of atmospheric aerosols, their origin presents a very fascinating problem and will thus continue to be investigated.

Comparison of the Total Amounts of Aerosols

Table 7 gives a summary of the total amount of soluble substance found by our chemical analyses. The figures are not strictly comparable because no analysis for NO_3 and Na was made in Frankfurt and none for Na on Hawaii. On the Island of Hawaii and in Florida it is difficult to give a reasonable value for the *large* particles, because a number of components were below the limit of detection. The values given in Table 7 are maximum values, obtained by inclusion of the limits of detection, which are influenced chiefly by the SO_4 method. The difference between these values and those of the average limit of detection gives us the lower limit.

From these data we can draw some interesting conclusions regarding the size distribution of aerosols.In (JUNGE, 1953) it was demontrated that the log number distribution of aerosols over continents for particles with radii larger than 0.08 μ can be well approximated by the formula $dN/d \log r = C \cdot r^{-\beta}$. In this equation, N is the total number of all particles ranging from the lowest limit up to radius r, C and β are constants, with the latter being equal to approximately 3. The total number of particles in the radius interval $\log r$ to $\log r + d \log r$ is

Table 7. Total concentration (in γ/m^3) of soluble substance in aerosols for various locations

Place and number of values	Large particles	Giant particles	Components analyzed
Frankfurs — winter 12	28.00	4.60	NH_4, SO_4, Cl
Frankfurt — summer 25	6.11	3.17	NH_4, SO_4, Cl
Round Hill 27	5.50	4.30	NH_4, SO_4, Cl, Na, NO_3
Florida 13	0.55 (0.45) [1]	3.00	NH_4, SO_4, Cl, Na, NO_3
Hawaii 10	0.45 (0.39) [1]	5.84	NH_4, SO_4, Cl, NO_3

[1]) Average total limit of detection, given essentially by the high value of the sulfate analyses.

thus $(dN/d \log r)\ d \log r$. The log scale was chosen simply because of the wide range of the r values from about 0.005 to about 20 μ, which is nearly four orders of magnitude.

Multiplication by $4/3\ \pi\ r^3$ gives the log volume distribution

$$\frac{dV}{d \log r} = \frac{4}{3}\ \pi\ c \cdot r^{3-\beta}$$

With $\beta = 3$, $\frac{dV}{d \log r}$ is constant. Within equal intervals log r, one may expect equal volumes or, in the case of a constant density of the aerosol material, equal masses. For this reason, our impactors were adjusted to collect the two particle-radius ranges 0.08—0.8 μ and 0.8—8 μ at normal humidities, so that $\triangle \log r = 1$. If β is equal to 3, the total mass of the large and the giant particles collected should be equal. We see from table 7 that this almost holds true for locations such as Frankfurt and Round Hill, but large deviations occur in Florida and on Hawaii.

These facts are demonstrated in Fig. 5. The solid line represents the log number distribution for $\beta = 3$. The radii 0.25 and 2.5 represent the center of gravity for both size ranges. Since we are interested here only in the shape of the curve (and not so much in the absolute values of particle numbers) we keep the value for the giant particles fixed. If the mass of the large particles is the same, the log number concentration can be represented by the solid line. This is indicated by the encircled dot lying on the solid line. If the mass of the large particles is larger (Frankfurt), these particles are more numerous than the solid line indicates and vice versa. For Florida and Hawaii we can only give the range between the maximum and the minimum values by a vertical line, the center of which is marked by a cross. However, these values still do not represent the pure maritime component. We know from the analyses that even in Florida and on Hawaii sea spray makes up only a fraction of the large particles, which could be estimated. Electron-microscope pictures made of large nuclei in Florida indicate that only about 10 per cent can be identified as sea spray. On Hawaii we did not make electron-microscope pictures, but obtained the *mass*

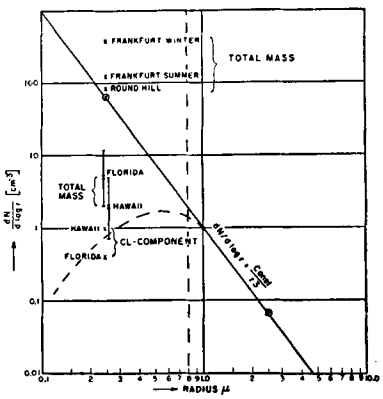

Fig. 5. Interpretation of the total-mass values of chemical analyses in terms of the size distribution of aerosol particles.

ratio of the large to the giant sea-spray particles. Taking into account all measurements, regardless of whether there was a small trace of Cl in the large particles or not, we found that in a pure maritime aerosol the Cl concentration of the large particles is ≤ 1.5 per cent of that of the giant particles (cf. JUNGE, 1955 a for detailed data). Using these values, we obtained the two points marked "Cl component" in Fig. 5. Considering the different localities and methods of estimation, the values show a satisfactory agreement. The dashed line represents the probable distribution of the pure sea-spray particles that would satisfy these values. This is, of course, only a very rough approximation, but since no direct size-distribution counts below a radius of one micron have been made in maritime air, this curve offers us the first information that we possess. The marked departure from the continental size distribution is obvious.

We believe that this basic difference should influence the condensation process in clouds, and may account for the different behavior of continental and trade-wind cumulus in rain formation. Plans are being made to investigate this question more carefully in the future.

We have included Fig. 6 (already published, see (JUNGE, 1955 b) for the log volume distribution which had been derived from the results of various observers. This figure quite clearly shows the complete lack of data on maritime aerosols below about $1 - \mu$ radius. We included the single point derived from our chemical analyses and extrapolated the marine curve for average wind speeds. Again the difference between the continental and the maritime aerosol distribution is evident. In coastal areas, of course, one may expect all kinds of intermediate distributions.

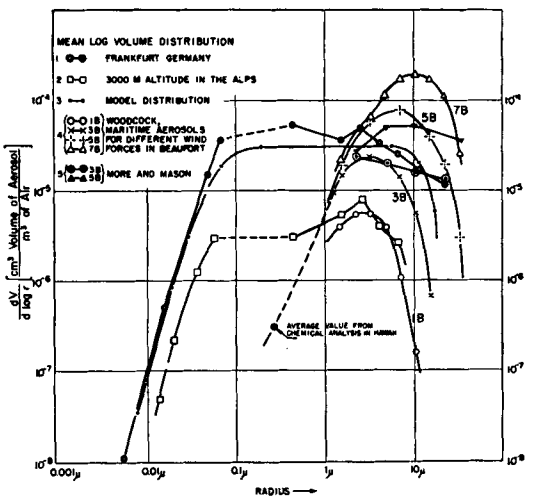

Fig. 6. Log volume distribution of continental and maritime aerosols. The curves for Frankfurt and the Alps represent continental conditions, the former approximated by a continental "model" distribution (see JUNGE, 1955 b). The curves of Woodcock and Moore (misspelled in the Figure) and Mason represent maritime aerosols for various wind speeds in Beaufort.

In this figure we note that our chemical analyses of aerosol particles with radii from 0.08—8 μ cover fairly well the portion of the distribution that actually contributes to the aerosol mass. Further, we see that the small but numerous Aitken nuclei (radius below 0.1 μ) do not contribute very much to the total mass, although they outnumber by far all larger particles over the continents.

Gas Traces

Basically, chemical trace substances in the air can be present as particles (droplets or solid particles) and as gases. Air chemistry is, therefore, incomplete if we deal only with substances concentrated in aerosols, or if the phases are not separated. The role of each component in the atmosphere can only be understood properly if independent measurements are made of each. Unfortunately, almost all previous work in air chemistry (e.g. CAUER, 1951, and EGNÉR, ERIKSSON, 1955) measures a mixture of particles and gases. *A real step forward in the understanding of the basic processes in air chemistry can be gained only if aerosols and gases are measured simultaneously but separately, and if the aerosols, in turn, are separated according to size.*

For this reason, we have supplemented our aerosol investigations in Florida and on Hawaii by measurements of the gaseous equivalents of the aerosol components: NH_3, SO_2, nitrogen oxides, and chlorine components. The air was bubbled through wash bottles *after removal* of the aerosols by Millipore filters. Because of the very low concentrations, some difficulties arose which were only partially resolved. The filters adsorbed a fraction of the gases (about 10—20 %). A certain (unknown) amount of the SO_2 was oxidized to SO_4 and escaped

analysis. Also, for chemical reasons, possibly only a fraction of all nitrogen oxides and of the chlorine components was measured because the catch solution was analyzed only for the ions NO_3 and Cl. All values must, therefore, be regarded as minima. Since we intend to demonstrate that the concentration of these gases is higher than that of the corresponding substances in the aerosol, these analytical defects are not too serious. The removal of the aerosols from the air entering the gas samples was carefully checked under field conditions, proving that the fraction of aerosol particles passing the filters was less than 1 per cent, and thus negligible (JUNGE 1955 a).

For a better comparison with aerosols, we present all data of NH_3 as NH_4, SO_2 as SO_4, the nitrogen oxides as NO_3 and the (unknown) chlorine component as Cl.

Fig. 1 shows the daily values of the Florida samples. Regarding the different scales for the particles and gases, we see that for NH_4, NO_3, and SO_4 the gas traces have concentrations about ten times higher than the aerosols. For Cl they are of the same order of magnitude. The NH_4, SO_4, and NO_3 gas components do not show much fluctuation from day to day. The exceptionally high NO_3 value of 20 July is probably due to some contamination from Miami, since on that morning we noted slight NE winds at the field site, located about 40 miles SW of that city. The fluctuations of the Cl gas components are more pronounced and seem to parallel those of the giant particles.

The results in Hawaii were very similar. The daily fluctuations were also small. We therefore give only the average values in Table 2. Comparison with Table 1 reveals that the concentration of SO_2 and NH_3 is about half as much as was observed in Florida. On the other hand, nitrogen oxides are a little higher on Hawaii. With the exception of Cl again and the SO_4 sea-spray component, the concentration of the gases on Hawaii is higher by one to two orders of magnitude than the corresponding aerosol concentrations.

These are interesting results. They indicate that the air chemistry in these maritime areas is largely controlled by the gas traces. The rain water in these areas, for instance, always contains NH_4, NO_3, and SO_4. Since the concentration of these substances in the aerosols is extremely small (Hawaii), a considerable fraction of the rain-water content is probably due to the gas traces. This is strongly supported by the observation that the NO_3 and NH_4 concentration in rain water varies only slightly with time and increasing distance from the shore, in contrast to the Cl content which drops rapidly.

Table 8. Calculated equilibrium concentration of NH_3 over the sea water for Hawaii

Distance from the coast	Near the coast	3 miles	10 miles
pH values of sea water ..	8.08	8.11	8.01
NH_3 content of sea water in γ/liter	36	37	44
Calculated equilibrium concentration of NH_3 in the air, γ/m^3	1.02	1.17	1.22

It is, of course, too early to speculate about the origin of the gaseous components. We have a little more information only in the case of NH_4. The NH_H content in the sea water as well as the pH value[1] were measured as far as ten miles upwind off the coast of Hilo, Hawaii. From these data the equilibrium pressure of NH_3 in the air can be calculated (EGNÉR 1932) as in table 8. Our observed average NH_3 concentration of 2.45 γ/m^3 is more than twice as high as the calculated values of this table. This would lead one to infer that the ocean acts as a sink for the NH_3 in the air and not as the source of it. However, measurements made during the night at an elevation of 9,500 feet (i.e. above the inversion layer) on the slopes of Mauna Kea contradict this hypothesis. The measurements were made at night for the very same reason given above in the case of the aerosol sampling. Table 9 gives the average values, reduced to surface pressure, so that they can be readily compared with the other Hawaiian data in table 2. All values are about one-half as large as those at sea level. It is now generally accepted that rather than a true material boundary the tropical trade-wind inversion is an easily penetrated internal interface generated by surface winds and subsiding air masses. Consequently, the gas traces should have the

[1] Mr. Erikson of the University of Stockholm kindly made these data available to me.

Table 9. Comparison of the average gas concentrations in γ/m^3 at sea level and on the Mauna Kea at 9500 feet altitude, Hawaii. The data on the Mauna Kea are reduced to surface pressure

	NH_4	NO_3	Cl	SO_4
Sea level.....	2.45	3.90	1.92	1.10
Mauna Kea	1.08	2.80	1.06	0.57 limit

same concentration above and below the inversion layer if the ocean would be without influence. Our data from Mauna Kea indicates that the ocean is a source, especially of NH_3. This conclusion appears also to be supported by the small difference between the values for Hawaii and Florida. However, we saw above that the sea-water content of NH_3 does not permit this conclusion. It might be that this discrepancy is due to the presence of films of organic decomposition products on the surface of the sea. These slicks, which are frequently observed, may well liberate NH_3 into the air and, to some degree, into the water, thus being a source for both sides. Further observations are, of course, necessary before we will be able to understand these interesting interrelationships. Table 10 includes some data on gas traces, gathered at Ipswich, in a rural surrounding, forty miles north of Boston. These data are fairly representative of continental conditions. The values for SO_2 were not reliable enough and thus have been excluded. No simultaneous aerosol measurements were made.

We see that the NH_4 concentration is about equal to that of Florida and Hawaii; whereas, the nitrogen oxides and the Cl-component are slightly higher. Although the increase is small compared to that of the corresponding substances in aerosols, which may be estimated from Figs. 3 and 4, it nevertheless appears that

Table 10. Gas concentrations in γ/m^3 for Ipswich; average from nine individual measurements, December—January 1954/1955

NH_4	NO_3	Cl
4.95	3.90	4.40

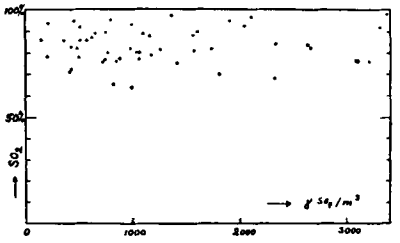

Fig. 7. Percentage of SO_4 of the total sulfur content of the air in polluted smelter areas as a function of the concentration, which is calculated as sulfate per cubic meter for comparison with the previous results. Data of KATZ (1952).

the concentration of gas traces are again higher than those of aerosols.

The lack of adequate data on the ratio of SO_2 to SO_4 in the aerosols may be compensated for by Fig. 7, which gives results from polluted atmospheres, according to KATZ (1952). Cities and industrial areas can be considered as a major source of SO_2 over land and the ratio of SO_4 in aerosols to SO_2 at this very source is interesting. About 80—90 per cent of all sulfur is present as SO_2, but the way these data were obtained suggests that this is a minimum value and that the true SO_2 percentage is still higher. The important result is, that the percentage is independent of concentration and that we found e.g. in Florida values of the same order of magnitude for the much lower concentrations in pure atmospheres.

These data are not complete enough to provide the basis for any definite conclusions; however, it seems that the concentration of such gas traces as SO_2, NH_3, nitrogen oxides and Cl-components are higher than the corresponding components in the aerosols over a wide variety of geographical locations, ranging from extreme continental to extreme maritime areas. This strongly suggests that, with the exception of the sea-spray Cl and SO_4, the gas traces are the primary sources of these substances in the aerosols. Current laboratory investigations seem to indicate that the essential process in the fixation of these materials in the aerosols occurs as the result of condensation of water vapor. The presence of NH_4, SO_4, and perhaps NO_3 would thus indicate that these particles are evaporated fog, cloud, or rain droplets. These are important problems dealing

with the very question of how our atmosphere is able to rid itself of the gaseous substances that are constantly being produced both artificially as well as naturally. Cities and industrial areas obtain immediate relief from their concentrations of pollutants through mixing with the unpolluted air of their surroundings, i.e. as the result of a large-scale mixing process. However, this process does not remove the material from the atmosphere. With the rapid, continued growth of industry, the second problem, i.e. the efficiency of the natural cleaning process of the atmosphere by water condensation, rain, etc. assumes increasing significance.

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