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The Yearly Circulation of Chloride and Sulfur in Nature; Meteorological, Geochemical and Pedological Implications. Part I

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Abstract

The circulation of air borne oceanic constituents is discussed to the extent available data permit. From data on sea salt particles in the atmosphere and their fall rate it is estimated that they are produced at a rate of the order of magnitude 1000 million tons a year over the ocean areas. About 90 per cent of this is precipitated over the oceans, the rest is carried into continents and is brought back to the sea in rivers. The estimated residence time for sea salt particles in the atmosphere is only a few days, higher for smaller particles, which lose their identity through coalescence, and lower for larger particles, lost by rainout or fallout. From the rate of production of sea salt particles in breaking waves it is concluded that about 0.3 per cent of the ocean areas is covered by breaking waves. On land the residence time of sea salt may vary from a few years in peripherally, drained humid areas to thousands of years in arid areas or areas without peripheral run-off.

Geochemical balance computations indicate that a major part of the sulfur in the atmosphere is of oceanic origin but does not originate as chloride through spray emitted from breaking waves. Of chemical reactions taking place in the atmosphere between sea salt constituents the release of HCl from sea salt particles due to absorption of oxidized sulfur dioxide seems to be quantitatively important and mainly responsible for variations in the Cl/Na ratio in precipitation. The deposition of chloride in precipitation over continents shows nicely the main areas of inflow of maritime air. Dry deposition of sea salt components seems to be an important process. The rate of which these constituents are carried to the ground from the air is about 1—2 cm per second, a figure concordant with the turbulent nature of air close to the ground.

As for proportions of sea salt components in precipitation some fractionation processes seems to take place at the sea surface (probably involving organic matter derived from surface films). In typical maritime areas there is always an excess cations over inorganic anions suggesting association of some cations with organic acid material in precipitation. The presence of sea salt components in groundwater can be taken advantage of in the estimation of regional evaporation using chloride as an indicator. Reduction of sulfur in groundwaters can cause precipitation of calcium and magnesium, thus modifying the chemical properties of groundwaters considerably. The role of air borne sea salt components for the development and properties of soils is discussed in principle.

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I. Introduction

It has been known for some time that oceanic salts are present in the atmosphere over continents and are found in precipitation, the earliest measurements dating back to the middle of the nineteenth century. The geochemical implication of this transport was visualized by Posephny, a Hungarian geologist already in 1877. In an extremely well written paper he discussed the origin of chloride in river water and recent saline deposits. At that time not much was known about the chemical composition of precipitation but he concluded from geological evidence that chloride in river water and various saline deposits must have originated in the sea and were carried inland by the atmosphere. He discussed also at some length the saline deposits of the Bonneville Basin—the present Great Salt Lake region in North America—an area which he visited and found that the older saline formations could not account for the present amounts of chloride.

Later investigations on rain-water in different places gave a qualitative support to Posephny's views. KÖHLER's (1921, 1922, 1925) investigations on cloud droplets and the role of sea salt particles in condensation processes stimulated the development of cloud physics in which field a good deal of recent useful data are found.

In the meantime the question about the circulation of oceanic salts in nature was discussed on occasions. In his well-known book "Data on Geochemistry" CLARKE (1924) discusses the oceanic elements in river water but gives a rather low estimate of the airborne part. He is, however, somewhat embarrassed by the presence of so much chloride and sulfur in river water. Clarke's attitude can be understood from his belief in the method of computing the age of the oceans by means of sodium in river water and his sceptical attitude towards the now acknowledged isotope methods of geological age determination.

A splendid effort was made by CONWAY in 1942 to reconstruct quantitatively the evolution of oceans. In this procedure he regarded all chloride in river water as cyclical, because weathering can hardly supply any. Most of this cyclical chloride he was led to believe is airborne, and, furthermore, he found that also a large part of the sulphur in river water must originate in the sea generated by some other mechanism than chloride is generated.

At present there is more information available on the composition of air and precipitation and on various physical and chemical processes in the atmosphere, allowing a rather complete reconstruction of the yearly circulation of oceanic salts in nature and the role of the atmosphere in this circulation. To some readers the present paper may seem to contain too much of speculation. There is, admittedly, some but only in the sense of trying to tie all pieces of information into a comprehensible pattern, resembling to a high degree of probability the pattern actually existing.

The present paper is thus mainly concerned with the release and transport of sea salts from oceans into continental areas. To understand these processes better a short description of significant chemical and physical properties of the atmosphere is given. Investigations on sea salt particles over the oceans are reviewed rather thoroughly as well as the generation of sea salt particles. After that a section is devoted to considerations on the yearly circulation of sea salts between oceans and continents as revealed by the use of geochemical data. Mechanisms of transfer to and removal by the ground of sea salt components are given in another section followed by considerations on the possible separation of sea salt components from sea salt particles. Existing data on precipitation of chloride and sulphur over land are then reviewed and their circulation schematically outlined.

The two last sections touch briefly on some problem of great interest in hydrology and soil science. They do not explore the subjects by any means but do show that such problems are intimately tied to atmospheric chemistry.

Some of the present material was included in a review report to UNESCO in 1957 (Eriksson 1958) like parts of section II and III, section IX and the whole of section X.

II. General features

1. *Average Composition of Tropospheric Air*

Available average data for minor constituents in the atmosphere have been compiled in table 2.1. This table is intended to give an impression of the order of magnitude of the constituents present. The table is by no means complete as it excludes among other things organic compounds which, presumably, are very numerous.

The estimates in the latter part of the table are based partly on data from the European chemical network described by Egnér and Eriksson (1955) and since then somewhat extended, and partly on data from a similar table compiled by Hutchinson (1959).

Gaseous constituents of principal interest here are those of carbon, nitrogen, sulfur and chlorine. The presence of sulfur dioxide has been known for quite a long time but does not exclude also some other forms of sulfur like H_2S. Its presence is mostly ascribed to industrial and domestic combustion of fossil carbon though, as will be shown later, this source is by no means sufficient to explain its incidence on a global scale.

The presence of *gaseous forms* of *chlorine* was indicated very recently in investigations by Junge (1956). There are only two possible gaseous compounds of chlorine in the atmosphere, namely hydrochloric acid and ammonium chloride. Free chlorine, Cl_2, can hardly exist in an atmosphere where hydrogen is present at a fifty times higher pressure.

The constituents in *particulate* state listed in table 2.1 are components of so called *condensation nuclei* which have recently been thoroughly discussed by Junge (1958), as well as of substances which normally would be classified as dust. All listed elements of the particulate matter may occur as soluble salts, and as such they can be components of the *hygroscopic particles* called condensation nuclei. Sodium, potassium, calcium and magnesium are, however, also constituents in common minerals, and as such they can be derived also from atmospheric dust which is, mainly, finely divided mineral matter.

Components invariably to be expected in particles of *marine origin* are primarily chloride, sodium and sulphate. These particles which are also called *sea salt particles* have been investigated quite extensively during the last years and will be discussed at some length in a later section. They occur as crystals or liquid droplets, depending on the relative humidity of the air, in a size range from about 0.1 μ (1 μ = micron = 10^{-4} cm) to 20 μ or even greater or, in weight, from 10^{-14} to 10^{-8} g or greater. The actual size distribution has been investigated on many occasions especially by Woodcock and co-workers (1949, 1950 a, 1950 b, 1952, 1953, 1955, 1957). The size distribution can within not too wide limits, be approximately described by the so-called inverse r^3 law originally proposed by Junge (1952).

$$\frac{dN}{d(\log r)} = \frac{k}{r^3} \qquad (2.1)$$

where N is the number of particles equal to or greater than the radius and k is a constant. The simple formula above implies that each logarithmic size interval contains the same mass of sea salts (see fig. 2.1.) Considering a wider range of particle sizes it can, however, be inferred when the frequency of particles is expressed as a function of the logarithm of

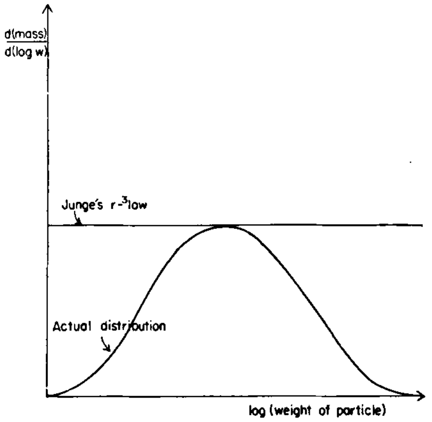

Fig. 2.1. Schematic mass-weight distributions of particles in the atmosphere.

size (or weight) that the mass is more or less normally distributed. (See fig. 2.1.)

The term *sea salt particles* should not be taken as indicating that the relative composition is exactly that of sea water. JUNGE (1956, fig. 2) has found that the larger particles contain sodium and chloride in approximately the same proportion as sea salts, but in smaller particles, sulphate is present in a greater proportion than in the sea. This phenomenon, which does not exclude the marine origin of the excess sulphate, will be discussed in more detail later. At present it will be understood that sea salt particles largely if not altogether represent constituents derived from the sea, though the proportions of these are not quite the same as in sea water.

Besides sea salt particles there are also smaller hygroscopic condensation nuclei, the so-called *Aitken nuclei* of a size less than 0.1 μ. Practically nothing is known about their chemistry but it has been inferred from experiments that condensation nuclei of similar size and properties can be produced in a number of processes such as combustion, photochemical reactions, etc. Their concentration in densely populated areas is very great, generally amounting to several ten thousands per cm^3. Over the sea as well as over sparsely populated areas they

TABLE 2.1

The chemical composition of the troposphere (1 atm. pressure)

	Compound	Partial pressure in atmospheres	Concentration in microgram per m^3	Remarks
Nitrogen	N_2	0.78101		constant
Oxygen	O_2	0.20946		constant
Water	H_2O	~ 0.02		very variable
Argon	Ar	0.00917		constant
Carbon dioxide	CO_2	3.3×10^{-4}		somewhat variable
Neon	Ne	1.82×10^{-5}		constant
Helium	He	5.24×10^{-6}		constant
Methane	CH_4	1.5×10^{-6}		constant
Krypton	Kr	1.14×10^{-6}		constant
Nitrous oxide	N_2O	5×10^{-7}		constant
Hydrogen	H_2	5×10^{-7}		constant
Ozon	O_3	$\sim 5 \times 10^{-7}$		very variable
Carbon monoxide	CO	1×10^{-7}		variable
Xenon	Xe	8.6×10^{-8}		constant
Sulfur dioxide	SO_2	1×10^{-8}		somewhat variable
Ammonia	H_2N	$\sim 5 \times 10^{-9}$		variable
Hydrochloric acid	HCl	$\sim 10^{-8}$		variable
Nitrogen dioxide	NO_2	$\sim 10^{-9}$		variable
Iodine	J_2	$\sim 2 \times 10^{-13}$		variable
Chloride	Cl		~ 1	very variable
Sulfate-sulfur	SO_4-S		~ 1	very variable
Ammonia nitrogen	H_3N-N		~ 1	very variable
Nitrate nitrogen	NO_3-N		~ 1	very variable
Sodium	Na^+		~ 1	very variable
Calcium	Ca^{2+}		~ 1	very variable
Magnesium	Mg^{2+}		~ 0.5	very variable
Potassium	K^+		~ 0.5	very variable

are usually low in number (cf. LETTAU 1939). An extensive review of Aitken nuclei distribution is given by LANDSBERG (1938). Quantitatively they cannot be as important as sea salt particles as they are mainly products of combustion.

Another important category of particles, which has been mentioned before, is the group of insoluble mineral particles classified meteorologically as *atmospheric dust*. Too little attention has been given to these, as it usually has been inferred that they are of local origin. They range in size from 10 to 0.1 μ. Obviously they are derived from soils and, more important, the bulk of them must originate in arid regions with little or no vegetative cover or in semi-arid areas with well developed agriculture. Conditions in humid regions do not as a rule favour the release of these particles from the soil surface.

Some information exists about dust in the atmosphere although no systematic collections have been made. The reports mostly concern "dust falls", i.e. cases where precipitation contains appreciable concentrations of dust. But actually it appears that dust is normally just as common as sea salts in precipitation. This can be inferred from analyses of snow collected in Finland during the late winter, published by VIRO (1953). The amount of silica (SiO_2) in his analyses, which must come from such dust, is quite substantial and is of equal geochemical importance as the sea salts.

2. *Circulation of atmospheric constituents*

The *circulation* of an *element* is defined as net transports of the element or a compound containing the element along closed paths in nature. It is clear from this definition that purely molecular exchange between, for instance, the atmosphere and the sea surface is not a part of a circulation unless a net transport takes place.

It can be shown (cf. ERIKSSON 1959) that practically all constituents in the atmosphere take part in circulations. They are added to the atmosphere in certain regions and withdrawn from the atmosphere in other regions. Every constituent thus spends a certain average time in the atmosphere, between the addition and the subtraction, this time being called *residence time* and is generally defined as the ratio of the amount of the constituent in the atmosphere divided by the rate at which it is added to the atmosphere in the particular circulation studied.

In many of the circulations the transported amount returns quantitatively to the regions where it is added to the atmosphere. A few elements, however, are radioactive and are consequently subjected to decay during the circulation. Of special interest are those who are formed in the atmosphere by cosmic radiation. In their circulations they resemble the corresponding inactive isotopes except for the continuous disappearance by decay.

Other radioactive isotopes, added from land surfaces are radon and thoron which, by their decay forms a series of elements that partly will accumulate on the deep sea floor as lead isotopes. This circulation is not closed in the sense defined but represents a net transport from one region to another without any foreseeable return.

Localities where a net addition of chemical constituents to the atmosphere takes place will be referred to as *source regions* as they often are of considerable areal extent. The regions where a net subtraction of chemical constituents from the atmosphere takes place are, consequently, called *sink regions*, also those of large areal extent.

The circulation path in the atmosphere can be both *zonal*, i.e. along latitude circles, or *meridional*, i.e. across latitude circles. The distinction between these two transports is significant for the following reason. The average air circulation is zonal and one could imagine a planet where it was strictly zonal. In such a case zonal transports would be simple advections but meridional circulations would be strongly impeded. The air circulation on the earth has, however, meridional components though no net transport of air takes place meridionally. These components can be rather steady features as in the subtropical high pressure systems over the oceans and, to some degree, in the blocking situations that can build up at higher latitudes. They can also be irregular in time and space as in the travelling cyclones or in the meandering jet stream at higher altitudes. All these features of the atmospheric motion greatly facilitates meridional transports of chemical and physical properties. In regions where they are irregular in time and space their effect can be looked upon as a large scale *diffusion process* (often called *large scale eddy flux*).

The large scale eddy flux of a compound in a region where irregular features of the air circulation prevail will manifest itself by time variations in the concentration of the compound in the air that passes a fixed point on the earth's surface. These variations are, of course, irregular, but their relative average magnitude defined in a suitable manner seems to be inversely related to the atmospheric residence time of the constituent studied.

Examples on meridional circulations of elements have been given recently by ERIKSSON (1959) who infers that all permanent gaseous constituents in the atmosphere must show a net transport in the atmosphere from equatorial-subtropical regions to temperate-polar regions, the return taking place in the oceans. The reason for this is the variation of solubility of gases in water with temperature, the difference in temperature of ocean surface water in low and high latitudes and the ocean circulation as manifested by the salinity distribution in the sea and the net evaporation pattern over the sea surface.

A typical and well recognized *meridional* circulation is shown by water, low latitudes being its source region for the atmosphere and high latitudes its sink regions. The residence time of water in the atmosphere in its meridional circulation is short, about a month, and the relative variations of water vapor pressure in the atmosphere are very large. Carbon dioxide has a similar circulation but as its residence time in this meridional circulation may be of the order of 100 years or so, its relative variation in the atmosphere is quite moderate, amounting to only a few per cent. Finally, a gas like argon, that also must circulate in the same manner, has a residence time of perhaps 100,000 years or more and any variation would probably be hard to detect by any known analytical procedure.

When illustrating the circulation of an element it is convenient to do this on a global scale and divide the nature into *reservoirs* between which the element is transferred. One of these reservoirs is logically the *atmosphere*, i.e. the gaseous phase of the globe. The liquid phase or the *hydrosphere*, represented practically entirely by the oceans, is another logical reservoir. The *solid inorganic phase* may be divided into two reservoirs, one is the *litosphere* and the other the *pedosphere*, i.e. the soil where plants are rooted and which is a medium where all three phases plus organic dead and living matter are intimately mixed. *Living plants* that use the sun's energy in assimilating carbon dioxide may be divided into a reservoir of land plants and another for marine plants. The distinction is significant because land plants take the carbon dioxide and possibly other elements from the atmosphere while marine plants use dissolved carbon dioxide and other elements in sea water.

The decay of plants takes place in many steps in which animals and other parasitic organisms take part. As they together with undecomposed organic matter represent a certain storage of not only carbon dioxide but also nutrients like nitrogen and sulphur they are conveniently regarded as a reservoir of *undecomposed organic matter* in nature. Again, a distinction should be made between a land reservoir and a marine reservoir of undecomposed organic matter.

3. *Vertical transports*

Vertical transport of properties in the atmosphere depends on four processes, namely convection, turbulent diffusion and molecular diffusion and in the case of particles, fall by gravity. Convection is a selective vertical transport of warmer air through the environment and is ultimately dependent on the vertical stability of the air.

Turbulent diffusion can be pictured as a random motion of air parcels of different size and is caused by wind shear which, together with the inertia of the air causes instabilities in an air stream leading to formation of eddies which move in all directions relative to the mean wind. These eddies are finally elongated to long filaments and across their large surfaces molecular diffusion causes them rapidly to lose their identity (cf. WELANDER 1955). By this mechanism rapid transports of properties can take place vertically, provided the earth's surface acts as a sink or a source. Close to the surface, however, in the so-called laminar boundary layer turbulent elements disappear so that molecular diffusion, or in the case of particulate matter, the fall by gravity and impingement are the ultimate transport mechanisms. The thickness of this layer is of the order of magnitude 0.1 cm.

Near the ground the effect of convection is difficult to separate from turbulent diffusion. For this reason it is included in the turbulent diffusion which then depends strongly on the vertical stability of the air. This is, of course, also true when vertical stability is such that no convection occurs. Even then the vertical stability influences the turbulent diffusion. But the dependence of turbulent diffusion on the stability cannot be of the same nature in a stable stratification and in an unstable.

The transport by turbulent diffusion can be expressed mathematically in the same way as molecular diffusion. If F is the vertical turbulent flux of a property present at a density of ϱ, the flux is related to the gradient of the property by

$$F = -K\frac{\partial \varrho}{\partial z} \qquad (2.2)$$

z being the vertical height coordinate and K the turbulent diffusion coefficient. Generally K increases rapidly with height which means that $\frac{\partial \varrho}{\partial z}$ decreases if F is the same at all levels. K is further a function of the wind velocity and the stability of the air. In general, K changes so rapidly near the earth's surface that $\frac{\partial \varrho}{\partial z}$ for any property is difficult to evaluate already at a few meters' height above the surface.

As K can be assumed to be the same for the vertical transport of all chemical constituents in the atmosphere the following relation can be taken advantage of. For a compound a and b we can write

$$F_a = -K\frac{\partial \varrho_a}{\partial z} \qquad (2.3)$$

$$F_b = -K\frac{\partial \varrho_b}{\partial z} \qquad (2.4)$$

and consequently

$$\frac{d\varrho_a}{d\varrho_b} = \frac{F_a}{F_b} \qquad (2.5)$$

Integrating between two levels z_1 and z_2 one gets (assuming F_a and F_b to be constant)

$$\Delta\varrho_a = (\varrho_a)_{z_2} - (\varrho_a)_{z_1} = \frac{F_a}{F_b}\left[(\varrho_b)_{z_2} - (\varrho_b)_{z_1}\right] = \\ = \frac{F_a}{F_b}\Delta\varrho_b$$

or

$$F_a = F_b\frac{\Delta\varrho_a}{\Delta\varrho_b} \qquad (2.6)$$

For many chemical constituents of interest their density at the interface air-ground (the ground taken to represent also surfaces of vegetation) may be zero. The density in free air at normal observation height (~ 2 m) can be easily assessed experimentally. Thus if F_b and $\Delta\varrho_b$ represent a property like water vapor and is known, merely measurements of the density in air of any other property makes it possible to calculate its flux. Assuming that we know $\Delta\varrho_{H_2O}$ and F_{H_2O} we can obviously define a kind of a vertical transport velocity w by

$$w = \frac{F_{H_2O}}{\Delta\varrho_{H_2O}}$$

which can be interpreted as the rate at which fresh air is steadily brought in immediate contact with the ground. This concept of a vertical velocity in the case of vertical transports of chemical quantities has been used earlier by EGNÉR (1932) when discussing nitrogen losses from soils and manure and recently by CHAMBERLAIN & CHADWICK (1953) in connection with absorption of radioiodine by soil and vegetation. If w is known, then apparently

$$F_a = w\Delta\varrho_a \qquad (2.7)$$

The velocity w averaged over a longer period also depends on the roughness of the ground. A value for the subtropical ocean regions can be estimated crudely in the following way. The evaporation in trade wind regions between 15 and 25° S or N of the equator is according to WÜST (1954) about 130 cm per year. This means that the daily flux is $\frac{130}{365} = 0.356 \text{ g} \times \text{cm}^{-2} \times \text{day}^{-1}$. In these regions the relative humidity from ship measurements, averaged over a year is around 80 per cent and as the water temperature is around 25° the density of water vapor at the surface must be 23×10^{-6} g × cm^{-3}. Thus, $\Delta \varrho_{H_2O} = 4.6 \times 10^{-6}$. Then w becomes 7.5×10^4 cm × day^{-1} or 0.87 cm × sec^{-1}.

This value may be regarded as a minimum value as the air is always slightly stable in trade wind regions (WYMAN-WOODCOCK expedition, unpublished). Over land, especially when heated in summer, the turbulent exchange is presumably greater due to convectional processes. On the other hand, low air inversion due to nocturnal cooling of land will reduce the turbulent exchange considerably at times. So from these points of view the value around 1,000 m per day may apply also to continents, maybe except for wooded regions where the roughness of the ground leads to very strong turbulence.

Particulate matter has also a certain settling velocity which will ultimately bring particles to the ground. For such particles the vertical transport is given by

$$F = -K\frac{\partial \varrho}{\partial z} + V\varrho \qquad (2.8)$$

where V is the fall velocity and is negative. From this

$$F = w\Delta\varrho + V\varrho \qquad (2.9)$$

which shows that the transport is made up of two quantities, one turbulent and one due to settling. In the case of particles, however, conditions in the laminar boundary layer differ vastly from conditions in the case of transport of molecules. Particles are practically uninfluenced by molecular processes so that no gradient whatsoever can be developed in the laminar boundary layer where fall velocity is the only transport means. This means that in a steady state process where the surface does not generate particles, $\Delta\varrho$ will be zero unless the fall rates are increased in the boundary layer.

When air is moving over land covered with vegetation, the inertia of particles can increase the apparent fall rate near the ground due to impingement of particles on leaves, needles and other obstacles. With the normally occurring wind speeds it can be shown that objects of a diametre of 1—2 mm are effective for removing larger particles by impingement. Pine and spruce needles should be effective in removing particles by impingement and in such a case a turbulent transport from higher levels will take place. One prerequisite for removal by impingement is, however, that the particles are retained for some specific reasons. This is mostly the case for sea salt particles because they are hygroscopic and wet even at low relative humidities.

A turbulent transport of gases can only take place if the gases are absorbed, or released, by the ground, i.e. soil and vegetation. Absorption can be predicted from the known properties of gases once the chemical properties of soil and vegetation are known.

4. *Sources of chemical constituents in the atmosphere*

a. Continental sources

We have been concerned so far only with the removal of chemical constituents from the atmosphere. The ground can also act as a source which is apparent from the existence of particulate matter or dust in the atmosphere. It is also clear that the ground can be a source of gaseous constituents.

Very obvious sources of both particulate and gaseous material due to human activities are found in densely populated districts with much industrial activity. Important areas in this regard can be found in western Europe and the north-eastern United States. The output of material into the atmosphere from these regions is obviously of great local importance and much work assessing atmospheric pollution has consequently been done. On the other hand the importance of these source areas on a global scale may have been considerably overestimated.

α. *Sources of particulate matter.* Atmospheric dust has been discussed earlier to some extent and it was inferred that the source regions must be the arid parts and agricultural areas of our continents. Dust appears in precipitation as well, therefore it may influence its composition. This influence depends, however, on the technique of analysis of precipitation samples as well as on the kind of dust which is carried by the atmosphere.

The composition of atmospheric dust must reflect the composition of the top soils in arid and agricultured regions. From the composition of these it can be inferred that the insoluble material consists of the three most common minerals, quartz, feldspar and mica, probably with a greater weight of quartz. Arid regions often contain calcium carbonate and calcium sulphate in the top layer; in this case these two could be present in the air representing compounds which are not readily soluble but still found in solution. Calcium carbonate, which is more frequent and which is probably easier to get into the air, would probably not exist as such for long when much sulphur dioxide is present in the air which on oxidation converts the carbonate into sulphate. Calcium sulphate is comparatively soluble, at least when considering such dilute systems as rain water. It is, however, of no use to speculate further on these two compounds as there is too little evidence concerning their presence in the atmosphere at present. It can be mentioned, however, that carbonate particles, which are easy to identify, have been detected in dust collected by impingement on glass slides in northern Sweden (unpublished results).

Salt efflorescences occur in large areas of the arid regions in top soils. It could perhaps be expected that these salts would be carried up into the air together with dust particles and thus be transported away from the arid regions. There is, however, some evidence that such a transport of easily soluble salts is not too important. Some salt particles may be carried into the air as observed by CROZIER & SEELY (1952) above the Mojave Desert in western United States. The number of such particles, however, was generally low compared to the number of salt particles encountered in maritime air masses above this region, and seemed to be correlated with the number of dust particles. In Quetta, situated on the Beluchistan highland in Pakistan, thick dust haze coming from the deserts to the west where large areas of salt waste are found is often experienced during summer. FOURNIER D'ALBE (1955) investigated the salt nuclei content in the surface air layer at this place and found no significant rise in the number of hygroscopic nuclei during these occasions. He thinks that the salts in the salt wastes are present on the surface as fairly large grains which, though raised by strong winds, rapidly fall out again under the influence of gravity. Therefore very little is actually carried away by wind from these regions. They may, however, influence the composition of precipitation locally.

There is thus far no evidence of any substantial transport of easily soluble salts from the arid regions.

The transport of insoluble mineral matter from arid regions into humid areas is, of course, a transport of great geochemical importance. The windborn soil material known as loess must be derived from such transports. The classical example of such soils is the extensive loess deposits in parts of China which are believed to be derived from the arid central part of Asia. The yearly amounts transported need not be great; in a few million years substantial deposits will be the result even if the yearly amount precipitated is of the order of only kg × ha^{-1} × $year^{-1}$.

From the fact that loess deposits are calcareous, i.e. contain calcium carbonate, it might be inferred that calcium carbonate is a significant constituent of atmospheric dust.

β. Sources of gaseous compounds. The land surfaces, or better, the continental surfaces can be sources of gaseous compounds. A well known example is the escape of radon from soil, produced by desintegration of radium in rock material. Other gaseous compounds produced in the soil are ammonia, carbon dioxide, nitrous oxide and probably hydrogen sulfide.

Hydrogen sulfide is easily formed by bacterial reduction of sulphate. This occurs where organic substances are present but oxygen is absent. The bacteria use the oxygen of the sulphate for oxidizing organic matter, and thereby gain energy necessary for their sustenance. This process occurs most frequently in swamps, bogs, soils with a high water table and in lakes with stable stratification. Even in normal well drained soils reduction processes can occur which may produce hydrogen sulfide. A good soil consists of aggregates of soil material and when wet, these are sites of anaerobic processes in which sulfur may participate.

In the reduction of sulphate ferrous sulphide may be formed. This is a rather common mineral in many soils high in organic matter, formed by sedimentation in water (for instance the "gyttja" soils of Sweden). If there is not a sufficient amount of ferrous iron present H_2S

will form. As the solubility of H_2S in water is rather moderate, its escaping tendency is great and it gradually diffuses into the atmosphere. Hydrogen sulfide is also formed during decomposition of sulfur containing organic matter.

The best known example of sulphate reduction in water is given by the Black Sea where the content of H_2S in deep water is very great (NIKITIN, 1931).

Lakes in tropical and subtropical regions often contain very stable stratified water as a result of warm surface conditions. This deprives deep layers of water of oxygen, and hydrogen sulphide forms as a consequence. Large lakes in tropical Africa, investigated by BEAUCHAMP (1953), are remarkably low in sulphate when compared with chlorine. It seems likely that large quantities of hydrogen sulphide are being released to the atmosphere. Similarly ANDERSON (1945) noticed a deficiency of sulphate in some south Australian lakes where he also was able to smell hydrogen sulphide. The limit of detection of H_2S by its odor is near $20\,\mu g \times m^{-3}$, consequently there must be appreciable concentrations in the atmosphere around these lakes.

The reduction of sulphate in ground waters makes them alkaline as pointed out by RIFFENBURG (1925). He found that when water seeps through sedimentary beds high in organic matter it becomes alkaline. Since H_2S is formed in such processes certainly some, if not the main part, must reach the atmosphere. H_2S which escapes to the atmosphere is oxidized to SO_2 and finally SO_3 which in turn is brought to earth again.

Release of HCl from the ground may occur with the help of sulphur trioxide. Sulphur trioxide which is very hygroscopic, is formed by oxidation of SO_2. With water it forms sulphuric acid which has a very low escaping tendency. Therefore both SO_3 and H_2SO_4 can be rapidly removed from the atmosphere or added to condensation nuclei. In salt waste regions rich in sodium chloride the presence of SO_2 in the air may lead to a loss of HCl. As SO_3 is formed it reacts with NaCl and water forming sodium sulphate and hydrochloric acid. This process is actually employed in the most common commercial method for the manufacture of hydrochloric acid.

b. Oceanic sources

The open ocean areas can contribute chemical constituents to the atmosphere in two ways. One is by mechanical disintegration of water into small droplets which evaporate, leaving droplets of concentrated solutions or crystalline matter as small particles in the atmosphere. The other is by gaseous diffusion through the interface water-air.

In addition to the open sea areas there are the borders of the sea in which the same two processes occur on a magnified scale. Production of sea salt particles in a surf has been known for long and the role of intertidal flats for production of various gases is obvious, considering the abundance of organic material and the anaerobic character of these deposits.

As to the mechanical processes of water disintegration these have been studied relatively recently by WOODCOCK, KIENTZLER, ARONS and BLANCHARD (1953a) who discovered that bursting bubbles in sea water eject a number of small droplets into the air which, upon evaporation, form small sea salt particles. Bubbles are, of course, produced by breaking waves which always occur frequently when the wind force exceeds four (Beaufort). BLANCHARD & WOODCOCK (1956) have, however, also discovered other processes of bubble formation. One is by impaction of drops on a water surface, another which produces very small bubbles takes place when snow flakes fall into water, air being entrapped as small bubbles.

All these processes have been studied in detail by BLANCHARD & WOODCOCK (l.c.) who related the number of particles produced and their size to the size of the bursting bubbles and they account satisfactorily for the amount and distribution of sea salt particles in air over ocean areas. Breaking waves seem to be quantitatively the most important and naturally one would expect the production of sea salt particles to be related to the wind force which is also the case as shown by WOODCOCK (1953).

Thus, a satisfactory mechanism exists by which disintegrated sea water is carried into the air. Once in the air the droplets formed are influenced by gravity which tends to carry them back to the sea surface. On the other hand they are influenced by the turbulence of the air which tends to distribute them in all directions. At the same time evaporation sets in which tends to reduce the gravitational settling by increasing their specific surface. The final distribution of sea salt particles in the atmosphere over a source region will largely depend on the rate of production of sea water droplets, their rate of evaporation and the turbulence of the air.

In the steady state which requires a constant source of the surface we have

$$-K\frac{\partial n}{\partial z}+Vn=0 \qquad (2.10)$$

where K is the turbulent diffusion coefficient, n the volume concentration of particles of a certain size, V the fall velocity and z the vertical coordinate. It is seen that provided K is constant the distribution will be simply exponential (V being negative), namely

$$n=n_0 \exp\,(Vz/K) \qquad (2.11)$$

As the flux down to the surface where K is very small is Vn_0, the rate of production must be the same. But this is the rate of production of sea salt particles, *in equilibrium with the relative humidity of the environment.* The equilibrium mass and volume of a sea salt particle (relative to the mass and volume of the corresponding sea water droplet of 35 % salinity) at different relative humidities can be calculated from available data on the vapor pressure of sea water at different salinities (ARONS & KIENTZLER 1954) and from the densities of sodium chloride solutions found in chemical handbooks. Table 2.2 gives the results of these computations for relative humidities between 75 and 100 per cent. RH is the relative humidity under equilibrium conditions, S the salinity in $\mathrm{g\cdot kg^{-1}}$, ϱ the density of sodium chloride solutions of the same satinity, ϱ/ϱ_0 the relative density, W/W_0 the relative volume, r/r_0 the relative radius and $V/V_0=\varrho/\varrho_0\,(r/r_0)^2$ the relative fall velocity. The last hold within the size range of particles considered here.

Table 2.2 shows that the decrease in fall velocity is appreciable already at 97 % RH when it has decreased to about 2/3 of the original. To decrease this value at 97 % RH to half, one has to decrease RH to 88 %. From 90 to 80 % the change in fall velocity is rather small, but an appreciable reduction occurs at around 75 % when NaCl crystallizes. Altogether, the fall velocity is reduced by a factor of about 7 by the complete evaporation of a sea water droplet.

TABLE 2.2

Salinity, density, relative volume, radius and fall velocity of sea salt particles at different relative humidities all at 25° C

RH per cent	Salinity S in $\mathrm{g\cdot kg^{-1}}$	Density ϱ $\mathrm{g\cdot cm^{-3}}$	Relative volume W/W_0	Relative radius r/r_0	Relative fall velocity V/V_0
98.2	35.2	1.024	1.000	1.000	1.000
98	39.2	1.026	.898	.966	.930
97	56.0	1.039	.620	.853	.739
96	73.2	1.051	.468	.777	.620
95	86.7	1.061	.392	.733	.556
94	99.3	1.070	.339	.698	.509
93	112.5	1.080	.297	.668	.469
92	124.3	1.089	.267	.645	.441
91	137	1.099	.240	.622	.414
90	147.7	1.107	.221	.605	.394
88	168.5	1.122	.191	.576	.364
86	189.5	1.140	.167	.551	.337
84	206.8	1.153	.151	.532	.319
82	225	1.168	.137	.516	.303
80	241	1.182	.1266	.502	.291
78	257	1.195	.1173	.490	.279
76	273	1.208	.1092	.478	.269
75	281 (sat)	1.215	.1057	.473	.266
75	1,000 (dry)	2.1	.01677	.256	.139

TABLE 2.3

Fall velocities of sea water droplets and of sea salt particles in equilibrium with 91.4 per cent relative humidity and time constants for changes in the fall velocity with changing relative humidity. *w* is weight of sea salt in particles in μμg; $r_{91.4}$ radius at 91.4 % RH

r_0 in μ	$r_{91.4}$ in μ	w in μμg	log w	V_0 cm · sec⁻¹	$V_{91.4}$ cm · sec⁻¹	τ in sec	$3\tau V_0$ cm
.872	.550	.100	—1.00	.0091	.0038	.022	$.6 \cdot 10^{-3}$
1.058	.667	.178	— .75	.0133	.0056	.032	$1.3 \cdot 10^{-3}$
1.28	.807	.316	— .50	.0195	.0082	.047	$2.8 \cdot 10^{-3}$
1.55	.976	.563	— .25	.0287	.0121	.070	$6.0 \cdot 10^{-3}$
1.88	1.178	1.000	± .00	.0420	.0176	.102	$1.3 \cdot 10^{-2}$
2.28	1.436	1.78	.25	.0618	.0260	.150	$2.8 \cdot 10^{-2}$
2.76	1.74	3.16	.50	.0905	.0380	.22	$6.0 \cdot 10^{-2}$
3.34	2.10	5.63	.75	.133	.056	.32	$1.3 \cdot 10^{-1}$
4.05	2.55	10.00	1.00	.195	.082	.47	$2.8 \cdot 10^{-1}$
4.91	3.09	17.8	1.25	.286	.121	.70	$6.0 \cdot 10^{-1}$
5.94	3.75	31.6	1.50	.420	.176	1.02	1.3
7.20	4.53	56.3	1.75	.618	.260	1.50	2.8
8.72	5.50	100	2.00	.905	.380	2.2	6.0
10.58	6.67	178	2.25	1.33	.56	3.2	13
12.8	8.07	316	2.50	1.95	.82	4.7	28
15.5	9.76	563	2.75	2.87	1.21	7.0	60
18.8	11.78	1,000	3.00	4.20	1.76	10.2	130
22.8	14.36	1,780	3.25	6.18	2.60	15.0	280
27.6	17.4	3,160	3.50	9.05	3.80	22	600
33.4	21.0	5,630	3.75	13.3	5.60	32	1300
40.5	25.5	10,000	4.00	19.5	8.20	47	2500

The evaporation will take a certain time which is a function of the relative humidity and the original size of the droplet. The evaporation rate can be approximated to a steady state for our purpose and with this assumption

$$\frac{dW}{dt} = -4\pi r D \Delta\varrho \qquad (2.12)$$

where W is the volume and r the radius of the drop, $\Delta\varrho$ is the vapor density difference between the surface of the drop and at infinity, i.e. that of the environment while D is the molecular diffusion constant which for water vapor can be put equal to 0.3 cm² × sec⁻¹. As $\frac{dW}{dt} = 4\pi r^2 \frac{dr}{dt}$ we get

$$r\frac{dr}{dt} = -D\Delta\varrho \qquad (2.13)$$

which shows that the decrease in radius is a parabolic function of time at least for the initial state. An approximate treatment of the problem can be done by putting

$$\Delta\varrho = \frac{36\,\overline{S}\,\varrho_0}{58\left(1+\frac{LD}{K}\frac{d\varrho}{dT}\right)} \cdot \frac{r^2-r_0^2}{r_0^2} \qquad (2.14)$$

where r_0 is the equilibrium radius and ϱ_0 the equilibrium vapor density, $\overline{S}$ the average salinity in g · g⁻¹ of the drop in the size interval studied, L the latent heat of evaporation, D the molecular diffusion coefficient for water vapor, K the heat conductivity of air and T the temperature. The term within brackets accounts for the effect of heat of condensation or evaporation on the vapor pressure of the droplet. Evaluation of

$$\frac{36\,\overline{S}}{58\left(1+\frac{LD}{K}\frac{d\varrho}{dT}\right)}$$

in the range RH 91.4 to 98.2 and 25°C and $\overline{S} = 87 \cdot 10^{-3}$ gives 0.0115 so we can write

$$\frac{d(r^2)}{dt} = -0.023\varrho_0 D \frac{r^2-r_0^2}{r_0^2} \qquad (2.15)$$

or

$$\frac{d(r^2)}{r^2-r_0^2} = -\frac{0.023\varrho_0 D}{r_0^2} \qquad (2.16)$$

which incidentally shows that the fall velocity which is proportional to r^2 changes approximately exponentially with a time constant τ

$$\tau = \frac{r_0^2}{0.023\varrho_0 D} \qquad (2.17)$$

Some values of τ for $\varrho_0 = 2 \cdot 10^{-5}$, $D = 0.3$ and various equilibrium radii is given in table 2.3 where also the weight of the salt in the particle is given as well as the fall velocity V_0 for a droplet in equilibrium with sea water and in equilibrium with 91.4 per cent relative humidity. In the same table also 3 τV_0 is calculated to show the magnitude of the distance travelled before the equilibrium velocity through evaporation is attained. It is seen that this distance is proportional to the forth power of the radius and is very small for small particles but appreciable for large particles. The calculations are made so that the time of evaporation for ejected sea salt droplets of different size can be estimated. It is evident that this time has some influence on the possibility of ejected sea salt droplet to be removed by turbulence into the air through the turbulence itself must be a much more important factor.

It is apparent that a selective process occurs at the sea surface whereby the smaller salt particles are favored compared to big ones. A given distribution of sea water droplets generated will be considerably modified in the layer close to the surface. A low relative humidity will favor the formation of larger sea salt particles because of a more rapid evaporation. As the main mass of salt is found in the larger particles, regions of low relative humidity like trade wind regions can be expected to be important source regions for sea salts in the atmosphere. Other areas also produce sea salt particles but production of the larger particles is impeded by the high relative humidity so that presumably smaller particles are produced in any number.

It is known that a substantial poleward transport of water vapor takes place carrying latent heat from subtropical into temperate zones. Similarly, a net transport of sea salt particles probably takes place from the subtropical regions into the temperate zones. This is strongly suggested by the fog water analyses carried out by CUNNINGHAM (1941) on the north-east coast of the U.S.A. He found much larger chloride concentrations in fog water from air masses of tropical origin than in polar air masses.

The main regions of sea salt particles generation in the temperate zones must be the cyclone tracks due to frequent high wind velocities though probably not in the warm sector of a storm. The cold air side of a cyclone has, of course, much more favorable conditions for sea salt generation as the air is being heated along its way.

Bursting bubbles in the sea can also be expected to remove organic matter in surface films that are always present on the sea surface. This mechanism for removal was discovered accidentally by WOODCOCK et al. (1953) in their experiments on bursting bubbles. It is felt that this is a geochemically important process which probably accounts for the presence of organic matter in rain and snow even when collected in places where hardly any vegetation grows and no human contamination is present.

The oceans are also sources of gaseous compounds, an aspect which has been discussed recently by ERIKSSON (1959) as mentioned earlier. There are, however, gaseous compounds that are formed in the biological cycle either in the surface layer or in shallow parts of the sea and reaches the atmosphere and are carried in over continents contributing to the circulation of these elements. An element of special interest is sulphur whose circulation is still puzzling. In order to balance the river run-off of sulphur CONWAY (1942b) hypothesized a production over the shelf areas of H_2S which reached the atmosphere and was carried in over the continents. The possible oceanic sources of sulphur will be discussed later. It may be sufficient at present to point out that intertidal flats which apparently are of a fair extent, may produce quite sizeable amounts of H_2S. It is possible that also the biological turnover in the sea produces sizeable quantities which are brought into the atmosphere.

III. Sea salt particles in the atmosphere

1. *General*

Most of the work on sea salt particles in the atmosphere over oceans has been carried out by A. H. WOODCOCK, Woods Hole Oceanographic Institution in connection with cloud physics studies. Sampling has been done from small aircrafts at different levels by the impaction method on glass slides and identification and measurements by the so-called isopiestic

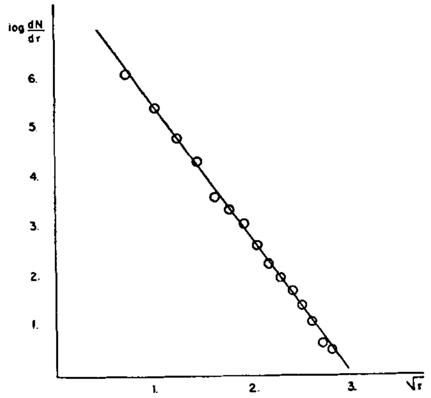

Fig. 3.1. Log $\frac{dN}{dr}$ as a function of $\sqrt{r}$. Average of 67 samplings from Hawaii (Woodcock 1957). N in number · m^{-3}, r in microns (μ).

method. The sampling slides are exposed to a controlled, constant humidity in which the salt particles grow to equilibrium at which their sizes are measured microscopically. The method is not specific for sea salts, as all easily soluble salts will react like sea salt particles. Over the oceans the assumption that these particles are sea salt particles is not entirely correct as will be discussed later though no serious error is introduced in most cases. Over land such a method may be more questionable unless sea salt components are identified in some other way. Twomey (1954) for instance used the phase transition method to establish the identity of sea salt particles samples over Australia. Chemical tests for chloride in sampled particles have been developed by Seely (1952) and later, in a more convenient form by Lodge (1954) enabling them to identify and measure the concentration of chloride particles over continents. Lodge (l.c.) has also developed similar techniques for sulfate and magnesium—ion particles.

Considering the oceans as the main source for sodium and chloride in the atmosphere, it is clear that the data obtained by Woodcock in his sea salt particle studies are most valuable as they may be used to obtain the average sea salt load of maritime air. How far this can be transported into continents can be surmised from investigation by Twomey (1955), Crozier and Seely (l.c.) and Byers et al. (1956) who all sampled from aircrafts. Ground sampling by impactor methods used by Fournier d'Albe (l.c.) in Pakistan seems to be excellenty suited for synoptic studies on a large scale and over longer periods where aircraft sampling would be prohibitively costly.

Some characteristic features of sea salt particle distributions will be discussed in the present section followed by a discussion on the vertical mass distribution at various places in the next section.

a. *Number-size distributions of sea salt particles.* It was mentioned earlier that the formula, developed by Junge (1952)

$$\frac{dN}{d(\log r)} = \frac{k}{r^3} \tag{3.1}$$

where N is the cumulative number of particles per unit volume with a radius smaller than or equal to r and k is a constant, cannot describe number distributions of sea salt particles properly. If (3.1) were valid then the mass of sea salt within each logaritmic size interval would be the same whereas in fact it is more like a normal distribution as pointed out earlier. From this it is apparent that the exponent of r must be a function of r.

It was found, however, from Woodcock's Hawaiian data (1957) that the number distribution could be expressed by a function

$$\frac{dN}{dr} = a \cdot e^{-\beta\sqrt{r}} \tag{3.2}$$

Fig. 3.1 shows the average of all 67 samplings from Hawaii when log $\frac{dN}{dr}$ is plotted as a function of $\sqrt{r}$. It is seen that the data fit relation (3.2) very well over practically the entire size range of sea salt particles. This does not, of course, mean that eq. (3.2) gives a physical interpretation of the whole complex of phenomena that leads to this distribution; the only purpose the equation can have is to describe the nature of the number-size distribution by a simple formula.

Woodcock (1953) summarized earlier values in order to show how the wind strength influenced the number-size distribution, anticipated from the known mechanism of sea salt particle production. The results as presented by Woodcock are shown in fig. 3.2 where N is plotted against w on a log-log scale. The weight w is given in $\mu\mu$g (10^{-12}g). It is

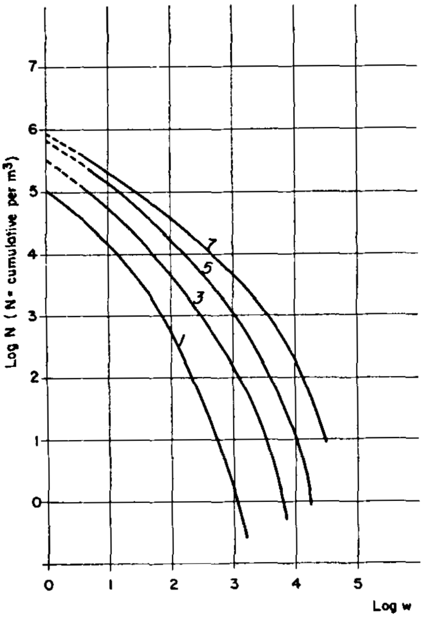

Fig. 3.2. Number-weight distributions of sea salt particles at different wind forces. Wind force in Beaufort. (From WOODCOCK 1953.)

found that these average curves for different wind force (in Beaufort) also seem to fit eq. (3.2) with some exceptions. A plot of the data in a way similar to fig. 3.1 is shown in fig. 3.3. Two things are, however, noted. Firstly, each wind force obeys eq. (3.2) in certain intervals. Below 2 μ the curves run nearly parallell but above that size they have different β values. It looks as if β is influenced by the wind force and actually by converting the wind forces given on the figure into corresponding wind speeds it is found that β most likely is inversely proportional to the square root of the wind velocity in this upper size range or at least inversely related to the wind velocity.

Fig. 3.3 indicates that the nature of the number-size distribution of sea salt particles as expressed by the parameter β is related to external factors at least above a certain size. Below that size β is presumably independent of wind force though the total number is still a function of wind strength.

Eq. (3.2) is not valid in all regions as will be pointed out in the next section.

b. *Mass-weight distributions of sea salt particles.* This kind of distribution is defined as the mass of sea salt per logaritmic weight interval and can be formulated

$$\frac{dm}{d(\log w)} = F(w) \qquad (3.3)$$

where m is the total mass of sea salt per unit volume and w is the weight of individual particles.

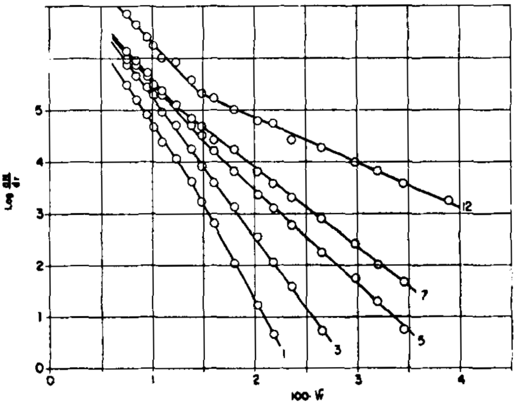

Fig. 3.3. Log $\frac{dN}{dr}$ as a function of $\sqrt{r}$ at different wind forces (in Beaufort), obtained from fig. 3.2. N in number · m⁻³, r in cm.

Considering that

$$dm = -wdN = -wNd(\ln N) \qquad (3.4)$$

it is apparent that the total mass m can be arrived at graphically in two ways. If wN is plotted as a function of $-\log N$ the area below the curve, which forms a kind of a statistical distribution, multiplied by 2.3 will be the total mass of sea salt per unit volume. From (3.4) we can also write

$$dm = -wN\frac{\partial(\ln N)}{\partial(\ln w)}d(\ln w) \qquad (3.5)$$

which shows that if $-wN\frac{\partial(\log N)}{\partial(\log w)}$ is plotted as a function of log w the area below this curve, multiplied by 2.3 will also be the total mass m. Both methods have been employed in the following for estimating the total concentration of sea salt.

The mass-weight distribution defined by $dm/d(\log w)$ have some interesting features. From WOODCOCK's number-weight distributions in fig. 3.2 the corresponding mass-weight distributions have been constructed, and the results are seen in fig. 3.4 where for comparison also the radius is given on top of the diagram. First it can be noted that the mass-log (weight) distributions are approximately normal with well defined maxima. It can also be noted that the maximum in mass density is situated at about 6 μ for the greatest wind force and is shifted towards smaller sizes for lower wind forces. Finally it is seen that the total mass of salt is strongly dependent upon the wind force.

The type of mass-weight distributions seen in fig. 3.4 are prevalent in most regions but there are interesting exceptions which will be discussed later.

2. *Vertical variations over ocean areas*

In section II the behaviour of particulate matter in the atmosphere was discussed and it was shown that at a steady state

$$-K\frac{\partial n}{\partial z} + Vn = 0 \qquad (3.6)$$

where n is the number concentrations of particles who have a fall velocity V (being negative), K is the turbulent diffusion coefficient and z the vertical coordinate. Further conditions implied in this equation are that the particles are conserved, i.e. no coalescence or disintegration of particles or removal by precipitation takes place and secondly that the horizontal gradient of n is zero.

As the fall velocity increases with the size of the particles it is obvious that the number-size distribution must vary in the vertical in such a way as to decrease the mass concentration. This is generally true too but important exceptions occur. MORDY (1959) has found that K in the eq. 3.6 can be computed from WOODCOCK's Hawaii data (1958) for some levels, and gives a value of K around 10^5 cm^2 $\times$ sec^{-1} in agreement with the K-value one can compute from the total evaporation in lower latitudes. At many levels, however, anomalies in the number-size distributions occur showing a far too great excess of large sea salt particles. WOODCOCK (personal communication) who also observed the abundance of large particles around clouds has explained this as due to coalescence of cloud droplets within a cloud and subsequent evaporation which will inevitably lead to an excess of larger particles at cloud level. These higher numbers occur as invisible clouds, often in the rear of tradewind clouds where evaporation of the cloud droplets normally occur. Another mechanism which may operate in cloud and favour large particles is visualized by WOODCOCK as follows. If the cloud is pictured as a ring vortex with moist, salt laden air flowing upward in the center, large salt particles will reach the largest sized cloud droplets. In the upper part of the cloud where the upward moving air diverges the velocity of the air stream decreases. Cloud droplets of the largest size will fall downward closest to the centre but on arrival at the bottom of the cloud they are evaporated and drawn into the upward moving air. Smaller droplets will be carried further out from the cloud before reaching the cloud base level and will have less chance of

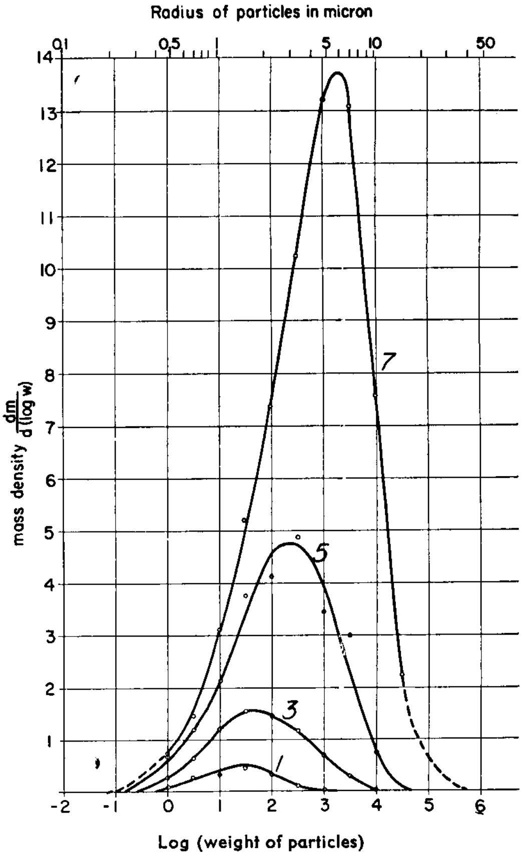

Fig. 3.4. Mass-weight distributions of sea salt particles at different wind forces. Obtained from fig. 3.2. Mass, m, in μg $\cdot$ m^{-3}, w in $\mu\mu$g (10^{-12} g) units.

being drawn into the cloud again than the larger salt particles forming the larger droplets. Such a cloud should thus tend to concentrate larger particles until it dissipates when it leaves an invisible cloud of larger salt particles.

Though these mechanisms explain the anomaly in the vertical number weight distribution of larger sea salt particles they do not explain the sometimes observed fact that the smaller particles which are hardly influenced by gravity under normal conditions, also increase upwards to some level. To understand this we must consider the nature of air flow in trade wind regions. The trades are not the uniform flow of air many times visualized though the steadiness of the winds are great. In these belts the flow of air has a wave-like nature so that winds increase and decrease more or less periodically. As these variations in wind force often are accompanied by wind shifts and weather phenomena like cloudiness and precipitation it has become customary to talk about weather disturbances in the form of waves that may move with the wind or against the wind (cf. Riehl 1954). Such disturbances are always accompanied by higher winds than usually due to convergence and release of latent heat by precipitation in the disturbances. The disturbances may occur on different scales and the best known are those recognizable on a synoptic scale. One significant fact in this connection is that the areal extent of the synoptic disturbances is much less than of the undisturbed regions. On a much smaller scale and much less active, such disturbances may be responsible for the often remarkably regular pattern of cloud areas, i.e. areas where trade wind clouds occur more or less densely distributed. Such patterns have been described by Starr Malkus (1957) from the Caribbean region and are sometimes even stationary, i.e. the air just passes through the cloud areas without moving the whole area.

All this indicates that wind velocities vary from time to time and from place to place and that the areal frequency of high winds is much less than of low winds. As the production of sea salt particles increases rapidly with increasing winds, one can apparently divide the whole trade wind belts into "source" areas and "sink" areas, the latter removing particles from the atmosphere.

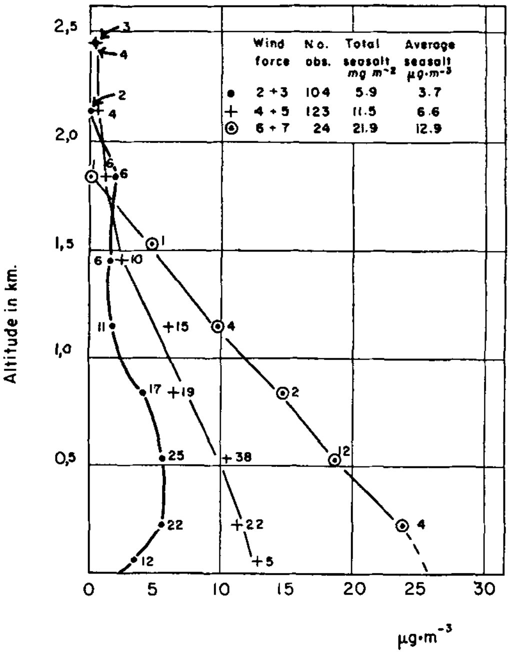

Fig. 3.5. Mass concentrations of sea salt particles as a function of altitude at different wind forces (in Beaufort). From Woodcock (unpublished).

Now, the application of eq. (3.6) is, of course, restricted. A more complete equation should read (considering only two dimensions)

$$\frac{\partial n}{\partial t} + u\frac{\partial n}{\partial x} + V\frac{\partial n}{\partial z} + \alpha n = \frac{\partial}{\partial z}\left(K\frac{\partial n}{\partial z}\right) \qquad (3.7)$$

where u is the wind velocity in the horizontal x-direction and αn is the rate at which particles disappear due to removal by coagulation, coalescence and precipitation. The equation is neglecting vertical motion of air and may be applicable in a sink region where occasional cloud formation and precipitation takes place.

Consider eq. (3.7) in a steady state ($\partial n/\partial t = 0$) when air is emerging from a source region. To demonstrate what happens neglect the fallout and the dispersive term. Then

$$u\frac{\partial n}{\partial x} + \alpha n = 0 \qquad (3.8)$$

which gives

$$n = n_0(z)\, e^{-\frac{\alpha}{u}x} \qquad (3.9)$$

Let $n_0(z)$, the vertical distribution at the source, be exponential of the form exp. $(-z/h)$, then

$$n = n_0 e^{-\frac{z}{h} - \frac{\alpha}{u} x} \tag{3.10}$$

Let u increase linearly with height, say by $u = u_0 z$. Then n has a maximum at

$$z = \sqrt{\frac{\alpha h}{u_0} x}$$

i.e. proportional to the square root of the distance. Thus, as we proceed from the source, a maximum in n is formed close to the surface and is shifted upwards, first rapidly, then more and more slowly.

Inclusion of the dispersive term cannot remove this maximum, only flatten it and inclusion of the fallout term would only shift its position to a lower altitude. The example above is simplified but on can expect such a maximum in the salt load to appear in a sink region whenever the wind increases with height because of more rapid advection from the source region at higher levels than at lower.

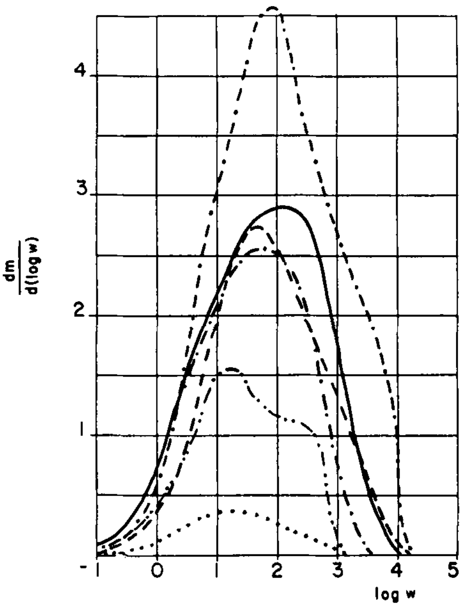

Fig. 3.6. Average mass-weight distributions of sea salts at different altitudes in Hawaii. Mass, m, in μg · m^{-3}, w in μμg (10^{-12} g). Data from WOODCOCK (1957).

———————— 500 feet altitude
— — . — — . 1,000—2,000 feet altitude
— — — — — — — 2,000—3,000 " "
— . — . — . — . 3,000—4,000 " "
— . . — . . — . . 4,000—5,000 " "
. . . . 5,000—8,000 " "

Now we can conclude that if sampling is done regularly at a certain place one would frequently find a maximum in the sea salt particle concentrations around the cloud base level in more normal wind conditions and a regular decrease with height when sampling in strong winds. This can actually be seen in fig. 3.5 (which has been received from WOODCOCK) where the average variations of mass of sea salt with height in three different groups of wind speeds are shown. It is seen that the lowest wind speeds give a clear maximum at about cloud base level. The next group of wind forces give a nearly constant mass with height up to the same level whereas the highest winds show a clear decrease all the way upwards.

Before discussing the mass-weight distributions further it should be remarked that excessive maxima may partly be due to an unfair large proportion of samples from cloud base level compared to lower levels.

Looking at mass-weight distributions at different levels, fig. 3.6 shows the distributions obtained from WOODCOCK's Project Shower data (1957). It is seen that there is a higher average mass density of sea salt in the atmosphere between 1,000 and 2,000 feet than at around 500 feet. From 2,000 feet it is fairly constant up to 4,000 feet which probably is not characteristic for Hawaii but may be influenced by the so-called Kona-storms which occurred in late November and early December in 1954. At higher levels the mass density decreases rapidly.

As to the mass-weight distributions themselves the one at the 500 feet level has a maximum around a particle weight of 100 μμg which corresponds to a radius of 2.2 microns. In the next layer, 1,000—2,000 feet, the maxima in the distribution is shifted somewhat to the left but there is an appreciable mass in large sea salt particles. There is at this level more mass in the interval 1,000—10,000 μμg than in the same interval at 500 feet which may depend on formation of larger particles in the clouds.

At higher levels it is seen that the mass of the larger particles is considerably reduced though the maximum in the distribution is nearly the same. In the highest layers, however, the maximum is shifted close to $w = 10$ μμg which is roughly about 1 micron radius.

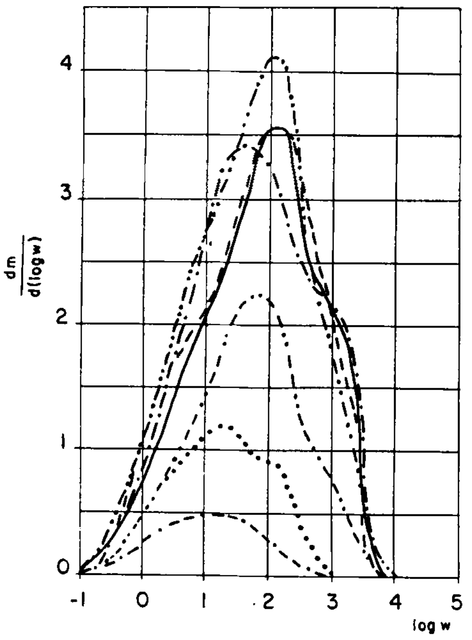

Fig. 3.7. Average mass-weight distributions of sea salts at different altitudes in the Caribbean area. Mass, m, in $\mu g \cdot m^{-3}$, w in $\mu\mu g$ (10^{-18} g). Data from Woodcock (unpublished).

——————— 100 feet altitude
—.—.—.— 500 " "
— — — — 1,000 " "
—..—.. 1,500 " "
— —..— —.. 2,000—2,500 feet altitude
. . . . 3,000—3,500 " "
— —.— —. 4,000—8,000 " "

The next set of mass-weight distributions at various levels shown in fig. 3.7 are from the Caribbean area. Data have been obtained by Woodcock (mostly unpublished) and the sampling was done at various places in the West Indies, from Puerto Rico to Barbados. Similar features to those from Hawaii are seen. The mass of salt per unit volume is nearly constant up to 1,000 feet but shows a maximum at 1,500 feet. From thereon it decreases steadily. The maximum in the mass-weight distribution is again around $w = 100 \mu\mu g$ except at the two highest layers where it is around 10 $\mu\mu g$ just as in the Hawaiian distributions.

Comparing figs. 3.6 and 3.7 one can conclude that there are hardly any regional differences neither in type of distributions, nor in mass of sea salts per unit volume and but small in the vertically integrated load of sea salts.

From these distributions which are obtained in oceanic areas we may proceed to the coast of Florida, a place which is close to a large continent. Woodcock's data from Pompano Beach in Florida have been worked up in a similar way as in figs. 3.6 and 3.7 and the results are shown in fig. 3.8. Here we see something entirely new, namely a bimodal distribution of mass with respect to log w at all levels. This type of distribution can apparently not fit eq. (2). The same type mass weight distribution is also found in a set of data published by Byers et al. (l.c.) to be discussed later. On this occasion they sampled chloride particles which were identified and measured on millipore-filters using Lodge's (l.c.) technique on a flight from New Orleans to Illinois.

One thing that is clearly seen in fig. 3.8 is that the first maximum is centered at $w = 10$

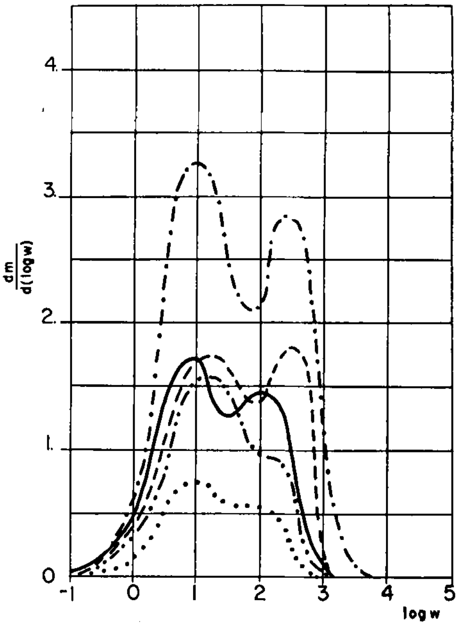

Fig. 3.8. Average mass-weight distributions of sea salts at different altitudes at Pompano Beach, Florida. Mass, m, in $\mu g \cdot m^{-3}$, w in $\mu\mu g$ (10^{-12} g). Data from Woodcock (unpublished).

——————— 100— 500 feet altitude
— — — — — — 800—1,100 " "
—.—.—. 1,400—1,600 " "
—..—..— 3,000—3,200 " "
. . . . 4,000—6,000 " "

$\mu\mu g$ very consistently whereas the second varies from 100 $\mu\mu g$ to 300 $\mu\mu g$. So even the distribution of larger particles is different from those in Hawaii and the Caribbean where the maximum was found close to $w = 100$ $\mu\mu g$ or somewhat below.

It is of little use speculating on the reasons for these differences. The sea salt particles in fig. 3.8 are most probably generated on the adjacent shelf area of the Atlantic and it may be possible that the biological turnover in these comparatively shallow waters give rise to different sea surface properties than in the "deserts" of the open trade wind regions. A special study of sea surface properties would probably shed light on this problem[1].

As to the vertical distribution of mass, a maximum is again found around 1,500 feet just as in the other regions.

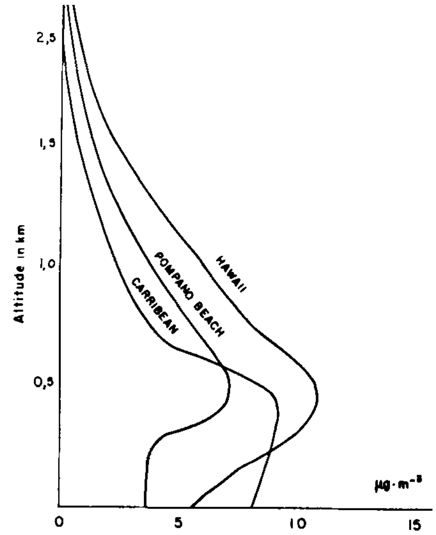

Fig. 3.9. Sea salt particle mass concentrations as a function of altitude at Hawaii, the Caribbean area and Pompano Beach, Florida. From fig. 3.6, 3.7 and 3.8.

There are, unfortunately, no data available from more temperate regions like the North Atlantic. Woodcock (1953) has some data from South Australia but they are too few to base a similar discussion on. The same is true for a couple of vertical profiles from off the isle of Nantucket on the New England coast.

From the mass-weight distributions in figs.

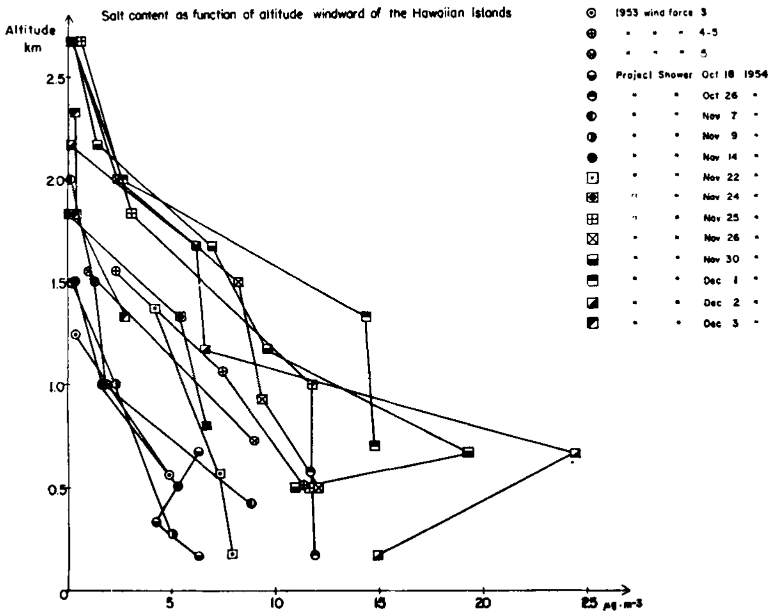

Fig. 3.10. Mass concentrations of sea salts as a function of altitude on various days in Hawaii. Data from Woodcock (1957).

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[1] Woodcock (personal communication) suggests that the anomaly in the Florida mass-weight distribution is due to outflow from the continent at higher levels of modified maritime air. This outflow is compensating the inflow at lower levels caused by heating of the land surface.

3.6, 3.7 and 3.8 the mass concentration at the different levels has been obtained by measuring the corresponding surface areas. Fig. 3.9 shows the average vertical mass concentration as a function of height for Hawaii, the Caribbean area and Pompano Beach. The maximum around 500 m is quite pronounced. Integrating these vertical distributions one obtains the average salt load per unit surface area which becomes

Hawaii	11.2 mg × m^{-2}
Caribbean	7.2 mg × m^{-2}
Pompano Beach	6.8 mg × m^{-2}

It is seen that average salt load is somewhat higher in Hawaii which no doubt is due to a unfair proportion of weather disturbances. The average for all three is 8.4 mg × m^{-2}. This may be taken as a representative figure for the amount of sea salt particles in the trade wind areas under fairly normal conditions. Whether the same load is found in higher latitudes is an open question. Under normal wind conditions it can, however, hardly be higher as the conditions for formation of large sea salt particles is somewhat limited by the higher relative humidity. The frequency of storms is, however, greater and this may contribute appreciably.

Nothing has been shown so far of the variations from day to day of the salt load of the air over the oceans. One can get a fairly good idea about the variability from WOODCOCK's Project Shower measurements. Some of the occasions when sampling was done at several altitudes have been chosen and are presented in fig. 3.10 as the mass concentration versus altitude. The variability is, as seen, great and yet no severe weather disturbances occurred during the time. In a region like the Caribbean and the coast of Florida the variability would certainly be greater due to the fairly regular occurrence of hurricanes in late summer in these areas. WOODCOCK (1950b) has measured the salt concentration from a lighthouse on the Florida coast during a hurricane when the wind force was 12 (Beaufort scale) and obtained extremely large sea salt particle concentrations.

Even more moderate weather disturbances in the Caribbean can give rise to quite large sea salt concentrations. One such case can be traced in data by LODGE (1955) in which the salt concentration reached well above 100 $\mu g \times m^{-3}$ at about 400 m altitude and the total salt load was about 100 mg × m^{-2}.

3. *Sea salt particles over land*

As pointed out before, data over land are scanty and very seldom so systematically collected as over the oceans and the information is many times qualitative. Yet those that exist are of considerable interest as they reveal interesting differences between land and sea.

TWOMEY (1955) investigated the maritime air flow south-west over the south-east part of Australia. On three occasions he followed the air by aircraft from the south-west and studied the change in the vertical distribution of sea salt particles that took place during its passage 600 miles inland. Two significant conclusions can be drawn from his work. There was a marked change in the vertical distribution of sea salt particles as the air entered the continent due to the increased turbulence and convection over land. Sea salts were thus transported upwards so that the vertical gradient decreased. This, of course, decreased the concentration of salt near the surface as the particles became more evenly distributed. Further, as he points out, if no precipitation or convective cloud formation took place there was no appreciable reduction in the sea salt concentration of the air during its long travel. Precipitation, and even convective cloud formation without apparent precipitation was very effective in removing the salt from the air. That even cloud formation alone could reduce the number of salt particles—as he actually measured—can be understood as coalescence of cloud droplets and subsequent evaporation forms a few large particles from many small and these really large particles soon fall out of the air.

The investigations undertaken by BYERS et al. (l.c.) also furnished very important information on sea salt particles over continents. They made some vertical samplings in Illinois on a few occasions. From their data fig. 3.11 has been constructed. It should be mentioned that the estimates of mass of salt made from their data are somewhat uncertain though they may be correct within ±30 per cent. The vertical distributions in fig. 3.11 shows relatively

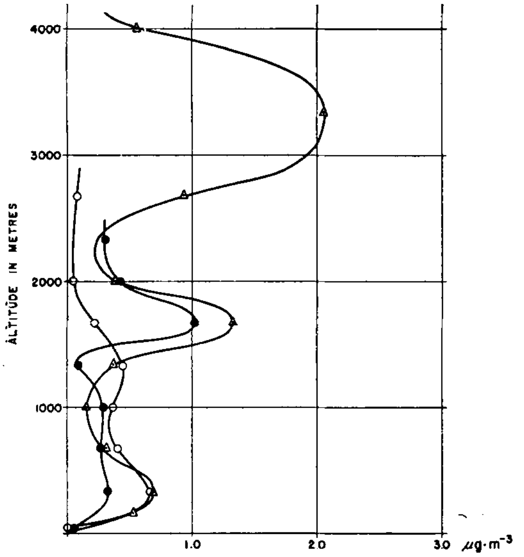

Fig. 3.11. Mass concentrations of chloride as a function of altitude in Illinois on three different occasions. Data from Byers et al. (1956).

● Nov. 10, 1954. 0.81 $\mathrm{mg} \cdot \mathrm{m}^{-2}$ up to 3,000 m
○ " 5, 1954. 1.09 " " " 3,000 m
△ June 11, 1954. 1.90 " " " 3,000 m
3.67 " " " 4,000 m

low mass concentrations but they can extend to great altitudes. In the June 11 case the air had moved from the Gulf of Mexico, but there is a marked stratification suggesting layers of somewhat different origin. In the other two cases the air flow was northerly and it may represent air from the North Pacific which has passed over the mountains to the west where a good deal of the sea salts got lost.

The most interesting is, however, the deep layer of salt at around 10,000 feet altitude. The lower part may have been washed out during the travel up to the Mississippi Valley. The Mississippi Valley is certainly important for the water vapor transport into the continent as well as for the sea salt transport as inferred earlier by Eriksson (1955a).

Byers et al. also made two horizontal sections along the Mississippi Valley sampling chloride particles. On June 6, 1954 they sampled at regular intervals at 5,000 feet elevation on the route from Illinois to the Gulf and on June 9 they returned flying at 2,500 feet altitude. Their results recalculated into μg salt × m^{-3} are shown below

Illinois									*Gulf*
June 6 5,000 feet	.23	.80	1.65	1.03	.85	.52	.09	.25	2.04
June 9 2,500 feet	.11	.35	.71	.97	.90	.95	.97	5.75	1.52

There is in the first place a maximum south of Illinois and a minimum close to the Gulf. In view of the vertical variability shown in fig. 3.11 the variations in the horizontal may simply be due to varying height of a strata situated around 5,000 feet indicating some wave character in the northward flowing air current. At lower levels the vertical variation is presumably less leading to a regular decrease northwards. It should be mentioned that the vertical profile in Illinois with the large concentration at high levels was made in the same air stream only two days after the return flight.

Another interesting feature of the return flight is found in the mass-weight distribution which was definitely bimodal at all places, just as the distributions at Pompano Beach in Florida.

Finally a more qualitative but extremely interesting investigation was carried out by Crozier, Seely & Wheeler (1952) in the western part of the United States. They also sampled from aircraft and though their technique does not give more than relative data on the largest salt particles the numbers they found per m^3 are certainly proportional to the salt concentration in the air.

In their first investigation they made a cross country flight at 10,000 feet elevation. Starting from Alberquerque in New Mexico they first flew westward. During the first part of the flight they were in what they call marginal Gulf of Mexico air and the number of chloride particles observed was around $500 \times m^{-3}$. Over California they passed through a tongue of air which had presumably originated in a tropical disturbance off the coast of SW Mexico which had dissipated two days earlier. The chloride particle concentration rose to about 3,000—$4{,}000 \times m^{-3}$ in the center of this tongue. Out over the Pacific they entered into descending stable air from the Pacific High which is a nearly permanent feature in this region. This air had a chloride particle content of only 100—$200 \times m^{-3}$. Off the coast of California they turned and flew in a north-east direction and once more they entered the Cl-particle rich tounge of air which they followed northward and were able to trace to Utah. From there on to Iowa the particle content was low as they where entirely in descending air. In Iowa they once more encountered Gulf of Mexico air with particle concentrations up to $1{,}000 \times m^{-3}$ and this air prevailed to eastern Illinois where they entered continental polar air with practically no chloride particles. The identification of air masses was made from ordinary weather maps.

The significant feature, apart from the Gulf of Mexico air which in summer penetrates far north, is the long tongue of air from the tropical disturbance. It is known that greater disturbances like hurricanes require an outflow of warm air at higher levels in order to maintain themselves (cf. RIEHL 1954) and this is presumably true for smaller disturbances too. CROZIER & SEELY (1952) continued to look for such chloride rich strata during a two weeks study and once more encountered a tongue over the Death Valley, this time originating in a disturbance off Baja California and with particle concentrations as high as $10{,}000 \times m^{-3}$.

The importance of these findings can hardly be overly stressed as it shows that chloride rich air can be transported at high levels into continents, thus passing over mountain barriers without washout of chloride. Once over continents mixing with colder air will cause precipitation of water and sea salt from such strata. The transport and subsequent accumulation of sea salt in the Bonneville Basin in Utah is thus easier to understand.

4. *Rate of production of sea salt particles*

The rate of production of sea salts in a "source" region must be equal to the rate of removal in sink regions. The removal is accomplished by two processes, removal by precipitation and removal by fallout. The rate of removal by precipitation is rather difficult to estimate directly but can perhaps be related to the rate of removal by fallout which is better suited for computations, using the average distributions presented earlier.

The fallout must be estimated at the sea surface in the so-called laminar boundary layer in which only molecular phenomena are supposed to take place, and consequently, where particles, falling into it, have no way of escape into the turbulent region again.

There are, however, a couple of problems involved in practice. In the laminar boundary layer the relative humidity is much higher than in the free air and this may influence the fall velocity of the particles. If they are small, equilibrium is probably so rapidly established that they essentially fall under equilibrium conditions. But if they are large, equilibrium is probably never attained and they fall through the laminar boundary essentially at the same rate as in the free air.

When the conditions in the boundary layer are defined, the rate of fallout can be simply computed from the concentration of particles in the boundary layer through multiplying with the appropriate fall rate. As to the concentrations of particles in the boundary layer, they are not known but a crude estimate can be done by extrapolating the vertical distributions to sea level. A check on the correctness of this procedure can be done afterwards by comparing the fallout rate with the turbulent diffusion coefficient in the free air to see if any appreciable gradient is needed for the transport down to the surface.

a. The boundary layer

The vertical transport mechanisms in the air at sea level has been thoroughly discussed by SVERDRUP (1951) on which the following discussion is mainly based. Of different assumptions made about the vertical transports the following seems to fit best the scanty observations made (cf. SVERDRUP): "Next to the surface there is a true diffusion layer of thickness $\lambda \nu / w_{*r}$ where w_{*r} applies to a rough surface. From the top of this layer the eddy diffusivity increases at the same rate as the eddy viscosity". In the formula above ν is the kinematic viscosity of air, λ is a constant and w_{*r} is the friction velocity. The rate of transport in the laminar boundary layer (= the true diffusion layer) is then

$$F = -D \frac{\partial \varrho}{\partial z} \qquad (3.11)$$

where D is the molecular diffusion coefficient. Above this layer

$$F = -K \frac{\partial \varrho}{\partial z} \qquad (3.12)$$

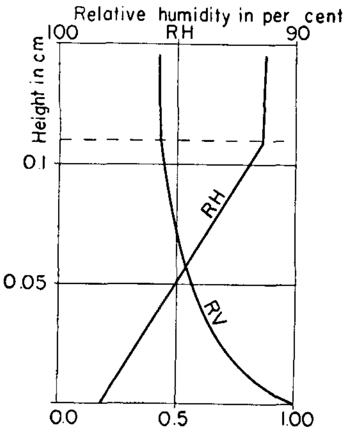

Fig. 3.12. The variation of relative humidity and fall velocity of a sea salt particle at equilibrium, in the laminar boundary layer over sea water.

where K is the turbulent diffusion coefficient. The following relations are to be used

$$K = k_0 w_{*r} (z + z_0) \qquad (3.13)$$

$$w_{*r} = \gamma w \qquad (3.14)$$

$$\gamma = \frac{k_0}{\ln \frac{z + z_0}{z_0}} \qquad (3.15)$$

where k_0 is Karman's constant ($= 0.4$) and z_0 the roughness parameter ($= 0.6$ over a rough sea surface) and w is the wind velocity at the level z.

As to λ which determines the thickness of the boundary layer, a value of 27.5 has been suggested for a rough sea surface, while $\lambda = 11.5$ has been suggested for a smooth surface.

Using $\lambda = 27.5$ and the values for the other constants as given one can compute the vertical vapor density profile from the average rate of evaporation and surface vapor density over tradewind areas (referred to in section 11) and an average wind speed at 8 m level of 6 m × sec^{-1}. These computations give a laminar boundary layer of 1.1 mm and a relative humidity at the top of the boundary layer of 91.4 per cent. As to the rest of the profile data have been tabulated in table 3.1. It is seen that the relative humidity at $z = 800$

TABLE 3.1

Vertical distribution of relative humidity over sea water and of relative volumes, radii and fall velocities of sea salt particles. Salinity of sea water 35.2 per mille, wind speed 6 m/s

Height in cm	Relative humidity in per cent	Relative volume of sea salt particles	Relative fall velocity of sea salt particles at equil.	Relative radius of particle	Remarks
0.0	98.2	1.000	1.000	1,000	Laminar boundary layer
0.11	91.4	.250	.424	.630	
0.2	91.2	.245	.419	.726	
0.3	91.0	.240	.414	.622	
0.4	90.8	.236	.409	.619	
0.5	90.6	.232	.405	.615	
0.8	90.2	.224	.397	.608	
1.0	90.0	.221	.394	.605	
1.5	89.5	.212	.385	.597	
2.0	89.2	.207	.380	.593	
3.0	88.7	.200	.372	.586	
4.0	88.2	.194	.366	.579	
5.0	87.9	.190	.362	.575	
10.0	86.5	.172	.343	.557	
20	85.7	.164	.334	.547	
30	85.0	.158	.327	.541	
50	84.2	.152	.320	.534	
60	83.9	.150	.317	.531	
100	82.9	.143	.309	.523	
200	81.8	.136	.301	.516	
300	80.8	.131	.295	.507	
500	80.3	.128	.292	.504	
600	79.9	.126	.290	.501	
800	79.5	.124	.288	.499	

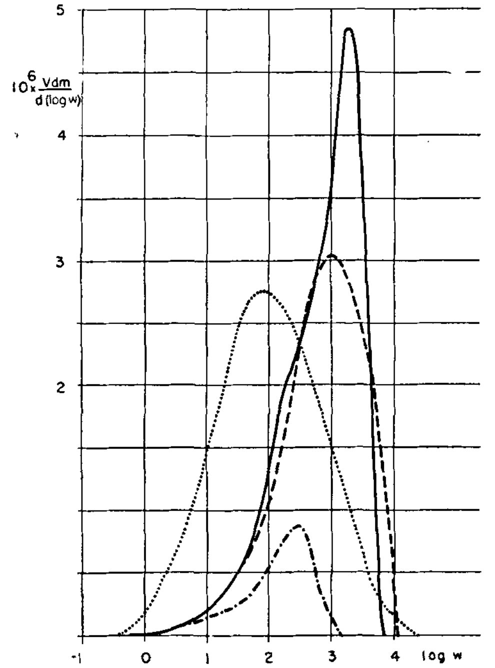

Fig. 3.13. Rate of fallout of sea salts and rate of production in breaking waves. Mass, *m*, in μg · m^{-3}, *w* in μμg (10^{-12} g).

——————— Hawaii
— — — — Caribbean area
—·—·—· Pompano Beach, Florida
. . . . . . Rate of production in breaking waves computed from data by BLANCHARD-WOODCOCK (1956). Note, original computed figures have been divided by 600.

cm is close to 80 per cent which is a good average for trade wind areas. In table 3.1 relative radii, volumes and fall rates are also shown. It is seen that above the laminar boundary layer the fall velocity is only 42 per cent of the value at saturation (98.2 per cent). The change in fall velocity further upwards is comparatively slow.

The conditions in the laminar boundary layer can be seen in fig. 3.12 where the fall velocity at equilibrium is given as a function of height. It is seen that the fall velocity changes but slowly until the surface is reached.

b. Fall rate and adjustment time to evaporation

One may thus assume that particles that arrive at the top of the boundary layer have a fall speed equal to about 40 % of that of equilibrium with sea water. Next we may try to estimate how long time they spend in the boundary layer before they fall into the water. Full saturation vapor pressure is not reached until the salt particles reach the very surface. One can compute the average fall velocity from the growth equation with some simplifying assumptions. This has been done and it is remarkable how little the average fall velocities differ from those on the top of the boundary layer. The greatest difference is in the small end of the size-spectrum but even there (at $w = 0.15$ μμg) the difference is less than 10 per cent. Considering that these small particles contribute very little to the fallout rate of mass one can compute the fallout with the simple assumption that the rate of removal is equal to the fall velocities of particles in equilibrium with the water vapor pressure at the top of the boundary layer.

c. The distribution of rate of fallout versus weight

The mass-weight distributions of the type discussed earlier can now be used to study the variation of the rate of fallout with size. Let ΔF be the rate of fallout of mass of particles in the interval $\Delta \log w$. Then we have

$$\frac{dF}{d(\log w)} = V\left[\frac{dm}{d(\log w)}\right]_{\text{boundary}}$$

and as boundary values we chose those at the lowest level presented in figs. 3.6, 3.7 and 3.8, while V is taken from table 2.3. It is obvious that no extensive turbulent transport need to take place in the lowest part of the atmosphere when the fall velocities of particles are only to a small extent influenced by the increasing relative humidity as we approach the surface. The assumption that the distribution of particles in the boundary layer is the same as that at say the 100 feet level or so therefore seems appropriate.

The results of the computations of rate of fallout are shown in fig. 3.13 for the three regions in question, Hawaii, the Caribbean and the coast of Florida. It is seen that this type of distribution naturally has its maximum in the large weight region, centered around $w = 10^3$ μμg. An exception is the Florida distribution where the maximum is centered at $w = 10^{2.5}$ μμg.

The total fallout can now be estimated from the area below the curves and becomes

Caribbean	$6.0 \times 10^{-6}\ \mu g \times cm^{-2} \times sec^{-1}$
Hawaii	$5.1 \times 10^{-6}\ \mu g \times cm^{-2} \times sec^{-1}$
Florida	$1.0 \times 10^{-6}\ \mu g \times cm^{-2} \times sec^{-1}$

The very low value for Florida is perhaps not representative for the sea as a whole, the other two are appreciably higher. As an average for trade wind areas a figure of $5.5 \times 10^{-6}\ \mu g \times cm^{-2} \times sec^{-1}$ may be used.

The average weighted fallout rates may now be estimated. The salt concentrations at the lowest levels are obtained from fig. 3 and are

Caribbean	$8.1\ \mu g \times m^{-3}$
Hawaii	$7.2\ \mu g \times m^{-3}$
Florida	$3.6\ \mu g \times m^{-3}$

so that average velocities become

Caribbean	0.74 cm $\times$ sec^{-1}
Hawaii	0.71 cm $\times$ sec^{-1}
Florida	0.28 cm $\times$ sec^{-1}

These figures can be compared to" deposition velocities" or vertical transport rates as defined earlier where, for the sea a value of 0.87 cm × sec^{-1} was estimated from evaporation data. They are thus comparable.

The rate of removal over the entire sea surface, using a fallout rate of $5.5 \times 10^{-6}\ \mu g \times cm^{-2} \times sec^{-1}$ becomes 540 million tons × year^{-1} and the corresponding chloride 300 million tons × year.

We may ask how much is removed by precipitation. We can then compare the fallout velocity over the sea with the deposition velocity over land which, as will be shown later, is about 2 cm × sec^{-1}. Over land about two times as much chloride is removed by dry fallout as by precipitation. Over the sea the dry fallout should consequently be less important relative to precipitation than over land maybe by a factor of 2. Thus one may assume that at least as much sea salt is removed by precipitation as by dry fallout. This gives a figure for the total removal over sea of more than 1,000 million tons a year. The rate of run-off from land is of the order of magnitude 100 million tons × year^{-1} so a figure of 1,000 million tons per year could represent the total production rate over the sea.

d. The production rate in breaking waves

BLANCHARD & WOODCOCK (1956) have made a thorough study of various mechanism for sea salt production. As to breaking waves, which presumably is the most important source for sea salt particles in the atmosphere, they made a study of the size and number of par-

TABLE 3.2

Data and computations of the rate of production of the mass of sea salt particles in a breaking wave. Data obtained from Blanchard and Woodcock (1956)

log w	v cm · sec^{-1}	$n\ (w)$	w^2	$\frac{dN}{dD}$	$\frac{dD}{dw}$	dm/d (log w)
—.50	.0128	.0	.1	$2.51 \cdot 10^3$	20.1	0
—.25	.0217	.2	.316	$7.95 \cdot 10^2$	19.2	36
.00	.0340	.5	1.0	$2.51 \cdot 10^2$	10.0	98
.25	.054	1.2	3.16	$7.95 \cdot 10^1$	7.1	266
.50	.0852	1.7	10.0	$2.51 \cdot 10^1$	5.04	419
.75	.136	2.3	31.6	7.95	3.56	645
1.00	.214	2.8	100	2.51	2.52	871
1.25	.34	3.3	316	$7.95 \cdot 10^{-1}$	1.79	1,160
1.50	.54	3.7	1,000	$2.51 \cdot 10^{-1}$	1.27	1,465
1.75	.78	4.0	3,160	$7.95 \cdot 10^{-2}$	.90	1,620
2.00	1.1	4.0	10^4	$2.51 \cdot 10^{-2}$	.64	1,635
2.25	1.6	3.8	$3.16 \cdot 10^4$	$7.95 \cdot 10^{-3}$	.45	1,580
2.50	2.1	3.4	10^5	$2.51 \cdot 10^{-3}$	.317	1,390
2.75	3.0	3.0	$3.16 \cdot 10^5$	$7.95 \cdot 10^{-4}$	.224	1,170
3.00	4.0	2.5	10^6	$2.51 \cdot 10^{-4}$	.159	920
3.25	5.3	1.9	$3.16 \cdot 10^6$	$7.95 \cdot 10^{-5}$	.113	660
3.50	7.0	1.3	10^7	$2.51 \cdot 10^{-5}$	.080	418
3.75	9.0	.6	$3.16 \cdot 10^7$	$7.95 \cdot 10^{-6}$	.0565	177
4.00	11.0	.4	10^8	$2.51 \cdot 10^{-6}$	.0400	102

ticles produced by breaking bubbles, the ejected height, the bubble size distribution in breaking waves and the rate of rise of bubbles of different sizes. All this information is contained in tables and diagrams and has been used in the following for computing the rate of production of sea salt droplets. This result depends much on the number of ejected droplets that can be considered to be carried away by the turbulence of the air above the laminar boundary layer. For small ejected particles with small fall velocities the most important requirement is that they penetrate the laminar boundary layer and in this way the probable number of successful droplets can be estimated. For large particles, however, turbulent conditions become more and more important and very little guidance is received from the height of the ejected heights. The choise of the number of successful droplets on this side of the distribution of ejected droplet becomes therefore more arbitrary but evidently they must decrease with increasing size. By this procedure the rate of production in a breaking wave can be computed as follows.

Let N be the cumulative number of bubbles arranged according to decreasing size and $n(w)$ the number of droplets that can possibly reach equilibrium above the boundary layer. Further let w be the weight of salt in each droplet and $D = \phi(w)$ be the relation between bubble size and weight of salt in a droplet ejected from the bursting bubble. Then we get for the mass m

$$\begin{aligned} dm &= v \cdot n(w)\, w\, dN = vn(w)w \frac{dN}{dD} dD = \\ &= vn(w)w \frac{dN}{dD}\frac{d\phi}{dw} dw = \\ &= 2.3 \; vn(w)w^2 \frac{dN}{dD}\frac{d\phi}{dw} d(\log w) \qquad (3.16) \end{aligned}$$

where v is the rise velocity of the bubbles. As to $n(w)$ this can be obtained as a smoothed function of log w applying principles discussed above. The units used are the same as in the computation of rate of fallout. It should be pointed out that the relations found by BLANCHARD & WOODCOCK have been extrapolated.

The computed $dm/d(\log w)$ shown in table 3.2 have been entered in fig. 3.13 on a scale that is directly comparable to the Caribbean fallout distribution, i.e. the surface areas below these curves are the same. To achieve this the data in table 3.2 were divided by 600. Considering the removal by precipitation it looks as if the rate of production in a breaking wave is 300 times the rate of removal. This can be interpreted to mean that about 0.3 % of the ocean areas is always covered with breaking waves.

The most striking thing about the distribution is, however, its position relative to the fallout curves. This really suggests a far reaching coalescence process in the air especially for the small-sized particles, shifting their mass to bigger sizes.

It should be pointed out that the right side of the distribution is tentative in a respect. It is certainly strongly influenced by the wind force because in a strongly turbulent air a greater number of the ejected droplets will be carried away by turbulence than indicated in table 3.2 For small-sized particles this influence is much smaller. We may have a reason here for the peculiarities in the dN/dr distributions discussed earlier. The nature of the distribution of larger-sized particles will be influenced by the wind much more than that of the small particles.

TABLE 3.3

Residence times of sea salt particles calculated both from fallout (τ_1) and from rate of production (τ_2)

log w	dM/d (log w)	$V\,dm/d$ (log w)	Rate of prod. dm/d (log w)	τ_1 days	τ_2 days
.00	9.9×10^4	.014	.33	82	3.5
1.00	2.4×10^5	.17	2.90	16	1.0
2.00	3.0×10^5	1.35	5.45	2.6	0.6
3.00	1.3×10^5	3.73	3.07	0.4	0.5

e. The residence time of different sized particles

With the material available we may also compute residence times for various sizes. Defining

$$dM = \int_{z=0}^{z=\infty} dm dz \qquad (3.17)$$

the amount of salt present in the air per unit area and logarithmic interval of w is dM/d (log w) and can be arrived at by plotting dm/d(log w) as a function of height for various values of w. Then the residence time can be formulated in two ways. If the fallout was the only process that removed the particles we would have

$$\tau = \frac{dM/d\,(\log w)}{V[dm/d\,(\log w)]_{z=0}} \qquad (3.18)$$

If there are other processes like coalescence that dominate we should use the production function discussed earlier, weighted by dividing the values in table 3.2 by 300, thus accounting also for removal by precipitation. Using the Caribbean distribution the computed residence times in days for selected values of w becomes those in table 3.3 for these two alternatives.

It is seen that the residence times computed on the basis of rate of fallout becomes extremely large for the small-sized particles and this is incompatible with the observed variability of particle numbers of these particles. Therefore, the residence time based on rate of production is much more reasonable and shows that they are fairly rapidly removed, naturally by coalescence, forming larger particles. As to the large particles fallout and removal by precipitation is, perhaps, much more important and, in fact, removes also particles that are formed by coalescence. Thus, the real residence time for these large particles is most probably smaller than indicated in the table.

It should be noted, however, that following a certain mass of salt as represented by a particle its residence time in the atmosphere will be appreciably greater than the values derived from the production of sea salt because it is constantly passing through increasing sizes before it is removed.

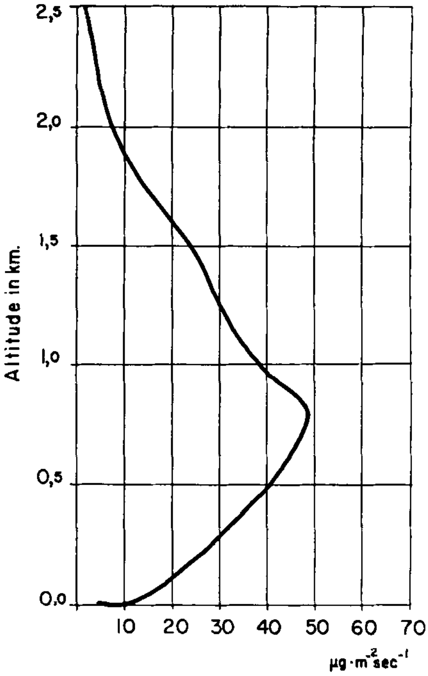

Fig. 3.14. Rate of advection of mass of sea salt from 60° at different altitudes windward of Hawaii. Computed from Project Shower data (Woodcock 1957, Amman 1957).

5. *Advection of sea salt as a function of altitude*

When considering the horisontal transports of the salts some information may be arrived at from the Project Shower data. Frequent rawin soundings during the operation make it possible to estimate the wind speeds and directions at various levels. The soundings were made at Hilo on the isle of Hawaii which is situated at the windward coast. Whether these soundings are representative for the trade wind areas as a whole is a question that will be left open but the influence of the land may not be too great. Anyway, the computation of the salt transport is at any rate representative for what happened at the windward side of Hawaii.

Data from the soundings have been compiled by Amman (1957).

The following days, when more complete data on the sea salt particle distribution existed were used. November 14, 22, 24, 25, 26 and 30 and December 1 and 2, 1954. As there were four soundings per day, those laying closest in time to Woodcock's sampling times were selected, plotted and the 60° components computed from the directions and wind speed.

For each of the days listed the product of the 60° wind speed and salt concentration in air were calculated at every 200 m level and from these an average of the 8 days calculated. The result is shown in fig. 3.14 where the product in $\mu g \times m^{-2} \times sec^{-1}$ is seen as a function of altitude.

The days chosen include the out of the trade wind season Kona-storm which, however, did not effect the average wind direction severely but had a considerable effect on the vertical stability. For this reason the salt transport at higher levels is probably somewhat larger than under average conditions.

There is a well marked maximum in the salt transport, namely at 800 m elevation. At that level the advection of sea salts is nearly five times larger than at sea level. The integrated transport amounts to 62 $mg \times m^{-1} \times sec^{-1}$. Thus, across each meter of the coast, perpendicular to the wind direction (60°) passes 62 mg sea salts per second as an average. This is ~ 5.4 $kg \times m^{-1} \times day$ or 5.4 tons $\times km^{-1} \times day^{-1}$.

One cannot, of course, expect the advection from the ocean to the continents to follow exactly this distribution but on the coast something similar will show up. The winds generally increase with height to some level of the order of 1,000 m and, if the mass distribution with height also shows maximum at that level, the maximum transport of sea salt will occur at the same level and be magnified in relation to the mass distribution. If the mass distribution was uniform a larger transport would still take place at higher levels.

How the advection looks like over land is entirely dependent on the stability of the air. In summer with vigorous convection due to heating greater vertical wind shears will not occur but in winter stratification of air over continents is quite common which will facilitate different advection rates of sea salts at different levels.

As pointed out earlier in connection with the observations by CROZIER & SEELY (l.c.) over the western U.S. advection of sea salt at higher levels is important because mountain barriers will not cause a rainout of the salt.

To be continued in Tellus 12: 1.