

## Characterization of Individual Giant Aerosol Particles above the North Sea

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■ In order to investigate the importance of giant airborne particles, air sampling was carried out using an aircraft which flew at different altitudes over the southern bight of the North Sea. A set of 25 samples was collected with a steel rod on top of the airplane. Some 12 500 individual particles were analyzed using electron probe X-ray microanalysis. Principal factor analysis allowed identification of four sources of giant aerosol particles: aluminosilicates, combustion processes, industrial processes, and marine sources. Hierarchical and nonhierarchical cluster analysis enabled us to classify the analyzed particles. A clear distinction was found between flights for which the associated air masses were marine or continental. The experimentally found size distributions for sea salts, sea salts enriched with sulfur, and organic,  $\text{CaSO}_4$ , and Fe-rich particles were fitted well by the log-normal distribution, and average sizes of these particle types were found to be  $\sim 3 \mu\text{m}$ . Aluminosilicates had a bimodal size distribution with average size maxima at 4 and  $15 \mu\text{m}$ .

### Introduction

The North Sea is surrounded by highly populated and heavily industrialized countries and consequently it is subjected to pollution of industrial, domestic, and agricultural origin through different channels. Input of contaminants, transported by rivers, and direct dumping into the North Sea have long been known as major sources of pollution. But it has been shown that atmospheric input of particulate matter or aerosols by wet and dry deposition processes contributes significantly to the North Sea pollution (1).

Every aerosol particle type differs in shape, size, density, and chemical composition. Each of these physical parameters has a strong influence on the behavior of the aerosol in the air.

Giant aerosol particles with a radius above  $1 \mu\text{m}$ , and especially those larger than  $10 \mu\text{m}$ , are of extreme importance to aerosol fluxes. Their concentration in the atmosphere is low, but it should be emphasized that a particle of, for example,  $10 \mu\text{m}$  has 1000 times more mass than a  $1-\mu\text{m}$  particle and its deposition velocity is ca. 100 times higher (2). Calculations by Dedeurwaerder (3) showed that deposition of giant particles explains 94% (Cd), 96% (Cu), 85% (Pb), and 88% (Zn) of the total dry deposition above the North Sea. Furthermore, if global aerosol production rates are estimated, discrepancies of 0.1–4000 tons/year occur, depending on whether particles with diameters up to 1 or  $1000 \mu\text{m}$  are included in the calculations (4). One should expect giant particles to be of local interest only, since a typical residence time of 1 day has been reported by Jaenicke (4); however, the presence of giant mineral aerosols has been observed in long-range transport (5). All these facts point to the extreme importance of giant aerosol particles for the total deposition process.

Due to their relatively low concentrations, it was not until the early 1970s that serious interest was taken in giant aerosol particles. Noll and Pilat (6) and Whitby et al. (7) pointed to the importance of these particles in the total deposition process and cloud and precipitation processes. They stated that, of the atmospheric aerosol mass distribution, approximately 81% of the total mass was ac-

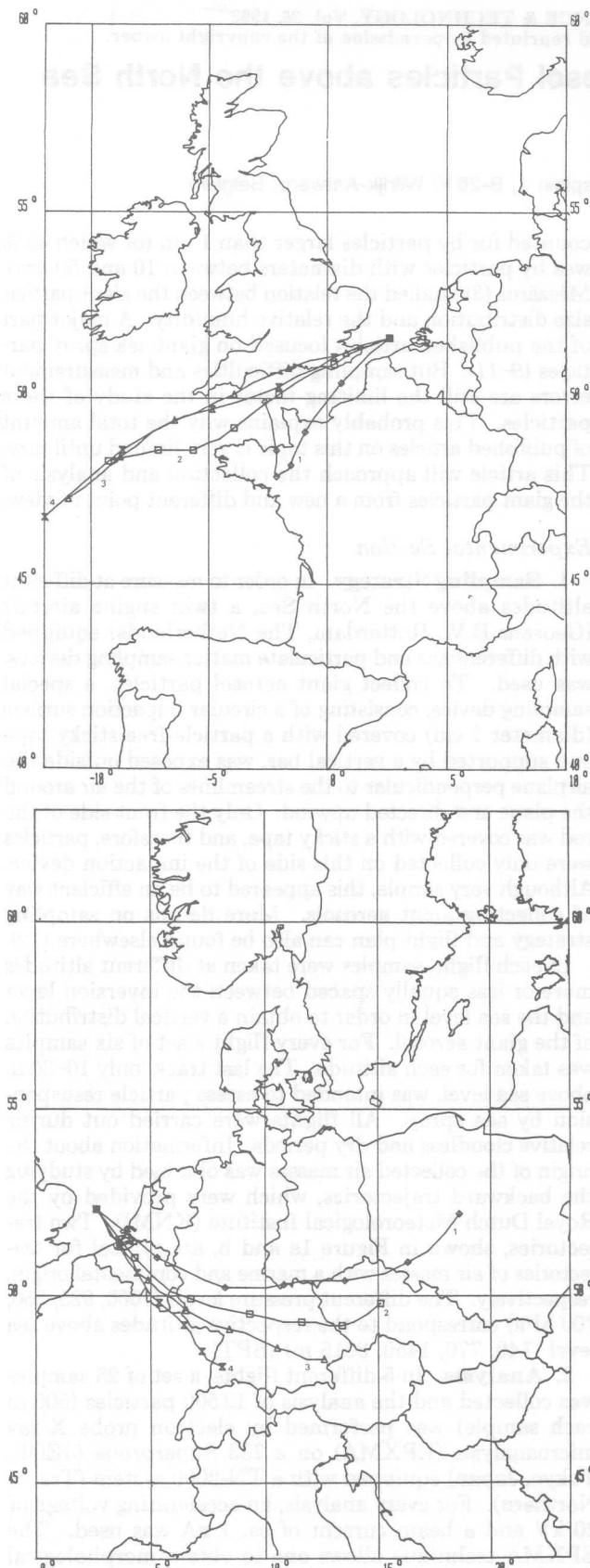
counted for by particles larger than  $1 \mu\text{m}$  (of which 45% was by particles with diameters between 10 and  $50 \mu\text{m}$ ). Mészáros (8) studied the relation between the giant particle size distribution and the relative humidity. A major part of the published articles focused on giant sea spray particles (9–11). But sampling difficulties and measurement errors are still the limiting factor in the study of these particles. This probably explains why the total amount of published articles on this topic is very limited until now. This article will approach the collection and analysis of the giant particles from a new and different point of view.

### Experimental Section

**1. Sampling Strategy.** In order to measure at different altitudes above the North Sea, a twin engine aircraft (Geosens B.V., Rotterdam, The Netherlands) equipped with different gas and particulate matter sampling devices, was used. To collect giant aerosol particles, a special sampling device, consisting of a circular impaction surface (diameter 1 cm) covered with a particle-free sticky tape and supported by a vertical bar, was exposed outside the airplane perpendicular to the streamlines of the air around the plane and directed upwind. Only the front side of the rod was covered with a sticky tape, and therefore, particles were only collected on this side of the impaction device. Although very simple, this appeared to be an efficient way of collecting giant aerosols. More details on sampling strategy and flight plan can also be found elsewhere (12).

In each flight, samples were taken at different altitudes more or less equally spaced between the inversion layer and the sea level in order to obtain a vertical distribution of the giant aerosol. For every flight a set of six samples was taken for each altitude. The last track, only 10–30 m above sea level, was intended to assess particle resuspension by sea spray. All flights were carried out during relative cloudless and dry periods. Information about the origin of the collected air masses was obtained by studying the backward trajectories, which were provided by the Royal Dutch Meteorological Institute (KNMI). Two trajectories, shown in Figure 1a and b, are typical for trajectories of air masses with a marine and continental origin, respectively. The different pressure levels (1000, 925, 850, 700 hPa) correspond to the respective altitudes above sea level (140, 770, 1450, 3015 m) (SPT).

**2. Analysis.** In 5 different flights, a set of 25 samples was collected and the analysis of 12 500 particles (500 in each sample) was performed by electron probe X-ray microanalysis (EPXMA) on a 733 Superprobe (JEOL, Tokyo, Japan) equipped with a TN-2000 system (Tracor Northern). For every analysis, an accelerating voltage of 20 kV and a beam current of ca. 1 nA was used. The EPXMA technique allows one to obtain morphological data such as average diameter and shape factor while the chemical composition can be derived from an energy-dispersive X-ray spectrum. The single-particle analysis program 733B (13) allowed us to perform automated individual particle analysis. Localization of a particle is obtained by successive horizontal scanning with the electron beam. During this process, contour pixels of a particle are stored into the memory. When all contour grid points have been stored, area, perimeter, and diameter are calculated and an X-ray spectrum is accumulated. All this



**Figure 1.** Backward trajectory of a flight with (a, top) a strong marine influence or (b, bottom), a strong continental influence: (1) 140 m, (2) 770 m, (3) 1450 m, (4) 3015 m.

information is stored on a disk.

**3. Multivariate Methods.** To allow interpretation of the obtained information, hierarchical and nonhierarchical cluster analyses were used to classify particles with similar

chemical composition into "particle groups".

Hierarchical cluster analysis was used to classify the 500 particles, measured in each of the 25 samples, into groups based on their chemical composition. It was then possible to calculate the percent abundance of each group in each sample. Here, the clustering was performed on the normalized X-ray elemental intensities of each analyzed particle. We used the software package DPP (14). Ward's method (error sum of squares) was chosen because it yields a maximal internal homogeneity (15). The condition for the joining of two groups, using Ward's method, is that the decrease in homogeneity is kept as small as possible. Thus, whenever a pair of clusters is joined, the homogeneity is calculated by determining the sum of square distances of each object to the centroid of the cluster. This calculation is done for each pair of clusters and those clusters will be joined which will lead to the smallest decrease in homogeneity.

Since the hierarchical clustering cannot be used for simultaneous classification of all measured particles in all samples due to the enormous amount of computer time calculating the distances between 12 500 particles in each cycle of a hierarchical clustering would take, we used the nearest centroid sorting technique. Nearest centroid sorting is a group of nonhierarchical cluster methods, which classifies objects (particles) in clusters according to their distance from the centroids of a fixed number of previously chosen training vectors, which are obtained by a hierarchical clustering. The distances between all objects and the training vectors are calculated. All objects that were incorrectly classified in the initial clustering are relocated with the nearest centroid method. The centroids of the new clusters are calculated. This procedure is repeated until convergence appears. The result of such a clustering is that objects in a cluster are very similar to each other, while the clusters themselves are well separated. More theoretical aspects on nonhierarchical clustering can be found in publications of Anderberg (16) and Bernard (17).

After the clustering, a standardless ZAF correction was carried out in order to convert the relative peak intensities into elemental weight compositions. Performing ZAF corrections on each of the measured particles separately would, in principle, be better, but would require an enormous amount of computer calculating time. Therefore, the ZAF correction is performed after the clustering.

To identify the different sources for giant aerosols, principal factor analysis (PFA) with orthogonal Varimax rotation was performed on the data set. PFA has already been used in many other atmospheric studies, e.g., by Henry and Hidy (18, 19), Rojas et al. (20), Schaug et al. (21), and Wolff et al. (22). The objective of PFA is to take  $p$  variables and find linear combinations of these to produce uncorrelated new variables (factors), which are ordered in decreasing order of importance so that the first one explains the largest amount of variance. It is a common practice to perform an orthogonal rotation of the original factors in order to facilitate their interpretation. In this case, the Varimax rotation was chosen. This type of orthogonal rotation consists of maximizing the variance of the squares of the factor loadings. Here the data matrix consisted of 13 variables (Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Cu, Zn, and altitude). An element was considered to be detected if the X-ray intensity of the element was found above detection limit in one of the 500 analyzed particles for each sample. Occasionally other elements such as Pb, Ni, Cr, Br, Ti and V were detected in a particle. However, when detected, these elements were found in particles that always contributed less than 0.5% of the total aerosol

**Table I.** Varimax Rotated Factor Loading Matrix for the 25 North Sea Giant Aerosol Samples<sup>a</sup>

variable	factor 1	factor 2	factor 3	factor 4	communality	standard deviation
Na	-0.42	0.69	0.36		0.814	0.09
Mg		0.75			0.627	0.13
Al	0.95				0.928	0.06
Si	0.96		-0.18		0.956	0.05
P	-0.40	-0.85			0.913	0.06
S		0.86			0.878	0.08
Cl	-0.31	0.73		0.46	0.883	0.07
K	-0.28			0.84	0.822	0.09
Ca	0.59	-0.60			0.773	0.10
Fe	0.90		-0.26		0.887	0.07
Cu	-0.30		0.83	0.25	0.867	0.08
Zn			0.85		0.813	0.09
height	0.38	-0.35	0.36	-0.52	0.672	0.11
eigenvalue	4.74	3.54	1.39	1.16		
% variance explained	36.3	27.1	10.6	8.9		
source ID	aluminosilicates	marine	industrial	combustion process		

<sup>a</sup>Absolute values for factor loadings smaller than 3 times their standard deviation were deleted for simplicity.

abundance. Therefore, they were excluded from the data matrix. One of the most important problems of PFA is the decision of the dimensionality of the model. The decision on how many factors should be retained is often rather subjective. But it is usually a "rule of thumb" to retain as many factors as there are eigenvalues greater than unity. More detailed information on the strategy for performing PFA on EPXMA data can be found elsewhere (23).

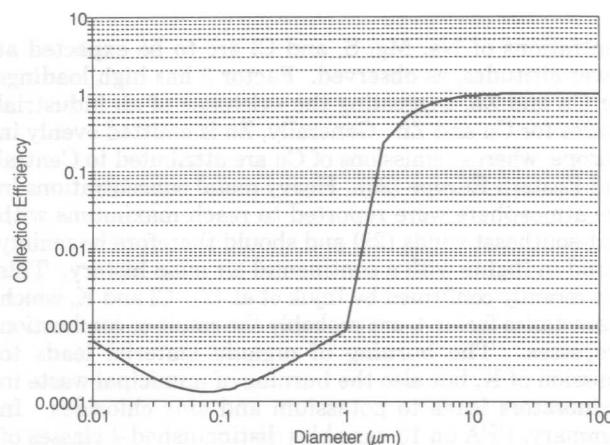
#### Collection Uncertainties

Collection of giant aerosols is not a straightforward matter. In aerosol sampling by filtration, suction velocities are usually too small to collect giant aerosols. Aerosol sampling by impaction as a function of particle size normally requires isokinetic conditions for representative sampling.

In order to calculate the collection efficiency  $E$  of the impaction rod on top of the aircraft, we assumed the same physics for the impactor as for the scavenging of particles by rain droplets; the impaction rod was considered as a droplet (diameter 1 cm) falling through the air with a speed equal to the speed of the airplane (75 m/s) during collection. For the calculations, the equations given by Slinn (24) were used. These equations treat the impaction surface as a sphere, but during the calculations this was corrected to the actual shape and dimensions of the impactor rod. Further theoretical background can be found elsewhere (25).

The results show (Figure 2) that an impaction rod, at aircraft speed, can be used to collect particles with a diameter above 0.8  $\mu\text{m}$ . This seems to compare well with the obtained EPXMA results, where the smallest detected particles had diameters around 0.6  $\mu\text{m}$ . The slight increase in collection efficiency for small particles is the result of collection by Brownian diffusion. Because Brownian diffusivity of particles increases as the particle size decreases, this effect is more distinct for small particles.

The upper size range of the collected particles is limited by bounce-off and reentrainment. When a particle strikes the surface, it can bounce off back into the gas stream or cause a previously collected particle to be knocked off the surface. In both cases, for single-stage impactors, this means that the concentration of particles collected is too small. These problems can be minimized by coating the surface of the impactor to absorb the kinetic energy of the particle. EPXMA results showed maximum diameters



**Figure 2.** Calculated collection efficiency for giant North Sea particles collected with a direct impaction rod.

around 25  $\mu\text{m}$ . Less than 1% of the detected particles were larger than 25  $\mu\text{m}$ .

#### Results and Discussion

**1. Principal Factor Analysis.** PFA, performed on the correlation matrix of the data set, which gives the pattern of relationships between the factors, resulted in four eigenvalues greater than 1 (4.74, 3.54, 1.39, 1.16), while the fifth and sixth eigenvalues were respectively 0.71 and 0.56. Therefore, further calculations were performed with the four-factor solution.

Results of the Varimax rotated factor analysis are shown in Table I. Only factor loadings greater than 3 times their standard deviation are shown, because only these are considered as statistically significant (26). The four factors together explain 83% of the total variance. Communalities are high for all variables, except for Mg, Ca, and "altitude". Factor 1 has high loadings for Al, Si, Ca, and Fe. Aluminosilicates, both windblown soil dust and fly ash, which have similar chemical compositions with respect to many elements, probably correspond to this factor. Factor 1 is positively correlated with altitude, which could be explained by the presence of a long-range-transported mineral aerosol at high altitudes. Factor 2 most likely represents marine impact. Furthermore, this marine source is slightly anticorrelated with altitude. If one considers the mechanism by which matrix and trace elements are injected from the sea into the atmosphere (27), high con-

**Table II. Results of the Hierarchical Clustering**

group no.	abund, %	av diam, $\mu\text{m}$	elements detected	identification
(a) Flights with Little Continental Influence				
1	31	3.5	Na, Cl, S	S enriched seaspray
2	18	3.3	Na, Cl	seaspray
3	16	2.9	Ca, S	gypsum
4	10	2.0	Fe	Fe-rich
5	8	3.9	S, Cl	sulfates
6	6	3.1	Ca, S, Cl	Cl enriched gypsum
7	5	3.2	Al, Si, Cl	aluminosilicates
8	5	3.1	none	organic
9	1	1.9	Na	Na-rich
(b) Flights with a Strong Continental Influence				
1	36	3.1	Ca (Si, P)	Ca-rich
2	17	2.1	none	organic
3	12	3.3	Ca, S	gypsum
4	11	4.3	Al, Si	aluminosilicates
5	4	2.7	K, Cl (Zn)	K, ZnCl
6	4	3.7	Cl, Na	seaspray
7	3	3.6	Fe	Fe-rich
8	2	2.6	Si	quartz

centrations of Na, Mg, S, and Cl are to be expected at lower altitudes, as observed. Factor 3 has high loadings for Cu and Zn, suggesting the existence of an industrial source for Cu and Zn. Generally, Zn is emitted evenly in Europe, whereas emissions of Cu are attributed to Central and Eastern Europe (28). Heavy metal concentrations in the atmosphere were reported to reach maximums with east-southeast winds (29) and should therefore be mainly found in flights with a continental air mass history. This was recently confirmed by Injuk et al. (1). Cl and K, which characterize factor 4, are probably the result of combustion processes. The burning of organic material leads to emission of K, but also the burning of municipal waste in incinerators leads to potassium and zinc chlorides. In summary, PFA on 13 variables distinguished 4 classes of giant aerosol sources: aluminosilicates (Al, Si, Ca, Fe), marine aerosols (Na, Mg, S, Cl), and aerosols from metallurgical processes (for Zn, Cu) and combustion processes (for K, Cl).

**2. Hierarchical Clustering.** Only 6 out of 25 samples correspond to a wind sector which is representative of marine air masses, whereas the remaining 19 samples correspond to other wind directions, which have as major sources Belgium, The Netherlands, Germany, Poland, Czechoslovakia, and Denmark. Depending on the sample, three to seven different aerosol groups were distinguished. Overall results of the hierarchical clustering for flights with, respectively, little and strong continental influences are listed in Table IIa and b. In these tables, average diameter, abundance (in percent), and the identification of each particle type are shown.

**(a) Marine Air Masses.** The flights with little continental influence are characterized by southwest wind directions. Then air masses come directly from the Atlantic Ocean through the English Channel, and anthropogenic influence is consequently low.

In these marine flights, mainly untransformed and transformed sea salts were found, accounting for up to 49% of the total aerosol abundance. Sea salt and transformed sea salt find their existence mostly in the mechanism of white cap formation during high-speed winds and bubble bursting. The sea-spray particles can then react with other compounds in the atmosphere. Eriksson (30) stated that the Cl loss in sea salt is the result of pH-lowering reactions between NaCl and acid atmospheric components such as  $\text{H}_2\text{SO}_4$ , and this was later confirmed by Hitchcock et al.

(31). As a result, degassing of HCl takes place and  $\text{Cl}^-$  is replaced by  $\text{SO}_4^{2-}$  (32). The abundance of the transformed sea salt enriched with S was positively correlated with altitude. This seems in agreement with the fact that these aged aerosols had a residence time long enough to allow chemical reactions with other compounds.

Ca-rich (and especially  $\text{CaSO}_4$ ) particles account for up to 22% of the total aerosol abundance. Ca-rich particles, which may or may not be associated with sulfur, were found in all flights.  $\text{CaSO}_4$  particles were very common in marine as well as in continental flights.  $\text{CaCO}_3$  could be transformed into  $\text{CaSO}_4$  in the atmosphere by  $\text{H}_2\text{SO}_4$  (33). Some of the  $\text{CaSO}_4$  particles contain  $\text{Cl}^-$ . This might point out that  $\text{CaSO}_4$  particles are partly of marine origin: interaction between marine  $\text{CaCO}_3$ , mainly coming from skeletons of pelagic organisms, and  $\text{H}_2\text{SO}_4$  in the air could be a possible source. Fractionated crystallization of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) out of sea spray and splitting off of the gypsum crystals could be another source (34). Other marine elements (such as Na, Mg, and K) were not observed in this type of particle.

In the lower tracks (under 300 m), a considerable part of the detected particles was of anthropogenic origin. The occurrence of these anthropogenic particles explains the aluminosilicates (5%) and organic (5%) and Fe-rich (10%) particles found in the hierarchical clustering. Particle resuspension could be a possible source for the anthropogenic particles, but more likely direct emission from land could explain the occurrence of these particle types. In the predominantly marine flights, air masses at lower levels came over the northwest of France. In the region of Roubaix and Le Havre (France) the iron industry is very intense, which could explain the high abundances of Fe in the lower tracks. Also the power plants in northwest France can partly explain the high abundance of  $\text{CaSO}_4$ .

**(b) Continental Air Masses.** Particle abundances during periods in which the air masses came from the continent were mostly dominated by Ca-rich, organic, and  $\text{CaSO}_4$  particles and aluminosilicates. Ca-rich particles and different combinations mainly containing Ca (e.g., Ca-P, Ca-Si-S, and Ca-Fe) yield 36% of the aerosol abundance. Abundances of Ca-rich and  $\text{CaSO}_4$  particles were always higher for flights with a continental air mass history than for marine flights. Ca-bearing particles can be related to high-temperature combustion processes as well: large quantities of  $\text{CaCO}_3$  are used in thermal power plants, as a desulfurization agent, to enhance the oxidation of  $\text{SO}_2$  and neutralize the  $\text{SO}_3$ ; this leads to sulfates. Furthermore, some of the  $\text{CaSO}_4$  particles were enriched with Si. This particle type is associated with coal combustion (35).

Particles with no major X-ray intensities were classified as organic (17%); they seem anticorrelated with altitude and could therefore be related to biogenic material such as pollen, spores, and bacteria. Organic particles are also emitted during combustion of fossil fuels.

Aluminosilicates are clearly less abundant in typical marine flights than in flights with continental influence, where they account for 11% of the particle abundance. The aluminosilicates can be divided into two groups: windblown soil dust and fly ash. Even though these particles have roughly the same chemical composition, they usually differ in morphology, as will be discussed later. A considerable amount of the aluminosilicates contained S, which can be related to the fact that a substantial part of these particles originates from coal combustion (fly ash). On the other hand, this might be a result of a sulfur layer formed on the soil dust particles, as reported by Winchester et al. (36, 37).

**Table III. Average Composition, Size, and Shape for the Groups Found by the Nearest Centroid Sorting Performed on the EPXMA-Analyzed North Sea Giant Particles**

group no.	group abund, %	diam, $\mu\text{m}$	relative abundance per element, wt %														
			Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Zn	O
1	22	3.2	0.6	0.5	0.6	2.7	0.6	1.3	1.1	0.1	61	0	0.9	0	0	0	31
2	21	4.2	14	1.0	0.1	0.8	0	3.7	75	1.6	2.3	0	0.3	0	0	1.1	0
3	20	3.0	0.9	1.5	0.7	2.2	0.1	21	2.0	0.7	22	0.1	2.4	0.3	0.1	0.1	46
4	17	2.7	1.6	4.0	2.7	4.2	3.1	6.7	11	10	5.0	0.4	5.7	0.6	1.1	11	32
5	14	3.8	0.1	0.5	8.1	28	0.1	1.6	1.2	2.0	6.1	0	4.7	0	0	0.1	47
6	5	2.6	0	0.3	0.3	1.7	0.1	0.1	1.4	0.2	1.5	1.8	60	0.6	0	0.2	31
7	1	2.2	69	0	0	0	0	2.1	0.8	0.4	0	0	0	0	0.3	0	27

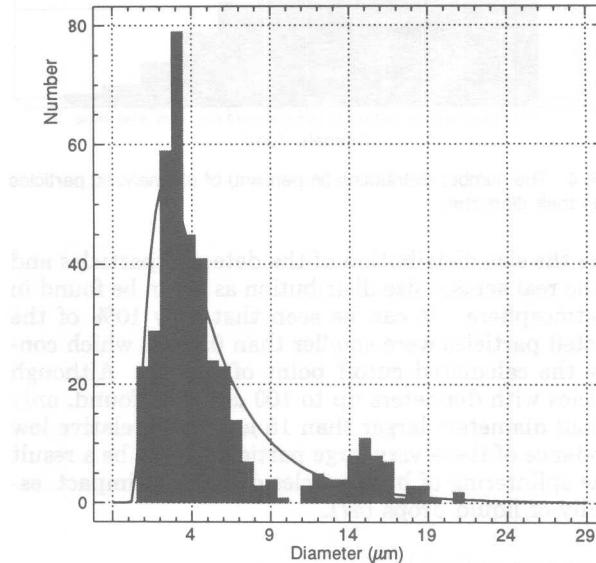
In flights with continental air mass history, potassium and zinc chlorides and phosphates were found. They probably result from burning organic material and municipal waste (38, 39). Results point to a low content of heavy metals in the giant particle size range. Since heavy metals are commonly emitted in high-temperature combustion processes, they are mostly drained into the atmosphere as gases, which condense from the vapor phase to predominantly submicrometer particles at sudden cooling. The occurrence of submicrometer aerosols containing heavy metals above the North Sea has indeed been reported in EPXMA results (40).

The sea-salt particles (4%) were only found in the lowest tracks (20 m). The iron-rich and quartz particles were only found in small amounts (3–4%).

In summary, in flights with air masses with marine influence, the samples were mainly characterized by sea salts, sea salts enriched with sulfur, and  $\text{CaSO}_4$  particles. Samples from flights correlated with air masses of a continental origin were high in aluminosilicates and Ca-rich, organic, and  $\text{CaSO}_4$  particles.

**3. Nonhierarchical Clustering.** To get an overall view on the particle types collected in all samples together, a nonhierarchical clustering was performed. In order to classify the 500 measured particles into 7 particle groups in each of the 25 collected samples, a hierarchical clustering (Ward's method) was performed on each of the 25 samples separately. The average elemental abundances of 175 ( $7 \times 25$ ) particle groups (7 in each sample), obtained from the clustering of the 25 samples, were clustered again, which provided us again with 7 groups of average elemental abundances now for all 25 samples together. These were further used as centroids for the nonhierarchical clustering. Results of the ZAF-corrected nonhierarchical clustering are given in Table III. The oxygen in Table III has been calculated by assuming all elements were present in the form of oxides.

From Table III it appears that 22% of the detected particles consist of Ca-rich (61% Ca) particles. Nearly as much (21%) of the North Sea giant aerosols are sea salts, while 20% of the particles are found to be  $\text{CaSO}_4$  particles. From Table III it can be seen that the Cl/Na ratio in group 2 is 5.4, which is greater than the seawater value. This is a result of the clustering. Since not all particles, which are brought together in the so-called "sea-salt" cluster, necessarily contain the same amount of Na and Cl, the Cl/Na weight ratio after the clustering may significantly differ from the actual Cl/Na seawater ratio. Group 4 can be identified as potassium, zinc chlorides. The abundance of this particle type (18%) is very high compared to the results obtained from the hierarchical clustering, it is likely that they have been mixed up in the nonhierarchical clustering with particles without major X-ray intensities, previously identified as organic particles. Group 5 is characterized by high contents of Al, Si, Ca, and Fe (respectively 8%, 28%, 6%, and 5%) and therefore it can be



**Figure 3.** The log-normal fitted size distribution of the aluminosilicates.

ascribed to aluminosilicates (14%). Group 6 contains Fe-rich (60% Fe) particles (5%), while the low-abundance group (1%) is identified by a high content of Na (69% Na). The size of the particles varies between 2.2  $\mu\text{m}$  for the Na-rich particles and 4.2  $\mu\text{m}$  for the sea salts.

**4. Particle Size and Distribution.** A description of the size distribution of several of the most abundant particle types was achieved by means of a log-normal distribution. The experimentally found size distributions of sea salts, sea salts enriched with sulfur, and  $\text{CaSO}_4$ , Fe-rich, and organic particles turned out to be fitted well by the log-normal distribution, and they also had average sizes between 1 and 3  $\mu\text{m}$ . Aluminosilicates, on the other hand, presented a bimodal distribution; the total distribution could be split up into two separate distributions with average diameters centered at 4 and 15  $\mu\text{m}$ . This suggests the presence of two completely different sources of aluminosilicates. Closer observation of the particle size and shape revealed that the smaller sizes were round in shape, while the fraction of the particles with diameters around 15  $\mu\text{m}$  were often irregularly shaped. This suggests that the smaller, spherical fraction originates from high-temperature combustion processes, which lead to fly ash. Especially when the sampled air masses came from Eastern Europe, these particles were responsible for the major part of the aluminosilicates (>60%). The irregularly shaped larger aluminosilicates, on the other hand, are windblown soil dust particles. The log-normal fitted size distribution of the aluminosilicates is shown in Figure 3.

In Figure 4, a number distribution for all 12500 particles as a function of their size is shown. Attention must be drawn here to the fact the size spectrum is cut off at the lower end by the impaction rod. Therefore, Figure 4 only

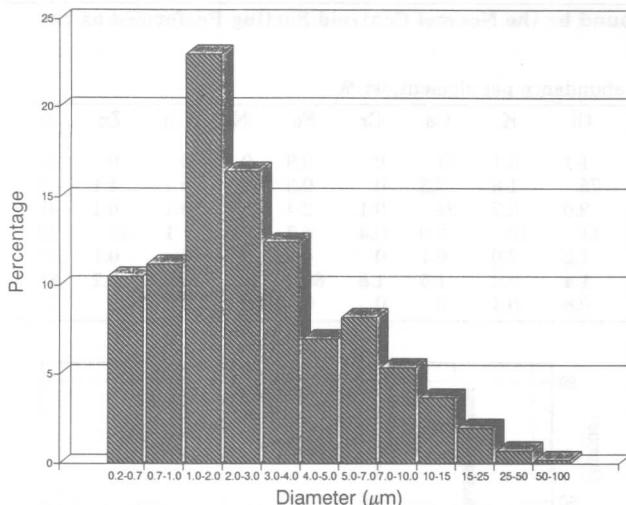


Figure 4. The number distribution (in percent) of all analyzed particles versus their diameter.

shows the size distribution of the detected particles and not the real aerosol size distribution as it can be found in the atmosphere. It can be seen that only 10% of the detected particles were smaller than  $0.7 \mu\text{m}$ , which confirms the calculated cutoff point of  $0.8 \mu\text{m}$ . Although particles with diameters up to  $100 \mu\text{m}$  were found, only 2% had diameters larger than  $15 \mu\text{m}$ . The relative low abundance of these very large particles might be a result of the splintering of big particles during the impact, especially of liquid drops (41).

### Summary and Conclusion

In order to investigate the importance of giant airborne particles, air sampling was carried out over the southern bight of the North Sea. Analysis of the collected samples was done by EPXMA.

Four sources of giant aerosol particles were found by PFA: aluminosilicates, combustion processes, and an industrial and a marine source. Hierarchical and nonhierarchical cluster analysis enabled us to find a clear distinction between flights for which the associated air masses were marine or continental.

The most abundant particle types were fitted with a log-normal size distribution. The experimentally found distributions for sea salts, sea salts enriched with sulfur, and organic,  $\text{CaSO}_4$ , and Fe-rich particles were fitted well by the log-normal distribution, while aluminosilicates had a bimodal size distribution with average size maximums at 4 and  $15 \mu\text{m}$ .

To confirm the importance of giant aerosol particles, further research on giant particle size distributions and collection efficiencies is needed. In the near future, more experiments with the impaction rod should lead to a method which enables us to calculate the upper size limits of the collected giant particles. The design and use of improved and new giant aerosol samplers should allow us to obtain a more precise view on the giant aerosol size distribution and composition.

**Registry No.** Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 7782-50-5; K, 7440-09-7; Ca, 7440-70-2; Fe, 7439-89-6; Cu, 7440-50-8; Zn, 7440-66-6; Cr, 7440-47-3; O<sub>2</sub>, 7782-44-7.

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