

## INFLUENCE OF CONTINENT ON THE DISPERSE AND CHEMICAL COMPOSITION OF AEROSOL IN THE NEAR WATER LAYER IN THE ATLANTIC

**M.V. Panchenko, V.V. Pol'kin, L.P. Golobokova, M.P. Chubarov, O.G. Netsvetaeva,  
and V.M. Domysheva**

*Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk  
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*The data on disperse and chemical composition of the adjacent to water aerosol of the north and central Atlantic are presented based on the results of scientific research performed during the 35th mission of the research vessel "Akademik Mstislav Keldysh." The influence of continental aerosol on the disperse and chemical composition of marine aerosol above the Atlantic is described.*

### INTRODUCTION

In the framework of a long-term program of the Institute of Atmospheric Optics SB RAS on the investigation of optical and microphysical characteristics of atmospheric aerosol in different geographical regions as well as above the ocean<sup>1-5</sup> in January–April 1995 the study of chemical composition and number density<sup>6</sup> of surface aerosol was continued. During the voyage of the research vessel "Akademik Mstislav Keldysh" the preceding studies have shown that the combination of the data on microstructure and chemical composition of atmospheric particles provides better grounds for estimating the contribution of different sources to aerosol formation in the layer adjacent to ocean water.

### EQUIPMENT AND METHOD OF INVESTIGATION

The measurements of aerosol number density were conducted using a photoelectric particle counter of AZ-5 type with 12 measuring ranges, the particle diameters being from 0.4 to 10  $\mu\text{m}$ . To improve the accuracy of the counter the electron scaling instruments were used, namely, the frequency meters of Ch3-63 and Ch3-57 type. The disperse composition was determined during daytime every two hours and occasionally during nighttime. Over the voyage period about 800 aerosol particle size spectra were obtained.

Along with measurements of number density, aerosol sampling with Petryanov filters (AFA-VP-20) was made. The air was pumped through the filter at a rate of 20 l/min. Samples were taken once or twice a day. Sampling lasted from 2 to 24 hours depending on meteorological situation. The analysis of samples was conducted in the laboratory conditions, and the ion composition was determined:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ . The anion

composition of soluble aerosol fraction after extraction from filters with bidistilled water was determined by the method of high-performance liquid chromatography (a "Milikhrom" chromatograph with an error of 4 to 7%). The cation composition was determined by the atom-absorption method (with an AAS-30 instrument, with an error of 4 to 6%).<sup>7</sup> The insoluble fraction of aerosol was studied simultaneously using different methods<sup>8</sup> and we do not discuss this in this paper.

### AREAS OF MEASUREMENTS

The investigations of aerosol properties have been made during the voyage of the research vessel along the route depicted in Fig. 1. Here the polygons, where the investigations were conducted, are denoted by small circles. The vessel route is shown by heavy solid curve. The direction of the dust from Sahara transported from the African continent is shown by arrows; geographic regions with similar aerosol characteristics are denoted by figures. In other figures we denote the regions, where the measurements were conducted, with figures in circles (1 is for Kaliningrad, North sea, Spain; 2 – Canary Islands; 3 – "Tradewind," 4 – Darkness sea, 5 – Equator).

The geographic regions, where the investigations were carried out, differ in aerosol characteristics. A brief description of the above regions along with climatic and optical aerosol characteristics is given in Ref. 6. The contrast of aerosol patterns in the regions shows that the possibility exists of estimating the degree of anthropogenic and terrigenous influence of dry land on the disperse and chemical composition of aerosol.

### ANALYSIS OF EXPERIMENTAL DATA

When analyzing the experimental material obtained on the chemical and disperse composition of

aerosol the authors attempted to separate the contributions to chemical composition of the near water oceanic aerosol from particles of purely marine origin and from the particles of continental origin. It was important to estimate the relation between the

aerosol particle size spectra and the content of some chemical elements in aerosol. These problems are important for understanding physicochemical processes of aerosols transformation and their removal from the atmosphere.

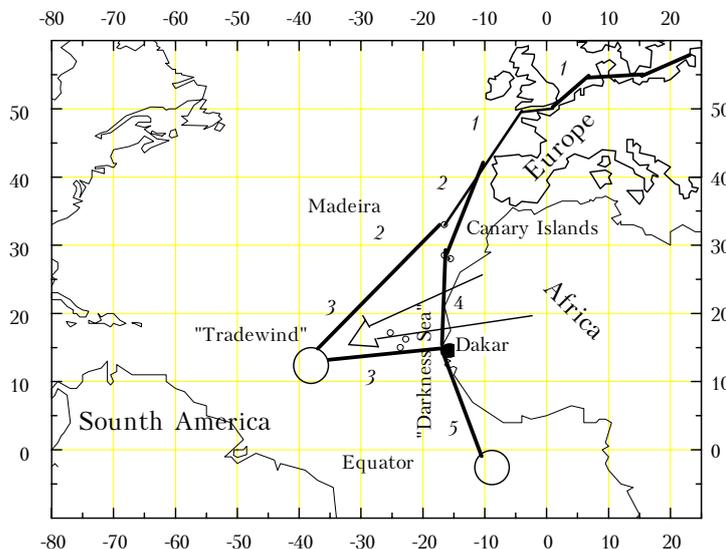


FIG. 1. Navigation chart of the route of the 35th mission of the research vessel "Akademik Mstislav Keldysh."

It is natural to assume that the main source of aerosol above the ocean is the salt in particles formed as a result of sea waves break and burst of air bubbles reaching the ocean surface. These mechanisms of aerosol formation should mainly govern the aerosol disperse and chemical composition. Therefore it is important to determine the content and relations of individual chemical elements typical for the sea water. This makes it possible to separate

out the particle contributions to chemical composition, of near water aerosol namely, the contribution from sources of purely marine origin and that from other sources located on the continent.

The content of ions in sea water is now better understood and most fully presented in Ref. 6. The analysis of the ratios between chemical elements for our measurements is convenient to be conducted using data in Fig. 2.

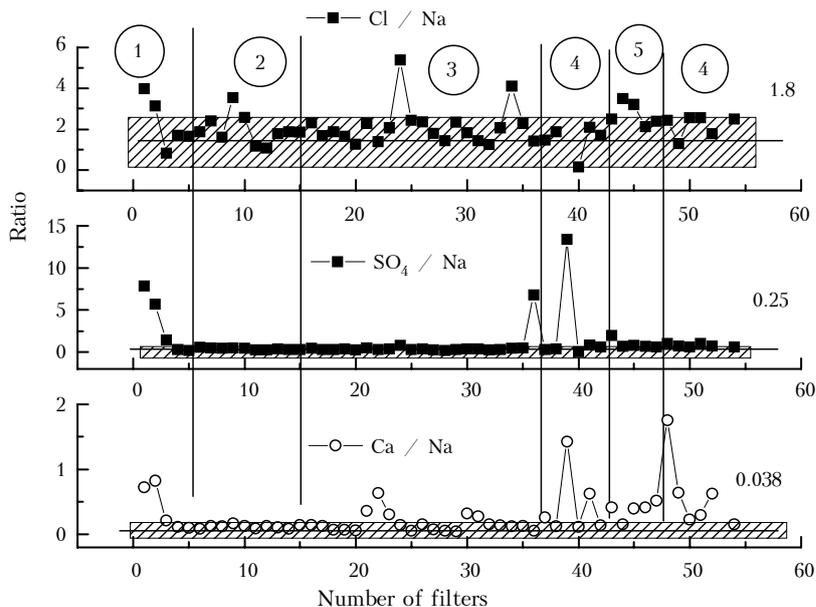


FIG. 2. Ratio between separate chemical elements.

In the figure the shaded areas show the corridor of the ratios for corresponding chemical elements measured by other authors.

The estimates of the ratios for the above-mentioned chemical elements show that the value of  $\text{Cl}^-/\text{Na}^+$  is close to the value typical for sea water practically in all measurements and equals to 1.8.<sup>9</sup> The ratio of Cl and Na ions in aerosol above the sea surface was also studied in Ref. 11. For example, from measurements on San-Nikola island (130 km far from Los Angeles) this ratio was obtained to be 2.4, that is, more than in sea water. Sometimes quite opposite situation occurred. The Cl losses (13% of the Cl content in sea water) were observed during the measurements in Puerto Rico and the Cl losses (54% of the Cl content in sea water) were observed in the gulf of San Francisco. On the basis of linear relation between the Cl losses and  $\text{NO}_2$  content in air the conclusion is drawn that the basic cause of Cl losses is the reaction  $\text{HNO}_3 + \text{NaCl} \rightarrow \text{HCl} + \text{NaNO}_3$ . It should be noted that in our measurements the ratio  $\text{Cl}^-/\text{Na}^+$  took the values within the above range varying about the value 1.8.

The ratio of ions  $\text{SO}_4^{2-}/\text{Cl}^-$  in samples analyzed is more than the typical values for sea water -0.14. This fact was noted in papers by other authors,<sup>10,11</sup> who conducted the measurements in the Atlantic ocean. The excess of sulfates relative to chlorides cannot only be explained by the processes of the sea surface break. In some cases the dominance of sulfates can be explained only by the presence of ions of continental origin. For the North Atlantic<sup>11</sup> the ratio of  $\text{SO}_4^{2-}/\text{Na}^+$  in the sea aerosol is three times as large as that in the sea water (0.25). In this case 50% of the excess ions of  $\text{SO}_4^{2-}$  are in particles of the diameter  $<0.45 \mu\text{m}$  that, probably, is indicative of gas phase

reactions of sulfates formation above the sea surface.<sup>12</sup> However, the ion-molecular reactions are more probable as well as catalytic and photocatalytic oxidation of sulfur compounds in small water droplets ( $\text{SO}_2 + \text{H}_2\text{O} + \text{O}_3 + \text{catalyst}$ ). This assumption is confirmed by the experimentally observed dependence of the sulfate concentration in the near water atmospheric layer on relative humidity.<sup>11</sup> The ratio of  $\text{Ca}^{2+}/\text{Na}^+$  in our measurements differ also from the ratio in the sea water (0.038), especially for the coastal areas. As was noted by Junge,<sup>9</sup> the ratio of  $\text{Ca}^{2+}/\text{Na}^+$  increases in aerosols, as compared with sea water on the average by 153%, that can be considered as the upper limit of sea surface spraying. In these measurements the above ratio is much larger in some cases that may only be explained the effect of the continent.

It is evident that the close ratio of ions of  $\text{Cl}^-$  and  $\text{Na}^+$  in the sea water<sup>9</sup> and in the near water layer enables us to take it as a basic one for calculating the contribution of purely marine substances to aerosol in near water layer. For this purpose the normalized excesses of ion content in aerosol were calculated as compared with the sea water by the formula

$$\Delta R_i = (R_i - k \cdot \text{Na}) / (k \cdot \text{Na}),$$

where  $R_i$  is concentration of the  $i$ th ion in aerosol; Na is the Na ion concentration in aerosol;  $k$  is the ratio of  $R_i$  to Na content in the sea water.<sup>9</sup> The results of calculations obtained are presented in Fig. 3.

Note that the excess of sulfates and calcium clearly manifests itself in measurements near ports (Kaliningrad) where the excess of  $\text{Mg}^{2+}$  and  $\text{K}^+$  is also observed during the periods corresponding to the moments of dust transport from the West Africa.

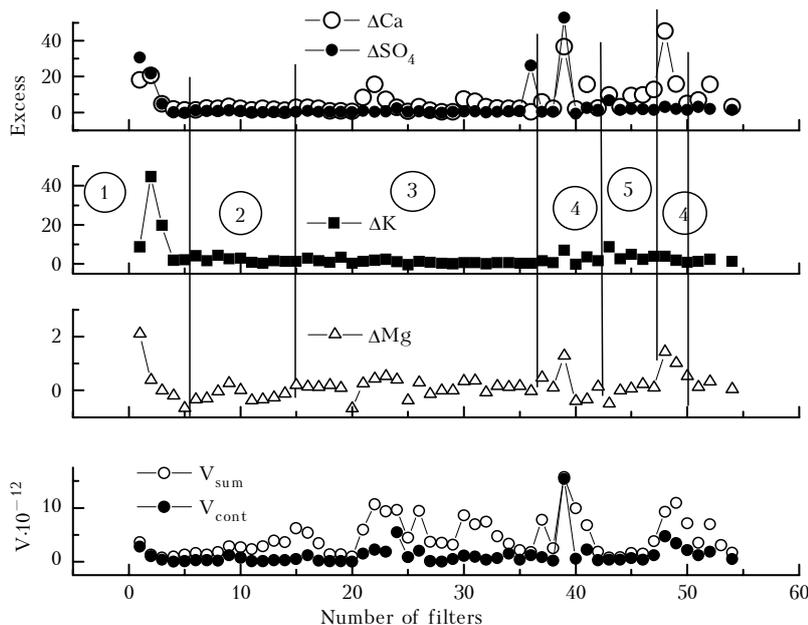


FIG. 3. Normalized "excesses" of ion content in aerosol as compared to that in sea water.

In order to isolate from near water aerosol the fraction of marine origin and that coming from other sources we have compared the total space factor with the space factor of aerosol from which the specific volume of aerosol of marine origin. Comparison used the formula

$$V_{\text{cont}} = V_{\text{sum}} \left\{ \frac{\sum_i (R_i - k \text{Na})}{\sum_i R_i} \right\},$$

where  $\sum_i R_i$  is the sum concentration of all ions in the aerosol, and  $\sum_i (R_i - k \text{Na})$  is the sum concentration of all ions excluding those of marine origin.

The behavior of the sum space factor and  $V_{\text{cont}}$  is shown in Fig. 3. The figure shows that the excess of calcium and sulfates corresponds to the moments when the values of  $V_{\text{sum}}$  and  $V_{\text{cont}}$  are close, i.e., when the near water aerosol composition is mainly determined by aerosol of not marine origin. These moments are consistent with the measurements conducted close to the European continent and maximum values of arid aerosol transport from Africa.

To evaluate the influence of a continent on chemical composition of the near water aerosol of particular interest in the analysis of ion content of samples of particles taken from the top mast of the

vessel (the height is more than 20 m above the sea level) at a period of greatest dust influx from the African continent. Since the aerosol was taken to filters onboard, in the immediate vicinity of the sea surface (about 4 or 5 m) and the particle samples were taken at a larger height, the ion composition of aerosol particles may be different. It is believed that chemical composition of particles measured on top of mast, may be the same as the chemical composition of dust to a greater degree, than the chemical composition of particles collected on the aerosol filters. The weight and relative concentrations of chemical elements are given in the Table I. The comparison of the content of chemical elements, made for ions of sea water<sup>9</sup> and dust, shows that the relative (normalized to  $\text{Na}^+$  concentration) content of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  is comparable with that for sea water and dust. The  $\text{Ca}^{2+}$  content in the dust differs greatly. When comparing the relative content of  $\text{Ca}^{2+}$  for the regions "Tradewind," "Darkness Sea," and the Sahara dust taken from the mast we can conclude that the  $\text{Ca}^{2+}$  content increases from that in the region "Tradewind," being at larger distance from Africa, to the value in the region "Darkness Sea" in the vicinity of the continent and reaches the value 0.4 for the dust taken on the mast. This fact demonstrates once more that the main source of  $\text{Ca}^{2+}$  for the surface atmospheric layer above sea is the dust from Sahara.

TABLE I. Weight concentration and relative content of some chemical elements for sea water and Saharan dust taken from the vessel mast. Relative content of chemical elements in aerosol for regions "Tradewind" and "Darkness Sea."

Chemical element	Weight concentration (mg/g)		Relative content			
	Sahara dust	Sea water <sup>8</sup>	"Tradewind"	"Darkness Sea"	Sahara dust	Sea water <sup>8</sup>
$\text{Na}^+$	60.0	10.56	1	1	1	1
$\text{K}^+$	3.2	0.38	0.066	0.044	0.05	0.036
$\text{Mg}^{2+}$	6.8	1.27	0.11	0.09	0.11	0.120
$\text{Ca}^{2+}$	23.2	0.40	0.13	0.22	0.40	0.038
$\text{Cl}^-$	185.5	18.98	1.81	0.81	3.09	1.800
$\text{SO}_4^{2-}$	21.7	2.65	0.41	0.18	0.36	0.250

Let us pay attention when analyzing the table, to the fact that relative content of sulfates in aerosol for the region "Tradewind" is larger than for the region "Darkness Sea." It is evident that this depends upon the fact that the fine aerosol fraction, enriched in sulfates to a greater degree than the coarse aerosol fraction, is transported by air masses at large distances and is also replenished with the sulfate anthropogenic aerosol from the north regions of Africa and Europe.

The reasons of difference of chemical composition of aerosol particles of various size are mainly conditioned due to peculiarities in creation and formation of aerosol particle size distribution from different sources, selectivity of processes of

removal from the atmosphere. Chemical composition of fine aerosol fraction is basically determined by the particle substance formed in the course of gas-phase transformations. Large particles are formed as a result of mechanical destruction of rocks. So, Junge<sup>9</sup> studied the content of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4$ , and  $\text{Cl}^-$  in aerosol and pointed out that the content of the first two ions is much the same that is indicative of the fact that these ions exist in the atmosphere mainly in the form of particles of ammonium sulfate with the maximum of particle size distribution below 1  $\mu\text{m}$ . For chlorides the distribution maximum is shifted towards larger particles.

In particular, the measurements made with the use of multistage impactor in the region of the city of Osaka have shown that Al and Ca are found mainly in the particles of the size more than  $3\ \mu\text{m}$ , and the contents of Na, Cl, K, Mn, Fe have two maxima in the distribution, which are observed more often within the size from 1 to  $3\ \mu\text{m}$ . The measurements in the city of Nagoya revealed different nature of particles of different size, i.e., the modal diameter of the mass particle distribution is  $0.5\ \mu\text{m}$  and it is due to ammonium sulfate and typical for winter months, and the modal diameter of  $40\ \mu\text{m}$  due to the presence of nitrate particles and is clearly observed in summer.<sup>11</sup> Dr. P.F. Svistov<sup>13</sup> has proposed models of chemical soluble aerosol material for two ranges of particle size, namely, for the coarse fraction of radius more than  $1\ \mu\text{m}$  with the basic ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and the medium-size fraction of radius less

than  $1\ \mu\text{m}$  with the basic ions  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ .

To analyze the behavior of fine and coarse fractions in different situations, and their connections with chemical elements the measurement range of photoelectric counter was divided into two ranges:  $0.4\text{--}1$  and  $1\text{--}10\ \mu\text{m}$  in diameter corresponding to fine and coarse aerosol fractions. The space factors for the above-mentioned ranges were calculated by the formula

$$V = \frac{4}{3} \pi \sum_{i=1}^n N_i r_{\text{mean}}^3,$$

where  $N_i$  is the particle concentration in the  $i$ th subrange (particles/l);  $r_{\text{mean}}$  is the mean particle radius in the  $i$ th subrange;  $n$  is the number of subranges in one of the above two subranges.

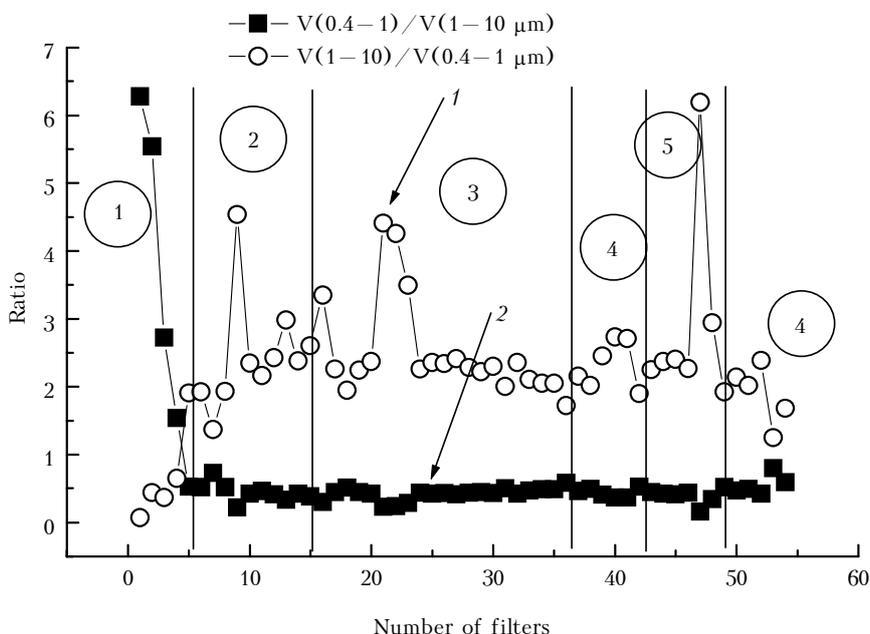


FIG. 4. The ratios of space factors of the fine and coarse aerosol fractions in the marine surface layer in the Atlantic.

In figure 4 the curves corresponding to the ratio of space factors of fine and coarse aerosol fractions are shown. Curve 1 shows the dominance of volume content of large particles and curve 2 shows the dominance of fine particles. The peaks in the first curve correspond to the moments of arid dust aerosol from the African continent, which were observed both near the northwest part of Africa (the region of Canary Islands) and in the area of constant tradewinds where much dust was transported far to the Atlantic ocean. The measurement data obtained in the port of Kaliningrad, in the North Sea and in the western part of the Spain coast are denoted by curve 2 (sharp initial increase of the curve).

We have obtained the following data when comparing the behaviors of the aerosol space factors

and the normalized excess of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ion content above the sea surface (Figs. 5 and 6). The enhanced sulfate content in the particle matter mainly corresponds to a larger relative content of fine aerosol in the marine air, and it is observed in the vicinity of European continent where, evidently, the aerosol of anthropogenic origin prevails. The excess of Ca corresponds mainly to the moments of dust transport from African continent. In dust normally large particles dominate. Figure 5 also shows the behavior of absolute content in soluble part of the Fe ion matter. Note that the maximum in Fe concentration are observed in the regions where the dust aerosol from Sahara is of crucial importance in the formation of total mass of aerosol matter above the ocean.

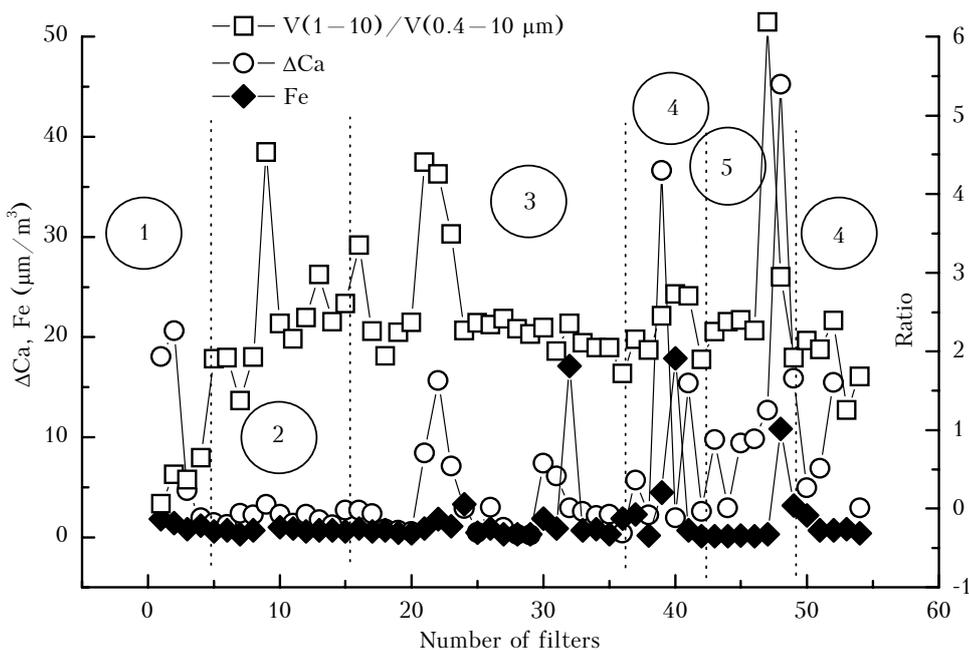


FIG. 5. Comparison of “excess” of Ca content and absolute Fe content with the ratio of space factors of coarse and fine aerosol fractions.

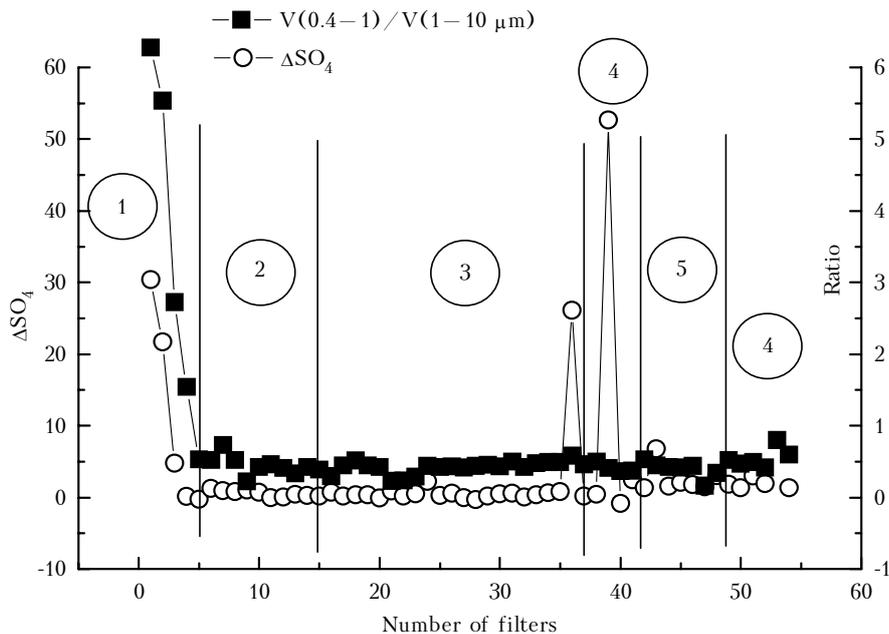


FIG. 6. Comparison of the “excess” sulfate content and the ratio of space factors of fine and coarse aerosol fractions.

**CONCLUSION**

The analysis made has shown that we can isolate, based on data on ion composition of soluble fraction of near water aerosol substance, the contributions to aerosol particles composition coming from the sea water and from dust transported from the continent. When we consider the variability of

specific volume of near water aerosol and the space factor of dust particles, the estimate can be made of the dust particle matter contribution to the composition of the near water aerosol.

When analyzing the variations of space factors of different fractions of aerosol particles and by comparing those with the behavior of excess of some chemical elements, we may surely say about

prevailing content of separate chemical elements in these fractions of aerosol particles.

The implementation of such an approach shows that in the regions of the Atlantic ocean, studied, the contribution of continental sources to the formation of the composition of near water aerosol is significant. For the Darkness Sea the contribution of the coarse aerosol from dust is from 30% to 100%, in the region of tradewind the above contribution is from 10% to 30%, in the equator it is about 30%. The aerosol of anthropogenic origin manifests itself close to the coast of Europe where in the near water layer the content of anthropogenic aerosol is, on the average, about 25% (of the total volume) and more than 60% of specific volume of submicron particles.

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