

Ion composition of near-water aerosol over White Sea in Augusts of 2003–2006

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The results of scientific studies of the chemical composition, number concentration, and microstructure of near-water aerosol of White Sea, obtained in August of each year (2003–2006) from onboard of Research Vessel *Professor Shtokman* are under discussion. The volume of the obtained data for different regions of White Sea makes it possible to more completely and correctly estimate the ion composition of aerosol substance and to study the interrelations of separate chemical elements (ions) with dispersivity of aerosol particles.

Introduction

The atmosphere is one of the important channels of exchange and redistribution of aerosol substance at northern latitudes of the Earth.

The study of the spatiotemporal variations of parameters of aerosol particles of near-water layer of the marine atmosphere is of extreme importance, as well as interrelation of the chemical composition and disperse aerosol properties. For these purposes, the aerosol microstructure, number concentration, and chemical composition had been studied in different regions of White Sea in August for a number of years (from 2003 to 2006) onboard the Research Vessel *Professor Shtokman*.^{1–5}

The volume of the obtained data in different years and in different regions of White Sea makes it possible to more fully and correctly estimate the ion composition of near-water aerosol and to draw statistically significant conclusions.

1. Instrumentation and methods of study

The aerosol disperse composition was studied using automated photoelectric particle counter of the type AZ-5 (256 measured size ranges of particles from 0.4 to 10 μm in diameter). The sampling device AZ-5 was located on the left side of the vessel in the laboratory at a height of about 4 m above water surface. The measurements were made round day hourly.

The aerosol samples for determination of the chemical composition of soluble aerosol fraction were collected using two installations: standard particle aspirator and 3-cascade impactor onto Whatman filters. For air pumping, we used air blower of the model 822 with productivity of 20 l/min in the aspirator channel and 5 l/min in the impactor channel. The installation for collection of aerosol

samples was mounted on direction finding deck in the zone of minimal disturbing effect of the vessel. In the cascade impactor, three cascades with slit diameters $d_1=7.9$, $d_2=5.0$, and $d_3=3.2$ mm were sequentially installed. Particles, not deposited on obstacles and having passed through the next cascade of the impactor, were collected on the filters. In impactor, test samples (in absence of cascade, i.e., without deposition of aerosol on obstacles) from the filter were also taken. The rate of aerosol sampling on the filters of aspirator was 1–2 times daily. In parallel, we took aerosol samples using impactor. The duration of aerosol sampling on the aspirator filters was between 4 and 14 h, and on the filters of impactor between 1.5 and 3 h per a cascade.

Concentrations of ions Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} , and pH of water-soluble aerosol fraction were measured under laboratory conditions. The chemical composition of the soluble fraction of aerosol substance was determined using modern analytical methods: high-efficiency liquid-state chromatography, the potentiometric method, the method of atomic absorption and spectrophotometry.⁶

2. Volume and characterization of the obtained data

In period from 2003 to 2006, we studied the spatiotemporal variations of the chemical composition of aerosol in the near-water marine atmosphere during 55, 64, 71, and 80th cruises of RV *Professor Shtokman*. For four cruises in the water basin of the White Sea, we performed about 1500 series of microphysical measurements, and collected aerosol samples on 48 filters of aspirator and 174 filters of impactor.

The map-diagram of sampling activities along the routs of vessel travel for entire measurement period 2003–2006 is presented in Fig. 1.

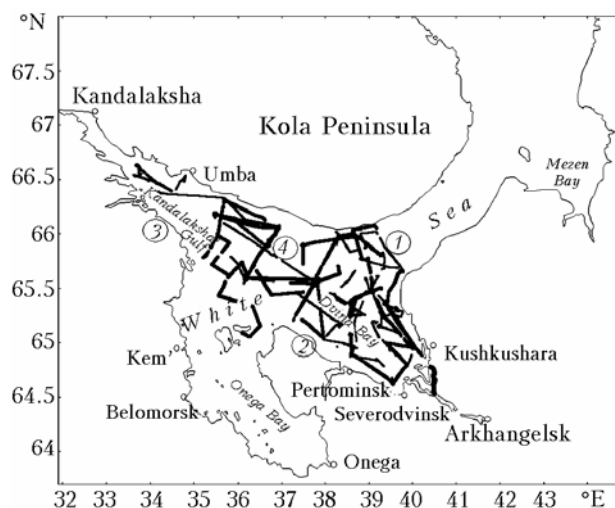


Fig. 1. Map-diagram of 55, 64, 71, and 80th cruises of RV *Professor Shtokman* with indication of regions of sampling with use of aspirator and impactor.

Thick lines indicate the regions of aerosol sampling with the use of aspirator and impactor, and numbers indicate the conditional regions.

3. Analysis of experimental data

3.1. Mean ion concentrations

The statistical analysis of ion concentrations was made for the array of aspirator data as most confident and representative in contrast to the impactor data. As much as 18 m^3 of air was pumped through the filters of aspirator, while a single cascade of impactor processed less than 1 m^3 of air; thus, the accuracy of concentration determination is much higher for aspirator than for impactor.

The table presents the results of the statistical processing of aspirator data on ion composition, obtained during all cruises.

Table. The data on ion composition of aerosol obtained using aspirator during all cruises in 2003–2006.

Ion	Mean value, $\mu\text{g} \cdot \text{m}^{-3}$	rms	Minimum value, $\mu\text{g} \cdot \text{m}^{-3}$	Maximum value, $\mu\text{g} \cdot \text{m}^{-3}$	Number of measurements
Cl^-	7.469	7.244	1.849	36.43	46
Na^+	3.832	3.465	0.840	17.37	46
Mg^{2+}	0.334	0.532	0.020	2.170	43
K^+	0.222	0.188	0.040	0.859	46
Ca^{2+}	0.656	0.885	0.040	3.960	46
SO_4^{2-}	3.275	2.652	0.404	14.55	46
NO_3^-	0.626	0.333	0.120	1.327	46
NH_4^+	0.885	0.810	0.030	2.670	46
HCO_3^-	1.685	1.268	0.320	4.473	14

We excluded from analysis the data sorted out in view of the evident fall of spray of sea waves upon the filtering material. Comparison of the mean values

obtained in our studies⁷ with data of other authors showed good agreement in absolute concentrations of ions Cl^- , Na^+ , and Mg^{2+} of marine origin. The difference lies in increased concentrations of ions Ca^{2+} , SO_4^{2-} , NO_3^- , and NH_4^+ for White Sea. When compared with data for Pacific and Indian oceans,^{8,9} these discrepancies may reach up to a factor of 3.4 for Ca^{2+} , up to a factor of 2.9 for SO_4^{2-} , up to a factor of 1.5 for NO_3^- , and up to a factor of 2 for NH_4^+ . These differences are explained by the fact that White Sea is actually an internal sea, experiencing more powerful influence of continental sources compared with other water basins of the World Ocean.

3.2. Variations of ion concentrations from one region to another in different years

The mean ion concentrations have large differences in absolute value; therefore, we consider the variations of the ratio of root-mean-square deviations to mean values of ion concentration, and these results are presented in Fig. 2.

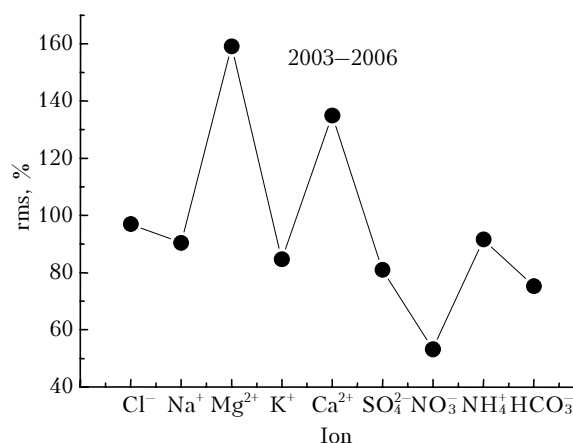


Fig. 2. Percentage values of rms deviation from the mean for ions obtained for entire array of 2003–2006 measurements.

Data are in percent of the mean value for entire array of the 2003–2006 measurements. It is seen that the maximum variations of concentrations of elements take place for ions Mg^{2+} and Ca^{2+} (about 160 and 135%, respectively). The minimum values are observed for NO_3^- (53%). Relative variations of other ions are intermediate in magnitude and vary in the range from 75 to 97%.

Consider the variations of ion mass concentration in different regions of White Sea. Figure 3 presents the percent variations V of ion mass concentrations from mean values during all cruises in 2003–2006 for chosen regions of measurements.

The variations V were calculated by the following formula:

$$V = 100 \cdot NX / NX_{av} - 100,$$

where NX is the average concentration of a chemical element for a year in a region; and NX_{av} is the average concentration of a chemical element for all cruises in 2003–2006.

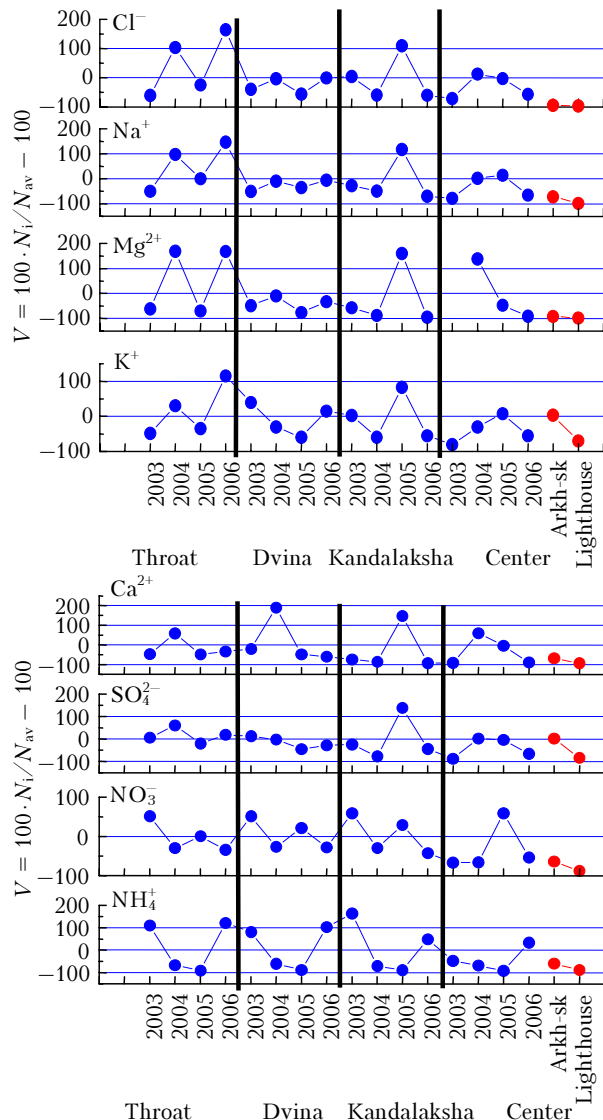


Fig. 3. Variations of concentrations of ions N_i , represented in percent of the average value for 2003–2006 over different years and regions.

We have chosen three regions of White Sea (see Fig. 1), which are subject to influence of continental sources with large probability. These regions are conditionally denoted as: 1) “Throat” (9 filters), i.e., sampling territories in the regions adjacent to narrowing of White Sea toward Mezen Bay and to the outlet to Barents Sea; 2) “Dvina” (13 filters), i.e., sampling territories in Dvina Bay; 3) “Kandalaksha” (13 filters), i.e., sampling territories in Kandalaksha Gulf. Number 4 in Fig. 1 denotes the central (“Center”, 11 filters) region of White Sea, least subject to the effect of continental sources. For comparison purposes, we also present data obtained on the continent in the region of

Arkhangelsk (“Arkhangelsk,” region of Summer coast of Dvina Gulf of White Sea, 3 filters) and in the region of Unsk lighthouse (“Lighthouse,” Marine hydrometeorological station “Unsk lighthouse,” 11 filters).

For the “Throat” region, maximum variations of concentrations of ions Cl^- , Na^+ , Mg^{2+} are recorded, and the largest deviations from mean values, characteristic for seawater, are 164, 146, and 169%, respectively. In this region we record the largest values of wind speed (18–20 m/s) and rough sea (up to 6 numbers), which, naturally, favored increased generation of salt aerosol from sea surface. The value of variation V , averaged over all ions and years for this region, was 71%.

The characteristic feature of “Dvina” region is that in all periods of observations, the concentrations of ions Cl^- , Na^+ , Mg^{2+} , inherent primarily to salt aerosol, differed little from the mean values. At the same time, this region has maximal variations of concentrations of ions Ca^{2+} in 2004 (about 200%); therefore, the increased calcium content in this case can be explained only by the influence of continental aerosol sources.

Among all the regions, the maximal values of V variation, averaged over all ions and years, are observed for “Kandalaksha” region, equal to 76%. For this region, in 2005 we observed concentration variations close to maximum practically for all ions with exception of nitrates and ammonium. Considering that these two ions are characteristic for continental sources, we should speculate that the presence of maximum of concentration for other ions is caused by increased generation of marine aerosol.

In absolute value, minimal variations of ion concentrations V are observed in all expeditions for the regions “Center” (60%) and “Dvina” (40%).

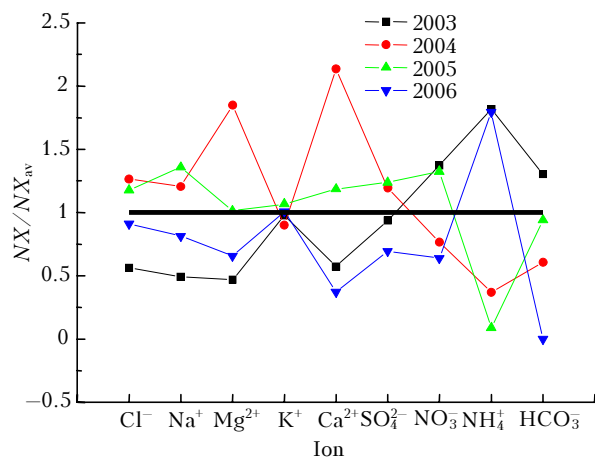
The variation V averaged over all ions and regions was found for 2003, 2004, 2005, and 2006 to be 57, 67, 61, and 71%, respectively.

3.3. Ion composition and its connection with ratio between finely and coarsely dispersed particles

Analysis of interrelation between ion composition and dispersion properties of aerosol was performed using integrated parameter introduced by ourselves in Ref. 10; it was calculated as the ratio of concentration of submicron fraction to coarsely dispersed fraction

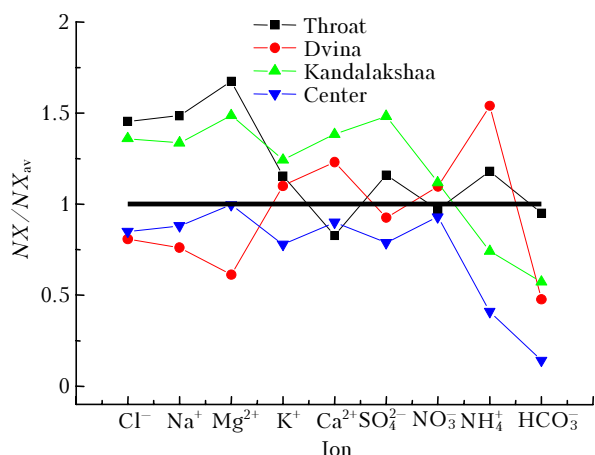
$$N_{sub}/N_{coars} = N(r = 0.2-0.5)/N(r = 0.5-1 \mu m).$$

Data on the concentrations are obtained using photoelectric counter of aerosol particles AZ-5. In Fig. 4, these data are given in the form of tables, which present the values of N_{sub}/N_{coars} , N_{sub} , and N_{coars} averaged over regions and for the expedition of each year. Also shown are the dependences of the ratios of the mean ion concentrations NX for a particular region and a year to the mean concentrations NX_{av} , obtained for the entire array of 2003–2006 measurements.



Year	$N_{\text{sub}}/N_{\text{coars}}$	$N_{\text{sub}}, \text{cm}^{-3}$	$N_{\text{coars}}, \text{cm}^{-3}$
2003	46.1	22.7	0.59
2004	9.95	20.4	3.4
2005	18.8	15.9	1.27
2006	14.8	12.9	1.75

a



Region	$N_{\text{sub}}/N_{\text{coars}}$	$N_{\text{sub}}, \text{cm}^{-3}$	$N_{\text{coars}}, \text{cm}^{-3}$
Throat	22.5	22.0	1.98
Dvina	28.6	21.7	1.37
Kandalaksha	15.1	9.94	1.23
Center	14.3	15.0	1.63

b

Fig. 4. Ratio of the mean ion concentrations NX for (a) different years and (b) regions to the mean concentrations NX_{av} obtained for entire array of 2003–2006 measurements.

In 2003 and 2006, the lowest NX/NX_{av} values were obtained for ions of marine origin Cl^- , Na^+ , and Mg^{2+} , as well as for ions Ca^{2+} and SO_4^{2-} , and the highest NX/NX_{av} values for NO_3^- and NH_4^+ , i.e., ions characteristic for continent. At the same time, in 2003 we obtained the highest $N_{\text{sub}}/N_{\text{coars}}$ and N_{sub} values and the lowest N_{coars} values. These facts indicate that the ion composition and the shape of particle size distribution function most closely correspond to continental aerosol.

For 2004 and 2005 (in comparison with 2003 and 2006), an inverse pattern in ion composition and behavior of the ratio $N_{\text{sub}}/N_{\text{coars}}$ is observed. Hence, the ion composition and the shape of the particle size distribution function more closely correspond to marine aerosol.

For the “Throat” region, the analysis of behavior of the ratios NX/NX_{mea} (Fig. 4, b) shows that it has the highest (relative to mean) concentrations of sea-derived ions (Cl^- , Na^+ , and Mg^{2+}), increased concentrations of K^+ , SO_4^{2-} , and NH_4^+ , and the lowest concentrations of calcium. The “Throat” region differs from other regions by the highest values of parameters $N_{\text{sub}}/N_{\text{coars}}$, N_{sub} and N_{coars} (the shape of the particle size distribution function closer corresponds to the continental aerosol). It should be noted that this region is characterized by the presence of large wind speeds and strong sea surface roughness. This leads to increased content of sea-derived ions in the chemical composition and to increased (in comparison with other regions) aerosol particle number concentration in size spectrum for entire working size range of the photoelectric counter.

The “Kandalaksha” region is characterized by the highest concentrations of ions of potassium, calcium, sulfates, and nitrates, high mean values of concentrations of sea-derived ions Cl^- , Na^+ , Mg^{2+} , but low concentrations of NH_4^+ and HCO_3^- . For this region, the value of N_{sub} is lower than for the “Throat” region, while the N_{coars} value is close to values of N_{coars} in other regions. Therefore, the particle size distribution function for this region is closer in shape to marine aerosol.

The highest NH_4^+ concentrations are detected in “Dvina” region. This region distinctly has high concentrations of K^+ , Ca^{2+} and NO_3^- , i.e., ions typical for continental sources, and also the lowest concentrations of Cl^- , Na^+ , and Mg^{2+} , i.e., ions typical for sea water. In this region, the N_{coars} value is low for high value of N_{sub} ; therefore, the shape of particle size distribution function most closely corresponds to continental aerosol.

In the central regions of White Sea (“Center” region) for ions K^+ , SO_4^{2-} , NO_3^- , NH_4^+ , and HCO_3^- we observe the lowest concentrations, and for other ions the concentrations are lower than the mean. The N_{coars} values are high in these region, whereas N_{sub} values are low; therefore, the ratio $N_{\text{sub}}/N_{\text{coars}}$ is the lowest of all regions and, hence, the shape of the particle size distribution function most closely corresponds to marine aerosol.

3.4. Estimate of connection between ion composition and disperse properties of particles according to impactor data

The use of impactor makes it possible to estimate the ion content in different-sized aerosol fractions. Deposition of particles with $r > 0.5 \mu\text{m}$ on the first cascade (slit diameter $d_1 = 7.9 \text{ mm}$) made

approximately 25% efficiency, deposition of particles with $r > 0.6 \mu\text{m}$ on the second cascade ($d_2 = 5 \text{ mm}$) – 40% efficiency, and deposition of particles with $r > 0.9 \mu\text{m}$ on the third cascade ($d_3 = 3.2 \text{ mm}$) – 60% efficiency.

The middle of the boundary separating aerosol particles into fractions lies in the region $r = 0.4\text{--}0.5 \mu\text{m}$.³ In analysis of the data, we note the strong differences in ion concentrations for different impactor cascades. This means that the ions are mostly in size range of coarsely dispersed particles with radii larger than $0.4\text{--}0.5 \mu\text{m}$. The absence of differences in ion concentrations means that the ion is contained in finely dispersed fraction of particles with radii less than $0.4\text{--}0.5 \mu\text{m}$. If these differences are small, then the ion is present both in finely and coarsely dispersed fractions.

For all 2003–2006 cruises we calculated the mean concentrations of ions for different cascades of impactor (Fig. 5).

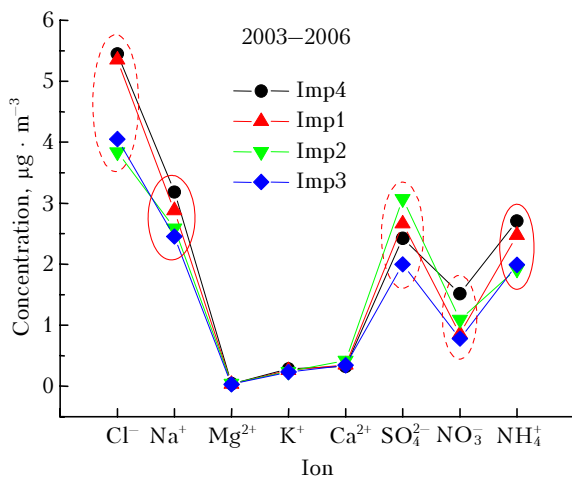


Fig. 5. Ion mass concentrations, averaged over entire array of 2003–2006 data, for different cascades of impactor: abbreviation “Imp” means sampling on the filter without preliminary deposition on the cascade; and “Imp1,” “Imp2,” and “Imp3” stand for the first, second, and third cascades.

Certain nonuniformity in separation of ion concentrations among cascades can be explained by different time of sampling in the presence of nonuniformity of aerosol concentration along the measurement path.

Analysis of Fig. 5 shows that the ions Cl^- and Na^+ , typical for seawater, are predominately present in coarsely dispersed fraction of aerosol particles. The ions SO_4^{2-} , NH_4^+ , and NO_3^- , typical for continental aerosol, are present both in coarsely and finely dispersed fractions. The ions Mg^{2+} , K^+ , and Ca^{2+} are present mainly in finely dispersed fraction.

Conclusion

Summarizing the results of the study of variations of ion concentration and interrelations of ion and disperse composition for different regions and

in different time intervals, we can conclude the following.

The main differences between the mean ion concentrations of soluble fraction of near-water aerosol over White Sea, as compared to aerosol from other regions of World ocean, are the increased concentrations of ions of continental origin: Ca^{2+} , SO_4^{2-} , NO_3^- , and NH_4^+ . The maximal differences may reach up to a factor of 3.4, 2.9, 1.5, and 2, respectively. The maximum variations of concentrations of elements are observed for ions Mg^{2+} and Ca^{2+} (160 and 135%, respectively), and minimal variations for ions NO_3^- (53%). The variations of other ions are intermediate in magnitude and vary by less than a factor of 2.

Large wind speeds (up to 18–20 m/s) and high sea rough (up to 6 numbers) of the sea surface lead to generation of sea-derived aerosol particles across entire size spectrum of the sensitivity range of the photoelectric counter AZ-5 ($> 0.2 \mu\text{m}$ in radius). This leads to increase of the concentration of the ions Cl^- , Na^+ , Mg^{2+} , increase of the concentration of particles of submicron N_{sub} ($r = 0.2\text{--}0.5 \mu\text{m}$) and coarse N_{coars} ($r = 0.5\text{--}1 \mu\text{m}$) ranges and their ratio $N_{\text{sub}}/N_{\text{coars}}$.

Sea-derived ions Cl^- and Na^+ are contained predominately in the coarse aerosol fraction. In the fine fraction, Mg^{2+} , K^+ , and Ca^{2+} are largely present. Ions, typical for continental aerosol, namely SO_4^{2-} , NH_4^+ , and NO_3^- , are present both in coarse and fine fractions.

Coastal zones of the water basin of White Sea can be considered as the regions, subjected to influence of continental sources, including anthropogenic ones. The central regions, removed from the coastal zones, can be considered relatively clean, not subjected to the influence of the continental sources.

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