

Comparison of the techniques for estimating the contribution of continental and marine sources into ion composition of near-water aerosol of the White Sea

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Two techniques for estimating the contribution of continental and marine sources into near-water aerosol composition formation is compared on the base of experimental data on the chemical composition of the water-soluble fraction of the aerosol over the White Sea. It is shown that the random root-mean-square error, obtained by the technique suggested by the authors of this paper, is several times less of those, found by the known techniques. Analysis of the empirical distribution functions of portion factors of the continental ion mass concentration, obtained by different techniques, has shown the suggested technique is better even for estimating neutral states of the atmosphere.

Introduction

Recently, the environmental study of the Earth's northern latitudes is of great importance, because the environment here is very sensitive to anthropogenic impacts. The atmosphere is one of the main channels of aerosol exchange and redistribution in these latitudes.¹

To estimate the influence of continental aerosol on the atmosphere of northern seas, microstructure and chemical composition of aerosol over the White Sea, special studies were conducted during 2003–2006 (August) onboard the *Professor Shtokman* research vessel.^{2–6} The aim of these researches was the spatiotemporal variability of the surface atmospheric layer.

To estimate the contribution of continental and marine sources into near-water aerosol formation, different techniques are used.^{7–11} In this work, the qualitative and quantitative comparison of these techniques is conducted, as well as atmosphere states by these techniques.

General information

The chemical composition of the water-soluble aerosol fraction was determined by means of aerosol Whatman filter sampling (1–2 times per day) using a standard particle aspirator; the sampling time was from 4 to 16 hours (see Refs. 7 and 8 for detail). During four years, aerosol over the White Sea was sampled by this technique 48 times.

Concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, NO₃⁻, HCO₃⁻, and SO₄²⁻ ions in the water-soluble aerosol fraction were determined in laboratory

conditions. The chemical composition of the matter soluble fraction was determined with modern analytical methods, i.e., high efficient liquid chromatography, potentiometer, atomic absorption, and spectrophotometry.^{7,8}

Estimations of random errors of portion factors by two techniques

Two techniques were suggested in Refs. 7–11, based on the analysis of mass concentration of continental and marine ions. To determine the contribution of continental and marine sources into the ion composition of aerosol, the portion factors FM_{cont} and FM_{ocean} were used in Refs. 7 and 8. The portion factor FM_{cont} is considered as the fraction of mass concentration of continental ions, while FM_{ocean} – as those of ions, formed of seawater. The relationship $FM_{\text{cont}} + FM_{\text{ocean}} = 1$ correlates the factors. The factor FM_{cont} is calculated by the equation

$$FM_{\text{cont}} = \frac{\sum_{i=1}^n (M_i^a - k_i^w M_X^a)}{\sum_{i=1}^n M_i^a}, \quad (1)$$

where $i = 1, \dots, n$ (n is the number of ions used for FM_{cont} calculation); M_i^a is the mass concentration of the i th ion in aerosol; M_X^a is the concentration of Na⁺ or Cl⁻ ions in aerosol; $k_i^w = M_i^w / M_X^w$ is the ratio of i th ion concentration M_i^w to Na⁺ or Cl⁻ ion concentration in seawater (M_X^w); $\sum_{i=1}^n M_i^a$ is the total mass concentration of all ions in aerosol, and $\sum_{i=1}^n (M_i^a - k_i^w M_X^a)$ is the total mass concentration of all

ions in aerosol minus the mass concentration of seawater-formed ions.

In this work, concentrations of six ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}) were used in the calculations. Note that the technique for FM_{cont} calculations with the use of the Na^+ or Cl^- concentration in Eq. (1) gives a quite close results.

To identify continental and marine aerosol sources, the authors of Refs. 9–11 use the ratios of mole concentrations of NH_4^+ and Na^+ cations to the basic anion SO_4^{2-} . Usually, the first cation is considered as the identifying attribute of a continental source and the second one is used for marine aerosol identification. In this case, the portion factors of continental and marine aerosol for NH_4^+ and Na^+ cations are written as^{9–11}:

$$FM_{\text{cont}} = M_{\text{NH}_4^+} / (M_{\text{Na}^+} + M_{\text{NH}_4^+})$$

and

$$FM_{\text{ocean}} = M_{\text{Na}^+} / (M_{\text{Na}^+} + M_{\text{NH}_4^+}).$$

Figure 1 shows the correlation between the portion factors of contribution of continental sources into the ion composition of near-water aerosol according to the techniques from Refs. 7, 8, 9–11 (dots), as well as the straight line with the unit coefficient of regression (slope).

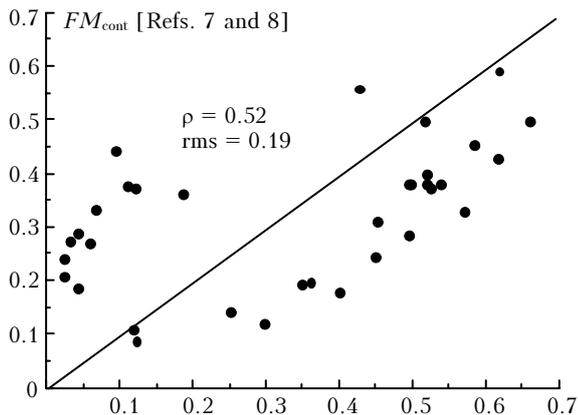


Fig. 1. FM_{cont} [Refs. 9–11].

The normalized correlation factor between the parameters under study is not high ($\rho = 0.52$); hence, they take into account the contribution of continental sources of atmospheric aerosol in different ways. The rms deviation of experimental FM_{cont} values from the regression line is 0.19. It is evident from Fig. 1 that the maximum spread in FM_{cont} values is higher and equal to 0.55 following the technique from Refs. 9–11 at FM_{cont} fixed by the technique from Refs. 7 and 8, while the maximum spread in FM_{cont} values is not higher than 0.35 following the technique from Refs. 7 and 8 at FM_{cont} fixed by the technique from Refs. 9–11. This points out to the fact that the calculation error is to be smaller in case of the technique from Refs. 7 and 8.

To compare the techniques for estimating the contribution of continental and marine sources into

the ion composition of near-water aerosol quantitatively, their random errors should be calculated. This can be done with the help of generalized linear regression formula, obtained with the accounting for random errors of the measured parameters.¹² Since the regression factor between the same parameters, obtained by different techniques, should be equal to 1, obtain their random errors. Calculations by the generalized formula¹² give FM_{cont} random rms errors equal to 0.02–0.04 for the technique from Refs. 7 and 8 with Na^+ and Cl^- ions and to 0.17–0.18 for the technique from Refs. 9–11 with the NH_4^+ and Na^+ cations. Their ratios to the average values are 6–13 and 52–56%, respectively. Thus, the random rms error by the technique with portion factors calculation^{7,8} is 4–8 times less than those by the technique with the use of the ratio of NH_4^+ and Na^+ cation mole concentrations to the basic anion SO_4^{2-} [Refs. 9–11].

Comparison of atmosphere states by two techniques

The empirical distribution functions (ω) of the portion factors of mass concentration of continental ions are shown in Fig. 2 for the whole set of experimental data, obtained by the techniques from Refs. 7–8 and 9–11. The increment is 0.25, because the FM_{cont} random rms errors vary significantly by different techniques, from 0.02 to 0.18. Percentages of the portion factors FM_{cont} of continental ions mass concentration are shown for intervals 0–0.25, 0.25–0.50, and 0.50–0.75. As is evident, the atmospheric states, determined by the two techniques (from Refs. 7–8 and 9–11), differ essentially.

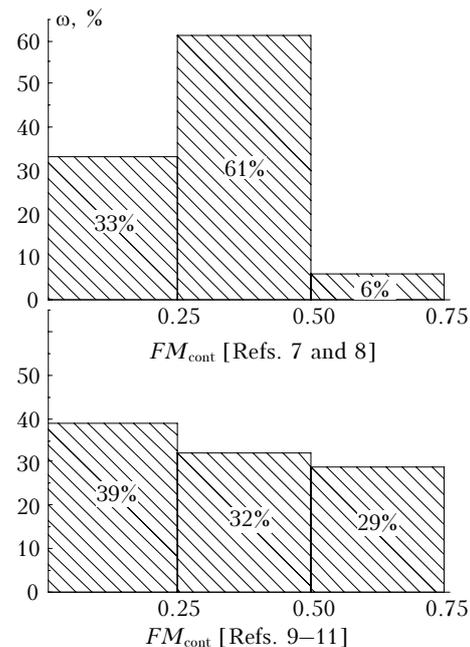


Fig. 2.

Thus, according to Refs. 7 and 8, maxima of the empirical functions fall into the 0.25–0.50 FM_{cont} interval, mean values – into the 0–0.25, and minima – into the 0.50–0.75 interval. In its turn, the technique from Refs. 9–11 gives a weak decrease of the empirical function with FM_{cont} increasing. To explain this difference, note that the random errors of the two techniques are 0.11 [Refs. 7, 8] and 0.5 [Refs. 9–11] with a confidence probability of 99%.

Hence, the FM_{cont} increment of 0.25 is sufficient only for estimating atmosphere states by the technique for portion factor calculations,^{7,8} while an increment of not less than 0.5 is recommended for the technique with the mole concentration ratio.^{9–11} Actually, for the 0.5 increment, values of the empirical function equal to 94 and 6% by the technique from Refs. 7, 8 and 71 and 29% by the technique from Refs. 9–11. In this case, a general downward trend of the empirical function is observed, though its values differ significantly.

Therefore, we recommend to use the technique from Refs. 7 and 8 to estimate even neutral atmosphere states with a step of less than 0.5.

Conclusion

Analyzing different techniques for estimating the contribution of continental and marine sources into near-water aerosol composition formation over the White Sea, the technique based on the analysis of mass concentration of continental and marine ions with portion factors calculation^{7,8} can be admitted more precise. According to this technique, the random rms error of the portion factor of continental ions mass concentration is about 0.04, while those of the portion factor FM_{cont} according to the technique from Refs. 9–11 is 0.17–0.18, which is several times larger than by the first technique. The reason is in the use of data accounting for total composition of basic ions in aerosol samples in the technique from Refs. 7 and 8, while the technique from Refs. 9–11 uses concentrations of only two cations, i.e., NH_4^+ и Na^+ , though they are characteristic for continental and marine sources.

Analysis of the empirical distribution functions of portion factors of continental ions mass concentrations, obtained by the two techniques, has shown that even neutral atmosphere states should be estimated by the technique from Refs. 7 and 8 with the 0.5 step. The results obtained by the technique from Refs. 9–11 noticeably differ from those obtained by the first technique.

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