

DEPENDENCE OF THE ION FRACTIONATION COEFFICIENT IN SEA AEROSOLS ON THE RATE OF EVAPORATION FROM THE SEA SURFACE

M. R. Kuznetsova, E. V. Karavaeva, and V. A. Tverdislov

It is shown that the difference between the chemical composition of sea aerosols and that of sea water may be due to irreversible processes of heat and mass exchange between the ocean and the atmosphere. These processes may cause changes in the chemical composition of the ocean surface microlayer, which generates aerosols.

The amounts of chemical elements contained in sea aerosols differ from their content in sea water [1]. The study of aerosol formation processes showed that aerosols are produced by water from a thin (below 20 μm) surface layer of the sea and that the specific composition of sea aerosols is related to a selective enrichment of this microlayer with various ions [2, 3].

Today it has been proved that redistribution of ions in a thin surface layer of the sea is irregular and depends on irreversible heat and mass exchange processes occurring at the ocean-atmosphere interface [4]. As far as we know, there are no direct observations of the dependence of aerosol composition on the rate of heat and mass exchange between the ocean and the atmosphere.

It is the intent of this paper to study the chemical composition of aerosols generated by the near-water layer of the atmosphere with different total heat fluxes from the ocean to the atmosphere which determine the thermal and chemical structures of the cold oceanic film. The main difficulty of such studies lies in that samples of sea aerosols may contain not only newly formed aerosols but also those which are already present in the air and which have formed under conditions that cannot be controlled. We believe that the influence of this factor can be minimized by sampling aerosols directly over the sea surface, i.e., near the aerosol generation source.

A convenient model system of aerosol formation for the purposes of this study may be a spatially-restricted process of waves breaking against a sea pier. It is also important that samples of aerosols can be taken from the ocean surface microlayer at the same point.

Full-scale investigations of the chemical composition of sea aerosols at different levels of the total heat flux from the ocean into the atmosphere were conducted during a Black Sea expedition (Katsiveli). Aerosols were collected by a Petryanov's filter during three hours. The rate of air flow through the filter was 0.85 m^3/h . Aerosol samples were collected from the pier at a distance of 25 m off the shore at 1.5 m above the sea surface. At the same time, samples of water were taken from the 300 μm surface microlayer of the sea with the aid of the Harret net as well as subsurface water samples at a depth of 0.5 m. The wind velocity V , water temperature t_w , air temperature t_a , and the relative air humidity φ were measured by standard meteorological methods. To make a chemical analysis of the substance collected on the filters the latter were subjected to wet ashing with concentrated H_2NO_3 and then the ash was dissolved in twice distilled water. Analysis of ionic concentration was made by the flame photometry method (concentration measurement accuracy 5%, confidence level 0.95). Water samples collected by the Harret net and subsurface water samples were analyzed potentiometrically (accuracy 0.4% with confidence level 0.95) [5]. The heat flux E from the ocean to the atmosphere (evaporation) was calculated by the method proposed in [6].

The data obtained were used to determine the fractionation coefficients for K^+ ions relative to Na^+ ions in a sea aerosol and in the surface microlayer (SML) with respect to sea water at a depth of 0.5 m:

$$F_{\text{Na}}^a(\text{K}) = \frac{(\text{K}^+/\text{Na}^+)_{\text{aerosol}}}{(\text{K}^+/\text{Na}^+)_{\text{depth}}}; \quad F_{\text{Na}}^{\text{SML}}(\text{K}) = \frac{(\text{K}^+/\text{Na}^+)_{\text{SML}}}{(\text{K}^+/\text{Na}^+)_{\text{depth}}}$$

Table 1

Fractionation Coefficients F_{Na}^a (K) and F_{Na}^{SML} (K), Relative Air Humidity φ , Water Temperature t_w , Air Temperature t_a , Wind Velocity V , Evaporation Heat Flux From Sea to Atmosphere, E ; Measurements Errors

Sample No.	F_{Na}^a (K)	F_{Na}^{SML} (K)	φ , %	t_w , °C	t_a , °C	V , m/s	E , W/m ²
1	1.00	0.98	56	18	19	0.5	95
2	1.62	1.00	59	17	14.8	2	235
3	1.78	1.04	49	17.5	17.6	1.5	310
4	2.06	1.00	53	17	17	2.5	246
5	2.48	1.02	57	17	17	3	264
6	3.08	1.02	67	17.5	19.2	5	476
7	3.74	1.02	54	17.5	15.6	3.5	413
8	3.85	1.05	70	17.2	16.4	4	430
9	1.20	0.99	57	17	15	6	778
10	1.57	1.00	70	17	15.2	8	796
11	1.30	—	61	17	15.2	8	927
12	1.17	—	46	17	15	7	1156
Relative measurement error, % (confidence level 0.95)							
	10.8	1.5	2	5	5	20	22

where K^+ and Na^+ are concentrations of potassium and sodium ions, respectively. To find the relations between the obtained values ($x_1 \dots x_n; y_1 \dots y_n$), the paired linear correlation coefficients were calculated:

$$R(X, Y) = \frac{\sum_1^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_1^n (x_i - \bar{x})^2 \sum_1^n (y_i - \bar{y})^2}}$$

The results of field observations are presented in Table 1. Here, the values of

$$F_{Na}^{SML} (K), \varphi, t_w, t_a, V, \text{ and } E$$

are averaged over five independent measurements made during three hours.

The data obtained suggest the following conclusions.

1. F_{Na}^a (K) averages 2.1 ± 0.1 , and F_{Na}^{SML} (K) averages 1.012 ± 0.008 .
2. There is a linear correlation between F_{Na}^a (K) and F_{Na}^{SML} (K) with a probability 0.9 (the coefficient $R(F_{Na}^a (K), F_{Na}^{SML} (K)) = 0.7$), which agrees well with the aerosol origin concepts.
3. Figure 1 shows the ion fractionation coefficients in aerosol (a) and in the sea surface microlayer (b) versus different heat fluxes due to evaporation from the sea into the atmosphere. Note that in the range of heat fluxes to 600 W/m^2 the fractionation coefficients and the heat flux are related linearly with a probability 0.9 ($R(F_{Na}^a (K), E) = 0.8$ and $R(F_{Na}^{SML} (K), E) = 0.7$). At higher heat flux values the linear relationship is upset, the ion fractionation coefficients for aerosol reduce to 1.31 ± 0.06 on the average, while for the surface microlayer they deviate from unity within the determination error. This phenomenon can probably be explained by the fact that heat fluxes exceeding 600 W/m^2 were observed in our experiments at wind velocities over 6 m/s , when the rate of destruction of the cold film by waves breaking, in the surf zone is much higher and, besides, marked changes occur in the thermodynamic structure of the sea surface

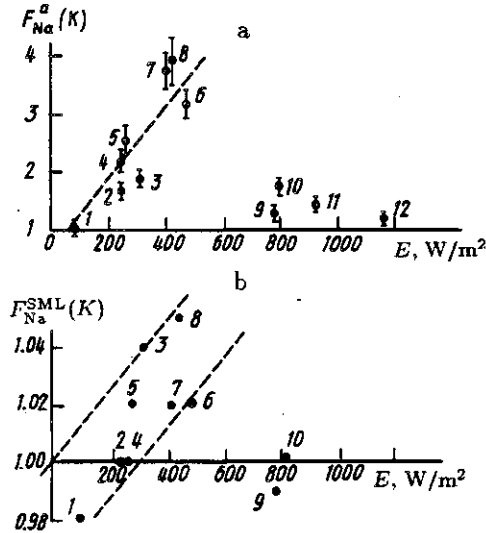


Fig. 1

Ion fractionation coefficients versus evaporation heat fluxes E in natural sea aerosols (a) and in the sea surface microlayer 300 μm thick (b). The same figures stand for simultaneously collected microlayer and aerosol samples.

layer [7]. As a result, there is no noticeable accumulation of the effects of ion redistribution in the surface microlayer, because, as has been shown in [8], formation of the sea surface layer requires time substantially greater than the characteristic diffusion process time.

Thus, the difference between the chemical composition of the sea aerosols and that of sea water may be due to irreversible processes of heat and mass exchange between the ocean and the atmosphere, which determine the chemical composition of the surface sea microlayer generating aerosols.

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28 January 1992

Department of Physics of Atmosphere
and Mathematical Geophysics