

## MEASUREMENTS OF NONEQUILIBRIUM PROCESSES AT THE SEA-ATMOSPHERE BOUNDARY: IMPLICATIONS FOR ECOLOGICAL PROBLEMS

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Marine surveys were carried out in the Black Sea to investigate variations of the fractionation coefficients of sea-water macrocomponents in a sea-surface microlayer as a function of temperature gradients in a cold sea film and to evaluate daily pH variations in a surface microlayer and in subsurface water.

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At the 1959 Congress of Oceanologists, P. Velander, a well-known Swedish scientist, declared: "Virtually all of the physical, chemical, and biological processes that operate in the sea are related to the fact that the sea has a free surface interacting with the atmosphere".

During the 40-year period since that statement, physicists established the existence of a so-called cold sea-water film (a surface water layer, a few millimeters thick, in which temperature gradients may be as high as 0.5-1.5 deg/mm) and evaluated the amounts of energy and material flowing through the ocean-atmosphere boundary [1].

Marine biologists discovered a significant concentration of various life forms in the upper 5-cm-thick sea-water layer which was thought, not more than 30 years ago, to be absolutely lifeless because of its specific properties: active absorption of solar ultraviolet radiation, high temperature gradients, liability to roughness, etc. They found that the population of protozoans, unicellular algae, and eggs and fry of many fish species was many times larger in this layer than in the water below. The concentration of saprophytic bacteria turned out to be a few thousand times higher in the surface layer (especially in foam) than in the water column. A great variety of organisms that adapted to the specific living conditions of the surface-sea film were recognized by marine biologists as a particular ecosystem and called neuston.

At the same time marine chemists discovered a remarkable ability of the sea-surface microlayer ranging between 100 and 300  $\mu\text{m}$  in thickness to concentrate organic materials, biogenic elements, heavy metals, and also pesticides and chlororganic toxic chemicals that are removed to the ocean by rivers. A new phenomenon was discovered, the redistribution of inorganic sea-water ions in the surface microlayer.

Examination of the sea aerosol produced by collapsing air bubbles at the sea surface revealed that the aerosol was enriched in the same elements and materials as the surface microlayer. It was established with certainty that pathogenic bacteria were removed from the contaminated sea to the atmosphere dropwise. In this context there arose an urgent problem of the potential contamination of the seaside environment.

Much attention is given now to the impact of human activity upon the surface layer of the sea as a habitat of neuston organisms which constitute, in the opinion of marine biologists, an important link in water ecosystems.

This brief review shows that the ocean-atmosphere boundary possesses a number of specific physical, chemical, and biological properties. However, relations between them are still poorly known. For instance, the temperature gradient in the cold film and the stable dissipation structures (Rayleigh and Marangoni convection cells) arising in the surface layer must cause a redistribution of components in sea water, affect

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the rate of O<sub>2</sub> and CO<sub>2</sub> gas exchange between water and air and, hence, modify the pH values of sea water in the surface microlayer. At the same time changes in sea water pH values and in the amount of oxygen dissolved in sea water are vitally important for protozoans inhabiting the thin surface layer, which serve as the first link in the trophic chains of marine ecosystems and as very important natural reworkers of the surface contaminants in the ocean. On the other hand, the presence of man-made organic films or of the products of sea organisms' activity, imposes a strong influence on the transfer of heat and material modifying the temperature gradient in the cold film.

An urgent modern problem related to the ocean surface and seaside areas is the systematic monitoring and study of the reciprocal influence of the physical and physicochemical processes operating in the sea microlayer and of the related biological behavior of the neuston.

In this context, teams of workers from the Faculty of Physics of the Atmosphere and the Faculty of Biophysics, Moscow State University, recently started investigating variations in the redistribution of sea water macrocomponents in the microlayer and in aerosol (compared to the sea water column) as a function of sea water evaporation [2] and wind velocity [3].

In this paper we describe the results of our observations which consisted in a series of simultaneous measurements of temperature gradients in the cold film and of the fractionation coefficients of sea water macrocomponents in a 300- $\mu$ m-thick microlayer performed at several sites in the Black Sea during August 1995 and September 1996 surveys. We also measured daily sea water pH variations in and below the surface microlayer. All measurements were made at intervals of one or two hours during a few days.

We chose the following sea water components for this study: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>. Compared to the water column, the degree of ion redistribution in the surface microlayer can be characterized by the ion fractionation coefficients which are usually found using the most conservative ions Na<sup>+</sup> or Cl<sup>-</sup>, for instance:

$$F(K/Na) = \frac{[K/Na]_{\text{surf}}}{[K/Na]_{\text{vol}}},$$

where [K/Na] is the ratio of K and Na ion concentrations.

We recorded temperature gradients using an equipment that had been designed at the Department of Physics of the Atmosphere, Moscow State University [1]. The measurement system consisted of a mobile thermoprobe (with a 30- $\mu$ m diameter of a copper-constantan thermocouple junction and a temperature measurement accuracy of 0.05 K), equipped with a drive mechanism, and a measurement amplifier, both placed inside a three-float buoy, and a recorder with a control panel and a start-up unit located in a shipboard laboratory. The buoy, a good monitor of sea roughness, was located at a distance of 70-80 m from the drifting ship, with a marine multiple-core cable serving as a communication line.

For the purpose of evaluating the fractionation coefficients of sea water macrocomponents in the microlayer, water samples were collected from a ca. 300- $\mu$ m-thick microlayer and from a depth of 0.5 m using the ship's boat and a Garrit sampler consisting of a capron sieve stretched over a chemically inert frame.

The water samples were analyzed at the shipboard laboratory immediately after their recovery. A combined electrode consisting of a glass (hydrogen) and a chlorsilver (reference) electrode was used to measure pH in the samples. The accuracy was 0.02 at  $P = 0.95$ . The concentrations of the Na<sup>+</sup>, and K<sup>+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup> ions were measured using a potentiometer equipped with appropriate ion-selective electrodes. The relative error was less than 4% with  $P = 0.95$  in all measurements.

The sulfate-ion (SO<sub>4</sub><sup>2-</sup>) concentration was measured by titration using a BaCl<sub>2</sub> solution. The relative error was 5% at  $P = 0.95$ .

Figure 1 shows the typical examples of the daily measurements made in the open sea in August 1995. Figure 1a displays a daily temperature gradient variation in the cold film; Fig. 1b shows the daily curves of the fractionation coefficients  $F(K/Na)$ ,  $F(SO_4/Cl)$ , and  $F(Ca/Cl)$ . The autocorrelation functions for the temperature gradients and cross-correlation functions between the temperature gradient in the cold film and for the fractionation coefficients of sea water macrocomponents in the microlayer are displayed in Fig. 1c and d, respectively. These curves were plotted with a time shift of less than 4 or 5 hours, because it was statistically unjustified to use larger time delays.

In September 1996 we carried out daily observations near the southern shore of the Crimean Peninsula

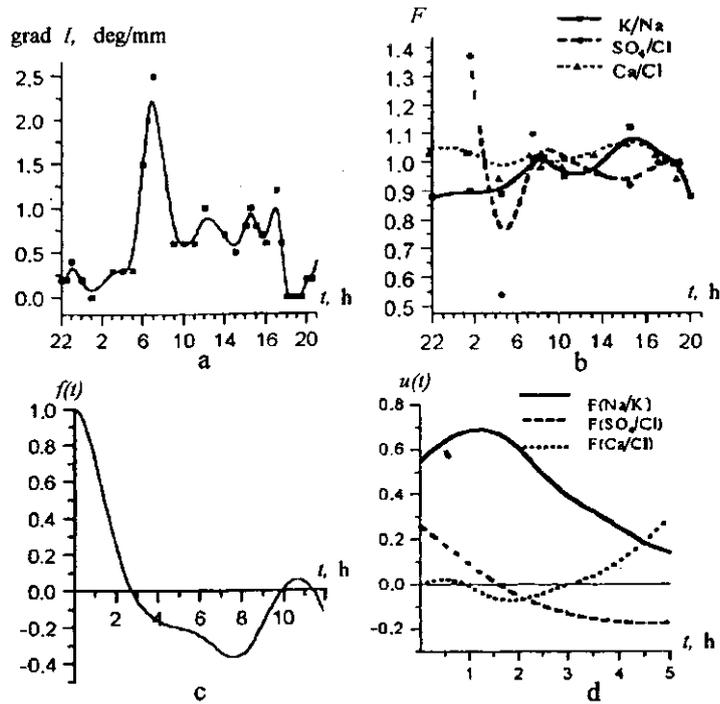


Fig. 1

Daily variations of temperature gradients in the microlayer (a) and of ion fractionation coefficients (b). Autocorrelation function  $f(t)$  for temperature gradient in the thin surface layer (c) and cross-correlation functions  $u(t)$  for ion fractionation coefficients and temperature gradient (d). Based on the results of the 1995 survey.

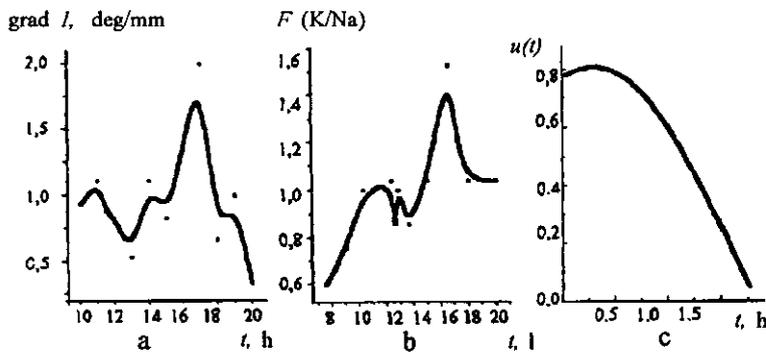


Fig. 2

Daily variations of temperature gradient in the surface layer (a) and of the ion fractionation coefficients of K relative to Na (b). Cross-correlation function  $u(t)$  for ion fractionation coefficient and temperature gradient (c). Based on the 1995 data.

(Katsiveli area) from a research platform installed at a distance of some 800 m from the shore. The most representative results are presented in Fig. 2.

The data displayed in Figs. 1 and 2 indicate that only one parameter, namely the K and Na fractionation coefficient, shows a linear correlation with the temperature gradient in the cold film: at small delay times its values range between 0.6 and 0.8 at  $P = 0.9$ . This means that the Na<sup>+</sup> and K<sup>+</sup> ion separation in the microlayer, compared to the water volume below, depends basically on the heat and material transfer

through the cold film. Note that the  $\text{Na}^+$  and  $\text{K}^+$  cation salts are strong electrolytes and are wholly dissociated into ions in water solutions. On the other hand, the oxidation–reduction potentials of these elements are too high to enter into oxidation–reduction reactions in natural conditions. Therefore, neither chemical transformations nor the activity of living organisms affect the  $\text{Na}^+$  or  $\text{K}^+$  concentrations in sea water. Our calculation of their fractionation coefficient, a parameter that characterizes ion redistribution due to thermal diffusion, yielded values that were substantially lower than the measured values for the observed temperature gradient. Apparently, calculations require the incorporation of nonlinear effects such as Rayleigh (thermogravitational) convection and Marangoni (thermocapillary) convection.

The  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions, relative to  $\text{Cl}^-$ , showed their notable redistribution in the microlayer, compared to the subsurface water volume, their fractionation coefficients undergoing significant daily variations and showing no correlation with the temperature gradient in the cold film. Apparently, the concentrations of these ions in the microlayer are strongly dependent on the extent of their participation in biochemical processes.

The acid–alkali balance of sea water is controlled basically by a carbonate system, whose major component is carbon dioxide. The solution of the latter in water produces carbonic acid which breaks down to protons, carbonate, and bicarbonate. Therefore, the concentration of hydrogen ions (pH) in sea water is strongly dependent on the content in water of dissolved  $\text{CO}_2$ , which, in its turn, depends on the intensity of photosynthesis and, hence, on solar radiation intensity: that is, pH variation in the surface microlayer must have a daily cycle.

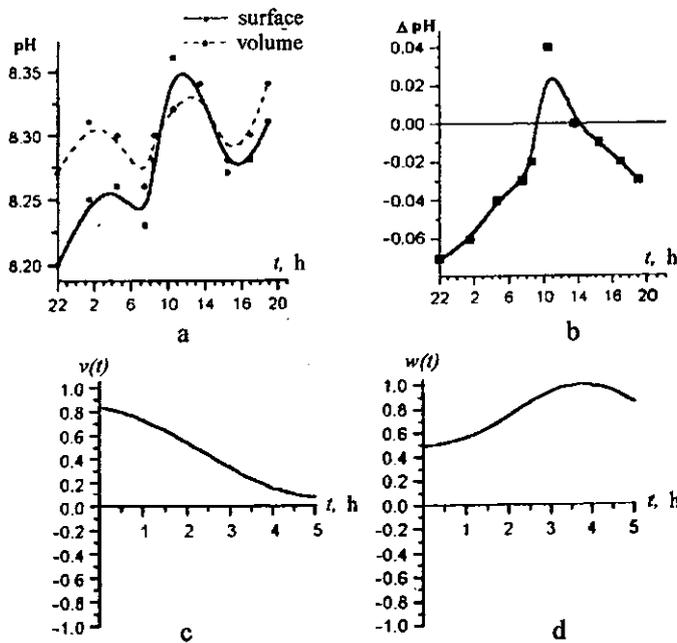


Fig. 3

Daily variations of pH in surface and subsurface water (a) and of a difference between the pH values in the surface layer and in subsurface water (b). Cross-correlation functions for pH variations in the surface layer and in subsurface water volume  $v(t)$  (c) and for a pH difference between the surface layer and subsurface water and temperature gradient in the cold film  $w(t)$  (d). Based on the 1995 data.

As seen in Fig. 3a and b, and Fig. 4a and b, the pH behavior in the microlayer and at a 0.5-meter depth shows a distinct daily variation with maximum values in the daytime, obviously because of the maximum intensity of phytoplankton photosynthesis and, hence, of the depletion of water in dissolved  $\text{CO}_2$ . It is important to note that the identity of the pH behavior in the microlayer and in the subsurface water suggests the same origin of pH variations in these water layers. This fact is indicated also by the behavior of

the cross-correlation function between the pH values in the microlayer and in the subsurface water (Fig. 3c). It appears that this behavior of the daily pH curves is the result of a complex interaction between the processes of CO<sub>2</sub> absorption and secretion by living organisms (photosynthesis–respiration), on the one hand, and the process of CO<sub>2</sub> transfer through the ocean–atmosphere boundary, controlled by the physical properties of both media, on the other.

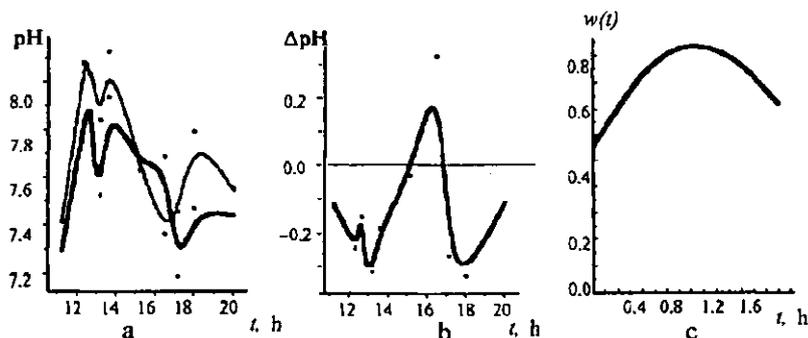


Fig. 4

Daily variations of pH in subsurface and surface water (a) and of a pH difference between surface water and subsurface water volume (b). Cross-correlation function  $w(t)$  for variation of a pH difference between surface water and subsurface water volume (b). Cross-correlation function  $w(t)$  for variation of a pH difference between the surface layer and subsurface water volume and temperature gradient in cold film (c). Based on the 1996 data.

It is likely that some amount of oxidation observed in the surface microlayer, compared to the water layers below, is basically caused by a higher carbon dioxide concentration near the ocean–atmosphere boundary where this gas is in equilibrium with atmospheric CO<sub>2</sub>. Worthy of mention is a somewhat higher alkali content in the microlayer relative to the subsurface water (Fig. 3b and Fig. 4b) in the daytime. This might be caused by a photosynthesis depression due to the too high intensity of illumination and the related pH decline of the subsurface water, or to a solubility decrease of carbon dioxide because of the increased average temperature in surface layers and its removal to the atmosphere through the surface microlayer.

The observed correlation between the daily variation of the temperature gradient in the cold film and the difference of the pH values in the microlayer and in the subsurface water (see cross-correlation functions in Fig. 3d and Fig. 4c) can be explained tentatively proceeding from the following reasoning. The difference between the carbon dioxide concentrations in the microlayer and in subsurface water is associated, in an obvious way, with the rate of CO<sub>2</sub> transfer between water and air and with the intensity of phytoplankton activity. The CO<sub>2</sub> transfer rate, in its turn, depends also on the intensity of the mixing process, which is controlled by the temperature gradient in the cold film. Therefore, a difference between pH values in the microlayer and in subsurface water must correlate with the temperature gradient in a thin surface layer. The observed delay (a few hours) in the pH difference relative to the temperature gradient can be associated with slow macroprocesses, e. g., with phytoplankton movements caused by changes in illumination and temperature.

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