

# Characteristics of aerosol-forming compounds measured in the Baikal region: physical properties and dynamics

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Results of complex measurements of mass concentration and diffusion coefficient of PreAerosol Compounds (PreAC) in the lower atmosphere performed at the Limnological Institute SB RAS on the Baikal lake shore in 2003–2005 are presented. A drop concentrator and diffusion aerosol spectrometer were used for the measurements. Seasonal and daily variability of the PreAC content, its correlation with meteorological parameters, and source characteristics are discussed.

## Introduction

Low-volatile PreAC by their physical properties take an intermediate position between gaseous aerosol precursors and aerosol nanoparticles. Low-volatile matters are the main source of submicron aerosol particles in the atmosphere; they either form the particles in the condensation or are absorbed by surfaces of present aerosol particles and, hence, determine optical, chemical, and toxic properties of the particles in the entire size range. Besides, low-volatile PreAC participate in natural cycles of such elements as nitrogen, carbon, and sulfur. Hence, the study of physical and chemical properties of atmospheric PreAC vapors is new and currently important research trend.

It was difficult to classify these compounds earlier, though their presence became undoubted beginning from a certain research stage of aerosol-forming processes.<sup>1</sup> At present, physical-chemical properties of PreAC vapors ground condensation models of aerosol forming.<sup>2</sup>

The developed water-absorption technique<sup>3</sup> 10000-fold accelerates the natural condensation process and allows real-time calculation of the weight content and diffusion coefficient of low-volatile PreAC vapors in air. The technique is based on entrapping of molecules and their clusters by water fog produced at fast liquid-nitrogen cooling of the atmospheric air.

Being guided by the principal purpose of the started PreAC research cycle, a run of measurements was performed to determined physical properties of PreAC immediately in the atmosphere.

Main tasks of this measurement cycle are:

- calculation of PreAC content and their physical parameters in the atmosphere,

- study of seasonal and diurnal variability of PreAC properties,
- detection and characterization of principal natural sources and sinks of PreAC,
- determining of the temperature dependence of PreAC emission rate.

## Measurements

The measurements were carried out at the scientific site of the Limnological Institute SB RAS, located near the Bolshie Koty village on the Baikal lake shore. Data of about four-month expedition measurements (from May to September, 2003–2005) are used in this work.

The mass concentration and diffusion coefficient of PreAC were measured using a drop concentrator, converting PreAC into traceable aerosol particles. The device operation is based on the principle of low-volatile admixtures concentration on atmospheric water drops. In our case, the formed particles were detected with a diffusion aerosol spectrometer (DAS).<sup>4</sup> The technique is described in Ref. 3 in more detail.

To evaluate the PreAC flux from the ground surface, a lavesan-film chamber of 0.7 m<sup>3</sup> in volume was used, covering 0.3 m<sup>2</sup> of the surface with plants. Lavesan is transparent for the main part of the solar spectrum and, hence, provides for the light conditions, close to ambient ones. In addition, it is not a source of aerosols and fume influencing experimental results.

The chamber was supplied with the redundant current (10 l/min) of air filtered out of aerosols and PreAC, which secures aerosol purity of the experiment. Normalizing the PreAC mass concentration, measured into the chamber, to the covered area and airflow, the flux of low-volatile aerosol-forming matter from

the ground surface can be estimated. To determine conditions, influencing the surface source power, the surface temperature was measured into the chamber.

In view of the aim to retrace the complete lifecycle of aerosol particles from gaseous precursors through PreAC to aerosol and environmental effect on this process, the following parameters were simultaneously measured during the experiment:

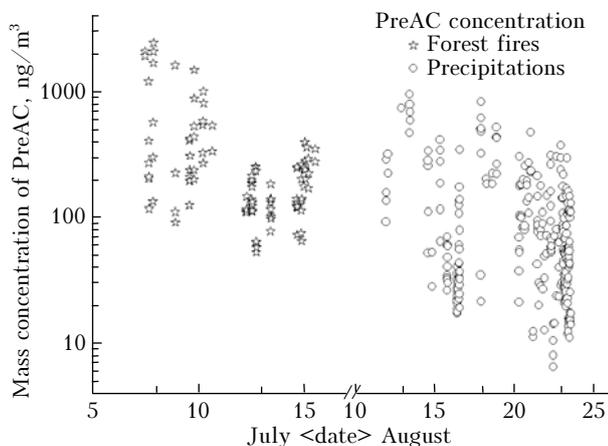
- mass concentration and average diffusion coefficient of PreAC in the surface atmosphere;
- PreAC flux from the ground surface;
- size distribution of aerosol particles within the range  $\varnothing = 3\text{--}200\text{ nm}$ ;
- surface and air temperature;
- brightness;
- ozone concentration;
- sulfur dioxide concentration;
- wind speed and direction.

They were measured every three hours. Instruments arrangement provided for minimization of anthropogenic effect on measurement results.

## Results and discussion

Previous assessments<sup>3</sup> have shown the characteristic mass concentration of PreAC in the surface atmosphere to be about  $100\text{ ng/m}^3$ . First measurement results of PreAC parameters have verified suggestions on the properties of these matters.

Figure 1 shows the measurement results for summer 2003. In July, characterized by forest fires, the average mass concentration of PreAC in the atmosphere was  $650\text{ ng/m}^3$ . Steady cloudiness and precipitations were observed in August, and the average PreAC concentration decreased down to  $170\text{ ng/m}^3$ . In view of variations of the diffusion coefficient and under the assumption of unit matter density and sphericity of PreAC particles, the mass concentration of aerosol-forming matters corresponds to clusters of  $1.5\text{ nm}$  in diameter at a concentration of  $4 \cdot 10^8\text{ cm}^{-3}$  in the period of fires and, respectively,  $2.3\text{ nm}$  at a concentration of  $0.5 \cdot 10^8\text{ cm}^{-3}$  in the precipitation period.

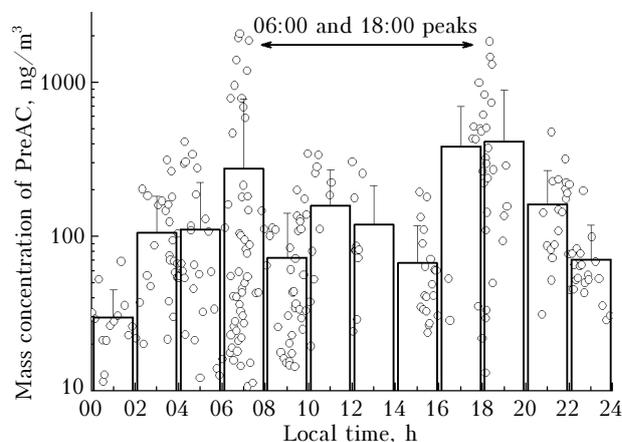


**Fig. 1.** Time behavior of the mass concentration of PreAC (summer 2003) in the surface atmosphere.

Note that the average size of air molecules is about  $0.2\text{ nm}$  and their concentration is about  $3 \cdot 10^{19}\text{ cm}^{-3}$ , while the minimum size of recorded aerosol particles is  $3\text{ nm}$  at a countable concentration of about  $10^3\text{ cm}^{-3}$ .

Thus, an intermediate position of PreAC by their physical properties between gaseous aerosol precursors and aerosol particles was experimentally confirmed. In addition, in view of smallness of PreAC mass concentration in comparison with aerosol and its gaseous precursors, one may state that the process of PreAC formation is the limiting stage of the gas-particle transformation.

Periodic character of PreAC parameters variations were ascertained only in the second measuring period (summer 2003) without fires, when two peaks of the mass concentration were revealed at about 06:00 and 18:00 of local time against common daily increase (Fig. 2). This may be caused by the diurnal variability of the vegetation activity.



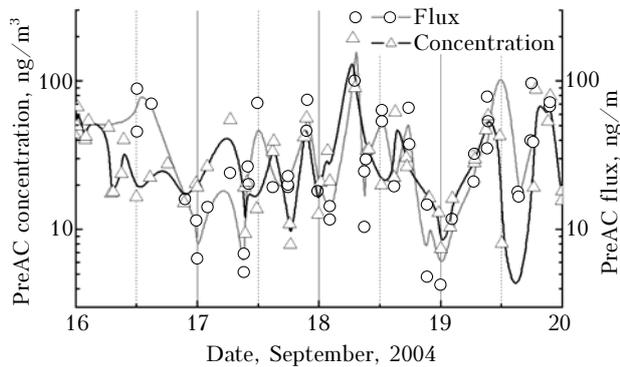
**Fig. 2.** Diurnal variation of the mass concentration of PreAC (columns correspond to the average values).

Atmospheric sources of PreAC can be conventionally divided, similar to aerosol sources, into primary and secondary (or surface and spatial) ones. Surface sources directly produce PreAC, their power should subject to vaporization and, correspondingly, surface temperature. Spatial sources of PreAC take their origin in chemical and photochemical reactions in air. First measurements of PreAC flux from the ground surface were carried out in summer 2004. To determine the contribution of surface sources, the mass concentration of aerosol-forming matters was measured consequently in the chamber and in atmosphere (Fig. 3). Comparison of time behavior of these variables gives information on which source is predominant.

The mass concentration of PreAC over the entire measurement period was  $20\text{--}60\text{ ng/m}^3$  and the flux from the surface was  $60\text{--}90\text{ ng/(m}^2\text{/h)}$  (see Fig. 3). The correlation between mass concentration of PreAC in the chamber and atmosphere points to surface source prevalence in our experiments.

The diurnal behavior and inter-day variability of PreAC formation from an underlying surface evidently depend in a complicated way on sun exposure, surface

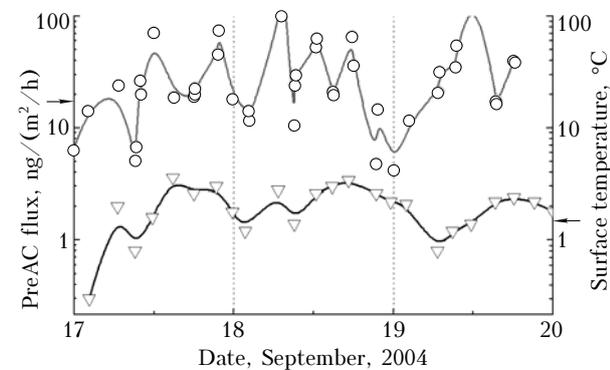
and surface air temperatures, which, in their turn, are defined by a complex of synoptical processes.



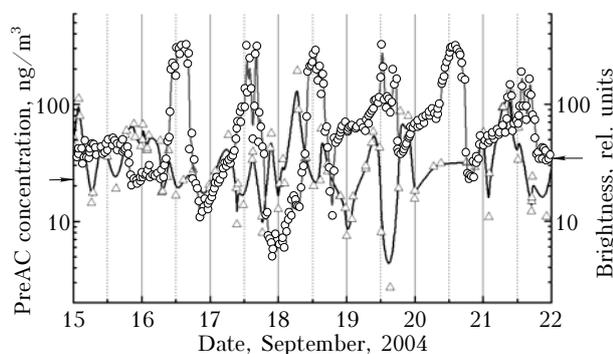
**Fig. 3.** Time behavior of the mass concentration of PreAC in the surface atmosphere and the PreAC surface source power. The correlation coefficient is 0.8.

To estimate the correlation between PreAC export processes and main energy parameters of the surface, variations of PreAC concentration, temperature, and lightness were analyzed simultaneously. The temperature of the surface depends on incident solar energy in many ways, while its heating and cooling inertia causes slower diurnal variability, as compared with the observed lightning variations.

Time behavior of PreAC flux and surface temperature are shown in Fig. 4 (correlation coefficient is  $-0.72$ ) and of mass concentration of PreAC and lightness – in Fig. 5 (correlation coefficient is  $-0.57$ ).



**Fig. 4.** Time behavior of PreAC flux and surface temperature; the correlation coefficient is  $-0.72$ .



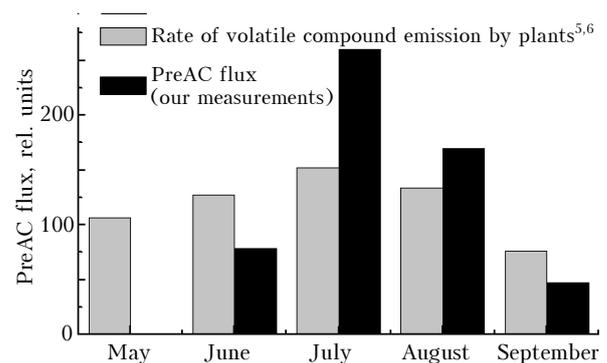
**Fig. 5.** Time behavior of the mass concentration of PreAC and lightness; the correlation coefficient is  $-0.57$ .

This probably implies that progressive surface heating or cooling affect the efficiency of a surface PreAC source in a more degree than rapid lightning variations.

Thus, on the base of the obtained data, it was stated that the prevailing PreAC source is surface vegetation, but not atmospheric reactions of gas precursors. Changes in surface PreAC fluxes seem to depend on integral soil heating more than on the current value of solar flux. It is reasonable to compare our results with the available reference data.

The concentration, chemical composition, and emission rates of volatile products of plant metabolism in boreal areas were measured in many works<sup>5–12</sup>; and the following regularities were ascertained.

1. Seasonal and diurnal dynamics are observed.
2. Seasonal peak of the emission rate falls on July (Fig. 6).
3. Emission of volatile matters is stronger in daytime than at night-time.
4. The emission rate noticeably increases after rain and may remain high for several days.<sup>10,11</sup>
5. The emission rate noticeably increases in flowering period.<sup>7,10</sup>
6. The emission rate weakly depends on the light level.<sup>7,10</sup>



**Fig. 6.** Seasonal dynamics of pine-tree volatile emission in the Krasnoyarskii Krai (rel.%)<sup>5,6</sup> and PreAC flux from the surface (B. Koty).

7. Emission cycles of volatile matters correlate with  $\text{CO}_2$  assimilation by plants (Ref. 5, p. 138).

8. The emission rate  $F$  mainly subjects to evaporation and, according to the experimental data,<sup>5,7,8,12</sup> is described by the following law:  $F = Ae^{-b/T}$ , where  $T$  is the temperature;  $A$  and  $b$  are the constants. This dependence is empirical, though it is similar to the equation correlating the saturated vapor pressure with temperature. Note, that this law uses Celsius temperature scale; the plant emission is vanishing at  $0^\circ\text{C}$ .

According to Refs. 5, 7, and 8, the constant  $b$  is  $16\text{--}10^4$  for different coniferous species growing at the territory of Russia. Based on these data, the total phytogenic forest emission for Russia and separate regions is estimated. Thus, it amounts to 7.9–13.9 mln tones per year for Asian territory of RF, where Eastern Siberia contributes most of all (3.4–6.5 mln tones per year).<sup>9</sup>

The comparison of our results and reference data points to common features of seasonal and daily variability of volatile phytogetic matter flux with PreAC emission (see Fig. 6). Therefore, there is a reason to suppose that PreAC, forming regional aerosol atmosphere, can be phytogetic products. At present, the main task for the authors are to find a temperature dependence of PreAC surface emission and to ascertain qualitative chemical composition of aerosol-forming matters.

## Conclusions

Physical parameters and fluxes of PreAC vapors in the atmosphere were calculated during expedition measurements at the Baikal Lake. The principal results are the following.

The weight content of PreAC in the lower atmosphere is about  $100 \text{ ng/m}^3$ .

About  $10^8$  PreAC particles of about 1 nm in size are contained in  $1 \text{ cm}^3$  of air.

Surface vegetation, but not reactions in air volume, is seemingly a prevailing source of PreAC.

The surface emission rate of PreAC is  $10\text{--}100 \text{ ng}/(\text{m}^2/\text{h})$ .

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