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Development and Application of the Drop Concentrator for the Investigation of the Physicochemical Characteristics of Low-Volatile Precursors of Atmospheric Aerosol

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Abstract

Technique of the determination of low-volatile admixtures in the atmosphere at concentrations down to 1 ng/m^3 was developed. The method is based on the absorption of molecules and their clusters by water fog obtained under sharp cooling of the atmospheric air with the vapour of liquid nitrogen. The designed and built experimental set-up was called drop concentrator. A simple and operative method of calibrating the equipment was developed. It was shown that the error of measuring vapour content using this method does not exceed 10 % within the mass concentration range from 10 to 3000 ng/m^3. Results of the tests of the set-up under laboratory and field conditions are reported. The diurnal and seasonal dynamics of the concentrations of aerosol-forming compounds in the vapour phase, their interconnection with the changes in meteorological parameters, source characteristics are considered.

Key words: gas-to-particle conversion, low volatile atmospheric admixtures

INTRODUCTION

The formation of the vapour of aerosol-forming compounds (VAFC) [1] is the limiting and less investigated stage of gas-to-particle conversion. Judging from their physicochemical characteristics, aerosol-forming compounds occupy an intermediate position among the gaseous precursors of aerosol and the aerosol particles. The vapour of aerosol-forming compounds may be formed either as a result of the direct emission or during atmospheric chemical reactions; they are represented by molecules and molecular clusters of low-volatile compounds that had not yet reacted with each other to reach a detectable size. They act as the precursors of atmospheric condensation nuclei. Uniting together or depositing onto the surface of already present aerosol particles, VAFC affect their optical, hygroscopic and other characteristics. So, the knowledge of the physicochemical properties of aerosol-forming compounds is necessary to understand the characteristics of aerosol particles, first of all those having the submicrometer size range.

For the experimental investigation of VAFC in real atmosphere, in view of the insignificant absolute content of these species in comparison with the formed aerosol, a procedure was developed at the Institute of Chemical Kinetics and Combustion (ICKC), SB RAS, and an experimental set-up was built for the determination of total concentration and diffusion coefficient of aerosol-forming admixtures in the atmosphere in concentrations down to about 1 ng/m^3. This method is based on the absorption of VAFC by the drops of atmospheric water appearing after sharp cooling of the air with the vapour of liquid nitrogen [2]. In this process, gaseous substances with vapour pressure less than 10^{-8} mm Hg get concentrated into detectable aerosol particles; the natural condensation process is thus accelerated by a factor of about 10 000.

Investigation of the gas-to-particle transformation in the atmosphere at the modern level implies detailed quantitative and kinetic description of the process. For this purpose, it is necessary to have a rapid, reliable and simple calibration method, in particular, for the work under the field conditions. For this goal, we developed a stabilized generator of the given concentration of low volatile vapour; for operation, it requires only power supply and a small amount of the substance with the known dependence of vapour pressure on temperature.

To study the VAFC in the environment, we made a series of measurements under the expedition conditions and for the first time determined the physical properties of VAFC directly in the atmosphere.

The following problems were to be solved while carrying out the cycle of measurements:

1. Determination of VAFC content in the atmosphere and investigation of the physical characteristics of these compounds.
2. Investigation of the seasonal and diurnal dynamics of VAFC properties.
3. Establishment and detailed investigation of the main natural sources and sinks of VAFC.
4. Establishment of the temperature dependence of VAFC emission rate.

METHOD OF DETERMINING THE MASS CONCENTRATION AND DIFFUSION COEFFICIENT OF AEROSOL-FORMING COMPOUNDS IN THE ATMOSPHERE

The principle of the method is based on the generation of a large number of water drops in a sample of real atmospheric air by means of sharp cooling with eth vapour of liquid nitrogen. Such a dispersing medium with enormous (in comparison with the standard atmospheric conditions) surface area strongly enhances sorption of molecules and their clusters. During subsequent evaporation of the water fog, the admixtures concentrated in each drop form nanometer-sized particles. The size and concentration of thus obtained particles may be reliably determined using the diffusion spectrometer of aerosol, developed at the ICKC, SB RAS [3]. The diffusion coefficient is independent of the density of the particle material; so, assuming that the particles have a spherical shape, the total filling factor per unit volume of the air may be calculated. This value is a kind of the potential volume of the condensed phase that may be formed from these molecules through their coagulation with each other or with the atmospheric aerosol particles. Assuming that the density of the condensed substance is equal to 1, this value may be in-

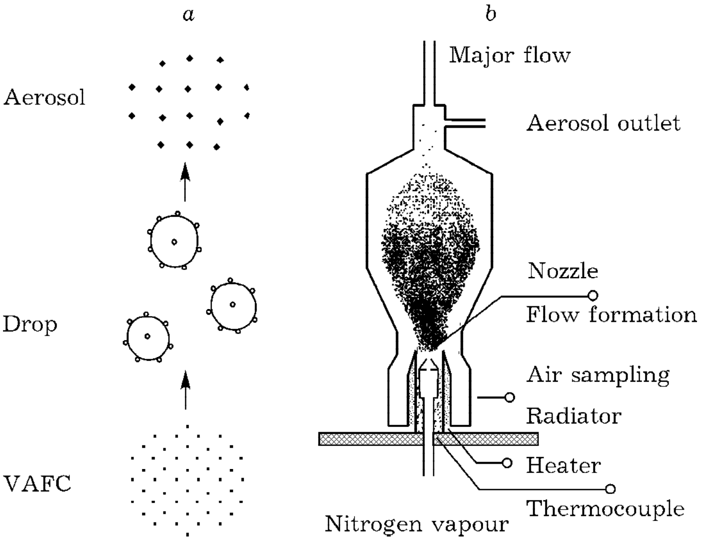

Fig. 1. Schematic cross-section (*a*) and illustration of the operation principle (*b*) of the drop concentrator.

terpreted as the mass concentration. For convenience, we will hold to this terminology.

The scheme of the set-up intended for the measurement of total concentration and diffusion coefficient of aerosol-forming admixtures in the atmosphere is presented in Fig. 1. On mixing the air with the vapour of liquid nitrogen, the concentration of the formed water drops is substantially larger than the concentration of natural aerosol. In order to decrease diffusion losses as substantially as possible, the set-up has no input lines; the air is admitted directly into the mixer of the set-up. The average drop size $\bar{r}$ depends on the humidity of ambient air, the ratio between the air and nitrogen flow rates, and the number concentration of fog particles (n). The time of absorption (τ) of admixture molecules can be estimated with the help of equations

$$dC_m/dt = -C_m/\tau \tag{1}$$

$$\tau = (4\pi D n \bar{r})^{-1} \tag{2}$$

$$\bar{r} = \sqrt[3]{\frac{3C_{w.s}(T)\eta Q_{air}}{4\pi n\left(Q_{air} + Q_{N_2}\right)}} \tag{3}$$

where C_m is the concentration of the molecules of the low volatile admixture; D is the diffusion coefficient of the molecules of the low volatile admixture; $C_{w.s}$ is the concentration of saturated water vapour; η is relative air humidity; Q_{air}, Q_{N_2} are the volume flow rates of the air and nitrogen, respectively; n is the number concentration of drops. The choice of the parameters of the set-up is reduced mainly to searching the conditions of complete absorption of admixtures by drops, that is, the conditions providing a smaller τ value than that the time of fog residence in the mixer and the time of diffusion loss on the walls.

As a result of preliminary studies, we chose the following basic parameters of the set-up. The total flow of the air and nitrogen through the chamber was about 1200 L/h. This flow rate provided (for the time of fog existence 2.5 s) insignificant diffusion losses on the walls (less than 1 %) and complete entrapment of the admixtures having the diffusion coefficient more than 0.01 cm^2/s. The flow rate of atmospheric air under investigation was varied from 150 to 600 L/h. Variation of air flow rate at the constant total flow rate was used to optimise measurement processes. The time of one measurement was 4 min. For the predetermined evaporation temperature (≈20 °C), it was possible to determine the concentrations of substances with saturated vapour pressure less than 10^{-8}–10^{-9} mm Hg.

To determine the average diffusion coefficient of PAFC, air was admitted to the mixer inlet through the tubes of different lengths. The ratio of the mass of aerosol-forming substances that passed through the tube to their total mass allows us to estimate the diffusion coefficient. Copper and polyethylene tubes with the inner diameter of 8 mm were used in these experiments. The length of the tubes (l) was 0, 10, 20, 40, 80 cm. To decrease the effect of natural fluctuations of concentrations, the experiments were carried out in long-term series using the sequence 0–10–0–20–0–40–0–80–0–10–0–20–0 *etc.* While processing the results, in the 0–l–0 sequence, the total concentration $\bar{C}(0)$ averaged over the two values was used to determine the overshoot coefficient $K(l)$:

$$K(l) = C_m(l)/\bar{C}(0) \tag{4}$$

No noticeable differences in the results for polyethylene and copper tubes used in experiments were detected.

Processing of the results was carried out within Gormley–Kennedy approximation [4]. In this approximation, the coefficient of particle overshoot through a round tube in the case of laminar flow $G(\mu)$ depends on a single parameter: $\mu = D\mathrm{Pe}$ (here D is diffusion coefficient, Pe is Pecle number which is equal to $\pi l/Q_{air}$):

for $\mu < 0.03$

$$G(\mu) = 1 - 2.56(\mu)^{2/3} + 1.2\mu + 0.177(\mu)^{4/3} \tag{5}$$

for $\mu \geq 0.03$

$$G(\mu) = 0.819\exp(-3.657\mu) + 0.097\exp(-22.3\mu) + 0.032\exp(-57\mu) \tag{6}$$

In the general case, the interconnection between the values determined experimentally and the calculated data may be represented in the form:

$$K(l) = AG(\mu) \tag{7}$$

where A is some parameter.

In view of the fact that the approximating curve in our case should pass through 1 at $l = 0$, then $A = 1$. Therefore, only the diffusion coefficient is to be fitted by means of the least squares.

CALIBRATION AND EVALUATION OF THE ACCURACY OF MEASUREMENTS

Aerosol-forming compounds in the atmosphere are characterized by very low concentration (~100 ng/m^3) [2] and low vapour pressure, so it is necessary to use special approaches in calibration procedures. For this purpose, we developed a stabilized generator of the necessary concentration of low volatile vapour.

Design of the generator of low volatile vapour

The operation principle of the generator is based on the introduction of a known amount of saturated vapour into the air flow under investigation. The scheme of the generator is shown in Fig. 2.

The generator is composed of a heat-insulated copper sleeve with a mass of 2 kg providing the stability of thermal mode. A quartz cell 220 cm^3 in volume is placed inside the sleeve. The substance which is a source of vapour is put into the cell. There is also nozzle in the sleeve; the vapour is fed through it into the calibration air. The nozzle and the cell are equipped with nichrome heaters. The temperature of the cell ((20–300)±2 °C) is set with the help of a contact thermometer commutating the circuit of the heater. To prevent condensation of the substance inside the generator, the mode is sustained in which the temperature of the nozzle is equal to the temperature of the cell; this is achieved with the help of a differential thermocouple and an electronic control unit.

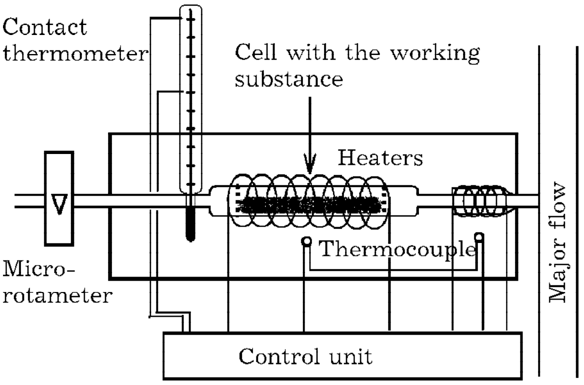

Fig. 2. Scheme of the generator of the required amount of low volatile vapour.

During the operation, the air purified with the help of the aerosol filter (at the flow rate of 10–200 m^3/min) passes through a microrotameter into the heated cell with the working substance. The air expands; the pressure of the working substance vapour in it becomes equal to the saturated vapour pressure at the temperature of the cell. Then the mixture passes through the nozzle into the main flow used for calibration.

Selection of the working substance of the generator

Physical properties were the major criterion for the choice of the working substance for calibration. Under normal conditions, its vapour pressure should not exceed the threshold value for the water absorption method (10^{-8} mm Hg), while its concentration at the generator outlet should be note less than 1 ng/m^3, which is determined by the sensitivity of the procedure. The substance should not undergo phase and chemical transformations within the temperature range of the generator. In addition, consistent reference data on the dependence of vapour pressure on temperature are to be available for the substance.

Among the substances available at the moment of calibration, the indicated criteria were met by selenium (Reakhim Co., ch. d. a. reagent grade, granules). Divergence between the literature data on vapour pressure [5, 6] within the temperature range 300–500 K does not exceed 2 %. Under normal conditions (293 K), the reference vapour pressure is $0.2 \cdot 10^{-12}$ mm Hg, vapour density 0.0029 ng/m^3. These characteristics provided non-recordable concentration of selenium at the generator outlet and the possibility to test the aerosol purity of the experiments.

In addition, selenium exhibits hydrophobic properties. Its use as the working substance to calibrate the drop concentrator allows one to decide a question that is arising permanent discussions and relates to the effect of the macrophysical properties of a substance with respect to water on measurement results.

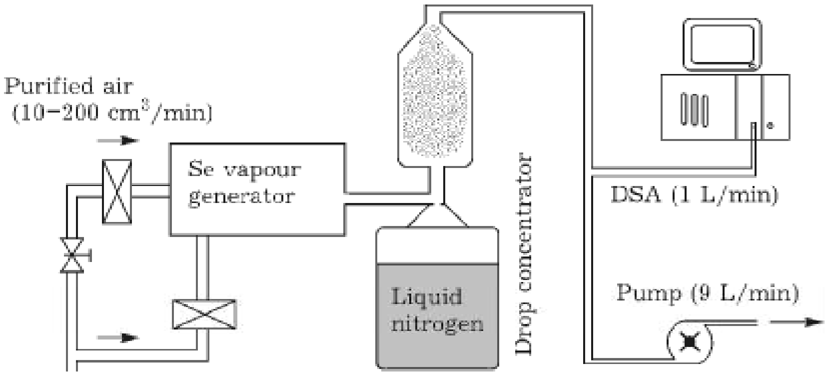

Fig. 3. Scheme of calibration of water absorption method using the generator of the required concentration of low volatile vapour.

Determiantion of the accuracy of water absorption method

Calibration scheme is presented in Fig. 3. Air purified from aerosol particles was saturated with selenium vapour in the generator are then got into the drop concentrator (total air flow rate was 10 L/min). Concentrations and size distribution of the particles formed in the concentrator were measured using the diffusion spectrometer of aerosol (DSA) after additional 20-fold dilution of the flow with the help of the capillary diluter.

It is necessary to stress that the aerosol purity of the whole set-up was tested before each experiment. With the generator cell heater switched off, no formation of particles was detected. The square mean fluctuations of the mass concentration of selenium vapour during a half an hour measurement series at a fixed cell temperature did not exceed 5 % of the average value. Measurements were carried out at the linear region of the dependence of vapour mass concentration on the rate of flow through the generator, which provided the reliability of the data on the correspondence of vapour pressure in the cell to saturated vapour pressure.

With such an arrangement of the experiment, the mass concentration of selenium vapour, on the one hand, can be calculated using the reliable reference data, on the other hand, can be obtained from the data obtained in measurements of the volume of aerosol formed from it in the drop concentrator. This is the essence of calibration process.

The density of selenium vapour in the generator cell M_{ref} was calculated from the tabulated reference data using equation

$$M_{\mathrm{ref}} = e^{A-B/T} \tag{8}$$

where A, B are reference values characterising the temperature dependence of Se vapour pressure, T is absolute temperature.

The density of selenium vapour in the generator cell (M_{fact}), taking into account the concentration and mean number concentration of the selenium aerosol measured with DSA at the outlet of the drop concentrator, thermal expansion and dilution, was determined using equation

$$M_{\mathrm{fact}} = \frac{\pi d^3}{6} N \frac{Q}{q} \rho \varepsilon \frac{T_0}{T} \tag{9}$$

where d is the mean number size of aerosol particles; N is the number concentration of particles; Q, q are total air flow rate and air flow rate through the generator, respectively; ρ is selenium density; ε is dilution coefficient at the inlet of DSA; T_0 is room temperature; T is the temperature of the generator cell.

A comparison between the reference and measured temperature dependencies of the density of selenium vapour is presented in Fig. 4.

The temperature of the generator cell was varied in experiments from 140 to 204 °C, the mass concentration of selenium vapour was varied from 10 ng/m^3 to 3 μg/m^3 of the air. Total number of measurements at different temperatures was 40. The difference of the average experimental values from the literature data did not exceed 8 %.

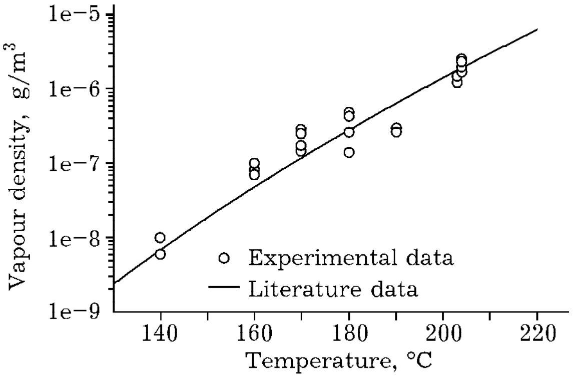

Fig. 4. Comparison between the reference and measured temperature dependencies of the density of selenium vapour.

So, we developed a simple and rapid method of calibrating the water-absorption method of measurement of the mass concentration of the vapour of aerosol-forming compounds in atmospheric air. Using the developed generator of the necessary concentration of low volatile vapour of a broad range of substances, it was demonstrated that the error of vapour concentration measurement using the water-absorption method does not exceed 10 % within the mass concentration range from 10 to 3000 ng/m^3.

MEASUREMENTS UNDER NATURAL CONDITIONS

Measurements were carried out at the research stationary ground of the Limnological Institute, SB RAS, situated near the Bolshiye Koty village (the southern coast of Lake Baikal). The basis of the material under analysis is formed by the data obtained in four cycles of expeditionary measurements made during the periods from May to September, 2003–2005.

To determine the flux of VAFC from the land surface, we used a chamber 0.7 m^3 in volume that isolated 0.03 m^3 of the surface of soil with vegetation. Lavsan was chosen as the material for the chamber because it is transparent for the major part of the solar spectrum and thus provides the illumination conditions in the chamber close to the natural ones near the land surface. In addition, lavsan cannot be a source of aerosol or vapour that might affect experimental results. An excess air flow was fed into the chamber (10 L/min); the air was purified from aerosol and VAFC, which ensured the aerosol purity of the experiments. Normalizing the mass concentration of VAFC measured in the chamber for the area of the coating and the air flow rate, we determined the flux of low volatile aerosol-forming compound from the soil surface. To control the conditions affecting the capacity of the surface source, soil temperature was measured in the chamber.

The goal of investigation was to follow the whole life cycle of aerosol particles from gas precursors through VAFC to aerosol, and also to determine the effect of external conditions on this process. In this connection, the following parameters were measured simultaneously during the field experiments:

1. Mass concentration and average diffusion coefficient of VAFC.
2. VAFC flux from the soil surface.
3. Size distribution of aerosol particles within the range 3–200 nm.
4. Temperature of soil and air.
5. Illumination.
6. Ozone concentration.
7. Concentration of sulphur dioxide.
8. Wind direction and velocity.

Measurements were carried out every 3 h. The devices were placed so that the anthropogenic effect on measurement results could be minimized.

Previous estimations [2] showed that the typical mass concentration of VAFC in the atmosphere is about 100 ng/m^3. The first results of measurements of VAFC characteristics confirmed the known scientific hypotheses concerning the properties of these compounds.

Results of measurements carried out in summer 2003 are shown in Fig. 5. The time of measurements (July) was characterized by forest fire events; the average mass concentration of VAFC was 650 ng/m^3. In August, the weather was characterized by permanent clouds and precipitation, thus the average concentration of VAFC decreased during this period to 170 ng/m^3. Estimations showed that, taking into account measurement of diffusion coefficient and assuming the unit density of substance and the spherical shape of VAFC particles, the mass concentration of aerosol-forming substances during the fire period corresponds to the clusters 1.5 nm in diameter, their concentration being $4 \cdot 10^8$ cm^{-3}, while during the period of precipitation cluster diameter is 2.3 nm and concentra-

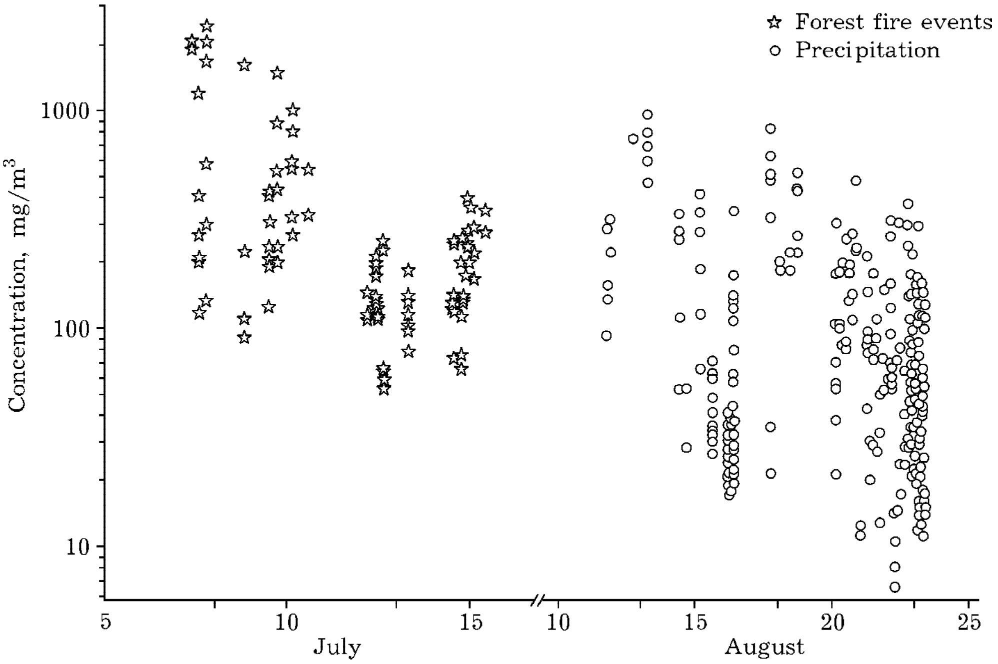

Fig. 5. Temporal variation of the mass concentration of VAFC (summer, 2003).

tion is 0.5 · 10^8 cm^{-3}. It should be noted that the average size of air molecules is about 0.2 nm, and their concentration is about 3 · 10^{19} cm^{-3}. The minimal size of recordable aerosol particles is 3 nm at the number concentration about 10^3 cm^{-3}.

So, we proved experimentally that the VAFC occupy an intermediate position in the physical properties between the gas precursors and aerosol particles. Taking into account the fact that the mass concentration of VAFC is much lower than the mass concentration of aerosol and its gas precursors, we may state that the process of VAFC formation is the limiting stage of gas-to-particle conversion.

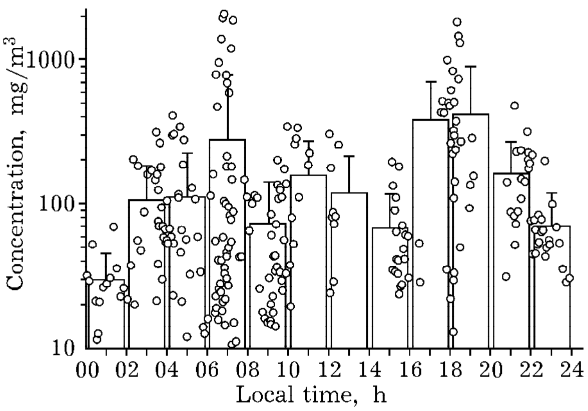

Fig. 6. Diurnal dynamics of the mass concentration of VAFC (average values are shown with bars).

Measurements of the diurnal dynamics of the mass concentration of VAFC revealed two maxima at the background of the general daily increase, corresponding to approximately 6.00 and 18.00 of local time (Fig. 6). This may be due to the diurnal cycles of vegetative activity and synoptic parameters.

Similarly to the case of aerosol sources, the sources of VAFC in the atmosphere may be divided conventionally into primary and secondary ones, or surface and volume, respectively. The surface sources serve directly as the sources of VAFC, their capacity should be determined by evaporation and correspondingly by the surface temperature. The volume sources of VAFC originate from chemical and photochemical reactions taking place in air volume. To determine the contribution from the surface sources, we measured the mass concentration of aerosol-forming compounds in turn in the chamber and in the atmosphere (Fig. 7). A comparison between the temporal dynamics of these data allows us to establish the dominating source.

The mass concentration of VAFC during the entire time of measurements in 2004 was 20–60 ng/m^3, the flux from soil surface was 60–

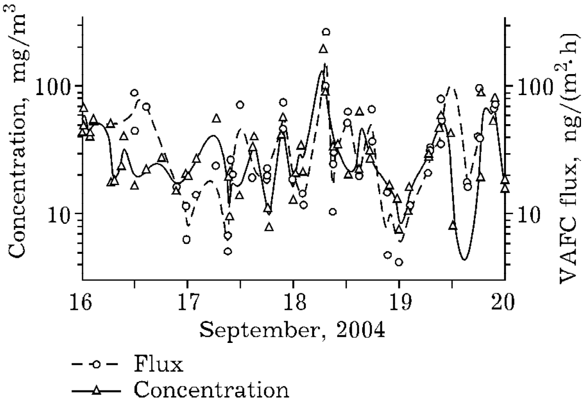

Fig. 7. Temporal variation of the mass concentration and the productivity of the surface source of VAFC. Correlation coefficient: 0.8.

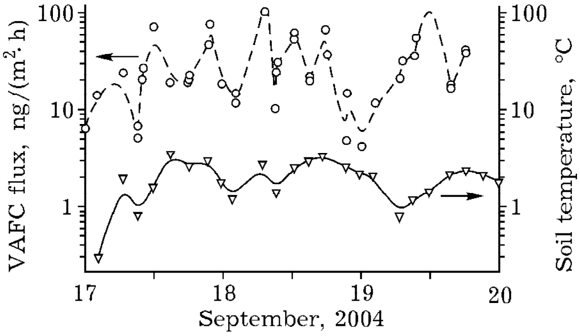

Fig. 8. Temporal variation of VAFC flux and soil temperature.

90 ng (m^2 · h) (Fig. 8). A correlation between the mass concentration of AFC in the chamber and in the atmosphere provides evidence of the fact that the surface source dominates for the measurement site.

Evidently, the diurnal variation of VAFC generation from the underlying surface and variability from one day to another depend on insolation, temperature of the surface and air near the land surface, which in turn are determined by a complicated set of synoptic processes. To estimate the interconnections between VAFC income and the major energy-related characteristics of the surface, we carried out a parallel analysis of changes in VAFC concentration, temperature and illumination. Evidently, soil surface temperature is strongly dependent on the amount of solar energy reaching it, but the inertia of soil heating and cooling ensures slower temperature variation in the diurnal process than the variations of observed illumination.

The temporal variation of VAFC flux and soil temperature is presented in Fig. 8; the correlation coefficient is 0.72.

For comparison, Fig. 9 shows a similar variation of the mass concentration of VAFC and illumination (correlation coefficient is 0.57).

Therefore, it may be concluded that gradual heating or cooling of soil has a stronger effect on the productivity of the surface VAFC source than rapid variations of illumination do.

So, changes of VAFC fluxes from the surface may be stronger dependent on the integral soil heating than on the current solar flux value. The prevailing source of VAFC is likely the on-land vegetation but not reactions within the air volume. In this connection, it is

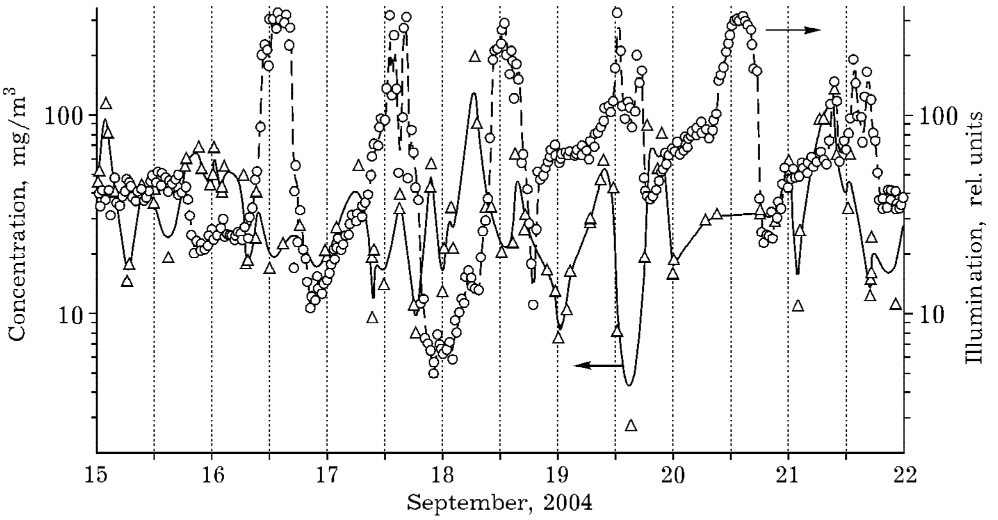

Fig. 9. Temporal variation of the mass concentration of VAFC and illuminance. Correlation coefficient: 0.57.

reasonable to compare our results with the available literature data.

Measurements of concentrations, chemical composition and emission rate for volatile products of plant metabolism in boreal zones were carried out by many authors [7–14]. The following regularities were established:

1. Seasonal and diurnal variations of these parameters are observed.
2. The seasonal maximum of emission rate is in July.
3. The emission of volatiles is higher in daytime than at night.
4. Emission rate increases noticeably after rain and may remain at a high level for some days [9, 10].
5. Emission rate increases noticeably during blooming [9].
6. Emission rate is weakly dependent on illumination level [9].
7. The cycles of emissions of volatiles are connected with the cycles of CO_2 assimilation by plants [7, p. 138].
8. Emission rate is mainly determined by evaporation and, in agreement with the literature experimental data, is described by the following law:

$$F = Ae^{-b/T} \tag{10}$$

This is an empirical dependence, but attention should be paid to its similarity with the equation binding saturated vapour pressure and temperature. The centigrade temperature scale is used in this law. At 0 °C, plant emission is absent.

According to the data of the authors of [9, 10, 12, 13], constant b for different coniferous species growing at the territory of RF is $16-10^4$. On the basis of these data, we may estimate the overall phytogenic emission from forests in Russia and separate regions. For example, for the Asian territory of our country, this emission is 7.9–13.9 million tons per year; the main contribution is made by the East Siberian region (3.4–6.5 million tons per year) [14].

A comparison between our and literature data points to the coincidence of general features of seasonal and diurnal variations of the flux of volatile phytogenic substances with the emission of VAFC (Fig. 10). Therefore, VAFC that form the aerosol atmosphere of the region may be a phytogenic product. At present, we are investigating the temperature dependence of VAFC emission rate from the surface and the qualitative chemical composition of aerosol-forming substances.

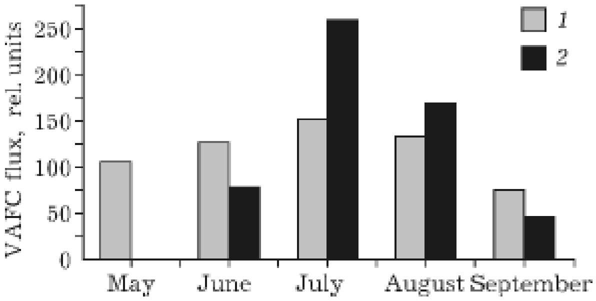

Fig. 10. Comparison between the seasonal dynamics of phytogenic emission and the concentration of aerosol-forming substances: *1* – volatile emissions of *Pinus sylvestris* in the Krasnoyarsk Territory (data from [8]); *2* – mass concentration of VAFC (Bolshiye Koty village, 2003–2005).

CONCLUSIONS

A procedure for the determination of concentrations of atmospheric admixtures down to a level of 1 ng/m^3 was developed. This procedure accelerates the natural process of collection of the vapour of low-volatile compounds from the air with the help of the drops of atmospheric water created artificially. The experimental set-up was called the drop concentrator. A simple and rapid method was developed to calibrate the drop concentrator with the help of the generator of a prescribed amount of low volatile vapour. It was shown that the error of measurement of vapour concentration using this method does not exceed 10 % within the concentration range 10–3000 ng/m^3.

The experimental set-up was tested during expeditionary measurements at Lake Baikal. The following major results were obtained:

1. The concentration of VAFC in the surface atmospheric layer is about 100 ng/m^3.
2. About 10^8 VAFC particles with a size of about 1 nm per 1 cm^3 of the air are present.
3. The prevailing source of VAFC is likely the ground vegetation bit not reactions with in the air volume.
4. The rate of VAFC emission from soil surface is 10–100 ng/(m^2 · h).

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