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OPTICS OF CLUSTERS, AEROSOLS, AND HYDROSOLES

Spatial Distribution of Potential Sources of Carbonaceous Aerosols in Central Siberia

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Abstract—We present the results of trajectory analysis of long-term measurements of organic (OC) and elemental (EC) carbon in aerosols sampled on quartz filters at an altitude of 300 m at ZOTTO station. The EC and OC concentrations were determined by the thermo-optical method. The resulted time series were supplemented with the HYSPLIT backward trajectories, and CWT and PSCF functions were calculated on a grid of 150 × 250 cells, which covered the geographical area of 30° × 20° centered at Zotino. These functions characterize the intensity of potential sources of carbon-containing aerosols in a cell. The results make it possible to identify the regions with the strongest organic and elemental carbon emissions and to estimate the seasonal variability of these emissions. In particular, in summer, the main sources of OC and EC are located to the east of Zotino, in the Podkamennaya Tunguska River region, and are most likely associated with wildfires. In cold seasons, most sources of carbonaceous aerosols are in the southwestern part of the geographical region under study, where large cities are located and the bulk of the population is concentrated. The regression analysis of CWT functions of organic and elemental carbon is shown to enable determining the dominant type of carbonaceous aerosol sources in some cases. Our results can be used for estimation of aerosol radiative forcing in Siberia.

Keywords: atmospheric composition, carbonaceous aerosol, trajectory method, elemental carbon, organic carbon

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INTRODUCTION

Aerosol particles are an essential element of the Earth's climate system, since they noticeably affect properties of the atmosphere, primarily radiation (direct and indirect aerosol forcing), and through them the temperature and dynamics of the atmosphere [1, 2]. In addition, the interaction of atmospheric aerosol with the Earth's biosphere plays an important role. On the one hand, aerosol pollution affects the living conditions of biological organisms, including human health; on the other hand, a significant part of aerosol particles in the lower atmosphere is biogenic [3]. They are not only bioaerosols (pollen, spores, and microorganisms and their defragmentation products), but also secondary aerosols resulted from the conversion of volatile hydrocarbons emitted by coniferous forests (isoprenes) [4], smoke particles from forest and steppe fires, etc. This interaction is of particular importance for large forest regions, including the boreal forest zone. Boreal forests occupy about 8% of the continental area of the planet and ~40% of the territory of the Russian Federation. Therefore, the study of aerosols on these territories is necessary to assess the climate change on both global and regional scales.

The peculiarity of natural forest systems is that global climate changes can produce various feedbacks in them, which, in turn, can increase climate variability [5, 6]. Thus, an increase in the surface temperature in Siberia can shorten the period when snow is lying, increase the duration of the growing season, and decrease humidity, which, in turn, intensifies the production of secondary organic aerosols by boreal forests and increases the wildfire risk [7]. As a result, the concentration of carbon-containing aerosols in the Siberian air basin rises, which changes the surface temperature due to direct and indirect radiation forcing.

The problem is that the positive or negative character of these feedbacks is determined by optical and hygroscopic properties of aerosols, which depend on the chemical composition and size of the particles. The lack of information about the physicochemical parameters of aerosol particles is one of the main sources of uncertainty in climate change [8]. Therefore, to improve the accuracy of estimates of aerosol climate effects, systematic observations of variations in the composition and concentration of aerosol particles and the study of the location and productivity of atmospheric aerosol sources are required.

There are many works devoted to such observations in Siberia [9–11], however, usually near large cities. In 2006, the international background observation station ZOTTO (Zotino Tall Tower Observatory) was

created in Central Siberia for long-term monitoring of the gas and aerosol composition of the atmosphere and analysis of the state of forest ecosystems. The large distance between the station and sources of anthropogenic pollution (the nearest large city, Krasnoyarsk, is spaced 600 km apart from the station) produces unique conditions for studying the composition of background aerosols in boreal forests. Since 2010, the station has performed regular filter measurements of organic (OC) and elemental (EC) carbon in atmospheric aerosols. The measurements made it possible to identify seasonal variations and long-term trends in the concentrations of these components [12].

Source-receptor models are commonly used for analyzing atmospheric data today. These models enable deriving the spatial distribution of potential sources of a pollutant from local measurements of its concentration at one point [13]. Trajectory methods are the most widely used in solving such problems; they are based on the analysis of a set of back trajectories of air masses outgoing from a measurement point. Quite a lot of such techniques are described in the literature, applicable to the analysis of both atmospheric gases [14] and aerosols [15].

The aim of this work is to derive information on the spatial distribution and relative intensity of sources of carbonaceous aerosols in Central Siberia by the concentration weighted trajectory method based on local measurements of EC and OC concentrations at ZOTTO station in 2010–2021 and classify these sources.

1. MEASUREMENT TECHNIQUE AND RAW DATA

The mass concentrations of OC and EC in atmospheric aerosol were determined from the analysis of aerosol samples collected on quartz filters at. ZOTTO station located near Zotino village in the Krasnoyarsk Krai (60° N, 90° E). Air was sampled from a 300 m high mast and pumped through filters [16] with an air flow rate of 19 L/min; filters were changed every 5–7 days. Thus, the total volume of air pumped through a filter was 150–200 m^3; the mass of aerosol deposited on a filter varied from 0.4 to 12 mg depending on air pollution level. A total of 705 aerosol samples were taken and analyzed during the period under study.

The amount of OC and EC in aerosol samples was determined by the thermo-optical method using a commercial analyzer (Thermal/Optical-Transmittance Carbon Aerosol Analyzer; Sunset Laboratory Inc., USA). Within this method, a quartz filter with aerosol under study is subjected to programmable heating in a flow of inert gas to a temperature of 870°C. While the temperature is rising, less and less volatile fractions of organic compounds evaporate from the filter, and elemental carbon sublimes at maximal temperatures. All carbon contained in different evaporated compounds is catalytically converted into CO_2; then, the gas flow is mixed with hydrogen and enters a methanator furnace, where CO_2 is converted into methane. Methane concentration is measured by a plasma ionization detector. Thus, the methane concentration can be used to determine the mass of carbon on a filter. The sensitivity (detection limit) of this method is 0.2 μg of carbon per 1 cm^2 filter; the random error does not exceed 6% of the mass of carbon material on a filter. The technique for analyzing filter samples is described in more detail in [12]. The mass concentration of carbon in atmospheric aerosol was determined from the ratio of the resulting mass of OC and EC on a filter to the volume of air pumped through the filter during sampling.

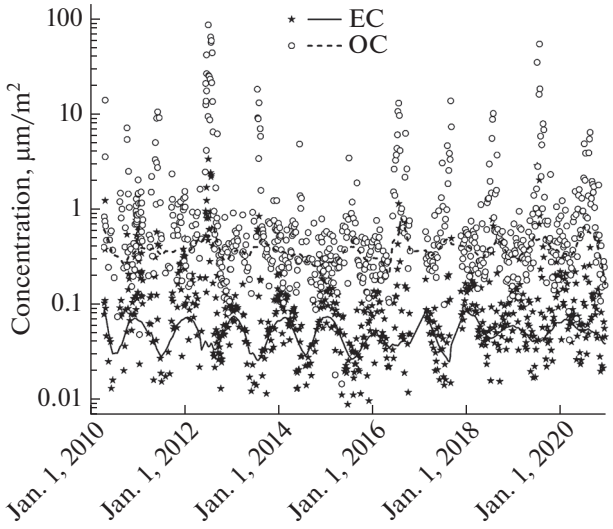

Fig. 1. Time variations in the mass concentrations of elemental and organic carbon in aerosol according to measurements at ZOTTO station in 2010–2021 (symbols correspond to measurement data and lines show calculated background concentrations).

The dynamics of the mass concentrations of OC and EC in atmospheric aerosols is shown in Fig. 1. Their strong variability is evident, maxima and minima of each component differ by more than two orders of magnitude. This variability is primarily due to the presence of high-power non-stationary regional sources of carbonaceous aerosol particles. In such situations, periods with high ("polluted") and low ("clean" or "background") content of atmospheric impurities are distinguished. The "background" conditions are understood as the state of the atmosphere without noticeable influence from local or regional sources of pollutants, but under the effect of natural emissions and pollutants transferred from distant sources. This division is substantiated and the algorithm for calculating the background concentrations of OC and EC is described in [12, 17, 18] as applied to ZOTTO station. The time variations in the calculated background concentrations for both carbonaceous components are shown in Fig. 1. The seasonal varia-

tions are clearly pronounced, with winter maxima and summer minima of the background concentrations for EC and vice versa for OC. This seasonal dynamics is associated with different prevailing processes of carbonaceous aerosol generation in winter and summer.

2. CONCENTRATION WEIGHTED TRAJECTORY METHOD

Long-term measurements of the concentration of an atmospheric pollutant at one point (receptor) make it possible, using receptor models, to estimate the spatial distribution of sources of this pollutant over the surrounding area. In this work, we use the concentration weighted trajectory method (CWT). Like all trajectory methods, the CWT method requires the calculation of a set of back trajectories of air masses outgoing from the point where an observation station is located at the time corresponding to the time of measurements. The geographic region where pollutant sources are looked for is divided by a coordinate grid into a two-dimensional array of cells. Each cell is matched to a trajectory-weighted concentration of an aerosol component C_{ij} calculated by the formula [15]:

$$C_{ij} = \frac{\sum_{l=1}^{N} C_l \tau_{ijl}}{\sum_{l=1}^{N} \tau_{ijl}},$$

where i and j are the cell indices; l is the trajectory number; N is the total number of trajectories; C_l is the concentration of the component measured at the observation point at the time of arrival of the lth trajectory; τ_{ijl} is the time for which the lth trajectory passes the cell with the numbers i and j. The parameter C_{ij} is often called the CWT function and has the meaning of the measurement time average concentration of an aerosol component brought to the observation point from the cell with the indices i and j. The higher C_{ij} value for a cell, the stronger sources are located in it.

In this work, the CWT function has been calculated in the geographical region 75°–105° E × 50°–70° N on a grid of 150 × 250 cells of ~10 km in size. Back trajectories of 120 h in duration have been constructed using the HYSPLIT model with 1 h intervals. Thus, the total number of processed back trajectories is ~80000. It should be noted that most trajectories came to the specified geographical region in less than 3 days. Since carbonaceous aerosol belongs to the submicron fraction, its lifetime in the atmosphere significantly exceeds the duration of back trajectories and it can be considered a conservative impurity to the first approximation,. The mass concentrations of EC and OC determined from the analysis of a filter sample were assigned to all trajectories arriving to the measurement point during the time of sampling to this filter.

The main sources of carbonaceous aerosol particles are located on the surface. Therefore, we suggest accounting in the formula for the CWT function only those sections of trajectories that pass over a cell at an altitude lower than the altitude of the mixing layer. These altitudes are calculated in the HYSPLIT model. This modernization of the algorithm reduces, in our opinion, the possible "masking" effect of air masses the trajectories of which pass over pollutant sources at high altitudes and, therefore, bring little pollution to the measurement point. In addition, when calculating the CWT function, the effect of washing out aerosol particles by precipitation is taken into account. When a trajectory passes over an area with precipitation intensity above 0.5 mm/h, the contribution from the earlier trajectory sections into C_{ij} sum is set to zero.

3. CALCULATED CWT FUNCTION FOR ORGANIC AND ELEMENTAL CARBON IN AEROSOL

To estimate the spatial distribution of sources of carbonaceous aerosols over the geographic region under study following the above described approach, the corresponding CWT functions are calculated for OC and EC based on measurements at ZOTTO from January 2013 to December 2021.

To analyze the annual variability of aerosol emissions, the annual measurement cycle is divided into warm ("summer") and cold ("winter") seasons. The cold period includes days when the ten-day average temperature at the measurement point is lower than the observation period average temperature (271 K). The calculation results are shown in Fig. 2. The zero CWT functions in the southeastern part of the region are due to the screening effect of the Sayan Mountains on the movement of air masses, i.e., no back trajectories arrive to the measurement point from this territory.

A strong correlation between the spatial distributions of EC and OC sources is observed in Fig. 2; the correlation coefficient between CWT functions for EC and OC $R_w = 0.96 \pm 0.02$ in warm seasons and $R_c = 0.90 \pm 0.02$ in cold seasons. These high values witness that EC and OC contained in aerosol particles are mainly generated by the same high-power sources, which provide high concentrations of carbon in aerosols at the measurement point. If we consider only the "clean" periods, when the carbon concentration in aerosol was lower than 150% of the background concentration (see Fig. 1), then the correlation between the CWT functions for EC and OC is significantly lower: $R_{w.bg} = 0.73 \pm 0.03$ and $R_{c.bg} = 0.64 \pm 0.03$ for summer and winter, respectively.

The results show the pronounced seasonal variation in the spatial distribution of carbonaceous aerosol sources. In the warm season, EC and OC emissions are significantly higher than in the cold season. Moreover, in summer, the main sources are concentrated to

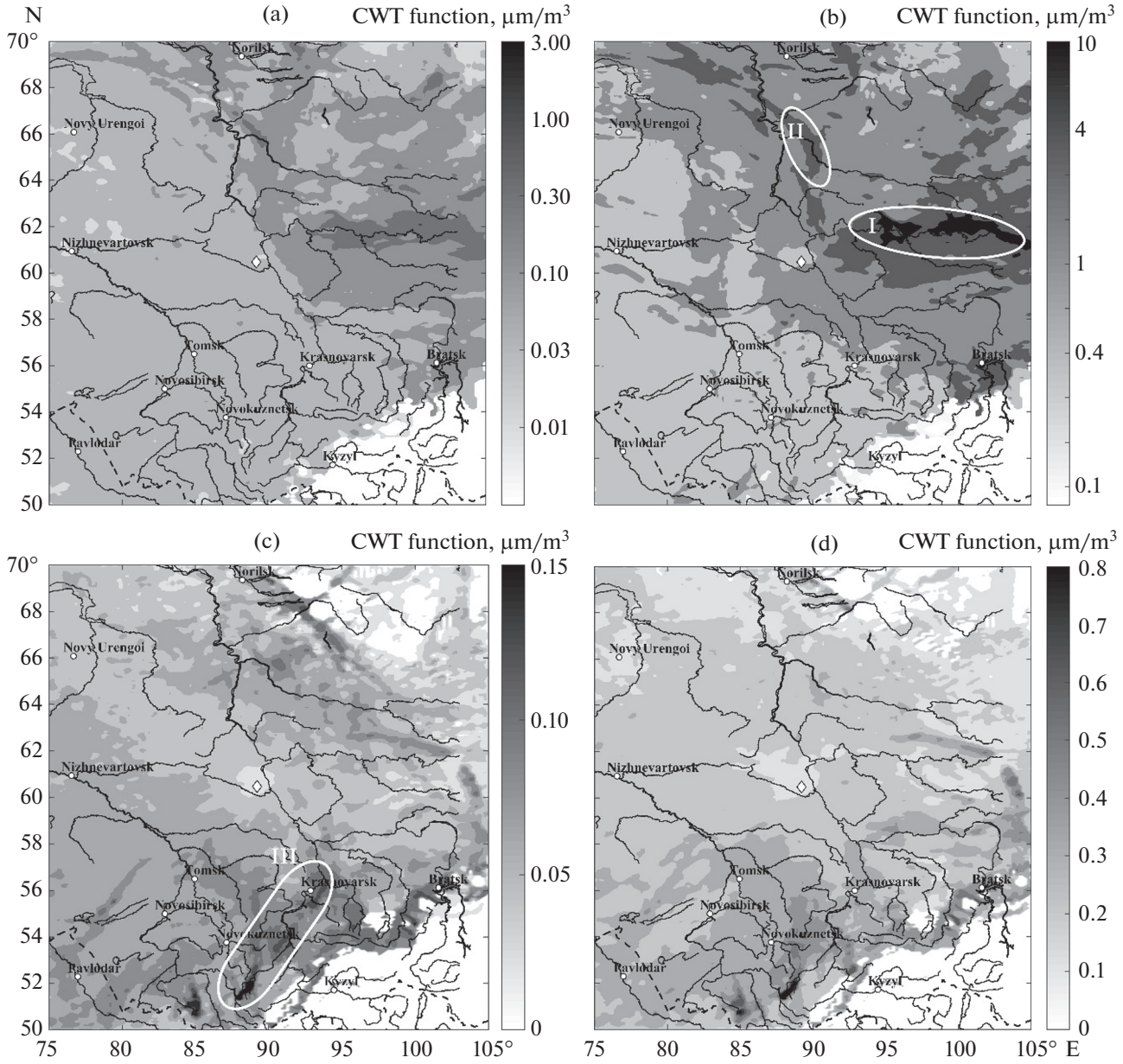

Fig. 2. CWT functions for (a and c) elementary and (b and d) organic carbon in aerosol in (a and b) warm and (c and d) cold seasons: regions for which regression coefficients have been determined are marked by I, II, and III (see explanations in the text).

the east and north of ZOTTO station along the Podkamennaya Tunguska and Yenisei rivers, and the CWT functions for these regions are more than an order of magnitude higher than for the rest of the territory under study. It is natural to match these high-power sources with wildfires, which cover a significant area of Central Siberia in summer. According to wildfire satellite monitoring data [19, 20], their average area in Siberia is ~ 60 thousand km^2 every year, and ~1 MT of fine aerosol ($PM_{2.5}$) is emitted into the atmosphere. The localization of numerous combustion sources varies both within a season (from April to September) and from year to year almost throughout the region under study. Long-term monitoring data [19] show a high concentration of wildfires to the east of the Yenisei, which is consistent with high CWT function values calculated in this work.

In the cold season, the CWT functions for OC and EC are an order of magnitude lower. The strongest sources of carbonaceous aerosol in winter are located in the vicinity of large industrial cities (Krasnoyarsk, Novokuznetsk, and Norilsk), mainly in the southern part of the region. They are most likely anthropogenic, i.e., emissions from industrial enterprises, transport, and all kinds of heating systems.

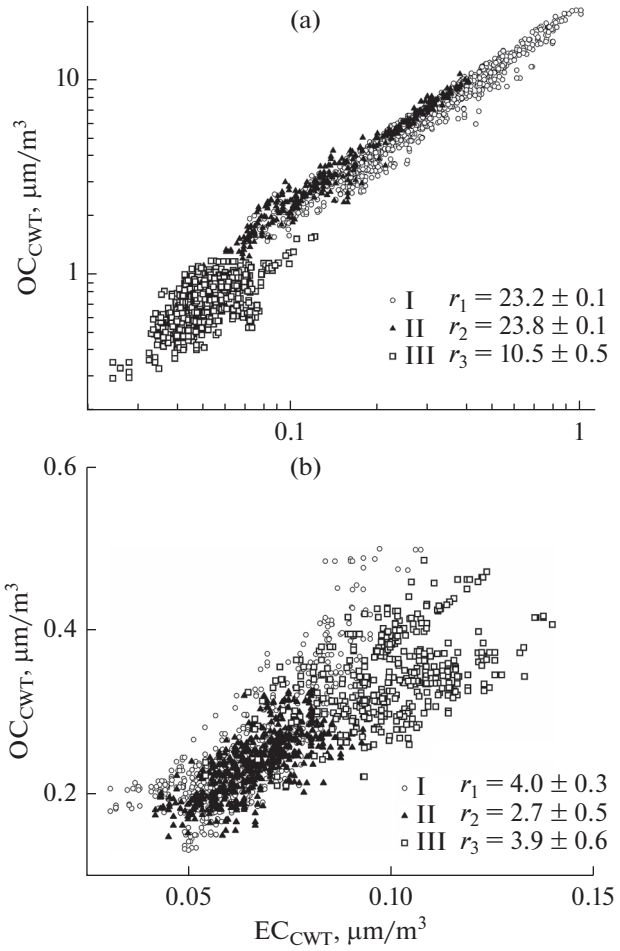

Fig. 3. Correlation between CWT functions for elemental and organic carbon in the selected regions in (a) warm and (b) cold seasons (see text for explanations).

4. CORRELATION BETWEEN AEROSOL OC AND EC EMISSIONS

As noted above, the bulk of aerosol carbon is emitted into the atmosphere during combustion of organic materials of various origins, when OC and EC are simultaneously produced. However, the ratio between these components varies depending on the fuel types and combustion conditions [21–23]. Therefore, the OC/EC emission ratio can be used as an indicator of the origin of aerosols. It is clear that the ratio of CWT functions for EC and OC is not identical to the emission ratio; however, we suggest that it also depends on the prevailing source types. Figure 3 shows the correlation between the CWT functions for OC and EC in warm and cold seasons for regions with high-power aerosol sources (these regions are marked in Figs. 2b and 2c). Each point in Fig. 3 corresponds to a specific cell of the geographic grid, and the coordinates of this point correspond to the CWT functions for OC and EC calculated for this cell.

One can see that the linear regression coefficients are close ($r \approx 23$) in the region of Podkamennaya Tunguska and the middle Yenisei (regions I and II) in summer. This indicates the identity of the aerosol carbon sources, which are strong wildfires. The regression coefficient for more populated areas (region III) is significantly lower ($r \approx 11$), as well as the CWT functions. In winter, the linear regression coefficients are even smaller ($r \approx 2.7$–4.0) for all the regions under study and their scatter is much larger. These values are apparently typical for sources associated with intensive combustion of various fossil fuels during the heating season.

Our results are consistent with the literature data on the emission ratios. According to estimates [21], the OC/EC ratio is 16 ± 6 for wildfires outside the tropics, 7 ± 4 for biofuel combustion, and 3.2 ± 0.3 for hard coal. The close coincidence of the emission ratios with linear regression coefficients for CWT functions for OC and EC allows the latter to be used to classify the predominant sources of carbonaceous aerosols in different regions.

CONCLUSIONS

The analysis of the concentration of organic and elemental carbon in aerosol measured at ZOTTO station using the CWT method made it possible to estimate the spatial distribution of sources of carbonaceous aerosols in Central Siberia (75°–105° E; 50°–70° N) and trace its seasonal variability. The simultaneous calculation of the CWT functions for OC and EC enabled us to identify regression relationships between them and classify the carbonaceous aerosol generation processes prevailing on different territories. It is ascertained that the main sources of OC and EC in summer are located east of ZOTTO, in the region of the Podkamennaya Tunguska River, and are most likely associated with wildfires, as indicated by the high linear regression coefficient between the CWT functions. During the cold seasons, main carbonaceous aerosol sources are detected in the southwestern part of the geographic area under study, where large cities are located and most of the population is concentrated. Low regression coefficients correspond to fuel combustion by transport and heating stations.

Modern trajectory methods have shown their promise for analyzing atmospheric pollution monitoring data. In addition to localizing sources, they make it possible to compare their intensity and type and to find areas that stand out from the rest (which are to be studied by other methods and means), thus significantly increasing the amount of information extracted from local measurements of atmospheric components.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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