
OPTICS OF CLUSTERS,
AEROSOLS, AND HYDROSOLES

Annual Dynamics of Aerosol Organic Components in the Free Atmosphere over South-Western Siberia

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Received June 24, 2015

Abstract—We study the annual behavior of the concentration of organic components of the atmospheric aerosol, sampled onboard the Tu-134 Optik airborne laboratory in the atmospheric layer of 500–8500 m. The concentration of the organic component in aerosol composition is found to be maximal during spring and minimal during fall. Compounds ranging from C₈H₁₈ to C₃₅H₇₂ are detected in the composition of aerosol particles. The range of hydrocarbons is the widest during the winter period (C₁₂H₂₆–C₃₅H₇₂) and during spring (C₈H₁₈–C₃₁H₆₄), and it is markedly narrower during summer (C₁₈H₃₈–C₃₃H₆₈) and during fall (C₁₆H₃₄–C₃₁H₆₄). One mode (*n*-alkane C₂₀H₄₂) predominates in aerosol composition throughout the year. A secondary maximum, corresponding to *n*-alkane C₂₉H₆₀, appears during the summer period.

Keywords: atmospheric aerosol, composition, hydrocarbons, *n*-alkanes

DOI: 10.1134/S1024856016010036

INTRODUCTION

Atmospheric aerosol plays an important role in many atmospheric processes. The report of the International Panel on Climate Change, published recently [1], indicated once more the ambiguous contribution of aerosol to the radiation budget of the planet and, correspondingly, to global climate change. In aerosol composition, there is a great number of dangerous compounds such as aromatic hydrocarbons and chlorine-, sulfur-, and nitrogen-containing species [2, 3], which explains the ecological significance of their study. Changes in the concentration of many organic components under the impact of human activity can change the whole structure of atmospheric processes to an extent difficult to predict [4].

It has long been believed [5] that the inorganic component dominates the chemical composition of atmospheric aerosols. The contribution of the carbon component does not exceed a few percent. Subsequent studies have shown that the inorganic component contributes 25–50% to the composition of microdispersed (nanoparticles) and submicron aerosol fractions, whereas organic species may account for from 40 to 65% in composition of the same particles [6], and this contribution is highly variable [7].

Moreover, experiments have shown that the contribution of the organic component can reach 80% in the microdisperse fraction [8], indicating that there are considerable deviations from the commonly accepted theory of binary and ternary nucleation in the atmosphere [9, 10], thus motivating a closer look at nanoparticle formation in the atmosphere. Recently, many hopes for a better understanding of the nature of nucleation are associated with recognition of an important role the Criegee radicals play in the chemical processes in the atmosphere [11, 12].

In the near-ground atmospheric layer, the organic component of aerosol has been studied quite intensively by a large number of research groups. For instance, the authors of work [13] compared data from 25 measurement sites and identified the main sources of organic particles. The natural organic gases include additions from plants and forest fires; among the anthropogenic contributions, combustion of different fuel types; and in maritime regions, dimethyl sulfide. It is noteworthy that the contribution of each source can vary from 10 to 80%, depending on region.

In the free atmosphere, the organic component of aerosol has been very poorly studied. The authors of work [14] showed that the concentration increases by

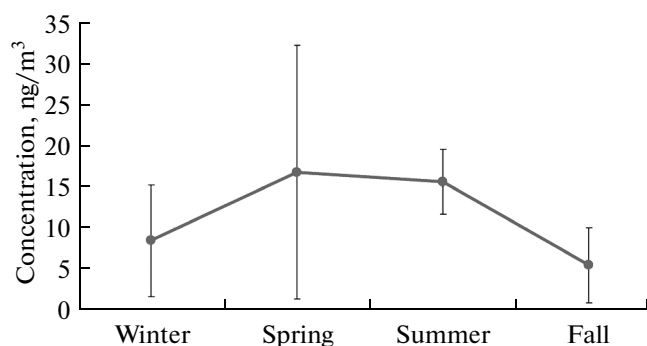


Fig. 1. Multiyear (2012–2015) average concentration of organic aerosol component in the free atmosphere over South-Western Siberia.

a factor of 2.5 when going from the Earth's surface to an altitude of 2 km, and levels off further upward. Authors of work [15] report neutral vertical behavior of concentration with altitude. In later works [16, 17], authors show that the concentration decreases with increasing altitude. Hence, the study of the organic component of aerosol in the free atmosphere is very important.

METHOD FOR SAMPLING AND SAMPLE ANALYSIS

Aerosol samples were collected onboard the Tu-134 Optik airborne laboratory in the atmospheric layer from 500 to 8500 m. The laboratory and the instrumentation used were described in [18]. Aerosol samples were collected in different periods from 2012 to 2015 in the course of regular flights in the region of the Karakansk pine forest, located on right bank of the

southern part of the Novosibirsk reservoir. Teflon analytical membranes Grimm 1.113A with pore diameters of 1.2 μm were used for concentrating the aerosol.

Collected samples were singly extracted with acetone, concentrated to 50 μL , with a subsequent analysis on a chromatato-mass-spectrometer Agilent 6890N as the temperature of analysis was raised from 50 to 250°C at a heating rate of 5°C/min; isotherms at initial and final temperatures were 3 and 45 min, respectively. The hydrocarbons were identified using libraries of NIST mass spectrum databases, as well as by comparing retention times of individual *n*-alkanes in a standard reference mixture (Alkane Standard Solutions C₈–C₂₀ and C₂₁–C₄₀ by SIGMA-ALDRICH). The analysis technique was described in more detail in [19].

To date, we accumulated 26 vertical profiles, allowing us to proceed from the analysis of individual samples [20] to a more general consideration of measurements performed.

RESULTS AND DISCUSSION

We will first consider how the total identified part of the organic component of aerosol behaves during the year. These data are shown in Fig. 1. For seasonal averaging, we used 9 samples for the winter season, 10 samples for spring, 4 samples for summer, and 3 samples for fall.

From Fig. 1 it can be seen that the organic component in aerosol composition has maximal concentration during spring and a little smaller concentration during summer. The smallest content of organic substance is observed during fall. Also, concentrations are most dispersed during spring period.

A similar annual behavior in the near-ground air layer is also recorded in other regions [21–23], primarily

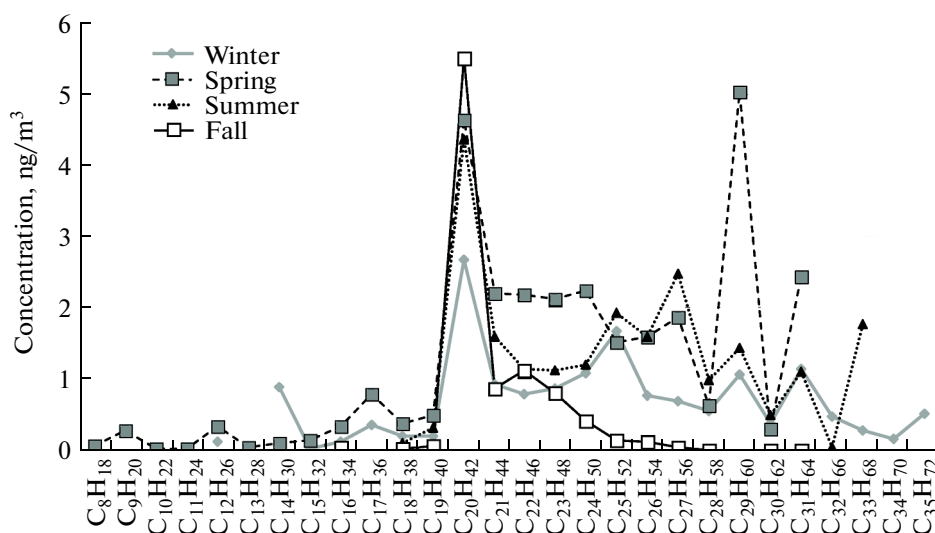


Fig. 2. Seasonal variations in the composition of organic compounds in aerosol in the free atmosphere.

because of the seasonality of the supply of organic precursor gases by plants for aerosol particle formation.

The organic component in particle composition has a much smaller concentration in the free atmosphere than in the near-ground air layer [24, 25]. On one hand, this confirms the result of work [16, 17], indicating that concentration decreases with altitude; on the other hand, this suggests that the source of the organic component of aerosol is located on the underlying surface.

The composition of aerosol-contained organic compounds is shown in Fig. 2, from which it can be seen that aerosol particles show marked seasonal differences in composition, with compounds ranging from C_8H_{18} to $C_{35}H_{72}$. Hydrocarbons show the widest range in composition during the winter season ($C_{12}H_{26}$ – $C_{35}H_{72}$) and during spring (C_8H_{18} – $C_{31}H_{64}$), and this range is markedly narrower during summer ($C_{18}H_{38}$ – $C_{33}H_{68}$) and fall ($C_{16}H_{34}$ – $C_{31}H_{64}$).

A single mode (*n*-alkane with composition $C_{20}H_{42}$) predominates throughout the year. A secondary maximum, corresponding to *n*-alkane with composition $C_{29}H_{60}$, appears during summer, probably due to forest fires [20].

Data, similar in species composition, were presented in a number of works, in which the organic aerosol component was studied [26–29]. They differed from our data by species concentrations, which are an order of magnitude smaller in the free atmosphere.

CONCLUSIONS

The identified part of the organic aerosol has a marked annual behavior, with a maximum in the spring period and a minimum during fall.

Hydrocarbons, ranging from C_8H_{18} to $C_{35}H_{72}$, are observed in the particle composition of the organic aerosol component in the free atmosphere. It is noteworthy that the composition markedly varies with season. Hydrocarbon composition varies in the widest range during the winter period and during spring, and in a markedly narrower range during summer and fall.

A single mode (*n*-alkane with composition $C_{20}H_{42}$) predominates throughout the year. The summer period is characterized by the appearance of a secondary maximum, corresponding to *n*-alkane with composition $C_{29}H_{60}$ and, possibly, caused by forest fires.

ACKNOWLEDGMENTS

This work was supported by Siberian Branch of the Russian Academy of Sciences (Interdisciplinary Project no. 35); Russian Foundation for Basic Research (grant nos. 14-05-00526 and 14-05-00590); Ministry of Education and Science (State Contract nos. 14.604.21.0100 (identification

no. RFMTFIBBB210290) and 14.613.21.0013 (identification no. RFMEFI61314X0013)), and Global Environmental Research Fund for National Institutes of the Ministry of Environment, Japan.

REFERENCES

1. *Climate Change 2013: The Physical Science Basis* (IPCC, 2013).
2. V. A. Isidorov, *Organic Chemistry of the Atmosphere* (Khimiya, St. Petersburg, 2001) [in Russian].
3. K. Ravindra, R. Sokhi, and R. Van Grieken, "Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation," *Atmos. Environ.* **42** (13), 2895–2921 (2008).
4. D. Fowler, K. Pilegaard, M. A. Sutton, P. Ambus, M. Raivonen, J. Duyzer, D. Simpson, H. Fagerli, S. Fuzzi, J. K. Schjoerring, M. Maione, P. S. Monks, J. Burkhardt, U. Daemmgen, J. Neirynek, E. Personne, R. Wichink-Kruit, K. Butterbach-Bahl, C. Flechard, J. P. Tuovinen, M. Coyle, G. Gerosa, B. Loubet, N. Altimir, L. Gruenhage, C. Ammann, S. Cieslik, E. Paoletti, T. N. Mikkelsen, H. Ro-Poulsen, P. Cellier, J. N. Cape, L. Horva, F. Loreto, U. Niinemets, P. I. Palmer, J. Rinne, P. Misztal, E. Nemitz, D. Nilsson, S. Pryor, M. W. Gallagher, T. Vesala, U. Skiba, N. Brüggemann, S. Zechmeister-Boltenstern, J. Williams, C. O'Dowd, M. C. Facchini, G. de Leeuw, A. Flossman, N. Chaumerliac, and J. W. Erisman, "Atmospheric composition change: Ecosystems–atmosphere interactions," *Atmos. Environ.* **43** (33), 5193–5267 (2009).
5. K. Ya. Kondrat'ev, "Aerosol as a climate-forming component of the atmosphere. 2. Direct and indirect impact on climate," *Atmos. Ocean. Opt.* **15** (4), 267–284 (2002).
6. X. Ge, A. S. Wexler, and S. L. Clegg, "Atmospheric amines—Part 1. A review," *Atmos. Environ.* **45** (3), 524–545 (2011).
7. P. Fu, K. Kawamura, and K. Miura, "Molecular characterization of marine organic aerosols collected during a round-the-world cruise," *J. Geophys. Res.* **116**, D13302 (2011).
8. G. Wang, K. Kawamura, M. Xie, S. Hu, J. Li, B. Zhou, J. Cao, and Z. An, "Selected water-soluble organic compounds found in size-resolved aerosols collected from urban, mountain and marine atmospheres over East Asia," *Tellus Ser. B* **63B** (3), 371–381 (2011).
9. G. J. Doyle, "Self-nucleation in the sulfuric acid–water system," *J. Chem. Phys.*, No. 35, 795–799 (1961).
10. M. Kulmala, H. Vehkamäki, T. Petaja, M. Dal Maso, A. Lauri, V. M. Kerminen, W. Birmili, P. H. McMurry, "Formation and growth rates of ultrafine atmospheric particles: A review of observations," *J. Aerosol Sci.* **35** (2), 143–176 (2004).
11. Liu Fang, J. M. Beames, A. S. Petit, A. B. McCoy, and M. I. Lester, "Infrared-driven unimolecular reaction of CH_3CHO Criegee intermediates to OH radical products," *Science* **345** (6204), 1596–1598 (2014).
12. M. Sipila, T. Jokinen, T. Berndt, S. Richters, R. Makkonen, N. M. Donahue, R. L. Mauldin, T. Kurten, P. Paasonen, N. Sarnela, M. Ehn, H. Jun-

- ninen, M. P. Rissanen, J. Thornton, F. Stratmann, H. Herrmann, D. R. Worsnop, M. Kulmala, V.-M. Kerminen, and T. Petaja, "Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO₂ and organic acids," *Atmos. Chem. Phys.* **14** (22), 12143–12153 (2014).
13. M. Crippa, F. Canonaco, V. A. Lanz, M. Aijala, J. D. Allan, S. Carbone, G. Capes, D. Ceburnis, M. Dall'Osto, D. A. Day, P. F. DeCarlo, M. Ehn, A. Eriksson, E. Freney, Ruiz L. Hildebrandt, R. Hillamo, J. L. Jimenez, H. Junninen, A. Kiendler-Scharr, A.-M. Kortelainen, M. Kulmala, A. Laaksonen, A. A. Mensah, C. Mohr, E. Nemitz, C. O'Dowd, J. Ovadnevaite, S. N. Pandis, T. Petaja, L. Poulain, S. Saarikoski, K. Sellegri, E. Swietlicki, P. Tiitta, D. R. Worsnop, U. Baltensperger, and A. S. H. Prevot, "Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach," *Atmos. Chem. Phys.* **14** (12), 6159–6176 (2014).
 14. T. Novakov, D. A. Hegg, and P. V. Hobbs, "Airborne measurement of carbonaceous aerosols on the East Coast of the United States," *J. Geophys. Res. D* **102** (25), 30023–30030 (1997).
 15. A. Asa-Awuku, R. H. Moore, A. Nenes, R. Bahreini, R. J. S. Holloway, C. A. Brock, A. M. Middlebrook, T. B. Ryerson, J. L. Jimenez, P. F. DeCarlo, A. Hecobian, and R. J. Weber, "Airborne cloud condensation nuclei measurements during the 2006 Texas air quality study," *J. Geophys. Res.* **116**, D11201 (2011).
 16. J. D. Allan, W. T. Morgan, E. Darbyshire, M. J. Flynn, P. I. Williams, D. E. Oram, P. Artaxo, J. Brito, J. D. Lee, and H. Coe, "Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA," *Atmos. Chem. Phys.* **14** (20), 11393–11407 (2014).
 17. B. T. Jones, J. B. A. Muller, S. J. O'Shea, A. Bacak, M. Le Breton, T. J. Bannan, K. E. Leather, A. M. Booth, S. Illingworth, K. Bower, M. W. Gallagher, G. Allen, D. E. Shallcross, S. J.-B. Bauguitte, J. A. Pyle, and C. J. Percival, "Airborne measurements of HC(O)OH in the European Arctic: A winter–summer comparison," *Atmos. Environ.* **99**, 556–567 (2014).
 18. G. G. Anokhin, P. N. Antokhin, M. Yu. Arshinov, V. E. Barsuk, B. D. Belan, S. B. Belan, D. K. Davydov, G. A. Ivlev, A. V. Kozlov, V. S. Kozlov, M. V. Morozov, M. V. Panchenko, I. E. Penner, D. A. Pestunov, G. P. Sikov, D. V. Simonenkov, D. S. Sinitsyn, G. N. Tolmachev, D. V. Filippov, A. V. Fofonov, D. G. Chernov, V. S. Shamanaev, and V. P. Shmarunov, "OPTIK Tu-134 aircraft laboratory," *Opt. Atmos. Okeana* **24** (9), 805–816 (2011).
 19. N. G. Voronetskaya, G. S. Pevneva, A. K. Golovko, A. S. Kozlov, M. Yu. Arshinov, B. D. Belan, D. V. Simonenkov, and G. N. Tolmachev, "Hydrocarbon composition of tropospheric aerosol in the south of Western Siberia," *Atmos. Ocean. Opt.* **27** (6), 547–557 (2014).
 20. N. G. Voronetskaya, G. S. Pevneva, A. K. Golovko, A. S. Kozlov, M. Yu. Arshinov, B. D. Belan, D. V. Simonenkov, and G. N. Tolmachev, "Spatial variability of aerosol organic component in the ground layer and in the free atmosphere," *Opt. Atmos. Okeana* **28** (9), 825–829 (2015).
 21. Jiyeon Park, Seungyong Lee, Minsoo Kang, Hee-Joo Cho, Kwangyul Lee, and Kihong Park, "Seasonal characteristics of submicrometer organic aerosols in urban Gwangju, Korea using an aerosol mass spectrometer," *Atmos. Environ.* **80**, 445–454 (2013).
 22. M. Vestenius, H. Hellen, J. Levula, P. Kuronen, K. J. Helminen, T. Nieminen, M. Kulmala, and H. Hakola, "Acidic reaction products of monoterpenes and sesquiterpenes in atmospheric fine particles in a boreal forest," *Atmos. Chem. Phys.* **14** (15), 7883–7893 (2014).
 23. T. Nieminen, A. Asmi, M. Dal Maso, P. P. Aalto, P. Keronen, T. Petaja, M. Kulmala, and V.-M. Kerminen, "Trends in atmospheric new-particle formation: 16 years of observations in a boreal-forest environment," *Boreal Environ. Res.* **19**, Suppl. B, 191–214 (2014).
 24. V. P. Shevchenko, D. P. Starodymova, A. A. Vinogradova, A. P. Lisitsyn, V. I. Makarov, S. A. Popova, V. V. Sivonen, and V. P. Sivonen, "Elemental and organic carbon in atmospheric aerosols over the northwestern coast of Kandalaksha Bay of the White Sea," *Dokl. Earth Sci.* **461** (1), 242–246 (2015).
 25. H. Timonen, D. A. Jaffe, N. Wigder, J. Hee, H. Gao, L. Pitzman, and R. A. Cary, "Sources of carbonaceous aerosol in the free troposphere," *Atmos. Environ.* **92**, 146–153 (2014).
 26. C. L. Blanchard, J. C. Chow, E. S. Edgerton, J. G. Watson, G. M. Hidy, and S. Shaw, "Organic aerosols in the southeastern United States: Speciated particulate carbon measurements from the SEARCH network, 2006–2010," *Atmos. Environ.* **95**, 327–333 (2014).
 27. I. Kourtchev, S. J. Fuller, C. Giorio, R. M. Healy, E. Wilson, I. O' Connor, J. C. Wenger, M. McLeod, J. Aalto, T. M. Ruuskanen, W. Maenhaut, R. Jones, D. S. Venables, J. R. Sodeau, M. Kulmala, and M. Kalberer, "Molecular composition of biogenic secondary organic aerosols using ultrahigh-resolution mass spectrometry: Comparing laboratory and field studies," *Atmos. Chem. Phys.* **14** (4), 2155–2167 (2014).
 28. J. E. Williams, G. Le Bras, A. Kukui, H. Ziereis, and C. A. M. Brenninkmeijer, "The impact of the chemical production of methyl nitrate from the NO + CH₃O₂ reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric ozone: A global modelling study," *Atmos. Chem. Phys.* **14** (5), 2363–2382 (2014).
 29. M. Shiraiwa, T. Berkemeier, K. A. Schilling-Fahnestock, J. H. Seinfeld, and U. Poschl, "Molecular corridors and kinetic regimes in the multiphase chemical evolution of secondary organic aerosol," *Atmos. Chem. Phys.* **14** (16), 8323–8341 (2014).

Translated by O. Bazhenov