UDC 504.3.054 + 543.544.054.9

DOI: 10.15372/KhUR20160405

Long-Term Trends in Black (Elemental) Carbon Concentrations in the Ambient Air of West Siberia and the White Sea Region

V. I. MAKAROV[1], S. A. POPOVA[1] and V. P. SHEVCHENKO[2]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

[2]*Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia*

Abstract

The work presents concentrations of elemental carbon (EC) in atmospheric aerosol samples, collected on fibreglass aerosol filters in the Novosibirsk region, in the northwest of the Siberian region, and in the White Sea Region from 1999 to 2015 and measured by the method of reaction gas chromatography. The year-to-year progress, seasonal and daily variations of EC concentration at observation sites, as well as the influence of distant wood fires on the content of EC in the sites with different degrees of anthropogenic stress. The HYSPLIT model is used to estimate the sources of the formation of EC-containing aerosols.

Key words: elemental carbon in the ambient air, long-term trends, thermal method, wood burning, West Siberia, the White Sea, HYSPLIT

INTRODUCTION

Black carbon (BC), often called elemental carbon (EC) or soot, is the by-product of the incomplete combustion of various fuels (in particular, coal and diesel fuel), and of biomass (forests, grass, agricultural wastes) [1]. The BC particles are in the submicron mode but grow in sizes upon propagation in the atmosphere. The mean lifetime of BC particles is about six days. Thus, these may be transported over hundreds and thousands of km from their source. While most of the suspended particles in the atmosphere reflect the solar radiation, BC strongly absorbs light in the visible and UV regions. It is thus assumed that BC is the second important component (after greenhouse gases, GHG) which affects the global warming [1]. In addition, carbon-containing particles may have a negative effect on human health [2].

The Siberian region is of particular interest, because (i) it directly neighbours the Arctic Seas, and (ii) includes the large clusters of oil and gas producing, mining, industrial, and agricultural enterprises, that contribute considerably to the technogenic pollution of the atmosphere and of other biospheres. On the other hand, as the Siberian region is very large (including Yakutia and Transbaikalia); there are vast territories here with minimal background pollution. Therefore, Siberia is a convenient "polygon" for investigations.

The Russian boreal (northern) forests are estimated to cover 700 million ha. The largest part consists of coniferous forests of Siberia. Satellite observations indicate that annually, in the world, fires occur over the area of more than a hundred million ha, including 10–14 million ha in the boreal and forest-steppe zones of Siberia. The burning forest combustibles evolve both gas combustion products and aerosol smoke particles. The mass fraction of gas and aerosol emission varies from 1 to 7 % of the amount of burnt biomass, depending on burning conditions. However, their role in atmospheric chemistry and heat-exchange is often dominating.

Some works report on the track above the territory of Siberia, along which atmospheric

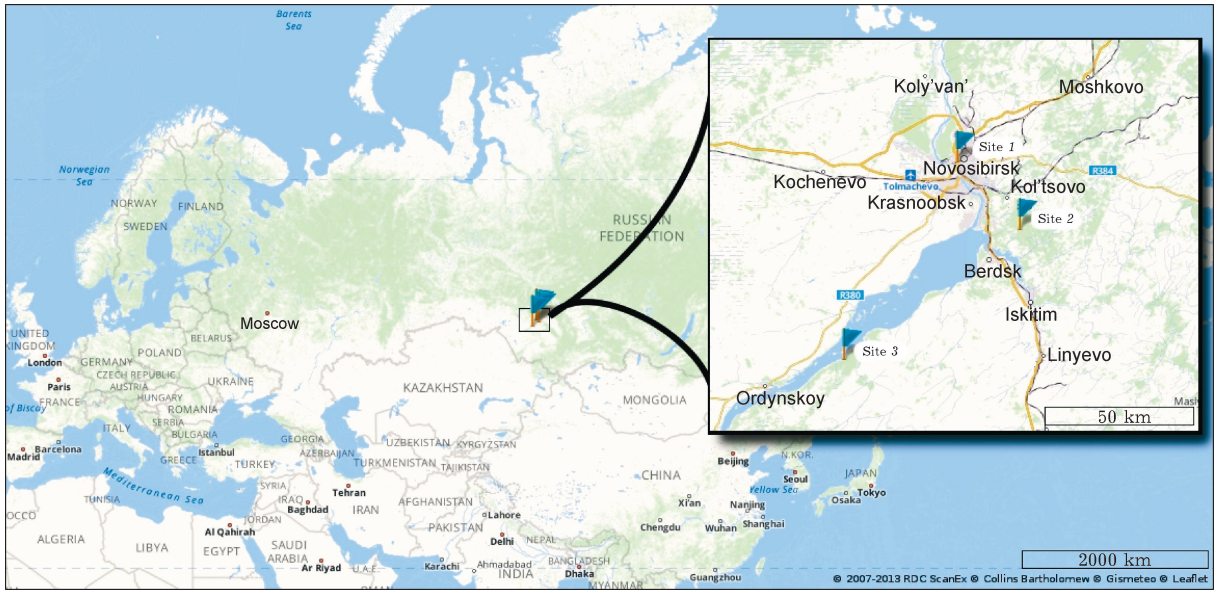

Fig. 1. Sampling sites.

aerosols are transported to the Arctic region [4]. Precipitation of BC on snow and ice may change surface albedo, contributing to the processes of warming and snowmelt. Considering the importance of Siberia as the source of materials for a distant transfer to the Arctic, from the beginning of the 90-th the project "Aerosols of Siberia" was initiated parallel to the International project "Arctic haze" [5]. One of the goals of this project was to extract quantitative data on the sources, the power, chemical, and disperse composition of gas-aerosol emission in the atmosphere of West Siberia. Since 1999, in the framework of this project, the mass concentration and the chemical and disperse composition of atmospheric aerosols were measured regularly at the sampling sites, characterized by the different degree of anthropogenic stress.

Thus, a wealth of experimental material was accumulated on the chemical composition of aerosols, in particular, on the content of elemental carbon which makes it possible to study the annual, seasonal, and daily distribution of EC.

EXPERIMENTAL

Sampling sites

The first point (1) is situated in Novosibirsk (55°N, 82°E) and characterizes urban zone. The main local source of EC here is motor transport and heat power stations. The second selection point (2) is located in the village of Klyuchi (54°N, 83°E), 30 km to the southeast of the city. This sampling site belongs to the rural area. Aerosol is assumed to form here due to natural processes with a small addition of contaminants of anthropogenic origin. Site (3) Sinemor'ye is situated in the forest zone, 15 km from the nearest village Zav'yalovo (54°N, 82°E) and 90 km from Novosibirsk. There are no local sources of anthropogenic pollution of atmosphere. Therefore, this site is called the background one (Fig. 1). In the northwest of Siberia the sampling was performed in communities Tarko-Sale (65°N, 78°E) (1999–2005), Krasnoselkup (65°N, 83°E) (2000–2003), and Samburg (67°N, 78°E) (1999–2003).

Thus, the seasonal sampling of aerosols allows determining their chemical composition, the mechanism of formation, sources and sink. A synchronous sampling at various sites makes it possible to determine and to compare the level of EC emission in the regions with the different degree of anthropogenic stress.

The work presents the results of the long-term studies performed since 2010 near the Pertsov Belomorsk Biological Station (Lomonosov Moscow State University) situated on the Kindo Peninsula on the northwest coast of the

Kandalaksha Bay (66.55°NL, 33.1°EL) in the framework of the project "The White Sea system" (leader – academician A. P. Lisitzyn). The sampling region can be considered as the background one, since the distance to the small railway station Poyakonda along the track Moscow–Murmansk is 15 km, and to the nearest town of Kandalaksha – 75 km.

Sampling collection and analysis

The sampling of atmospheric aerosols of West Siberia is performed annually in winter (January 20–February19), spring (April 20–May 19), summer (June 20–July 19), and autumn (September 20–October 19). To determine EC, the sampling is carried out on fibreglass filters (Whatman) 47 mm in diameter with a rate of 30 L/min for 24 h. At the Belomorsk Biological Station, the atmospheric aerosols were collected using an air sampler UAS-310, which pumps air through the fibreglass filters "Pall" A/E. The sizes of filter, on which the particles smaller than 2.5 μm ($PM_{2.5}$) precipitate, is 225×172 mm, and the rate of air pumping is 270 L/min. The collection of one sample takes about one week. After sampling, the filters are kept in sterile packets in a fridge.

The method of reaction chromatography was used to measure the average daily concentrations of organic (OC) and elemental (EC) carbon. The method makes it possible to determine the content of the organic and elemental carbon particles by their high-temperature separation in the inert atmosphere. Each component was oxidized to CO_2, converted into в CH_4, and recorded with a flame-ionization detector. Thus, when the sample (700 °C) is heated in the inert atmosphere, organic mixtures evaporate and are defined as organic carbon, and the elemental one is determined upon combustion in the oxidative atmosphere [6].

Air trajectory data

The HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) was used to reveal a possible source of pollution on a regional and global scale. The air trajectories were calculated using the archival meteorological data (the GDAS archive) of the National Oceanic and Atmospheric Administration of the USA. The archive includes the basic meteoparameters at 14 levels from the ground surface up to 20 mbar, which allows one to construct trajectories with regard to vertical shifts. For a detailed description of the model and of the algorithm for calculating air trajectories see [7].

RESULTS AND DISCUSSION

Figure 2 shows averaged seasonal concentrations of EC and the annual trend (since 1999 – more than 15 observations) at three sampling points. Since in the village of Zavr'yalovo the sampling was performed only in summer, the figure demonstrates the annual trend by

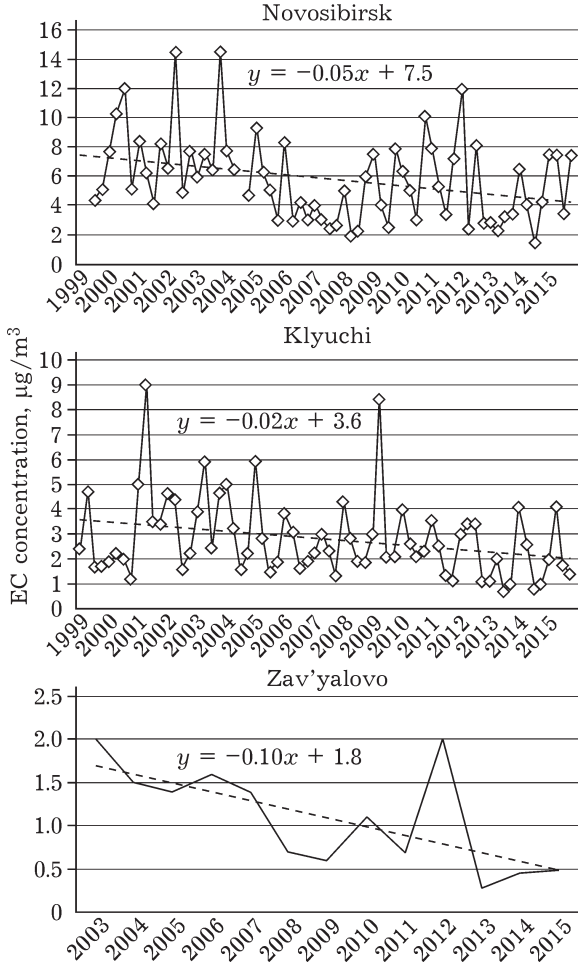

Fig. 2. Long-term trends in EC concentrations for the sampling sites.

TABLE 1

Seasonal concentrations of EC in 1999–2015 (mean±SD, μg/m^3)

Periods	Zavryalovo	Klyuchi	Novosibirsk
January–February	–	3.5±1.3	7.1±2.1
March–April	–	3.9±2.1	5.6±3.3
June–July	1.1±0.6	1.9±0.74	4.4±2.6
September–October	–	1.9±0.94	6.0±3.1

TABLE 2

Average concentrations of EC at various sites, μg/m^3

Sites	Concentration
Novosibirsk	5.8±2.9
Klyuchi	2.8±1.6
Zavryalovo	1.1±0.6
Tarko-Sale	1.8±0.6
Krasnoselkup	1.4±0.7
Samburg	1.1±0.5

summer measurements. During the entire observation period the average EC concentrations measured at sampling sites 1, 2 and 3 amount to (5.8±2.9), (2.8±1.6) and (1.1±0.6) μg/m^3, respectively. The linear regression line indicates that the decrease in EC concentration occurred during the entire period of measurements which is particularly evident for the background region (see Fig. 2).

The seasonal variations in EC concentration are not very strong and are presented in Table 1. In winter, the maximal EC concentrations depend on both heat power station (HPS) operation and motor transport. The minimal values are recorded in summer and obviously due to the absence of specific, local sources of EC over the territory of the Novosibirsk Region.

Thus, the temporal variations of EC may be used to estimate the background concentrations as well as sources and sinks in the regions with the different degree of anthropogenic stress (Table 2).

In July of 2012, the observation sites of the Novosibirsk Region were covered with flumes of aerosols due to wild fires. The fireplaces of boreal forests were located in the Tomsk Region and in the Krasnoyarsk Territory. The highest burning power was observed in the first part of July (July 5–7, 2012) [8].

The HYSPLIT model was used to calculate the back air trajectories that confirmed the origin of a smoke plume above the city and its region [9]. When measuring the aerosol characteristics of this period, we have recorded a substantial increase in total suspended particulate (TSP), submicron fraction (PM_1) and organic matter (OM). The EC concentrations were either average or varied negligibly (Fig. 3). This observation testifies to a local EC source in atmospheric smoke in the Novosibirsk Region. The EC variability was also confirmed by the calculations of the factor analysis (the method of principal components). As follows from Table 3, in the village of Klyuchi (rural zone) and at background site 3, there is a high correlation of TSP, PM1, organic carbon (OC) and secondary organic carbon (SOC). These components compose one factor which testifies to their common source. In the town, the effect of distant fires is graded by local sources [9].

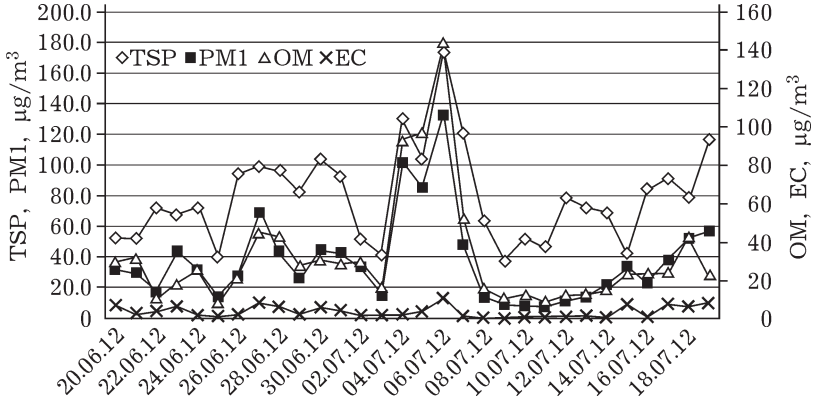

Fig. 3. Temporal variations in TSP, PM_1, OM, EC at site Klyuchi over June–July, 2012.

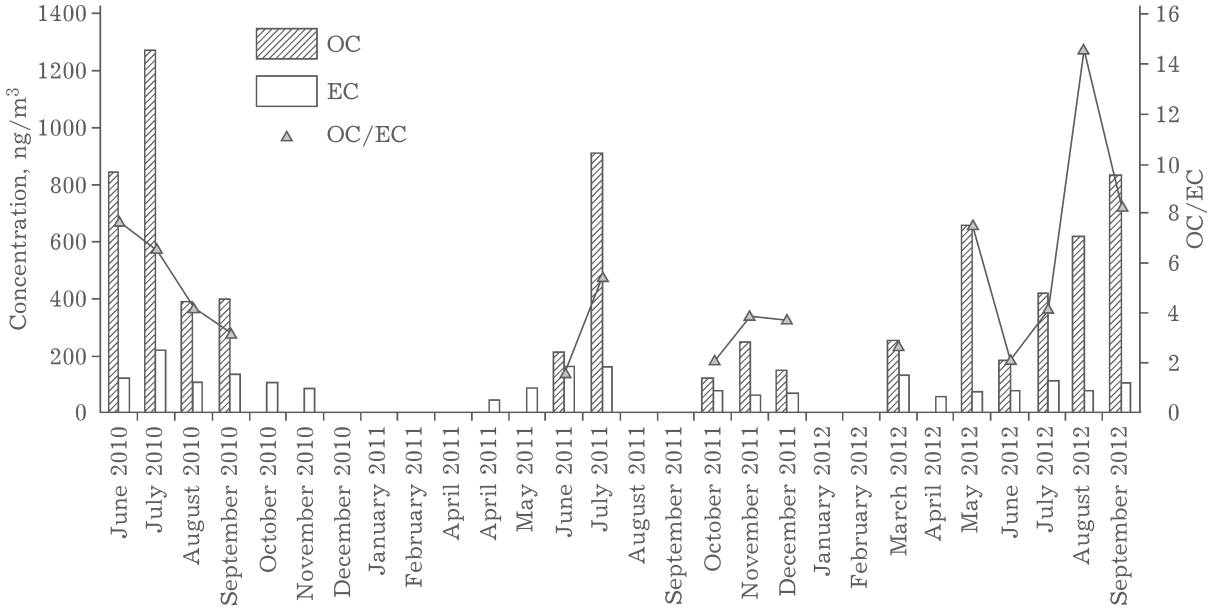

Fig. 4. Distribution of monthly average concentrations of EC and OC (ng/m^3) and of OC/EC ratios.

It is worth noting that in summer of 2012, there was actually no effect of distant fires on EC concentration at observation sites. This is verified by the results of work [10], which show that at large distances from the source (on order of several hundred km) the atmosphere is cleaned from elemental carbon due to the precipitation on soil and plants.

TABLE 3

Varimax rotated factor loading matrix for the aerosol characteristics over the BB period in summer 2012 for sites ***1–3*** with loadings >0.7 in bold typeface

Characteristics	Site								
Components	***1***			***2***			***3***		
	1	2	3	1	2	3	1	2	3
TSP	**0.799**	0.420	0.297	**0.772**	0.178	0.298	**0.794**	0.559	0.034
PM_1	0.018	**0.918**	−0.155	**0.879**	−0.150	0.048	–	–	–
OC	0.085	**0.922**	−0.122	**0.923**	−0.140	0.099	**0.949**	0.076	0.028
SOC	−0.041	**0.864**	−0.132	**0.923**	−0.136	0.144	**0.905**	−0.045	0.025
EC	0.322	**0.769**	0.054	0.316	−0.050	−0.117	0.528	0.442	0.021
WSIs	**0.809**	−0.283	0.432	0.110	**0.797**	0.506	0.313	**0.768**	0.520
$Ca^{2+} + Mg^{2+}$	**0.829**	−0.269	0.393	0.167	**0.847**	0.421	0.187	**0.861**	0.297
NH_4^+	**0.788**	0.188	0.027	0.164	0.024	**0.914**	−0.053	−0.145	**0.963**
Na^+	−0.066	−0.258	**0.745**	0.090	0.122	0.391	0.330	0.392	0.506
K^+	0.866	0.195	0.079	0.695	−0.160	0.322	**0.865**	0.300	0.137
HCO_3^-	0.534	−0.488	0.527	−0.297	**0.878**	−0.317	0.080	**0.913**	−0.290
$F^- + HCOO^-$	0.284	**0.786**	0.468	**0.710**	−0.342	0.348	**0.800**	0.415	0.013
Cl^-	0.329	0.151	**0.838**	**0.706**	0.031	0.337	**0.843**	−0.186	0.123
NO_3^-	**0.871**	−0.007	−0.109	0.635	−0.022	0.396	**0.792**	0.090	0.094
SO_4^{2-}	**0.870**	0.199	0.097	0.255	0.023	**0.930**	0.048	0.021	**0.962**
pH	0.094	−0.584	0.290	−0.368	**0.842**	−0.219	−0.211	**0.774**	−0.501
Variance (%)	34.2	29.5	14.2	35.5	20.3	20.2	37.7	25.1	19.0

To reveal the ingress of aerosol substances in the White Sea region, the HYSPLIT program was used to calculate the back trajectories of air masses entering the BBS of MSU at 20 m level with a 12 h step. The three-day trajectories were calculated for summer months, and the five-day ones – for the others. The results obtained indicate that in the surface aerosols of the coast of the Kandalaksha Bay of the White Sea, the OC concentration is characterized by a strong seasonal and annual variability. It is shown that in summer, the local and distant wild fires are another source of OC. In summer of 2010 the OC concentration in air was anomalously high, probably, due to the condensation of gaseous OC, resulting from the vital function of trees at the beginning of summer and from wild fires in the middle of summer. In autumn, winter and spring, OC comes from the industrial regions of the Kola Peninsula [11].

The EC concentration in this region is at the background (for the Arctic) level and is characterized by negligible seasonal and annual variations. A substantial source of EC is the western transfer from the industrial regions of northern Europe, including the gas jets of the oil deposits of the North Sea. In summer, wild fires are the additional source of EC (see Fig. 4).

CONCLUSION

1. The results of more than the 10-year EC measurements performed in the atmosphere of Novosibirsk and its suburbs and upon expeditions in the area of the White Sea show that the content of EC in the total particulate matter is 5–15 %.

2. The annual pathway of EC concentrations is demonstrated. The EC distribution was not uniform. For instance, the high content of EC was observed in 2000–2003 and in 2009–2010 despite the absence of continuous and stable increase in EC concentration.

3. The average levels of EC concentration were established for the zones of anthropogenic stress and moderate effect, and for the "background" territories (Novosibirsk – 6 $\mu g/m^3$; Kluchi – 3 $\mu g/m^3$; Tarko-sale – 1.8 $\mu g/m^3$; Krasnoselkup – 1.4 $\mu g/m^3$; Sumburg – 0.76 $\mu g/m^3$).

4. The seasonal variability of EC with the maximal values in winter and the minimal ones in summer is shown.

5. Note that in summer of 2012, there was actually no effect of distant fires on the concentration of elemental carbon at observation sites. This is confirmed by the results of work [10], which indicate that at large distances from the source (on order of several hundred km) the atmosphere is cleaned from elemental carbon due to precipitation on soil and plants.

Actually, the work presents the profiles of EC concentration levels in the regions with the different degree of anthropogenic stress that may be used in mathematical models for calculating BC effect on the climate of the Earth.

REFERENCES

1 Quinn P. K., Stohl A., Arneth A., Berntsen T., Burkhart J. F., Christensen J., Flanner M., Kupiainen K., Lihavainen H., Shepherd M., Shevchenko V., Skov H., Vestreng V., The Impact of Black Carbon on Arctic Climate, Oslo, 2011, p. 72.

2 Ahmed T., Dutkiewicz V. A., Khan A. J., Husain L., *Atmos. Res.*, 137 (2014) 49.

3 Rom W. N., Samet J. M., *Am. J. Respir. Crit. Care Med.*, 173 (2006) 365.

4 Shevchenko V. P., Lisitzin A. P., Vinogradova A. A., Smirnov V. V., Serova V. V., and R. Stein, *Optika Atmos. i Okeana*, 13 (2000) 510.

5 Koutsenogii K. P. (Ed.), Aerosols of Siberia (SB RAS Integration Projects), issue 9, Novosibirsk, 2006.

6 Makarov V. I., Koutsenogii K. P., Koutsenogii P. K., *J. Aerosol Sci.*, 30 (1999) 659.

7 Draxler R. R., Rolph G. D., 2003. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access *via* NOAA ARL READY. NOAA Air Resources Laboratory, Silver Springs, MD.
URL: http://www.arl.noaa.gov.hysplit4.html

8 Smolyakov B. S., Makarov V. I., Shinkorenko M. P., Popova S. A., Bizin M.A., *Environ. Pollution*, 188 (2014) 8.

9 Bizin M. A., Popova S. A., Chankina O. V., Makarov V. I., Shinkorenko M. P., Smolyakov B. S., Koutsenogii K. P., *Optika Atmos. i Okeana*, 26 (2013) 484.

10 Bond T. C., Doherty S. J., Fahey D. W., Forster P. M., Berntsen T., DeAngelo B. ., Flanner M. G., Ghan S., Koch D., Kinne S., Kondo Y., Quinn P. K., Sarofim M. C., Schultz M. G., Schulz M., Venkataraman C., Zhang H., Zhang S., Bellouin N., Guttikunda S. K., Hopke P. K., Jacobson M. Z., Kaiser J. W., Klimont Z., Lohmann U., Schwarz J. P., Shindell D., Storelvmo T., Warren S.G. and Zender C. S. , *J. Geophys. Res.: Atmos.*, 118 (2013) 5380.

11 Shevchenko V. P., Starodymova D. P., Vinogradova A. A., Lisitzin A. P., Makarov V.I. , Popova S. A., Sivonen V. V., and Sivonen V. P., *Doklady Akademii Nauk*, 461 (2015) 242.

УДК 504.3.054 + 543.544.054.9

DOI: 10.15372/KhUR20160405

Многолетние измерения концентраций черного (элементного) углерода в атмосфере Западной Сибири и района Белого моря

В. И. МАКАРОВ[1], С. А. ПОПОВА[1], В. П. ШЕВЧЕНКО[2]

[1]Институт химической кинетики и горения им. В. В. Воеводского Сибирского отделения РАН, Новосибирск, Россия

[2]Институт океанологии им. П. П. Ширшова РАН, Москва, Россия

Аннотация

Приведены данные о концентрации элементного углерода (ЕС) в пробах атмосферного аэрозоля, отобранных на стекловолокнистые аэрозольные фильтры в Новосибирской области, на северо-западе сибирского региона и в районе Белого моря в период с 1999 по 2015 годы. Данные получены методом реакционной газовой хроматографии. Рассмотрены межгодовой ход, сезонные и суточные вариации концентраций ЕС в точках наблюдения, а также влияние удаленных лесных пожаров на содержание ЕС на участках с разной степенью антропогенной нагрузки. С использованием модели HYSPLIT оцениваются источники образования аэрозолей, содержащих ЕС.

Ключевые слова: углеродсодержащие аэрозоли, черный (элементный) углерод, долгосрочные тренды, горение биомассы