Chemical composition and disperse characteristics of aerosol smoke emission from fires in boreal Siberian forests

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Field experiments with forest fires have shown that the amount of aerosol matter, emitted into the atmosphere during fires is 0.2–1 t/ha. This represents 1–7% of the total biomass (15–25 t/ha) burned out during a typical forest fire in Siberia. It has been found that 3–10 million tones of aerosol materials are emitted into the atmosphere from forest fires. The analysis of chemical composition of the sampled smoke matter has indicated that 3–15% of their masses are of mineral (soil) origin (Na, Si, Ca, K, Fe, Zn, etc.). The carbonic aerosols appeared due to incomplete burning out of the biomass range from 60–90% of the total emitted aerosol. The fraction of aerosols-containing elemental carbon (graphite, soot, black carbon) is 7–15%. More than 80% of smoke emission consists of aerosol particles with sizes less than 3 μm.

Introduction

Spontaneous biomass burning ("wild" fires) is a natural phenomenon; at which 3–5 billions tones of biomass have burned annually. This is comparable with the amount of organic fuel (oil, coal) utilized by the mankind. Though the problem of biomass burning and accompanying environmental, chemical, optical, and climatic aspects are connected with all Earth regions, fires in boreal (north) Siberian forests were the object of our studies. Russian boreal forests occupy 700 million ha, most of them are almost completely coniferous forests of Siberia.

The statistics underestimates the scales of forest fires in Russia; nevertheless, satellite data show[1,2] that yearly fires occur at an area of 10–14 million ha in forest and forest-steppe zones of Siberia (this phenomenon is the third at the scale of natural fires after seasonal fires in African savannas and (sub)tropical forests). Both gaseous products of combustion and aerosol smoke particles are evolved when combustible materials (wood, shrubs, grass, moss, lichen, etc.) are burning.

The mass fraction of aerosol emission varies from 1–2 to 5–7% of the amount of the burned biomass depending on burning conditions (proper and reference data), but it often dominates in atmospheric heat exchange. This is due to the presence of fine particles, consisting of elemental carbon (soot, graphite), in the smoke emission. Such particles, residing in the atmosphere for a long time, absorb and scatter solar radiation, i.e., influence the heat exchange between the atmosphere, surface, and solar radiation and, hence, the local weather and global climate.

Therefore, it is necessary to note that the potential climate effect of aerosol emission (fall of temperature) is compensative with respect to the effect of gaseous products of burning (carbon dioxide and oxide, methane), hypothetically leading to the global warming. Therefore, quantitative data on the intensity, chemical and disperse composition of smoke emission from large-scale forest fires are necessary for development and verification of computer models, forecasting the global or regional weather-climatic trends. They are important in the study of optical and chemical properties of the atmosphere, as well as in estimation of the respiratory quality of the surface air.

In this work, we present experimental results obtained in 2000–2007 within integrated researches of fires in taiga coniferous forests at the Krasnoyarsk Territory, carried out jointly by Russian (Institute of Forest SB RAS, Institute of Chemical Kinetics and Combustion SB RAS), American (USDA Forest Service), and Canadian (Canadian Forest Service) researchers. The investigations in 2000–2003 were conducted mainly in coniferous forests; their results were partly published.[3–5] Fire experiments in 2006–2007 were carried out in larch forests with a large part of other woody species. Different types of forests concern with different types of soil and landscape features, they are characterized by different types of ground flora, shrubby, woody, and other types of forest combustible materials. Hence, representative and comparable experimental data are required about the fire behavior in different types of forests, the intensity of gas-aerosol smoke emission in different conditions, chemical composition and disperse characteristics of smokes.

Organization of natural-model forest fires and the aerosol sampling technique

The experiments were carried out in the form of natural and modeled fires at four taiga areas in the region of middle Yenisei and Angara (Yartsevo,

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2000–2002; Govorkovo, 2002; Khrebtovyi, 2003, Nevonka, 2006–2007). A forest site of 200 × 200 m = = 4 ha (sometimes 100 × 100 m = 1 ha) was prepared for each fire experiment with guard bands around (cuttings and/or mineralized (soil) bands) to prevent fire propagation out of the site. Preliminary, the quantity and distribution of forest combustible materials at different levels (ground cover, moss, lichen, grass, shrubs, sprouting, mature trees, and so on) were bio-ecologically and pyrologically estimated and documented.

Similar estimates were made after fire experiments, which allowed quantitative and qualitative accounting for fire effect on the forest ecosystem, in particular, determination of the amount of consumed biomass per unit of area. A "grid" of accountable points was formed on the fire area (49 points with 25 × 25 m spacing), where devices were located for measuring the travel rate of fire front and temperature characteristics at different heights (up to 10 m from the burning surface). On-line digital data were transmitted and stored at data loggers, overheat-protected by a soil layer. A helicopter hovered at a height of 1000 m and recorded with an IR digital camera thermal parameters of the burning area and fire front travel. The firing was initiated in the form of "fire band" throughout the length of the windward area, usually in the second half of the day. The travel rate of fire front depended on experimental conditions (amount of combustible material on the area, its dryness, intensity of the ground wind) and varied from 0.5 to 9 m/min.

Data of pre-fire and in-fire measurements were recorded in a note-book, thus saving the information on conditions and the character of each forest fire. The controllable and recordable conditions of natural-modeled experiments are the important advantage, allowing integrated study of forest fires, which is virtually impossible during spontaneous fires.

With the purpose of aerosol and gas sampling, the helicopter periodically flew through a smoke plume at different heights from 100 to 300 m (data on the concentration and composition of gas-aerosol emission at different heights are not considered in this work). Simultaneously, aerosol was sampled near the surface via pumping the smoked air through aerosol filters of two types: fine-fiber polymeric AFA-KhA (Petryanov) and fiberglass Gelman ones. They were preliminary dried off during seven days in a hermetic glass exsiccator above a layer of freshly ignited zeolite till their utmost dryness, weighed, and kept in plastic bags till the fire experiments. On finishing the sampling, the filters were again dried off and weighed in laboratory conditions. Thus, the mass of aerosol matter from each filter was determined, then mass concentrations of smoke emission at sampling points were calculated (the volume velocity and pumping duration were registered in a note-book; in addition, the total volume of pumped smoke was recorded with a SG-2 gas-meter).

To determine disperse characteristics of the emitted smoke, particles of different sizes were separately deposited from smoke plume on glass plates of inertial impactors of two types, i.e., particles between 30–40 and 1–3 μm were deposited on a 5-step rectangular cascade impactor and particles of 10–100 μm – on the open-type rotating impactor.[4,5] The glass plates were preliminary coated with a thin adhered layer of Apiezon, dried, and weighed. They were again dried and weighed after experiments to determine the amount of the deposited aerosol matter of one or another size fraction. The plates with particles were photographed with the Axioscope 2 plus digital microscope. The software, described in Refs. 5 and 6, was used to determine disperse characteristics of the photographed size fractions. In addition, the PKZV-906 photoelectric aerosol counter was used in fire experiments to measure the size spectrum of fine fraction (0.3–3 μm) in the smoke plume.

The chemical composition of the emitted aerosol was determined in laboratory conditions by high-sensitivity methods, i.e., the synchrotron-radiation excited X-ray fluorescence (SR XRF) for elemental analysis of AFA-KhA-filtered aerosol and the reaction gas chromatography for measuring Gelman-filtered organic matters and elemental carbon. Chemical elements with atomic numbers beginning from potassium (sometimes from sulfur or chlorine) and further according to the Periodic Table were recorded by the SR XRF method.

The method sensitivity was investigated earlier,[7] it varied from about 0.05–0.1 $\mu g/cm^2$ for calcium and potassium to 0.0004–0.001 $\mu g/cm^2$ for Sr, Zr, and Mo. The sensitivity is represented here as minimally recordable quantity of an element on unit filter area, i.e., as its surface concentration. When experimentally measured concentration was essentially lower than this threshold, it was considered as zero. Such procedure allowed the insufficiently reliable measurements to be excluded from the consideration (it is important in case of their mean-geometric averaging, while this procedure is immaterial for arithmetic mean calculations).

The amount of carbonic organic matter in aerosol samples was measured by the reaction gas chromatography method at the setup, described in Refs. 5 and 8. The method is based on catalytic combustion of Gelman-filtered organic matters into carbon dioxide with its following catalytic conversion into methane, the amount of which was measured with a high-sensitive flame-ionization detector.

As is evident, each carbon atom from an organic molecule first transforms to CO_2 and then to CH_4 molecules. In other words, the method measures the number (mass) of carbon atoms being in a sample under study in the form of organic compounds independently of their specific chemical composition.

The total carbon mass in organic matter of aerosol samples was determined from a preliminary defined calibration dependence "detector signal – carbon mass in the reference sample"; several organic compounds of known chemical composition were used as the reference substances. However, when determining the total mass of organic matters in smoke samples, it is necessary to take into account the fact that molecules of organic compounds include oxygen, hydrogen, and nitrogen atoms along with carbons. Organic components of smoke aerosols are of chemical origin from typical forest combustible materials: cellulose $(C_6H_{10}O_5)_n$, hemicellulose $(C_5H_8O_4)_n$, lignin, gums. The mass fraction of carbons in such compounds varies from 45 to 55% and is 50% on the average.[9] Hence, the experimentally measured carbon mass should be doubled to determine the total mass of organic matters in the aerosol sample. The amount of elemental carbon (in the form of graphite, soot, or black carbon) in a smoke sample was determined by us at the same setup and oxidized into the carbon dioxide at the first stage. In this case, there was no need in doubling the measured mass, since the amount of elemental carbon in the given aerosol sample was directly determined.

Mass concentration and total amount of smoke aerosol emission

Surface aerosol was sampled by means of pumping the smoked air through filters. Volume velocities and pumping rates were 130 l/min and 3–6 min for AFA-KhA filters and 30 l/min and 7–15 min for Gelman ones. This allowed us to collect 4–8 samples on fiberglass and 6–12 samples on polymeric filters hourly during the fire experiment (usually, for 2–3 h). The samples were collected at several points along the side boundary of a fire site, where the smoke plume from the burning area was carried away by slightly oblique wind. The sampling points moved along with fire front from the initial upwind boundary to the terminal downwind boundary of the fire site. Filter holders were placed just over the smoking (burning) surface at a height of 0.5–1 m. At such position, freshly-forming aerosols, still non-exposed to physical transformations (e.g., atmospheric saturation) and to chemical reactions in free atmosphere (e.g., with nitrogen and sulfur oxides, acid admixtures), fell on the filters. Besides, near-vertical lofting of hot smoke was observed here.

From the measured lofting speed ($U \approx 0.5 \div 1.5$ m/s), duration of active smoking at a certain point ($t \approx 10$–40 min), and the mass concentrations of smoke emission C (mg/m^3), the amount of aerosol M (t/ha), emitted from the unit of area during a fire, can be assessed:

$$M = 6 \cdot 10^{-4}\, CUt. \qquad (1)$$

“Bending” of smoke plumes and their mixing with ambient air took place at a height of 2–3 m and higher. Therefore, the smoke concentration, measured at an arbitrary height, characterized the current concentration at a given point, but it would be difficult to obtain generalized “fire” data from this quantity.

The aerosol concentrations, measured and averaged in different fire experiments in 2000–2003 [Refs. 3–5] and 2006–2007 are given in Table 1.

The concentration at each sampling point was calculated from the filter weight gain after pumping the smoke through the filter and from the volume of the pumped smoke. The measured in such a way concentrations in samples, collected at different points and different time, strongly varied in magnitude even for one fire experiment (see Tables 2 and 3 below). Such strong variations were caused by the fact that the burning and the smoking proceeded not uniformly both over burning area and in time. This is mostly connected with continuous fluctuations of wind direction and intensity near the burning surface, therefore, periodically either a strong smoke flow came to a filter-holder or passed by it. Hence, the substance amount can differ by several times even at neighboring filters. Therefore, it was important to collect a sufficient number of samples during fire experiments and to repeat experiments in order to obtain average values, characterizing smoke emissions in different conditions.

Table 1. Averaged mass concentrations of smoke emission

Fire experiments in					
pine forests				larch forests	
2000	2001	2002	2003	2006	2007
2 experiments	4 experiments	5 experiments	2 experiments	2 experiments	3 experiments
Averaged concentrations of smoke aerosol emission, mg/m^3					
88; 57; 73; 65	73; 54; 44; 50; 41; 40; 54; 60	50; 19; 13; 30; 28; 42; 21; 20; 43; 39	55; 46; 40; 35	58; 29; 36; 25	57; 47; 69; 74; 64; 60
Average value, mg/m^3					
46				51	

Note. Data for both polymeric AFA-KhA and fiber glass Gelman filters are included; therefore, the total number of data is more than the number of fire experiments (18) for the whole period.

As follows from Table 1, the averaged concentrations for different fire experiments varied from 13 to 88 mg/m^3, but they were mostly within a range 40–60 mg/m^3 (48 mg/m^3 on the average). The average amount of smoke matter $M \approx 0.5$–0.6 t/ha (within a range 0.2–1 t/ha for different fires), emitted in air from 1 ha of the burnt forest, was obtained from Eq. (1) at the average concentration $C \approx 48$ mg/m^3, average speed of lofting smoke $U \approx 1$ m/s, and smoking duration $t \approx 20$ min. Taking into account the fact that usually 15–25 t of plant material (our own measurements[3–5,10] and literature data[11,12]) are consumed in a forest fire, we conclude that from 1–2 to 5–7% of consumed biomass transforms to the aerosol smoke emission depending on the fire type and intensity (this also corresponds to previous estimates[3–5] and literature data[11–13]).

The comparison of concentrations measured in fires in (conventionally) larch forests (2006–2007, 25–74 mg/m^3, the average value is 51 mg/m^3) with those in pine forests (2000–2003, 13–88 mg/m^3,

Table 2. Concentration of microelements in smoke fire emission (fire experiments in conventionally larch forests, 2007)

Sample No.	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Zr	Nb	Mo	Pb	Sample mass, mg	Total concentration, mg/m^3	Fraction of element, %
Amount of microelement in a sample (AFA-KhA filter), μg																							
Fire experiment on July 10, 2007																							
1	13	0	1.1	0.2	0.2	0.4	2.6	0.02	0.08	0.12	0.2	0	0	0.02	0.02	0.01	0.03	0	0.011	0.06	3.7	6	5
2	39	40	4.0	0.2	0.5	2.6	9.4	0	0.04	0.06	0.1	0.01	0	0.11	0.06	0.16	0.04	0.01	0.004	0.03	11.3	19	9
4	26	17	1.0	0	0.3	0.9	2.2	0.04	0.01	0.11	0.1	0.03	0	0.10	0.03	0.04	0.01	0.00	0.014	0.03	15	25	3
5	132	88	2.6	0.2	0.7	9.8	6.6	0.04	0.06	0.14	0.9	0.03	0	0.42	0.15	0.29	0.05	0.01	0.003	0.09	84.4	141	3
6	51	38	5.4	0	0.4	2.9	16.5	0.05	0.03	0.10	0.3	0.01	0.04	0.18	0.09	0.13	0.04	0	0.016	0.03	43.2	72	3
7	53	67	2.8	0	0.1	3.6	9.9	0.03	0.07	0.20	0.4	0.03	0.07	0.16	0.05	0.22	0.01	0	0	0	39	65	4
8	106	172	6.9	1.1	0.3	6.4	12.5	0.01	0.09	0.29	0.4	0.02	0.11	0.14	0.07	0.65	0.04	0	0.010	0	32.9	55	9
9	60	102	4.6	0.9	0.6	10	8.3	0.05	0.12	0.16	0.4	0.02	0.03	0.27	0.07	0.28	0.04	0	0.008	0.04	57.7	96	3
10	22	13	3.7	0.2	0.2	0.7	5.7	0.07	0.03	0.03	0.3	0.02	0.02	0.04	0.04	0.08	0.03	0	0.006	0	15.1	25	3
																					Average:	57	5
July 15, 2007																							
11	71	31	1.3	0.2	0.5	2.1	4.6	0	0	0.09	0.7	0.02	0	0.51	0.08	0.05	0.01	0	0.013	0.10	6.4	11	18
12	56	43	1.5	0.3	0.2	2.4	3.5	0.07	0.01	0.03	0.1	0.01	0	0.22	0.04	0.05	0	0.01	0	0.07	36.3	61	3
13	693	124	9.5	0.4	0.6	10.0	20.4	0.20	0.17	0.67	5.2	0.04	0	1.79	0.44	0.14	0.06	0.01	0.035	0.63	29.7	50	29
14	287	56	3.9	0	0.3	2.9	6.5	0	0.08	0.44	2.1	0.02	0.05	0.88	0.23	0.04	0.04	0.01	0	0.14	34	57	11
15	62	59	2.5	0	0.8	2.2	6.7	0.09	0.16	0.45	0.8	0.03	0	0.34	0.07	0.06	0.03	0.01	0.009	0.12	29	48	5
16	70	134	2.8	0.3	0.3	7.0	7.0	0	0.03	0.10	1.0	0	0	0.26	0.06	0.20	0.03	0.01	0.017	0.06	30.5	51	7
18	84	58	8.1	0.8	0	5.1	13.8	0.03	0.07	0.38	0.6	0.03	0	0.18	0.09	0.08	0.05	0.01	0	0.13	27.5	46	6
19	145	1251	13.6	4.8	0.2	76.4	7.5	0	0.11	1.10	1.7	0.02	0.02	0.26	0.07	2.63	0.06	0.02	0.023	0.10	79.5	133	19
20	48	160	1.6	0.3	0.5	7.7	13.2	0.14	0.16	0.63	4.7	0.03	0	0.27	0.04	0.26	0.05	0.01	0.012	0.21	45.4	76	5
22	85	35	3.2	0.2	0.1	2.2	5.8	0.03	0	0.06	2.1	0.02	0	0.58	0.13	0.08	0.05	0.01	0	0.04	8.2	14	16
23	36	4	0.4	0.2	0	0.9	0	0	0	0	0.4	0	0	0.28	0.03	0	0	0	0.005	0.10	3.9	6	11
24	53	57	1.9	0.5	0.1	2.5	3.2	0	0.06	0.49	1.6	0.02	0	0.45	0.08	0.05	0.01	0	0.003	0.09	7.2	12	17
																					Average:	47	12
July 17, 2007																							
25	83	23	14.2	0.4	0.6	2.3	25	0.10	0.07	0.11	0.2	0.02	0	0.10	0.10	0.09	0.11	0.03	0.014	0.03	14.2	24	10
29	240	880	11.3	1.8	0.2	68	32	0.16	0.09	0.39	3.4	0.07	0	0.23	0.11	1.03	0.09	0.01	0.004	0.08	70.4	117	18
30	870	1520	14.5	2.1	0	134	29	0.13	0.11	1.03	9.5	0.08	0	0.27	0.23	1.79	0.07	0.01	0.007	0.18	67.3	112	38
31	280	418	12.4	1.1	0.0	38	27	0.12	0.03	0.14	3.4	0.02	0.07	0.23	0.12	0.50	0.09	0.01	0.123	0	23.1	38	34
32	162	173	2.3	0	0.4	11	2.9	0	0.06	0.13	1.6	0.01	0	0.12	0.06	0.17	0	0.01	0.008	0.01	26.6	44	13
33	69	67	2.0	0.4	0.2	4.2	0	0.02	0.01	0.06	0.5	0	0	0.07	0.02	0.05	0.01	0	0.009	0.01	24.6	41	6
34	119	268	5.7	0.7	0.1	25	11	0	0.03	0.10	1.4	0.02	0	0.08	0.05	0.31	0.04	0	0	0.09	38.5	64	11
35	95	78	0.4	0	0.4	3.6	0.0	0.03	0	0.13	0.2	0.05	0.05	0.01	0.02	0.07	0.02	0	0	0	102.2	170	2
36	69	136	2.4	0.3	0.1	10	3.3	0	0	0.07	0.4	0.02	0.04	0.02	0.03	0.15	0.03	0	0.025	0	13.3	22	17
37	126	396	13.0	1.6	0.1	26	25	0.08	0.06	0.18	1.4	0	0	0.48	0.15	0.34	0.07	0	0	0.26	26.5	44	22
38	98	82	6.1	0.6	0.4	7	9.4	0.05	0.02	0.03	0.2	0.07	0	0.02	0.05	0.09	0.03	0.01	0.003	0.04	65	108	3
																					Average:	69	16

46 mg/m^3) shows the absence of essential distinctions (with accounting for large variances of local and even average values). This reflects the fact that the total amount (41–62 t/ha in pine forests and 49–78 t/ha in larch ones, our own data) of species, and morphological composition of forest combustible material though differ in different taiga forests but vary comparatively slightly; therefore, type, behavior, and, hence, smoke intensity are mainly determined by dry weather in the pre-fire period (this predetermines pyrologic quality of combustible materials) and weather conditions during the fire.

Is there a correlation between the fire character, e.g., intensity of its burning (expressed quantitatively and qualitatively[10]) and the strength of smoke emission and/or variations in chemical and disperse composition of smoke particles? Such dependence should exist, and it is observed in laboratory conditions when burning forest materials. Actually, the amount of smoke, originating from intense (fiery) biomass burning is significantly less even visually as compared to the following smoldering. Besides, sedimentation on the filter from "fiery" smoke visually (black, probably, because of carbon substance) differs from those of "smoldering smoke" (yellow-brown, sometimes oily). However, this correlation for real forest fires is smoothed due to above-mentioned variations of moving smoke plumes, coming to an aerosol sampling point. During pumping through the filter (5–15 min), smokes from both the burning and smoldering zones can come to the filter; this can mask the desired correlation.

Nevertheless, two fire experiments, carried out one after another at the forest region Govorkovo in 2002, are demonstrative (see Table 1). One of these fires was very intensive both visually and according to measured temperature and rate of the fire front movement; another one was quite moderate. However, the mean concentration of smoke emission in the second fire (50 mg/m^3) was much higher than those of the intensive fire (19 mg/m^3).

It can be reasonably assumed that biomass particles and vapors of organic compounds, continuously escaped from the warmed vegetative material, can hardly pass the fiery burning zone without strong burnout. This leads to a decrease of aerosol concentration in smoke emission (i.e., incompletely combustible organic material). At the same time, a stronger burnout of the total amount of combustible materials takes place in the intensive fire; hence, the total aerosol emission can be even higher than at a slow burning/smoking.

Composition of microelements in smoke aerosol emission and their origin

In the course of fire experiments of 2000–2003 in typical pine forests of Central Siberia, concentrations of microelements (potassium, calcium, titanium, iron, and other 10–15 elements) were measured by the SR XRF method. It has been shown that partial amounts of one or another elements can differ from each other by 2–3 orders of magnitude, which reflects different natural content of the elements in soils and/or plant tissues.[7,14,15]

Based on the data from Refs. 3–5, the summary fraction of all the measured elements could be assessed as 0.3–1% of the total aerosol mass; the main their part is formed from five or six elements: potassium, calcium, iron, manganese, titanium, and zinc. These elements exist in nature in the form of salts, oxides, or complex compounds; the SR XRF method is low sensitive to "light" elements (natrium, aluminum, silicon, oxygen, etc.), which are contained in natural soils in 10–20-fold excess; hence, the summary fraction of mineral-soil matters was assessed as 3–15% of the total mass of the initial smoke emission.

Experiments of 2006–2007 in larch forests confirmed these data in general. For example, SR XRF measurements of 20 elements (from potassium to lead) in samples of two fire experiments in 2006 have shown that their total amount (with accounting for the above-mentioned "light" elements) varied from 7 to 19% (13% on the average).

Similar data, obtained for three fire experiments in 2007 (Table 2), have shown that surface smoke emission contains from 5 to 16% of mineral-soil elements (11% on the average).

An evident dependence of the quantity of mineral-soil matters on a random or natural dustiness of the surface cover and flora (moss, leaf and needle litter), upper vegetation-soil layer, and stems/trunks; all they are accumulated during months and years, and manifest themselves in the form of increased emission when burning (the case of artificial dustiness of moss was noted[5] in experiments of 2003, resulted in atypical 20–40% mineral-soil emission).

At the same time, the above manifold excess of "light" elements in soil and, hence, in smoke emission relates in fact only to those elements (silicon, aluminum, calcium, etc.), which are carried out from the burning surface by currents of hot air in the form of specks of soil dust. It is known, that some elements (potassium, calcium, manganese, bromine) are required for functioning of plant cells; they abound directly in plant tissues. When burning plant biomass, these elements are emitted in the atmosphere as parts of smoke emission (the technique allowing discrimination between elements of soil and vegetation origin is known and has been used in Refs. 3–5).

As is evident from Table 2, potassium and calcium mainly contribute (more than 90%) in mineral-soil emission in experiments of 2007. Potassium is undoubtedly originated from plant biomass burning (probably, in the form of K_2CO_3), while calcium ($CaCO_3$) partly comes to air from burnt vegetation tissues and mineral soil particles. Therefore, the mineral-soil emission fractions in experiments of 2006 and 2007 (13 and 11%) are overestimated (they are about 6%, if consider soil as a main source of calcium and the burning biomass – as a source of potassium).

Data on elemental composition of smoke emission in fire experiments of 2007, given in Table 2, their comparison with the results of 2006 (are not given in Table 2), and data for 2000–2003 [Refs. 3–5] evidence that no distinctions are observed in microelement composition of fire emissions in forests of different types. Only variations in absolute and relative concentrations of different elements are observed; they are either random or reflect the peculiarities of the SR XRF method. This was expected since no geochemical anomalies in natural or anthropogenic origin were observed in soils of all four forest areas, which could manifest themselves in emission of one or another element-marker.

From the mean fraction of mineral-soil matter (about 10%) and the above-calculated total smoke emission (0.2–1 t/ha), we obtain that 20–100 kg of mineral-soil matters are emitted to the atmosphere from 1 ha of the burnt forest, i.e., annually about $7 \cdot 10^5$ t in the Asian part of Russia. However, note, that here we discuss the primary emission, measured directly over burning/smoking surface. It is reasonable to believe that the main part of mineral emission consists of quite large particles (soil particles of several tens of microns), which fall on the surface near the burning forest (kilometers/tens of kilometers); therefore, only mineral substances (elements) belonging to small particles (about 10 μm and smaller) participate in regional (hundreds of kilometers) and, moreover, global atmospheric transfer.

Carbonic substances in smoke aerosol emission

Table 3 presents the amount of organic matters and elemental carbon, measured in smoke aerosol emission during the fire experiments in 2006 and 2007. As is evident, the main fraction of smoke emission (70–90%) consists of organic substances of unknown chemical composition (there are undoubtedly compounds, included in pine tar, lignin, and thermally decayed cellulose) and 2–18% of the emission (8% on the average) consists of elemental carbon. Integrally, these results correspond to the data earlier obtained for fires in pine forests. Thus, both concentrations and mineral-soil and carbonic composition of the emission are similar for fires in forests of different types. Weather conditions in the pre-fire period and during the fire experiments, which were similar in 2000–2003 and 2006–2007, played probably the key part.

Is there some correlation between the forest fire intensity and carbonic composition of smoke emission (we do not discuss possible variations of elemental composition of the mineral-soil fraction)?

Table 3. Amounts of carbonic substances in smoke aerosol emission (fire experiments in (conventionally) larch forests, 2006–2007)

Sample No. (Gelman filter)	Total mass in sample, mg	Mass concentration, mg/m^3	Mass of organic matter, mg	Fraction of organic matter, %	Mass of elemental carbon, mg	Fraction of elemental carbon, %	Total fraction of carbonic matters, %	Filter color
Fire experiment on July 23, 2006								
2	11.8	39	8.4	71	0.57	5	76	
3	9.9	30	7.6	77	0.53	5	82	
4	6.1	31	6.7	110	0.37	6	116	
5	8.3	42	8.4	101	0.6	7	108	
	On average:	**36**		**90**		**6**	**96**	
August 3, 2006								
7	3.7	19	2.4	65	0.68	18	83	
8	7.2	24	4.9	68	0.26	4	72	
9	6.7	22	4.4	66	0.22	3	69	
10	5.1	17	4.4	86	0.17	3	90	
11	3.8	13	3.5	92	0.08	2	94	
13	11.6	37	7.6	66	0.96	8	74	
	On average:	**25**		**74**		**6**	**80**	
July 10, 2007								
07-2	1.9	16	1.2	64	0.2	10	74	black
07-3	40	133	26	65	3.4	9	73	yel-brown
07-4	16.3	54	11.4	70	1.8	11	81	black
07-7	30.6	102	25	82	3.7	12	94	brown
	On average:	**76**		**70**		**11**	**81**	
July 15, 2007								
07-5	19.1	64	13.2	69	1.5	8	77	yel-brown
07-6	18.6	62	17.5	94	1.9	10	104	brown
07-8	21.9	73	21.5	98	2.7	12	110	brown
07-9	9.8	33	7.1	72	0.7	7	79	brown
07-10	43.7	146	31.9	73	2.9	7	80	black
07-11	6.1	20	4.3	71	0.8	13	84	black
07-13	24.1	80	15.7	65	1.3	6	71	black
07-14	11.4	38	9.9	87	1.2	11	97	brown
	On average:	**64**		**79**		**9**	**88**	
July 17, 2007								
07-15	7.4	25	5.4	73	0.4	6	79	yellow
07-16	10.9	36	6.7	62	0.6	6	68	yel-brown
07-17	15.5	52	14.3	92	1.4	9	101	black
07-18	26.6	89	26.6	100	1.7	7	107	yel-brown
07-19	12.4	41	6.5	53	0.6	5	58	black
07-20	11.4	38	6.4	56	0.9	8	64	black
07-21	26.1	131	15.2	58	1.7	7	65	black
07-22	16.8	84	20.8	124	1.0	6	130	yel-brown
07-23	9.2	46	4.9	53	0.8	8	61	black
	On average:	**60**		**75**		**7**	**82**	

As was mentioned above, the sedimentation of smoke particles on filters in intensive (fiery) burning was less in mass and differed in color and morphology as compared to aerosols from the smoldering zone. Aerosol layers on filters from fiery zone were black and visually consisted of hard particles. Filters from the smoldering zone were yellow-brown or brown, sometimes oily. Black color is undoubtedly caused by aerosols, completely or partly consisting of carbonized material, i.e., elemental carbon (graphite, soot, black carbon). Yellow-brown color and oiliness are caused by tar substances from burning conifers.

The increased concentration of elemental carbon, seemingly, should be expected in "black" filters, but this is not confirmed by the results (see Table 3). As for summary content of organic matters, some their increase on yellow-brown and brown filters ("smoldering" aerosols) is not excluded. Although similar conclusions were obtained in Refs. 4 and 5, they need further refinements.

Disperse characteristics of smoke aerosol emission

Disperse characteristics of fire emission along with its chemical composition are of the greatest interest. First, because of the dependence of the efficiency of solar light absorption and scattering on disperse sizes and chemical composition of atmospheric aerosol particles. Submicron particles are the best light scatterers, while particles of carbonized materials are the best absorbers. At the same time, the mass of an individual particle is proportionate to its cubed diameter; therefore, median-mass parameters, i.e., mass distribution over size fractions, are also important to characterize smoke aerosol emission.

Second, the hover time of aerosol particles in the atmosphere also strongly depends on their sizes, "fire" submicron and near-micron particles are formally able to reside there for months (in real atmosphere, such particles live for 10–15 days, since they are washed out with rain); however, particles of 40–50 μm in diameter should settle on the Earth surface for a day (it is supposed that smoke column/plume at forest fire rises to a height of 0.5–1 km (our observations); at a large-scale conflagration, smoke rises to 3–5 km [Ref. 16]).

Figure 1 presents the mass distribution histogram of smoke emission, collected separately on 5 steps of an inertial rectangular cascade impactor, based on 90° rotations of air-smoke current for each cascade/step (RCI model, worked out at ICKC SB RAS). First four steps are glass plates coated with a thin adhered layer of Apiezon; the fifth step, collecting particles of less than 3 μm in size, is the AFA-KhA filter.

It is seen in Fig. 1, that the main part of smoke emission falls on particles of less than 5–7 μm (moreover, mainly of the 5th step, i.e., less than 3 μm). However, some amendment is required.

First, as is known, it is very difficult to deflect large particles (30–40 μm and larger), transported with air (smoke) by wind, and suck in the receiving aperture of the impactor with air current and than deliver onto the 1st step without large loss.[17,18]

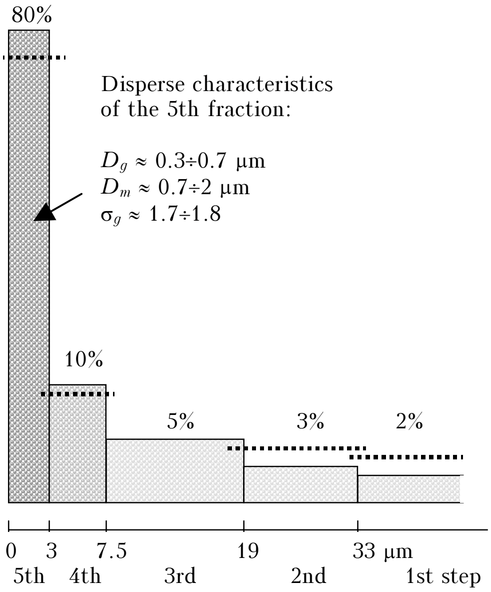

Fig. 1. Mass distribution of smoke aerosol emission over separate steps (fractions) of the cascade impactor. Characteristics of the fine 5th fraction are given on top: D_g is the mean countable diameter, D_m is the median-mass diameter, σ_g is the standard geometrical deviation for the logarithmically normal distribution.

Second, we deal with quite large aerosols, originating due to organic matter burnout from an initial biomass grain.

After (almost) full organic burnout, a particle is formed consisting of residual mineral substance, probably, of K_2CO_3 and $CaCO_3$ mixture (soot particle). This particle is most likely nonspherical (e.g., lamellar) and mechanically unstable.

When such particle is captured by an accelerated air current at the first and next steps or collides with a glass plate/step, it can mechanically collapse, giving smaller particles able to pass and settle on the next steps (similar processes are known and described in Ref. 17).

This undoubtedly takes place in our experiments, so, a true histogram should somewhat differ, namely, somewhat more substances should be on the 1st and 2nd steps, but less at the 4th and 5th (this is shown in Fig. 1 by horizontal dotted lines).

The presence of significant amount of the coarse matter in fire emission is seen in Fig. 2, taken from Ref. 5.

Here smoke particles, collected with the help of the open-type rotational impactor, are shown. This impactor, in contrast to the RCI, most efficiently collects the coarse smoke aerosols (10–20 μm and larger), but is incapable of collecting fine particles, e.g., 5–7 μm and smaller. It is evident from Fig. 2 that there are many particles of 10–20 μm in diameter and larger in the smoke emission.

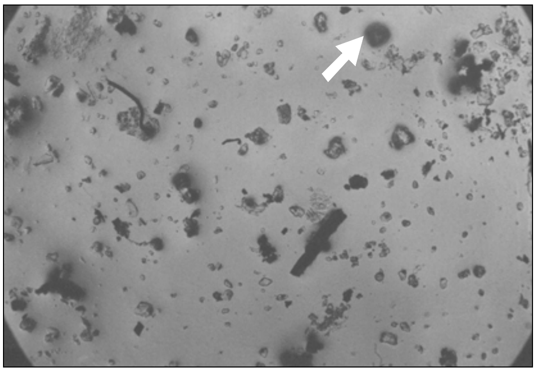

Fig. 2. Smoke particles, settled on a plate of rotational inertial impactor (the arrow points to the particle of about 20 μm in diameter).

Nevertheless, our experimental measurements and *a priori* knowledge approve that the mass fraction of small particles (3–5 μm and smaller) prevail in the smoke emission. In particular, in-fire measurements of the fine fraction of smoke emission with a PKZV photoelectric counter have shown (see Fig. 1) that the median-mass diameters D_m vary within 0.7–2 μm limits in different experiments and at different smoke concentrations (mean countable diameters D_g is within the 0.3–0.7 μm range). This can be important for computer simulation of smoke emission effect on the atmospheric heat exchange, since the main mass of emission falls in the fine range, the most "dangerous" for solar radiation scattering.

Conclusion

1. Mass concentrations of smoke aerosol emission, measured directly over burning/smoking surface, vary within a range from 10–15 to 80–100 mg/m^3 (48 mg/m^3 on the average). This results in emission into the atmosphere of 0.2–1 t of aerosol from 1 ha of the burnt forest area, which is from 1–2 to 5–7% of the total amount of the consumed biomass, depending on the forest fire type and intensity.

2. Aerosol smoke emission consists of three types of chemical matters:

a) mineral-soil substances, either trapped by an upward hot currents from the surface of "burning" soil and burning dusty plants (iron, titanium, calcium, silicon, etc.) or initially entering the consumed biomass (potassium, calcium, zinc, bromine, etc.). The summary fraction of mineral-soil matters is 3–15% of the total mass of the aerosol emission;

b) organic matters, characteristic for chemical composition of vegetation (thermally decayed cellulose, tar, lignin); their summary fraction is 60–90% of the total aerosol emission;

c) elemental carbon (graphite, soot, black carbon) resulted from deep carbonization of organics; its fraction is 7–15%.

3. The main part of smoke emission (more than 80%) is within the 5–7 μm size range (mainly less than 3 μm). These particles mainly consist of organic matter and elemental carbon (with an impurity, less than 1%, of potassium in the form of K_2CO_3).

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