Content of microelements in the aerosols emitted from fires in boreal forests of Central Siberia

K.P. Koutsenogii, Yu.N. Samsonov, T.V. Churkina,[1] A.V. Ivanov,[1] and V.A. Ivanov

Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
[1] V.N. Sukachev Institute of Forest,
Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk

Received January 4, 2003

Microelement (mineral) composition of the particulate matter emitted from fires in boreal forest was investigated by X-ray fluorescence analysis using synchrotron radiation (the XRF SR method). About twenty different chemical elements with atomic numbers from potassium K and higher were detected and measured quantitatively in the aerosol particles sampled. Total microelement (mineral) fraction was estimated to be about 5–10% of the total particulate matter. Both the total particulate matter emission and the mineral one were evaluated for fires in boreal forests of Siberia.

Introduction

Chemical elements, such as iron, calcium, potassium, molybdenum, and many others, are components of atmospheric aerosols. Most of them are met in aerosols, but having very low concentration, so that they can be conditionally called microelements. As applied to the continental territories of Western and Central Siberia, their main source is soil erosion due to weathering of surface soil layers. The chemical composition of aerosol particles coming to the atmosphere in such a way could reflect both mineral and dispersion characteristics of soils, and these particles could consist almost completely of mineral elements (unlike microelements mentioned above).

Such mineral particles actually exist in the atmosphere, and they are objects for investigation of their microstructure (morphological) and chemical characteristics, for example, using X-ray or proton microanalyzers.[1,2] However, it should be taken into account that atmospheric aerosols are a mixture of particles of different chemical and disperse origin coming to the atmosphere and mutually transforming under various meteorological, physical, and chemical processes. As a result, particles of soil-mineral origin may make up a relatively small fraction in the total mass of atmospheric aerosols.

Another source of microelements in the atmosphere is aerosol emission from extensive forest fires occurring regularly in summer in Siberia (about 10^7 ha a year). Microelements are lifted into the atmosphere by upward convective flows of hot air (smoke) in the form of fine particles of forest soil subjected to intense heating both during the passage of the burning front and during the following smoldering combustion of forest combustibles (grass, lichen, moss, shrubs, trees). In addition to particles coming to the atmosphere during a forest fire directly from the surface, a part of aerosol emission of mineral origin is associated with dustiness of surface of forest plants. Plants can accumulate dust for a long time before a fire, and this accumulation is especially intense in dry season. In principle, long-term accumulation of dust on the plant surface could lead to some selection of dust particles by their disperse and chemical composition as compared to the composition of the initial soil. At plant burning, these dust particles are emitted into the atmosphere.

Some chemical elements present, in marked amounts, in the natural chemical composition of the plant material itself. For example, potassium is a vitally essential element for functioning of vegetation cells. At burning of plant mass, these elements partly remain in the ash residue and partly are emitted as aerosol into the atmosphere.

High-temperature heating of forest soil during fires significantly changes the initial chemical composition of soil particles leading to burning-out (thermal destruction) of organic (humus) substances contained in them. Such aerosol particles will be higher mineralized than the initial forest soil.[3] On the other hand, burning combustibles intensely emit particles consisting of the initial vegetation (wood) organic material (cellulose, hemicellulose, lignin, etc.) subjected to high-temperature pyrolysis, oxidation, thermal sublimation, and condensation. Such particles are obviously carbonic. Thus, the total fire aerosol emission is a mixture of particles of both mineral and organic origin. This mixture may be rather specific for forest fires, widely different in the concentration, disperse and chemical composition from ordinary atmospheric aerosols. Certainly, these differences can be most strong just near a fire until fire aerosol mix with other atmospheric particles or undergo physical and chemical transformations changing their primary chemical composition.

This paper presents the data on the content of microelement (mineral) substances measured in

0235-6880/03/05–06 424-04 $02.00

aerosol samples collected in summer of 2000–2002 during forest fires in Krasnoyarskii Krai.

Methods of aerosol sampling and microelement detection

Investigations were conducted on the forest testing ground of the Institute of Forest SB RAS (Krasnoyarsk) situated 700 km to the north from Krasnoyarsk. The testing ground was roughly 3×2 km isolated forested area surrounded by marshes. This “island” was divided into 200×200 m parts separated by fire-prevention barriers (ditches, sandy strips, cleared spaces). Some of these parts were meant for control burning, that is, for natural imitation of forest fires (a total of 11 parts were burned out in the period of 2000–2002).

Burning was conducted after some preparation, including estimation of the combustible amount and installation of measuring instrumentation at 49 positions all over the territory (to form the 25×25 m grid). The instrumentation included equipment for measuring the speed and direction of motion of the fire front, as well as thermocouple meters of fire temperature at five height levels from the ground to 10 m above the surface. The current information from these sensors during a fire was transmitted in the digital form to storage electronic devices (dataloggers) protected against overheating by a soil layer with the following re-recording for long-term storage and processing of the data collected.

The fire movement process was recorded with a video camera placed in a heat-shield jacket and set in the burning zone. From a helicopter hovering at the height of 1000 m over the fire zone, infrared recording of the fire was conducted. In spite of high smoke density, this record allowed us to follow the movement of the fire front and delayed burning in the back part of the fire.

Ground-based sampling of aerosol was carried out near a side edge of the fire zone by pumping the smoked air through AFAKhA aerosol filters (pumping rate of 20 l/min, pumping time of 2–10 min, sampling height of 0.5–1 m above the ground). For pumping smoke through the filters, we used a pneumatic pump operated from a portable 220 V electric generator. In addition, aerosol was sampled onto filters from the helicopter flying at the height of 100–200 m through the smoke plume from the lee side of a burning forest area. A pump with the flow rate of 100 l/min (pumping time ~ 1–2 min) was operated from the onboard power line (24 V dc).

AFAKhA aerosol filters are circles of 70-mm diameter (working diameter of about 50 mm, working area of 20 cm^2) made from a fine-fiber polymeric material. Before the experiments, all filters (including the check ones) were dried for 5–7 days in a tight glass dessicator over the layer of NaX-type freshly calcinated zeolite granules until they achieved the constant mass. Filters were weighted in a closed plastic Petri dish to prevent their humidification in open air. Once aerosol sampling was completed and the filters were returned into the laboratory, the above drying and weighting procedures of the filters (including the check ones) were repeated. Thus, we determined filter weight increments associated with deposition of aerosols from the smoked air pumped through the filters. These increments were ~ 1–10 mg depending on the smoke intensity and the pumping time. Measurements of that small increments, first, required for the above drying and weighting procedures to be performed very carefully and, second, formed a source of significant experimental errors in determination of the relative content (concentrations) of microelements and other substances in aerosol.

The content of chemical elements deposited onto a filter was determined by the method of X-ray fluorescence using synchrotron radiation (the XRF SR method).[4,5] This method was applied to detect chemical elements with atomic numbers starting from that of potassium K and higher. The sensitivity of the XRF SR method to different elements was studied in various versions and varied from ~ 0.05–0.1 μg/cm^2 for calcium or potassium to ~0.0004–0.001 μg/cm^2 for strontium, zirconium or molybdenum (the sensitivity here means the minimum detectable amount of an element normalized to the unit filter area, that is, it has the dimensionality of the surface concentration of an element under study). In the cases, when an experimental measurement nominally gave the value of the surface concentration significantly lower than the limit mentioned above, zero value was assumed to this measurement. This procedure allowed us to exclude measurements with low reliability from the consideration, which was very important in the case of their geometrical mean values.

Results and discussion

Table 1 presents the data on the content of some chemical elements on the filters from the ground-based samples collected in field fire experiments of 2001. The data obtained in the experiments of 2000 and 2002 were very close to the results of 2001, and therefore they are omitted here. As applied to the aim of this paper, the element contents in Table 1 are given as volume concentrations in the smoked air pumped through the filters.

To calculate these volume concentrations, we used, besides the surface concentrations determined by the XRF SR method, some additional data on the amount of smoke pumped through the filters. These data are omitted in the paper, but in Table 1 element concentrations are given as calculated from them (including the total mass concentration of aerosol substance C_0) in every aerosol sample separately, which is characterized in Table 1 by the number of an experimental filter (in experiments, we registered every filter along with the characteristics of burning plant materials, burning conditions, and pumping rate and time).

Table 1. Microelement content in aerosol emission from forest fires (ground-based aerosol sampling, 2001)

	Total mass concentration of aerosols C_0 and partial concentrations of chemical elements, μg/m^3															
Filter number	C_0	K	Ca	Ti	Cr	Mn	Fe	Co	Zn	As	Se	Br	Rb	Sr	Zr	Mo	Pb
1	30800	445	72	5.9	0	6.0	27.9	0.52	11.1	0	0.23	4.3	2.2	0.14	0	0	2.5
2	33300	416	37	0	0	2.1	11.6	0	15.1	0.31	0.34	23.7	1.5	0	0	0	0.5
4	14700	141	129	14.7	0	5.0	24.1	0	3.8	0	0	0.5	0.8	0.08	0	0	2.4
5	243900	85	139	0	0	9.5	25.4	0.32	4.9	0	0	0.6	0.2	0.49	0.38	0	0.9
6	35700	439	54	0	5.0	0.4	22.5	1.04	6.1	0	0	2.6	1.8	0.06	0	0.25	3.1
7	38500	233	100	2.1	1.9	11.0	49.2	0.31	3.3	0.94	0	0.8	0.9	0.14	0	0.09	0
9	30000	23	39	0	1.7	0.3	7.5	0.02	0	0.12	0	0.5	0	0.05	0.04	0.05	0.2
10	78100	144	53	0	5.6	3.8	33.1	0	0	0	0	0.4	0	0.13	0	0.38	1.0
12	43500	113	174	10.9	7.4	2.2	28.3	0	0	0	0	5.6	0	0	0	0.45	3.6
15	35700	270	70	29.3	1.4	6.4	18.9	0	1.6	0.16	0	1.3	1.9	0.27	0.06	0	0.8
16	76900	915	46	0	7.7	0	69.2	1.77	2.3	0.85	0	5.8	4.8	0.09	0.17	0.85	3.7
17	37700	455	38	0	0	2.3	10.0	0	14.5	0	0.26	2.3	1.8	0	0	0	1.3
20	22000	88	70	1.8	2.6	19.6	9.5	0.11	0	0	0	0.2	0.3	0.10	0	0	1.0
21	37000	106	25	0	0	1.2	17.5	0	0.7	0	0	0.6	0.4	0	0	0	0
23	63800	25	102	14.5	11.9	8.5	24.7	0	0	0	0	0	0	0	0	0	0
25	42100	185	61	3.0	0	4.6	11.4	0	1.7	0.27	0.13	0.9	0.8	0.03	0	0.12	0.7
27	56600	25	34	0	0	0	16.6	0	0	0	0	0	0	0	0	0	0
28	29100	206	274	16.5	5.2	10.9	13.4	0	2.7	0.8	0	0.4	0.6	0.20	0	0	0
29	76200	30	53	6.5	0	6.1	12.4	0	0.2	0.7	0.06	0.5	0.1	0.42	0.38	0	0.1
32	50000	205	65	0	8.5	0	5.0	0	1.5	0.35	0.25	1.1	0.8	0	0	0.27	0.9
34	31900	364	311	12.8	5.3	25.7	19.6	0	6.2	0	0	2.3	1.1	0.61	0	0	0.9
45	32800	398	39	0	0	1.5	9.2	0	2.6	0	0	0.4	1.6	0	0	0	0
46	30000	619	49	1.8	0	9.0	4.1	0.24	5.7	0	0.09	1.9	2.8	0.11	0.06	0	0.8
47	20800	54	94	0	1.9	5.6	7.1	0.08	0	0	0.13	0.2	0.2	0.15	0	0	0.6
48	15400	54	77	0	0	8.9	12.0	0	0.6	0	0	0	0.1	0.17	0	0	0
51	48200	22	29	1.7	2.2	0	6.0	0.27	0	0	0	0.1	0.2	0	0.1	0	0.7
52	111100	83	10	2.9	0	1.0	15.6	0	0	0	0	0.3	0.5	0.18	0	0	1.5
56	74400	815	142	8.9	3.5	12.2	13.4	0.13	6.9	0.23	0.10	2.4	3.0	0.20	0	0.15	0.9
57	40000	685	125	0	0	12.0	15.6	0.37	5.3	0	0.05	3.6	3.5	0.20	0.10	0.04	1.4
58	29800	412	17	3.9	0	1.8	8.2	0.33	5.3	0	0.12	4.9	1.7	0	0	0	2.6
Mean value	50300	268	86	4.6	2.4	5.9	18.3	0.18	3.3	0.16	0.06	2.3	1.1	0.13	0.04	0.09	1.1
RMS deviation	42500	248	70	7.0	3.2	6.1	13.7	0.37	4.1	0.29	0.10	4.4	1.2	0.15	0.10	0.19	1.1
Error in mean value	7800	45	13	1.3	0.6	1.1	2.5	0.07	0.8	0.06	0.02	0.8	0.2	0.03	0.02	0.03	0.20

It can be seen from Table 1 that the XRF SR method allows us to detect 15–20 chemical elements from potassium to lead (some elements, e.g., nickel and copper are omitted in Table 1) in aerosol samples. However, it can also be seen that the concentrations of different elements in smoke may differ by two to three orders of magnitude, what reflects different natural content of these elements in natural soils (the so-called element clarkes). On the other hand, from the available literature data on the values of clarkes of that or other element in typical soil (clay, rock, sedimentary materials) it is possible to determine the elements, which originate, to a higher degree, in the fire emission from burnt vegetation (wood) mass than from the soil emission. For this purpose, in Table 1 we should normalize the measured concentrations of different elements to the iron concentration, since the principal source of iron in aerosols is just the soil. The data re-normalized in such a way (the so-called relative element clarkes) are given in Table 2 (for simplicity, Table 2 presents only re-normalized mean values of the relative clarkes) along with the reference relative clarkes of the same elements for typical soils taken from Refs. 6–8. Comparing the experimental and reference values, it is possible to judge on the origin of that or other element in aerosol emission from forest fire. It can be seen from Table 2 that the appearance of such elements as potassium, chrome, zinc, selenium, bromine, molybdenum and, probably, manganese is caused by burning of vegetation tissue. At the same time, such elements as titanium, strontium, zirconium, (probably, calcium) and some others are likely of soil origin.

Probabilistic judgment on the origin elements in aerosol emission is connected with the fact that the reference values of natural clarkes (given in Table 2) can vary widely depending on the geolandscape conditions. Consequently, only in the cases, when the measured relative clarke of some element many times exceeds the natural (reference) value, we can draw a reliable conclusion on the predominantly plant origin of this element in fire aerosols (for example, potassium or zinc).

Based on data from Table 1 we can obtain that the total fraction of all microelements detected in aerosols makes up about 1% of the total aerosol mass. However, it should be taken into account that the XRF SR method used fails to detect such elements as oxygen, nitrogen, sodium, aluminum, silicon, chlorine, and sulfur. At the same time, it is well-known[6,7] that just these elements are components of many soil materials and in far larger (10–20 times) total amount than that of the elements included in Table 1.

Table 2. Relative element clarkes

Relative clarke (for Fe)	K	Ca	Ti	Cr	Mn	Fe	Co	Zn	As	Se	Br	Rb	Sr	Zr	Mo	Pb
Reference	0.58	0.55	0.11	0.0023	0.017	1	0.0005	0.002	0.00012	0.00002	0.0007	0.004	0.001	0.0045	0.0001	?
Experiment	14.6	4.6	0.25	0.13	0.32	1	0.01	0.18	0.0087	0.0033	0.13	0.06	0.007	0.0021	0.005	0.058
Exp./Ref.	25	8	2	56	19	1	20	90	73	165	185	15	7	0.5	50	?

Thus, it is quite reasonable to believe that the total fraction of aerosol components of mineral (soil) origin can reach 5–10% of the total aerosol mass. The rest substance of fire aerosols (about 90%) consists of carbonic substances, which follows from our measurements (the technique and results of our carbonic measurements will be published elsewhere), and also agrees with the literature data.[9]

Although the mineral fraction in particles seems to be small (5–10%), the absolute amounts of mineral substances coming to the atmosphere at forest fires are quite significant. Table 1 gives the data on the total smoke concentration C_0 at forest fires varying from ~ 15 to 240 mg/m^3 with the mean value ~50 mg/m^3. Note that fluctuations of the smoke concentration are random and connected with experimental conditions. First, fire zones were small (no larger than 200×200 m), and therefore the landscape conditions of burning were quite inhomogeneous. Second, for safety reasons, aerosol samples were collected after passage of the fire front near the side edge of an area without going in depth of the fire territory. In view of both of these reasons, the smoke intensity at sampling sites fluctuated widely, and this was observed visually. Nevertheless, in spite of these fluctuations, the mean (over all experiments) aerosol concentration must characterize the total smoke-forming ability of forest fires. As can be seen, the mean concentration of fire emission (~50 mg/m^3) exceeds, roughly by 1000 times, the mean concentration of aerosols in the free atmosphere (10–60 μg/m^3). Therefore, even at the 5–10% fraction of mineral components the total amount of mineral emission from extensive forest fires to the atmosphere is a significant factor.

Based on the data obtained on the mean smoke concentrations and assuming that the mean speed of convective lifting of hot air near the surface is ~ 0.5–1 m/s and the mean time of local plant burning (that is, the mean time of intense smoke formation) is ~ 5–10 min, it is easy to estimate the total amount of aerosol emission from a unit area of burning forest territory. This value is ~ 10–30 g/m^2 (100–300 kg/ha), and the fraction of mineral emission can be estimated as 5–30 kg/ha. The total aerosol emission estimated above makes up 1–3% of the total amount of combustibles burnt in a fire (~ 1 kg/m^2, ~ 10 t/ha, our measurements), which correlates closely with the estimates obtained from measurements of the amount of carbon dioxide emitted at forest fires.[3,9]

Conclusion

Using the XRF SR method, we have determined the content of some chemical microelements of mineral-vegetation origin in aerosol emission from forest fires in Central Siberia. It has been shown that the total fraction of mineral-vegetation elements is 5–10% of the total amount of aerosol emission. The specific production rate of the aerosol emission of microelements from forest fires has been estimated.

Acknowledgments

The financial and organizational support from NASA (Project 99–ICA–076), LCLUS, CRDF (Grant RBI–2416–KY–02), USDA Forest Service (Project 99–ICA–076), Canadian Forest Service, Russian Foundation for Basic Research (Grant No. 01–04–49340), Siberian Branch of the Russian Academy of Sciences (Grant No. 64) are strongly appreciated.

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