Results of direct measurements of aerosol composition in emissions from several enterprises in Russia and Kazakhstan

Belan, Boris, Arshinov, Mikhail, Simonenkov, D., Tolmachev, Gennadii

Boris D. Belan, Mikhail Yu. Arshinov, D. V. Simonenkov, Gennadii N. Tolmachev, "Results of direct measurements of aerosol composition in emissions from several enterprises in Russia and Kazakhstan," Proc. SPIE 3108, Combustion Diagnostics, (23 May 1997); doi: 10.1117/12.274768

SPIE.

Event: Environmental Sensing III, 1997, Munich, Germany

RESULTS OF DIRECT MEASUREMENTS OF AEROSOL COMPOSITION IN EMISSIONS FROM SEVERAL ENTERPRISES IN RUSSIA AND KAZAKHSTAN.

B.D.Belan, M.Yu.Arshinov, D.V.Simonenkov, G.N.Tolmachev.
Institute of Atmospheric Optics SB RAS
1, Akademicheskii ave., Tomsk, 634055, Russia

ABSTRACT

These measurements have been carried out directly by sampling on filters in the emission plumes by means of airborne laboratory. Then filters have been analyzed in laboratory conditions. The analysis allowed the determination of the concentration of 12 ions and 27 elements. Average concentration of each emission component has been determined from known air volume passed throughw the filter. Wind speed has been measured at the crossing of the emission plume whose area is found from lidar data. This allows us to find the average concentration of contaminants in the emission as well as the emission gross yield.In this paper we present the data on the composition of emissions from enterprises of Pavlodar, Khabarovsk, Komsomolsk-on-Amur, Nizhnevartovsk,and Nizhnii Tagil.

Key words: **aerosol composition, concentration, emission**

Many estimates made recently indicate that anthropogenic aerosol is a significant portion of the total mass of suspended substances in the atmosphere.[1,2] However, the data on its properties and particularly on its chemical composition are very limited that makes it difficult to be taken into account in many problems. For example, in ecological problems it is important to know what portion of metals contained in raw materials and fuel is emitted into the atmosphere in the process of industrial production. The estimates[1,2] give the difference in values of about two orders of magnitude. As the author of Ref. 3 thinks, the knowledge of the anthropogenic aerosol chemical composition would allow identification of the regions which are the aerosol sources in the long distance transport of air pollution. The methodical aspects of such an identification are described in Refs. 4 and 5. The account for the anthropogenic aerosol is also very important to numerical modeling of the climate radiative characteristics.[6]

In this paper we present the data on chemical composition of aerosol emitted by enterprises in some regions during 1989–1991. The data were obtained by collecting air samples from the emission plumes from onboard the An-30 airborne laboratory "Optik-E". The airborne laboratory is described in Ref. 7, and the techniques for its use as a complex are described in Ref. 8. Let us remind that aerosol was sampled on the AFA-HP and AFA-HA-20 filters when the aircraft crossed the emission plume at a distance of 100–200 m from the stack mouth. Filters were exposed only in the plume. Its geometrical cross section was determined either by means of a lidar or from the data of photoelectric particle counter operating continuously assuming that the section is close to a circular one. The samples collected in such a way were handled at the laboratory of analytical chemistry at the Tomsk State University headed by Z.I. Otmakhova. The laboratory is now accredited in the Russian Standard Agency, and the techniques are certificated in the Institute of Standards (Ekaterinsburg). The techniques listed below were applied to the analysis, and the errors were the following.

Element or compound	Method	Detection threshold, μg/filter	Error, %
Al, Co, Cr, Mo, Ni, Ti, Zn, B, Si	atom-emission	0.02	20
Ag, Ba, Cu, Pb, Sn, V, Mg, Mn	–"–	0.01	20
Fe, Ga, W	–"–	0.1	20
Ca, Cd	–"–	0.2	20
In	–"–	0.002	20
As^{5+}, Zn^{2+}	inverse volt-ammetry	0.02	15
Cd^{2+}	–"–	0.04	15
Na^{+}, K^{+}	flame photometry	0.20	10
Fe, Cl^{-}	high-effective liquid chromatography	0.20	10
$SO^{2-}{}_{,4}$	–"–	2.00	15
$NO^{-}{}_{,3}$	–"–	0.60	10
F^{-}, $NH^{+}{}_{,4}$, $NO^{-}{}_{,3}$	ionometry	0.20	10

TABLE I. Aerosol chemical compopsition of the industrial emissions (μg/m³).

Chemical elements	City												
	Khabarovsk		Pavlodar						Ermak	Samotlor			
	Plant												
	Power heat station 1	Power heat station 3	Power heat station 1	Aluminium Plant	Power heat station 2	Tractor Plant	Power heat station 3	Oil processing Plant	Power heat station	Plume			
										Oil plume		Gas plume	
Na^+	675	153.3	5.6	<	176.6	1	6.1	<	76.7	18.3	10.5	5.2	3.6
K^+	820	316.7	9.4	32.9	119.9	1.2	3.4	28.8	40	<	<	<	<
Cl^-	665	443.3	147.2	152.9	196	116	116	83.5	69.5	112.1	48.8	<	<
F^-	–	–	–	–	–	–	–	–	–	<	<	<	<
$NH^+{}_4$	<	346.6	7.8	128.6	150	60	83.3	34.6	225	<	<	<	<
Br^-	<	<	1.6	22.9	1.4	10.7	0.9	10	80	<	<	<	<
$NO^-{}_3$	<	<	0.7	<	0.2	0.3	0.5	30	<	<	<	<	<
P^{5+}	–	–	36.1	61.4	9.7	13.3	40	6.9	55	<	<	<	<
$SO^{2-}{}_4$	<	<	15.5	9.9	426.1	39.1	105.3	16.5	201	<	<	<	<
Hg^{2+}	1.9	<	0.9	0.8	7	0.4	2.1	2.2	45	<	<	0.2	<
As^{5+}	<	46.8	88.9	11.4	35.7	26.7	51.3	1.9	53.3	<	<	<	<
Zn^{2+}	33.5	22.4	0.9	3.7	6.3	0.5	0.3	0.6	4.5	<	<	<	<
Cd^{2+}	<	<	<	0.4	<	<	<	0.04	0.2	<	<	<	<
Fe	580	200	250	480	186.7	66.7	250	240	520	4.4	8.8	6.1	1.7
Mn	3.3	2.5	16	29	4	1.9	0.6	0.7	10	0.1	0.1	0	0
Mg	110	51.7	23.3	0.2	0.2	<	6	27.5	23.3	4.3	4.1	<	1.1
Pb	<	<	0.1	1.8	<	<	0.7	<	0.3	0.1	<	0.1	0
Cr	<	2.7	3.3	18.5	6.8	7.3	<	8.3	50	0.1	0.1	<	0.1
Ni	16	2.7	–	–	–	–	–	–	–	0.4	0.1	0.1	0.2
Al	620	333.3	520	910	340.5	233.3	380	460	1100	242.5	3.6	3.2	3.8
Cu	14	0.5	0.1	0.2	<	<	0.5	0.1	8	0.3	2	2.1	1.2
V	6	1	0.5	1.2	<	<	0.5	0.1	1	0.1	<	<	0
B	2	0.3	–	–	–	–	–	–	–	0.1	<	<	0.1
Zn	36	12.8	10	76.2	<	2.3	10.5	0.1	39	–	<	<	<
Mo	5.8	1	–	–	–	–	–	–	–	<	0.1	<	<
Ca	1700	1016.7	62.5	125	<	28.7	62.5	107.5	255	13.8	7.9	3.5	2.5
Si	7100	1266.7	500	1050	333.3	434	620	450	943	0.6	0.4	0.1	0.2
Ti	–	–	50	140	33.3	7.3	24.5	8	80	12	5.8	5.3	10.8

Note: < denotes the concentration less than the detection threshold; – denotes that element was not determined.

TABLE I. (continued).

Chemical elements	City							Kamchatka	References 9–17	
	Megion	Nizhnevartovsk	Nizhnii Tagil							
	Plant									
	Boiler station	Boiler station	Coke battery plant	Power heat station	Carriage-building plant	Ural chemical plastpolymer plant	Metallurgical works	Mt. Klyuchevskoi	Coil μg/g	Liquid fuel μg/g
Na^+	5.3	1.3	<	<	11.7	<	<	5.9	0.16–600	14–15
K^+	<	0.1	<	<	3.3	<	<	<	0.25–210	1.1–2.0
Cl^-	<	13.8	72.4	<	1439.7	281.8	108.5	0.8	8–200	400
F^-	<	<	2.1	20.8	24.4	113.6	<	–	1.2–240	2
$NH^+,_4$	<	12.7	265.4	<	749.1	<	<	15.2	–	–
Br^-	<	<	97.6	<	1378.2	1090.9	65	–	0.2–15	1.8
$NO^-,_3$	<	<	16.8	129.2	387.9	<	117.1	<	–	–
P^{5+}	<	<	–	–	–	–	–	–	5–1550	130
$SO^{2-},_4$	2.3	<	97.6	<	235.5	<	<	18	–	–
Hg^{2+}	0.1	0.3	5.5	<	1.4	6.4	3.7	<	0.05–60	0.06
As^{5+}	<	<	<	35	<	17.7	<	–	0.1–2000	0.2–4
Zn^{2+}	0.1	<	<	<	<	<	8.9	<	0.2–1300	0.2–130
Cd^{2+}	<	<	<	<	<	<	1	<	0.5–200	0.3–0.5
Fe	3.5	6.5	138.3	<	105.1	52.2	207.5	19.5	2.5–5000	4.6–600
Mn	0	0.1	2.1	<	0.8	<	<	0.5	0.7–1300	0.3–1
Mg	1.9	1.7	37.5	15.2	70.9	19	5	2.6	0.3–20	0.6–65
Pb	0	0.1	<	<	<	<	0.5	<	0.02–250	–
Cr	0	1.1	12.3	0.4	11.4	7.9	12.5	0.2	0.5–360	0.5–12
Ni	0.2	0.3	2.3	3	0.2	1.6	17.3	0.5	0.3–500	0.1–600
Al	10.8	5.3	8.6	<	17.7	<	14.8	9.1	9–1500	0.8–5900
Cu	0.3	1.2	2.2	4.4	1.2	1.6	21.8	0.1	0.6–600	0.5–200
V	0	0	0	0.2	0.2	0.3	<	0.1	0.8–220	25–700
B	0	0.1	<	<	<	<	2.5	0	2.5–250	8
Zn	<	<	–	–	–	–	–	–	0.2–1300	0.2–130
Mo	<	0	–	–	–	–	–	<	0.1–200	1
Ca	10.3	10.9	431.3	518.5	451.9	279	2	3.9	0.4–560	0.3–130
Si	0.8	0.3	20.7	<	<	<	<	13.4	1.5–1500	2–2200
Ti	4.9	3	9.1	<	1.8	1.1	<	3.5	3.4–6000	–

The results of determining the aerosol composition in the emissions of some enterprises in Russia and Kazakhstan are listed in Table I, as well as the data obtained in the plume of Mt. Klyuchevskoi volcano (Kamchatka) and the data from Refs. 9–17 on the concentration of substances in the coal and liquid fuel ashes.

It is seen from Table I that almost all elements and ions to be determined are found in the plant emissions. Concentrations of one or another component can differ by 5 orders of magnitude, what is probably indicative of the properties of the fuel used or the technological peculiarities. The enhanced content of Si, Ca, Al, Mg, and Zn in ashes fraction is characteristic of the enterprises in Khabarovsk and Pavlodar, which used coal during the period of measurements. In addition, high concentration of the water soluble fraction of ions NH_4^+, SO_4^-, and Br^- is observed in the emissions of enterprises in Pavlodar, that is indicative of the specific peculiarities of the coal burnt. The concentration of Na^+, K^+, and Cl^- is higher in the plumes observed in Khabarovsk.

According to Ref. 18, up to 10% of Al, Co, Fe, Mn, and Sc, up to 30% of Cr, Cu, Ni, and V, and up to 100% of As, Br, Hg, Sb, and Se from all possible sources is emitted into the atmosphere when burning the coal. The data from Table I partially confirm this conclusion, especially for such toxic substances as As, Hg, and Br.

In the emissions from oil burning plants the mass concentration of suspended substances is essentially lower, mostly it is the ash fraction (Samotlor, Megion, and Nizhnevartovsk oil deposits). Water soluble fraction is absent in these plumes. The emission of Nizhnii Tagil enterprises is the particular case of the emitted aerosol chemical composition. We almost did not find such widespread ions as Na^+ and K^+ in its composition. The ash fraction (Ca, Fe, Al) is a small part of the whole concentration of pollutants while water soluble fraction represented by the ions Cl^-, F^-, NH_4^+, Br^-, and NO_3^- is maximum of all the regions studied. Evidently, not only the effect of the fuel properties is revealed here, but also the peculiarities of the technologies used.

The comparison of our results with other data shows that in the majority of events the concentrations we measured are within the range noted in Ref. 9–17. But in some cases we obtained the concentrations of some substances exceeding the known ones. These are Na^+, K^+, Ca, Si, and Mg (Heat Power Station No. 1, Khabarovsk), Cl^- and Br^- (Carriage-Building Plant, Nizhnii Tagil). One can explain the high level of Na^+, K^+, Ca, Si, and Mg concentration at Heat Power Station No. 1 in Khabarovsk by the fuel peculiarities, but it is doubtful that one could explain high concentration of Br^-, which, according to Refs. 1–3, is primarily of natural origin. This is especially true since it was not revealed in the power station emissions of this city. The absence of the ions Na^+ and K^+ excludes the marine origin of its formation. It is quite probable that it comes with the technological water that is used in the production cycle, because the high concentration of Br^- is observed at other enterprises of Nizhnii Tagil. However, this fact requires a separate study.

The aforementioned data show high efficiency of the airborne sounding as a complex method of studying emission composition.

REFERENCES

1. S.G. Malakhov and E.P. Makhan'ko, Uspekhi Khimii **59**, No. 11, 1777–1798 (1990).
2. V.S. Savenko, *Natural and Anthropogenic Sources of Atmospheric Pollution* (VINITI, Moscow, 1991), 211 pp.
3. A.A. Vinogradova, Izv. Ros. Akad. Nauk, Fiz. Atmos. Okeana **29**, No. 4, 437–456 (1993).
4. K.A. Rahn, Atmos. Environ. **15**, No. 8, 1457–1464 (1981).
5. K.A. Rahn and D.H. Lowenthal, Science **228**, No. 4697, 275–284 (1985).
6. K.Ya. Kondrat'ev, ed., *Aerosol and Climate* (Gidrometeoizdat, Leningrad, 1991), 542 pp.
7. V.E. Zuev, B.D. Belan, D.M. Kabanov, et al., Atmos. Oceanic Opt. **5**, No. 10, 658–663 (1992).
8. B.D. Belan, Atmos. Oceanic Opt. **6**, No. 2, 124–135 (1993).
9. N.A. Damburg and L.L. Pelekis, in: *Nuclear Physics Methods of Analysis in Environmental Monitoring* (Gidrometeoizdat, Leningrad, 1987), pp. 47–48.
10. S.M. Katchenkov, *Minor Chemical Elements in Sedimentary Rocks and Oils* (Gostekhizdat, Leningrad, 1959), 271 pp.
11. D.P. Partsev, I.A. Danilychev, A.A. Bekker, and A.A. Pavlov, Tr. Tsentr. Gidrometeorol. Obs., No. 19(2), 19–24 (1987).
12. P. Bacci, M. Del Monto, A. Longhetto, et al., J. Aerosol Sci. **14**, No. 7, 557–572 (1983).
13. R.E. Bickelhaupt, Envir. Sci. and Technol. **9**, No. 4, 336–342 (1975).
14. J.W. Winchester and G. Nifong, Water, Air, and Soil Pollut. **1**, No. 1, 50–64 (1971).
15. S.K. Friedlander, Envir. Sci. and Technol. **7**, No. 3, 235–240 (1973).
16. W.M. Henry and K.T. Knapp, Envir. Sci. and Technol. **14**, No. 4, 450–456 (1980).
17. D. Havlicel, R. Pribil, and B. Kratochvil, Atmos. Environ. **23**, No. 3, 701–706 (1989).