CHEMICAL COMPOSITION OF INDUSTRIAL AEROSOL IN SOME REGIONS

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We present here data on aerosol chemical composition obtained from onboard the airborne laboratory when sounding the industrial emission plumes in some regions of Russia and Kazakhstan. It is shown that some ingredients in the plumes had concentrations exceeding the values known from literature. The enrichment coefficient of some elements in plumes is calculated relative to their concentration in ambient air at the same height.

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-EB. 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 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_4^{2-}	–"–	2.00	15
NO_3^-	–"–	0.60	10
F^-, NH_4^+, NO_3^-	ionometry	0.20	10

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The laboratory is now accredited in the Russian Standard Agency, and the techniques are certificated in the Institute of Standards (Ekaterinsburg).

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. Comparison of the results obtained at different enterprises has revealed a drawback in the technique of the airborne laboratory use as a complex.[8] The point is that the samples were collected just near the stack mouth in order to catch even giant particles emitted into the atmosphere. Then it occurred that many gaseous substances are not yet condensed at such a short distance, and, hence, they are not settled on the filter. Such substances are NO, NO_2, and SO_2 which have the dew point[19] from 35 to 155°C. Therefore, these substances would condense and transform to aerosol particles at the distances proportional to temperature of the emitted air, depending on the heating of the emission jet from the stack. Thus, one should carry out sounding of a plume at least twice: near the stack mouth, in order to efficiently collect the solid components, and at some distance, in order to collect the condensed ingredients. Evidently, using the difference, one can additionally estimate the composition and volume of the gaseous component of the plume. As to the distance, when the second section is to be done, it should be determined empirically in the specially prepared experiment.

Although the concentrations of aerosol chemical components measured in the plumes are of certain interest, they are not completely informative because the amount of pollutants emitted into the atmosphere depends on the source power, meteorological conditions, solar radiation that favors the transformation of impurities, etc. The air samples were additionally collected at the same heights outside the plume, hence, one can estimate the enrichment of the ambient air by the emissions. These data are shown in Table II.

It follows from Table II that the excess of some ingredient concentrations in the plume over their concentration in the ambient air can vary from 2642 (Carriage-Building Plant, Nizhnii Tagil) to the background ones, equal to unity. The average enrichment coefficients for the water soluble fraction are greater than those for metals. The exception is the ion SO_4^{2-} and Zn, respectively. Possibly, it is the effect of the joint mass, which appears in the free atmosphere due to condensation, chemical reactions, and moistening of the particles, while the ash or soil fraction is hydrophobic.[20] As is seen from Table II, in the majority of events the ratios between the concentrations in plume and background values are within the range from ten to hundred.

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_4^{2-}	<	<	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_4^{2-}	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	–

TABLE II. Ratios of concentrations of aerosol components in plumes and background conditions at the same height.

Chemical elements	City														Maximum
	Khabarovsk		Ermak	Pavlodar						Nizhnii Tagil					
	Plant														
	Power heat station-1	Power heat station-3	Power heat station	Power heat station-1	Power heat station-2	Power heat station-3	Aluminum Plant	Tractor Plant	Power heat station	Coke battery plant	Power heat station	Carriage building plant	Ural chemical plastpolymer plant	Metallurgical works	
F^-	–	–	–	–	–	–	–	–	–	21	208	344	1136	<	1136
Na^+	133	30	8	7	117	4	<	8	<	260	<	75	<	<	260
K^+	256	99	8	2	200	6	55	2	48	<	<	132	<	<	256
Cl^-	138	92	10	70	93	55	73	55	40	72	<	2642	282	109	2642
Br^-	<	<	114	2	2	1	33	15	14	12	<	288	136	8	288
NH_4^+	<	1733	49	2	33	18	28	13	8	442	<	2272	<	<	2272
NO_3^-	<	<	75	2	1	1	<	1	1	8	59	353	<	55	353
SO_4^{2-}	<	<	42	3	89	22	2	5	4	23	<	66	<	<	89
Hg^{2+}	8	<	32	1	5	2	1	4	2	15	<	4	18	124	124
As^{5+}	<	187	59	99	40	57	2	30	2	<	20	<	10	<	187
Zn^{2+}	67	45	5	1	7	1	4	1	1	<	<	<	<	27	67
Cd^{2+}	<	<	1	<	<	<	<	<	<	<	<	<	<	50	50
Al	248	133	177	84	55	61	147	38	74	122	<	200	<	211	248
Ca	187	112	319	78	<	78	156	36	134	135	162	264	87	1	319
Fe	170	59	167	81	60	81	155	22	77	51	<	39	20	77	170
Mn	37	28	33	53	13	2	97	6	2	68	<	3	<	<	97
Mg	208	98	4	<	<	5	1	1	<	188	76	655	95	25	655
Si	634	113	155	82	55	102	198	71	74	83	<	<	<	<	634
Pb	<	<	27	140	<	75	180	<	<	<	<	<	<	500	500
Cr	<	13	125	3	17	<	46	18	21	103	3	186	66	103	186
Ni	160	27	–	–	–	–	–	–	–	10	13	1	7	78	160
Cd	<	167	189	86	<	<	172	<	87	–	–	–	–	–	189
Cu	280	10	22	<	<	2	1	<	<	17	34	9	12	167	280
V	50	8	67	33	<	33	80	<	7	30	32	65	43	<	80
Zn	1800	640	390	100	<	105	762	23	1	–	–	–	–	–	1800

The enrichment coefficients are usually calculated relative to the element content in soil or fuel,[1–3] so we have nothing to compare the data of Table II with. Nevertheless, they are of interest, because they show the contribution into the pollution of the region and with what ingredients coming from a particular source.

As follows from the above, the anthropogenic aerosol includes many toxic elements to be regulated in content, the concentrations of which reach high values in plumes, and the enrichment relative to the background values can be thousand times, that is indicative of the technologies and fuels used at the enterprises.

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