Some Characteristics of Dust Particles in Atmosphere of Kemerovo City According to Pollution Data of Snow Cover

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Abstract. The given paper presents the study results of solid particles contained in snow samples, taken on 10 sites in Kemerovo city in spring 2013. The sites were chosen in such a way as to prevent particles flow into the snow cover in other ways, except with atmospheric precipitation. Kuzbass Botanical Garden was chosen as the check point. In 7 out of 10 sampling sites on the territory of Kemerovo city the presence of particles that are particularly dangerous for human health was found. In one of the areas the particles of 200-400 nm size and with a specific surface area of 14,813.34 cm^2 / cm^3 were detected in ecologically significant quantity (8%).

1. Introduction

Kemerovo Region is located in the south-eastern part of the West Siberian Low Land and is among other regions of Russia which endure the greatest development pressure on the natural environment – here 1,560 industrial enterprises are located [1], and they release thousands tons of contaminants (pollutants) into the atmosphere.

As follows from the *Report on Environment Situation and Protection Measures in Kemerovo Region in 2012* [2], the climate peculiar properties and the geographical location of the Kemerovo region contribute to the fact that most of the industrial pollutants, with the effect of deposition on the surface, are not driven out of the area, but precipitate on terrestrial ecosystems of the Kuznetsk Basin. In the immediate vicinity of emission sources (industrial towns) during light winds the photochemical smog is produced, causing the formation of secondary pollutants, which together with the main ones impact negatively the public health and the biosphere conditions.

For a long time Kemerovo city has contuniued to be one of the most polluted cities of the Russian Federation, especially in terms of specific pollutants, and in a disease structure has a very high proportion of ecological dependent diseases among the population [3-7].

The objective of this work was to undertake the analysis of snow samples taken on 10 sites in Kemerovo in spring 2013 (March 18-21).The selected sites were located both in highly polluted areas, and in relatively clean ones. The aim of the analysis was to identify the total amount and dispersed composition of pollutants for various parts of Kemerovo, and to determine the content of particles, the size of which is the most dangerous for health (less than 10 microns) and also to evaluate heavy metals content in a water-soluble form. In the first case a laser granulometry method was used, and in the second – the one of a high resolution mass spectrometry.

2. Materials and methods

Snow samples were taken on 10 sites of Kemerovo city. A checkpoint 10 designed to characterize the background-contamination of snow, was chosen on the territory of Kuzbass Botanical Garden (Figure 1 and Table 1).

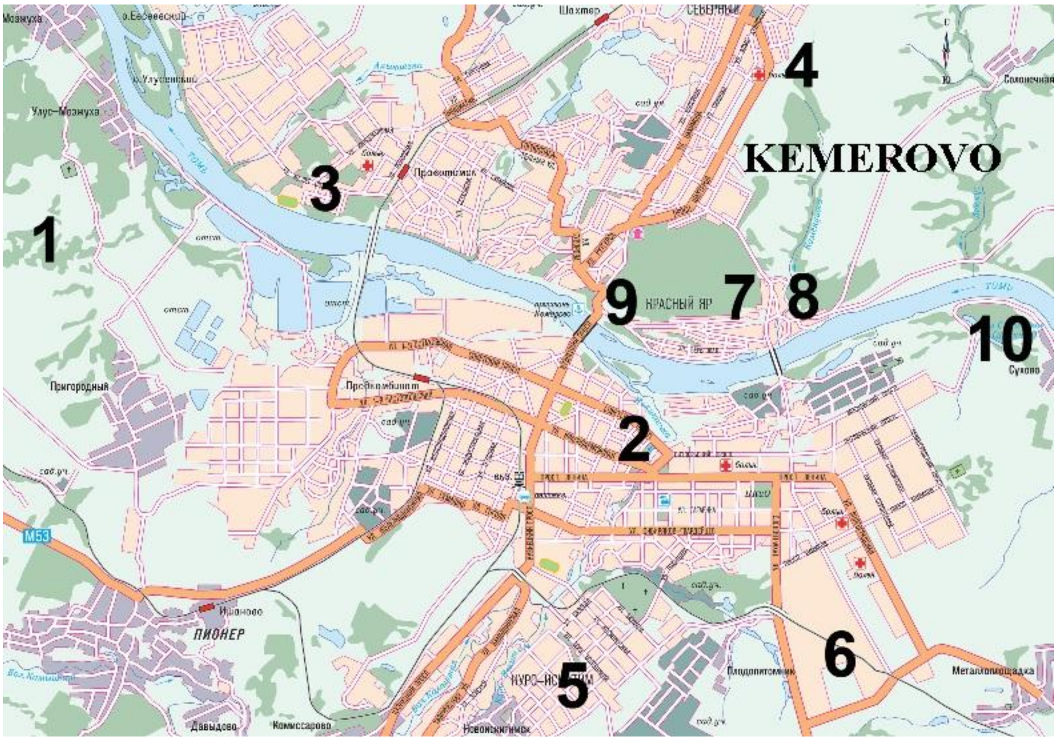

Figure 1. A schematic map of snow sampling locations in Kemerovo city (deciphering is given in Table 1)

Table 1. Areas of sampling in Kemerovo

Stations	Description of sampling locations
1	Outskirts of Zavodskoy district. St. Shaturskaya. Production cooperative "Kemerovo mounting cooperative-1" (KMC-1)
2	Centralnii district. St. Ostrovskogo. Recreation Park.
3	Kirovskii district. St. Initiative. Birch Grove.
4	Outskirts of Rudnichnii district. Miners Avenue. On a wasteland
5	Outskirts of Yuzhnii district. Between the parking lot and garage cooperative.
6	Outskirts of Leninskii district. A wasteland between unfinished buildings and warehouses.
7	Pinery.Central part. Rudnichii district. .
8	Pinery.Eastern part. Rudnichii district.
9	Pinery.Western part. Rudnichii district.
10	Leninskii District. Territory of Kuzbass Botanical Garden

Snow samples were taken in early spring 2013 prior to the period of an active snowmelt. The used snow sampling tubes allowed to capture snow to a full thickness of the snow layer. Snow samples were placed in sterile containers of 1 liter capacity. In a couple of hours, after the snow melted in the container, 60 ml of liquid was taken from each sample to be analyzed with a laser particle analyzer Analysette 22 NanoTec (company Fritsch), allowing in a single measurement to establish a particles size distribution scheme, as well as to determine their shape and some morphometric parameters. Measurements were carried out in a «nanotec» mode with «carbon / water 20^0C» settings.

Also 10 ml of liquid was taken from each sample and analyzed on a high resolution mass spectrometer with the inductively coupled plasma Element XR (Thermo Scientific). The measurements were implemented using the procedure CV 3.18.05-2005 FR.1.31.2005.01714 (method for measuring the elemental composition of drinking, natural, waste water and precipitation by mass spectrometry with ionization in inductively coupled plasma).

For comparison with the results of snow samples analysis the model estimate of total winter precipitation of dust particles emitted into the atmosphere of Kemerovo by industrial plants and motor vehicles was conducted. Simulation was carried out both for sampling sites and for the whole city to obtain schematic maps of snow dust pollution.

For calculations a local long-term model of aerosol deposition on the underlying surface was used [8]. The model is implemented in software and is integrated into the program complex "ERA" (www.logos-plus.ru) which is widely used for regulatory calculation of air pollution in the Siberian region. Thus, regulatory inventory data on emissions sources accumulated within the formats of this complex may be used for research.

In particular, the parameters of emission sources for this very calculation are taken from the consolidated city volume of maximum permissible emission (MPE) of Kemerovo [9]. Totally, benchmark sources inventory data consider about 200 industrial enterprises (3,200 stationary sources), that emit into the atmosphere 185 pollutants, incorporated into the list [10], a portion of which is dust particles. Automobile transport is specified in the benchmark data in the form of 195 line sources, representing straight portions of the city's main roads, and of 60 point sources, set for controlled junctions. It should be noted that vehicle emissions are presented in inventory data only with settling substances produced by fuel combustion in engines (soot and benzapyrene). At the same time the road in winter time is a source of dust particles formed as a result of icing reagents, roadbed wear products, brake pads, tires, etc. emitting from the roadway. Therefore, the sampling points are taken far enough from the roads, where the influence of these unaccounted emissions is negligible.

It should be also noted that using for dispersion modeling emission sources inventory data relate to the operation mode of industrial plants and transport in 2003. Changes in sources composition occurred within the last 10 years were considered in an expert way, taking into account performance rate changes of enterprises and the growth of vehicles number and structure.

For each source all emitted pollutants with sedimentation effect are aggregated into a single pollutant "suspended solid", using a special software procedure and further, for each source, they emission rates are automatically divided into 5 fractions of particles with dimensions: up to 1 micron; 1-10 micron; 10-50 microns; 50-100 microns and more then 100 microns. For each fraction the particles loss rates (deposition velocities) are calculated depending on the average density of particles, surface roughness parameter and average winter meteorological conditions.

Meteorological parameters that define conditions of pollutants dispersion in the atmosphere are obtained by processing results of standard observations data received at Kemerovo Weather station for the period from the 1st November 2012 to the 21st March 2013 (data taken from the site www.rp5.ru). For the indicated period, based on these data, a real wind rose is built and the wind speed distribution defined.

3. Results and discussion

Previously, while analyzing suspended particles contained in the city atmosphere, the authors divided them by particle sizes, based to the laser analyzer data, into seven classes: 1) up to 1 micron (corresponding to PM1), 2) from 1 to 10 (corresponding to PM10), 3) from 10 to 50, 4) from 50 to 100, 5) from 100 to 400, 6), from 400 to 700, 7), more than 700 microns, which allows to correlate the environmental hazard and particles size [11]. The first two classes are the most dangerous in this case,

and relates to particles of an average danger the third dimension class [12].
The particles size distribution of suspended fractions, found in snow of Kemerovo city, is given in Table 2.

Table 2. Distribution of particles in snow by fractions in sampling stations

∅, µm	1	2	3	4	5	6	7	8	9	10
Less than 1	0.2-0.4 8%									
1 - 10		1.5-2.5 2% 2.5-3.5 3% 4-5 8%				1.5-2 8% 4-8 77%	2-3 3% 4-7 8% 7-15 34%	4-5 4%		
10 - 50	20-30 2% 30-50 28%	10-15 23% 18-25 58% 30-40 6%	15-20 85% 25-35 15%	15-100 100%		18-25 15%	20-40 39%	12-20 48% 25-35 25% 35-50 10%	35-50 4%	25-35 2%
50 - 100					60-200 100%		40-70 9%	55-80 13%	55-90 5%	
100-400							80-150 7%			150-200 3%
400-700									500-750 70%	350-500 18%
More than 700	800-1000 62%								800-1000 21%	800-1000 77%

As shown in Table 2, the most contaminated regions of Kemerovo, in terms of having a significant number of particles of 1 and 2 size classes are - 1 (KMC factory), 2 (city center), 6 (industrial area) and 7 (part of pinery, which is adjacent to the transport interchange). All these areas are characterized with the presence of stationary (industrial zone) and mobile (transport) sources of dust particles emissions

It should be noted that suspended particles found in the vicinity of the station 1 have a sufficiently large arithmetical mean diameter (621.62 µm), but at the same time have an extremely high surface area (about 15,000 cm^2 / cm^3) due to the presence of particles with less than 1 micron size, which makes them predictively dangerous to the public health (Table 3).

Relatively favorable areas for living include 9 and 10 sites, which is not surprising, since both areas are adjacent to the green zone. Station 5 is located on the edge of the neighborhood and is also characterized with particles of a large diameter (arithmetic average diameter – 124.16 µm) and a low specific surface area (505.46 cm^2 / cm^3).

The rest of sampling sites in Kemerovo (3, 4, 5, 8) showed a strong (on average, their share is more than 90%) degree of air pollution with particles of a 3 size class, possessing an adverse health effects and which are likely to be soot from the power stations and particles of vehicle exhaust [12].

Table 3. Physical parameters of dust particles contained in snow in different sampling sites

Parameters /sampling site	1	2	3	4	5	6	7	8	9	10
The arithmetic mean diameter, (μm)	621.62	18.64	18.01	39.19	124.16	8.12	27.07	27.23	647.06	839.18
Mode (μm)	1003.38	21.92	16.29	41.21	125.49	5.76	25.43	16.29	619.27	1003.38
Median (μm)	928.44	21.29	16.49	37.41	122.06	5.78	20.95	18.58	633.59	957.44
Deviation (μm)	204880.3	65.16	23.46	187.83	692.77	40.7	842.79	275.86	48925.25	63444.13
RMS deviation (μm)	452.64	8.07	4.84	13.71	26.32	6.38	29.03	16.61	221.19	251.88
Coefficient of deviation (%)	72.82	43.3	26.88	34.96	21.19	78.57	107.24	60.9	34.18	30.01
Specific surface area, cm² / cm³	14813.34	4817.44	3518.89	1733.87	505.46	10838.21	4783.45	3071.82	167.97	134.16

Table 4. Average concentrations of S (μg/L) toxic metals in snow samples on sampling sites in Kemerovo [a]

	Cd^{111}	Ba^{138}	Pb^{207}	Al^{27}	Cr^{52}	Mn^{54}	Fe^{56}	Ni^{59}	Cu^{63}	Zn^{66}
1	0.03± 0.01	2.04± 0.31	0.06± 0.01	1.33± 0.2	0.18± 0.03	4.24± 0.64	1.03± 0.16	1.35± 0.2	1.86± 0.28	14.19± 2.13
2	0.03± 0.01	1.9± 0.28	0.19± 0.03	0.76± 0.11	0.25± 0.04	4.44± 0.67	0.53± 0.08	0.53± 0.08	0.46± 0.07	25.2± 3.78
3	0.11± 0.02	1.55± 0.23	0.14± 0.02	1.49± 0.22	0.360 .05±	10.9± 1.64	1.62± 0.24	0.54± 0.08	0.86± 0.13	27.6± 4.14
4	0.04± 0.01	5.64± 0.85	0.65± 0.1	6.06± 0.91	0.52± 0.08	12.9± 1.93	4.15± 0.62	0.45± 0.07	0.17± 0.03	54.61± 8.19
5	0.03± 0.01	8.42± 1.26	0.3± 0.04	4.21± 0.63	0.46± 0.07	33.1± 4.96	3.38± 0.51	2.7± 0.41	1.86± 0.28	4.87± 0.73
6	0.01± 0.002	0.84± 0.13	0.05± 0.01	3.89± 0.58	0.13± 0.02	2.03± 0.3	1.63± 0.25	0.42± 0.06	0.6± 0.09	2.58± 0.39
7	0.01± 0.002	0.72± 0.11	0.03± 0.01	0.38± 0.06	0.06± 0.01	1.41± 0.21	0.23± 0.03	0.27± 0.04	0.45± 0.07	1.99± 0.3
8	0.02± 0.003	1.91± 0.29	0.1± 0.01	1.35± 0.2	0.24± 0.04	20.8± 3.11	1.11± 0.17	0.45± 0.07	0.73± 0.11	10.37± 1.56
9	0.03± 0.01	1.89± 0.28	0.1± 0.01	1.15± 0.17	0.23± 0.03	10.4± 1.57	0.8± 0.12	0.52± 0.0.08	0.33± 0.05	10.1± 1.51
10	0.01± 0.002	1.01± 0.15	0.05± 0.01	0.39± 0.06	0.13± 0.02	1.93± 0.29	0.2± 0.03	0.43± 0.06	0.47± 0.07	3.92± 0.59

[a] inaccuracy of made analyzes is estimated by a mean-square deviation, the value of which does not exceed 1-5%, when determining the elements listed in the table

Study results of heavy metals in dissolved form obtained by the method of high resolution mass spectrometry are shown in Table. 4.

Mass spectrometry data indicate low concentrations of heavy metals in dissolved form in snow, but it doesn't exclude their being in the form of solid particles. A more comprehensive conclusion may be made after electron microscopy and energy dispersive analyses of suspended particles are performed.

Figure 2 shows isolines of modeling estimation of pollution P (g/m^2) of the snow cover with dust particles emitted by industrial plants and main highways for the winter period of 2012-13 yrs.

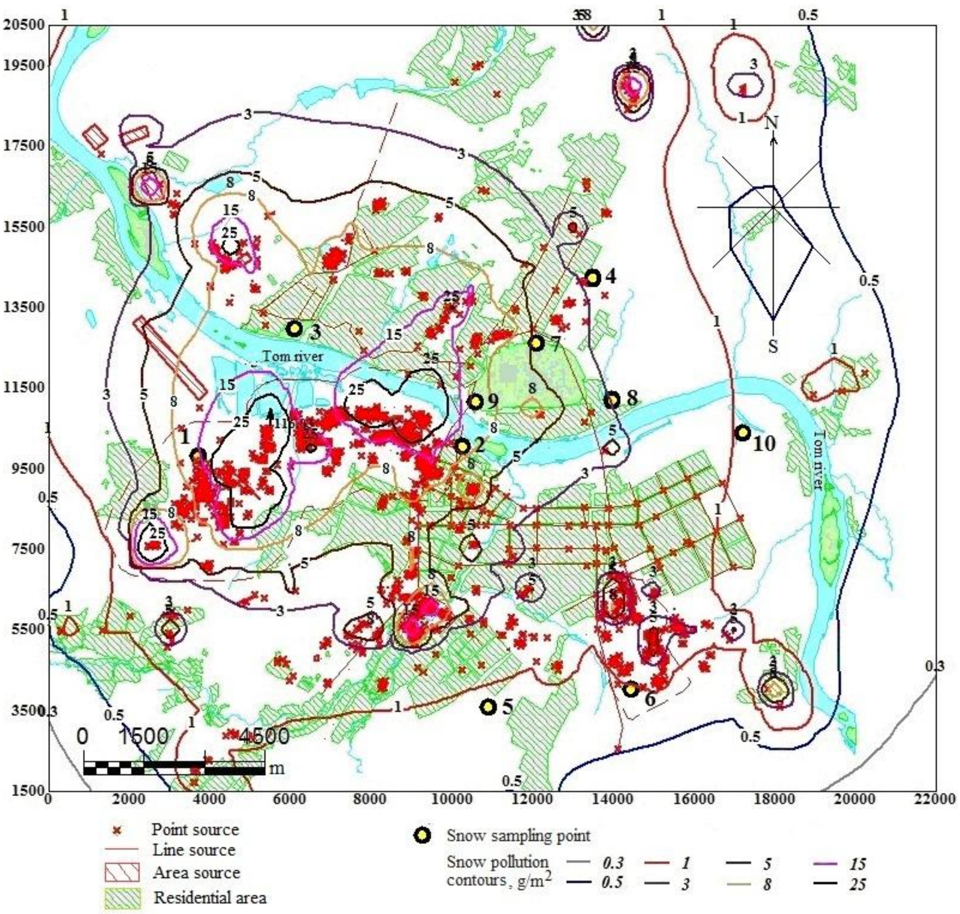

Figure 2. Isolines of calculated pollution P (g/m^2) of the snow cover with dust particles of industrial sources and of vehicles for the winter period of 2012-13 yrs

Figure 3 shows a comparison of the average sums of toxic metals concentrations S, μg/dm^3 (sum of columns of Table 4) and the estimated value of the total dust load P g/m^2 on the snow cover for the winter period on sampling sites. Since the concentration S is a result of municipal emission sources, then S should depend upon the total content P of dust particles in snow, calculated with involvement of all the accounted emissions sources data.

Because dimensions of values S and P are different, and Figure 3 is only intended to demonstrate the trends of snow pollution on sampling sites, the S value is multiplied by 0.17 to bring the average values of calculations and measurements to a single value.

Samples, taken on sampling sites 4 and 5 and containing the maximum concentration of metals according to measurements data, appeared to be notably clean according to modeling estimates. This is most likely due to the fact that these areas are currently under the most intense city housing, which is not accounted for in the official inventory data for 2003 emissions.

The obtained data allow to conduct an initial environmental-hygienic zoning of Kemerovo city according to dimension of particles contained in atmospheric suspension. As a result, based on the size composition of suspensions and their potential health hazard, it becomes possible to allocate tentatively three groups of areas:

- unfavorable for living (containing particles of 1, 2 and 3 size class) – sampling sites 1, 2, 6, 7;
- tentatively unfavorable for living (containing 3 and 5 size class particles) – sampling sites 3, 4, 8;
- conditionally favorable for living (containing mainly particles of 5, 6 and 7 size class) – sampling

sites 5, 9, 10.

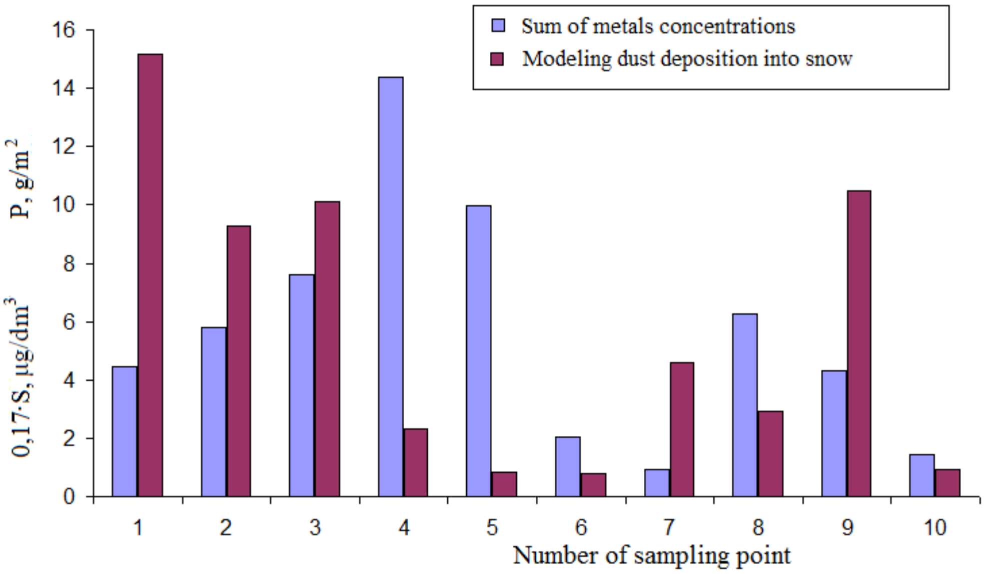

Figure 3. Comparison of the calculated dust load on the snow cover P with the overall concentration of metals S on sampling sites

4. Conclusion

Analysis of the size composition of atmospheric suspensions in Kemerovo confirms its status of a town with a strong anthropogenic (industrial and automobile transport) pressure, which is manifested by the presence of particles of dangerous size classes in the atmosphere of almost all city districts.
On the whole, our data are consistent with the results of the constant monitoring of Kemerovo city atmosphere (in terms of suspended solids and heavy metals) contained in the "Report on the status and protection of the environment of the Kemerovo region in 2012" Year (Report 2013).

The authors think that the results obtained in this work should be considered when developing the ecological security strategy for Kemerovo Region, the implementation of which is scheduled for near-term outlook.

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