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Technogenic Atmospheric Pollution of the Karakan Coal Cluster

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Abstract

The paper presents the results of the study on the effects of objects of the Karakan coal cluster (Kuzbass) on the atmosphere. Observation of the composition of atmospheric suspension was carried out for 3 years – from 2012 to 2014. It was demonstrated that particles of less than 1 and 10 μm were found in a considerable proportion (to 50 and 71 %, respectively) in atmospheric suspension of a number of sampling points throughout the observation period. These points are located near technological and motor roads, quarries. The qualitative composition of suspended particles demonstrated high contents of coal particles with multiple inclusions of native metals and their compounds (including rare earth elements). Rare-earth phases have a potentially hazardous inhalable size – from nanoscale to tens of microns. As a whole, as demonstrated by our three-year observation, all studied regions of the Karakan coal cluster are unfavourable for living from the viewpoint of air quality.

Key words: atmospheric suspension, Kuzbass, microparticles, coal, technogenic particles

INTRODUCTION

Coal dust is one of the strongest air pollutants in mining sites with a pronounced negative effect on human health [2, 32]. Particle transport processes in the atmosphere are extremely ambiguous and heterogeneous [7, 13–16, 18, 21–24, 29–31, 33]. There is a belief that the maximum sickness rate on the majority of classes of diseases is observed during treatment of coke and fat coal that are biologically aggressive and most adverse in fibrogenic respect and on dust factor [9, 25, 36, 38].

That, it was demonstrated that hygienic assessment of employment conditions of people working under conditions of constant atmospheric pollution with coal dust was characterized by a set of unfavourable factors of the working environment and labour process, which is accompanied by increased illness rates [9, 19]. An extremely high level of the effects of coal dust on the environment and disease incidence has been noted in China [2]. Additionally, it is observed that the negative impact on the environment from coal pollution is so great that it can be compared with atomic stations [8].

A work goal is to assess the effect of a large coal object on atmospheric suspension composition under the conditions of a 3-year observation.

EXPERIMENTAL

The Kuznetsk (Kuzbass) coal basin that is one of the biggest coal basins in the world was selected as a study object (as a large technogenic source of dusting).

The most complex environmental conditions are developing in the territory of the Karakan coal cluster where 15 opencast coal mines are planned to be built.

It is located in the northeastern part of the Erunakovo geologic and economical district of Kuzbass, 35 km from the city of Belovo and occupies the northwestern part of syncline of the Karakan deposit. Coal is mined by open-pit method, overburden rocks and coal are transported to coal depots by motor transport, additionally, and excavator loading of coal to railway wagons is carried out.

The snowpack is considered by us as deposit environment accumulating for a certain period of time chemical elements contained in the composition of emissions of coal mining enterprises. The dynamics of distribution of harmful impurities in the environment can be traced by studying the chemical composition of snow samples and comparing it to that of enterprises emission [3].

The selection of snow samples to account for contamination was carried out in perpendicular to the Karakan ridge along the wind rose from the west to the east. The total length of the transect is 12 km, on which 7 sampling points are located (Fig. 1).

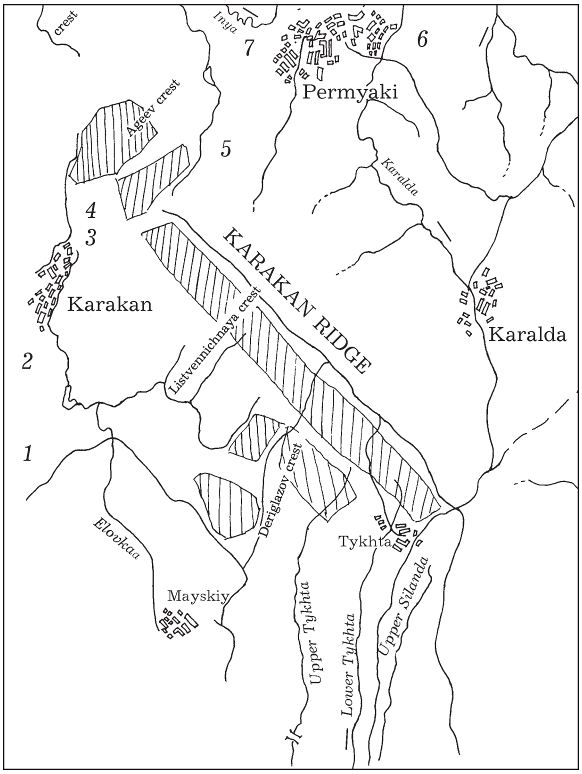

Fig. 1. Sampling places of snow samples in the area of the Karakan coal cluster. Existing and under construction coal sections are shaded. See text for transcript of sampling points.

Point *1.* The neighbourhood of the Yevtyukhovo village, in a birch forest, 250 m from a motor road. Anthropogenic impacts are associated with car emissions that are somewhat delayed by a rare birch forest. Visible changes in the landscape and business activities did not happen for three years of observations.

Point *2.* The neighbourhood of the Karakany village, a technological road from the cut to the coal warehouse. The latter began to be built just in 2012, and currently it is the main source of pollution of the surrounding territory.

Point *3.* Near the Dunayevsky section, between technological roads. In 2012, the section was found under development; technological roads are used year-round and represent the major sources of technogenic pollution.

Point *4.* Between Dunayevsky and Permyaki sections, virgin soil, disturbance of vegetation occurred by repeated ploughing, located in the territory of the mining allotment of the section Dunayevsky. In 2010, the area was a vast accumulation. With the development of the section, the deposit territory constantly decreases. The main source of pollution is ash transport of particles from the quarry and nearby dumps.

Point *5.* Between the western slope of the Karakan ridge and the Permyaki village, 400 m to the side of the Karalda village. The territory is presented by open willow and aspen thickets, with numerous glades. It is protected from the effects of dumps and sections by the Karakan ridge and can be considered as reference.

Point *6.* The eastern edge of the Permyaki village. The territory is partially a paddock, partially – a deposit. The main factor of winter pollution is particles of carbon black, coal, chemical elements generated from household coal combustion.

Point *7.* A road in the direction of the Novokhudyakovo village, 1.5 km from the Permyaki village to the north. The area is a vast meadow stretching down to the river Inya. The former is protected from emissions from coal sections and the Permyaki village by large forest plantations and can be considered as a reference.

Cutting out the cores to the depth of the snowpack was carried out using a cylindrical sampler ∅ 50 mm. An area where a triangle with sides of no less than 10 m could be built was selected for sampling. Discount areas 1 × 1 m were located in the vertex of the triangle. Three discount areas were obtained. Sampling was carried out by the envelope method – by 5 samples from each discount area. The snow core was collected in the full depth of the snow cover. All 15 samples were mixed and formed one weighted-mean sample. Cups with samples were placed in a refrigerator prior to analysis.

To study suspended particles a complex method of study of atmospheric suspensions particles including laser granulometry, high resolution mass spectrometry, scanning electron microscopy with energy dispersive analysis was used.

In two hours, when the snow in containers melted, 60 mL of the liquid was collected from the container and analysed using an Analysette 22 NanoTec particle analyser (Fritsch Company) that allowed setting particle size distribution during one measurement, and defining their shape and a number of morphological parameters. The measurements were carried out in nanotech mode using a carbon/water 20 °C setup. Also, 10 mL of the liquid was collected from each sample and analysed using Element XR inductively coupled plasma high resolution mass spectrometer (Thermo Scientific). The method TV 3.18.05–2005 FR 1.31.2005.01714 was used for the measurements (Method of measurement of the elemental composition of drinking, natural, waste water and atmospheric precipitations by means of mass-spectrometric technique with inductively-coupled plasma ionization). Samples were filtered from a solid precipitate using a filter of 0.47 μm. Substantial analysis of suspensions was performed on an lSMZ1000 light microscope (Nikon, Japan) and S-3400N scanning electron microscope (Hitachi, Japan) with Ultra Dry energy dispersive spectrometer (Thermo Scientific, the USA).

Research was conducted using equipment of the Center of Collective Use of the "Interdepartmental Centre of Analytical Control of the Environment" of the Far Eastern Federal University.

RESULTS AND DISCUSSION

Granulometric analysis

The composition of snow adequately reflects atmospheric pollution. This indicator becomes especially informative in regions with steady multi-month snowpack. Accumulation in snowpack of elements that dominate in the composition of atmospheric aerosols is typical in north regions during winter season. The snowpack quality clearly demonstrates the effect of various sources of atmospheric air pollution above ground, and allows tracking pollutant space distribution on the territory and receiving a reliable picture of zones of influence of specific technological objects.

According to the modern classification [5], atmospheric suspensions are divided by particle sizes, according to our classification, by seven classes (μm): <1, 1–10, 10–50, 50–100, 100–400, 400–700, >700, which allows correlating environmental hazard and dimensionality [4]. The first two classes are considered to be most hazardous in this case, and the third size class should be referred to medium hazard particles [5]. Specific surface, from the environmental hazard viewpoint, is the second most important particle feature. According to the laser analyser data, particles were divided by us according to specific surface values (cm^2/cm^3): 1) more than 7000 (most hazardous), 2) from 1000 to 7000, and 3) less than 1000 (least dangerous). Table 1 gives particle distribution in snow by sampling points.

More detailed features of suspension particles detected in snow and also obtained using a laser detector are given below (Table 2).

According to the results of 2012–2014, a territory between two technological roads (near the Dunayevsky section, point *3*) is characterised by the most adverse conditions. Here, nanoparticles of 100 nm (50 %) and microparticles up to 10 μm (to 100 %) are consistently detected in the samples. Most likely, their origin is related to the coal-mining industry (crushing, loading). Open coal mining is most likely an alleged source of these nanoscale particles, which is not something unusual during similar mining processes [3].

Probes from sites *1–4* and 7 have significant specific surface areas (to 1 832 750 cm^2/cm^3),

TABLE 1

Particle distribution in snow by fractions along sampling points during the period of 2012–2014, %

Particle diameter, μm	Years	Sampling points, %						
		1	*2*	*3*	*4*	*5*	*6*	*7*
<1	2012	3	2	24^a	5	1		2
	2013			15^a	50^a			
	2014		5	34^a				
1–10	2012	3	28^b	44^b	45^b	11		17^b
	2013	7	4	31^b	46^b			
	2014	71^b	20^b	66^b	6	2		12
10–50	2012	94	20	32	50	20	52	70
	2013	93	56	54	4		100	
	2014	29	46		47	8	100	40
50–100	2012		50			10	48	
	2013		40					
	2014		32		32	4		48
100–400	2012					13		
	2013							
	2014				15			
400–700	2012					6		
	2013					100		
	2014							
>700	2012					45		3
	2013							
	2014					76		

[a]High danger for human health.

[b]Middle danger for human health.

which also indicates adverse conditions for the adverse living conditions due to a serious load for respiratory organs. Their high health hazard is driven by the ability to sorb a large number of toxins on its surface [10]. Regions that are found between coal strip mines are characterized by the finest fractions.

According to a number of morphometric particle indicators (diameter, surface area), regions near the Karakany village, technological road from the cut to the coal warehouse *2* in the eastern outskirts of the Permyaki village *6* can be referred to the number of relatively adverse areas.

In dimensions of suspensions in almost all points, particles of the third of fourth size classes are detected in meaningful proportions (10–100 μm). They are most likely exhausts of cargo motor transport [5]. Although these particles do not refer to the most hazardous dimensional forms (to 10 μm), they have sizes that allow them falling into and staying in the respiratory tract increasing the load on the lungs.

Large size particles (from 100 μm and higher) with low specific surface areas (to 1000 cm^2/cm^3) are only observed in the points that are found far from mining and coaling sites (sites *5* and *6*).

As a whole, it is necessary to ascertain the fact that virtually all the points located near the Karakan coal cluster (except for the leeward side of the Karakan ridge, point *5*) are harmful for health by atmospheric suspension particles.

Numerous inclusions of native elements and their compounds have been found in coal dust; however, the abundance of mineral phases containing rare earth elements (REE) is especially noteworthy. Rare earth phases have a size from nanoscale to tens of microns. They are mainly

TABLE 2

Morphometric parameters of suspension particles contained in snow in various selection regions for the period of 2012–2014

Parameters	Years	Latitudinal transect						
		1	*2*	*3*	*4*	*5*	*6*	*7*
Arithmetic mean diameter, μm	2012	15.98[b]	33.19[b]	7.47[a]	14.59[b]	468.95	44.1[b]	38.8[b]
	2013	28.50[b]	37.23[b]	11.83[b]	5.06[a]	476.45	23.1[b]	–
	2014	10.25[a]	27.64[b]	4.45[a]	49.11[b]	839.92	13.76[b]	46.21[b]
Mode, μm	2012	16.91	55.46	15.12	26.39	1003.38	69.29	15.12
	2013	41.20	30.62	21.92	8.99	477.55	23.61	–
	2014	8.35	57.55	7.47	66.76	1003.38	10.05	80.38
Median, μm	2012	16.43	30.15	4.54	21.26	239.66	39.41	15.91
	2013	22.95	32.85	8.36	0.23	471.25	23.01	–
	2014	9.07	20.94	3.61	30.23	957.85	10.55	31.13
Deviation, μm^2	2012	12.49	735.21	44.46	139.48	183 993.1	639.59	15 866.16
	2013	181.87	522.42	97.57	53.09	8173.76	4.38	–
	2014	11.44	441.78	19.01	1981.33	97 716.22	106.01	1154.6
Mean square deviation, μm	2012	3.53	27.11	6.67	11.81	428.94	25.29	126.04
	2013	13.48	22.85	9.88	7.29	90.41	2.09	–
	2014	3.38	21.02	4.36	44.51	312.6	10.3	33.98
Deviation coefficient, %	2012	22.12	81.68	89.29	80.94	91.47	57.34	324.80
	2013	47.31	61.39	83.50	143.87	18.97	9.05	–
	2014	32.98	76.04	95.84	90.62	37.21	74.81	73.52
Specific surface area, cm^2/cm^3	2012	7142.07[b]	10 126.58[a]	24 903.82[a]	19 854.22[a]	1986.36	2036.59	10 340.97[a]
	2013	2924.12	2701.05	177 136.7[a]	704 498.3[a]	130.56	2617.99	–
	2014	6453.56[b]	17894.48[a]	134 844[a]	2684.1	431.52	7013.44[b]	3065.68

[a]High danger for human health.

[b]Middle danger for human health .

presented by phosphates of light REE – the composition is close to monocyte and of heavy REE – the composition is close to xenotime. Single micron-sized grains of REE silicate.

The presence itself of REE in Kuzbass coals is quite usual, especially since Kuznetsk coal was assessed as rare earth raw materials [1, 11].

A large amount of rare earth minerals in coal dust is interesting. According to experimental data, only the amount of 10–20 % of REE in coal is found as own minerals, 1–2 % – isomorphous impurities, and 80–90 % – as complex humates.

In a typical sample taken in the neighbourhood of the Yevtyukhovo village (point *1*), particles were defined in descending order: coal > natural minerals (aluminosilicates and quartz prevail) > plant detritus > Fe-containing particles (technogenic iron alloys, iron oxides, pyrite). In a sample taken near the Karakan village (point *2*), the following minerals were met in descending order: coal > natural minerals > Fe- and Ti-containing particles > hardly detectable anthropogenic particles > plant detritus. Particles containing rare earth elements as monazite were also found in samples.

The finest particles (coal microparticles totally prevail) were detected between technological roads near the Dunayevsky coal section (point *3*). Additionally, particles containing rare earth elements close to orthite by composition have also been detected in this region.

Dynamics of heavy metals in snow samples

A site situated between the western slope of the Karakan ridge and the Permyaki village with the least pollution of samples by cadmium, lead, chromium, manganese, iron, nickel,

TABLE 3

Average concentrations of toxic metals in snow samples at selection sites (average for 2012?2013), μg/L (ppb)

Sites	Cd^{111}	Ba^{138}	Pb^{207}	Al^{27}	Cr^{52}	Mn^{54}	Fe^{56}	Ni^{59}	Cu^{63}	Zn^{66}
1	0.03	2.16	0.17	0.80	0.25	6.14	3.04	0.67	2.55	11.04
2	0.04	23.0	0.23	107.60	0.41	10.29	38.33	1.58	1.58	14.72
3	0.06	0.87	0.46	0.15	0.16	5.38	17.8	1.13	2.06	120.00
4	0.02	10.0	0.20	206.90	086	9,72	27.7	1.57	1.44	22.00
5	0.01	1.37	0.08	0.27	0.06	3.73	2.25	0.53	1.63	2.75
6	0.04	0.43	0.27	0.08	0.06	19,20	3.96	0.49	1.33	108.61

zinc is distinguished at monitoring sites located near the Karakan ridge. The maximum pollution of snow samples by cadmium, lead, nickel, zinc, iron is located between the technological roads on the south west side of the Karakan ridge. Contamination level is average in other sampling points (Table 3).

Cadmium contents in monitoring sites within transects are approximately identical and amount to 0.03 μg/L (ppb). Lead content is maximum between technological roads is 0.46 μg/L (ppb). The chromium content is changed in large limits, but its maximum amount was detected in a deposit between Dunayevsky and Permyaki sections (point *4*) – 0.86 μg/L (ppb), and near a road to coal warehouses (point *2*). Manganese content is maximum at the eastern outskirts of the Permyaki village (point *6*) –19.2 μg/L (ppb). The maximum amount of iron (38.33 μg/L, ppb) was detected in samples of site *2* (outskirts of the Karakan village). The maximum content of nickel (1.13–1.58 μg/L, ppb) was detected in sites with strong technogenic pollution (points *2–4*). The nickel content in all options is in the limits. Copper is present in samples in large quantities prevails in samples of points *1* and *3* – 2.55 μg/L (ppb) and 2.06 μg/L (ppb), respectively. The maximum content of zinc (120.00 and 108.61 μg/L, ppb) was found between technological roads (point *3*) and the outskirts of the Permyaki village (point *6*).

All the studied regions of the Karakan coal cluster are unfavourable for living from the viewpoint of the material composition of atmospheric suspensions [6].

Micro-sized coal dust saturated with mineral particles and technogenic dirt was recorded in all regions. The origin of the latter is mainly related to the coal-mining industry (coal mining, crushing, loading).

The origin of rare earth phases is most likely natural – rare earth minerals often occur in coal and rocks. The frequent occurrence and predominantly phosphate occurrence form of rare earth metals in coal were earlier noted by S. I. Arbuzov [1].

By the quantitative composition (the proportion of coal particles and metal compounds) and a number of visual morphometric indicators, the following transect region can be referred to the number of most adverse: *3* (between technological roads), and to the number of relatively adverse regions – regions *2* (near a technological road), *6* (the Permyaki village) and 7 (a motor road near the village of Khudyakovo).

As is known rare earth minerals cause some professional diseases, for example, pneumoconiosis [20, 27, 34, 35, 37], which increases their potential hazard for human health.

On the other hand, other effects on living organisms, including non-toxic effects of rare earth elements on biochemical processes and positive effects on plants and tissue regeneration, have been demonstrated and discussed in literature [12, 17, and 26]. For example, it has been demonstrated that lanthanum ions are able to increase amplitudes of GABA-activated signals on CA1 pyramidal neurons of the gene observed in the hippocampus of the brain [26].

As a whole, it is noteworthy that coal dust contained in atmospheric suspensions of the Karakan coal cluster can be a source of potentially hazardous compounds, such as rare earth minerals [27, 34]. Upon combustion of this coal, these elements may fall into the air of big cities and undoubtedly affect an increase in human sickness rate and environmental pollution [35].

It is important that coal dust and REE particles are present in the nano and micro range. As is known precisely small-sized particles have the maximum reactivity right up to toxic affection.

CONCLUSION

Assessing environmental pollution of the Karakan coal cluster, it is necessary to note that atmospheric suspension particles related to highly hazardous for biological objects are contained near coal mining, stevedoring centers, and coal transportation.

Pollution level is somewhat decreased to the east to opencast coal mines located along the western slope of the Karakan ridge of opencast coal mines but increased near settlements.

Neither of the studied sites cannot be considered clean on the content of technogenic suspensions, indicating high technogenic load in the entire territory of the Kuzbass coal basin.

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