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Distribution, sources and forms of mercury occurrence in the street dust of Mezhdurechensk (Kemerovo Region)

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ABSTRACT. The aim of this study was to investigate mercury concentration and forms of its occurrence in the dust component of the atmospheric air (street dust) to assess the geo-ecological condition of the area where coal is mined, processed and transported. The mean mercury concentration of 29 street dust samples collected along a uniform network throughout the city was 36.4 ± 4.7 ng/g, with a minimum (4.6 ng/g) and a maximum (104.6 ng/g) value, respectively. This value was much lower than the mean concentration in soil samples taken previously at the same sites (58.4 ng/g) but higher than the mean concentration in snow solids (29.8 ng/g), which was likely due to precipitation that washed out mercury from the street dust and to the wind blowing.

The method of successive chemical extraction revealed a weakly bonded water-soluble form, inorganic poorly sorbed mercury compounds, an organic form of mercury, and mercury associated with minerals. The proportion of each fraction accounted for on average 10.94%, 10.32%, 44.76%, and 33.97%, respectively. Water-soluble and acid-soluble mercury forms were less common. The bulk of mercury had metal-organic and sulfide forms.

The study of mercury distribution based on particle size indicated that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction with a diameter of 20 to 50 μm contained the bulk of mercury, which stayed in suspension form for a long time before settling on the surface.

Keywords: mercury in depositing environments, forms of mercury occurrence, street dust, particle size distribution of street dust

1. Introduction

The city of Mezhdurechensk is part of the Kemerovo Region, the area of which allocates the Kuznetsk Coal Basin, the largest in the country and the world. Interest in the study of street dust arises from the functioning of the large Russian coal mining enterprises near this city (3 to 12 km). There are losses of the components of raw materials and their redistribution in environmental objects, which are hazardous for biological systems, including humans. Even with a possible slight decrease in coal production in Kuzbass, a rapid improvement of the ecological condition in the region should not be expected because it takes a long time and requires appropriate measures to reduce the level of compounds and substances accumulated in depositing environments. Mercury concentrations in depositing environments (soil and dust) of urban agglomerations are of special interest in the areas with technogenic pollution. Compounds of this toxic element can migrate and be found in different phase states as well as accumulate in plant and living organisms and be redistributed metamorphically and biogenically. The distribution of mercury in areas of intensive coal mining and coal processing requires an individual study. A rough estimate of mercury emission indicates that, with mean mercury concentrations in coals, at the clarke level, of 0.08 mg/kg, mercury distribution coefficient in the atmosphere of 81 % and the volume of coal burnt annually at the thermal power plant of 947041 tons of equivalent fuel (Report…, 2017), 61.4 kg of mercury enter the atmosphere. At the same time, mercury concentrations in the Kuzbass coals can reach even higher values.

This study aims to investigate the mercury concentration in the street dust from Mezhdurechensk (Southern Kuzbass) where a large number of mines and quarries in the immediate vicinity of the city form a certain level of pollution. The constant inhalation of dust-loaded air is a risk factor for public health.

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2. Materials and methods

For a comprehensive study of the chosen area, samples (29 samples) were taken within the city limits of Mezhdurechensk according to the sampling procedure: along a uniform areal network (Scale: 1:25 000) and at sites accessible for sampling where the maximum accumulation of dust emissions transported from coal objects during drilling and blasting, as well as from thermal power facilities, towards the city is possible. In choosing the sampling sites, we tried to avoid the influence of vehicles. The samples were taken by sweeping with clean plastic brushes with hard bristles in the asphalted areas, following the methods described in (Vlasov et al., 2015; Lau and Stenstrom, 2005). A statistically significant number of samples was taken. Samples weighing at least 500 g were placed in tight plastic bags. Thereafter, the samples were dried under laboratory conditions at room temperature, sifted through sieves with a mesh size of 1 mm to separate the samples from street and domestic waste and divided into granulometric fractions by sieving using a standard set of sieves to obtain fractions of 1000-100, 100-50 and 50-20 μm according to (Ljung et al., 2008).

Additional experiments were carried out to obtain a fine fraction of 20-4.5 μm by elutriation according to the procedure presented in (Ljung et al., 2008; Kasimov et al., 2016). A sample with a fraction less than 20 μm was dispersed in distilled water, followed by filtration of the resulting solution with a fine suspension through membrane filters with a pore size of 4.5 μm to obtain a fine fraction (20-4.5 μm).

Mercury concentration in the street dust was determined by atomic adsorption on an RA 915+ mercury analyzer with a PYRO-915+ attachment (PNDF 14.1:2:4.243-07, 2007). This technique is based on the reduction of bound mercury in the sample by pyrolysis, followed by the air transfer of the formed atomic mercury from the atomizer to the analytical cuvette. A standard soil sample (SDPS-3) with a mercury concentration of 290 ± 58 ng /g was used as a standard.

The sample aliquots that were preliminarily crushed and dried at room temperature were (45.0-60.0) ± 0.1 mg. The limits of relative measurement error ranged from 20 to 28% depending on the mercury mass fraction in the samples with a confidence level of 0.95 and three parallel measurements.

To determine the forms of mercury occurrence in the soil, the method of sequential or autonomous soil extractions was used (Bloom et al., 2003). The most mobile (water-soluble) forms were extracted with double distilled water; ion exchange forms associated with clay minerals, oxides and hydroxides of Al, Fe and Mn, as well as acid-soluble forms (with different migration ability), were extracted with a mixture of 0.1 acetic and 0.01 M hydrochloric acids. The solubility in 0.1 M NaOH solution characterised the amount of mercury associated with organic matter. Strongly bound forms were extracted with concentrated 12M nitric acid. Each extraction included intensive stirring for 10-12 hours and centrifugal sedimentation of the insoluble part, followed by decantation.

3. Results and discussion

The mean mercury concentration in street dust of urban area was 36.4 ± 4.7 ng/g, 26.3 ± 5.3 ng/g in the Western district and 41.8 ± 6.3 in the Eastern district. Intervals of minimum and maximum values for the entire city and the Eastern district were 4.6 to 104.2 ng/g and 7.7 to 4.7 ng/g for the Western district (Table 1). The next summer, with fewer number of samples along the sparse network, the mean value of mercury was 26 ± 5 ng/g; the minimum value – 6 ng/g, and the maximum value – 70 ng/g. We obtained significant positive correlations between mercury concentrations at different time intervals (correlation coefficient was 0.92). With the unchanged volumes of coal mining and processing, provided that climatic conditions have not changed in one year, this is a good evidence of the possibility and reliability of using street dust as an indicator of environmental quality in the summer. Maximum mercury concentrations in coal dust are formed under the influence of coal mining objects that are moved towards the city during drilling and blasting.

Table 1. Hg concentration and concentration coefficient (CC) in street dust of Mezhdurechensk

Indicators	City	Eastern district	Western district	Clarke, ng/g (Kasimov and Vlasov, 2015)
Number of samples	29	19	10	
C Hg, ng/g	36.4 ± 4.7	41.8 ± 6.3	26.3 ± 5.3	
C min, ng/g	4.6 ± 4.7	4.6 ± 6.3	7.7 ± 5.3	
C max, ng/g	104.2 ± 4.7	104.2 ± 6.3	64.7 ± 5.3	
$CC_{(Yaroshevskiy)}$	3.64	4.18	2.63	10
$CC_{(Vinogradov)}$	0.43	0.50	0.32	83
$CC_{(Beus)}$	1.10	1.26	0.79	33
$CC_{(Grigoriev)}$	0.56	0.64	0.40	65
CC_{MPC}	Do not exceed maximum permissible concentration			2100

Note: C Hg is the mean Hg concentration in dust; C min is the minimum Hg concentration in dust; C max is the maximum Hg concentration; CC (Yaroshevskiy, etc.) is the concentration coefficient relative to clarke according to Yaroshevskiy A.A., clarke according to Vinogradov A.P., clarke according to Beus A.A., and clarke according to Grigoriev A.P.

Table 2 compares mercury concentrations in street dust, soil and snow solids. The mean mercury concentration in street dust was slightly lower than in soil samples that had previously been taken at the same sites (58.4 ng/g) but higher than that in snow solids (29.8 ng/g). This was likely due to the atmospheric precipitation that washed out mercury from the street dust and to the wind blowing.

We determined the following ratio of mercury occurrence forms: mobile (water-soluble) was 10.94% (9.8% to 28.6% mercury), ion exchange form associated with clay minerals, oxides and hydroxides of Al, Fe and Mn – 10.32% (8.8% to 26.0% mercury) and mercury associated with organic matter – 44.76% of its total concentration, with a minimum value of 34.6% and a maximum value of 62.5%. The proportion of strongly bound mercury that was soluble only in concentrated nitric acid and is likely of 'coal' origin was 33.97%, with a minimum value of 13.3% and a maximum value of 70.13%. A wide range of values indicates the uneven nature of the mercury distribution in the samples depending on their sampling site and total concentration. The greater the bulk mercury concentration in the sample, the greater the contribution of the water-soluble form.

The study of the mercury distribution based on the particle size of street dust revealed that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction contained the bulk of mercury.

4. Conclusions

The obtained data, as well as data on the composition of dust and aerosol fallouts in the area of Mezhdurechensk and adjacent areas in the winter, indicated that they differed in much higher (two- or threefold) mercury concentrations than those in the background area. At the same time, the proportion of coal particles accounted for 20% to over 80% of the volume of solid fallouts. With a mean mercury concentration in Kuzbass coal of 0.08 mg/kg, the contribution of coal dust to the total amount of mercury in dust and aerosol can range from 45% to 90%. In fact, coals in the south of the Kuznetsk Coal Basin are much richer in mercury than the average estimates for Kuzbass, and their real proportion in the balance of the element in the soil may exceed 90%. For example, according to (Arbuzov et al., 2015; Osipova et al., 2019), coals of the Mezhdurechensky coal mine contain 0.75 mg/kg of mercury. Similar values were also obtained for other coal mining enterprises in the south of Kuzbass. Therefore, coal dust, along with coal combustion products, determines mercury accumulation levels in street dust and adjacent areas. The study of the mercury distribution based on particle size of street dust revealed that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction with a diameter of 20 to 50 μm contained the bulk of mercury. Fine dust formation is especially hazardous because it remains in suspension form of for a long time before settling on the surface, and mercury is concentrated in this dust. Particle-size analysis combined with the method of selective chemical extraction indicated the presence of mercury with different degrees of bonding and, hence, different migration abilities, which allowed us to more objectively assess the risk of pollution and identify sources of mercury emissions.

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Conflict of interest

The authors declare no conflict of interests.

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Table 2. Comparison of Hg concentrations (ng/g) in street dust, soil and snow solids

	Soil			Street dust			Snow		
	City	Eastern district	Western district	City	Eastern district	Western district	City	Eastern district	Western district
C Hg, ng/g	58.4	63.9	55.5	36.4	41.8	26.3	29.8	30.8	27.8
C max, ng/g	173.6	173.6	116.9	104.2	104.2	64.7	49.0	49.0	35.0
C min, ng/g	10.2	11.8	10.2	4.6	4.6	7.7	15.0	15.0	20.0

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