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CHEMICAL COMPOSITION OF ROAD DUST AS AN INDICATOR OF THE ECOLOGICAL STATE OF URBAN LANDSCAPES (BY THE EXAMPLE OF THE CENTRAL ADMINISTRATIVE OKRUG OF MOSCOW)

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Abstract: An indicator of urban environmental pollution can be road dust, which is formed by the participation of many anthropogenic sources. For Moscow, the main source of heavy metals and metalloids (HMMs) is motor transport which emissions are toxic. Pollutants in fine fractions of road dust are easily blown into the air, then enter the human body and pose a health risk. This work is devoted to assessing the spatial distribution and environmental hazard of HMMs accumulation in road dust and its fine fractions PM_{1-10} and PM_1 in the Central Administrative Okrug (CAO) of Moscow based on field data for 2023. The list of priority pollutants coming with technogenic emissions in the CAO includes Sb, Zn, Cu, and Cd, as well as Sn, Pb, Mo, and W. In fine fractions, the mean content of these HMMs is an order of magnitude higher; its variability is lower, while the differences in the contents of the elements in dust from roads with various traffic intensities become more contrasting. Differences between the roads are caused by intensity, average speed, and mode of the traffic, as well as by the composition of the vehicle fleet and the frequency of traffic jams. Extremely high and dangerous pollution in the PM_1 fraction was found in about 85% of samples; the average for the okrug total pollution index for this fraction is 1.4 times higher than for the PM_{1-10} fraction.

Keywords: particle size fractions; enrichment; non-exhaust emissions; microparticles; pollution

1. Introduction

Currently, about half of the world's population lives in cities, and by 2050, the share of urban population will increase to 68% (Our World in Data, 2023). For residents of many cities, the quality of the urban environment is becoming one of the priority indicators of the standard of living. It is controlled by many factors, the most important of which is the ecological and geochemical state of urban landscapes. Geochemical studies are especially relevant in large cities, where a large number of man-made sources of pollution are concentrated. The most informative indicators of the ecological state of the urban environment include road dust, which is formed with the participation of many sources, including emissions from vehicles, industry, urban construction projects, the fuel and energy complex, as well as particles of contaminated roadside soils and aerosols coming from neighboring regions by atmospheric

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transfer (Amato et al., 2011; Haynes et al., 2020; Wang et al., 2021). Unlike urban soils, which accumulate pollutants over many years and even decades, the chemical composition of road dust characterizes the impact of modern pollution sources affecting the ecological state of urban landscapes (Acosta et al., 2015; Long et al., 2021). At the same time, the chemical composition of road dust is significantly influenced by roadside soils and atmospheric precipitation accumulated in the snow cover, as indicated by the common parageneses of heavy metals and metalloids (HMMs) in these landscape components (Kasimov et al., 2023).

Particle-size fractions of road dust are enriched with pollutants in different ways (Kong et al., 2012; Lanzerstorfer, 2018). The finest fractions of solid particles, which are not captured by industrial filters and have a high sorption capacity for toxic chemical elements, such as HMMs, usually enter the environment with emissions from transport and industrial enterprises (Alves et al., 2018; Amato et al., 2016; Ivaneev et al., 2024). Therefore, the chemical composition of PM_1, $PM_{2.5}$, and PM_{10} road dust particles (the number shows the maximum diameter of particles in micrometers), which are easily blown into the air, thus creating a threat to the human respiratory system, is the most actively studied (Golokhvast et al., 2015; Ramírez et al., 2019; Revich, 2018; Tager, 2004).

In Moscow, the largest and northernmost megalopolis in Europe, studies of the contents of HMMs in road dust were carried out in individual districts of Moscow (Ivaneev et al., 2023; Kasimov et al., 2020; Ladonin & Mikhailova, 2020; Ladonin & Plyaskina, 2009; Vlasov et al., 2022, 2023). The most complete survey of Moscow roads was carried out in 2017 when the contents of 23 HMMs were determined in 220 samples of road dust and its PM_{10} fraction collected in 9 districts of Moscow on roads with different traffic intensities and in courtyards with parking lots (Vlasov et al., 2021).

Owing to the developing street and road network and public transport, as well as due to improving fuel quality, emissions from motor vehicles in Moscow tend to decrease; from 2012 to 2022, they decreased by 2.9 times (Kulbachevsky, 2023). Nevertheless, motor vehicles remain an important source of many HMMs: fuel combustion products emit Sb, Zn, Cu, Pb, and Mo into the atmosphere; road surface abrasion, Zn, As, W, Cr, V, and Co; tire wear, Sb, Cd, Zn, Pb, Cu, Co, Ni, and Cr; brake pad wear, Sb, Zn, Cu, Pb, Ni, W, and Cr (Fussell et al., 2022; Grigoratos & Martini, 2015; Vlasov et al., 2023). In terms of emissions from motor vehicles (318.5 thousand tons per year), Moscow holds the first place among Russian cities, while emissions from industrial enterprises are lower and amount to 66.7 thousand tons per year (Kulbachevsky, 2023). Significant supplies of dust particles to the urban environment are due to construction works, including the construction of new highways and the modernization of old highways, as well as the implementation of the housing stock renovation program. Therefore, the task of assessing and monitoring the polluting impact of anthropogenic sources on urban landscapes in the Moscow megalopolis remains very relevant.

Of particular interest is the Central Administrative Okrug (CAO) of Moscow, which has the highest density of the street and road network and traffic intensity. Owing to the large number of cars and traffic jams, the most severe pollution of road dust and its PM_{10} fraction is observed in the CAO compared to other administrative okrugs of Moscow (Vlasov et al., 2021). The purpose of this work is to assess the current pollution of the transport zone in the

CAO of Moscow by HMMs and its environmental hazard based on the chemical composition of road dust and its fine fractions PM_{1-10} and PM_1. The particular objectives of the study were:

– to determine the bulk contents of HMMs in PM_{1-10} and PM_1 fractions of road dust on the roads with different traffic intensities and in the courtyards with parking lots in the CAO of Moscow;
– to identify priority HMM pollutants and their possible sources; and
– to assess the environmental hazard of pollution of bulk road dust samples and their fine fractions on the roads of CAO.

The information basis for this study was obtained during the geochemical survey of the CAO in the summer of 2023.

2. Study area

The CAO is the historical and cultural center of Moscow megalopolis; it has a permanent population of 775,000 people and is annually visited by about 25 million tourists (Department of the Federal State Statistics Service for Moscow and the Moscow Region, 2024). The CAO area is 66,000 km^2.

A larger part of the CAO is located on the low spurs of the Smolensk–Moscow Upland, which is an accumulative-erosional plain with flat areas composed of glaciofluvial sediments alternating with gentle moraine hills (Ishkov & Ilyin, 2000). The southern and southwestern part of the CAO occupy the floodplain and the first, second, and third terraces of the Moskva River. Small areas to the east of the Yauza River in the eastern part of the CAO are attributed to the Meshchera Lowland with glaciofluvial sediments. In the territory of the CAO, native soils have been preserved only in small areas in parks and forest parks; due to the anthropogenic loads, most of the soils have been significantly transformed into anthropogenic soils, mainly Urbic Technosols (Gerasimova et al., 2003).

The CAO of Moscow is characterized by a moderately continental climate with mean monthly temperatures of –4.7°C in February and +18.2°C in July and the mean annual precipitation of 650–700 mm (Ishkov & Ilyin, 2000). In 2023, Moscow received 150 mm of precipitation above the climatic norm (Department of Nature Management and Environmental Protection of the City of Moscow, 2024). A "heat island" often forms over the CAO with temperature contrasts between the city center and the suburbs of about 1.5–2°C due to fuel combustion in the winter, as well as changes in the albedo of the underlying surface in the summer (Alekseeva et al., 2017; Varentsov et al., 2018). The location of the CAO at the junction of two physiographic regions, the boundaries of which are the valleys of the Moskva and Yauza rivers, and the absence of natural orographic barriers and low-rise historical buildings in the city center contribute to the active transfer of air masses and the dispersion of pollutants.

Compared to other okrugs of Moscow, the CAO is characterized by the highest density of roads with high traffic intensity (Bityukova & Mozgunov, 2019), such as the Third Ring Road, Garden Ring, and radial highways with 2–3 lanes in each direction. On 55% of the roads in the CAO, vehicles emit from 100 to 500 t/km^2 of pollutants, while the density of transport emissions of 3000–5000 t/km^2 is recorded on 10% of the roads from the total pavement area, mainly on the Third Ring Road (Bityukova & Mozgunov, 2019; Popov et al., 2016). There are also six railway stations and railway infrastructure facilities on the territory of

the CAO, which are potential sources of pollutants. This makes transport the main supplier of emissions in the CAO (about 95% of the total emission of pollutants into the atmosphere).

Significant deindustrialization and reorganization of 15 industrial zones in the CAO led to the placement of residential complexes, business centers, educational, cultural, and social institutions on their territory (Official website of the Mayor of Moscow, 2020; Saulskaya, 2018). However, some industrial zones and thermal power plants, such as combined heat and power plant (CHPP-7), hydroelectric power plant (HEPP-1), Mezhdunarodnaya thermal electric power station, and district heating plants Pereyaslavskaya and Krasnaya Presnya remain on the territory of the CAO. In the northeastern part of the CAO, there is the Mitkovskaya Vetka industrial zone, which includes the Babaevsky confectionery concern, Dollezhal Design Institute of Power Engineering, and warehouses; in the eastern part, the Tupolev aircraft plant, the Mosgaz enterprise, the Pluton enterprise for the production of vacuum tubes within the Kurskaya industrial zone, and automobile repair and maintenance shops in the Magistralnye Ulitsy industrial zone. In the southern part of the CAO, a part of the Paveletskaya industrial zone (refrigeration plant and warehouses) and the Udarnitsa confectionery factory are located. Depending on weather conditions, wind rose, and wind speed, the territory of the CAO may be affected by emissions from industrial enterprises adjacent to the CAO borders, mainly from the southeast, east, and northeast.

3. Materials and methods

Road dust samples in the CAO were collected in August 2023 on roads of various sizes, as well as in the courtyards of residential buildings with parking lots (Figure 1). In accordance with the width of the roadway and the number of lanes, all roads were divided into four categories with different traffic intensities: the Third Ring Road (TRR); large highways with 3–4 lanes in one direction; medium highways with two lanes; and small highways with one lane in one direction. Sampling was carried out in dry weather, at least 24 hours after rain. Samples were collected along the curb on both sides of the road using a plastic scoop and a brush in 3–5 replicates with sampling points spaced apart at 3–10 m from one another; one mixed sample was prepared from them. On the TRR and large highways, samples were collected from the dividing strip, courtyards, and parking areas. A total of 25 samples were taken, including three samples from the TRR, seven samples from highways, nine samples from medium roads, three samples from small roads, and three samples from courtyards with parking lots.

Particle-size distribution in road dust samples was determined at the Ecological and Geochemical Center of the Lomonosov Moscow State University using a laser particle sizer Analysette 22 MicroTec plus (Fritsch). Ultrasonic dispersion of dust samples was used to isolate the $PM_{1\text{-}10}$ and PM_1 fractions, followed by centrifugation (Bezberdaya et al., 2023). The resulting solutions were filtered through membrane filters with a pore diameter of 0.45 μm (EMD Millipore) on a vacuum filtration unit.

The contents of Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, La, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sn, Sr, V, W, and Zn were determined in $PM_{1\text{-}10}$ and PM_1 fractions and the bulk road dust samples using mass-spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES) with inductively coupled plasma on an iCAP Qc (Thermo Scientific) mass spectrometer and an Optima-4300 DV (Perkin Elmer) atomic emission spectrometer, respectively. The analysis

was carried out in the laboratory of the N.M. Fedorovsky All-Russia Research Institute of Mineral Resources (VIMS) using certified methods (NSAM 499-AES/MS, 2015), standard reference samples, and blank samples. The VIMS laboratory is accredited by the International Accreditation System Analytics (AAC.A.00255), and the International Organization for Standardization (ISO 17034:2016 and ISO/IEC 17025:2017).

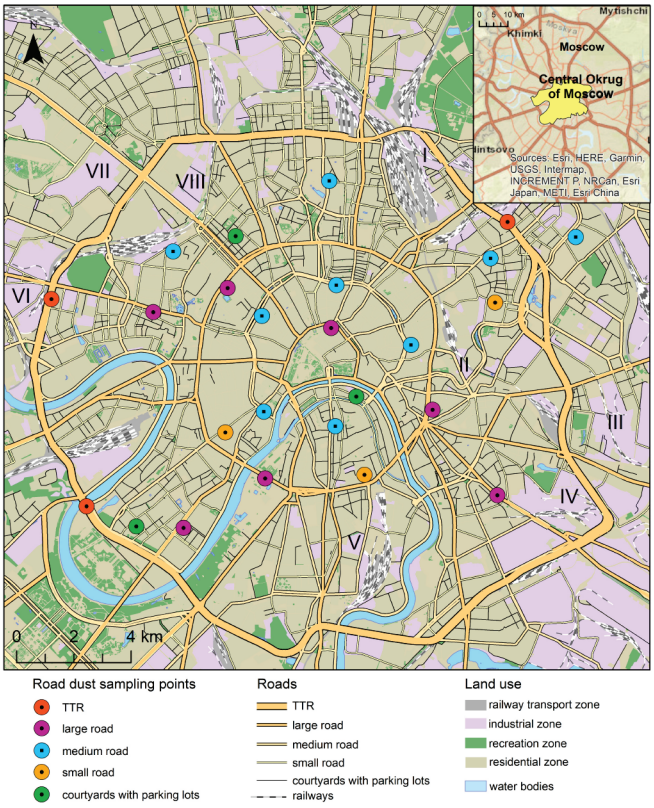

Figure 1. Land use zoning of the CAO and location of sampling plots. Industrial zone: I – Mitkovskaya Vetka, II – Kurskaya, III – Hammer and Sickle, IV – Volgogradsky Prospekt, V – Paveletskaya, VI – Magistralnye Ulitsy, VII – Botkin passage, VIII – Pravda Street..
Note: The maps are based on the authors' own analytical data.

The contents of HMMs in bulk samples of road dust (C_{bulk}) and in the fine particulate matter fractions (C_{PM}) were compared to modern data (Rudnick & Gao, 2014) on the abundances of elements in the upper continental crust (UCC) and relative abundances of elements (pollution index, *PI*) were calculated as $PI = C_{bulk(PM)}/UCC$. The crustal abundances were used as a comparison standard due to the lack of a background analogue for road dust, which is a specific technogenic object. The total pollution with HMMs was judged from the total pollution index $TPI = \Sigma PI - (n - 1)$, where n is the number of chemical elements with $PI > 1.0$. The *TPI* index has five gradations: <16 – low, non-hazardous, 16–32 – medium,

moderately hazardous, 32–64 – high, hazardous, 64–128 – very high, very hazardous, >128 – maximum, extremely hazardous pollution (Kasimov et al., 2016).

The contribution of particulate matter fractions to the overall dust pollution was determined by the ratio between C_{PM} and C_{bulk}. The coefficient $Dx = C_{PM}/C_{bulk}$ was calculated as an indicator of particle-size fractionation of HMMs in the road dust.

The influence of technogenic sources of HMMs on the chemical composition of individual fractions and bulk samples of road dust was assessed using the enrichment factor $EF = (C_i/C_{ref})/(K_i/K_{ref})$, where C_i and C_{ref} are the contents of the i-th and reference (normalizing) elements in the sample, and K_i and K_{ref} are the abundances (clarkes) of these elements in the upper part of the continental crust, respectively. The normalizing element Al was chosen because of its minimal participation in technogenic processes in the study area. There are no generally accepted gradations of the *EF* indicator. We used *EF* gradations according to (Sutherland, 2000) that are widely applied in the study of road dust pollution: < 2 – minimal enrichment and, accordingly, minimal pollution, 2–5 – moderate, 5–10 – significant, 10–50 – very high, and ≥ 50 – extremely high enrichment and pollution.

The danger of road dust and its particulate matter contamination with HMMs was assessed by calculating the frequency *P* (%) of the excess of maximum permissible concentration (MPC_i) or tentatively permissible concentration (TPC_i) and the coefficients of environmental hazard of individual elements $Ko = C_i/MPC(TPC)_i$. In the absence of standards for road dust, calculations were carried out for MPC and TPC standards established in the Russian Federation for eight elements in soils (SanPiN 1.2.3685-21, 2021). For V and Sb, the MPC values of 150 and 4.5 mg/kg were taken, respectively; for the remaining six elements, the TPC values established for loamy or loamy sandy (depending on the texture of the sample) neutral soils with pH > 5.5 were used: As (10 and 2 mg/kg), Cd (2 and 0.5), Ni (80 and 20), Pb (130 and 32), Cu (132 and 33), and Zn (220 and 55).

Visualization of geochemical data was performed in the ArcGIS 10 package. Data from the OpenStreetMap project were used as the cartographic basis for geochemical maps. The size of the roads was determined by analyzing Yandex street panorama photographs.

4. Results and discussion

4.1. Bulk contents and distribution of HMMs by particle-size fractions of road dust in the CAO

The polluting impact of motor vehicles and other anthropogenic sources on road dust in the CAO was manifested in the high total content of Sb (*PI* = 7.5), Zn (5.7), Cu (3.8), Cd (2.8), Sn, Pb and Bi (2.5–1.6) relative to the average composition of the upper part of the continental crust. The contents of W, Fe, and V were close to clarke values, while the contents of the remaining elements in Moscow road dust were lower than in the upper part of the continental crust (Table 1). Many HMMs are characterized by a strong variability in their contents in road dust (*Cv* > 50%), especially those whose content is significantly higher than the global clarke, which attests to a significant contribution of technogenic sources and to the spatial heterogeneity of the technogenic load. For HMMs with contents less than the clarke values, the variation coefficients are significantly smaller; for most of these elements, the *Cv* is within 15–30%.

Table 1. The contents of HMMs in road dust and its PM_1 and PM_{1-10} fractions in the CAO of Moscow in 2023

Element	PM_1 fraction				PM_{1-10} fraction				Bulk samples of road dust				Dx_1	Dx_2	UCC, mg/kg
	mean	min–max	*PI*	*Cv*, %	mean	min–max	*PI*	*Cv*, %	mean	min–max	*PI*	*Cv*, %			
	mg/kg				mg/kg				mg/kg						
Sb	35	3.1–301	**89**	**162**	25.9	2.6–192	**65**	**141**	2.8	0.49-9.7	**7.1**	**74**	**12.5**	**9, 2**	0.4
Zn	3205	1024–11747	**47**	**72**	2254	735–9075	**34**	**80**	380	91-1168	**5.7**	**77**	**8.4**	**5.9**	67
Cd	2.4	0.86–9.0	**27**	**87**	1.86	0.56–9.57	**21**	**118**	0.26	0.07-1.56	**2.8**	**122**	**9.6**	**7.3**	0.09
Sn	41	9.89–85	**20**	48	27	9.3–45	**13**	35	5.1	1.99-11.2	**2.4**	51	**8.1**	**5.3**	2.1
Bi	2.52	0.65–5.2	**16**	44	1.81	0.42–3.9	**11**	43	0.26	0.01-0.88	**1.6**	**71**	**9.9**	**7.1**	0.16
Pb	254	89–401	**15**	33	158	64–380	**9.3**	45	37	14.3-98	**2.2**	53	**6.9**	**4.3**	17
Cu	370	104–952	**13**	60	302	91–844	**11**	60	107	12.8-396	**3.8**	**97**	**3.5**	**2.8**	28
Mo	13.2	2.5–95	**12**	**138**	10	1.85–63	**9.1**	**119**	2.78	0.98-5.8	**2.5**	46	**4.8**	**3.6**	1,1
W	16.3	3.83–33	**8.6**	44	17.4	6.3–37.8	**9.2**	41	2,3	0.79-6.4	1,2	**79**	**7.0**	**7.5**	1.9
As	8.6	3.58–14.6	**1.8**	36	8.6	2.8–14.5	**1.8**	35	1.99	0.82-3.7	0.4	39	**4.3**	**4.3**	4.8
Ni	78	50–114	**1.7**	22	66	45–113	1.4	20	26	12.3-47	0.6	32	**3.0**	**2.5**	47
Fe	61441	36319–115958	**1.6**	26	61406	29790–115268	**1.6**	27	28473	10522-48265	0.7	33	**2.2**	**2.2**	39200
Cr	143	69–257	**1.6**	28	105	49–138	1,1	22	56	19,1-93	0.6	37	**2.5**	1.9	92
V	149	109–205	1.5	19	136	97–201	1.4	16	75	21.8-160	0.8	47	2.0	1.8	97
Co	22	12.6–33	1.3	20	22.2	11.5–35.6	1.3	25	8.9	2.8-16	0.5	35	**2.5**	1.5	17.3
Mn	847	646–1152	1,1	16	837	696–1201	1,1	13	422	251-651	0.5	24	1.9	1.9	774
La	29	22–47	0.9	20	28	22–52	0.9	21	13	8.0-22	0.4	21	**2.2**	**2.1**	31
Ba	516	330–733	0.8	22	539	359–733	0.9	18	304	226-359	0.5	10	1.7	1.8	624
Sc	11.5	8.1–17.5	0.8	21	12.5	7.6–19.7	0.9	20	6.9	2.5-13.3	0.5	37	1.7	1.8	14
Rb	66	43–101	0.8	23	61	45–102	0.7	22	31	23-50	0.4	18	**2.1**	2.0	84
Be	1.41	0.94–2.1	0.7	22	1.4	1.01–2.3	0.7	18	0.62	0.47-0.92	0.3	18	**2.3**	**2.2**	2.1
Al	48618	34634–73156	0.6	18	48988	37097–62290	0.6	13	25810	17046-34577	0.3	14	1.9	1.9	81529
Sr	140	98–299	0.4	26	175	128–216	0.5	12	154	112-217	0.5	16	0.9	1.1	320

Note. Elements with *PI* > 1.5, *Cv* > 60%, and *Dx* > 2 are highlighted in bold. Elements are ranked in descending order according to *PI* in the PM_1 fraction. Dx_1 and Dx_2 are the values of the coefficient *Dx* for fractions PM_1 and PM_{1-10} of road dust in the CAO. The indicators presented in the table were obtained by processing the original analytical data.

Particulate matter particles PM_1 and PM_{1-10} have increased sorption capacity compared to road dust as a whole (Jayarathne et al., 2017; Khademi et al., 2020; Ramírez et al., 2019). The elements accumulating most intensively in the PM_{1-10} particles are the same as in the bulk road dust samples, but the accumulation intensity is significantly higher, with *PI* in the range of 11–65 (Table 1). In addition, W (*PI* = 9.2) and Mo (9.1) are added to the list of accumulating elements. The most contrasting values relative to the bulk content with *Dx* = 9.2–5.3 are Sb, W, Cd, Bi, Zn, and Sn; for another five elements (Pb, As, Mo, Cu, and Ni), the *Dx* coefficients are quite high (2.5 to 4.3); the remaining HMMs weakly accumulate in the $PM_{1–10}$ fractions.

The variability in the contents of HMMs, except for Mo, Sb, and Ba, in the PM_{1-10} fraction is slightly less than that in the bulk samples of road dust, which can be explained by the more uniform composition of particles coming mainly from motor vehicles. At the same time, the bulk samples of road dust are distinguished by a more variegated composition: coarse fractions consist mainly of quartz grains, feldspars, carbonates, and asphalt fragments, while fine fractions contain carbon compounds, fragments of paint, glass, plastic, brick, and other substances (Prokofieva et al., 2015; Seleznev et al., 2021).

Fraction PM_1 is characterized by an even more significant accumulation (*PI* from 89 to 8.6) of the same elements as in the fraction $PM_{1-10.}$ The differences in the levels of accumulation of these elements in the bulk road dust samples and in the PM_1 fraction (*Dx* values) are within 7.0–12.5. At the same time, the variability of concentrations of most of HMMs (except for Sb, Sn, and Mo) in PM_1 particles remains at the same level or becomes smaller than that in PM_{1-10} particles, which indicates a high homogeneity of fines particles, most likely coming only from emissions of motor vehicles.

This is confirmed by data on the size distribution of particles forming during the movement of vehicles: brake pad wear produces particles with an average size of 0.8–2.2 μm; tire wear, 2–4 μm; road surface abrasion, 6–7 μm, and more than 12 μm (Harrison et al., 2021). Road dust particles released into the air when blown out (resuspended) by moving vehicles are larger than particles formed during the wear of tires and brake pads (Tanner et al., 2008). Their average diameter is about 5 microns, and some particles exceed 10 μm (Rienda & Alves, 2021). At the same time, in the total emissions of PM_{10} and $PM_{2.5}$ particles, non-exhaust emissions from motor vehicles currently predominate, accounting for 67% and 49%, respectively, in the EU countries (Harrison et al., 2021).

4.2. Accumulation of priority pollutants on roads with different traffic intensities

The average bulk content of HMMs in road dust on roads with different traffic intensities varies slightly. The highest contents of HMMs are observed on small roads, where the speed of traffic is low, and the traffic regime is intermittent because of a large number of traffic lights, pedestrian crossings, and public transport stops (Table 2). The lowest contents of HMMs are noted on large roads and in courtyards with parking lots. The group of HMMs with maximum accumulation (*PI* 11–4) in the road dust includes three elements: Zn, Sb, and Cu; Pb, Cd, and Mo accumulate moderately; and Sn and Bi, weakly.

Table 2. Pollution of road dust and its PM1 and PM1-10 fractions with HMMs on different types of roads

Object	Road type	*PI* levels				*TPI*
		> 20	10–20	5–10	2–5	
PM_1 fraction	TRR	$Sb_{62}Zn_{29}Cd_{25}$	$Cu_{13}Bi_{13}Sn_{12}Pb_{12}$	Mo_9W_6	$As_2Fe_2Ni_2V_2Cr_2$	173
	LR	$Sb_{114}Zn_{34}Sn_{29}Bi_{23}$	$Cd_{17}Mo_{16}Cu_{14}Pb_{12}W_{12}$	–	$As_2Fe_2Ni_2V_2Cr_2$	267
	MR	$Zn_{42}Sb_{41}Cd_{38}$	$Sn_{18}Pb_{17}Bi_{14}Cu_{13}$	W_8Mo_7	$As_2Fe_2Ni_2$	192
	SR	$Sb_{273}Zn_{119}Mo_{33}Cd_{31}Pb_{21}$	$Sn_{19}Cu_{18}Bi_{15}$	W_7	$As_2Fe_2Ni_2Cr_2$	522
	CY	$Zn_{55}Sb_{22}$	$Cd_{15}Pb_{11}$	$Sn_9Bi_8W_7Cu_7$	$Mo_4As_2Ni_2$	132
	CAO	$Sb_{90}Zn_{47}Cd_{27}Sn_{20}$	$Bi_{16}Pb_{15}Cu_{13}Mo_{12}$	W_9	$As_2Fe_2Ni_2V_2Cr_2$	24 3
PM_{1-10} fraction	TRR	$Sb_{70}Zn_{19}$	$Cd_{14}Sn_{14}Cu_{13}Bi_{10}$	$Pb_7Bi_7Mo_7W_7$	As_2Fe_2	154
	LR	$Sb_{77}Zn_{20}$	$Bi_{16}Sn_{14}W_{12}Mo_{12}Cu_{11}Cd_{10}$	Pb_6	Fe_2	173
	MR	$Sb_{34}Cd_{34}Zn_{30}$	$Sn_{18}Pb_{12}Cu_{11}Bi_{10}$	W_9Mo_6	As_2Fe_2	152
	SR	$Sb_{175}Zn_{82}Cd_{22}Mo_{22}$	$Pb_{14}Cu_{14}Sn_{12}Bi_{11}$	W_8	As_2	35 4
	CY	Zn_{40}	$Sb_{14}Sn_{10}$	$Cd_9Bi_8Pb_6W_6Cu_5$	Mo_2As_2	92
	CAO	$Sb_{65}Zn_{34}Cd_{21}$	$Sn_{13}Bi_{11}Cu_{11}$	$Pb_9W_9Mo_9$	As_2Fe_2	175
Bulk sample	TRR	–	Sb_{11}	Cu_6	$Zn_4Mo_2Sn_2Bi_2Cd_2Pb_2$	24
	LR	–	–	Sb_7	$Mo_4Zn_4Cu_3Sn_2Bi_2$	17
	MR	–	–	Sb_7Zn_5	$Cd_4Cu_3Sn_3Pb_2Mo_2$	22
	SR	–	Zn_{11}	Sb_9Cu_7	$Pb_2Cd_3Sn_3Bi_2Mo_2$	34
	CY	–	–	Zn_8	$Sb_3Cu_2Sn_2Cd_2Bi_2Pb_2$	16
	CAO	–	–	Sb_7Zn_6	$Cu_4Mo_3Cd_3Sn_2Bi_2Pb_2$	21

Note. The indicators presented in the table were obtained by processing the authors' own analytical data. The *PI* values are given in subscripts. Dashes mean the absence of an indicator fitting the accepted grade (only the elements with $PI \geq 2$ are shown). Road types: TRR – Third Ring Road, LR – large roads, MR – medium roads, SR – small roads. CY – courtyards with parking lots; CAO – average for the whole okrug.

In the PM_{1-10} fraction of road dust, the contents of HMMs increase several times; in the PM_1 fraction, by an order of magnitude, and the differences in the contents of priority pollutants on roads with different traffic intensities become more contrasting. The list of priority pollutants is complemented with W. Extremely high concentrations of HMMs are observed on small roads and relatively low concentrations on the TRR and medium-sized roads. Courtyards with parking lots are distinguished by minimal accumulation of HMMs in the fine fractions of road dust. Differences between the roads are due to the intensity, average speed, and mode of the traffic, as well as due to the structure of the vehicle fleet and the likelihood of traffic jams. On large highways, high average speed promotes the blowing out of the most polluted fine particles from road dust, in which coarse fractions of weakly sorbing HMMs predominate (Kasimov et al., 2019; Vlasov et al., 2021).

4.3. Sources of HMMs in road dust and its fine fractions

Heavy metals and metalloids in the fine fractions of road dust can be clearly divided into four groups according to the enrichment factor values (Table 3, Figure 2). The first group with a pronounced anthropogenic impact and an extremely high enrichment level (*EF* > 50) includes $Sb_{162}Zn_{88}$ in the PM_1 fraction and $Sb_{112}Zn_{60}$ in the PM_{10} fraction (subscripts are average *EF* values). The second group with a very high enrichment level consists of Cd, Sn, Bi, Pb, Cu, Mo, W (10 < *EF* < 50); for these elements, the enrichment levels in the PM_1 fraction are 1.3–1.6 times higher than those in the PM_{10} fraction, except for W with *EF* = 15 in both fractions. All these elements get into the road dust of the CAO with exhaust and non-exhaust emissions of motor vehicles.

Table 3. Mean and maximum enrichment factors in the PM_1 and $PM_{1\text{-}10}$ fractions and in the bulk road dust mass

Element	PM_1 fraction		$PM_{1\text{-}10}$ fraction		Bulk road dust mass	
	*EF*mean	*EF*max	*EF*mean	*EF*max	*EF*mean	*EF*max
Sb	162	1566	112	935	23	88
Zn	88	365	60	264	19	66
Cd	49	236	36	178	9.4	65
Sn	34	73	22	37	7.8	19
Bi	27	49	19	38	5.0	18
Pb	26	45	16	32	7.0	18
Cu	23	71	18	49	12	44
Mo	22	179	16	112	7.8	14
W	15	28	15	27	3.9	9.8
As	3.0	4.8	3.0	4.7	1.4	3.,1
Ni	2.9	4.6	2.3	3.9	1.8	3.2
Fe	2.7	5.6	2.6	4.8	2.3	3.6
Cr	2.7	5.3	1.9	2.5	1.9	2.9
V	2.6	3.5	2.3	2.9	2.4	4.5
Co	2.2	3.6	2.1	3.3	1.6	2.7
Mn	1.9	3.4	1.8	2.5	1.7	2.3
La	1.6	2.3	1.5	2.4	1.3	2.3
Ba	1.4	2.2	1.4	2.2	1.6	1.8
Sc	1.4	1.6	1.5	1.9	1.5	2.2
Rb	1.3	1.7	1.2	1.8	1.2	1.9
Be	1.1	1.5	1.1	1.5	0.9	1.4
Sr	0.7	1.4	0.9	1.4	1.5	2.2

Note. The indicators presented in this table were obtained by processing the authors' own analytical data.

The third and fourth groups of HMMs in the PM_1 and $PM_{1\text{-}10}$ fractions are characterized by moderate (As, Ni, Fe, Cr, V, Co) and minimum (Mn, La, Ba, Sc, Rb, Be, Sr) enrichment levels. The presence of elements from the third group in the fine fractions of road dust in the CAO is caused by mixed natural and human-made sources, such as building materials and dust and particles of contaminated soils. Elements of the fourth group are mainly derived from natural sources: particles of soil-forming rocks, various mixtures used to replace contaminated roadside soils, etc.

The enrichment of the bulk samples of road dust in the CAO with metals from the first two groups remains very high, although 3.3–4.7 times lower than in the fine fractions, which

confirms the supply of these elements from technogenic sources. The differences in the *EF* for the third and fourth groups of HMMs in the bulk samples and fine fractions are insignificant. All of them are characterized by low values, i.e., the concentrations of these elements are determined mainly by natural sources with a weak participation of technogenic emissions.

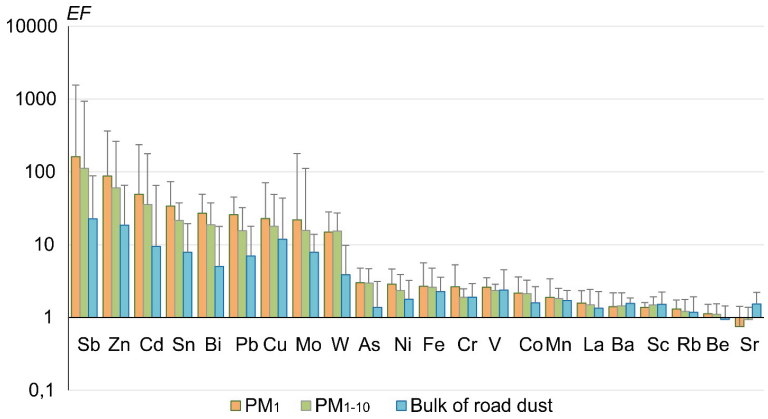

Figure 2. Enrichment of bulk samples of road dust and their PM_1 and PM_{10} fractions with HMMs. Vertical lines indicate maximum *EF* for each HMM; boxes indicate mean *EF* values.
Note: The graph is based on the authors' own analytical data.

4.4. Environmental hazards of pollution of road dust with HMMs in the CAO

The assessment of the environmental hazard of road dust pollution with HMMs via comparison with the MPC/TPC values for individual elements showed the most frequent excess of the permissible concentrations (*P*) in the PM_1 fraction (Table 4). In this fraction, the frequency of excesses of MPC/TPC values for Sb, Zn, Cu, and Pb is close to 100%, while Zn is in the lead in terms of the mean (39.5) and maximum (214) values of the environmental hazard coefficient *Ko*. Sb is in the second place with *Ko* 8.2 and 66.7, respectively. For two other metals – Cu and Pb – the average excesses of the TPC are 7.4 and 5.3, and the maximum excesses are 28.9 and 12.5. For Cd and Ni, the frequency *P* = 72%; and for As and V, 64 and 52%, respectively. The average *Ko* value varies from 1.1 for V to 4.1 for Cd, and the maximum *Ko*, from 1.4 for V to 17.0 for Cd. On different types of roads, the *P* and *Ko* indicators vary quite significantly, reaching maximum values for most elements on small roads and decreasing to minimum values on the TRR.

In the PM_{1-10} fraction, the frequency and multiplicity of exceeding the permissible concentrations generally decrease. Frequencies *P* close to 100% are noted for three elements: Zn, Sb, and Cu, with the mean *Ko* of 27.7, 6.2, and 6.1 and maximum *Ko* of 165, 42.7 and 25.5, respectively. Zn still leads in terms of the mean and maximum *Ko* values. The second group of elements – Pb, As, Cd, and Ni – has a frequency *P* varying from 52 to 72%, the mean *Ko* is from 3.3 to 4.2, and the maximum *Ko* is from 5.7 to 19.1. The last place belongs to V, which has an excess frequency *P* = 28% with the mean *Ko* = 1.1, and the maximum *Ko* = 1.3. Just as for the PM_1 fraction, among the different types of roads, small roads with the highest indicators of environmental hazard stand out, while the most favorable situation is observed on the TRR, where significant excesses of permissible concentrations both in frequency and in magnitude were found only for Zn, Sb, and Cu.

Table 4. Mean and maximum values of environmental hazard coefficients *Ko* for the bulk content of HMMs in the road dust and for its PM_1 and PM_{1-10} fractions in the CAO

Fraction	Zn	Sb	Cu	Cd	Pb	As	Ni	V
				Mean *Ko*				
PM_1	39.5	8.2	7.4	4.1	5.3	3.9	3.2	1.1
PM_{1-10}	27.7	6.2	6.1	4.1	4.2	3.8	3.3	1.1
Bulk sample	5.1	1.7	3.3	1.2	1.7	1.5	1.6	1.04
				Maximum *Ko*				
PM_1	214	66.7	28.9	17.0	12.5	6.8	5.7	1.4
PM_{1-10}	165	42.7	25.6	19.1	11.9	7.3	5.7	1.3
Bulk sample	17.5	2.2	10.1	1.4	3.1	1.9	2.4	1.1

Note. The indicators presented in the table were obtained by processing the authors' own analytical data.

The contents of HMMs in the bulk mass of road dust are characterized by a further decrease in the frequency of exceeding the MPC/TPC values for all elements, except for Zn with the mean *Ko* = 5.1, and the maximum *Ko* = 17.5. The second group includes Cu (*P* = 60%), Pb (32%) and Ni (40%) with the mean *Ko* 3.3, 1.7, and 1.6 and maximum *Ko* 10.1, 3.1, and 2.4, respectively. The third group consists of As (*P* = 24%), Sb (12%), Cd (8%), and V (8%), with the mean *Ko* values of 1.04–1.7 and maximum *Ko* values of 1.1–2.4. Among all road types, the maximum excesses of the MPC/TPC values for Zn, Cu, Sb and Cd were recorded on small roads; Ni and As dominate in the pollution of courtyards with parking lots, and Sb dominates on the TRR.

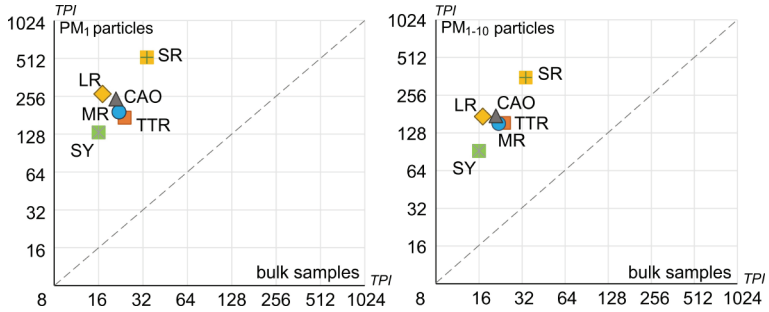

Figure 3. The ratio of the total pollution index *TPI* of road dust and its fractions PM_{1-10} and PM_1 on different types of roads in the CAO of Moscow. Road types: TRR–Third Ring Road, LR–large roads, MR–medium roads, SR–small roads. CY–courtyards with parking lots; CAO–average for the whole okrug.
Note: The graphs are based on the authors' own analytical data.

The integral indicator (*TPI*) for the association of toxic elements in the road dust and its PM_1 and PM_{1-10} fractions has been used to assess the degree of contamination and the environmental hazard of HMMs contained in the road dust and its fine fractions. The most dangerously polluted PM_1 fraction is characterized by high *TPI* values on all types of roads: the average *TPI* in this fraction for the CAO is 243, which is 11.6 and 1.4 times higher than the *Zc* values for the bulk mass of road dust (Figure 3) and for the PM_{1-10} fraction, respectively. Extremely high, extremely hazardous contamination of the PM_1 fraction was detected in

approximately 85% of samples, and the most dangerous environmental situation (*TPI* = 1137) was identified in the historical part of Moscow on Prechistenka Street (Figure 4a, small road).

The total pollution of the PM_{1-10} fraction with HMMs on all types of roads is at the maximum, extremely hazardous level; on small roads, it is more than two times higher than the pollution on other types of roads (Figure 3). Courtyards with parking lots are an exception: the total accumulation of HMMs in the PM_{10} fraction of road dust corresponds to a very high, very hazardous level. The contrast of all anomalies in the PM_{1-10} fraction decreases in comparison with the contrast characteristic of the PM_1 fraction. An extremely high pollution level was noted in 70% of samples. The center of the anomaly with an extremely high, extremely hazardous level of contamination of the PM_{1-10} fraction (*TPI* = 763) is located in the same place as the center of the anomaly for PM_1 (Figure 4b).

The intense accumulation of pollutants in fine dust fractions on this street is explained by the prevalence of passenger cars and passenger vehicles with relatively low speeds and intermittent traffic patterns, which contributes to an increase in the amount of pollutants entering the atmosphere. The main pollutants here are Sb and Zn, which enter the dust as part of fine particles formed by the wear of tires and brake pads; their contents are more than 100 times higher than the abundance of these elements in the upper part of the continental crust.

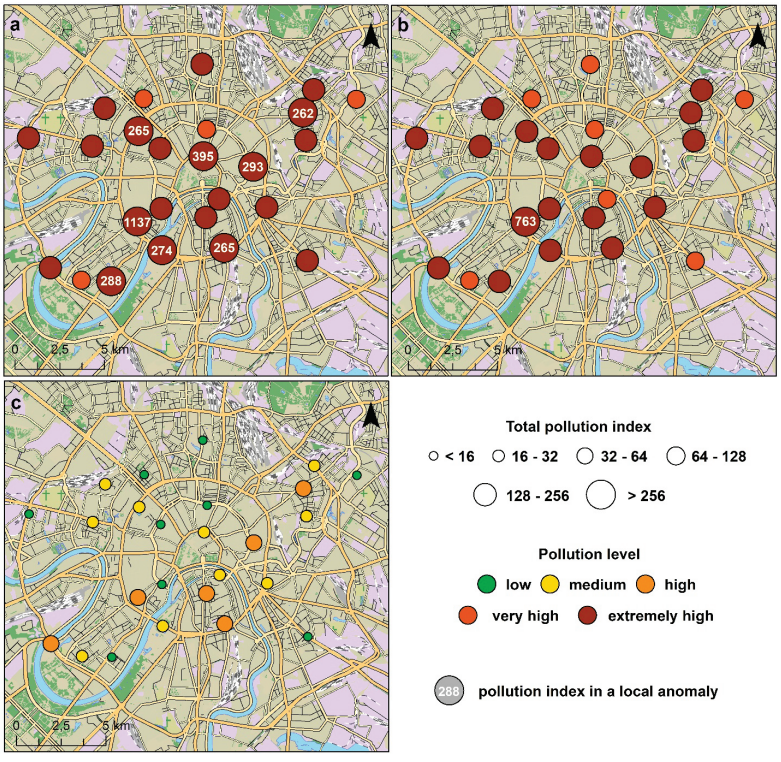

Figure 4. Spatial distribution of the total pollution index (*TPI*) of the (a) PM_1 fraction, (b) PM_{1-10} fraction, and (c) bulk mass of road dust in the CAO of Moscow.
Note: The maps are based on the authors' own analytical data.

With respect to a decrease in the average values of *TPI* in fine fractions, road types are arranged in the following sequence: SR > LR > MR ≥ TRR, i.e., except for small roads, fine fractions are heavily polluted on large roads. They compose the Garden Ring with very high traffic intensity. This sequence ends with parking lots in courtyards (Figure 3); there the traffic intensity is minimal, but the degree of road dust pollution is only slightly inferior to that on the roads. This can be explained by dense, albeit low-rise residential blocks, which often form so-called closed courtyards–wells with favorable conditions for the deposition of fine dust particles (Kosheleva et al., 2018).

Thus, the integral contamination of PM_1 and PM_{1-10} particles is an order of magnitude higher than that of road dust as a whole and is manifested in the formation of a large number of highly contrasting local multielemental anomalies.

The total pollution of road dust in the CAO with HMMs is generally low and not hazardous, except for small roads, where the total content of HMMs reaches a moderately hazardous level. The greatest contribution to the total pollution is made by Sb and Zn, as well as by Cu and Cd. In descending order of average *TPI* values in the bulk road dust mass, road types form the following sequence: SR > TTR > MR > LR. About 75% of the samples of bulk road dust mass have a low, non-hazardous, and moderate, moderately hazardous level of total pollution (Figure 4c). In the remaining 15% of sampling points, high, hazardous pollution is noted. Road sections with extremely hazardous and very hazardous levels of pollution of road dust have not been detected.

5. Conclusions

A comprehensive analysis of the chemical composition of the road dust and its fine particulate matter fractions PM_{1-10} and PM_1 in the Central Administrative Okrug of Moscow allows us to draw the following conclusions. Road dust in the okrug is characterized by moderate accumulation of Sb, Zn, Cu, Cd, Mo, Sn, Pb, and Bi relative to the upper part of the continental crust with significant variability in the contents of these elements due to the participation of many anthropogenic and natural sources, including roadside soils and atmospheric fallout, in the formation of road dust. In the fine fractions, the contents of these elements are, on average, an order of magnitude higher, and the spatial variability is lower. A greater enrichment of fine fractions of road dust with HMMs can be explained by their high sorption capacity, and the reduction in variability can be explained by a greater homogeneity of particles coming predominantly from vehicle emissions.

The priority pollutants accumulating in the road dust are Sb, Zn, Cu, and Cd; for fine fractions, this list is expanded by Mo, Sn, Bi, Pb, and W. All of these elements are undoubtedly of technogenic origin, as indicated by the high values of the enrichment factor *EF*, and come primarily from non-exhaust and exhaust emissions of motor vehicles. The presence of As, Ni, Fe, Cr, V, and Co in road dust has a mixed natural-technogenic genesis (building materials and dust, particles of contaminated soils). Minimum enrichment of road dust with Mn, La, Ba, Sc, Rb, Be, and Sr indicates the predominance of natural sources of these elements (particles of soil-forming rocks, various mixtures used to replace contaminated soils, etc.).

The differences in the bulk contents of HMMs in the road dust sampled from the roads with different traffic intensities are small and are manifested only for elements entering

mainly with vehicle emissions. The highest concentrations of HMMs are observed on small roads, the lowest on large roads, and in courtyards with parking lots. In the PM_{1-10} fraction of road dust, the contents of HMMs increase several times in the road dust and by an order of magnitude in in the PM_1 fraction, while the differences in the content of priority pollutants on the roads with different traffic intensities become more contrasting due to the intensity, average speed, traffic mode, vehicle fleet, and the frequency of traffic jams.

The greatest environmental hazard is represented by the PM_1 fraction of road dust, in which the highest frequencies *P* and the highest rates of excess of sanitary and hygienic standards (*Ko*) were detected for individual elements. On different types of roads, the *P* and *Ko* indicators vary quite significantly, reaching maximum values for most elements on small roads and decreasing to minimum values on the Third Ring Road. In the PM_{1-10} fraction, the frequency and multiplicity of exceeding the MPC/TPC generally decrease, but not significantly. The content of HMMs in the bulk road dust mass is characterized by a further decrease in the environmental hazard.

The contamination of fine fractions PM_1 and PM_{1-10} is an order of magnitude higher than that of road dust as a whole and manifests itself in the formation of high-contrast multielemental anomalies on small and large roads. The PM_1 fraction is most dangerously polluted with the association of toxic elements; extremely high and extremely hazardous contamination of the PM_1 fraction was found in about 85% of samples, the average integral pollution index *TPI* value for the okrug is 1.4 times higher than that of the PM_{10} fraction. In the road dust as a whole, only 25% of samples have a high, hazardous level of the integral contamination. The dust on large roads is the least polluted due to the high speed of movement, which contributes to the blowing out of small fractions.

The obtained results showed the importance of monitoring the chemical composition of road dust and its fine fractions in large cities, which gives an integral characteristic of the quality of the urban environment that reflects the influence primarily of non-exhaust and exhaust emissions of motor vehicles. A comparison of the contents of HMMs in the road dust as a whole and in its fine particulate matter fractions revealed a significantly, by order of magnitude, higher accumulation of pollutants in the latter, which indicates the need to control their trace element composition of fine particles.

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