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PHYSICOCHEMICAL PROPERTIES OF ROAD DUST IN MOSCOW

ABSTRACT. Road dust is a composite substance formed due to wear of different components of transport infrastructure and motor vehicles. In 2017, 214 road dust samples were collected in Moscow to analyze pH, electrical conductivity (EC), and organic carbon (C_{org}) content that controls the ability of dust to fix pollutants. The road dust was dominated by sand and silt size particles (the share of PM_{10} particles varies from 2.3% to 39%) and had alkaline pH (6.4–8.1), high EC (33–712 μS/cm) and C_{org} (0.17–6.7%). The road dust is alkalinized by detergents and particles formed by abrasion of roadways and blown out from construction sites. A three-fold excess of the EC over the background values (dust in parks) is mainly due to the use of the de-icing agents and roadway maintenance. But the concentration of C_{org} in the Moscow's road dust is on average 2 times lower compared to the background values; the increased content of C_{org} in the courtyards is associated with the application of organic fertilizers. The most significant factor that determines the physicochemical properties of the dust was the type of a road. The dust on large roads including the Third Ring Road had higher pH (7.0–8.0) and EC (98–712 μS/cm); it contained higher proportions of the fine particle-size fractions compared to other roads. The C_{org} content in the road dust was minimum on Moscow's major radial highways due to the insignificant contribution of soil particles. The spatial trends in variability of the physicochemical properties of the dust in Moscow were not evident as they were to a large extent masked by other factors: proximity to industrial zones and large forest parks, differences in the de-icing agents used, unequal frequencies of road cleaning, and the various contribution of soil particles that vary in composition and genesis in different parts of Moscow.

KEY WORDS: megacity, urban pollution, particulate matter, accumulation potential, geochemical transformation, spatial variability

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INTRODUCTION

Road dust is a multicomponent substance formed as a result of washing out and deflation of roadside soils, wear of different components of transport infrastructure and vehicles, crushing of solid waste and residues of de-icing agents (DIAs), and atmospheric precipitation of particulate matter (Ladonin and Plyaskina 2009; Nazzal et al. 2013; Prokofieva et al. 2015). Road dust originates from various sources and indicates pollution level of urban landscapes, since its particles are the carriers for many pollutants, including heavy metals and metalloids (HMMs). In turn, road dust itself may be a source of secondary pollution of the atmosphere and roadside soils. Road dust is lifted into the air by traffic and it is one of the six most important sources of suspended particulate matter (PM) in urban atmosphere (Belis et al. 2013; National Emissions Inventory 2017).

In the major cities of the world, road dust is increasingly being considered as an object of environmental and geochemical monitoring (Vlasov et al. 2015; Demetriades and Birke 2015; Jayarathne et al. 2017; Yang et al. 2017). Extensive literature is devoted to elemental composition of road dust; however, the physicochemical properties inherited from its different components have been studied to a much lesser extent, although they are the ones that determine the potential of the dust to fix pollutants. Usually, such parameters as pH, organic carbon content (C_{org}), electrical conductivity (EC), and particle size distribution are evaluated (Wang and Q_{in}, 2007; Al-Khashman 2007; Hu et al. 2011; Acosta et al. 2011). The studies of atmospheric dust focus on particles with an aerodynamic diameter of 10 µm or smaller (PM_{10}). This PM fraction is the most important indicator of air quality in many cities around the world, since it can penetrate the human respiratory tract, cause asthma in children and increase the risk of mortality from diseases of the cardiovascular system (Tager 2005; Fonova 2017; Report… 2017). The same particle size fraction is also important when studying road dust, since the particles PM_{10} contain up to 40–60% of the total amount of HMMs and the concentrations of Cd, Ag, Sb, Sn, Se, Cu, Bi, Pb, Zn, Mo, and W in this fraction are 4–22 times higher than their abundances in the upper continental crust (Vlasov et al. 2015; Vlasov 2017).

When road dust settles on the surface of urban soils it changes their physicochemical properties. Road dust has a weak alkaline reaction and can form or increase the capacity of the existing alkaline geochemical barrier, which control the accumulation of many HMMs (Kosheleva et al. 2015). The presence of organic matter in dust causes the formation of organo-mineral geochemical barrier, and the occurrence of various-size dust particles leads to the appearance of sorption-sedimentation geochemical barriers.

In this study for the first time a comprehensive analysis of the road dust properties and their spatial distribution has been made for the entire urban area of Moscow, the largest megacity of Russia and Europe. Moscow has numerous industrial enterprises, heating power plants (HPPs), an extensive road and transport network, and over 4.6 million cars. Similar but limited in scope studies were previously conducted only for individual districts of Moscow (Ladonin and Plyaskina 2009; Vlasov et al. 2015; Prokofieva et al. 2015; Bityukova et al. 2016; Ladonin 2016). The purpose of this study was to evaluate the main physicochemical properties and the accumulation potential of the Moscow's road dust with respect to pollutants as its chemical composition is one of the important indicators of urban environment quality.

The specific objectives of the study were:

– to obtain a representative data set for the territory of Moscow that characterizes the dust on its roads in regard to various traffic intensity in different administrativedistricts (okrugs) of the city;

– to determine main physicochemical parameters of the road dust: pH, EC, C_{org}, and particle size distribution;

– to identify their spatial trends within the city;

– to assess the extent of technogenic geochemical transformation of the dust properties on the roads and to evaluate its accumulation potential with respect to inorganic pollutants (e.g., HMMs).

SOURCES OF ROAD DUST

Motor transport. It is the main source of air pollution in Moscow that presents up to 95% of total emissions, or 880–930 thousand tons per year (Report… 2017; Bityukova and Saulskaya 2017). The length of Moscow roads is 3,600 km, they occupy about 8% of its area (Fig. 1). The density of the road network is 4.2 km/km^2, including the main network 1.54 km/km^2 (Khusnullin 2013). At the beginning of 2017, the automobile fleet of Moscow was about 4.6 million units of which 90.4% were passenger cars, 8.5% were trucks, and 1.1% buses. The number of vehicles is constantly increasing; the car ownership level is 340 per 1000 people.

Deposition of atmospheric aerosols resulting from anthropogenic emissions is one of the factors controlling the accumulation of road dust. Motor transport emissions consist of carbon monoxide (63%), nitrogen oxides (22%), and volatile hydrocarbons (13%) (Report… 2017). Particulate matter accounts for about 1% of the traffic emissions and non-exhaust emissions coming from abrasion of the road surface and road marking, break and tire wear, which ranges, according to various estimates, from 2.5 to > 5 thousand tons per year depending on traffic conditions – type, speed, and numbers of maneuvers (Nazzal

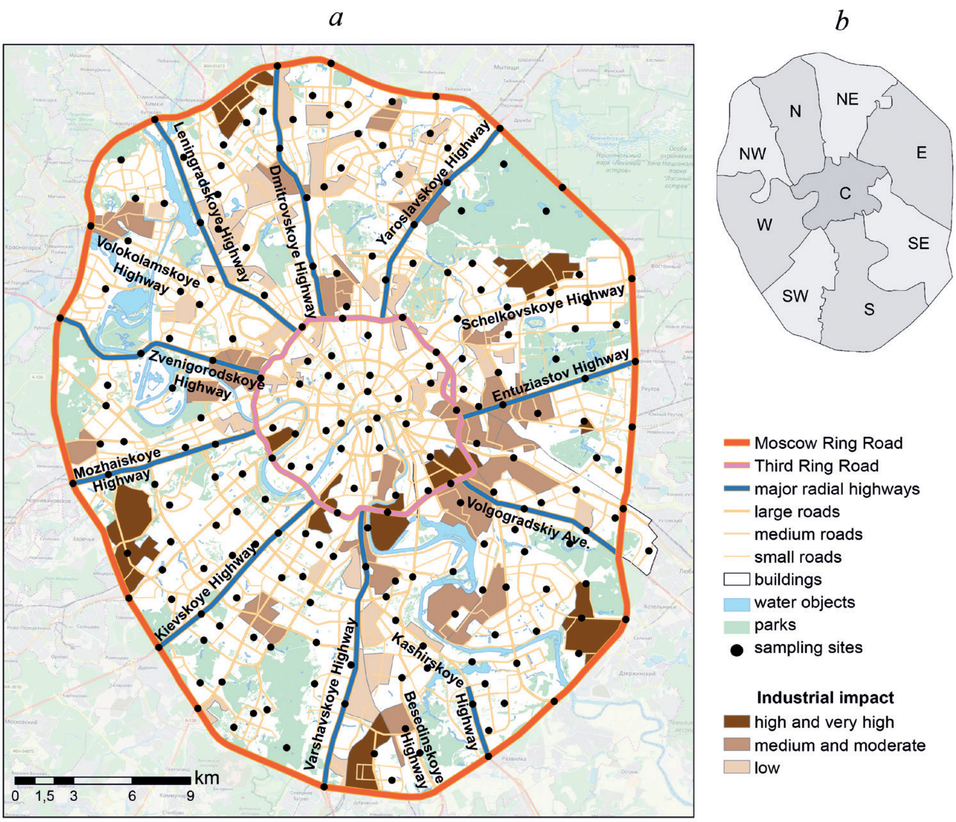

Fig. 1. Mobile and stationary sources of technogenic impact and road dust sampling locations in Moscow (a) and the administrative districts of Moscow within the Moscow Ring Road (b)

Impact levels of industrial zones are given according to Bityukova and Saulskaya (2017). Capital letters indicate the names of administrative districts (okrugs): N – Northern, NE – North-Eastern, E – Eastern, SE – South-Eastern, S – Southern, SW – South-Western, W – Western, NW – North-Western, C – Central et al. 2013). The particulate fraction PM_{10} is largely associated with emissions of diesel cargo transport (61%) and buses (29%), despite the fact that their number is much smaller than that of passenger transport; however, they have higher emission intensity and mileage and a smaller share of engines of high environmental classes. An apportionment of the sources of PM_{10} in Hatfield Tunnel (United Kingdom) showed that 60% of the particulate fraction is composed of particles originated from wear of road surfaces, tires, and brake pads, and re-suspension of the dust (i.e. non-exhaust emissions); while engine exhausts produce only 40% of PM_{10} (Lawrence et al. 2016).

The maximum concentrations of pollutants in the air are observed in close proximity to roads. Within a distance of 1 m from a roadway the average dust load is 1.77 g/m^2 per day and at a distance of 5 meters it is 0.47 g/m^2 per day, which is 262 and 67 times higher, respectively, than the background level (Achkasov et al. 2006). Even in the eastern industrial part of Moscow, the dust load near roads is 1.2–2 times more intensive than near industrial areas (Kasimov et al. 2012, 2017).

The generation of particles during braking of vehicles due to friction between parts of the brake system is one of the significant sources of road dust (Garg et al. 2000). Therefore, the contribution of the road dust loading to suspended PM in urban environment can be quantitatively assessed using markers of particles originated from brake and tire wear, which include Cu and Sb (Weckwerth 2001), as well as tracers of road wear – Ca, Al , Si, Ti, and Fe (Diapouli et al. 2017).

De-icing reagents. The DIAs used in Moscow are chloride-based. They comprise at least 93% of technical salt (sodium chloride). The salt is usually mixed with marble chips that after snowmelt mark the places where the DIAs were applied (Nikiforova et al. 2016). A single road treatment requires 80–200 g/m^2 of the DIA (Sister and Koretsky 2004). The total permitted salt load in Moscow reaches 420–500 thousand tons (as dry matter) during the winter season, or 37 kg of the DIAs per person (Khomyakov 2015). The DIAs include combined (solid and liquid) agents. The municipal services of Moscow use liquid DIAs at temperatures higher 16ºC; at lower temperatures combined agents which include 50–60% of marble chips, crystals of calcium chloride, and formic acid salts are applied. The solubility of marble is low; with decreasing chip-size, it increases in the presence of dissolved calcium chloride and particles of road surface (Greinert et al. 2013). In the courtyards and adjacent areas, sidewalks, and pedestrian streets, only combined DIAs are allowed to be applied. Additionally, grains of crushed granite with a diameter of 2–5 mm can be used, mainly in yard areas and on dangerous road sections.

Industrial enterprises and construction. In Moscow, there are over 30,000 stationary sources of pollutant emissions concentrated in the industrial zones (Fig. 1 a). In different years, the total emission load ranged from 60 to 70 thousand tons per year with a contribution of solids of about 3%. Thirteen HPPs in Moscow account for almost 50–65% of atmospheric emissions from stationary sources, while 20–30% comes from oil refineries, 2–3% and about 2% are derived from engineering enterprises, and from food processing and building materials production, respectively (Bityukova and Saulskaya 2017).

The sources of aerosol emissions to the atmosphere also include about 700 objects of urban construction – residential buildings, urban infrastructure, road and transport facilities (Bityukova and Saulskaya 2017). Many stages of construction are accompanied by intense dust generation. In the near future, the number of construction projects in Moscow is expected to increase owing to the adoption of the law aimed at renovation the old housing stock. Accordingly, about 5,000 buildings needs to be demolished and rebuilt. Besides, in Moscow, some industrial zones are being redeveloped into residential areas.

Soil deflation. Dust contamination of roads increases due to wind erosion of poorly vegetated soils. Within the Moscow Ring Road (MRR), artificially created or highly transformed soils called urbanozems

(Prokofieva and Stroganova 2004) dominate; they have more alkaline pH, higher levels of C_{org} and readily soluble salts, increased accumulation potential and higher proportion of clay, which controls binding of HMMs in soils (Kosheleva et al. 2015). Extraneous material of anthropogenic origin, e.g., construction and household waste, are common in urban soils.

The composition of solid atmospheric fallout on the roadside areas of Moscow reflects its mixed origin. The coarse fractions consist mainly of quartz grains, feldspars, carbonates, and asphalt fragments; the fine fractions, in addition, carry carbon-containing matter, paint, glass, plastic, brick and other fragments (Prokofieva et al. 2015). The $PM_{2.5}$ fraction (particles with an aerodynamic diameter of 2.5 µm or smaller) is formed by soluble inorganic salts, mainly sulfates and nitrates (4–32% of the aerosol mass), insoluble mineral particles, carbon-containing material (1.2–48%) usually represented by elemental carbon (Privalenko and Bezuglova 2003; Da Costa and Oliveira 2009).

MATERIALS AND METHODS

The road dust was tested in Moscow within the MRR on roads with different traffic intensity in June–July 2017 in 9 administrative districts (Fig. 1), as well as inside courtyards with local driveways and parking lots. The courtyards protected from the winds often act as traps for inorganic pollutants which are accumulated in urban soils of residential areas (Kosheleva et al. 2018b). The sampling grid density was defined as one sample per approximately 4 km^2 (Demetriades and Birke 2015; Kasimov et al. 2016). The dust samples that represent geochemical background in urban environment were collected on pedestrian paths in natural forest parks (the Losiny Ostrov, the Izmaylovsky and Bitsevski parks), at the most remote locations from the highways. In total, 173 dust samples were collected on the roads, 36 – in the courtyards, and 5 – in the forest parks.

In terms of traffic intensity, all roads were divided into several types by the width of the roadway and the number of lanes: (1) MRR, (2) the Third Ring Road (TRR), (3) major radial highways with more than four lanes in one direction, (4) large roads with three to four lanes, (5) medium roads with two lanes, and (6) small roads with one lane, and (7) local driveways and parking lots of courtyards. Table 1 shows the number of samples taken on different types of roads.

The fieldwork period was characterized by wet and rainy weather conditions; in June–July 2017 the precipitation norm for Moscow was exceeded nearly twice (Weather and Climate, 2017). The accumulation of the road dust was hampered by intensive surface drainage and daily road cleaning by public utilities. The sampling was carried out in days as dry as possible and no earlier than 24 hours after the rain and full road drying. Composite 300–500 g samples were collected along the curb on both sides of the road with a plastic scoop and brush, in 3–5 replications at a distance of 3–10 m from each other. On large and major radial roads, the samples were taken on the dividing strip; in the courtyards they were collected from the parking lots.

The main physicochemical properties of the dust samples were analyzed at the Ecological and Geochemical Center of the Faculty of Geography, Lomonosov Moscow State University. The pH values were measured in aqueous solutions (dust:water 1:2.5) by the potentiometric technique, the electrical conductivity (EC) – in aqueous solutions (dust:water 1:5) using EC meter,the content of organic carbon (C_{org}) was determined by the Tyurin (wet oxidation) method followed by titration, and the analysis of particle size distribution was performed by laser granulometry. The definition of particles is given according to the classification of N.A. Kachinsky adopted in Russia.

The obtained data were analyzed by statistical methods. For each district and road type, the following measures were calculated: sample averages (m), their errors, standard deviations σ, variation coefficients *($Cv = \sigma/m \cdot 100\%$)*, minimum and maximum values. The variation of the parameters depending on a set of factors (type of road, spatial location of the sampling point in the city, particle size class, base-acid reaction, and C_{org} content) were estimated by the regression trees method in *S-Plus* package (MathSoft®). The visualization of the geochemical data was done in *ArcGIS 10* package.

RESULTS AND DISCUSSION

The physicochemical properties analyzed (Tables 1, 2), in general, fall into the range of values comparable to what has been found in other cities of the world where pH, C_{org} content and EC varied between 7–9, 1–17%, and 100–2800 µS/cm, respectively (Wang and Qin 2007; Al-Khashman 2007; Ladonin and Plyaskina 2009; Acosta et al. 2011; Yisa et al. 2011; Hu et al. 2011; Sutherland et al. 2012).

The results of multivariate regression analysis (Fig. 2) revealed the leading factors determining the physicochemical properties of road dust.

Table 1. Physicochemical properties of the dust collected from different road types

Roads (number of samples)	pH		EC, µS/cm		C_{org}, %		Share of PM_{10}, %	
	Average (min–max)	Cv,, %	Average (min–max)	Cv, %	Average (min–max)	Cv,, %	Average (min–max)	Cv,, %
forest parks (5)	7.1 (6.7–7.4)	3.2	70 (66–88)	17	4.1 (2.5–7.4)	42	13 (6.3–18)	37
MRR (20)	7.3 (6.8–7.9)	3.1	256 (98–521)	41	2.7 (1.5–4.9)	33	18 (5.4–31)	36
TRR (10)	7.4 (7.0–7.6)	2.4	277 (136–712)	57	2.8 (0.85–3.6)	29	18 (6.2–22)	25
major radial (19)	7.5 (7.1–8.0)	3.5	256 (118–537)	45	2.0 (1.0–4.0)	36	15 (4.1–29)	63
large (47)	7.4 (6.9–8.0)	3.9	257 (88–523)	49	2.1 (0.17–4.8)	41	16 (5.7–33)	44
medium (44)	7.4 (6.8–8.1)	3.7	174 (33–450)	55	2.3 (0.87–4.6)	38	13 (3.2–27)	52
small (34)	7.4 (6.4–8.1)	4.2	193 (47–525)	58	2.4 (0.91–4.8)	36	14 (4.0–39)	52
courtyards (36)	7.2 (6.6–8.1)	3.7	162 (63–483)	50	4.1 (1.1–6.7)	32	14 (5.2–28)	45

Note. Hereinafter, share of PM_{10} represents the share (%) of particles with a diameter of 10 µm and smaller in a bulk sample of the road dust (considering particles of all diameters).

Table 2. Physicochemical properties of the road dust collected in different administrative districts (okrugs) of Moscow

District (number of samples)	pH		EC, µS/cm		C_{org}, %		Share of PM_{10}, %	
	Average (min–max)	Cv, %	Average (min–max)	Cv,, %	Average (min–max)	Cv,, %	Average (min–max)	Cv,, %
Eastern (21)	7.4 (7.0–8.0)	3.8	174 (33–519)	67	2.2 (0.17–4.9)	51	14 (6.7–30)	46
Western (29)	7.4 (6.9–8.1)	4.0	183 (98–376)	40	2.5 (1.1–5.67)	45	16 (4.1–28)	41
Northern (12)	7.3 (7.1–7.9)	2.9	211 (97–537)	58	2.6 (1.4–3.8)	22	19 (6.9–28)	34
North-Eastern (23)	7.3 (6.4–7.7)	3.7	199 (65–352)	40	3.1 (1.6–5.1)	34	17 (6.7–29)	34
North-Western (16)	7.2 (6.7–8.0)	4.6	248 (90–459)	45	2.7 (0.85–5.1)	38	18 (7.2–29)	35
Central (32)	7.3 (6.8–8.1)	3.9	243 (80–712)	56	2.4 (0.85–4.8)	46	14 (4.2–24)	47
Southern (27)	7.4 (6.8–8.1)	4.2	214 (73–483)	42	2.8 (1.3–6.6)	49	12 (5–26)	55
South-Eastern (30)	7.4 (6.6–8.0)	4.3	242 (47–525)	64	2.7 (0.91–6.7)	46	15 (3.2–39)	62
South-Western (20)	7.4 (7.1–7.8)	2.4	176 (53–521)	61	2.4 (1.4–4.7)	38	14 (4.1–34)	55
Moscow (210)	7.4 (6.4–8.1)	3.9	211 (33–712)	56	2.6 (0.17–6.7)	44	15 (3.2–39)	48

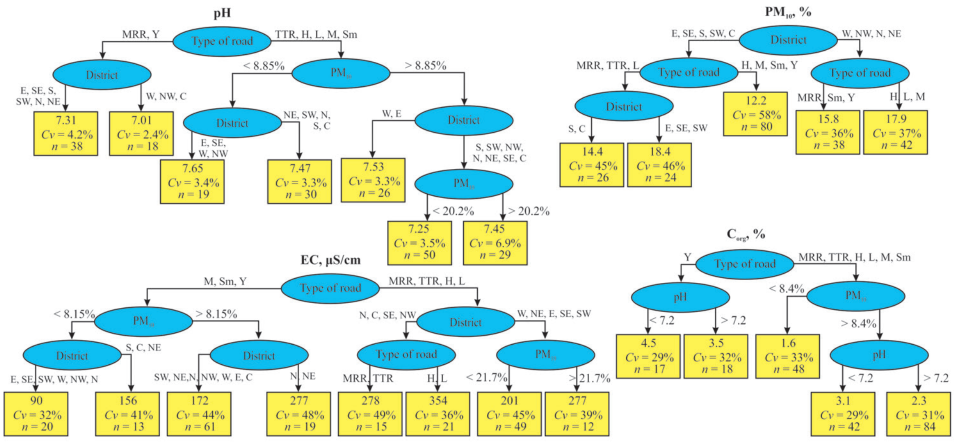

Fig. 2. Differentiation of the physicochemical properties of the Moscow's road dust in relation to the type of the road, the administrative district, and the particle size distribution

For each terminal node, the average value of the parameter, the coefficient of its variation Cv, and the number of sampling points n are given. Types of roads: H – major radial highway, L – large, M – medium, Sm – small, Y – courtyards. For the names of the districts please see the footnote of Fig. 1

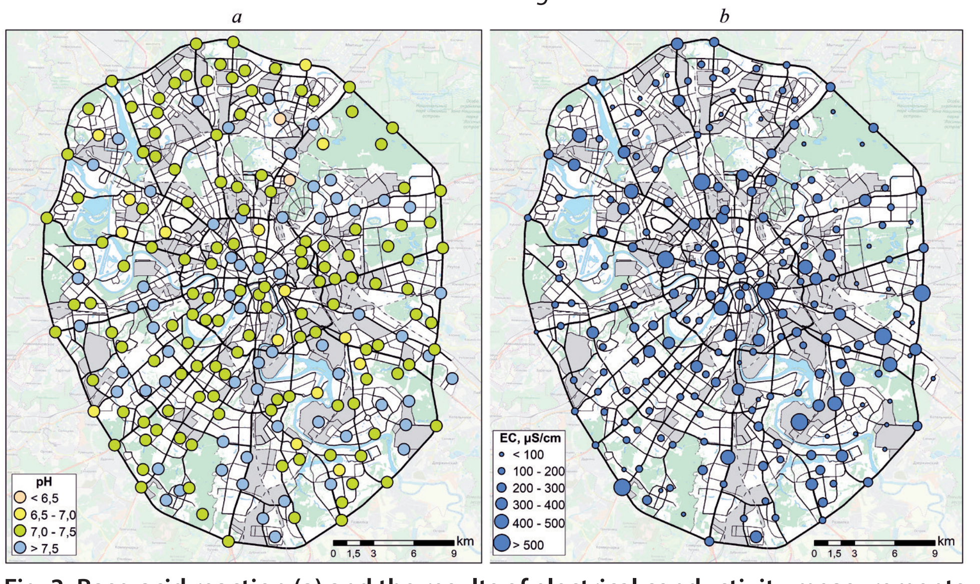

Fig. 3. Base-acid reaction (a) and the results of electrical conductivity measurements of the road dust in Moscow (b)

Urbanized background. The road dust in the urban forest parks (Table 1) had the lowest values of pH (7.1) and EC (70 µS/cm). The DIAs are not applied in these territories; there is no pollution by particles formed during mechanical deterioration of vehicle parts, and atmospheric deposition is hampered by vegetation. The main components of the dust in these background areas are plant residues and soil particles. In the forest parks, natural sod-podzolic soils (Retisols) with slightly acidic reaction and the prevalence of fulvic acids in the surface horizon owing to plant litter (Prokofeva et al. 2013, Rozanova et al. 2016) are still present. Foliage residues serve as a natural source of C_{org}, which determined its increased concentrations – 4.1%, on average. Unlike the forest parks, fallen leaves are removed from the public gardens and parks, as well as in many

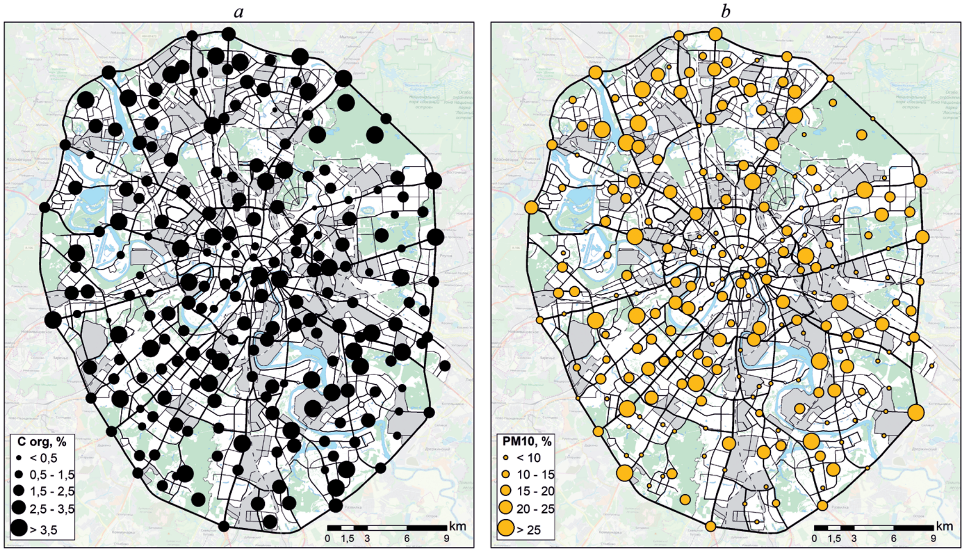

Fig. 4. The C_{org} content (a) and the proportions of PM_{10} fraction in the road dust samples in Moscow (b)

residential yards and green lawns, thereby reducing the new addition of organic matter into the soil. Also, the background dust had specific granulometric composition: in all 5 samples collected, a coarse particle size fraction 250–1000 μm prevailed (> 50%).

Base-acid reaction. The average pH of the dust sampled on the roads and in the courtyards is 7.4. The differences between the administrative districts were insignificant; the values that exceed the maximum and the average pH were typical of the western, southern and eastern parts of Moscow, while minimum values were observed in its northern part (Table 2, Fig. 3a). The lowest average pH of 7.2 was recorded in the North-Western district due to the prevailing northerly winds which contribute to the translocation of alkaline technogenic dust to the south of Moscow (Lokoshchenko 2015) – the road dust pH in the Southern, South-Eastern and South-Western districts, as well as in the Eastern and Western districts, exceeded the value of 7.4. The coarse sand fraction (particles with diameter >500 μm) is suspended at wind speeds exceeding 10 m/s; the coarse silt (with diameter 10–50 μm) and smaller particles may suspend in fairly weaker winds. Particles with diameter of 1–2 μm at wind speeds of 2–3 m/s are removed from the soil surface, enter the surface aerosol, and remain suspended for quite a long time (Gendugov and Glazunov 2007). The particles' pH rises when their size decreases. Thus, in Western district, the pH in the aqueous extract of PM_{50} (with diameter ≤50 μm) was 0.6 units higher than that of $PM_{>50}$ (with diameter >50 μm); on large roads, this difference increased to almost 1 unit (Bityukova et al. 2016).

High pH values (≥8) in most cases are caused by the influx of alkalinizing substances during the repair of the roadway and laying paving slabs (Greinert et al. 2013). The maximum pH of 8.1 turned out to be lower than the average (8.2) and maximum (8.9) pH of road dust collected in the summer of 2013 for the eastern part of the city (Vlasov et al. 2015) when the weather was rather dry and hot. Low pH values in the summer of 2017 may be associated with intensive removal of carbonate dust by precipitation and surface runoff.

The pH values of the dust correlate well with the types of roads. The pH tends to increase in the following order: courtyards and small roads → large and major radial roads. The exception is the road dust collected on the MRR which shows the intermediate pH values. The lowest average pH is restricted to the inner yard territories (7.2), while the highest – is registered for the major radial highways (7.5); which supports the idea that pH increases with the increasing road width and intensity of traffic. Roadway abrasion is higher on large roads (even small ruts are formed here), the material of which has a slightly alkaline reaction with a pH of 7.4. The highest pH variability with both the minimum (6.4) and maximum (8.1) values was observed on small roads.

The pH rise with increasing road-size might be explained by a more active use of strong alkaline detergents on large roads. During summer period, roads are cleaned daily by sweeping dust and periodic washing of the road surface. Detergent products with high pH (9–11) are used ("Chistodor," "Tornado"). After deposition on road surfaces and drying they become one of the significant dust alkalinizing agents. The pH of the dust is minimal on parking lots in courtyards and on the MRR as they are not regularly washed (Fig. 2) while the road dust pH is much higher on the TRR, major radial, large, medium, and small roads, especially in Eastern, South-Eastern, Western and South-Western districts.

The predominance of the coarse particle size fractions in the road dust (Fig. 2) determines a more alkaline environment, which is associated with the input of slightly soluble particles of marble chips in winter season. The bulk of the DIAs used consists of particles with a diameter of 1–10 mm; the number of particles <1 mm does not exceed 15–20%.

Electrical conductivity. The Moscow's road dust has high EC, which is due to the presence of large quantities of soluble substances of technogenic and natural origin, detected in aqueous extracts. The average EC value of Moscow road dust was 211 μS/cm, which is about 3 times higher than the background value in the forest parks (70 μS/cm). The EC varies between the districts from 173 (Eastern district) to 248 μS/cm (North-Western district) and within the districts, where the EC variation coefficients are also significant (*Cv* 40–67%).

In winter time, the main source of readily soluble salts are the DIAs. With their excessive application, some of the reagents are not removed by the melt water, but remain in the solid form on the roadway, increasing the road dust EC. With decreasing particles' size, their EC rises: in Western district, the EC of PM_{50} is 2 times higher than that of $PM_{>50}$ (Bityukova et al. 2016).

The clear relationship between road-size and the EC was detected: the EC values on medium and small roads and in courtyards were 1.5 times lower than those on the MRR, TRR, major radial highways and large roads, especially in Northern, Central, South-Eastern and North-Western districts (Fig. 2) due to a high content of PM_{10} (Table 2). A similar effect was observed in Amman, Jordan (Al-Khashman 2007). The smallest average EC (161 μS/cm) was typical of courtyards with parking lots, while the highest (277 μS/cm) of the TRR. The minimum value was found on the medium-size roads in Eastern district (33 μS/cm), and the maximum (712), at the crossroad of the Zvenigorodskoye Highway and the TRR.

The map (Fig. 3b) shows that increased EC are confined to the area stretching from the North-West to South-East. Most likely, the high EC values in this area are associated with greater density of the road transport network and industrial facilities. Outside this area in the North-East of Moscow, there is a large forest park Losiny Ostrov, and in the South-West, the Bitsevski forest park.

Organic carbon. The pool of carbon in road dust is formed by soil particles containing humus and organic compounds of technogenic origin. In the traffic zone, the composition of organic matter is dominated by insoluble organic compounds, generally not susceptible to destruction by soil microorganisms, which increases their accumulation. Sources of these compounds are asphalt pavement and emissions from industries and motor vehicles (Faure et al. 2000). In the recreational and residential areas (forest parks and courtyards), the organic matter usually consists of natural fractions of humus (Lodygin et al. 2008); it is possible that in wet conditions (as it was in summer 2017), the fungi mycelium was an additional source of organic carbon (Prokofieva et al. 2015). The increase in the C_{org} content in the forest parks is caused by the decomposition of plant litter as a natural source of C_{org}; in the courtyards, it is associated with the application of organic fertilizers (Vodyanitskii 2015).

The average content of C_{org} in road dust of Moscow was 2.6% ranging from 2.2% in Eastern district to 3.1% in North-Easterndistrict with the variation coefficient up to 50% (Table 1, Fig. 4a). In dust of different types of roads, the minimum content of C_{org} of 2.0% was associated with the major radial highways and large roads; the maximum of 4.0%, close to the background level of 4.1%, was observed in the courtyards (Fig. 2), where organic matter comes from soil particles that are blown out from lawns and carried on wheels of cars parked on bare ground. The lawn soils have a high content of C_{org} and nutrients, primarily nitrates (Kosheleva et al. 2018a). The addition of organic matter also occurs during idling of car engines responsible for increased emissions of soot and other organic compounds.

The C_{org} content in the road dust is positively correlated with PM_{10} fraction, which is partially derived from automobile exhaust containing various organic compounds, including soot particles and lubricating oils (Grigoriev and Kissel 2002). The fine particle size fraction in the road dust also includes fine topsoil particles (1–2 μm), which are blown out by moving vehicles (Gendugov and Glazunov 2007). The smaller are the particles, the greater is the likelihood of them being blown out of the soil surface and getting into the dust. This explains the direct relationship between C_{org} and PM_{10}. The effect of pH on the C_{org} content (Fig. 2) relates to the contribution of soil particles, which, compared with technogenic material, have a more acidic reaction.

Particle size distribution. The granulometric composition of the Moscow's road dust was fairly uniform; it mainly contains sand (50–1000 μm) and coarse silt (10–50 μm) fractions, consisting predominantly of quartz and feldspar, respectively (Prokofieva et al. 2015). There were no significant differences in the particle size distributions between the road dust samples collected in different administrative districts and on different road types; the differences did not exceed 2–6% (Table 1, 2, Fig. 4b). Within the district groups, the share of PM_{10} in the road dust varied depending on the type of roads (Fig. 5). The road dust in Southern, South-Eastern and South-Western districts and on the large roads and the MRR was slightly dominated by PM_{5-10} and PM_{10-50} fractions (Fig. 5).

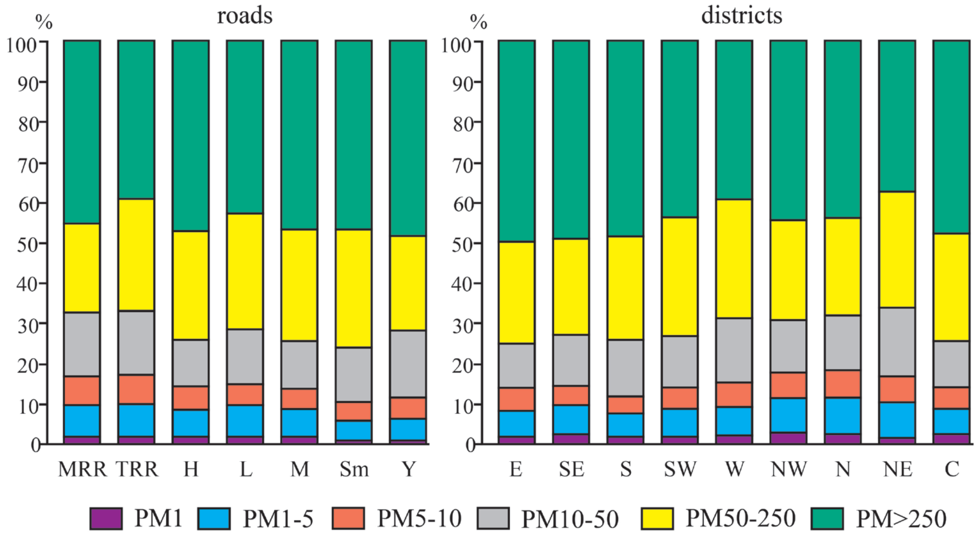

Fig. 5. The particle size composition of the road dust on various types of roads and in different administrative districts of Moscow. Types of roads are deciphered in Fig. 2.

The dust with a high content of the PM_{10} was typical for the Leningradskoye and Yaroslavskoye Highways, some of the busiest highways in Moscow, and for large roads at some distance from TRR and the city center. The PM_{10} content increases as a result of daily congestion of vehicles with long idling, which leads to an increase in emissions of fine particles and soot. This is especially pronounced in local depressions of the relief, where the most favorable conditions for the deposition of particles are formed.

The maximum content of coarse fractions was observed on the medium and small roads, as well as in Central, Eastern, South-Eastern and South-Western districts. The most likely reason for the predominance of coarse fractions in the road dust of the South-Eastern district is the coarse parent material of Meshchera lowland; there, a flat sandy plain is composed of fluvioglacial sands and sandy loam (Kasimov et al. 2016).

Technogenic transformation of the dust properties and the dust ability to accumulate pollutants.

Physicochemical properties of the road dust in the city are affected by technogenic sources. The comparison of the road dust with the dust sampled in the forest parks allowed us to estimate the intensity of the technogenic transformation of its properties (pH, EC, C_{org}, and the PM_{10} content) within Moscow. However, a comprehensive assessment of such transformation is difficult due to differences in the units of measurement and the variability of the parameters studied. To bring the heterogeneous data to a single scale, physicochemical properties of the road dust were normalized (Tikunov 1997):

$X'_i = |X_i - X_b| / |X_{ex} - X_b|$,

where X_i, X'_i are the initial and normalized values of a property at the *i*-th sampling point, respectively; X_b is the background value of the property in the dust of forest parks; X_{ex} is the extreme value of the property (X_{max} or X_{min}) most deviating from the background value X_b. As a rule, $X_{ex} = X_{max}$. If $|X_{min} - X_b| > |X_{max} - X_b|$, then $X_{ex} = X_{min}$. Then the *degree of technogenic transformation* (R) at the *i*-th sampling point can be defined as the total value of the normalized deviations of all parameters from the background values of $\Sigma X'_{ij}$, where *j* is the considered physicochemical property (in our case *j* = 1, 2, 3, 4). We set the approximate gradations of R depending on its range in the study area $\Delta R = R_{max} - R_{min}$ (Table 3).

Analysis of the spatial distribution of R (Fig. 6a) showed that the greatest transformation of the physicochemical properties of road dust was associated with the sections of major radial highways located near the industrial zones and bus depots: in Southern district – it was the Varshavskoye Highway (electrical substations, meat processing plant, bus and trolleybus depots, factory for the production of optoelectronic devices); in Eastern district – Schelkovskoye Highway (HPP-23); in Northern district – Dmitrovskoye Highway (bus depot, mechanical plants); in North-Western district – Volokolamskoye Highway (bus depot, reinforced-concrete plant) and

Table 3. Levels of technogenic transformation (R) of the road dust physicochemical properties

Level of technogenic transformation	Limit values of R	Ranking categories of R for Moscow
very low	$R \le R_{min} + 0.1 \cdot \Delta R$	$R \le 0.417$
low	$R_{min} + 0.1 \cdot \Delta R < R \le R_{min} + 0.25 \cdot \Delta R$	$0.417 < R \le 0.776$
medium	$R_{min} + 0.25 \cdot \Delta R < R \le R_{min} + 0.5 \cdot \Delta R$	$0.776 < R \le 1.374$
high	$R_{min} + 0.5 \cdot \Delta R < R \le R_{min} + 0.75 \cdot \Delta R$	$1.374 < R \le 1.972$
very high	$R_{min} + 0.75 \cdot \Delta R < R \le R_{min} + 0.9 \cdot \Delta R$	$1.972 < R \le 2.330$
extremely high	$R > R_{min} + 0,9 \cdot \Delta R$	$R > 2.330$

Zvenigorodskoye Highway (bus depot and HPP-16); in Western district – Mozhaiskoye Highway (HPP-25, wood processing plant, champagne wines plant, beer and non-alcoholic beverages plant); and in Central district – the Garden Ring road.

An increase in the pH, C_{org} and the PM_{10} contents in soils leads to the formation of technogenic alkaline, organo-mineral, and sorption-sedimentation geochemical barriers (Vodyanitskii 2008, 2015), whose capacity increases with the growth of these parameters (Kosheleva et al. 2015). Considering that roadside soils play an important role in the formation of the mineral part of road dust and supply a significant amount of toxic chemical elements and compounds, an increase in pH, C_{org} and the PM_{10} content in the road dust, as in other mineral components of urban landscapes will contribute to the growth of its accumulation potential in relation to many HMMs.

To assess the spatial variability of the accumulation potential of the Moscow's road dust with respect to HMMs, the normalized index $Q = \Sigma X'_{ij}$ was calculated, with $j = 1, 2, 3$; $X'_i = (X_i - X_{min}) / (X_{max} - X_{min})$. The following ranking categories were adopted for the accumulation potential (Q) of road dust in Moscow taking into account its range in the study area $\Delta Q = Q_{max} - Q_{min}$ (Table 4).

Table 4. Ranking categories of the accumulation potential (Q) of the road dust

Accumulation potential	Limit values of Q	Ranking categories of Q for Moscow
very low	$Q \le Q_{min} + 0.1 \cdot \Delta Q$	$Q \le 0.796$
low	$Q_{min} + 0.1 \cdot \Delta Q < Q \le Q_{min} + 0.25 \cdot \Delta Q$	$0.796 < Q \le 1.052$
medium	$Q_{min} + 0.25 \cdot \Delta Q < Q \le Q_{min} + 0.5 \cdot \Delta Q$	$1.052 < Q \le 1.478$
high	$Q_{min} + 0.5 \cdot \Delta Q < Q \le Q_{min} + 0.75 \cdot \Delta Q$	$1.478 < Q \le 1.905$
very high	$Q_{min} + 0.75 \cdot \Delta Q < Q \le Q_{min} + 0.9 \cdot \Delta Q$	$1.905 < Q \le 2.160$
extremely high	$Q > Q_{min} + 0.9 \cdot \Delta Q$	$Q > 2.160$

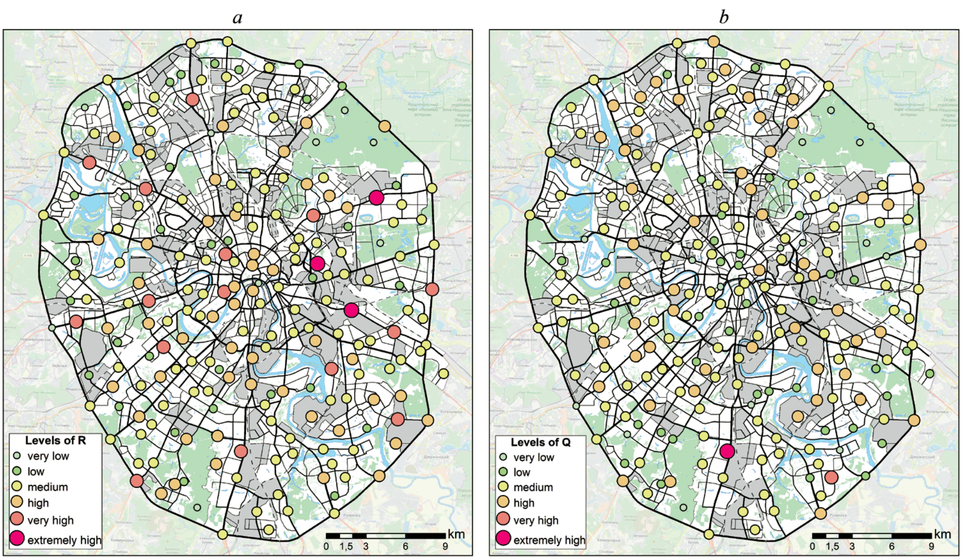

Fig. 6.The degree of technogenic transformation (R) of physicochemical properties (a) and the accumulation potential (Q) of the road dust (b)

The spatial distributions of the two indices – Q and R – differed for several reasons. First, the calculation of Q did not take into account the data on the EC of the aqueous extract of the road dust, since the EC's effect on the accumulation potential of mineral components has not been sufficiently studied. Secondly, the accumulation potential considers only the increase in pH values and the content of C_{org} and PM_{10}, whereas the index of technogenic transformation R summarizes both positive and negative deviations from the background conditions.

The analysis of the Q index distribution suggests the predominance of road dust with high and average accumulation potential in the traffic zone in all districts of the city. Medium levels of technogenic transformation and accumulation potential were typical of the MRR and the TRR, which is might be explained by rapid "regeneration" of dust material as a result of frequent road sweeping by municipal services. The largest accumulation potential of the road dust was detected in south of Moscow (along the Varshavskoye Highway), in the south-east (in courtyards and on medium-size streets between the Kashirskoye and Besedinskoye Highways), and in the north of Moscow (along the MRR and medium-size streets near the HPP-21, pipe plant, and fish and meat processing plants).

CONCLUSIONS

The dust in the urban forest parks of Moscow is mainly derived from the natural sources with minimal impact of anthropogenic fallout. Formed mainly by soil particles, it has the background properties most similar to those observed in the upper horizon of zonal sod-podzolic soils. It has neutral pH (average 7.1), low EC (70 µS/cm), high content of C_{org} (4.1%) and a significant amount of the coarse particle size fraction (> 250 µm). The high content of C_{org} in the forest parks is caused by decomposition of plant litter.

The dust on the roads has a more alkaline reaction (pH 7.4), high EC (211 µS/cm), and lower content of C_{org} (2.6%), which is explained by motor vehicles emissions and the proximity to the industrial areas, as well as with a large volume of DIAs applied. The road dust is alkalinized by detergents and particles formed by abrasion of roadways and blown out from construction sites. A three-fold excess of the EC over the background values is mainly due to the use of the DIAs and roadway maintenance. The concentration of C_{org} in the Moscow's road dust is on average 2 times lower compared to the background values. In the courtyards, the increased content of C_{org} is associated with the application of organic fertilizers. In general, the road dust is composed mainly of sand-size particles (50–1000 µm) and coarse silt (10–50 µm) fraction. The variations in the share of particle size fractions by districts and different types of roads, as a rule, do not exceed 2–6%.

The most significant factor determining the physicochemical properties of the road dust is the type of road. The dust on large roads including TRR has higher pH, EC, and PM_{10} values, which is caused by the intense traffic and, as a result, the greater amount of particles formed through roadway and vehicle wear. The content of C_{org} in the road dust is reduced due to the lower contribution of soil particles. The spatial trends in the dust properties across the city territory are poorly expressed; to a large extent they are masked by other factors such as proximity to industrial zones and to large forest parks, the DIAs composition, frequency of the roadway cleaning and washing, and the contribution of soil particles of various genesis in different districts of Moscow.

The settling of airborne technogenic substances in the traffic zone increases the accumulation potential of the road dust with respect to pollutants binding compared to the dust of the forest parks. The most pronounced transformation of the road dust properties was found along some segments of the major radial highways that are located near the industrial areas and bus depots, especially in Southern, Eastern, Northern, North-Western, Western and Central districts. In Southern, South-Eastern and Central districts dust has the greatest accumulation potential. Cleaning roadways by municipal services reduces technogenic transformation of the road dust properties and thereby diminish its ability to bind pollutants, what is most pronounced on MRR and TRR. Therefore, regular cleaning of all types of roads, including those in courtyards of residential areas, is an effective measure to improve the quality of urban environment by reducing the level of its contamination with dust and dust associated pollutants. Thus, these results and the approved methodology for studying the physicochemical properties of road dust can be useful in assessment of urban environmental pollution, as well as in planning and rationalizing activities for cleaning streets from road dust.

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