ORIGINAL PAPER



Benzo[a]pyrene in Moscow road dust: pollution levels and health risks

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Received: 29 November 2021 / Accepted: 19 April 2022 © The Author(s), under exclusive licence to Springer Nature B.V. 2022

Abstract Benzo[a]pyrene (BaP) is one of the priority pollutants in the urban environment. For the first time, the accumulation of BaP in road dust on different types of Moscow roads has been determined. The average BaP content in road dust is 0.26 mg/kg, which is 53 times higher than the BaP content in the background topsoils (Umbric Albeluvisols) of the Moscow Meshchera lowland, 50 km east of the city. The most polluted territories are large roads (0.29 mg/ kg, excess of the maximum permissible concentration (MPC) in soils by 14 times) and parking lots in the courtyards (0.37 mg/kg, MPC excess by 19 times). In the city center, the BaP content in the dust of courtyards reaches 1.02 mg/kg (MPC excess by 51 times). The accumulation of BaP depends on the parameters of street canyons formed by buildings along the roads: in short canyons (< 500 m), the content of BaP reaches maximum. Relatively wide canyons accumulate BaP 1.6 times more actively than narrow canyons. The BaP accumulation in road dust significantly increases on the Third Ring Road (TRR), highways,

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10653-022-01287-9.

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Published online: 18 May 2022

medium and small roads with an average height of the canyon > 20 m. Public health risks from exposure to BaP-contaminated road dust particles were assessed using the US EPA methodology. The main BaP exposure pathway is oral via ingestion (> 90% of the total BaP intake). The carcinogenic risk for adults is the highest in courtyard areas in the south, southwest, northwest, and center of Moscow. The minimum carcinogenic risk is characteristic of the highways and TRR with predominance of nonstop traffic.

Keywords Polycyclic aromatic hydrocarbons \cdot Street canyons \cdot Regression trees \cdot Road dust \cdot Health risks \cdot Benzo[a]pyrene

Introduction

Road dust is a multicomponent medium formed during the settling of aerosol particles derived from the engine and industrial emissions, wear and tear of vehicles and transport infrastructure, washing out and blowing out of roadside soils, the comminution of garbage, and from residues of deicing mixtures (Aguilera et al., 2021; Pachon et al., 2021; Seleznev et al., 2020; Zhang et al., 2019a). Its particles are the carrier phase of many pollutants, primarily polycyclic aromatic hydrocarbons (PAHs, or polyarenes) and heavy metals and metalloids (HMMs) (Alves et al., 2020b; Jayarathne et al., 2019; Vanegas et al., 2021; Wiseman et al., 2021; Vlasov et al., 2022). Therefore,



in large cities, road dust increasingly often becomes an object of ecological and geochemical monitoring (Demetriades & Birke, 2015; Ramírez et al., 2019; Sager, 2020; Vlasov et al., 2021; Yang et al., 2017). Road dust particles, particularly those with a diameter of less than 10 μ m (PM₁₀), are easily blown out from the roadways into the air, and the related pollutants enter human bodies through inhalation, ingestion, or dermal contact (Levesque et al., 2021; Lloyd et al., 2019; Rienda & Alves, 2021). Road dust is an essential source of particulate matter in the urban atmosphere, especially within street canyons (Kauhaniemi et al., 2011; Stojiljkovic et al., 2019). Moreover, road dust is a significant source of suspended particles in the atmosphere of the USA, supplying more than half of the mass of PM₁₀ and about a quarter of PM_{2.5} (NEI, 2020). In the form of dry precipitates, road dust enters urban soils, as well as the surface of plants, contributing to their pollution, particularly, during mechanical cleaning of the roadway by city services (Polukarova et al., 2020). Migrating with storm runoff, it exerts a negative impact on urban water bodies, increasing the content of suspended matter and the concentrations of most HMMs, PAHs, salts, and nutrients (Lloyd et al., 2019; Nawrot et al., 2020). In the absence of snow cover, the chemical composition of road dust appears an informative indicator of the ecological state of the urban environment and the primary sources of pollution (Kasimov et al., 2019a; Ladonin & Mikhaylova, 2020; Švédová et al., 2020).

PAHs are distinguished as carcinogens and mutagens (IARC, 2010). Pyrogenic PAHs are mainly formed during the combustion of organic substances in motor vehicles and industrial plants; petrogenic PAHs are found in petroleum products. PAHs included in the polymeric materials, tires, and road surfaces can be classified as both pyrogenic and petrogenic (Stogiannidis & Laane, 2015). Among PAHs, the most dangerous is benzo[a]pyrene (BaP), which belongs to hazard class I substances, the ingestion of which into the human body can cause cancer (Dat & Chang, 2017; Jacob, 2008; US EPA, 2017). In cities, BaP is most often formed during incomplete combustion of fuels at industrial enterprises, transport facilities, and in heating systems, as well as during biomass burning (Konstantinova et al., 2020a; Liao & Yu, 2020). PAHs in road dust have been the subject of many studies, especially in Asian cities with high amounts of road dust and with numerous sources of PAHs (Anh et al., 2019; Gbeddy et al., 2021; Khpalwak et al., 2019; Konstantinova et al., 2020b; Ma et al., 2017; Majumdar et al., 2017; Soltani et al., 2015; Wei et al., 2015). In the road dust of Moscow the largest megacity of Russia and Europe-the dustiness of the roads is also quite high (Bityukova & Mozgunov, 2019). However, most of the studies of PAHs in Moscow are devoted to soils (Agapkina et al., 2007, 2018; Belinskaya et al., 2015; Kasimov et al., 2017; Kogut et al., 2006; Nikiforova & Kosheleva, 2011; Nikiforova et al., 2019; Nikolaeva et al., 2017; Smagin et al., 2021; Zavgorodnyaya et al., 2019), river water (Eremina et al., 2016), bottom sediments of water reservoirs (Kramer & Tikhonova, 2015), snow cover (Galitskaya & Rumyantseva, 2012; Kasimov et al., 2017; Khaustov & Redina, 2019; Lebedev et al., 2012; Zavgorodnyaya et al., 2019), atmospheric precipitation (Polyakova et al., 2018), and aerosols (Popovicheva et al., 2020).

So, the behavior and distribution of BaP in Moscow road dust have not been studied in detail, there are only a few single measurements of the content of BaP in road dust on some city roads (Bykova et al., 2021; Karpuhin et al., 2017), although road dust is an important link reflecting the relationships between the urban environments—soils, water bodies, and atmospheric aerosols (Kasimov et al., 2020). In the road dust of Moscow, only HMMs were previously analyzed in detail (Ermolin et al., 2018; Fedotov et al., 2014; Kasimov et al., 2021; Ladonin & Mikhaylova, 2020; Vlasov et al., 2021). An important role in the distribution and accumulation of HMMs and BaP is played by the physicochemical properties of road dust, determining dust capacity to fix pollutants (Acosta et al., 2011; Hu et al., 2011; Kasimov et al., 2019b), and by the artificial relief: under urban conditions, buildings can both protect against pollution and contribute to the enhanced accumulation of pollutants (Kasimov et al., 2017; Kosheleva et al., 2018). Air pollution, and probably as a result, road dust, is especially high in deep street canyons with heavy traffic (Lv et al., 2020; Yuan et al., 2014). The isolation of street canyons from adjacent urban blocks leads to the fact that about 70% of the equivalent black carbon released into the atmosphere from intracanyon sources (vehicles) (Barreira et al., 2021). Owing to the turbulent air mixing in street canyons, a uniform distribution of PAH concentrations over height can be observed (De Nicola et al., 2013). BaP is one of



the priority pollutants in Moscow soils; its contribution to the total equivalent toxicity of 16 PAHs is 37.5% (Agapkina et al., 2018). Road dust in Moscow is an important source of particles in the atmosphere (Gubanova et al., 2021), and increased concentrations of BaP in the surface air are one of the causes of population mortality in the city from cancer (Andreeva et al., 2016). Thus, the study of road dust pollution with BaP in Moscow is extremely relevant. However, despite the serious danger of BaP for the city's population, the associated public health risks have not yet been estimated.

Our work aimed to characterize the content and leading factors contributing to the increased accumulation of BaP in the road dust in dependence on the type of road and geometry of street canyons in Moscow, to compare BaP contents in road dust and other urban environments, and to evaluate non-carcinogenic and carcinogenic risks to public health.

Sources of road dust pollution

The main source of road dust pollution in Moscow is motor transport; in 2019, its emissions amounted to 345,000 tons, or 85% of the total volume of emissions into the atmosphere (Kul'bachevskii, 2020). Roads occupy about 8% of the city's area; their total length at the end of 2019 was 6625 km (Rosstat, 2020). With the area of Moscow reaching 2561 km², the density of the road network in the city is 2.6 km/km². In 2019, Moscow's car fleet totaled about 4419 thousand units, including 90% of cars, 9% of trucks and light-duty vehicles, and 1% of buses. The level of motorization was 349 units/1000 people. The average growth rate of the vehicle fleet in Moscow in 2014–2019 reached 18.2 thousand units/year, or 0.5%/year (Kul'bachevskii, 2020).

In Moscow's motor transport emissions (excluding abrasion of the road surface, markings, tires, and brake pads of cars), carbon monoxide accounts for 63%, nitrogen oxides 22%, volatile hydrocarbons 13%, and particulate matter about 1%. The largest amount of PM_{10} is emitted by freight transport (61%) and buses (29%), although the number of these vehicles is an order of magnitude smaller than that of light cars. This is because of considerably higher specific emissions and mileage of heavy trucks and buses and a lower share of engines of high ecological classes corresponding to Euro-4, Euro-5, and higher

European emission standards (Kul'bachevskii, 2020). The average dust load on the surface of roadside soils (within a 1 m zone) in the early 2000s was 1.77 g/m² per day, decreasing to 0.47 g/m² per day at a distance of 5 m from the road, which was 262 and 67 times higher, respectively, than the background dust deposition (0.007 g/m² per day) level (Achkasov et al., 2006). At present, dust deposition from the atmosphere within a few meters from the MRR averages 0.13 g/m² per day; it decreases to 0.10 g/m² per day near major highways and 0.03–0.04 g/m² per day near medium and small roads; in courtyards of residential buildings with parking lots, it is about 0.02 g/m² per day (Vlasov et al., 2020).

Exhaust emissions of BaP per 1 km of the mileage reach up to 0.1 mg for mopeds and motorcycles, 3.87 mg for cars, 2.03 mg for light trucks, 0.97 mg for heavy trucks, and 0.90 mg for buses (Riccio et al., 2016). In addition to vehicle exhausts, the source of BaP in the traffic area is non-exhaust emissions, among which the most significant contribution is due to tire and roadway wear. The content of BaP in automobile tires can reach 1.39-2.5 mg/kg, in addition, the intensity of the supply of polyarenes during tire wear increases with increasing tire mileage or the degree of wear (Alves et al., 2020a). A significant source of PAHs and BaP in the traffic area is represented by railway transport facilities associated with diesel engine exhaust gases; abrasion of brakes, wheels, and rails; dust blowing during the transportation of bulk minerals and slags; and wear and tear of sleepers and objects treated with various chemical compounds (Kim et al., 2016; Levengood et al., 2015; Lovett et al., 2018).

Emissions from industrial plants also contribute to road dust pollution. There are more than 30,000 stationary emission sources in the industrial zones of Moscow (Fig. 1).

In 2019, the volume of their emissions amounted to about 60,000 tons, with a share of solids of about 3% (Kul'bachevskii, 2020). Stationary sources are responsible for only 15% of the total emissions of pollutants in Moscow, of which 50–65% are due to 13 combined heat and power plants (CHPs); 20–30%, to oil refinery plants; 15–20%, to processing industries; and up to 7%, to machine-building enterprises, incinerators, and production of food and construction materials (Bityukova & Saul'skaya, 2017). Very high and high levels



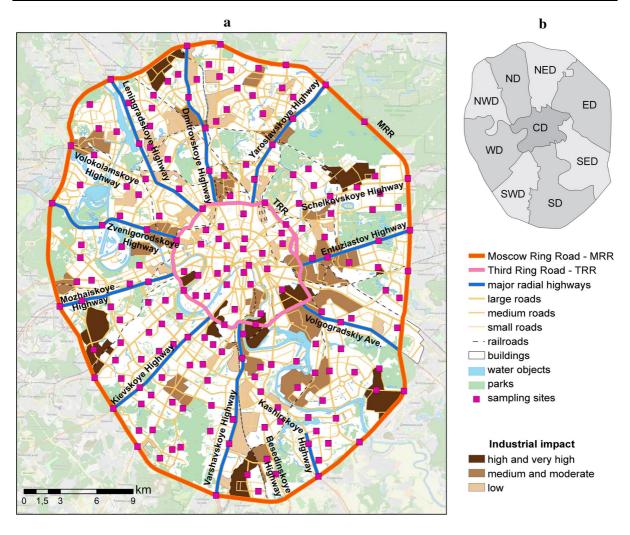


Fig. 1 Sources of industrial impact and road dust sampling sites (summer 2017) in Moscow (a) and the administrative districts of Moscow within the Moscow Ring Road (b): ND is Northern district. NED is Northeastern. ED is Eastern. SED

is Southeastern, SD is Southern, SWD is Southwestern, WD is Western, NWD is Northwestern, CD is Central district. Industrial impact levels are given according to Bityukova and Saul'skaya (2017)

of anthropogenic impact are characteristic of 11 industrial zones, which occupy more than 20% of the total area of industrial territories and supply more than 70% of the gross pollution from all city's industrial zones (Bityukova & Saul'skaya, 2017). These industrial zones are located mainly in Moscow's eastern, southern, and southeastern sectors, often adjacent to the TRR or MRR. Industrial zones with medium and moderate levels of anthropogenic impact also occupy large areas near the TRR in these sectors. Dust sources are also represented by about 700 urban construction sites. These are residential buildings, urban infrastructure, and road and

transport facilities. In addition, Moscow is currently redeveloping industrial zones into residential ones (Saul'skaya, 2018).

The dustiness of roads increases due to the wind-blowing of urban soil particles and the use of deicing mixtures (DIMs). Artificially created or intensely transformed soils—Technosols—prevail on territories bounded by the MRR (Prokof'eva et al., 2017). These soils are specified by higher pH values, contents of soluble salts, organic matter, PM₁₀ particles, and sorption capacity in comparison with the natural background soils (Umbric Albeluvisols), which contributes to the fixation of BaP in the urban



soils (Kasimov et al., 2019b). In Moscow, DIMs of the chloride group (NaCl, CaCl₂) mixed with marble chips are applied. In 2019, 324 thousand tons of DIMs were purchased by the City Hall, so for every 1 m² of road surfaces and courtyards (in total they occupy about 162 million m²) accounted for 2 kg of DIMs (Voronov et al., 2019).

Materials and methods

Sampling and chemical analyses of road dust

Road dust was sampled in June-July 2017 within the territory limited by the MRR (Fig. 1). Sampling was carried out during the summer, since in autumn, winter, and spring the roadway is wet for a long period (due to snow melting or low temperatures that prevent the rapid evaporation of moisture), and in the summer, there is a high probability of road dust resuspension from the roadway surface after a dry antecedent period and release it into the atmosphere, which poses a potential risk to public health. Samples were taken in all districts of the city on roads with different traffic intensities: MRR (number of samples n = 19), Third Ring Road (TRR) (7), major radial highways with more than four lanes in one direction (17), large roads with three-four lanes (46), medium roads with two lanes (42), and small roads with one lane in one direction (29). Overall, 160 dust samples were collected on highways and 33 dust samples in courtyards with parking lots (Table S1 in the Supplementary materials). The period of field work was rainy; the rainfall exceeded the average value by almost two times. Light rains with a volume of < 5 mm fell on June 1-3, 16, 22, and on July 9, 16, 21; rainfall events with a volume > 5 mm occurred on June 5, 13-15, 19, 21, 26, and on July 1-4, 8, 12-14, and 31. The accumulation of road dust was impeded by surface runoff and cleaning of roads by municipal services. So, sampling was performed under dry weather conditions, no less than 24 h after the rains with volume < 5 mm and no less than 72 h after the rains with volume > 5 mm, when the road surface was completely dried out. Samples were taken along the curb on both sides of the roads using a plastic dustpan and a brush in three-five replicates at a distance of 3-10 m from one to another; one mixed sample was composed of them. On the major radial highways and large roads, samples were taken from the dividing strip; in the courtyards, samples were taken from parking areas. The bulk samples were then stored in self-sealed polyethylene bags for transportation to the laboratory.

All dust samples were dried for 48 h at room temperature and then were sieved through 0.25-mm sieves to remove debris particles and gravel. The BaP content was determined in samples at the Laboratory of Carbonaceous Substances of the Biosphere (Faculty of Geography, Lomonosov Moscow State University) by high-resolution spectrofluorimetry at the temperature of liquid nitrogen (Shpolskii spectroscopy) using a Fluorat-02-Panorama (Lumex Instruments, Saint-Petersburg, Russia) device supplemented with an LM-3 monochromator and a CRYO-1 cryogenic attachment. This method is widely used in the study of PAH concentrations in soils and mineral objects. The methodology is described in detail elsewhere (Tsibart et al., 2014). Briefly, 3 g of road dust samples were extracted with n-hexane (5 mL) at room temperature. The degree of extraction was controlled by the absence of extract luminescence under UV light. In cases of the presence of extract luminescence, the extraction was continued with 5 mL of n-hexane. The extract was frozen in liquid nitrogen (77 K). Then, the mixture in the frozen extract was irradiated by light, and the BaP luminescence spectra were recorded. The wavelengths of the excitation and emissions of luminescence used for the BaP identifications are 367 nm and 402 nm, respectively. High selectivity of the method is obtained by using a spectra selection of BaP in the solution by scanning the narrow excitation wave band (Alekseeva & Teplitskaya, 1981). Identification and quantitative estimations of BaP were made by comparison of fluorescence and excitation spectra with the international certified reference standard solution 2260a of the National Institute of Standards and Technology (USA). The limits of detection (LOD) and quantification (LOQ) for BaP were 0.0001 mg/kg and 0.0005 mg/kg, respectively. The average error in determining BaP was 10-15% with a maximum error (near LOD) of 25%.

Data processing

Statistical data treatment was performed in the Statistica 8 software package. The mapping of geochemical data was performed in the ArcGIS 10 package. Maps



from the OpenStreetMap project (www.openstreet map.org) served as a cartographic basis for maps. The classification of numeric fields when using graded symbols was carried out using the Jenks natural breaks algorithm.

The method of regression trees in the S-PLUS software package was used to assess the effect of the physicochemical properties of dust, the uneven anthropogenic load in certain areas of the city, and the geometry of street canyons on the BaP content in road dust (Rawls & Pachepsky, 2002). The result of multiple partitioning of the matrix with predictor variables and the BaP content in Moscow road dust is a dendrogram reflecting the levels of the pollutant content for various combinations of quantitative and qualitative factors. For each terminal node of the dendrogram, the average content of BaP and the coefficient of variation Cv ($Cv = \sigma/\text{mean} \times 100\%$, where σ is standard deviation) were calculated for n sampling points. The following properties of road dust were taken into account: particle-size distribution, pH and the electrical conductivity (EC) of the water solution, and the organic carbon (C_{org}) content. A detailed analysis of these properties of Moscow dust was made previously (Kasimov et al., 2019b), and the brief results are given in the Supplementary Materials (Text S1, Table S2). The anthropogenic impact of transport was characterized by the type of road, from which dust samples were taken, and by its belonging to one of the nine districts. The parameters of street canyons—height H, width W, canyon proportions H/W, length L, and orientation (direction) θ —were determined for each sampling point using the Open-StreetMap data following the methodology described below.

The environmental hazard of road dust pollution with BaP was determined using the environmental hazard coefficient $K_h = C/\text{MPC}$, where C is the content of BaP in road dust, and MPC is its maximum permissible concentration. As the MPC of BaP for road dust has not been developed, the MPC for soils equal to 0.02 mg BaP/kg soil (SanPiN1.2.3685-21, 2021) was used as a hygienic standard. The reasons why we used MPC of BaP in soils are as follows: (1) the contribution of soil particles to the road dust mass in Moscow is significant (Vlasov et al., 2021), (2) soils are often used as a background in the study of road dust (Men et al., 2020), (3) resuspension of road dust particles from the roadway into the atmosphere

and their further deposition on the soil surface can be an important source of urban soils pollution (Zhang et al., 2019b), (4) the same approach is used to assess the potential risk to public health from the exposure of road dust and soil particles (Gabarrón et al., 2017b).

Determination of parameters of street canyons

The size of the road (the number of lanes) is an insufficient characteristic for analyzing the spatial distribution of pollutants within the urban area and quantitatively assessing its impact on the accumulation of BaP since this characteristic does not take into account the urban development surrounding the road. Previously, we have shown that building characteristics have a significant impact on the pollution level of the urban environment in Moscow (Kosheleva et al., 2018). Buildings can both prevent the transfer of pollutants from the streets to the surrounding areas (which can increase the level of dust pollution on the roads), and in some cases, on the contrary, certain building characteristics can contribute to the blowing of pollutants off the streets, which can potentially reduce dust pollution by various contaminants. Therefore, we expanded the set of parameters characterizing the geometry of streets with traffic flows and used formal methods of its description within the framework of the concept of urban canyons. An urban canyon is a three-dimensional volume bounded by the surface of the Earth from below and by the walls of buildings from both sides of the street and open at the top (Fig. S1a, Supplementary materials). This concept is widely used in urban climatology to model the processes occurring in the interaction zone of the boundary layer of the atmosphere, the Earth surface, and urban built-up (De Nicola et al., 2013; Fellini et al., 2020; Nunez & Oke, 1977; Oke, 1987). The micro-canyon is defined by a pair of neighboring buildings, but dispersion of pollutants in urban environment appears in a larger scale, specifically along the streets, which are formed by multiple canyons arranged in a row. To formalize such arrangement, Samsonov et al. (2015) introduced the concept of the macro-canyon (Fig. S1b, Supplementary materials). With the correct planning of the street network in relation to the wind rose, the macro-level canyons are ventilation corridors, along which the urban



atmosphere is blown through, and the concentration of pollutants in it decreases (Ren et al., 2018). In this work, macro-level canyons are called *street canyons*.

The main parameters of the micro-canyon are the height h and the width w, which determine the proportions of the canyon, the h/w ratio (Text S2, Supplementary Materials). The similar parameters H, W, and H/W of the street canyon are determined by averaging the h, w, and h/w values for its constituent micro-canyons (Samsonov et al., 2019). Additional geometric characteristics of the street canyon are its length L and orientation (direction) θ , which is defined in the range from 0° to 180° (because mutually opposite orientations are equivalent). Street canyon characteristics for each sampling point in Moscow were determined based on the data from OpenStreet-Map. The variability of the characteristics is shown by their distributions (Fig. 2), and their characteristic

values are shown in the bottom line of Table 1. The average values of the canyon's height H and width W are 17.5 m and 120.3 m, respectively, which determines the prevalence of small values of the canyon proportions (H/W < 0.5). The distribution of canyon lengths also suggests that shorter canyons (< 3000 m in length) are more common. The main mode of orientations corresponds to the direction 102.2°, while the directions perpendicular to it are also widespread (for clarity, the directions $0^{\circ}-180^{\circ}$ are duplicated in the graph by equivalent directions $180^{\circ}-360^{\circ}$).

The average characteristics of the street canyons are expected to differ depending on the type of road along which the canyon is located. The corresponding distribution densities are shown in Fig. 3; mean values of H, W, L, and H/W and modal values of θ are given in Table 1. It can be seen that the change in the type of road from the courtyard roads to the MRR is

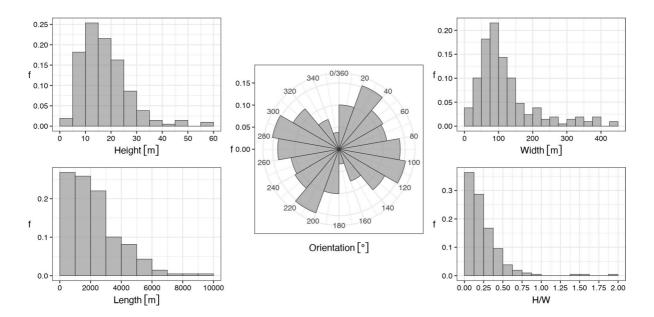


Fig. 2 Distribution of the parameters of street canyons at sampling sites (frequencies of occurrence) in Moscow

Table 1 Typical values of street canyon parameters in Moscow

Road	Height (H) , m	Width (W) , m	Length (L) , m	H/W	Orientation (θ) , °
MRR	12.1	304.1	4,650	0.053	110.6
TRR	13.4	157.1	2,232	0.110	120.7
Major radial highways	16.7	143.2	4,424	0.136	61.6
Large	17.8	129.2	2,744	0.166	34.9
Medium	15.9	92.7	1,675	0.213	41.6
Small	18.2	76.9	1,170	0.284	74.1
Courtyards	23.0	58.5	588	0.522	92.6
All roads	17.5	120.3	2,199	0.240	102.2

Mean values are given for H, W, L, and H/W; modal values are indicated for θ



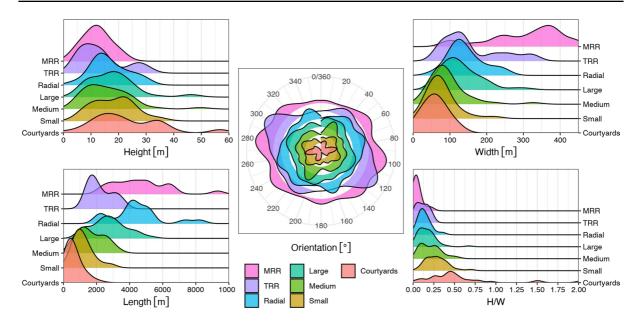


Fig. 3 Distribution densities of the parameters of street canyons by types of roads in Moscow

accompanied by a regular decrease in the mean height of the canyons from 23 to 12.1 m, an increase in the mean width from 58.5 to 304.1 m, an increase in the mean length from 588 to 4650 m, and a decrease in the canyon proportions from 0.522 to 0.053. This general pattern is interrupted by relatively short TRR canyons with the mean length of 2232 m, which is obviously due to the higher curvature of the TRR, at which the rectilinear sections are relatively short. Another exception is represented by canyons along medium roads, which are less high (15.9 m) than canyons along small (18.2 m) and large (17.8 m) roads, which can be explained by the peculiarities of street development. However, there is no complete differentiation of the parameters of the canyons depending on the types of roads; their distributions partially overlap one another. This determines the need to consider all the parameters of the canyons when analyzing the factors of BaP accumulation in the road dust of Moscow.

Assessment of public health risks

The health risks of adults and children were assessed using a model developed by the US EPA (US EPA, 1989, 2002), which takes into account three pathways of the entry of contaminated road dust particles into the body: oral via ingestion (ingest), dermal via

skin contact (dermal), and respiratory via inhalation (inhal). For BaP, the risk is determined by the average daily dose (ADD) of chronic consumption of contaminated dust coming in three ways:

$$ADD_{ingest} = \frac{C_{u} \times IngR \times EF \times ED}{BW \times AT} \times CF,$$
 (1)

$$ADD_{inhal} = \frac{C_{u} \times InhR \times EF \times ED}{BW \times AT \times PEF},$$
(2)

$$ADD_{dermal} = \frac{C_{u} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF,$$
(3)

where C_u is the content of BaP in road dust (mg/kg), IngR and InhR are the amounts of ingested (mg/day) and inhaled (m³/day) particles, EF is the exposure frequency (days/year), ED is the exposure duration (year), BW is the average human body weight (kg), AT=ED×365 is the average time of BaP influence (days), CF is the conversion factor $(1\times10^{-6} \text{ kg/mg})$, PEF is the particle emission factor $(1.36\times10^9 \text{ m}^3/\text{kg})$, SA is the surface area of the skin in contact with road dust particles (cm²), AF is the coefficient of dust adhesion to the skin (mg/cm²), and ABS is the absorption coefficient of BaP. The values of the variables differ for adults and children (Table 2).



Table 2 Values of variables for adults and children used in the assessment of public health risks

Variable	Value		References		
	Adults	Children			
IngR (mg/day)	30	60	(US EPA, 2002)		
InhR (m ³ /day)	21.4	16.74	(US EPA, 2011)		
EF (days/year)	350	350	(US EPA, 2002)		
ED (year)	72	6	(US EPA, 2002)		
BW (kg)	80	15	(US EPA, 1989, 2002)		
AT (days)	26,280	2190	(US EPA, 2002)		
SA (cm ²)	5700	2800	(US EPA, 2002)		
AF (mg/cm ²)	0.07	0.2	(US EPA, 2002)		
ABS	0.13	0.13	(RSL, 2017)		

The danger of BaP is determined by the ratio of ADD_i to the reference dose RfD:

$$HQ_{ingest} = \frac{ADD_{ingest}}{RfD_o},$$
 (4)

$$HQ_{inhal} = \frac{ADD_{inhal}}{RfD_{i}},$$
(5)

$$HQ_{dermal} = \frac{ADD_{dermal}}{RfD_{ABS}}.$$
 (6)

Reference dose RfD is a daily dose, which, being consumed for a long period, does not lead to the development of pathological changes or diseases detected by modern research methods at any time in the life of the present or subsequent generations. To date, the following reference doses have been established for BaP: for oral intake, RfD_o= 3×10^{-4} mg/kg per day, and for inhalation, RfD_i= 2×10^{-6} mg/kg per day (RSL, 2017; US EPA, 1989). According to the recommendations by the US EPA (2002), RfD_{ABS} is calculated by multiplying the reference dose for oral intake by the gastrointestinal absorption coefficient, which equals 1.0 for BaP (RSL, 2017). Thus, RfD_{ABS}=RfD_o.

Hazard index $HI = \sum (HQ_{ingest} + HQ_{inhal} + HQ_{dermal})$ considers the admission of contaminated dust particles in all possible ways. Indicators HQ_i and HI are graded into four levels of hazard for human health: none (<0.1), low (0.1–1), moderate (1–10), and high

(>10) (Lei et al., 2016; Lemly, 1996; Man et al., 2010; US EPA, 2002).

The carcinogenic risk for adults was assessed by calculating the incremental lifetime cancer risk (ILCR) under the impact of BaP (AT=72 yr=26 280 days) (US EPA, 1989, 2002):

ILCR_i = ADD_i × CSF_i ×
$$\sqrt[3]{BW/70}$$
, (7)

where $\mathrm{CSF_i}$ is the cancer slope factor (mg/kg per day) for different pathways of dust particles into human body ($i = \mathrm{ingest}$, dermal, inhal): $\mathrm{CSF_{ingest}} = 7.3$, $\mathrm{CSF_{inhal}} = 3.85$, $\mathrm{CSF_{dermal}} = 25$ (Knafla et al., 2006; Peng et al., 2011; Yang et al., 2014). The total carcinogenic risk (TR) under the influence of BaP arriving in various ways was determined as the sum of individual risks:

$$TR = \sum ILCR_i$$
 (8)

Indicators ILCR_i and TR are graded into five levels (Fryer et al., 2006; US EPA, 1989): very low ($<10^{-6}$), low ($10^{-6}-10^{-5}$), medium ($10^{-5}-10^{-4}$), high ($10^{-4}-10^{-3}$), and very high ($>10^{-3}$).

Results and discussion

The contents and spatial distribution of BaP in road dust

The mean BaP content in the road dust of Moscow is 0.26 mg/kg (Table 3, Table S3 in Supplementary materials), which is almost 53 times higher than the background level (0.005 mg/kg) in the natural topsoils (Umbric Albeluvisols) of the Meshchera lowland, 50 km east of the city (Kasimov et al., 2017), the level in postagrogenic soils (0.005 mg/kg) in the east of Moscow (Kasimov et al., 2017), and the level in natural soils of the Losinyi Ostrov National Park (0.008 mg/kg) in the northeast of Moscow (Zavgorodnyaya et al., 2019). In the soils of forest parks, which fall under the influence of industrial facilities and transport, the BaP content is only 1.5–1.6 times lower than that in the road dust of Moscow and averages 0.16 mg/kg for the eastern industrial part of the city with variation from 0 to 0.80 mg/ kg (Kasimov et al., 2017). In Moscow's northeastern and northern parts, the BaP content in the dust



Table 3 Mean, minimum and maximum concentrations (mg/kg), and environmental hazard of BaP in the dust on different types of Moscow roads and parking lots in courtyards (summer 2017)

Roads (number of samples)	Mean ± σ	Min	Max	Cv, %a	K _h ^b
MRR (19)	0.26 ± 0.20	0.030	0.91	77	13.1
TRR (7)	0.14 ± 0.11	0.045	0.33	81	7.1
Major radial highways (17)	0.17 ± 0.98	0.022	0.36	58	8.5
Large roads (45)	0.29 ± 0.19	0.026	0.77	68	14.4
Medium roads (42)	0.25 ± 0.13	0.042	0.56	54	12.3
Small roads (29)	0.22 ± 0.13	0.036	0.56	59	10.8
Courtyards (33)	0.37 ± 0.21	0.101	1.02	57	18.6
All roads (193)	0.26 ± 0.18	0.022	1.02	67	13.2

^aCv is the coefficient of variation ^b K_h is the environmental

hazard coefficient

of forest parks averages 0.17 mg/kg with variation from 0.04 to 0.49 mg/kg. The BaP content in soil fractions < 1 μ m and 1–2 μ m is higher (0.27 mg/kg and 0.45 mg/kg, respectively) than that in road dust because of the high sorption capacity of clay particles (Kogut et al., 2006). Comparison of BaP concentrations in road dust with the level in the background and urban soils is carried out quite often (Men et al., 2020) since there is no background analog for road dust (all roads are of anthropogenic origin), and soils are an important source of road dust material and its PM_{10} particles in Moscow (Vlasov et al., 2021) and other cities (Ramírez et al., 2019).

The highest content of BaP was determined in road dust from courtyards in residential blocks (mean, 0.37 mg/kg; maximum, 1.02 mg/kg) (Table 3). This is due to the impact of organized and unorganized car parking, low vehicle speeds, and frequent vehicle maneuvers in courtyards. In addition, the accumulation of BaP can increase in specific "trap wells" in courtyards, where the velocity of airflows decreases and more active fallout of aerosols takes place (Kosheleva et al., 2018). Among different types of roads, road dust is most contaminated with BaP on large roads and the MRR with the high traffic intensity and a large number of trucks. On the contrary, in the road dust of medium and small roads, the BaP content is lower because of lower traffic intensity induced by public transport and numerous traffic lights and turns, which increase the number of maneuvers and contribute to traffic congestion. The least contaminated is the road dust from radial highways and TRR because of the absence of traffic lights and regular renewal of the dust during sweeping and washing of the roadbed by city services.

Thus, the environmental hazard of BaP pollution is maximal in courtyards with parking lots

(mean K_h =18.8, maximum 51), the second place belongs to major radial highways (mean K_h =15, maximum 33.5), and road dust from the MRR ranks third (mean K_h =13, maximum 40.5) (Table 3). The share of dust sampling points, in which K_h exceeds 10, on different types of roads decreases in the following order: courtyards with parking lots (79%)>MRR (63%)>medium roads (60%)>large roads (57%)>small roads (48%)>radial highways (35%)>TRR (29%). The points with the highest contamination (K_h >30) are found in courtyards with parking lots (12% of the total number of sampling points in courtyards), on major radial highways (7%), and the MRR (5%) (Fig. 4).

The distribution of BaP in road dust of Moscow is uneven; the highest mean contents are typical for the Northern, Southeastern, Eastern, Central, and Southern administrative districts (Fig. 5), where traffic jams are frequent and large industrial facilities are located. Waste incineration plants are located in the Eastern, Southern, and on the border of the Northern and Northeastern districts. Many heat power plants are located in the Southern district and on the border of Southern and Southwestern districts. The maximum content of BaP (1.02 mg/kg) in the road dust exceeding the background level in Umbric Albeluvisols by more than 200 times was found in the Central district, where the density of the road network is higher than in other districts of Moscow, and the minimum content (0.022 mg/kg), in the Southern district. The lowest mean BaP content (0.10 mg/kg) was in the road dust from the Southeastern district. We obtained a value close to the previously reported (0.13 mg/kg) for this area (Karpuhin et al., 2017).

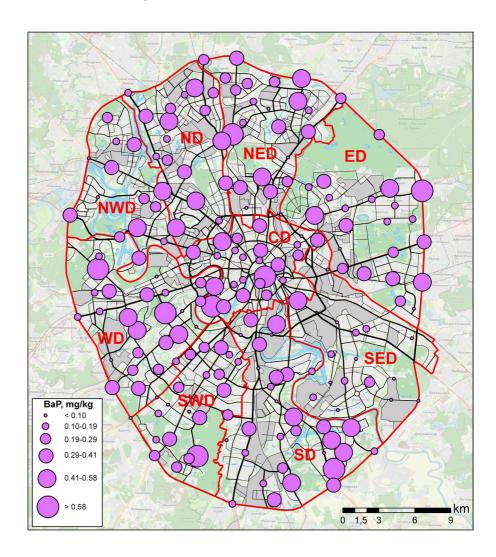
On most of Moscow's highways, a hazardous environmental situation has developed with an excess of the MPC for BaP by 13–15 times. The maximum



Fig. 4 Percent of road dust samples with different levels of K_h in the districts and on different types of roads. The decoding of the designations of the administrative districts is given in the caption to Fig. 1. Roads: MRR is Moscow Ring Road, TRR is Third Ring Road, RH is radial highways, LR is large roads, MR is medium roads, SR is small roads, YA is yards with parking lots

Districts Roads % of samples % of samples 100 100 90 80 80 70 70 60 60 50 50 40 40 30 30 20 20 SD SWD WD NWD CD MRR TRR HR LR MR *K*_h ■ 1-2 ■ 2-5 **□** 5-10 **20-30 ■**>30 **■**10-20

Fig. 5 Distribution of BaP in road dust of Moscow (summer 2017)



excesses with the coefficient of environmental hazard $K_{\rm h} = 30{\text -}50$ are observed near large industrial zones within the TRR and the area between the TRR and

the Moscow Central Circle railroad (Table 3). Only the Southeastern district is characterized by a low excess of the BaP content in the road dust relative



to the MPC (on average, by 2.2 times), which can be explained by the predominance of volatile low-molecular-weight PAHs (naphthalene homologs) in the emissions of the oil refinery. According to the percentage of dust sampling points, in which K_h exceeds 10, relative to the total number of sampling points (Fig. 4), the districts of Moscow can be arranged into the following sequence: ND (75%)>SED (74%)>SWD (65%)>WD (59%)>CD and SD (58%)>ED (57%)>NWD (56%)>SED (7%). The most polluted points with $K_h>30$ were found in WD (7% of samples), CD (6%), ED and SWD (5%), and SED and NWD (4%).

Comparison of BaP contents in road dust and other components of Moscow environment

Since there were no previous assessments of road dust pollution in Moscow with BaP, it was impossible to understand what "place" in terms of pollution level road dust occupies among other environments of the city. This is important because it is not clear whether further detailed studies on the distribution of BaP and other PAHs in road dust are needed, or research needs to be focused on other environments to assess public health risks. So, the chemical composition of road dust as an indicator of urban pollution can be assessed by comparing it with the composition of atmospheric precipitation in the form of snow and rain, soils, and bottom sediments in watercourses and reservoirs.

Precipitation

The fallout of PAHs with snowfalls onto the earth surface near roads in Moscow is 3–6 times higher than that in the recreational area and residential blocks (Zavgorodnyaya et al., 2019) (Fig. 6, Table S3 in Supplementary materials). The BaP concentration in the filtrate of melted snow near major roads often exceeds the MPC for water (0.005 mg/L) (Mazur et al., 2021), reaching 0.003 mg/kg to 0.140 mg/kg near major highways (Khaustov & Redina, 2019), and 0.005–0.493 mg/L near the MRR (Lebedev et al., 2012). The insoluble phase in the city's snow (dust component of the snow) accounts for about 90% of the total BaP content (Galitskaya & Rumyantseva, 2012). In the dust component of snow of the high-rise

residential, agricultural, and recreational areas, the BaP content is slightly lower than that in road dust. In the low-rise and middle-rise residential areas and near roads it rises up to 0.60 mg/kg, 1.22 mg/kg, and 5.73 mg/kg, respectively, which is several times higher than in road dust (Kasimov et al., 2017).

In spring, the BaP concentration in the rainwater of Moscow varies within 0.0006–0.03 mg/L and, in most cases, exceeds the MPC for water (Polyakova et al., 2018). High correlation coefficients between the contents of BaP and pyrene, fluoranthene, chrysene, benzo[a]anthracene, indeno[1,2,3-c,d]pyrene, and benzo[g,h,i]perylene in atmospheric aerosols of Moscow indicate the supply of PAHs with emissions from combustion of natural gas and the operation of domestic heating plants together with emissions from combustion of gasoline and diesel fuels by vehicles (Popovicheva et al., 2020).

Urban soils

According to the long-term monitoring data, the BaP content in the soils of different land-use zones of Moscow averages 0.02-0.04 mg/kg and varies from 0.003 to 2.30 mg/kg (Kosheleva & Tsykhman, 2018; Kul'bachevskii, 2020), which is generally less than that in the road dust. However, most publications provide averaged data on the BaP content in the soils of several land-use zones, including slightly polluted recreational zones, which underestimates the BaP pollution of urban soils. According to these estimates, the average BaP content in soils is 0.023 mg/ kg in the south of the city (Maksimova et al., 2014), 0.043 mg/kg in the northeast (Namestnikova, 2017), and 0.080 mg/kg in the southeast (Karpuhin et al., 2017), though averages of 0.115-0.125 mg/kg in different parts of the city have also been reported (Agapkina et al., 2007; Belinskaya et al., 2015).

In soils of the residential zone, the BaP content is varying from 0.035 mg/kg in new high-rise residential areas to 0.075 mg/kg and 0.084 mg/kg in the densely built-up and low-rise residential areas (Kasimov et al., 2017; Zavgorodnyaya et al., 2019). These values are almost three times lower than the BaP content in road dust. However, in old medium-rise residential blocks, where a large number of people who own vehicles live for a long time, the BaP content in soils increases to an average of 0.28 mg/kg (Kasimov



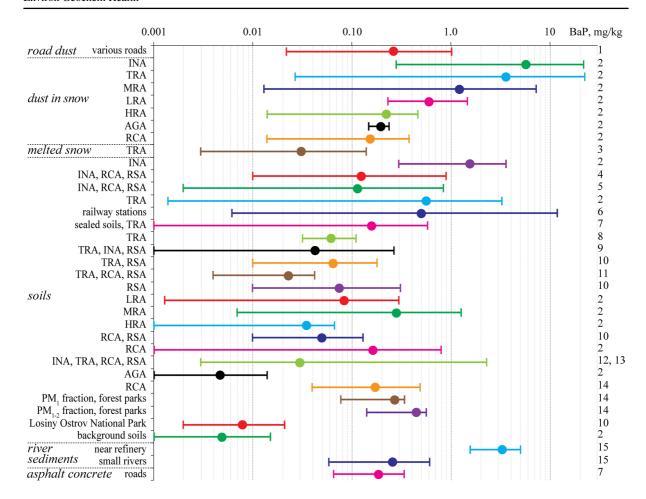


Fig. 6 Contents of BaP in the urban environments of Moscow. Lines indicate the ranges, and bubbles indicate the mean concentrations. Information on the components of the urban environment and land-use areas (INA is industrial, TRA is traffic, RSA is residential, LRA is low-rise residential, MRA is medium-rise residential, HRA is high-rise residential, AGA is agricultural, RCA is recreational) are indicated in the left columns. The numbers in the right column indicate reference

sources: 1—this study; 2—Kasimov et al. (2017); 3—Khaustov and Redina (2019); 4—Belinskaya et al. (2015); 5—Agapkina et al. (2007); 6—Makarov (2014); 7—Nikiforova et al. (2019); 8—Nikolaeva et al. (2017); 9—Namestnikova (2017); 10—Zavgorodnyaya et al. (2019); 11—Maksimova et al. (2014); 12—Kul'bachevskii (2020); 13—Kosheleva and Tsykhman (2018); 14—Kogut et al. (2006); 15—Kramer and Tikhonova (2015)

et al., 2017), which is comparable to its content in road dust.

In the soils of the traffic zone, the highest concentrations of PAHs are observed within 30–50 m from roads, which indicates a significant supply of PAHs from roads, especially in densely built-up areas (Nikolaeva et al., 2017; Zavgorodnyaya et al., 2019). This is confirmed by a threefold increase in the ratio of BaP to benzo[g,h,i]perylene in urban soils as compared to undisturbed soils of forest parks (Zavgorodnyaya et al., 2019). In the soils of the traffic zone in a 50-m strip along the

roads, the BaP content averages 0.062–0.065 mg/kg (Nikolaeva et al., 2017; Zavgorodnyaya et al., 2019), increasing to 0.57 mg/kg within few meters from major highways and ranging from 0.001 to 3.28 mg/kg (Kasimov et al., 2017), which is twice as more as in the road dust. In the traffic zone near large railway stations, the BaP content in soils varies from 0.006 to 11.9 mg/kg with an average of 0.50 mg/kg (Makarov, 2014), which is almost two times higher than in the road dust.

In industrial zones, a significant source of BaP is emissions from enterprises of various industries;



therefore, the average concentration of BaP in soils is 1.56 mg/kg varying from 0.30 to 3.61 mg/kg, which is higher than in the traffic zone (Kasimov et al., 2017) and is almost six times higher than in road dust.

A more intense accumulation of BaP in roadside soils compared to road dust was previously found in some other cities (Bezberdaya et al., 2022) and could be associated with increased organic matter content in soils treated with peat-compost mixtures, contributing to the active fixation of polyarenes on the geochemical sorption barrier (Kosheleva & Nikiforova, 2011). In addition, soils accumulate BaP for decades, whereas the accumulation time in road dust is limited to a few days or weeks in the warm season because the dust material is regularly renewed due to its partial blowing and road cleaning by communal services. The road surface provides an additional supply of BaP to soils and road dust. The average BaP content in the asphalt concrete pavement of Moscow is 0.19 mg/kg with a variation from 0.066 to 0.34 mg/kg, and its content in sealed soils under the asphalt pavement averages 0.16 mg/kg, increasing to 0.51 mg/kg in some places (Nikiforova et al., 2019), which is about 1.5 times lower than in the road dust.

With an increase in the number of benzene rings, the rate of PAH biodegradation decreases (Patel et al., 2020); therefore, the concentration of high-molecular-weight BaP during its long-term accumulation in soils is 2.5 times higher than in melted snow, which accumulates BaP during several cold months (Zavgorodnyaya et al., 2019). However, at the first stages of the operation of new sources of BaP, and owing to the active replacement of contaminated soil material with a cleaner one, soils become relatively depleted (four–seven times) in BaP compared to the dust component of snow (Kasimov et al., 2017).

Bottom sediments

When particles contaminated with BaP enter the watercourses, they accumulate actively in the bottom sediments of small rivers. Thus, in bottom sediments of the Los' River in the Losiny Ostrov National Park in the northeast of Moscow, the BaP content is 0.059 mg/kg; in bottom sediments of the Nishchenka River in its southeastern part, it increases from 1.58 to 5.05 mg/kg along the river course, which is due to the strong industrial impact, including that of the old refinery located near the river (Kramer & Tikhonova,

2015). Due to low solubility in water, BaP molecules migrate mainly together with fine particles as part of sorption organic and organomineral complexes (Kogut et al., 2006). Therefore, despite the fairly high levels in soils and road dust, BaP in the Moskva River virtually does not migrate in dissolved form (Eremina et al., 2016). In bottom sediments of small rivers of Moscow—the Los', Kotlovka, Businka, and Tarakanovka—the mean BaP content is 0.26 mg/kg with a variation from 0.059 to 0.61 mg/kg, which is close to its content in road dust (Kramer & Tikhonova, 2015) and attests to a significant role of emissions from vehicles and washing off road dust in the pollution of water bodies in the city.

So, the BaP content in Moscow road dust is, on average, several times lower than that in winter atmospheric precipitation and is close to that in the soils of most land-use zones and bottom sediments of watercourses of the city. This is due to the supply of dust contaminated with BaP both from the atmosphere and from the blown out soil particles. Lower levels of BaP in road dust and soils compared to snow are due to a higher degradation rate of BaP in the warm season, the removal of contaminated dust material from roads by communal services, and the addition of clean material to the urban soils.

Factors of BaP accumulation in road dust

The role of various factors of BaP accumulation in road dust was determined using the method of regression trees, which makes it possible to estimate the BaP content under different combinations of influencing factors according to the dendrogram. To construct it, the following groups of factors were used: (1) physicochemical properties of dust (Table S2, Supplementary materials); (2) the level of anthropogenic load, determined by the type of road and its allocation within a particular part of the city (administrative districts) as well as the geometry of street canyons (its length L, height H, width W, H/W ratio, and orientation of the canyon θ relative to the cardinal points). The inclusion of physicochemical properties among the factors in regression analysis is reasonable, since organic matter, its composition and structure, as well as the presence of clay minerals and fine particle fractions (especially PM₁₀ and PM₂ due to the large surface area, negative charge, and high content of organic



matter), play a significant role in the accumulation of PAHs and BaP; the degradation of PAHs depends on the pH and EC values, which determine the activity of microbial communities (Gennadiev et al., 2015; Gabarrón et al., 2017b; Dehghani et al., 2018; Emoyan et al., 2018). In general, physicochemical properties of road dust in Moscow (Text S1, Supplementary materials) fit into the range of values typical for other cities of the world: pH 7–9, C_{org} 1–17%, EC 100–2800 μ S/cm (Abbasi et al., 2017; Acosta et al., 2011; Bartkowiak et al., 2017; Dong et al., 2020; Gabarrón et al., 2017a, 2017b; Gelhardt et al., 2021; Padoan et al., 2017; Sutherland et al., 2012; Wu & Lu, 2018). Other factors used in regression trees are analyzed above.

The results of regression analysis made it possible to determine the threshold values of the influencing factors and showed a significant role of the geometry of street canyons in the accumulation of BaP in road dust (Fig. 7). With a canyon length L < 500 m, which is typical for courtyards with parking lots, the BaP content in road dust is maximum, on average, 0.39 mg/kg. In relatively wide street canyons (H/W < 0.5), BaP accumulation in road dust is 1.6 times more intense than in narrow canyons. This can be explained by a larger number of cars in wide canyons and the protective role of buildings in narrow canyons that act as barriers preventing air flows

contaminated with BaP from entering the courtyards. Previously, an inverse relationship was revealed; air pollution in canyons with high *H/W* values was higher than in canyons with low *H/W* values (Merbitz et al., 2012). However, such a relationship was observed in a large street canyon with heavy traffic.

A secondary factor of BaP accumulation in short (L<500 m) and wide (H/W<0.5) canyons is the acid-base properties of dust; in a neutral medium, the BaP content is 1.6 times higher than in an alkaline medium, which can be explained by dust acidification by nitrogen oxides with an increase in traffic load. In short (L < 500 m) and narrow (H/W > 0.5) canyons, a positive relationship between the BaP and organic matter contents is observed, which is caused by a significant proportion of soil particles in the road dust of courtyards. The organic matter of the traffic zone mainly consists of difficultly soluble compounds, the sources of which are the asphalt pavement and emissions from the industrial sector and vehicles (Faure et al., 2000), and the influence of organic matter on the sorption of PAHs is generally known (Minkina et al., 2019).

Most of the samples (about 80%) were taken in relatively long (L>500 m) canyons, where the average concentration of BaP is 0.24 mg/kg with some differentiation by road type. On the MRR and major highways, the average BaP content reaches 0.28 mg/

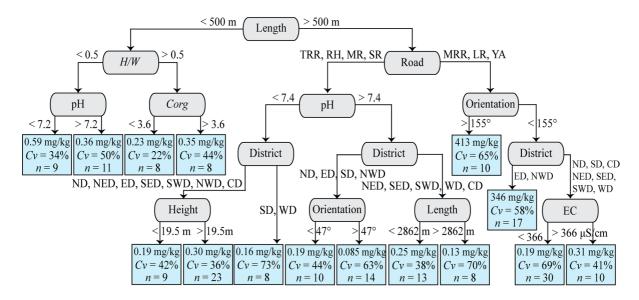


Fig. 7 Factors of BaP accumulation in road dust of administrative districts in Moscow. The decoding of the designations of the administrative districts is given in the caption to Fig. 1, the types of the roads—in Fig. 4



kg with an increase in accumulation when the canyon is directed from north to south ($\theta > 155^{\circ}$). With a different orientation of the canyons, various intensities of polyarene accumulation are seen in different parts of the city, as well as in dust with various EC caused by the use of DIMs (Fig. 7). An increase in EC by 1.7 times enhances the accumulation of BaP, which is confirmed by soil studies in the Eastern district of Moscow (Kosheleva & Nikiforova, 2011), as well as in Tyumen city (Konstantinova et al., 2020a).

In long (L>500 m) canyons on the TRR, radial highways, medium and small roads, as well as in short wide (L < 500 m, H/W < 0.5) canyons, pH has a noticeable effect on the BaP content in road dust; in a neutral medium (pH < 7.4), it is 1.5 times higher than in an alkaline medium. High pH values (pH \geq 8) are due to the input of alkalizing materials during repair works on the roads and the laying of paving slabs (Greinert et al., 2013). A similar negative relationship between the pH value of the water extract of road dust and the BaP content was established in Tyumen (Konstantinova et al., 2020a). Moreover, the excess of the average height of the canyon H > 20 m on these types of roads in all districts of Moscow, except for the Southeastern district, leads to a noticeable (1.6 times) increase in the accumulation of BaP because of the slowing down air flows in the canyons (Kauhaniemi et al., 2011).

Hence, the maximum accumulation of BaP in the road dust of Moscow occurs in relatively wide (H/W < 0.5) and short (L < 500 m) canyons, and is favored by the neutral reaction of the dust typical of courtyards with parking lots, and meridional orientation of segments of major roads (MRR, radial highways) perpendicular to the direction of the prevailing winds, which impairs blowability of these segments.

Assessment of environmental hazard of BaP and human health risk

The health risk of the urban population is determined by the chronic average daily dose (ADD) of BaP-contaminated dust. The consumption of BaP with dust particles which enter the body of an adult and a child by different pathways varies greatly from 2.8×10^{-9} mg/kg to 4.75×10^{-3} mg/kg per day. The ADD values averaged for the administrative districts of Moscow decrease in the following order: ND>N ED>ED>CD>SD>WD>SWD>NWD>SED.

There is also a strong differentiation of this indicator depending on the type of road (Table 4).

Ingestion of dust particles with food and while playing, walking, etc., is the main pathway of BaP intake into the bodies of both adults and children. ADD values indicate that adults and children receive 90.6% and 93.3% of BaP orally, respectively. BaP entering human bodies through skin contact is 9.3% and 6.7% of the total ADD for these two groups, respectively. Less than 0.2% of BaP is received through inhalation. The total hazard index HI is highly differentiated by administrative districts of the city with the highest average values both for adults and children in the Northern district and the lowest values in the Southeastern district (Fig. S2, Supplementary materials).

For adults, average HI values do not exceed 3.34 in all districts of Moscow, which corresponds to the moderate level of health hazard. However, children are more susceptible to exposure to pollutants per unit weight because of their physiological and behavioral characteristics, such as ingestion of significant amounts of soil and dust during playing and walking outdoors, increased gastrointestinal absorption of certain substances and air consumption per unit weight, etc. (Gabarrón et al., 2017b; Qu et al., 2012). Thus, for a child, average HI values in administrative districts of Moscow vary from 3.37 to 8.62, corresponding to the moderate health hazard level. The maximum HI (28.9) was determined for courtyards in the Central district, where children are more likely to contact contaminated dust particles during walks. The lowest HI values were found in the Southeastern district, which can be explained by the predominance of volatile low-molecular weight PAHs in the refinery emissions.

Almost all values of the carcinogenic risk associated with the oral and dermal exposure ways are in the range from 10^{-5} to 10^{-3} , which corresponds to moderate and high risk levels; the risk associated with inhaled BaP is very low: 10^{-9} to 10^{-7} . Therefore, the total risk (TR) is high and very high with TR> 10^{-4} . The highest average value of the TR= 4.43×10^{-3} is in the Central district. Increased contents of PAHs in road dust and other environments lead to an increased risk of developing cancer cells, including lung, skin, and bladder cancer (Abdel-Shafy & Mansour, 2016; Armstrong et al., 1994; Boström et al., 2002; Kim et al., 2015; Zhang



Table 4 Average daily doses of BaP (10⁻⁵ mg/kg per day) entering the bodies of adults/children with contaminated road dust particles on the roads with different traffic intensities

District	MRR	TRR Radial highways			Carretannala			
District WIKK TKK		IKK	Radial highways	Large	Medium	Small	Courtyards	
Oral pathway: ADD _{ingest}								
ND	8.1/86.7	n/a	9.1/96.7	n/a	10.9/116.3	14/149.2	9.8/104.3	
NED	10.8/114.8	n/a	7.9/84	17.3/184.8	6.3/66.8	6.6/69.9	12.2/129.6	
ED	20.1/214	n/a	10.1/107.6	6.4/68.4	9.3/99.5	7.4/78.7	12.4/132.7	
SED	5.6/59.6	5.4/58.1	7.5/79.8	4.7/49.8	3.7/39.3	3.1/33.3	4.7/49.6	
SD	6.7/71.3	n/a	3/32.3	8.8/93.8	13.3/142	5.8/61.6	15.3/162.8	
SWD	7.6/81.3	n/a	8.3/88.6	9.4/100.1	7.1/75.8	8.5/90.7	14.5/154.7	
WD	7.7/82.1	n/a	4.6/48.8	13.2/140.9	4.4/46.5	10.3/109.6	11.8/125.4	
NWD	3.5/37.8	n/a	5/53.1	9.4/100.1	11.8/126.2	6.3/66.7	12.2/129.9	
CD	n/a	5.1/54.2	n/a	9.8/104.5	10.2/109.1	9.5/101.1	23/245.4	
-			Derr	nal pathway: ADD _{der}	mal			
ND	14.1/105.2	n/a	15.7/117.3	n/a	18.9/141.1	24.2/181	16.9/126.6	
NED	18.6/139.3	n/a	13.6/101.9	30/224.2	10.8/81.1	11.3/84.8	21/157.3	
ED	34.7/259.7	n/a	17.4/130.5	11.1/83	16.1/120.7	12.8/95.5	21.5/161	
SED	9.7/72.4	9.4/70.5	12.9/96.8	8.1/60.4	6.4/47.7	5.4/40.4	8/60.2	
SD	11.6/86.6	n/a	5.2/39.2	15.2/113.8	23/172.3	10/74.7	26.4/197.5	
SWD	13.2/98.7	n/a	14.4/107.5	16.2/121.5	12.3/91.9	14.7/110.1	25.1/187.7	
WD	13.3/99.6	n/a	7.9/59.2	22.8/170.9	7.5/56.5	17.8/132.9	20.3/152.2	
NWD	6.1/45.8	n/a	8.6/64.5	16.2/121.5	20.5/153.1	10.8/81	21.1/157.7	
CD	n/a	8.8/65.8	n/a	16.9/126.8	17.7/132.3	16.4/122.6	39.8/297.7	
			Inhal	ation pathway: ADD	inhal			
ND	0.0043/0.0178	n/a	0.0048/0.0198	n/a	0.0057/0.0239	0.0073/0.0306	0.0051/0.0214	
NED	0.0056/0.0236	n/a	0.0041/0.0172	0.0091/0.0379	0.0033/0.0137	0.0034/0.0143	0.0064/0.0266	
ED	0.0105/0.0439	n/a	0.0053/0.0221	0.0034/0.014	0.0049/0.0204	0.0039/0.0162	0.0065/0.0272	
SED	0.0029/0.0122	0.0029/0.0119	0.0039/0.0164	0.0024/0.0102	0.0019/0.0081	0.0016/0.0068	0.0024/0.0102	
SD	0.0035/0.0146	n/a	0.0016/0.0066	0.0046/0.0192	0.007/0.0291	0.003/0.0126	0.008/0.0334	
SWD	0.004/0.0167	n/a	0.0044/0.0182	0.0049/0.0205	0.0037/0.0155	0.0045/0.0186	0.0076/0.0318	
WD	0.004/0.0168	n/a	0.0024/0.01	0.0069/0.0289	0.0023/0.0096	0.0054/0.0225	0.0062/0.0257	
NWD	0.0019/0.0078	n/a	0.0026/0.0109	0.0049/0.0205	0.0062/0.0259	0.0033/0.0137	0.0064/0.0267	
CD	n/a	0.0027/0.0111	n/a	0.0051/0.0214	0.0054/0.0224	0.005/0.0207	0.0121/0.0504	

Here and in Table 5, n/a denotes the absence of data. Colors (from green to red) indicate increasing ADD values for each type of road, each administrative district, and each pathway of BaP intake into human bodies

et al., 2020). In addition to carcinogenic effects, a direct relationship has been established between the long-term exposure to microparticles contaminated with polyarenes and the decrease in birth weight (Wilhelm et al., 2012), poor cognitive development (Edwards et al., 2010), obesity, and the risk of diarrhea (Wu et al., 2021). The contribution of different ways of entry to the total risk follows the sequence: ingestion > skin contact > inhalation, which is consistent with the results obtained by other researchers

(Alghamdi et al., 2021; Gope et al., 2018; Jiang et al., 2014; Mihankhah et al., 2020; Zhang et al., 2020).

The variation in the TR values depending on the type of roads in different districts of Moscow is given in Table 5. The highest average values are observed in the Southern, Southwestern, Northwestern, and Central administrative districts (Fig. 8) for courtyards with parking lots, which is most likely associated with the idling of cars while waiting for passengers.

Table 5 Total carcinogenic risk (TR) associated with traffic intensities on different roads

District MRR		TRR	Highways	Street roads			Courtyards	Assaucas in district
		IKK		Large	Medium	Small	Courtyards	Average in district
ND	1.56×10 ⁻³	n/a	1.74×10 ⁻³	n/a	2.10×10 ⁻³	2.69×10 ⁻³	1.88×10 ⁻³	2.11×10 ⁻³
NED	2.07×10 ⁻³	n/a	1.52×10 ⁻³	3.33×10 ⁻³	1.21×10 ⁻³	1.26×10 ⁻³	2.34×10^{-3}	2.01×10 ⁻³
ED	3.86×10 ⁻³	n/a	1.94×10 ⁻³	1.23×10 ⁻³	1.79×10 ⁻³	1.42×10 ⁻³	2.39×10^{-3}	1.97×10 ⁻³
SED	1.08×10 ⁻³	1.05×10 ⁻³	1.44×10 ⁻³	8.98×10 ⁻⁴	7.09×10 ⁻⁴	6.01×10 ⁻⁴	8.96×10 ⁻⁴	8.25×10 ⁻⁴
SD	1.29×10 ⁻³	n/a	5.84×10 ⁻⁴	1.69×10 ⁻³	2.56×10 ⁻³	1.11×10 ⁻³	2.94×10 ⁻³	1.93×10 ⁻³
SWD	1.47×10 ⁻³	n/a	1.60×10^{-3}	1.81×10 ⁻³	1.37×10 ⁻³	1.64×10 ⁻³	2.79×10^{-3}	1.78×10 ⁻³
WD	1.48×10 ⁻³	n/a	8.81×10 ⁻⁴	2.54×10 ⁻³	8.40×10 ⁻⁴	1.98×10 ⁻³	2.26×10^{-3}	1.88×10 ⁻³
NWD	6.82×10 ⁻⁴	n/a	9.59×10 ⁻⁴	1.81×10 ⁻³	2.28×10 ⁻³	1.20×10 ⁻³	2.34×10^{-3}	1.77×10 ⁻³
CD	n/a	9.79×10 ⁻⁴	n/a	1.89×10 ⁻³	1.97×10 ⁻³	1.82×10 ⁻³	4.43×10 ⁻³	1.94×10 ⁻³

Colors from green to red indicate a rise in the average TR value for different types of roads in each administrative district



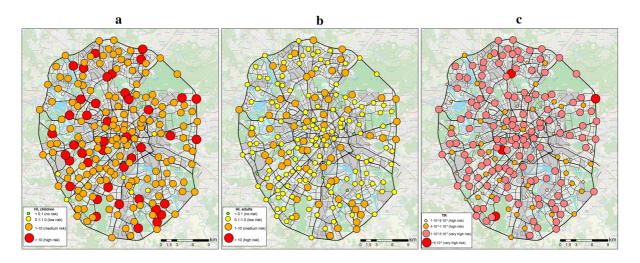


Fig. 8 Distribution of the total hazard index HI for a children and b adults; c total carcinogenic risk TR at sampling points of Moscow road dust (summer 2017)

In the Central, Northeastern, and Western districts, maximum TR values are typical of the roads with several lanes. In the Eastern and Southeastern districts, maximum TR values are allocated to the MRR and major radial highways, respectively, due to frequent traffic congestions since many residents from the southeastern suburbs commute to work on these roads every day.

Limitations of the study

Our results are a first assessment of risk for public health from road dust polluted with BaP in Moscow megacity based on snapshot observations during one of the seasons of the specific year. Therefore, the risk assessment results in our study have the following limitations. Firstly, the sampling represents only one season, which did not allow taking into account the inter-annual variability in the accumulation of dust on the roads. To assess seasonal differences in the level of pollution of the urban environment with BaP, a comparative analysis of pollutant concentrations in various environments, such as snow cover which characterizes pollution during the cold period, urban soils, and bottom sediments of water bodies which are indicators of long-term pollution, was carried out. For a more accurate risk assessment, further studies of the distribution of BaP in road dust in different seasons and under various meteorological conditions are required. Secondly, the study of only BaP did not make it possible to do a source apportionment study using receptor models and statistical methods such as principal component analysis or positive matrix factorization. Further expansion of the list of analyzed pollutants could remove this limitation. Thirdly, the distribution of BaP in various particle size fractions of road dust of Moscow has not yet been studied, which may affect the assessment of the risk to public health, since the ability of particles to be blown off the roadway, as well as their ability to penetrate the human body, largely depends on particle size. For a more detailed assessment of the health risk, it is necessary to determine the content of BaP in different particle size fractions of road dust. Finally, the obtained results show the risk levels averaged over various types of roads and different administrative units of the city. In the absence of knowledge about the degree of road dust pollution with BaP in Moscow, the task was to obtain the average level of contamination in order to understand whether further more detailed studies of BaP in road dust in Moscow are needed. It will be helpful to take into account the spatial variability of BaP concentrations in road dust when assessing health risks in future, for example, applying Monte Carlo simulation or using not only mean concentrations, but also the median, 90th and 95th percentiles of BaP concentrations.



Conclusions

For the first time, the pollution levels and the spatial distribution of BaP in road dust in Moscow were determined considering the geometry of street buildings (canyon effect) and the physicochemical properties of the dust. In addition, the health risks of the adult and child population arising from BaP contamination were assessed, including the average daily dose of contaminated dust, the hazard index, and the carcinogenic risk under the influence of BaP entering the human body through dermal, ingestion, and inhalation pathways.

The average BaP content in Moscow road dust is 53 times higher than the background level in Umbric Albeluvisols and 1.6 times lower than the BaP content in dust fallout from the atmosphere. The highest contents and environmental hazard of BaP pollution with a maximum in the Central district of Moscow are confined to the courtyards with parking lots. The pollution with BaP in these places is intensified due to the formation of "trap wells" creating zones of air stagnation and deposition of aerosols. Road dust pollution with BaP depends on the type of road: large street roads and the MRR with high traffic intensity are the most polluted, while radial highways and the TRR with a low number of traffic lights are the least polluted roads.

Important factors of BaP accumulation in road dust of Moscow are geometry patterns of street canyons. The BaP content in road dust is maximum when the canyon length is less than 500 m, and relatively wide canyons accumulate BaP 1.6 times more actively than narrower street canyons. In longer canyons, road dust pollution with BaP is less pronounced, but the pollution level is not the same on different types of roads and depends on their orientation relative to the cardinal points. On the TRR, radial highways, and medium and small street roads with high (> 20 m) street canyons, there is a noticeable increase in the accumulation of BaP. The influence of the physicochemical properties of road dust and allocation in different districts of the city is manifested locally.

On most of Moscow's highways, an extremely dangerous environmental situation has developed with an excess of the MPC for BaP by 13–15 times. The maximum excess of the MPC (K_h 30–50) is observed near large industrial zones within the TRR and in the territories between the TRR and the Moscow

Central Circle railroad. The high content of BaP in road dust negatively affects the health of citizens. The main way of BaP intake by adults and children is oral ingestion, which accounts for more than 90% of the total BaP intake. For adults in all districts, the HI index corresponds to a low–moderate level of danger, for children, to a moderate level with a maximum in the central part of the city. The carcinogenic risk is the highest in the courtyards of the Southern, Southwestern, Northwestern, and Central districts.

The results showed the need for further study of BaP in the road dust of Moscow, seasonal dynamics of pollution and the effect of precipitation on the washing of dust from roads. The results can be useful for identifying urban areas with the most dangerous level of BaP pollution and for increasing the efficiency of road cleaning measures.

Acknowledgements The authors are grateful to L.A. Bezberdaya, I.S. Kapustina, N.Yu. Kuzminskaya, K.S. Nabelkina, A.V. Ryzhov, A.G. Tsykhman, and G.L. Shinkareva for participation in field and laboratory work, as well as to N.I. Khlynina for the determination of BaP in road dust samples.

Author contributions NEK involved in conceptualization, formal analysis, data curation, investigation, writing—original draft, writing—review and editing, project administration, and funding acquisition. DVV involved in conceptualization, formal analysis, investigation, writing—original draft, writing—review and editing, and visualization. IVT involved in formal analysis, investigation, writing—original draft, writing—review and editing, and visualization. TES involved in formal analysis, investigation, data curation, writing—original draft, and visualization. NSK involved in conceptualization, writing—review and editing, supervision, and funding acquisition.

Funding The determination of BaP in road dust samples was performed under agreement 04/2017-I with the Russian Geographical Society. Analysis and interpretation of data on road dust pollution with BaP were carried out with the financial support of the Russian Science Foundation (Project No. 19-77-30004); health risk assessment, within the framework of the Development Program of the Interdisciplinary Scientific and Educational School of the Lomonosov Moscow State University "The Future of the Planet and Global Environmental Changes." Calculations of the characteristics of urban canyons were carried out on the computer equipment of the Collective Use Center "Geoportal of Moscow State University." The comparison of BaP contents in road dust and other components of Moscow environment was made in the framework of the grant of the Ministry of Science and Higher Education of the Russian Federation (Project Number 075–15–2021–574).



Data availability Data are available within the article and its supplementary materials. Additional data are available on request from the corresponding author.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Research involving human and animal rights Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

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