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Pollution Level, Partition and Spatial Distribution of Benzo(a)pyrene in Urban Soils, Road Dust and Their PM_{10} Fraction of Health-Resorts (Alushta, Yalta) and Industrial (Sebastopol) Cities of Crimea

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Abstract: Polycyclic aromatic hydrocarbons (PAHs), in particular benzo(a)pyrene (BaP), are priority organic pollutants coming from various anthropogenic sources. The levels of accumulation and the spatial distribution of BaP in urban soils, road dust and their PM_{10} particles (with a diameter of less than 10 microns) were for the first time determined for various land use zones and roads of different size in the cities of Crimea—Alushta, Yalta and Sebastopol. The average content of BaP in soils and road dust in Alushta is 60 and 97 ng/g, in Yalta—139 and 64 ng/g, in Sebastopol—260 and 89 ng/g, respectively, which considerably exceeds the background level (1 ng/g). The BaP concentrations in PM_{10} particles of soils and dust are up to 11 and four times higher, respectively, than the total contents; they concentrate 35–70% of amount of the pollutant. The accumulation of BaP in soils and dust depends on the type of land use and size of roads. The exceedance of BaP standards in soils and road dust indicates a hazardous environmental situation in three cities of Crimea. The most dangerous are PM_{10} particles, which form anomalies with extreme levels of BaP contamination.

Keywords: microparticles PM_{10}; benzo(a)pyrene; urban soils; road dust; polycycic aromatic hydrocarbons; type of land use; traffic; environmental hazard

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of widespread organic compounds containing two or more benzene rings; many of them are considered toxic environmental pollutants [1,2]. PAHs can enter the environment from natural and anthropogenic sources. Natural sources include fires, volcanic activity, weathering of rocks, and biological processes [3,4]. Anthropogenic PAHs are formed during the production of asphalt, energy production, incomplete combustion of fuel, wood or waste [5–7]. PAHs with 2–3 rings, belong to low molecular weight compounds and come mainly from petrogenic sources, i.e., from rocks and oils. High-molecular PAHs have 4–6 benzene rings and are more persistent toxic pollutants coming from pyrogenic sources or generated by the combustion of various organic materials [8–10].

In total, about 160 PAHs have been studied in nature, but only 16 of them are included by the US Environment Protection Agency and the European Union in the list of priority pollutants in various natural environments [11] and are strictly regulated in many countries of the world. Among the most toxic PAHs, benzo(a)pyrene (BaP) stands out. It could accumulate for a long time in various components of landscapes. It is carcinogenic and mutagenic to all living organisms, causing allergic skin reactions and increasing the incidence of skin, lung, and gastrointestinal cancers in animals and humans [2,7,12]. BaP is the only PAH included in the list of pollutants subject to state control in the field of environmental protection in Russia.

BaP enters the urban road dust primarily from vehicle emissions of gasoline and diesel engines [13], as well as from non-exhaust emissions due to abrasion of tires, brake pads and asphalt pavement [14,15]. BaP is also generated by heating systems and the incineration of household waste. When BaP falls out of the polluted atmospheric air as part of aerosols, it accumulates on the road surface and is firmly fixed in the upper soil layer due to the high sorption capacity of soil organic matter and the low solubility of BaP [1,16–18].

Pollution of urban soils and road dust is dangerous for the population because they are susceptible to blowing out, which increases the air pollution with particulate matter and accumulated PAHs. At the same time, the intensity of blowing out soil particles and road dust increases with decreasing diameter. Microparticles with a diameter of <10 μm (PM_{10}, where PM stands for "particulate matter" and the number is the maximum particle diameter in the fraction) have a high sorption capacity and play an important role in the accumulation of many pollutants [19–21]. In the absence of maintenance and cleaning of roads, up to 50% of PM_{10} dust particles enter the atmospheric air when the vehicles move [22]. If blown out, PM_{10} particles could remain suspended for several days and be transported hundreds of kilometers from the source [23]. The increased danger of these fractions is associated with their accumulation in the human upper respiratory tract, frequent adhesion to hands and passage through the gastric mucosa, as well as their adsorption in tissues [24]. PAHs formed as a result of combustion at high temperatures enter the atmosphere mainly with fine particles [1,25]. More than 50% of them are formed during the movement of vehicles and are in the less than 0.5 μm fraction; other combustion sources emit polyarenes with particles of 0.5–1 μm in size [26].

Recently, a large number of studies on the levels of PAH accumulation in soils and road dust, sources of their intake and risks to human health have been carried out in many countries of the world, especially in the USA [27], European countries [28–32] and Asia [33–37]. In Russia, PAHs have only been studied in a few large cities, such as Moscow, St. Petersburg, and Tyumen [38–43]. Long-term monitoring of the accumulation and distribution of BaP in soils was carried out in Moscow from 1990 to 2006 [44] and in the zone of influence of the largest thermal power plant in the Rostov region from 2002 to 2011 [45]. Most of these studies deal with the PAH content in the total mass of soils and road dust without a detailed analysis of their fractional structure, i.e., PAH content in particular particle size fractions. There are practically no data on the contamination of particles of various sizes, in particular PM_{10}—small and environmentally most hazardous fraction.

Ecological and geochemical assessment of the state of the environment is most often carried out in large industrial centers or cities with high population. Small coastal cities have been studied less, since it is believed that the pollution of landscape components is low there and does not pose a serious environmental hazard for residents [31]. Tourism is the main branch of the economy in such cities, in addition various industries are developed in coastal cities, i.e., power production, ship repair, construction industry, waste processing and incineration, etc. They provide a geochemical load on urban landscapes due to vehicles, tourist services and industrial emissions. In this regard, the increased health risks are produced for local population and a large number of tourists, or the "seasonal population", which makes it relevant to assess the pollution of recreational centers and resort towns.

The intensive development of tourist activity on the Black Sea coast of Crimea makes it necessary to study the ecological state of seaside resort towns. Some of them, for example, Sebastopol, are at the same time large industrial centers; others are characterized by heavy vehicular traffic, which supplies a large amount of BaP. Alushta and Yalta are also agro-industrial centers for the cultivation of grapes, the quality of which depends on environmental pollution, especially soil contamination. Sanatorium-resort enterprises of Alushta and Yalta treat the diseases of respiratory system, hearing and vision, as well as the diseases of cardiovascular and nervous systems, and musculoskeletal system.

Soil contamination with heavy metals and metalloids (HMM) was previously estimated in Sebastopol [46] and Alushta [47]; the BaP contamination of soil microparticles and road dust in Crimean cities is studied for the first time. The aim of our work is to assess the levels of BaP accumulation and its spatial distribution in urban soils, road dust and their PM_{10} microparticles for the resort cities of Alushta and Yalta and the industrial and recreational center of Sebastopol.

2. Materials and Methods

2.1. Study Area: Natural Conditions

The seaside resort towns of Alushta (44°40′34″ N; 34°24′45″ E) and Yalta (44°29′46″ N; 34°10′13″ E) are located on the South Coast of Crimea (SCC), which occupies a strip of the Black Sea coast at the southern slope of the Main Ridge of the Crimean Mountains (Figure 1). The climate of the SCC is subtropical Mediterranean with average temperatures of +2.5 °C in February and 22.9 °C in July in Alushta and 4.2 °C and 23.2 °C respectively in Yalta [48]. Prevailing winds come from the east and southeast. Natural landscapes are represented by coastal xerophytic juniper-oak forests with Cambisols on eluvium-diluvium and eluvium of siltstones, mudstones, shales, limestones, and sandstones [49].

Figure 1. Study objects.

The city of Sebastopol (44°36′29″ N; 33°33′29″ E) is located at the Black Sea coast in the southwestern part of the Crimean Peninsula (Figure 1). The relief of the territory is formed by numerous bays and deep gullies. The climate of the territory of Sebastopol is similar to subtropical. The average air temperature is +2.6 °C in February and +22.4 °C in July [48]. Westerly and north-westerly winds prevail in summer, and northeasterly ones in winter. The climate of the northern part of Sebastopol is maritime temperate continental, the landscapes are represented by feather grass-fescue vegetation with Haplic Kastanozems on limestones. The southern coast of Sebastopol has subtropical Mediterranean climate, resulting in the formation of Cambisols under the juniper-oak forests.

As a rule, zonal soils within the territory of cities are significantly transformed or created artificially [50]. The soils of the urban areas of Alushta, Yalta and Sebastopol are mainly represented by Urbic Technosols.

2.2. Study Area: Sources of Pollution and Land Use Zoning

Most of the cities of the Crimean peninsula are popular densely populated resorts on the Black Sea coast. In 2020, about 6.5 million people visited Crimea, of which 50% stayed in the cities of the South Coast.

Yalta is the largest resort center of the South Coast, where 78,000 people reside permanently and which is annually visited by about 700,000 people. Alushta is a small tourist town with the population of less than 35,000 people, but it ranks second after Yalta among the resort cities of Crimea in terms of the number of tourists (about 200,000 people a year) [51,52]. The large number of tourists, 65% of whom come by private vehicles and the lack of parking spaces lead to heavy traffic congestion and traffic jams. The motor vehicles, including transit ones, are the main source of emissions of pollutants into the atmosphere of Alushta and Yalta, accounting for more than 90% of their total volume. In 2017 and 2018 total volume of emissions amounted to 276 and 268 tons, respectively, in Alushta and 314 and 518 tons in Yalta [53,54]. In addition to motor transport, industrial enterprises producing heat and electricity, building materials, concrete and cement, as well as the food industry play an important role in the pollution of the environment in these cities. These sources provide high average annual concentrations of nitrogen dioxide, suspended solids and carbon monoxide in the atmospheric air and inorganic pollutants (Pb, Zn, Co) and hazardous BaP in the soils of Yalta [55]. Intensive accumulation of Sb, Zn, Pb, Cu emitted by vehicles was noted in the soils of Alushta [47].

Sebastopol, with the population of 510,000 people, is a large industrial city and seaport of Crimea. There are enterprises dedicated to mechanical engineering and metalworking, shipbuilding and ship repair, petrochemistry and food industry, and also the production of construction and paint and varnish materials within its territory. The city has the Sebastopol Commercial Sea Port, which provides transportation and storage of sand, coal, oil products, metals and other goods. Large sources of pollution are thermal power plants and boilers, which were fueled with coal for a long time. Annually up to 5000 tons of pollutants enter the atmosphere of Sebastopol from these sources, and every year the volume of emissions increases, primarily due to the increasing capacity of thermal power enterprises [53]. Solid waste landfills and dumps, which annually receive about 200,000 tons of waste, play a significant role in the pollution of the city. Due to its location, Sebastopol is also a cultural, historical and recreational city, which attracts a large number of vacationers and tourists annually.

In addition, the use of coal for heating private residential buildings contributes significantly to the pollution of the three cities by releasing PAHs, including BaP, into the environment.

The distribution of pollution sources and the formation of technogenic anomalies of pollutants are dictated by the functions of urban areas. Basing on the analysis of satellite images Sentinel-2 and WorldView-2, the following zones with different types of land use were identified in Alushta, Yalta and Sebastopol (Figure 1): traffic (T), industrial (I), residential with multi-storey (Rm) and low-rise (Rl) residential buildings, recreational (R). The residential-recreational (Rr) and agrogenic (A) zones were additionally specificated in Alushta and Yalta. The roads in the traffic zone were divided by width and traffic intensity into large (three or more lanes in one direction), medium (two lanes) and small (one lane and driveways in the courtyards).

2.3. Sampling

Field studies were carried out in 2016–2018 by the staff of the Crimean Expedition of the Russian Geographical Society and the Lomonosov Moscow State University (LMSU), Faculty of Geography. Geochemical survey of Alushta, Yalta and Sebastopol included sampling of the upper layer (0–10 cm) of anthropogenically transformed soils and road dust on a 500–700 m grid (Figure S1). Road dust was collected from the surface of large, medium and small roads using plastic brush and shovel; from several individual samples taken at a distance of 5–10 m, one mixed sample was made. Mixed soil samples were made of 5 separate samples taken at a distance of 5–10 m from each other in all land use zones of three cities. In total, 49 soil samples and 29 samples of road dust were collected in Alushta; 69 and 57 samples in Yalta; and 69 and 70 samples in Sebastopol, respectively. The background level of BaP was estimated by analyzing 10 samples from the upper horizon of Cambisols, taken 2 km northwest of Alushta on the southern slope of the Demerdzhi Ridge, and 10 samples of Haplic Kastanozems, taken 2 km to the north-east of the city of Sebastopol.

2.4. Analytical Methods

Soil and road dust samples were dried, and plant roots and debris inclusions were taken away. The pH values in soil and dust samples were measured at the LMSU Ecological and Geochemical Center, using a potentiometric method with an EXPERT-pH pH meter (Econix-Expert Ltd., Moscow, Russia); and specific electrical conductivity (EC) was measured using a SevenEasy S30 conductometer (MettlerToledo, Greifensee, Switzerland) at a soil to water ratio of 1:2.5. The content of organic carbon (Corg) in soils and road dust was determined by the Tyurin method with a titrimetric ending [56], and the particle size distribution was analyzed using a laser granulometer (Fritsch, Idar-Oberstein, Germany).

To isolate the PM_{10} fraction from soils and road dust, the samples were dispersed using wet grinding. The mixture was then put into a 1 L glass cylinder filled with distilled water, and the PM_{10} fraction was isolated by precipitation according to the Stoke's law [57]. The resulting solutions were filtered through membrane filters with a pore diameter of 0.45 μm.

The BaP content in soils, road dust and their PM_{10} fractions was analyzed at the LMSU Biosphere Carbonaceous Substances Laboratory by the Shpolsky low-temperature spectrofluorimetry method [58] using the international standard 2260a of the National Institute of Standards and Technology (Lumex Instruments, Mission, BC, Canada), the determination accuracy is ±25%.

2.5. Data Analysis

The levels of BaP pollution of soils, road dust and their PM_{10} fraction in Alushta, Yalta and Sebastopol were evaluated by the contamination factor $CF = Ci/Cb$, where Ci is the content of pollutant in the soil, road dust or their PM_{10} fraction in a city, mg/kg, Cb is the BaP content in background soils or their PM_{10} fraction, mg/kg.

To characterize the fractional composition of soils and road dust, that is, the proportion of BaP in the PM_{10} fraction relative to its bulk content, we used the formula [19]: $D_{10} = (C_{10} \bullet P_{10}/Cdust * 100) * 100$, where C_{10} is the BaP concentration in PM_{10}, ng/g; P_{10}—PM_{10} fraction in dust and/or soils, %; $Cdust$—bulk concentration of BaP in soil or road dust, mg/kg.

The environmental hazard of BaP pollution of soils, road dust or their PM_{10} fraction was assessed by comparing with the maximum permissible concentration (MPC) and calculating the environmental hazard coefficient $Kh = Ci/MPC$, where Ci is the concentration of BaP in soils, road dust or their PM_{10} fraction. Since the hygienic standards for road dust and PM_{10} particles of road dust and soils have not been developed, we used the MPC adopted for soils, which is 20 ng/g [59]. The Kh values were divided into five levels: <1—non-hazardous, 1–2—moderately hazardous, 2–5—hazardous, >5—extremely hazardous. These indicators are widely used for ecological and geochemical monitoring and assessment of the state of the environment in the Russian Federation.

Statistical data were processed using the Statistica 10 package (Statsoft/Dell, Tulsa, OK, USA). The mean m, minimum and maximum values, standard deviations σ, and variation coefficients $Cv = \sigma/m * 100\%$ were calculated for soil and road dust parameters and the BaP content. The maps of BaP pollution of soils, road dust and PM_{10} fraction were compiled in the ArcGis 10.4 package (Esri, Redlands, CA, USA), using graded symbols for visualization.

3. Results

3.1. Benzo(a)pyrene in Background Soils

The level of BaP accumulation in the soils of background territories most often depends on the input of pollutant from local and regional sources, and the composition and properties of soils, which influence the processes of sorption, degradation, leaching, and volatilization of polyarene [60]. The background content of BaP in the mineral part of most soils ranges from 0.1 to 5 ng/g; for some chernozems the BaP level can reach 15–20 ng/g, due to increasing content of organic matter and the structure of soil microbial community in these soils.

In Crimea, the BaP content in all samples of background Cambisols and Haplic Kastanozem corresponds to the detection limit (LP) of the pollutant by the analytical method used, i.e., 1 ng/g. The obtained value is several times lower than in the background soils of Norway [60], developed under pastures (3.0 ng/g) and coniferous forests (9.3 ng/g), as well as in Albic Luvisol in Meshchera near Moscow (4.9 ng/g) [44] and Luvic Phaeozem under fallow lands in the south of Western Siberia (6.0 ng/g) [43]. This could be explained by the higher rate of biological decomposition and degradation of PAHs in subtropical regions, more sunny days, and higher air temperatures [4].

3.2. Content and Spatial Distribution of BaP in Urban Soils

3.2.1. Alushta

The average BaP content in urban soils is 60 ng/g, which is 60 times higher than the background value (1 ng/g). The BaP concentration increases to 73 ng/g in PM_{10} microparticles of soils. The average BaP content in urban soils and their PM_{10} fraction in different land use zones of Alushta varies from 8.3 to 111 ng/g in the total soil mass and from 7.9 to 152 ng/g in PM_{10} (Table 1). Increased levels of pollutant accumulation in soils and PM_{10} particles were found in the traffic zone, and the lowest in the agrogenic zone (Figure 2).

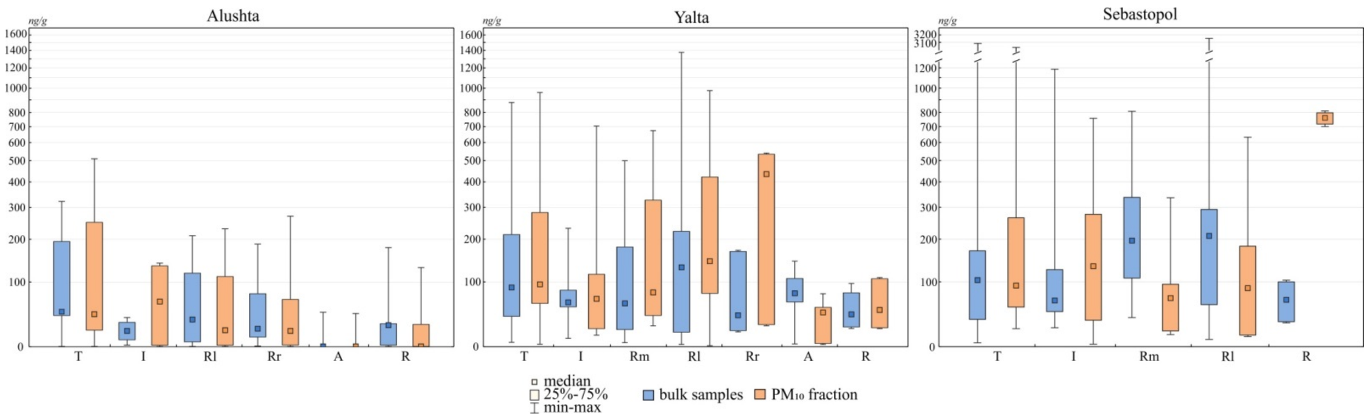

Figure 2. The content of BaP in soils and their PM_{10} fraction in the land use zones of Alushta, Yalta and Sebastopol. Zones: T—traffic, I—industrial, Rm and Rl—residential with multi-storey and low-rise buildings, A—agrogenic, Rr—residential and recreational, R—recreational.

Table 1. The content of benzo(a)pyrene in urban soils and their PM_{10} fraction of land use zones in Alushta, Yalta, and Sebastopol.

Parameters	Alushta		Yalta		Sebastopol	
	Bulk Samples	**PM_{10} Fraction**	**Bulk Samples**	**PM_{10} Fraction**	**Bulk Samples**	**PM_{10} Fraction**
Traffic						
mean, ng/g	111	152	140	195	217	225
min–max, ng/g	0.5–322	0.5–510	5.3–878	3.0–962	4.7–2638	23–1642
CF	111	152	140	195	217	225
Kh	5.5	7.6	7.0	9.8	11	11
Industrial						
mean, ng/g	20	67	85	166	207	196
min–max, ng/g	2–39	0.5–140	10–232	14–704	24–1186	3.0–757
CF	20	67	85	166	207	196
Kh	1.0	3.4	4.2	8.3	10	9.8
Multi-storey residential						
mean, ng/g	–	–	124	180	244	104
min–max, ng/g	–	–	5–499	27–673	39–809	15–335
CF	–	–	124	180	244	104
Kh	–	–	6.2	9.0	12	5.2
Low-rise residential						
mean, ng/g	65	65	240	290	437	152
min–max, ng/g	0.5–210	0.5–230	2.8–1375	1.3–979	8.9–3146	13–632
CF	65	65	240	290	437	152
Kh	3.2	3.2	12	15	22	7.6
Residential-recreational						
mean, ng/g	49	47	77	334	–	–
min–max, ng/g	1–187	0.5–270	19–171	27–540	–	–
CF	50	47	77	334	–	–
Kh	2.5	2.4	3.9	17	–	–
Recreational						
mean, ng/g	48	32	52	61	67	760
min–max, ng/g	0.5–178	0.5–130	23–97	23–109	31–103	718–801
CF	48	32	52	61	67	760
Kh	2.4	1.6	2.6	3.0	3.4	38
Agrogenic						
mean, ng/g	8.3	7.9	79	37	–	–
min–max, ng/g	0.5–47	0.5–45	3.4–145	2.7–78	–	–
CF	8.3	7.9	79	37	–	–
Kh	0.4	0.4	4.0	1.8	–	–

Note. Dash—no data available. Contamination factor (*CF*) is the ratio of the content of pollutant in the soils or PM_{10} fraction in a city to the content of BaP in background soils or their PM_{10} fraction. Environmental hazard coefficient (*Kh*) is the ratio of the content of BaP in soils or PM_{10} fraction to maximum permissible concentration (MPC) adopted for soils, which is 20 ng/g.

The BaP content in the soils of Alushta and their PM_{10} fraction shows a high variability with *Cv* values of 134% and 156%, respectively. The BaP content varies from 0.5 to 322 ng/g in the total soil mass and from 0.5 to 510 ng/g in PM_{10} particles, thus indicating the formation of local BaP anomalies within the city under the influence of anthropogenic sources. The spatial position of BaP anomalies in the total soil mass and fine PM_{10} particles differs only slightly (Figure 3). The former shows four contrasting anomalies with very high level of BaP accumulation, i.e., 210–322 ng/g, and an excess of the background values by more than 300 times. One of them was formed in the residential area under the influence of personal vehicles and stove heating of private houses. Other anomalies were formed in the roadside soils of the northwestern, southwestern and central parts of Alushta. The anomaly in the city center (211 ng/g) ranges along the major highway near bus station and gas station; their operation provides the emission of automotive fuels and oils containing BaP. The contrast of this anomaly is even higher in the PM_{10} fraction of soils, and the BaP content reaches an extremely high level—510 ng/g, which is 2 times the total soil concentration and more than 500 times the background one. The pollutant content reaches 250–394 ng/g near the busiest highways of the city (Yalta highway, Lenin, Komsomolskaya and Naberezhnaya streets). A very high level of BaP accumulation in the PM_{10} fraction of soils (230 ng/g) was also recorded in the east of the city, on the floodplain of the Ulu-Uzen River as a result of active accumulation of BaP in subordinate positions. The pollutant is hydrophobic and poorly soluble in water, which results in its slow biodegradation and long-term accumulation in floodplain soils [3].

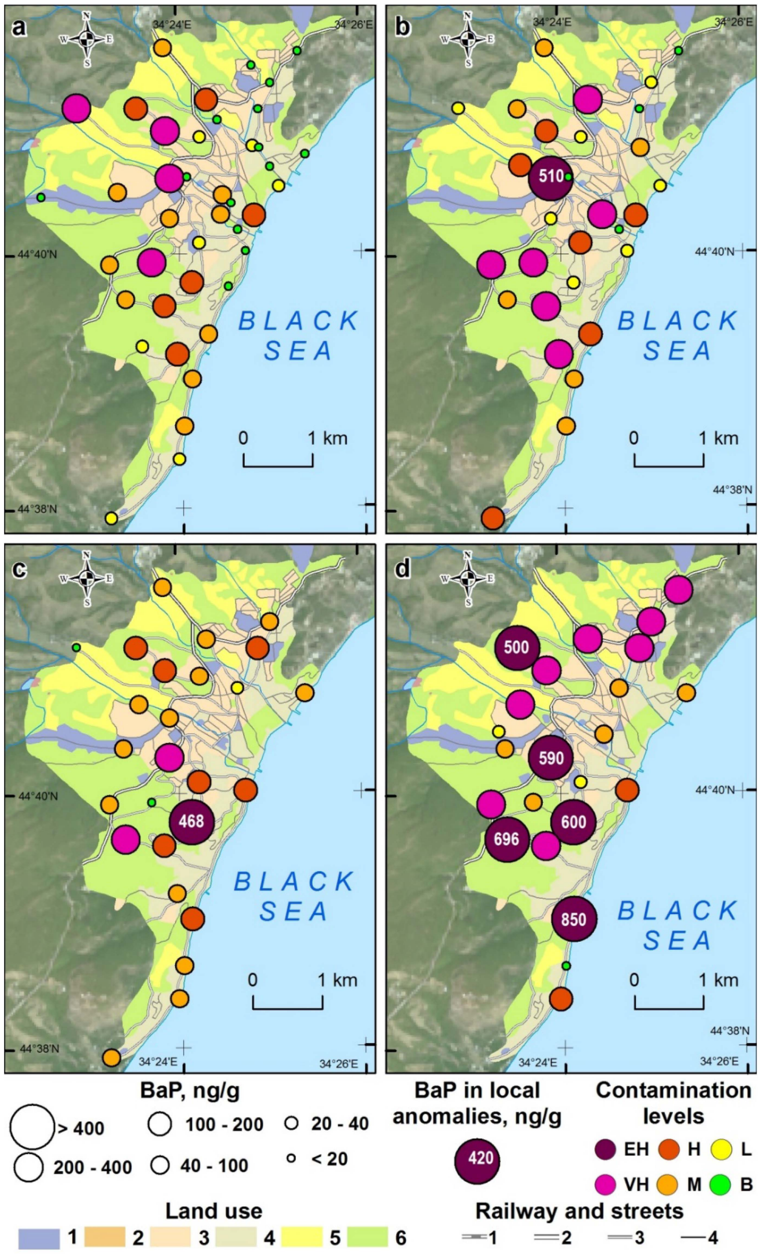

Figure 3. Distribution of BaP in soils (**a**) and their PM_{10} particles (**b**), road dust (**c**) and its PM_{10} particles (**d**) within the territory of Alushta. Contamination levels: EH—extremely high, VH—very high, H—high, M—moderate, L—low, B—background. Land use zones: 1—industrial, 2—multi-storey residential, 3—low-rise residential, 4—residential and recreational, 5—agrogenic, 6—recreational. Railway (1) and streets with: 2—large roads, 3—medium roads, 4—small roads.

3.2.2. Yalta

The average BaP content in urban soils is 139 ng/g with a 139-fold increase of the background values. The PM_{10} fraction of soils is characterized by a higher concentration of BaP—265 ng/g, which is 2 times higher than the total content in soils and 265 times higher than the background. The BaP content in different land use zones of Yalta varies from 52 to 240 ng/g in the total soil mass and from 37 to 334 ng/g in PM_{10} microparticles (Table 1). The most contaminated soils are in the residential zone (Figure 2) with low-rise residential buildings (mean *CF* value is 240), which is mainly due to the coal-based heating residential buildings [10]. In comparison with the total content, PM_{10} fraction of soils is the most polluted in the residential and recreational zone, where the concentration of the pollutant is 334 times higher than the background values. The lowest BaP contents were recorded in the soils of the recreational zone and PM_{10} particles of the soils of the agrogenic zone (*CF* 52 and 37, respectively), due to the absence of pollutant sources. A strong variation in the concentration of the pollutant was found in the soils of Yalta—from 2.8 to 1375 ng/g (Cv = 151%), and in their PM_{10} fraction—from 1.3 to 979 ng/g (Cv = 120%).

The largest BaP anomaly in urban soils with an excess of the background by a factor of 1375 was found in the residential area with low-rise buildings near a boiler house emitting coal combustion products (Figure 4). PM_{10} particles are characterized by the higher number of anomalous zones, the spatial position of which differs from the anomalies for soils as a whole. Extremely high levels of BaP accumulation in PM_{10} particles were recorded in the residential sector in the northern (808 ng/g), central (979 ng/g) and southwestern (421–492 ng/g) parts of the city. The BaP content exceeds the background level by 421–979 times, which confirms the effect of emissions from the heating of private houses. High concentrations of BaP were also found in roadside soils near highways and major roads, where its content in soils as a whole exceeds the background values by up to 878 times, and by up to 962 times in the PM_{10} fraction. Other BaP anomalies in the PM_{10} fraction of soils (434–540 ng/g) were formed in the city center near the embankment, recreation areas and hotel complexes, i.e., in the areas with the highest congestion of vehicles and tourists. BaP intensively accumulates in soils and their PM_{10} particles in the northwestern part of Yalta on the territory of the industrial zone and motor depots, where its concentration is more than 700 times higher than in background soils.

3.2.3. Sebastopol

The average BaP content in soils is 260 ng/g, exceeding the background values by 260 times. The intensity of polyarene accumulation in the PM_{10} fraction of soils decreases to 201 ng/g, which is 201 times higher than the background. The concentration of BaP varies by land use zones from 67 to 437 ng/g in soils and from 104 to 760 ng/g in fine particles (Table 1). The residential zone has the highest pollution of soils with BaP (Figure 2). This is due to the ingress of the pollutant with emissions from vehicles in the near-house areas. The recreational zone of Sebastopol is characterized by the maximum BaP accumulation in the PM_{10} fraction (760 ng/g on the average). High contents in the PM_{10} fraction of soils in this zone were found in the northern part of the city on the floodplain of the Belbek River and in the park area of Primorsky Boulevard (Figure 5), where there are a large number of tourists, catering and leisure facilities in summer. The concentrations of the pollutant at these points are 718 and 801 times higher than the background values and 10 times higher than its content in the bulk samples of the soils. The influence of vehicles, e.g., emissions of exhaust gases and engine oil leaks, tire and roadway abrasion, results in the high content of BaP in soil (*CF* 217) and its PM_{10} fraction (*CF* 225) in the traffic zone of Sebastopol. An additional technogenic impact comes from the industry, as indicated by the increased concentrations of BaP in soils and their PM_{10} fraction in the industrial zone of Sebastopol, which exceed the background values by 207 and 196 times, respectively.

The soils and the PM_{10} fraction are characterized by the high variation of the BaP content, which exceeds 100% in almost all land use zones and indicates the presence of large sources of the pollutant. The pollutant content varies greatly within the city: from

4.7 to 3146 ng/g in soils (Cv = 281%) and from 3.0 to 1641 ng/g in the PM_{10} fraction of soils (Cv = 134%). At the same time, the variability of BaP in soils is, on average, two times higher than in their PM_{10} particles, which confirms the accumulation of BaP in larger particles.

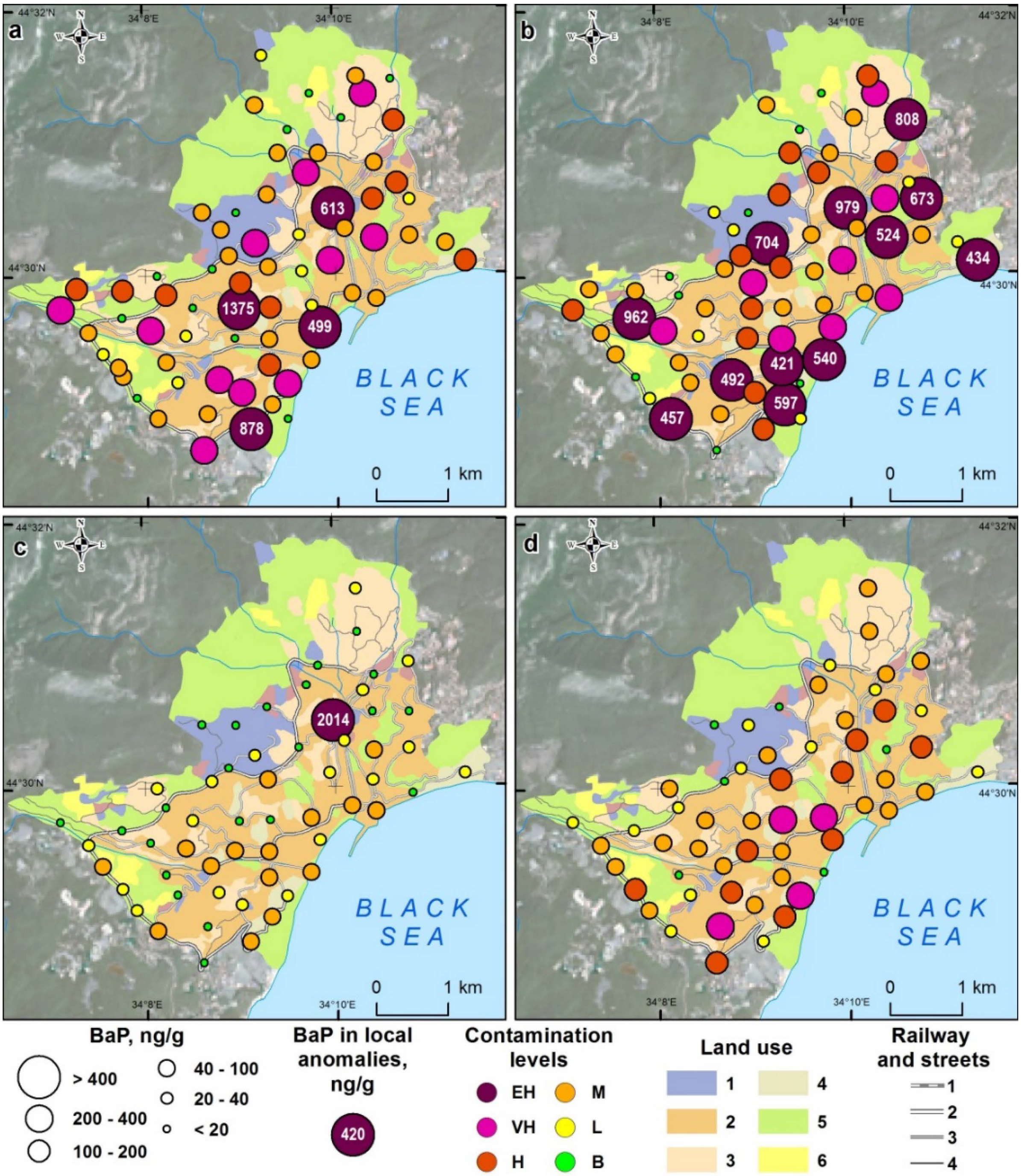

Figure 4. Distribution of BaP in soils (**a**) and their PM_{10} particles (**b**), road dust (**c**) and its PM_{10} particles (**d**) within the territory of Yalta. Contamination levels: EH—extremely high, VH—very high, H—high, M—moderate, L—low, B—background. Land use zones: 1—industrial, 2—multi-storey residential, 3—low-rise residential, 4—residential and recreational, 5—agrogenic, 6—recreational. Railway (1) and streets with: 2—large roads, 3—medium roads, 4—small roads.

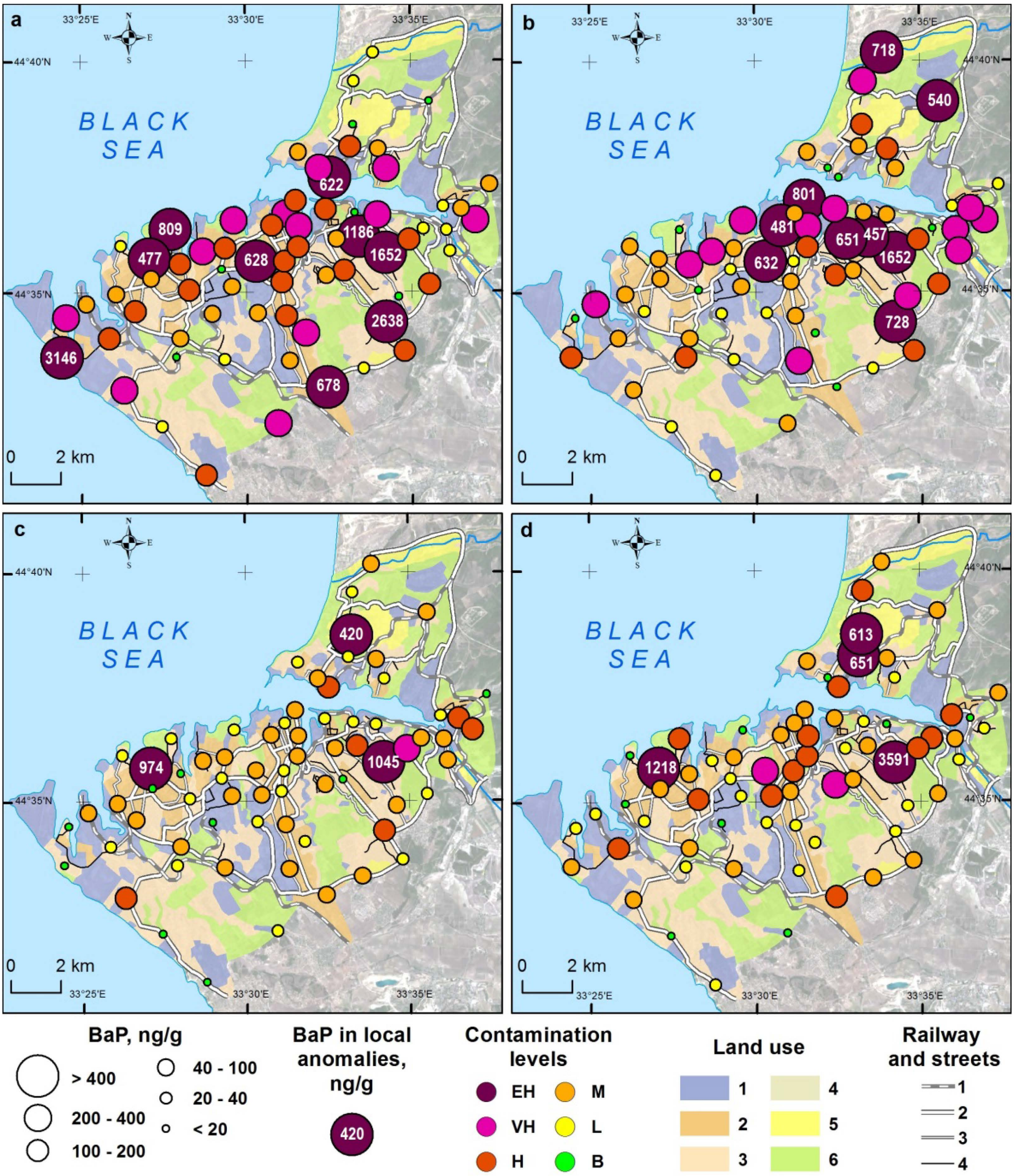

Figure 5. Distribution of BaP in soils (**a**) and their PM_{10} particles (**b**), road dust (**c**) and its PM_{10} particles (**d**) within the territory of Sebastopol. Contamination levels: EH—extremely high, VH—very high, H—high, M—moderate, L—low, B—background. Land use zones: 1—industrial, 2—multi-storey residential, 3—low-rise residential, 4—residential and recreational, 5—agrogenic, 6—recreational. Railway (1) and streets with: 2—large roads, 3—medium roads, 4—small roads.

3.3. Content and Spatial Distribution of BaP in Road Dust

The background analogs for road dust are not available, therefore the levels of BaP accumulation in the dust of Crimean cities were evaluated relative to its content in background soils (1 ng/g).

3.3.1. Alushta

The average content of BaP in the road dust of Alushta is 97 ng/g, i.e., exceeding the background concentration in soils by 97 times, and varies from 0.5 to 468 ng/g, *CF* is up to 468. The BaP concentration in the PM_{10} fraction is approximately 2.5 times higher, i.e., in line with the previously established pattern of enhanced accumulation of the pollutant in smaller fractions [19,22,61]. The average BaP content in PM_{10} particles is 238 ng/g, exceeding the background content by 238 times and varying from 0.5 to 850 ng/g, *CF* is up to 850 (Table 2). The intensity of BaP accumulation in road dust differs slightly on the roads of different size (Table 2; Figure 6), increasing in the following order: large (*CF* = 84) < small (93) < medium (106). The accumulation of BaP in PM_{10} road dust particles follows another sequence: small (*CF* = 113) < medium (256) < large (327).

Table 2. The content of benzo(a)pyrene in the bulk samples of road dust and its PM_{10} fraction and its environmental hazard in Alushta, Yalta and Sebastopol.

Parameters	Alushta		Yalta		Sebastopol	
	Bulk Samples	PM_{10} Fraction	Bulk Samples	PM_{10} Fraction	Bulk Samples	PM_{10} Fraction
Large roads						
mean, ng/g	84	327	34	68	101	123
min–max, ng/g	0.5–210	0.5–590	7.4–92	8.1–196	20–974	7.4–1218
CF	84	327	34	68	101	123
Kh	4.2	16	1.7	3.4	5.1	6.1
Medium roads						
mean, ng/g	106	256	28	74	55	75
min–max, ng/g	12–301	15–850	3.3–86	11–332	18–151	4.3–228
CF	106	256	28	74	55	75
Kh	5.3	13	1.4	3.7	2.7	3.7
Small roads						
mean, ng/g	93	113	144	111	108	232
min–max, ng/g	0.5–468	0.5–600	7.9–2014	5.9–113	13–1045	4.5–3591
CF	93	113	144	111	108	232
Kh	4.7	5.7	7.2	5.6	5.4	12

Note. Contamination factor (*CF*) is the ratio of the content of pollutant in the road dust or PM_{10} fraction in a city to the content of BaP in background soils or their PM_{10} fraction. Environmental hazard coefficient (*Kh*) is the ratio of the content of BaP in road dust or PM_{10} fraction to maximum permissible concentration (MPC) adopted for soils, which is 20 ng/g.

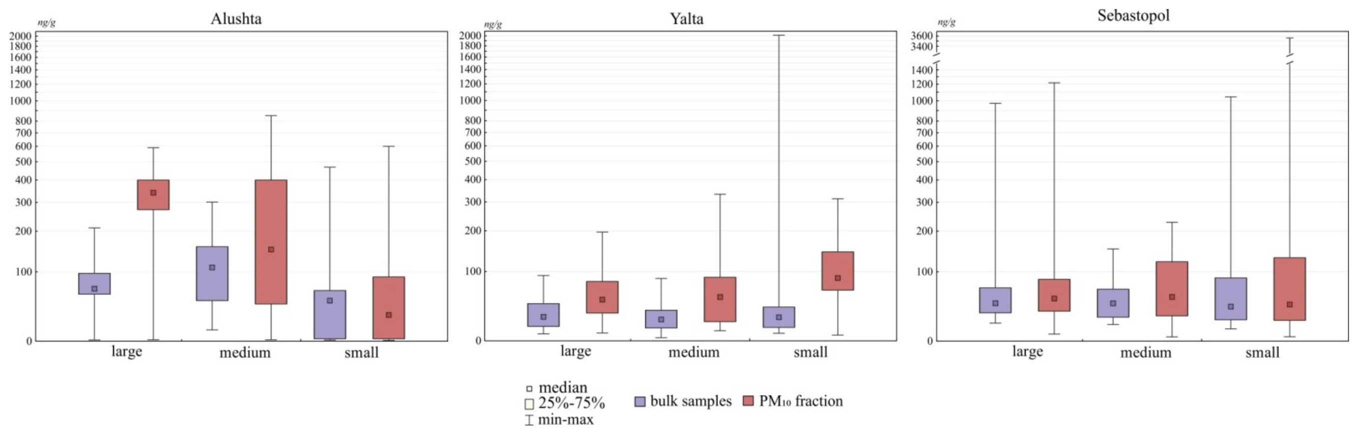

Figure 6. The content of benzo(a)pyrene in road dust and its PM_{10} fraction for different types of roads in Alushta, Yalta and Sebastopol.

The spatial pattern of BaP anomalies in the total mass of road dust and its fine PM_{10} particles is shown in Figure 3. An extremely high level of BaP accumulation in road dust is observed in the northwestern, southwestern and eastern parts of the city on large and medium-size roads. An increased accumulation of BaP in PM_{10} fraction was found on the roads with the most intense traffic flow of trucks and cars (Yalta highway, *CF* 600), as well as on the road along the city embankment, where the BaP content is more than 800 times higher than the background values.

3.3.2. Yalta

The BaP content in the road dust of Yalta averages 64 ng/g and is characterized by high spatial variability, ranging from 3.3 to 2014 ng/g. The average BaP content in PM_{10} fraction of road dust was 83 ng/g, varying from 5.9 to 332 ng/g, i.e., exceeding the total content in dust by 1.3 times on the average, and up to 10–15 times at some points. At the same time, the average content of BaP in road dust and its PM_{10} is approximately 2 and almost 3 times less than in soils and their PM_{10} fraction, respectively. The intensity of pollutant accumulation in dust on different types of roads increases in the following sequence (Table 2; Figure 6): medium (*CF* 28) < large (34) < small (144). The same dependency of BaP accumulation was found for PM_{10} dust particles: fine fractions from small roads are 1.5 and two times more enriched in pollutant compared to medium and large roads, respectively.

An extremely high level of polyarene accumulation in road dust (2014 ng/g) was recorded just in one local anomaly in the center of Yalta (Figure 4) on a small road near a residential low-rise zone, which may be associated with coal heating of private houses. An extremely high accumulation of BaP in PM_{10} fraction of dust is characteristic of small roads in the central and southwestern part of the city in a multi-storey residential area. Another anomaly was found in the southern part of the city on the roads near residential areas and within the residential and recreational zone with hotel complexes, sanatoriums and recreational areas.

3.3.3. Sebastopol

The BaP content in the road dust of Sebastopol is 203 ng/g, varying from 4 to 851 ng/g. Atmospheric fallout plays a significant role in the pollution of road dust and aquatic ecosystems of Sebastopol, with storm runoff supplying oil hydrocarbons and PAHs to city bays [62]. The BaP content in the urban air usually does not exceed the MPC; however, in winter when the fuel is burned to heat the houses the concentration of the pollutant is about 3 times higher than in summer and spring and 1.5 times higher than in autumn [63]. The BaP concentration in PM_{10} fraction of road dust is approximately 1.4 times higher than in the bulk samples. It averages 292 ng/g, ranging from 6 to 1546 ng/g. The accumulation of BaP in road dust and PM_{10} particles decreases in the following sequence of roads (Table 2; Figure 6): small roads (*CF* 108 and 232) > large (101 and 123) > medium (55 and 75), which coincides with the Yalta sequence.

The maximum content of BaP in road dust is on the large road, i.e., the Sebastopol highway in Inkerman near the commercial seaport (Figure 5). An extremely high level of BaP accumulation in road dust is also found on roads with intensive motor-vehicle traffic and proximity to the seaport and railways, which provide a large volume of cargo transportation by land and sea. Coal is a main cargo in the Sebastopol port, and its dust contains a large amount of BaP and other PAHs. An additional source of BaP in road dust of Sebastopol are emissions from boiler houses of the city [64]. In Guangzhou (China) where the seaport is also located major origins of PAHs inputs to road dust were identified as vehicle emissions (52%) and coal combustion (27%) [65].

The centers of BaP anomalies in PM_{10} fraction in part coincide with the centers of its anomalies in road dust. The maximum content of BaP in PM_{10} dust particles was found on the middle road (Rosa Luxemburg St.) near the railway tracks. An extremely high level of BaP accumulation in the PM_{10} fraction of dust is also observed in the coastal part of the city, where fine dust particles which are formed during the construction of urban and transport infrastructure, asphalt paving and its wear during road operation are released into the atmosphere and then deposited. This is confirmed by the positive correlation between the BaP content in PM_{10} dust and the proportion of these particles in road dust samples in the coastal zone (r = 0.6), while there is no such correlation in other parts of Sebastopol (r = 0.15).

3.4. Fractional Composition of BaP in Urban Soils, Road Dust and Its PM_{10} Fraction for Different Types of Land Use and Roads

3.4.1. Distribution of BaP in Land Use Zone Soils

The dependence of pollutant accumulation on the type of use of urban areas has been confirmed by many studies [41,47,66–68]. Pollution of soils and their PM_{10} particles is also different in the land use zones of Alushta, Yalta and Sebastopol (Figure 7).

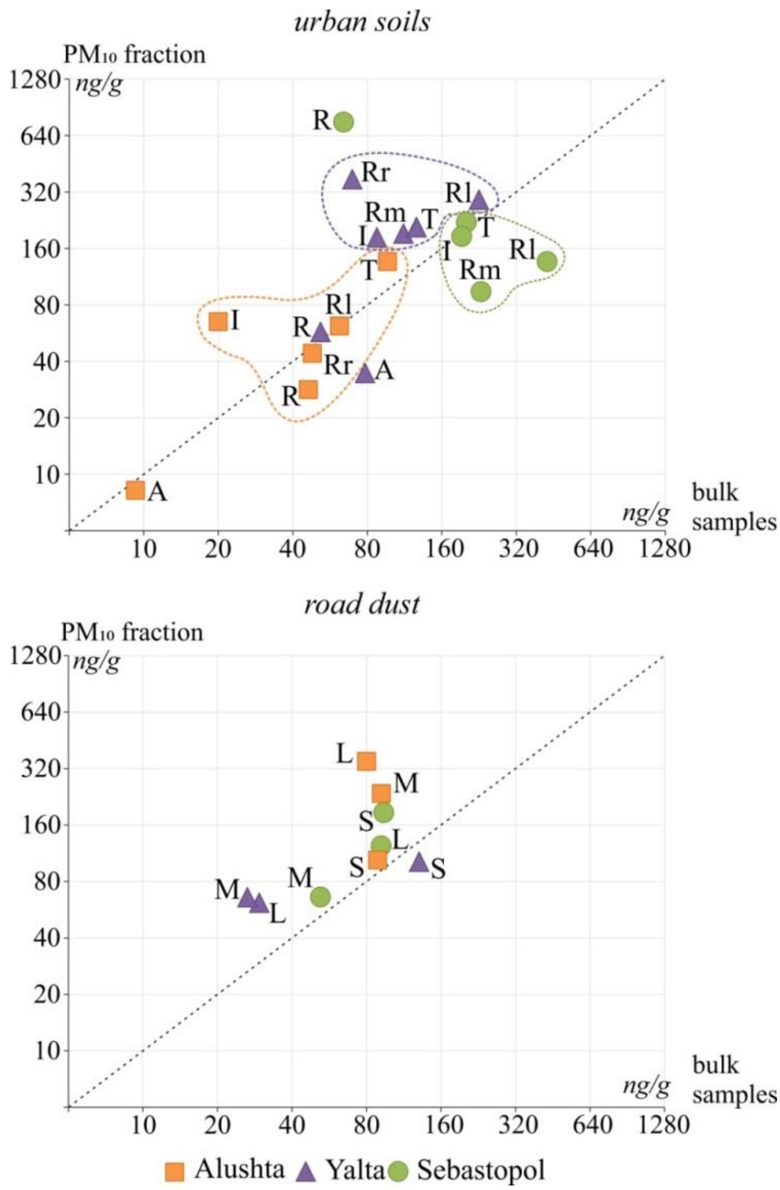

Figure 7. Fractionation of benzo(a)pyrene in soils and road dust in Alushta, Yalta and Sebastopol. Land use zones: T—traffic, I—industrial, Rm—residential multi-storey, Rl—residential low-rise, Rr—residential and recreational, A—agrogenic, R—recreational. Road type: L—large, M—medium, S—small.

Soils of the *traffic zone* in Alushta are the most polluted; in Yalta and Sebastopol they come after the residential zone soils. PM_{10} particles of soils in this zone in Alushta and Yalta are more contaminated with BaP than soils in total; its concentrations in soils and microparticles in Sebastopol are practically the same (Figure 7). This is due to the fact that the main source of PAHs in the first two cities is vehicle emissions, in which fine particles rich in these pollutants are formed, as a result of incomplete combustion of gasoline and diesel fuel, as well as weathering of pads and tires [1,26,69]. Industrial sources with a wider range of particle sizes make a significant contribution to BaP pollution in Sebastopol. Similar results were obtained in Beijing, where PAH concentrations in six soil fractions near the industrial zone demonstrate a bimodal distribution with a maximum content in larger particles of 250–500 µm in size [70].

Soils of *the industrial zone* are minimally polluted with BaP in all three cities, while the contribution of PM_{10} fraction to the total pollution increases along the sequence of Sebastopol–Yalta–Alushta (Figure 7). The more intense accumulation of BaP in small soil particles in the industrial zones of Alushta and Yalta can be explained by the influence of emissions from the thermal power complex, i.e., the main source of PAHs.

Residential zones of different storey number in Yalta and Sebastopol have the maximum BaP content in soils; the soils of low-rise residential areas in Alushta are less polluted than the roadside soils. PAHs in low-rise residential areas are formed from the combustion of automotive fuel, wood and coal, which are often used to heat the houses [10,27]. Soils of all residential zones in Yalta show higher pollutant concentrations in PM_{10} particles, while in Alushta the BaP content in dust fractions is no different from the total content. An invert correlation is typical of Sebastopol where the highest accumulation of BaP occurs in soils as a whole, i.e., the contribution of PM_{10} microparticles to total pollution decreases. The same pattern was found in Xuzhou (China), where PAHs accumulate more intensively in soil particles > 75 µm in diameter [71].

Soils of *recreational zones* in all cities are characterized by low level of BaP accumulation, while its content in fine particles differs significantly. The maximum accumulation of BaP in PM_{10} fraction of soils in Sebastopol is associated with the air transport of small contaminated particles from roads and industrial zones; a minimum is observed in Alushta with a lower technogenic load and better conditions for self-purification of the atmosphere.

A relatively low content of BaP in soils and their PM_{10} fraction was recorded in the *agrogenic zone* of Alushta, which is explained by its remoteness from technogenic sources of PAHs. Total soil mass accumulates BaP more actively than PM_{10} particles in Yalta, which is probably associated with the content of organic matter, which most often forms a similar distribution with PAHs [72].

3.4.2. Distribution of BaP in Dust on Different Types of Roads

Many pollutants in road dust are generated by road traffic and their accumulation depends on the composition and intensity of traffic flow, vehicle speed, and the number of brakeages and accelerations [73]. Therefore, the BaP pollution of road dust and its PM_{10} fraction in many cities varies on the roads of different sizes.

The intensity of BaP accumulation in the dust of *large roads* decreases in the following order: Alushta–Sebastopol–Yalta, with a corresponding increase in the enrichment of PM_{10} dust particles. This is mainly due to the accumulation of contaminated dust particles produced by transit vehicles, trucks and intercity buses on the large roads in Alushta. The lower accumulation of BaP on the major roads of Yalta and Sebastopol is apparently caused by higher travel speeds, which contribute to the removal of dust particles away from the roadbed.

The highest rate of BaP accumulation in road dust and PM_{10} fraction on *medium roads* is characteristic of Alushta (Figure 7). The contribution of PM_{10} particles to the total BaP content increases in the sequence of Sebastopol–Yalta–Alushta. Intensive accumulation of pollutant in fine dust particles of medium-size roads of Alushta could be explained by the prevalence of passenger vehicles with lower speed, intermittent traffic and frequent stops, thus the amount of pollutants emitted into the atmosphere increases.

A different pattern is characteristic of the accumulation of BaP on *small roads*: the total mass of dust is more contaminated with BaP than PM_{10} particles in Yalta, while in Alushta its concentrations in soils and microparticles are practically the same. The increased concentration of BaP in the total mass of road dust is probably associated with the input of predominantly large asphalt particles during the destruction of the road carpet which contains various mixtures of hydrocarbons [73]. A higher contribution of PM_{10} to the total pollution of dust with BaP was recorded on small roads in Sebastopol, which is in line with its increased accumulation in microparticles relative to the dust in general. This can be explained by emissions from vehicles in the vicinity of houses as a result of engine warming up. The combustion of coal and various wastes in the garden plots could also contribute to the accumulation of pollutants in the dust of small roads [65,74].

Thus, the intensity of BaP accumulation in PM_{10} dust particles is higher than in the total dust samples practically on all types of roads in all cities under study (Figure 7). This is in line with survey results from other cities. For example, the intensity of BaP accumulation in the city of Xincheng (town within the Yangtze River delta in China) is higher in finer road dust particles < 63 μm in size compared to coarse fractions for all zones of the city [75]. Dust particles < 40 μm in diameter in Beijing also have the highest concentrations of PAHs resulting from the vehicle exhaust emissions [76].

4. Discussion

4.1. Soil and Road Dust Properties as Factors of BaP Accumulation

The behavior and accumulation of PAHs in soils and road dust depend on their physicochemical properties [6,77]. The intensity of PAH sorption primarily determines the composition and amount of organic substances and clay minerals [78]. The main physicochemical properties of background soils, urban soils and road dust of Alushta, Yalta and Sebastopol were analyzed to assess this dependence, namely pH and electrical conductivity (EC), Corg content and particle size distribution (Table S1), and linear correlation coefficients (r) between BaP content and the physicochemical properties of soils and road dust were calculated (Table 3). The results of correlation analysis (Table 3) showed a significant statistical relationship between the BaP content and the properties of soil and road dust in Alushta and Yalta. However, such relationships were not revealed in Sebastopol, which can be explained by greater geochemical heterogeneity of the studied depositing media, due to larger number of both motor transport and industrial sources of BaP pollution. As a result the correlations are not identical in different land use zones of the city and there are no correlations in the general sample as a whole.

Table 3. Correlation coefficients between the benzo(a)pyrene content in soils, road dust and their physicochemical properties in Alushta, Yalta and Sebastopol.

Properties of Soils and Road Dust	Alushta		Yalta		Sebastopol	
	Soils	Dust	Soils	Dust	Soils	Dust
PM_1, %	−0.28	−0.13	−0.11	−0.15	0.01	−0.07
$PM_{1–10}$, %	−0.28	0.06	−0.04	−0.10	0.03	−0.11
$PM_{10–50}$, %	−0.14	0.24	0.15	0.00	0.13	−0.02
$PM_{>50}$, %	0.26	−0.08	−0.02	0.07	−0.1	0.01
pH	−0.06	−0.32	−0.25	−0.18	−0.18	0.14
Corg, %	0.38	0.42	0.22	0.31	0.11	−0.03
EC	0.19	0.02	0.09	0.25	−0.01	−0.05

Note. The values of r that are significant with a probability of $p > 0.9–0.95$ are highlighted in red.

The grain-size composition of soils is largely determined by the lithology of parent rocks. However, it undergoes strong technogenic transformation in cities, especially in the areas near industrial and transport facilities and residential buildings. Soils of the studied cities are generally medium loamy with an average physical clay content of 31–38%. Soil texture varies within the cities from sandy loam (with a physical clay content of 10–19%) to light clay (63–65%), mainly due to the input of new earth materials of various compositions. The heavier texture of urban soils could also result from the deposition of technogenic fine aerosol on soil surface [79]. The content of PM_{10} particles in road dust in three cities varies greatly, i.e., from 7% to 35% in Alushta and from 15–20% to 55–65% in Yalta and Sebastopol. That is, Yalta and Sebastopol, in comparison with Alushta, are characterized by accumulation of the heavier road dust on the road surface.

The influence of soil texture on pollutant distribution became evident as an inverse correlation dependence ($r = -0.28$) between the proportion of PM_1 and $PM_{1–10}$ particles in soils of Alushta and the content of BaP in them and a direct relationship with PM > 50 ($r = 0.26$). This indicates the accumulation of BaP in fine, medium and coarse sand fractions, which is in line with the results of many studies. For example, the highest PAH content in floodplain soils of the Moselle River (Germany) was found in particles > 500 μm, while particles < 63 μm had lower concentrations of pollutants [80].

The urban soils are slightly alkaline (pH 7.6) in Alushta and medium alkaline (pH 8.4) in Yalta and Sebastopol, while the background soils—Cambisols and Haplic Kastanozems—are on average neutral (pH values 6.7–7.1) due to the predominance of carbonate rocks. Alkalinization of urban soils is typical for many cities, such as Moscow [79], Berlin [81], Krakow [31], etc. The road dust in Alushta is weakly alkaline with an average pH value 7.5, while in Yalta and Sebastopol it is on average strongly alkaline (pH 8.7–8.9), sometimes reaching pH values of 10 to 11. The pH values ≥ 8 in many cities result from the input of carbonate dust and alkalizing materials from construction sites, as well as during road repairs and paving slabs [38,82]. Cement, brick and construction debris are often highly alkaline (pH 9–10). The road dust in Yalta and Sebastopol is more alkaline, in comparison with Alushta, probably due to wider occurrence of carbonate rock outcrops, as well as application of highly alkaline detergents, mainly on larger roads in city centers.

The reaction of the environment affects the microorganisms involved in the biodegradation of BaP [83]. BaP decomposes two times faster in more acidic soils with pH 6.5 and oxidizing conditions, than under pH 8.0. The accumulation of BaP decreases with increasing pH of the alkaline soils of Yalta and road dust of Alushta, which is demonstrated by inverse correlations with $r = -0.25$ for soils of Yalta and $r = -0.32$ for road dust of Alushta (Table 3). The revealed trend disaccords the known regularity and could be explained by the fact that the higher traffic intensity on highways is accompanied by both the higher input of BaP to the urban environment, and by emissions of nitrogen oxides, which acidify road dust and roadside soils [84].

The content of Corg in soils of Alushta, Yalta and Sebastopol averages 3–4%, and 1.5–2% in road dust. Higher values of Corg in road dust of Sebastopol (5%) and in soils of Alushta and Yalta (11% and 16%) are related to its input as a result of pollution with bitumen-asphalt mixtures and soot. The sources of pollutants are mainly asphalt pavements, exhaust fumes and automotive oils. Organic carbon is an important factor controlling the concentration of PAHs in soil [4,72,78,83,85]. Their concentrations usually increase at high Corg values [70,80,86]. The soils and dust of Alushta and road dust of Yalta are also characterized by a positive correlation ($r = 0.31–0.42$) between the pollutant concentration and the content of Corg.

Specific electrical conductivity of urban soils and road dust in Alushta, Yalta and Sebastopol varies from 280 to 540 μS/cm, which is on average 2–4 times higher than in background soils. The maximum EC values (1150–5150 μS/cm) in three cities were found near the Black Sea coast due to the input of salts with sea aerosols. A positive relationship between the content of readily soluble salts and BaP in road dust was recorded for Yalta ($r = 0.25$). A similar pattern was noted in Moscow, where the salinization and alkalization of urban soils due to the introduction of anti-ice reagents are the main factors of the BaP accumulation [44]. The reason is the influence of electrolytes, which cause the coagulation of colloids and the sorption of PAHs on their surface.

4.2. Environmental Hazard of Urban Soil and Road Dust Contamination with BaP

4.2.1. Alushta

The zone of extreme ecological hazard of BaP contamination of soils and their PM_{10} fraction (>5 MPC) in Alushta covers about 25% of the urban area owing to almost regular grid of soil sampling (Figure 8). Approximately 20% of the territory has a hazardous level (2–5 MPC), and more than half of the territory is characterized by moderately hazardous and non-hazardous levels of BaP contamination of soils and their PM_{10} fraction. The ecological and geochemical state of road dust and its PM_{10} fraction in terms of BaP content is more unfavorable compared to soils. Extremely dangerous and dangerous contamination was found in about 70% of samples (Figure 8) on the Yalta and Sudak highways, and the Naberezhnaya, Lenin, Partizanskaya and Vinogradnaya streets. Moderately hazardous contamination is characteristic of only 3% road dust samples and 7% of PM_{10} fraction; only 17% and 21% of samples, respectively, are classified as non-hazardous.

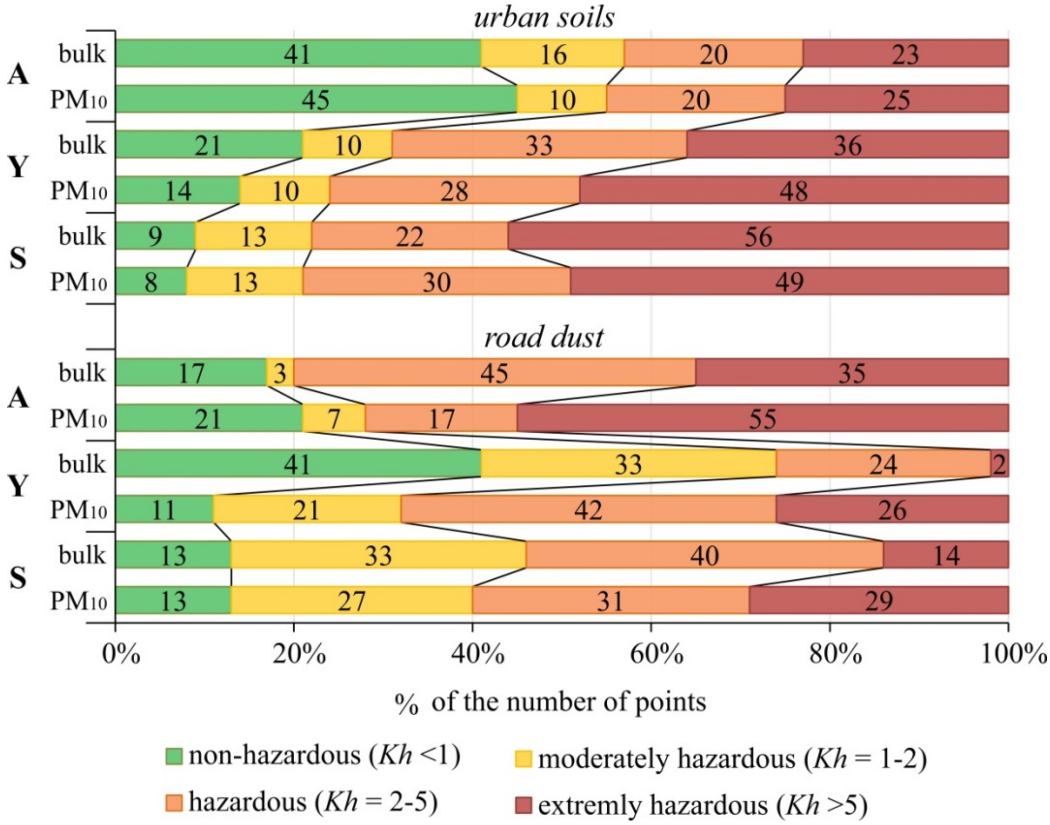

Figure 8. Levels of environmental hazard of benzo(a)pyrene contamination of urban soils, road dust and their PM_{10} fractions in Alushta (A), Yalta (Y) and Sebastopol (S).

4.2.2. Yalta

Pollution of soils and their PM_{10} fraction in Yalta reaches an extremely hazardous level, which is characteristic of 36 and 48% of the urban territory, respectively. The most hazardous are PM_{10} microparticles with high intensity of pollutant accumulation and large number of anomalies with extremely high level of pollution (*Kh* 21–49). The anomalies are developed near private residential houses, hotels and resort areas, thus creating an environmental hazard for urban residents and tourists. Hazardous contamination of the upper soil horizons and their PM_{10} particles was detected for 33% and 28% of the urban area, respectively, while non-hazardous and moderately hazardous levels for 31% and 24% (Figure 8). An extremely hazardous level of BaP contamination of road dust with *Kh* = 100 was recorded just in one local anomaly on a small road near a residential low-rise zone in the city center, which is most likely associated with the coal heating of private houses. Hazardous contamination of road dust and its PM_{10} fraction was recorded in 24% and 42% of samples, respectively, and moderately hazardous in 33% and 21% of samples. Samples of road dust and PM_{10} fractions with a non-hazardous level of contamination in Yalta account for 41% and 11%, respectively (Figure 8).

4.2.3. Sebastopol

The environmental hazard of soil contamination with BaP reaches an extremely hazardous level over 56% of the urban territory practically in all land use zones, except for the recreational one. The highest level of contamination for the PM_{10} fraction of soils was found at 49% of the territory. A hazardous level of BaP accumulation in soils and their PM_{10} particles was recorded at 22% and 30% of the urban area, respectively (Figure 8). For the rest of the territory the ecological situation is assessed as non-hazardous or moderately hazardous. Road dust is less polluted. About 14% of road dust sampling points are classified as having the extremely hazardous levels of contamination, 40% as hazardous, 33% as moderately hazardous and 13% as non-hazardous. Road sections with extremely dangerous and dangerous levels of pollution of PM_{10} particles are the most widespread and account for 29 and 31%, respectively, with moderately dangerous—27% and non-hazardous—13% of the city's road network.

The highest urban soil pollution within the three Crimean cities under study was found in the industrial and recreational city of Sebastopol, where the environmental hazard of BaP is, on average, three and 1.5 times higher than in the resort centers of Alushta and Yalta, respectively (Figure S2). This stems from the functioning of large industrial facilities, a seaport with oil storage facilities and repair shops in Sebastopol, which provides transportation of coal, oil products, grain and other goods. A large number of enterprises of the heat and power complex in Yalta, 15 of which have up to 90% equipment wearing [54], causes a greater environmental hazard of soil contamination with BaP in comparison with Alushta.

Another tendency is typical for the intensity of BaP contamination of PM_{10} fraction of soils. The maximum environmental hazard of BaP was recorded in Yalta, which is 3.5 and 1.3 times higher than the danger of soil PM_{10} particles contamination in Alushta and Sebastopol, respectively. Higher *Kh* coefficients for PM_{10} particles of Yalta soils result from the intensive traffic load, leading to traffic congestion, especially in summer when the number of tourists increases. The situation is aggravated by poor air circulation in the streets caused by the urban topography, namely high and steep slopes of the Yalta Yayla stepping directly to the seacoast.

The danger of BaP contamination of road dust and its PM_{10} particles in Alushta is about 1.5 and three times higher, respectively, than in Yalta, which can be explained by the greater share of transit passenger and freight transport that supply BaP to the atmosphere. Despite the fact that Alushta is a seaside recreational city with a large difference in altitude, many sunny days and high air temperatures and, consequently, an increased intensity of biological decomposition of BaP [4,83], its concentration in the road dust is high, indicating the presence of powerful sources of modern urban pollution. The environmental hazard coefficients *Kh* for the road dust in Sebastopol correspond to their values in Alushta and are about 1.5 times higher than in Yalta. However, PM_{10} dust particles in Sebastopol have a lower environmental hazard (*Kh* is 1.5 times lower) than in Alushta, but are two times more polluted than in Yalta.

5. Conclusions

(1) The environmental state of the coastal resort towns Alushta and Yalta on the South Coast of Crimea is largely dictated by the proximity of the Crimean mountain range to the sea. The transit traffic flows pass directly through urban areas, causing the contamination of soils and road dust with pollutants, primarily PAHs, including benzo(a)pyrene. The BaP sources are the increased emissions of vehicles during brakeage and at the start of movement and the combustion products of coal and wood under stove heating.

(2) Distribution of BaP in urban soils and road dust is largely governed by their physicochemical properties. A direct correlation between the content of BaP and Corg was found in soils and road dust of Alushta and Yalta, and on the content of coarse

fractions PM > 50 in Alushta. An inverse correlation between the pH value and BaP accumulation was found in the soils of Yalta and the road dust in Alushta.

(3) The BaP content in soils and road dust of the resort towns are comparable to those in the larger industrial city of Sebastopol. The content of BaP in soils and road dust exceeds background values in soils by an average of 60 and 90 times, respectively, in Alushta, by 139 and 64 times in Yalta, and by 260 and 89 times in Sebastopol. The levels of BaP in soils and road dust indicate a dangerous environmental state in these towns. About half of the Sebastopol area has an extremely hazardous level of soil contamination; in Yalta and Alushta such soils occupy 35 and 25% of the urban areas, respectively. In 35% of the road dust samples taken in Alushta a high environmental hazard of contamination with BaP was recorded. The Yalta town shows less contamination indicated by only 2% of dust samples with the extremely hazardous BaP content. Local BaP anomalies with extremely high concentrations in urban soils and road dust were determined in the residential areas and inner-yard passages of residential zones.

(4) The PM_{10} fraction of soil and road dust is significantly more polluted in all three towns, than the total dust. PM_{10} particles are important carriers of BaP, concentrating from 35 to 70% of the pollutant. Urban soils are most polluted with BaP in industrial Sebastopol, indicating a long-term anthropogenic impact. The accumulation of BaP in road dust and particularly its PM_{10} fraction indicates the intensifying modern recreational and transport load in the resort towns of Alushta and Yalta, especially in summer. The fine particles migrate actively in the air over long distances; after depositing from the atmosphere, they accumulate in soils and on the surface of roads, affecting the health of residents and vacationers.

(5) The similar environmental state can be expected in other resort towns experiencing a significant long-term anthropogenic load of motor vehicles running on gasoline and diesel fuel. This study shows once again the need to reduce traffic flows within resort cities and to replace internal combustion engine vehicles with electric cars.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14040561/s1, Table S1: Physicochemical properties of background soils, urban soils and road dust in Alushta, Yalta and Sebastopol. Figure S1: Points of urban soils and road dust sampling within the territory of Alushta, Yalta and Sebastopol. Figure S2: *Kh* coefficients and levels of environmental hazard of BaP contamination of urban soils, road dust and their PM_{10} fractions in Alushta, Yalta and Sebastopol.

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