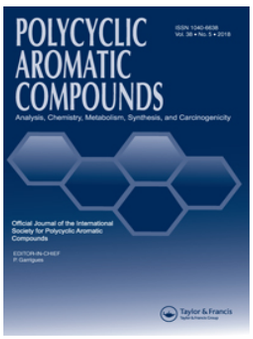

Polycyclic Aromatic Compounds

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Polycyclic Aromatic Hydrocarbons in the Snow Cover of Moscow (Case Study of the RUDN University Campus)

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ABSTRACT

The major objective of this study are polycyclic aromatic hydrocarbons (PAHs) in the snow cover of the RUDN-University campus. The campus is located in the south-west of Moscow, in a relatively clean zone of the city. However, the atmospheric pollution introduces a significant amount of the contaminants into this area, including PAHs. The area is affected by several anthropogenic sources, and the major highways are the largest contributor of air pollution. The presence of PAH in the snow cover is also due to these sources. The paper investigates interrelation of pollution character and transport activity mode. The pyrogenic genesis of pollution was confirmed using indicator ratios of PAH isomers. This method can demonstrate significant errors; therefore, the study investigates the informative value of the indicators. Implementation of a complex of ratios confirmed pyrogenic pollution. Due to the complexity and originality of the local conditions of scattered pollution the profiles of the prevalence of PAHs in the snow cover of the campus practically do not correspond to theoretical models. The study revealed dominant pollutants, i.e. Flu, Py, Phen, BbFlu, in contrast to earlier findings, traditionally used to describe the distribution of PAHs in media (soil, snow etc.). It draws on the specificity of migration and accumulation of PAHs, which may be due to the phase-structural transitions in the "snow-water" system, occurring during thaws and cold spells, and the specificity of pyrogenic pollution

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Introduction

As a depositing media, snow cover is one of the most interesting objects "preserving" pollution in itself. An analysis of its state makes it possible to identify the effects of the spread of pollutants from natural and anthropogenic sources and to evaluate their contribution to the formation of a picture of pollution. Due to the seasonal accumulation of substances, the genesis and behavior of super toxic compounds, which include polycyclic aromatic hydrocarbons (PAHs), are very precisely monitored when analyzing snow cover. Studies of the concentration of PAHs in the glacier and snow cover over more prolonged periods demonstrate clear connection between emission sources and the level of accumulation of PAHs as shown in previous studies.[1]

Due to their structural features, PAHs can most representatively reflect the essence of the kinetics of the processes of vertical and horizontal migration of natural and human-made hydrocarbon flows in the environment. PAHs are characterized mainly by electrophilic substitution reactions, and this leads specific migration behavior, in particular during phase transitions, compared with substances that are characterized by addition reactions.[2,3]

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpol.

Due to flat structure and aromatic nature of PAHs lipophilic molecules, they tend to adsorb to many surfaces. The low solubility of PAHs explains the absence of their high concentrations in the hydrosphere. Traditional representatives of PAH in water are naphthalene (Naph), fluoranthene (Flu), phenanthrene (Phen), pyrene (Py) and anthracene (An). They are more soluble than the heavy PAHs with 5–8 benzene rings. Therefore, light PAHs are a good indicator of many processes (e.g., pollution) in the case of increasing the concentration of PAHs in snow and water.

Despite extremely low concentrations of PAHs in environments, polyarenes have been widely investigated by academic community due to their high toxicity and total distribution, as well as marker properties (binding to certain natural and human-made processes). It has been established that combinations of PAHs with other substances may enhance the toxicity of pollutants (synergistic effect).[4–6]

In addition to the importance of studying PAHs as indicators of anthropogenic stress, the relevance of the study is also associated with the almost complete or selective transition of PAHs accumulated over the season in the snow, into the soil, and then into the plants. Extremely high concentrations can gradually lead to degradation of vegetation cover. In addition, PAHs were considered as one of the indicators of the total anthropogenic load: the study confirmed that the transport load (and not long-range transport from elsewhere) is the main source of PAH in the snow. In fact, an analysis of the distribution of PAHs allowed us to obtain a model for the formation of the total anthropogenic load on the studied local area.

Because of the high toxicity of PAHs, the maximum permissible concentration (MPC) levels must be established, but the justification approaches and lists of the substances to be controlled differ for different countries. For example, in EU there are MPC for 6 PAHs in water (according to the Council Directive 98/83/EC). The United States Environmental Protection Agency's (US EPA) list of the priority pollutants includes 16 PAHs to be monitored. The set of their "critical levels" includes different MPC, threshold levels, target values, etc. This list has become a subject of discussion: it is suggested, the list needs to be extended.[7] The variety of approaches to the justification of MPC or another critical pollution levels results in ambiguity in the choice of the critical level of the pollutant. According to the World Health Organization (WHO) recommendation, the total concentration of 6 of the 16 priority PAHs in drinking water should not exceed 0.2 ng/dm^3. In Russia, the following MPCs are established for PAH in water: 10 μg/dm^3 for Naph and 5 ng/dm^3 for BaP in drinking water; 10 μg/dm^3 for Naph and 1.0 ng/dm^3 for BaP in water bodies for drinking and cultural and domestic water use; 4 μg/dm^3 for Naph in fishery water bodies. It is possible to see that the PAHs concentrations in water environments are sometimes too low, and in this case, one should implement analytical approaches with caution.

Review of works[1,8–15] and earlier studies indicated that relatively light PAHs are traditionally dominating in snow cover, and the presence of multiring substances is most often associated with solid particles of natural or human-made origin. Thus, predominantly heavy PAHs are sorbed, whereas polyarenes with 2–4 rings are more often present in the gaseous phase.[3,16] The accumulation of light PAHs in atmospheric precipitation occurs due to their accumulation on snowflakes: polyarene molecules associate with the boundary between the air and the solid phase. The values of concentrations of PAH in snow cover vary from 5.6 ng/l (snow cover of Alpine lakes[11]) to 49 ng/l on fallow lands in the Tver region[9] and to 92,500 ng/l in snow samples from Bratsk city (vicinity of aluminum smelters, the largest PAHs emitters). And in snowmelt water in the zone of influence of technogenic sources the content of PAH is from 21.3 to 446.5 ng/l.[8]

According to the generally accepted opinion, PAHs differentiate depending on the genesis: Py and BaP are typical for objects of pyrogenic nature; naphthygenesis is characterized by the accumulation and transformation of Naph, Phen; for biogenesis, Phen, Chr, and perylene are representative.[3,15] Indicators of industrial pollution are Py, Flu, benzo[g,h,i]perylene (Bghi), benzo[b]fluoranthene (BbFlu) and 2,3-o-phenylenepyrene etc. In megacities and large cities vehicle pollution plays the key role. Numerous measurements have shown that the emissions of

internal combustion engines are dominated mainly by Flu, Py, BbFlu, Bghi in the form of unsubstituted structures. It is believed that the car emits an average of up to 1 μg of PAH per minute.[17]

The contribution of tire abrasion (respectively, the formation of solid particles containing and transporting PAHs) to the release of PAHs, as shown,[3,18] is even higher (55–60%) than the exhaust gases of some cars. The content of PAH in the tread of passenger car tires reaches 234.4 mg/kg. Such concentrations are explained by the fact that PAHs are contained in mineral oils, which are introduced into rubber compounds to give them plasticity properties (up to 20% of mineral oils with a high content of aromatic compounds).

General information intends to clarify, what sources of the pollution could form the current state of the snow cover on our object and to underline the role of some sources in a long-term atmospheric pollution.

Accumulation of PAHs in media is selective, which is confirmed by their comparative analysis in the vehicle exhaust and concentrations in the snow. So, in the exhaust content of Phen, Flu and Py are about 10 times more than the BaP. In snow, Flu and Py accumulate intensively in disproportionately higher ratios.

The migration of PAHs to the environment is facilitated by the increased temperature of the tire materials during friction, as well as by the wear of the tire tread and the renewal of the road surface. Also, PAHs can interact with other released substances to form nitro-PAH, chloro-PAH (dioxins), hydro-PAH, etc. as shown in the Ref. 10. Carcinogenicity of PAH derivatives, e.g., 6-nitrobenz(a)pyrene, is higher than PAH. Nitration of BaP also produces 1-nitro and 3-nitrobenzo[a]pyrenes.

In extracts of a three-carbon used in the manufacture of tires, BaA, BaP, BbFlu, BkFlu, BjFlu, Dibenz (a, h) anthracene, Naph, Py, Phen, etc. are identified. It has been established that oil distillation fractions containing 4–6 nuclear PAHs, in which the concentration of BaP or BaA is 0.4% are the most carcinogenically dangerous ones. According to the available data, the largest number of different PAHs contain aromatic oils, which also contain An, Phen, Flu, cyclopenta[c,d]pyrene.

Analysis of air pollution in the proximity of highway with moderate traffic indicated the presence of 3800–6900 individual fragments of tires in 1 m^3 of air; the size of more than 58% of them are no higher than 10 microns. These particles can easily penetrate the respiratory tract. It is calculated that a resident of Sweden is exposed to about 6 g of tire dust per day, a resident of the United States – more than 13, in the Moscow region, this figure is even higher: only in Moscow the characteristic content of PAH (by BaP) is 20 MPC, the content of volatile N-nitrosamines is about 4 MPC as demonstrated in Ref. 18.

There is scarcity of reliable data for asphalt, since the mixtures for its preparation have a very different composition, including the residues from burning garbage. According to available data, the total contribution of air pollutants may reach 10–15%, and for PAHs, this value may be even higher when operating vehicles in hot weather. It has been established in the study[19] that during the year, about 4 mm of asphalt pavement is abraded due to interaction with tires.

The methodology of the monitoring used in our study allows to quantify the technogenic (transport) pressure caused by a combination of highways, one of which is the largest highway with a stream of cars of more than 100 thousand/day. Previously published works on the presence of PAHs in the snow uncovers issues of long-distance transport of these compounds, transboundary transport, etc. Such studies are really very actual, given the persistence of PAHs in the environment and the ability to migrate hundreds of kilometers. But the contribution of local sources to the formation of a cumulative picture of pollution has been given insufficient attention. Perhaps, stationary industrial sources (aluminum production, petrochemistry, etc.), which create maximum PAH concentrations in adjacent media, are most often considered. Transport load as a source of PAH is given much less attention. Further will be presented the model of the distribution of PAHs from a linear source of local pollution for the Moscow conditions. The

model has been developed as a base for the projecting of an optimal local monitoring system able to identify the local effects of the PAHS distribution and accumulation in close proximity to the pollution source (transport). The following steps of the development of such a monitoring must allow to trace the PAHs fate in the surrounding media, incl. soils and plants. This approach requires to use quite precise model of the spatial distribution of pollutants on the local area; some one-time measurements without understanding of the variations of the pollution fields are surely not enough.

Objects and research methodology

This paper investigates the snow cover on the campus of the RUDN University and the surrounding area (South-West of Moscow). Specialized research has been implemented in connection with the participation of RUDN in the international movement of "Green universities". RUDN successfully participates in this program and in 2018 placed 41st in the world ranking and first in Russia. Among Russian universities, RUDN is one of the few universities with campus infrastructure and a unique territory with a large green area. A campus is a place of compact residence of thousands of students from 157 countries, the place of work of hundreds of employees. Therefore, this study provides an exciting opportunity to advance our knowledge of the ecological status of the campus. The objects surrounding the territory (highways, gas stations, neighboring institutions), create a significant anthropogenic load. This study has been conducted within the framework of a unique environmental monitoring program.

The snow sampling was carried out on 03.04.2017, using the specially designed uniform grid with plots 5×5 m by the method of "envelope" according to the standard regulations and the existing approaches to sampling.[20] Samples from 31 points were taken at full capacity by snow collectors from a chemically resistant polymer material. Then for each sampling point, a sample was prepared with a mass of at least 1 kg, which was placed in special containers of chemically resistant polymeric material. As the samples melted, the water was filtered into blue tape filters, packed in a glass dish and placed in a refrigerator.

Increased attention to sampling is associated with our special studies, which revealed active leaching of PAHs during storage of water samples from polyethylene packages. An attempt was also made to avoid traditional sampling errors. It was established that 10% of the total error in the analysis of persistent organic pollutants in waterfalls on the signal measurement stage, 30% on sample preparation and 60% on sampling.[21] It has been confirmed by previous findings that the sampling error can reach 100% or more, which is caused by non-equilibrium, non-uniformity, phase differences of controlled media. For snow, this is extremely important, since under conditions of Moscow in winter there are frequent thaws, leading to significant variations in the moisture reserves in the snow with the corresponding phase transitions of the medium accumulating PAHs.

In our study, we identify and model the distribution of 10 PAHs from the EPA list. Extremely low concentrations (beyond the reliable quantitative detection limit of the method used) of the "light" PAHs (Naph, Ace, acenaphthylene) can be attributed to a set of factors.

1. A short decay period in the natural media (including the photolysis). Current study confirms their presence in the trace concentrations;
2. We do not deny their formation during the vehicle functioning, but there is also a probability of thermal destruction or combustion of these substances in the engine exhaust;
3. Probability of the phase transitions "snow-water";
4. Use of a standard (state approved) detection method[22] cannot provide high accuracy (only 25–44%).

Table 1. Measuring ranges and QA/QC characteristics.

	According to the PND F Method 14. 1: 2: 4.70–96				Current analysis		
Substance	Measurement range, μg/dm^3	Recurrence rate (standard deviation of recurrence), σ_r, %	Reproducibility Index (standard deviation of reproducibility), σ_R, %	Accuracy index (relative error margin at $P = 0.95$), $\pm\delta$, %	Recovery rate	LOD, ppb	LOQ, ppb
Naphthalene	**0.02** to 5.0 incl.	17.5	21	44	90	0.011	0.034
	Over 5.0 to 500 incl.	10	12	25			
Acenaphthene	**0.006** to 5.0 incl.	16	19.5	40	92	0.006	0.018
	Over 5.0 to 50 incl.	12	14.5	30			
Fluorene	**0.006** to 5.0 incl.	17	20,5	42	98	0.006	0.021
	Over 5.0 to 100 incl.	11	13.5	28			
Phenanthrene	**0.006** to 5.0 incl.	16	20	41	95	0.002	0.006
	Over 5.0 to 250 incl.	11	13.5	28			
Anthracene	**0.001** to 1.0 incl.	15	21	43	96	0.001	0.003
	Over 1.0 to 100 incl.	10,5	14.5	30			
Fluoranthene	**0.02** to 5.0 incl.	18	22	45	99	0.001	0.002
	Over 5.0 to 250 incl.	12	14.5	30			
Pyrene	**0.02** to 5.0 incl.	16	20	41	97	0.002	0.007
	Over 5.0 to250 incl.	10.5	13	27			
Benzo[a]anthracene	**0.006** to 5.0 incl.	17.5	21.5	44	97	0.002	0.005
	Over 5.0 to 50 incl.	11	14	29			
Chrysene	**0.003** to 5.0 incl.	18	22	45	95	0.001	0.003
	Over 5.0 to 50 incl.	11.5	14	29			
Benzo[b]	**0.006** to 5.0 incl.	17,5	21.5	44	98	0.001	0.003
fluoranthene	Over 5.0 to 20 incl.	10.5	14,5	30			
Benzo[k]	**0.001** to 1.0 incl.	15	21	43	97	.002	0.007
fluoranthene	Over 1.0 to 20 incl.	10	12	25			
Benzo[a]pyrene	**0.001** to 1.0 incl.	15	21	43	100	0.001	0.003
	Over 1.0 to 20 incl.	9	11,5	24			
Dibenzo(a, h)anthracene	**0.006** to 5,0 incl.	16	20	41	96	0.002	.004
Benzo(q, h, i)perylene	**0.006** to 5.0 incl.	16	20	41	97	0.004	0.012
Indeno(1,2,3-cd)pyrene	**0.02** to 0.1 incl.	SO	27.5	55	94	0.002	0.007
	Over 0.1 to 10 incl.	00	23	45			

The samples were analyzed at the NORTEST accredited test center (Moscow) following the PND F Method 14. 1: 2: 4.70–96 ("Quantitative chemical analysis of water. Methods of measuring the mass concentrations of PAHs in drinking, natural and waste waters using high performance liquid chromatography") with a standard test procedure according to the current regulations. Mass concentrations of PAHs are measured by HPLC with fluorescent detection after extraction from an aqueous sample with hexane and concentration of the extract by evaporation. The document establishes a methodology for the quantitative chemical analysis of various types of water in order to measure the mass concentrations of PAHs. The method applies to the following objects: drinking water, including those packaged in containers; natural waters, including surface and groundwater sources; industrial wastewater, domestic wastewater, stormwater and purified. The technique can be used to analyze samples of snow cover and melt water.

In our study the analyses have been carried out using the LC-20 Prominence Shimadzu Liquid Chromatograph, Spectrofluorimetric Detector RF-10AXL. The precision data according to the PND F Method 14. 1: 2: 4.70–96 methodology and QR/QC characteristics of analyses presented in the Table 1.

The mapping of the amounts of PAH concentrations was carried out using interpolation in ArcGis. Maps are made in 1: 10,000 scale.

A set of methods are used, to identify the source of pollution including multivariate methods, such as principal components analyses (with variations and extensions like positive matrix

factorization), cluster analyses etc. Currently also some specific approaches and techniques are developed for the identification of sources of the pollution (used as models integrated into the software i.e. like Unmix). But some of them are rather aimed at the local pollution models. It is to be noted, that in case of PAHs the migration on the large distances (up to hundreds of km) is possible,[23] which makes it sometimes impossible to associate the presence of these substances in the studied objects with the nearest source.

Results and discussion

Data at sampling point 1 (maximum distance from highways) were taken as a background. Here, the minimum values of the PAH sum are fixed, and the concentrations of some polyarenes vary within the accuracy of the analysis. In general, the amount of PAHs ranged from 0.144 to 7.86 μg/g of snow at almost a constant ratio in the stationary levels of PAHs. The maximum values are fixed in the adjacent to the road part of the campus. Minimum levels are at a considerable distance (up to 1 km or more) in the Park area, the most remote from Leninsky Prospekt and Miklukho-Maklaya Street (point 1).

It is to be noted that we use the parameter of "sum of PAHs" as a primary description of a pollution, to show the general distribution and presence of PAHs on the territory. This characteristic objectively reflects the arrival of pollutants from the atmosphere at the expense of vehicles. The individual composition of the PAH pollution, estimates and models of the "fate" of individual PAHs will be presented and described further. Also, on the basis of the ratios of individual kinetic and thermodynamic compounds, the genesis of PAH will be determined.

The behavior of some individual substances is a result of interaction of a number of factors. The detection method is also of great importance, as shown above. Therefore, the findings of current study do not support previous research. In particular, our results differ from Ref. 24 estimates on the content of some light PAH in the snow obtained on the basis of the method EPA-8827. The present study does not draw on the findings of the paper mentioned above, as it sheds light on the issues of pollution in the Arctic regions and global processes. For us, however, local patterns in the formation of pollution fields are of greater interest. Therefore, the organization of sampling is of great importance. In our case, the emphasis was on regularity. The sampling point system has been developed as a uniform network according to the impact monitoring methodology. In such approach, errors in analytical definitions are detected more reliably than in a single sampling without taking into account local sources.

The obtained data are consistent with those of the previous study.[25] For the transport zone of the Eastern District of Moscow during the two years (2012–2013) of observations of the PAH aerial supply, concentrations of 8.22 and 8.79 μg/g, respectively, were established. At the same time, in the natural, recreational zone (park of the Elk Island) the amount of PAH in the snow exceeded the concentration for the transport zone and averaged 10.7 and 9.53 μg/g for the years studied. Taking into account the errors of analytical definitions (up to 40%), it is encouraging to compare our data with that found by Ref. 25. It should also be emphasized that our distribution of PAHs concentrations is in accordance with some another previous studies demonstrating the role of a transport pollution of snow.[26,27]

The spatial distribution of the sum of PAHs is shown in Figure 1.

A geochemical field is a quite regular localization. Its maximal values are confined to the part of Miklukho-Maklaya Street adjacent to Leninsky Prospekt. The intensive thickening of the PAH isolines can be attributed to two reasons related to the change in the mode of traffic.

The first of them is slowing down of traffic speeds at stops and before traffic lights. It is known (for example, the variability of the concentrations of BaP) that during the period of deceleration and acceleration the concentrations of PAH in the exhaust of cars increase almost by 10 times. In this period occurs an excessive abrasion of the tire with the saturation of the air with

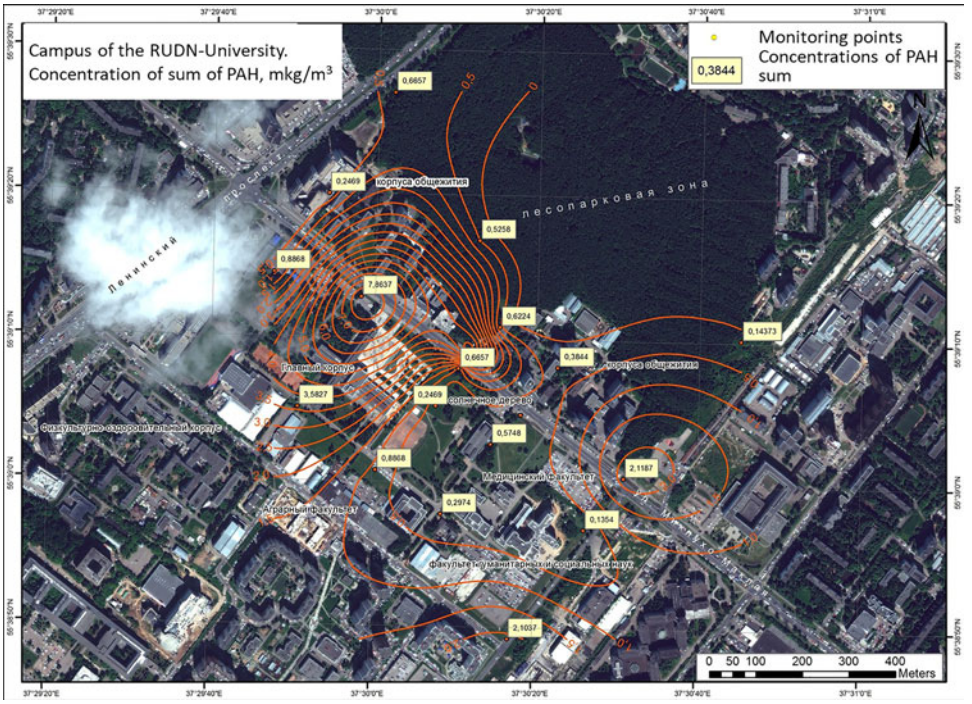

Figure 1. Spatial distribution of the amount of PAHs in the snow cover of the campus area.

tiny particles that are actively adsorbed PAHs because of their lipophilic properties. This favorable situation leads to an active accumulation of polyarenes in the snow cover on the adjacent part of the highway. Similar conditions in the zone of the second maximum are created at the crossroads at the entrances to the campus zone from the Volgina Street.

The second reason for the intensive accumulation of PAHs is associated with the heating of cold engines at the exit from the parking lot on the territory of the university. Emissions from the parking lots aggravate the already existing unfavorable traffic situation. It has been empirically proved that when starting a cold engine, a tenfold increase in the concentration of PAHs in the exhaust gases also occurs.

Judging by the distribution of PAH concentrations, the maxima of their concentrations in snow can be traced at 600–700 m along Miklukho-Maklaya Street and 250–300 m perpendicular to its direction. The size of the zone of influence is due to the shielding effect of campus buildings, the density of which is maximum in the residential zone, directly adjacent to the Park area. At the same time, the administrative and educational part of the campus, adjacent to Miklukho-Maklaya Street, has a dispersed distribution of educational buildings with sports and functional recreational areas, which led to the formation of a more sparse field of PAHs concentrations. The minimum amounts of PAHs were recorded in the park area adjacent to the campus of RUDN. Here you can see the distance to which the exhaust vehicles distribute PAH. So, from the Leninsky prospect, they penetrate through the air at 150–200 m distance. From the Miklukho-Maklaya Street, identical emissions reach the distances up to 400–500 m. Although the park zone is influenced by emissions of vehicles standing at the crossroads of streets, traffic with correspondingly large amounts of emissions is detected by the accumulation of PAHs in the snow.

The second maximum is also formed at the intersection of Miklukho-Maklaya Street and Academician Oparin Street. The spread of PAHs from this intersection is also fixed in the park area at a distance of 400–500 m. The configuration of the PAH contamination field of such a

Table 2. PAHs content (μg/g) in snow samples on campus of the RUDN University.

PAH	Limits of variation and mean	Coefficient of variation	% of PAH sum	Background value (point 1)	Maximum background excess, μg/g (%)
Phen	0.006–0.570 (0.161)	0.832	9.55	0.014	0.556 (3971.4)
An	0.001–0.210 (0.033)	1.201	1.94	0.001	0,209 (33233.3)
Flu	0.034–**4.180 (0.881)**	1.060	**52.34**	0.034	4.146 (12194.1)
Py	0.011–**2.190 (0.345)**	1.223	**20.51**	0.011	2.179 (19809.1)
BaA	0.001–0.037 (0.010)	0.863	0.62	0.002	0.035 (1661.9)
Chr	0.003–0.150 (0.043)	0.872	2.58	0.006	0.144 (2280.9)
BbFlu	0.005–0.220 (0.053)	0.983	3.13	0.006	0.214 (3337.5)
BkFlu	0.002–0.075 (0.019)	0.972	1.12	0.002	0.073 (3471.4)
BaP	0.003–0.140 (0.031)	0.942	1.87	0.006	0.134 (2122.2)
Bghi	0.005–0.190 (0.051)	1.183	3.04	0.005	0.185 (3553.9)

depositing environment as snow cover clearly indicates the role of green areas of urban settlements that actively prevent the spread of impurities even in the winter period (Table 2).

The data presented in the table indicate the same genesis of the formation of unsubstituted PAHs in the vehicle's emissions. The snow cover accumulates the typical products of the emissions of internal combustion engines, i.e. Flu and Py intensively. The absence (or concentration at the level of sensitivity of the analysis) of light PAH such as Naph, acenaphthene, Phen, and diphenyl, a representative for the background regions, indicates the formed stable spatial and temporal vehicular pollution. Such industrial markers as dibenz(a, h)anthracene, indeno(1,2,3-c, d)pyrene are practically not recorded in the snow. For the latter one, a biogenic genesis is also not excluded.

Further, according to the values of concentration following the more toxic BbFlu and BkFlu and Bghi and the most toxic BaP (its content in the composition of PAHs is up to 1.87%). This is quite a significant value for multi-ring (massive) structures, which indicates the absence of special devices on cars for afterburning exhausts. In addition to Flu and Py, BbFlu has a high contribution to a sum of PAHs (3.13%). This is the most objective marker of air pollution by vehicle exhaust products. The accumulation of these polyarenes in the snow near highways is quite natural compared to the clean background regions, where the light PAHs Naph and Phen prevail.

Principal component analysis is a widely used method for the understanding or the pollution fields. The above shown data on PAHs distribution on sampling points have been processed to clarify the interaction between the PAHs complex. As a result of decomposition of the matrix by orthogonal factors, we obtained the values of the vectors at the observation points. This made it possible to establish a close relationship within the data set (close correlations: high factor loads on the first factor of almost all the considered substances except An, this PAH formed an independent factor 2) and to indicate anomalies from the total set of points. Such kind of distribution of PAHs relative the principal components can be due to the physico-chemical properties of the polycyclic compounds. The distribution of points in the plane of the first and second principal components is shown in Figure 2. The most visible anomalies are indicated in points 3, 11, 26; the less apparent one – in point 28. Their specifics is due to the following:

- points 3 and 11: a high concentration of anthracene and relatively low amounts of other PAHs;
- point 26: the most significant concentrations of almost all PAHs compared to all other points;
- point 28: relative high concentration of all PAHs, especially BbFlu and BkFlu and highest level of Bghi.

Almost all of the identified anomalous points are confined to objects with an active traffic load (parking, pre-light traffic zones with active exhaust of buses and partially freight transport, etc.).

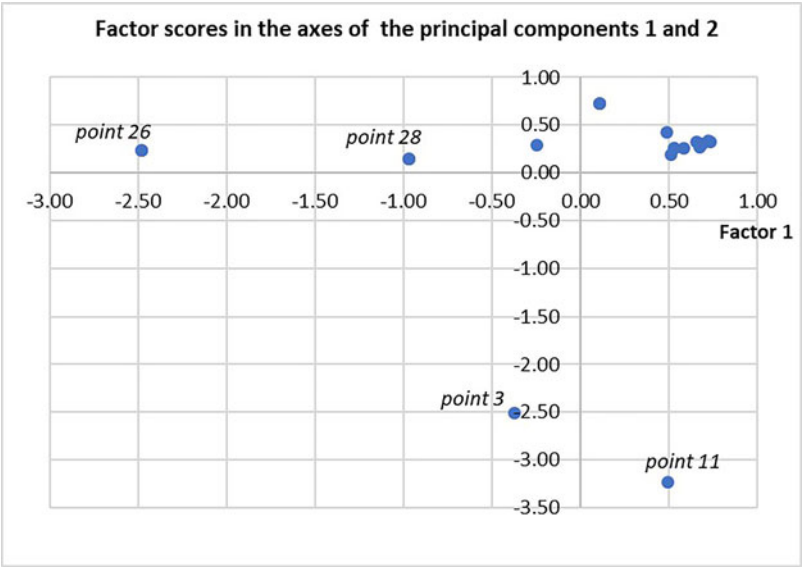

Figure 2. Factor scores in the axes of the principal components 1 and 2.

Table 3. Physico-chemical properties and prevalence series in the environments and migration activity of PAHs.[a]

PAH properties	The sequence of PAH descending properties
Solubility of PAHs in fresh water	Naph > Phen > Flu > Py > An > Chr > Pl > BaP
Hydrophobicity characteristic – lgKow	Pl > BaP > Chr > Flu > Py > Phen > An > Naph
Structural and molecular stability[3]	Phen > Flu > Naph > Chr > Py > BaP > Pl > An
Prevalence in natural environments[3]	BaP > Py > Flu > Phen > Chr > Naph > An > Pl
prevalence of PAHs in the snow cover of the RUDN University campus in Moscow	Flu > Py > Phen > Ba(b)Flu > Bghi > Chr > An > BaP > (IP) > (Naph) > Ba(k)Flu > BaA > (DBA) > (Fluor) > (Ace)
PAHs content in a solid atmospheric aerosol[3]	Chr > Py > Bghi > Phen > Flu
PAHs content in alpine firn (1860–1870)[1]	Phen > Flu > Py > An > Chr = BbFlu = BkFlu = BaP > (Bghi = IP)

[a]Concentrations in parentheses are below the detection limit.

In this regard, it is interesting to refer to the juxtaposition of the properties of the PAHs themselves (Table 3) and to compare the obtained PAH distributions in a real situation with the data established as a result of modeling the properties of PAHs and in assessing the molecular structural stability.

The analysis included such indicators as the solubility of PAH in fresh water and the hydrophobicity index (the distribution of PAH in the octanol-water system, Kow). This characteristic is opposite to solubility, but it also characterizes the presence of media – sorbents, favorable to the accumulation of PAHs. Theoretically, the physicochemical properties of PAHs should largely determine their migration activity and prevalence in homogeneous and heterophase media. However, as demonstrated in the Table 3, there are very significant differences between the theoretically based distributions and the empirical results obtained. In our opinion, such differences are due to the role of multiple phase transitions in the aerosol system "water–crystal phase" even in the conditions of the same type of pollution genesis.

The problem of assessing the genesis and transformation of PAHs

The speed and transformation paths of PAHs are very diverse. So, in the soil, some PAHs can persist depending on geochemical stability from tens to hundreds of years. This is mainly due to their chemical composition and kinetics of decomposition processes. Pyrogenic PAHs have a

Table 4. Values of the indicator ratios of PAHs with pyrogenic snow pollution.

Indicator ratios	Min	Max	Average	Values for pyrogenic objects	% of match
Phen/An	0.34	48.46	15.19	<10	5
Flu/Py	0	0.54	0.15	<1[15] >0.4[29]	100
An/178	0.02	0.74	0.12	<0.10	85
Flu/208	0.66	0.91	0.78	>0.50	100
(Py + Flu)/(Chr + Phen)	1.46	8.85	4.11	>0.5	100
BaA/228	0.1	0.46	0.21	>0.20	0
IP/(IP + Bghi)	0.09	0.79	0.54	>0.20	75

strong affinity for volatile organic particles (soot, biogenic suspensions) that can travel long distances due to atmospheric phenomena. The first to undergo decomposition are PAH with a small number of benzene rings. Alkylated PAHs exhibit various degradation abilities (including microbial) depending on the number and length of alkyl groups. The consequence of degradation is a change in the composition of hydrocarbon contamination. Considering the rate of degradation and the initial component composition of pollution, it is possible to predict the further metamorphosis (track) of pollutants.

PAH isomers differ in the heat of formation and reactivity. "Kinetic" (less stable) isomers are the isomers with a relatively higher heat of formation, while "thermodynamic" isomers are the more stable (their heat of formation is minimal). So, in a pair "Phen–An" An is the kinetic isomer, and Phen is thermodynamic one; in the pair "Py and Flu" Flu is the kinetic isomer, and Py is the thermodynamic one, etc.

This approach (as well as the use of indicator ratios to determine the genesis of pollution) is difficult to automatically transfer to all pollution conditions. This is due to the difference in natural conditions, including seasonality. It is well known that in different modes of illumination, temperature and humidity PAH stability series in winter and summer are different.[3] According to the results of previous findings, for the petrogenic pollution,[28,29] these estimates are not always unambiguous, and many boundary values of indicator ratios in some cases need to be corrected. Let us demonstrate this by the example of estimating the informative coefficients for pyrogenic pollution of campus snow cover. The limited area and density of testing allow such assessments to be carried out with a high degree of reliability and certainty (Table 4).

The data of Table 4 indicate that such ratios as Phen/An and BaA/228 are practically unsuitable for assessing the source of pyrogenic PAH in the snow cover. In addition, we previously found an erroneous value of the ratio Flu/Py > 0.4 for pyrogenic hydrocarbon combustion processes.[29] Using the example of a number of objects, the recommended value of this ratio is <1.

Conclusions

On the territory of Moscow and, in particular, the campus of RUDN, the presence of PAH with solid aerosol deposition can be attributed to intense traffic.

Depending on the shielding effect of buildings and green spaces, the spatial distribution of the amount of PAHs on campus varies from 0.144 to 7.86 μg/g of snow.

The specificity of the spatial distribution of PAHs is related to their additional emissions in exhaust gases, tire and asphalt abrasion at the front-light part of the intersection of Miklukho-Maklaya Street and Leninsky prospect (highway), as well as close to public transport stops. This corresponds in general with the PAHs sources role distribution for the industrial countries (as indicated in Ref. 30). The second most important source is the internal and external parking of passenger cars on campus, which create additional emissions of polyarene during warming up of cold engines.

The main pollutants are "light" polyarenes: Flu (52%), Py (21%) and Phen (10%); followed by the 5-6-ring isomers of benzofluoranthene (1–3%), Bghi (3%), Chr (2.5%), BaP (2%).

The profile of the prevalence of PAHs in the snow cover of the campus contradicts theoretical models (generally accepted) of the prevalence of polyarenes in environments. This may be due to phase-structural transitions in the snow-water system, occurring during periods of thaw and cooling, as well as the local specifics of pyrogenic pollution. The extremely low concentrations (beyond the reliable quantitative detection limit of the method used) of Naph, acenaphthene, and Flu, as well as the calculations of specific markers, clearly indicate the genesis justified above.

The park zone creates certain "oasis" to atmospheric pollution with polyarenes and other compounds even in the winter period, which indicates the most important environmental protection role of green spaces in the urban environment.

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