

# Input and behavior of polycyclic Aromatic Hydrocarbons in Sub-urban and Urban soils under Pollution from a Local Industrial Source

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The increased interest in polycyclic aromatic hydrocarbons (PAHs) is related to the carcinogenic and mutagenic activity of some of them, which poses a human health risk. One of the main ways of PAHs contamination of soils is their accumulation from the atmosphere, where, in turn, they are released by industrial enterprises. Meanwhile, in the literature, these processes are not illuminated sufficiently; features of PAHs accumulation on soil surface in urban and suburban areas from the atmosphere and transformation in soil cover have been studied in rare works. For a better understanding of their behavior in the environment it is necessary the further research characterizing features of income, accumulation and transformation of these compounds in the soil.

The aim of this study was to compare the PAHs content in snow and soil cover in urban and suburban areas under pollution from a local industrial source, identification and testing of the indicator significance of the individual polyarenes ratios to establish the characteristics of their accumulation from the atmosphere and transformation in soils at different combinations of natural and anthropogenic factors. In the literature there is no information on the comparison of different PAHs ratios according to the degree of their stability in soil and snow samples, this approach is applied for the first time.

The studied key-site was subjected to the technogenic impact, mainly related to the technical carbon-producing plant for a long time. The studies were conducted along a transect directed from the source of industrial emissions (industrial zone of the technical carbon-producing plant) to the east. The transect included six soil-testing plots with a total length of 11 km. There were no other industrial enterprises along the transect, except the initial plot occurring in the industrial zone.

Earlier in the specified paper the authors described the content of different hydrocarbon compounds in soils of studied key-site: the bitumoids, free and held hydrocarbon gases and polyarenes (Gennadiev et al., 2016). However, that work have been devoted exclusively to the content of these substances in soils. In this paper, the focus was on a comparison of polyarenes contents in soil and snow, as well as a calculation of various ratios of individual PAHs as an indicator of their stability and degradation.

Soil samples were taken from genetic horizons in soil profiles. Snow samples were taken at the same points where the soil profiles were previously studied. Sampling the snow was conducted in sealed plastic containers by special trumpet samplers with fixed diameter. Snow was melted in a container at room temperature. Melted snow water was filtered through a membrane filter (pore diameter of 0.45 microns) on a vacuum filtration unit. At each sampling point was determined snow water reserve by the volume of snow and snow moisture.

Polycyclic aromatic hydrocarbons in soil and snow samples were analyzed by spectrofluorimetry at low temperatures (Shpol'skii spectrometry). The analysis of PAHs was performed on a Lumex Fluorat-Panorama spectrofluorometer equipped with an LM-3 monochromator and a Cryo-1 accessory. The identification and quantification of individual hydrocarbons were performed from characteristic lines in the fluorescence spectra of bitumoid solutions at  $-196^{\circ}\text{C}$  using the certified international standard NIST 2260a. The analysis of highly diluted solutions was performed using spectral fractionation, which involved the selection of characteristic excitation and fluorescence wavelengths for each compound.

The following conclusions are made on the basis of the results obtained. On the major part of the studied territory, especially in the suburban zone, PAHs get into soils mainly because of atmospheric transfer. Only within the most industrial area and in the close vicinity of it there are inclusions of solid material with some hydrocarbon containing products in soils.

As a result differences in the radial distribution of PAHs and their penetration depth among the soils of urban and suburban area are established. In suburban soils under forest, the radial distribution of PAHs is of accumulative character. Four-, five-, and six-ring PAHs are detected only in the upper 5-cm-thick layer of soils under natural vegetation. In forest soils with morphological indices of old plowing, the penetration depth of heavy four-, five-, and six-ring PAHs corresponds to the lower boundary of the old plow horizon. In the cultivated soils, the penetration depth of PAHs is slightly greater than in the soils of forested areas. The contents of four-, five-, and six-ring PAHs in all plow horizons are maximum in the profile, and their contents in the subsurface horizons decrease abruptly to the trace level. The maximum penetration depth of heavy PAHs in tilled soils coincides with the lower boundary of the plow horizons.

In urban area high contents of PAHs throughout the profile are noted in the toxic industrial sites and chemozones. On some plots in the industrial zone, the maximum contents of total PAHs are observed at a depth of 50–75 cm.

Volume of PAHs income, defined by their reserves in the snow cover, within the study area is high. They range from 1.5 to 85 mg/m<sup>2</sup> in different sampling points, which corresponds to the following average annual PAHs entering to the territory: about 1 g/ha per year – on average in a suburban area (forest, arable and fallow land) and about 45 g/ha per year on average near the source of pollutants. These rates correspond to PAHs receipt data in the literature, according to which in urban areas and close to major industrial centers the rate of receipt of PAHs ranged from 4 to 40 g/ha per year (Wilcke, 2000). It should be noted that such high rates of PAHs income on the territory take place, despite of the fact that in the last decades of soot production was dropped sharply and the plant was almost completely redeveloped for production, much less conducive to PAHs enter to the environment. Probably, high PAHs content revealed in snow samples, due to the scattering of the previously manufactured product that was accumulated over a century of operation of the plant on the surface of buildings and other elements of enterprise infrastructure and adjacent to the plant site.

It was also identified a clear trend of a sharp increase in PAHs reserves as well as coefficient of variation of PAHs reserves both in the soil and in the snowpack when approaching to the industrial zone.

Monodominant phenanthrene association of PAHs prevailed in the snow and the soils, which is found in almost all sampling points, regardless of the distance from the source of pollutants and land use types. In addition to the dominance of phenanthrene characteristic of PAHs identified associations for all sampling points is the lack of fluorene and biphenyl in all snow samples. The absence of these polyarenes in snowy samples is probably caused by the fact that diphenyl and fluorene are light 2-3-ringed hydrocarbons, which may be in the atmosphere in gaseous phase (Baek et al., 1991, Shimmo et al., 2004). In the soil samples the fluorene and biphenyl are present, but in small quantities (in the majority of samples less than 1% of the amount of PAHs).

Analysis of the data indicates that in suburban area the intensity of PAHs transformation is more intense and depends on land use. Under the forest about half polyarenes have a similar share of the amount of PAHs in soil and snow; on the croplands almost all polyarenes have different proportion of the amount of PAHs in soil and snow. Conversely in urban soils near the source the transformation of PAHs in soil is weak and polyarenes association in snow and soil are similar in composition.

In urban area the proportion of reserves of individual polyarenes in the snow to the reserves in soils are minimal and have a small range of variation for different compounds; in suburban area range of variation for different compounds is much higher an order.

Also there was analyzed the relationships within the selected pairs of polyarenes, which are isomers, but with different resistance to transformation, in snow and soil. In particular, there were considered proportions of benzo(a)pyrene to pyrene (BP/P) and anthracene to phenanthrene (A/F). It was revealed that the ratios of BP/P have a higher indicator potential compared with ratios A/F in terms of assessment of the intensity of the transformation of PAHs in soil for various land use regimes. Nevertheless both indicators (BP/P and A/F) confirmed that the most intense transformation of PAHs is typical for soil plowed land, less intensive – for soils under forest and the lowest – to the urban soil, on the territory near the source of pollutants.

Amplification of the transformation of PAHs in the soils of suburban agricultural land may be due to their better aeration and more intensive photo-destruction of PAHs under conditions of turbation of ar-

able horizon during the plowing. Slowing the transformation of PAHs in the urban soil near the source, probably due to inhibition of microbial activity due to the toxic effect of extremely high concentrations of polyarenes.

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