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Polycyclic aromatic hydrocarbons in post-pyrogenic soils of drained peatlands in West Meshchera (Moscow Region, Russia)

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants and they arrive to the environment from numerous anthropogenic and natural sources, but the data on their natural sources which include wildfires remains insufficient. The level of contamination and the composition of PAHs in soils of the areas affected by wildfires were studied in this work. The study was conducted in Moscow Region (Russia) on the territories occupied with drained peatland and strongly damaged by fires of 2002, 2010 and 2012. The features of PAHs accumulation and profile distribution in histosols and histic podzols after the fires of different time were analyzed. It was shown that new soil horizon form after the fires – Cpir, Hpir and incipient O horizons, and these horizons differ in PAHs accumulation rate. Maximal total concentrations of 14 PAHs were detected in charry peat horizons Hpir (up to 330 ng g^{-1}) and in post-pyrogenic incipient O horizons (up to 180 ng g^{-1}), but the high-molecular weight PAHs (benz(ghi)perylene, benz(a)pyrene, benz(k)fluoranthene) were revealed only in charry peat horizons. The trends to higher PAHs concentrations were found in cases of incomplete burning out of peat horizons while in cases of almost complete pyrogenic destruction of He horizons total PAHs concentration were no more than 50 ng g^{-1} . Also the PAHs accumulation in upper horizons of soils near the sites of latest fires was observed.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are high molecular weight organic compounds, many of them have carcinogenic and mutagenic activities and pose a hazard for human health. These pollutants contain two or more benzene rings and depending on the position and number of benzene rings PAHs could be subdivided into different groups. PAHs are formed in natural and technogenic processes and are ubiquitous in different landscape components. So the scientific interest in PAHs remains high during

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the last decades (Wilcke, 2000; Haritash and Kaushik, 2009; Cai et al., 2008; Gennadiev et al., 1996; Bandowe et al., 2014; Maisto et al., 2006; Baek et al., 1991).

Most PAHs form during the processes of organic matter **heating**. So far pyrogenic anthropogenic sources of PAHs (automobile exhausts, various industrial and power plants emissions) are well studied (Khan et al., 2008; Mastral and Callen, 2000; Tsi-
bart and Gennadiev, 2013; Wilcke, 2000, 2007; Agarwal, 2009; Kwon, 2014; Mu et al., 2013). Moreover in developed countries there is a trend of reducing environment contamination with PAHs because of improvement in technologies (Guo et al., 2011).

And the level of PAHs arrival into the environment with natural pyrogenic sources (wildfires, volcanism) remains uncertain. Numerous works are devoted to PAHs formation from vegetation components influenced by **combustion and smouldering**. It was shown that burning conditions (the temperature, the amount of available oxygen) and the type of vegetation define the amount and composition of PAHs (Ramdahl and Bech-
ler, 1982; Jenkins, 1996; Nussbaumer, 2003; Medeiros and Simoneit, 2008; Simoneit, 1999; Schauer et al., 2001; Nakajima et al., 2007; Fitzpatrick et al., 2008; Kakareka et al., 2004).

The publications devoted to pyrogenic PAHs on the territories affected by wildfires cover not the all range of questions related with this problem. For instance, the peculiarities of PAHs composition in the air after the wildfire were studied in several works (Radojevic, 2003; Masclet et al., 1995; Maioli et al., 2009; Freeman and Cattell, 1990; Yuan et al., 2008), but there is an obvious lack of information on pyrogenic PAHs accu-
mulation in soils. Some publications were focused on PAHs in different organo-mineral soils, which were subjected to the fire (Gennadiev and Tsi-
bart, 2013; Dymov et al., 2014; Gonzalez-Vila et al., 1991; Garcia-Falcoan et al., 2006; Vergnoux et al., 2011). It was shown that PAHs accumulate in these soils in small amounts, which pose no
danger for humans. However PAHs accumulation after **smouldering fires** causing deep changes in soil profile was investigated insufficiently (Vane et al., 2013; Gennadiev and Tsi-
bart, 2013; Bojakowska and Sokołowska, 2003).

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Peat fires differ from other fire types, because the burning material in this case is not only the vegetation, but also directly the soil organic matter. The conditions of peat burning and smouldering act as factor of PAHs formation because peat fires propagate slowly and surface and deep soil horizons are affected by high temperature (Rein et al., 2008; Hartford and Frandsen, 1992). The smouldering process occurs under the conditions of **small amount of oxygen in the flame**. These conditions favour the processes of organic radicals recombination and PAHs forming.

It is worth noting that the combustion products differ depending on the peat type, moisture and the completeness of combustion. The combustion products include in various proportion the mixture of gases and particles, they contain **carbon**, sulphur, potassium, nitrogen oxides (Blake et al., 2009) and metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn) (Betha et al., 2013). PAHs are part of the peat combustion products in most cases and after the fires they generally **accumulate** across the whole soil profile (Vane et al., 2013; Kakareka et al., 2004; Blake et al., 2009).

In most cases scientific literature contains data on pyrogenic PAHs in undrained peat soils. The drained soils, affected by fire, are not studied from this context, although they are very vulnerable for wildfires (Blake et al., 2009; Zaidel'man et al., 2007). Large amounts of organic matter burn out during the fires and deep transformations occur in the profiles in comparison with the soils of undrained territories (Zaidel'man et al., 2007, 1999). The drained peat soils are widespread in densely populated areas of European part of Russia and currently important task is to reveal levels of accumulation of PAHs in these areas.

So the aim of this study was to reveal the features of PAHs accumulation in soils of drained peatlands affected by wildfires. The objectives included: (1) the comparison of PAHs distribution and levels of accumulation in different post-pyrogenic soils – histosols and podzols; (2) the identification the parts of post-pyrogenic soil profiles with maximal PAHs accumulation; (3) the detection of the trends of different PAHs groups accumulation; (4) the comparison PAHs accumulation in soils after fires of different time.

2 Materials and methods

2.1 Study area

The current study was conducted in the soils of Shatura District (Moscow Region, Russia). The burned area is located at coordinates 55°39' N, 39°36' E with an elevation of 120 m a.s.l. The investigated site is situated 15 km to the North of Shatura (Fig. 1) and 200 m to the west of village Dolgusha (Fig. 2).

The territory represents West Meshchera fluvioglacial plain. The major part of the area is covered by fluvial-glacial deposits, alluvial deposits also occur. The absolute altitude are within the limits of 120–126 m, and the range of altitude is low (Wetlands of Moscow Region, 2008; Zonov and Konstantinovich, 1932).

The investigated area is covered with peatlands, laying on the ancient alluvial deposits, which are located above the confining clay layer. The development of wetlands is caused by flattened relief and shallow horizon of waterproof clay. The bogginess of this part of Meshchera plain is 15–16% (Wetlands of Moscow Region, 2008; Zonov and Konstantinovich, 1932; Kudravtseva, 1973).

The investigated plot belongs to Petrovsko-Kobelevskoe high-moor peat which is a part of Shatura wetland area. Its total area is 6443 ha, before the peat extraction the thickness of peat layer reached 7.5 m and its average thickness was 2.5–4 m (Zonov and Konstantinovich, 1932).

The large areas were transformed during the drainage and peat mining. From the end of 18th century the peat bogs of Moscow Region were used as peat **minefield**. The demand for it increased in 1920s, when peat-burning power station including Shaturskaya station were constructed (Wetlands of Moscow Region, 2008; Simakin, 1958). The peat deposits in Shatura district started to mine from 1920s (Timashev, 1932). Nowadays the mining is stopped and the most of peat-hags in Meshchera bog province are in the stage of renewing (Wetlands of Moscow Region, 2008).

As a result of peat mining natural bog complex was changed to large open pits, connected with the system of channels and distributaries and the fields of peat mining

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at different stages of overgrowing. The birch–aspen forests grow on the banks. On the plots with flooded peat pits the process of bog restoration starts and it will take several centuries before peat deposits will start to accumulate (Sushkova, 2008).

Because of changes in hydrological regime the number and areas of peat fires increased dramatically in this region (Wetlands of Moscow Region, 2008). According to Zaidel'man (2003) there is a repeating pattern of the fires in drained peatlands. Almost every 10 years large fires occur (1972, 1972, 1992, 2002). In 2010 the wildfires in Russia damaged large areas and in Moscow region they caused significant air pollution, degradation of ecosystems and health impacts for the population (Donkelaar et al., 2011; Shvidenko et al., 2011).



The soil cover of the area is presented by gleyic histosols, histic podzols and sod podzols (WRB, 2006) in a varying degree altered with the wildfires. In this work peat soils affected with fire of 2010 were studied, moreover the sod podzols were studied after the fire 2002 and the site of new burned area (2012) was studied. The field work and sampling were conducted in 2012, and in total it was studied 12 soil pits (Fig. 3).

Background soils are represented by histosols and histic podzols. The histosols have the following horizons O-H-Hp-He-Ha-C and typical profile of histic podzols has – O-A-E-EBhs-Bhs-Cs horizons. After the smouldering fire and burning out the peat layer the new ash horizons (Cpir) form up to 5 cm depth, they are underlaid by *peat cherry horizons* (Hpir) with 2–3 cm and *pyrogenic muck peat* horizons (Ha,pir) with 2–3 cm thickness.

Post-pyrogenic histic podzols (Fig. 5) are confined to the peripheral part of peatlands, the parent material for them is bare quartz sands, and typically their profile has the following horizons O-Cpir-Hpir-He-Ha-E-EBhs-Bhs-Bh-BC-C. Post-pyrogenic gleyic histosols occupy large areas and form in the central parts of peatlands, their profile consists of O-Cpir-Hpir-He-Ha-Ch-Cs-Cg.

It should be pointed out that the thickness of horizons in soils affected with the fire distinguishes dramatically depending on the initial peat thickness and the intensity of

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thermal impact. The depth of organogenic horizons in soil pits varies from 10 to 30 m at a distance of several meters.

2.2 Soil sampling and laboratory analysis

Soil pits were excavated to a depth of 50–100 cm depending on the depth of parent material. Detailed morphological descriptions of soil profiles were taken. Samples were collected from each genetic horizon and in cases of thick horizons (more than 10 cm) samples were taken from each 10 cm. Samples were stored in plastic bags and taken to the laboratory, where they were air-dried, homogenized and sieved through 0.25 mm sieve.

In soil samples the concentrations of 14 PAHs, which are widely spread in the environment, were analyzed – naphthalene, pheanthrene, chrysene, pyrene, anthracene, benz(a)anthracene, benz(a)pyrene, benz(ghi)perylene, fluorene, dibenztiophene, triphenylene, benz(e)pyrene, benz(k)fluorantene, coronene.

The quantitative analysis was conducted with spectrofluorometry method at the temperature of liquid nitrogen (Spolskii spectroscopy) (Alexeeva and Teplitskaya, 1988). The measurements were done on a Jobin Yvon Fluorolog-3-22 spectrofluorimeter. Soil were extracted with n-hexane, and the extract was frozen in liquid nitrogen. Then, the mixture of PAHs in the frozen extract was irradiated by light with optimum wavelengths for each compound, and the PAH luminescence spectra were recorded. After that the calculation of PAHs concentration was completed. In total 110 soil samples were analyzed for PAHs concentration.

2.3 Statistical analyses

The results were analyzed with STATISTICA 8.0 program. Analysis of Variance (ANOVA) was used to analyze the statistical differences in the means of the study parameters. Cluster analysis was conducted to find similarities in the individual PAH compounds distribution.

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3 Results

The studied soils varied highly in PAHs concentrations; their total content changed from 5 to 330 ngg⁻¹. In the **histosols not affected by fire** (pit 12), PAHs were contained in the amounts 20–100 ngg⁻¹ within the profile, their composition was presented only with naphthalene, benz(a)anthracene and phenanthrene. In the **background his-**
5 **tic podzols** (pit 7) the total PAHs concentration varied from 32 ngg⁻¹ in A horizon to 0.2 ngg⁻¹ in BC horizon. Naphthalene and pyrene were prevailed components. In mineral horizons Bhs only naphthalene and sporadically pyrene occurred. Phenanthrene and benz(a)anthracene were found only in organic horizons (Table 1).

3.1 Profile distribution of PAHs in soils of different types

The common features of PAHs distribution in *post-pyrogenic histosols* (pits 2, 11, 3) were the following (Fig. 5, Table 2). These soils had the ash horizon Cpir at depth 2–5 cm and typically at these sites they had low PAHs concentrations (5–8 ngg⁻¹). Below and above of Cpir horizon there were two maximums of PAHs concentration –
15 in surface incipient horizon O (20–70 ngg⁻¹), where mainly 2–3-nuclear compounds (naphthalene, phenanthrene, anthracene) occur. **And the second maximum was below** Cpir in pyrogenic peat horizon which presents the fragments of charred peat (Hpir). In these horizons total PAHs concentration reached 255 ngg⁻¹. The PAHs composition in these horizons was also different. Cpir horizons had predominantly the low-molecular
20 weight compounds 2-nuclear naphthalene and 4-nuclear pyrene. In Hpir horizons 5–6-nuclear compounds prevailed – benz(ghi)perylene, benz(e)pyrene, benz(k)fluoranthene and naphthalene occurred in a lower concentrations. In underlying organic horizons He and Ha benz(a)anthracene occurred. In humic-infiltrated horizon Ch the low PAHs concentrations (up to 5–10 ngg⁻¹, coefficient of variation for total PAHs 106 %) were
25 registered and hydrocarbons were presented mainly by naphthalene.

Post-pyrogenic histosols had certain differences in PAHs distribution. Thus in pit 3 the thickness of undestroyed peat horizons were maximal among the investigated

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soils (approximately 30 cm), and PAHs concentrations were maximal in this case – up to 255 ng g^{-1} , moreover PAHs concentrations were relatively high within the all depth of organic layer. The PAHs composition was presented by a wide range of compounds – from low-molecular weight to 5–6-nuclear compounds – benz(ghi)perylene, benz(e)pyrene and benz(k)fluorantene. In cases of more complete combustion of peat (pits 2 and 11), where mineral material underlayed from 10–14 cm, the total PAHs concentrations were much lower – from 5 to 25 ng g^{-1} (Fig. 5).

It may be noted that total PAHs concentrations in residual peat horizons of post-pyrogenic histosols changed from 10 to 255 ng g^{-1} , coefficient of variation in He horizon was 118 % and in Ha horizon – 155 %. In sites with more complete combustion of peat, PAHs molecules accumulated at a lesser amount ($10\text{--}20 \text{ ng g}^{-1}$). And in cases of incomplete burning their concentrations in peat horizon were more than 200 ng g^{-1} .

According to analysis of variances PAHs had shown significant difference in total PAHs concentration between different horizon types (Fig. 6). Mineral horizons (Ch, Cs, C) had minimal ranges and mean values and organogenic horizons (Hpir, He, Ha) had maximal ranges and mean values, which was statistically confirmed.

Sod-podzols and histic podzols (pits 5, 6, 8, 9, 10) subjected to wildfires were slightly different in peculiarities of PAHs accumulation. Also there were two maximums of total PAHs concentrations in these soils. The first maximum was most frequently confined to pyrogenic organogenic soil horizons (He, pir, Ha,pir, Apir, He, Ha), they contained up to $40\text{--}60 \text{ ng g}^{-1}$. The composition of hydrocarbons in these horizons and the contribution of separate components to PAHs associations differed slightly. In most cases PAHs were presented by naphthalene, anthracene, pyrene. In particular cases high-molecular weight PAHs (perylene, benz(ghi)perylene, benz(k)fluoranthene, baez(a)anthracene) appeared (Fig. 7, Table 2).

Furthermore, occasionally Cpir and post-pyrogenic O horizons of pits 5 and 6, closer adjacent (50 m) to burnt area of 2010, contained up to 150 ng g^{-1} PAHs. These sites were affected by fire 2002, but layed directly nearby the site of recent burnt area (Fig. 3).

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With a distance from the place of the last fire the Cpir horizons (pits 8 and 9) (Table 2), formed in the fire of 2002, contain PAHs in low amounts – up to $2\text{--}3\text{ ng g}^{-1}$, in some cases – to $10\text{--}12\text{ ng g}^{-1}$, naphthalene prevailed in hydrocarbon composition, in soil pit 9 3–4-nuclear PAHs – chrysene, pyrene, anthracene were added. The post-pyrogenic surface incipient horizons O in these soils contained from 3 to 40 ng g^{-1} PAHs. The PAHs composition was presented by naphthalenes and in traces by benz(a)anthracene, perylene, benz(ghi)perylene.

In contrast with histosols the sod-podzols are characterized by eluvio-illuvial translocation of hydrocarbons. For instance, eluvial horizons E contained from 0.7 to 5 ng g^{-1} PAHs with coefficient of variation 98 %, in particular cases hydrocarbons were not detected. The PAHs are represented in these horizons only by naphthalene and in trace amounts – phenanthrene and pyrene. The upper parts of illuvial Bh horizons had total concentrations in amounts up to 12 ng g^{-1} , PAHs composition included mainly naphthalene, but benz(a)anthracene, fluorene, benz(e)pyrene and benz(k)fluorantene occurred in some cases (Fig. 7). So as contrasted with background sod-podzols the post-pyrogenic soils tended to have certain migration of high-molecular weight compounds to illuvial soil horizons (Fig. 7).

As opposed to histosols the upper O, Cpir, Apir horizons of histic and sod podzols had high range, which exceeded the range in pyrogenic organogenic horizons (Fig. 8).

In the investigated soils PAHs tended to form groups different in their distribution, which was confirmed by cluster analysis (Fig. 9). So low-molecular weight 2- and 3-nuclear compounds had similar distribution, both in histosols and podzols they occurred within the whole profile. The 5–6-nuclear compounds had resembling distribution and they were detected only in organogenic horizons Hpir, Ha, He.

Also in investigated samples the coefficient of variation was high for high-molecular weight compounds, especially in Hpir horizons, benz(a)pyrene (283 %), benz(ghi)perylene (283 %), benz(k)fluorantene (437 %), chrysene (195 %). The variation of low-molecular weight compounds was lower, in H horizons naphthalene had 131 % and phenanthrene had 126 %.

3.2 The PAHs accumulation in soils of burnt sites of different time

Certain differences in the intensity of PAHs accumulation could be noted in soils of different age burnt sites. On the site subjected to the fire in 2012 the post-pyrogenic histosol of burnt area (pit 13) and histosol situated nearby the burnt site and containing charred peat layers from previous fires (pit 14) were studied. In the soil of latest burnt site the total PAHs concentrations were maximal for investigated territory. They corresponded 330 ng g^{-1} and were confined to charry peat horizon Hpir (Table 3). The PAHs composition was represented by naphthalene and anthracene. In a deeper horizon He of pyrogenic histosol without charry material high-molecular weight compounds – benz(ghi)perylene and benz(e)pyrene occurred. The same compounds were detected in soil, adjacent to the burnt area, but in a lesser amount, the total PAHs concentration did not exceed 140 ng g^{-1} . In comparison with the histosols of 2 year burnt area (pits 2, 3) this site is characterized by higher PAHs concentration.

In the case of sod-podzols affected with the fires of 2002 and 2010 (pits 6 and 10) the pyrogenic organogenic horizons had similar PAHs concentrations (Fig. 7). The differences in the intensity of eluvio-illuvial process were not detected.

The ANOVA showed the significance of the time factor (Fig. 10) for several first years after the fire. The organogenic horizons of fire 2012 had higher PAHs concentrations. In the surface ash horizons Cpir of burnt places 2002 the tendencies of PAHs concentration decreasing were not detected.

4 Discussion

4.1 Profile distribution of PAHs in soils of different types

These data on PAHs concentration and composition in soils not affected with fires corresponded with results obtained for soils of other territories distant from PAHs sources

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(Gennadiev and Tsibart, 2013; Wilcke, 2007; Rovinskii, 1988; Gabov et al., 2007; Krasnopeeva, 2008).

The producing of PAHs in Hpir horizons of *histosols* is caused by peat heating at sites adjacent to the seat of fire. Under the conditions of smouldering and low oxygen access PAHs may actively form in combustion zone (Blomqvist et al., 2006., Jenkins et al., 1996; Mastral et al., 1999). Moreover the intense PAHs formation during the longtime heating was shown in literature (Gonzalez-Vila et al., 1991), so in cases of incomplete burning of peat horizons the conditions for high PAHs production created. Also, possibly, during the fire not only Hpir horizon, but all peat layer was subjected to heating, and PAHs formation could take place in organogenic horizons at the all depths.

In addition, the possible factor causing different PAHs concentrations in peat horizons, was amount of peat remained after the burning. The more residual mass of peat was the more sorption of PAHs by this mass took place. At the same time allowing for high variability of absolute PAHs concentrations in residual peat horizons it could be registered that they tend to accumulate 5–6-nuclear compounds, which could indicate processes of peat combustion. Vane et al. (2013) also pointed out the presence of low- and high-molecular PAHs in soils after peat fire. However, 5–6-nuclear compounds (benz(ghi)perylene, benz(a)pyrene, benz(e)pyrene, benz(k)fluoranthene) could be considered as the indication group, marking the peat combustion.

The soils with very shallow peat horizons remained after fire had low PAHs concentrations due to the fact that all organic matter was totally burned out. **The combustion products were only CO₂ and H₂O and PAHs as products of incomplete burning were not formed** (Belis et al., 2001). High coefficients of variation of PAHs in residual peat horizons could be caused by different duration and depth of heating of these horizons at different sites. The depth of changes in soils differs depending on the fire intensity and location characteristics (various moisture content, microrelief and peat thickness) (Efremova and Efremov, 2006; Grishin et al., 2013).

In surface incipient horizon O (20–70 ngg⁻¹), where mainly 2–3-nuclear compounds (naphthalene, phenantrene, anthracene) occur, these compounds are presum-

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ably sorbed by new organogenic horizons from the atmosphere. Sorption is one of the leading PAHs-involving process in soil (Trapido, 1999; Wicke, 2000), and the factors determining the rate of sorption are the content of organic matter and the presence of clay minerals (Maliszewska-Kordybach, 2005; Maliszewska-Kordybach et al., 2010).

5 So it was quite high in new-formed organic horizons.

The PAHs concentrations in pyrogenic organogenic horizons (He, pir, Ha,pir, Apir, He, Ha) of *podzols* were lesser than in analogous horizons of histosols as these soils had lesser amount of available organic material for burning and PAHs formation.

Also in comparison with histosols Cpir and post-pyrogenic O horizons of podzols had rather high PAHs concentrations. It could be explained by the fact that these sites were affected by fire 2002, but layed directly nearby the site of burnt area of 2010 (Fig. 3). These horizons have sandy loam texture and humus horizons (Zaidel'man et al., 2006), so they have high sorption capacity. Presumably, the accumulation of low-molecular weight compounds formed during the last fire could take place in these sites.

15 In contrast with histosols the sod-podzols are characterized by eluvio-illuvial translocation of hydrocarbons, which was also found in study of Gabov (2007), so PAHs distribution follows the soil-forming processes in wet climate of taiga zone. The increased migration of PAHs after the fire was, probably, caused with vegetation destruction during the fire and following intense percolation of the soil profile.

20 4.2 The PAHs accumulation in soils of burnt sites of different time

The histosols, affected with fires in 2012 had higher PAHs concentration in comparison with the histosols after the fire of 2010. On the one part it is caused by the fact that arriving PAHs, especially low-molecular weight compounds, may degrade after the fire. On the other part in the investigated case the organic horizons of latest burnt place were not completely burnt out, this fact favours the intense sorption and accumulation of polycyclic aromatic hydrocarbons in these soils. But it is worth mentioning that the time of pyrogenic PAHs presence in soil could differ depending on the conditions. Thus, even in geological scale the elevated PAHs concentration in the deposits of Cretaceous and

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Jurassic periods could be explained by ubiquities distribution of wildfire (Killops and Massourd, 1992; Marynowski et al., 2011; Belcher, 2006). From the other hand, according to Garcia-Falcoan (2006) the concentrations in the burnt organo-mineral soils remained high only during the first three months after the fire and then PAHs were involved in soil processes including degradation and migration.

In the case of sod-podzols the organic horizons O of fire 2002 the accumulation of compounds from the latest fire could take place and influence of latest fires occurred, so trends on PAHs degradation with the time were not so prominent.

Considering the soils of drained peatlands it is necessary to emphasize that in both post-pyrogenic sod-podzols and histosols, the total PAHs concentrations could be rather high – up to hundreds of ng g^{-1} . These peculiarities differ from the features founded in our previous researches – in Polistovo natural Reserve (Pskov Region, Russia), where after the fire organogenic peat soils have higher PAHs concentration in comparison with sod-podzol soils (Gennadiev and Tsibart, 2013). Moreover, the undrained soils the total PAHs concentrations did not exceeded 150 ng g^{-1} . Presumably, in Shatura district the deep changes in hydrological regime occurred after the drainage and the level of groundwater decreased. So the fire touched the soil cover of the area to a great extent and new horizons having different capacity for PAHs accumulation formed. Also after the catastrophic influence of the fire the inhomogeneity of soil cover increased, and it was resulted in very contrast soil profiles and spatial PAHs distribution.

However it should be noted that even under conditions of catastrophic fires on the drained peatlands in studied cases the PAHs concentrations, especially high-molecular weight compounds were relatively low, for instance benz(a)pyrene concentrations did not exceed 3 ng g^{-1} .

It corresponds to some literature results. For instance, Vane et al. (2013) note that PAHs concentrations in peat soils after the fire are lower the amount dangerous for biota. Also there are no evidences that amounts of PAHs accumulated after the fire are dangerous for human, as they are lower the levels determined for soils. But the variation

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of high-molecular weight PAHs in soil horizons was high as these compounds occur not in all horizons, and their formation is more complicated process in comparison with low-molecular PAHs.

5 Conclusions

5 So the conclusions are the following:

1. The wildfires on the drained peatlands caused the change of morphological properties of soils; new soil horizons C_{pir}, O, H_{pir}, Ha_{pir} different in PAHs accumulation rate were formed. Maximal PAHs concentrations were revealed in charry peat horizons and in post-pyrogenic incipient O horizons.
- 10 2. Post-pyrogenic histosols and histic podzols differed in profile PAHs distribution. In both cases maximal PAHs concentrations occurred in the organogenic pyrogenic horizons, but in cases of histic podzols their slight accumulation of PAHs in illuvial horizons was possible.
- 15 3. 5–6-nuclear compounds were formed in pyrogenic horizons Ha_{pir} and He_{pir}, their production was possible in smouldering processes under condition of lack of oxygen, this group could be considered as indicative group of peat combustion. 2–3-nuclear PAHs occurred within the whole profile, in sod-podzols and histic podzols their migration to illuvial horizons was registered. In studied cases PAHs composition of pyrogenic horizons did not a changed in different soil types.
- 20 4. The tendencies to higher PAHs accumulation in soils were revealed in cases of incomplete burning out of peat horizons. The PAHs sorption in upper horizons of soils near the sites of latest fires was observed.

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Table 1. PAHs concentrations in soils of unburnt area.

Horizon depth, cm	Horizon	Naphthalene	Phenanthrene	Chrysene	Pyrene	Anthracene	Benz(a)anthracene	Benz(a)pyrene	Benz(ghi)perylene	Fluorene	Dibenzophene	Perylene	Triphenylene	Benz(e)pyrene	Benz(k)fluoranthene	Coronene	Total PAHs
Histic podzol (pit 7)																	
0–1	O	8.7	26.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	35.4
1–10	A	2.7	6.3	0.0	0.0	0.3	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.2
10–18(21)	A	6.9	11.8	0.0	0.0	0.0	12.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	1.3	0.0	32.3
18(21)–26	E	3.3	2.3	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.6
26–37(40)	E/Bhs	5.3	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.4
37(40)–55(57)	Bhs	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0
55(57)–65	Cs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.2
Histosol (pit 12)																	
0–5	He	11.0	0.0	0.0	0.0	0.0	8.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	19.6
5–10	He	29.1	36.1	0.0	0.0	3.4	11.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	80.2
10–15	He	40.6	49.3	0.0	0.0	0.0	19.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	109.6
15–20	He	34.7	38.0	0.0	0.0	0.0	9.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.3
20–30	Ha	32.5	0.0	0.0	0.0	0.0	16.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	48.7
30–40	Ha	45.9	0.0	0.0	0.0	0.0	12.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	57.9
40–50	Ha	63.5	27.2	0.0	0.0	0.0	46.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	137.2

Table 2. PAHs concentrations in post-pyrogenic histic podzols, sod-podzols and histosols.

Horizon depth, cm	Horizon	Naphthalene	Phenanthrene	Chrysene	Pyrene	Anthracene	Benz(a)anthracene	Benz(a)pyrene	Benz(ghi)perylene	Fluorene	Dibenzofluorene	Perylene	Triphenylene	Benz(e)pyrene	Benz(k)fluoranthene	Coronene	Total PAHs
Histosol (Pit 11)																	
0–0.5	O	55.5	19.4	0.0	1.1	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	76.5
0.5–2(4)	Cpir	8.3	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.5
2(4)–7	Hpir	0.9	0.6	0.0	0.0	0.0	0.1	0.0	2.6	0.0	0.0	0.0	0.0	2.4	0.0	0.2	6.7
7–8	He	1.4	0.4	0.0	0.0	0.0	0.3	0.0	3.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.9
8–14	He	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3
14–26	Ch	1.2	0.0	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5
26–38	Cs	1.2	1.5	0.0	0.2	0.0	6.5	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	9.7
38–50	Cs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
50–60	C	1.8	0.0	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1
60–70	C	1.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2
70–80	C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
80–90	C	0.5	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7
Sod-podzol (pit 5)																	
0–2(3)	O	9.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	9.7
2(3)–3(4)	Cpir	11.2	38.8	24.0	0.8	62.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.9	0.0	0.0	146.4
3(4)–6(7)	Apir	48.2	0.0	0.0	0.8	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	49.6
6(7)–10(14)	E	5.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5
10(14)–20(22)	Ha	6.1	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	3.7	0.0	0.0	10.3
20(22)–30(33)	Ha	4.4	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.5
30(33)–40	Bhs	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6
40–50	Bhs	1.4	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6
50–60	Bhs	3.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7
60–70	BC	1.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9
Sod-podzol (pit 8)																	
0–1(1.5)	O	36.2	0.0	0.0	0.0	0.0	5.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	41.7
1(1.5)–2(3)	Apir	10.7	0.0	0.0	0.1	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.3
4(5)–7	H	40.2	11.6	0.0	8.2	0.0	0.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	64.2
2(3)–7	Hpir	42.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	42.4
7–9	Ha	5.4	0.0	0.0	0.0	1.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.8
9–14	Ha	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0
14–25	E	1.3	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5
25–30	E	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30–40	Bs	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2
40–50	Bs	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7
Sod podzol (Pit 9)																	
0–1(2)	O	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1
1(2)–4	Cpir	11.5	0.0	0.0	0.3	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.3
4–5	Apir	30.2	22.6	0.0	0.0	13.2	3.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	69.5
5–7	A	10.7	7.8	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	19.7
7–12	E	1.6	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2
12–20	EB	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5
20–30	Bs	3.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3
30–40	Bs	12.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.2
40–50	B	11.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.4

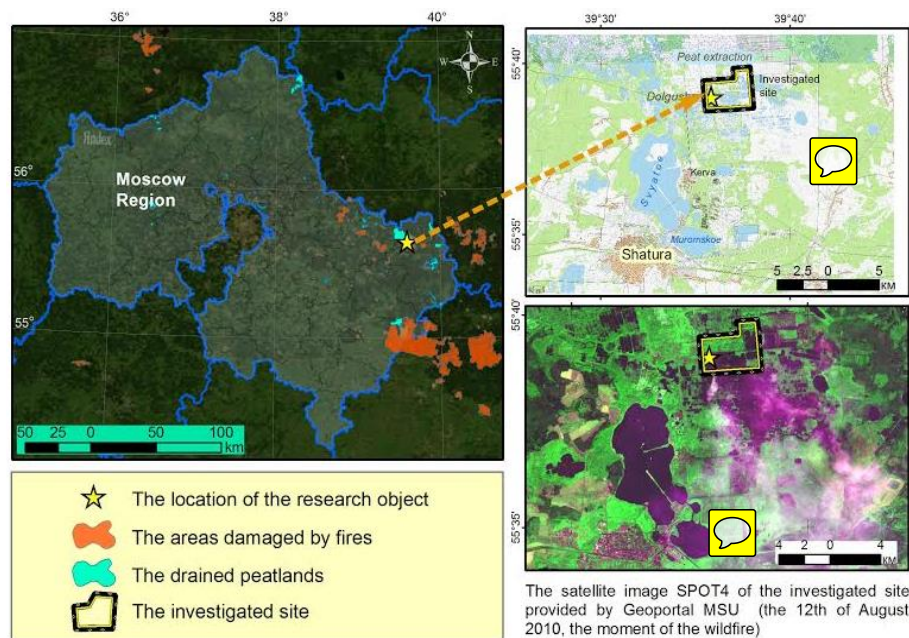


Fig. 1. The location of the research object.

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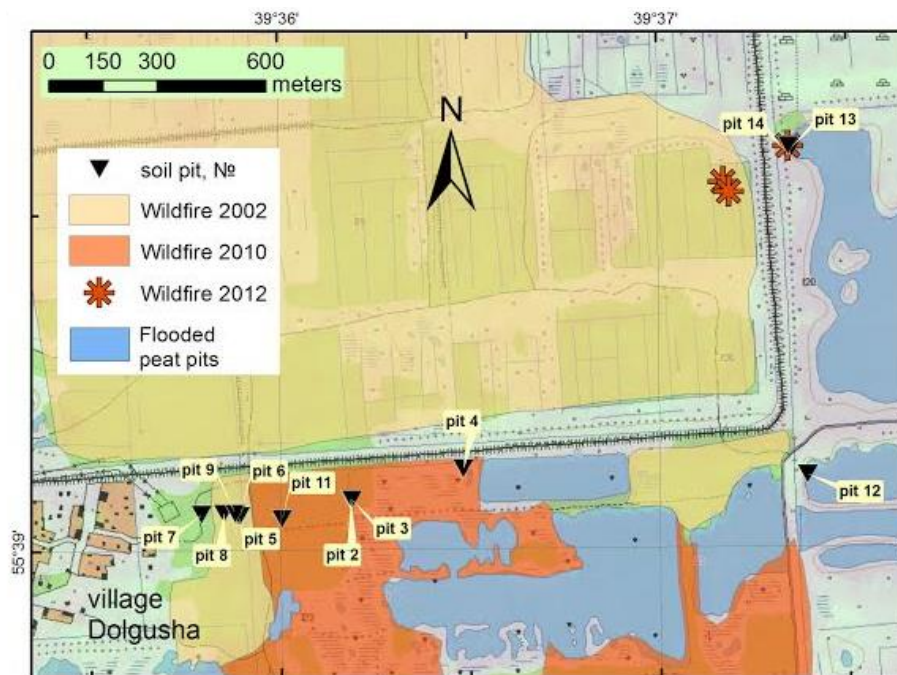


Fig. 2. The location of the investigated soil pits.

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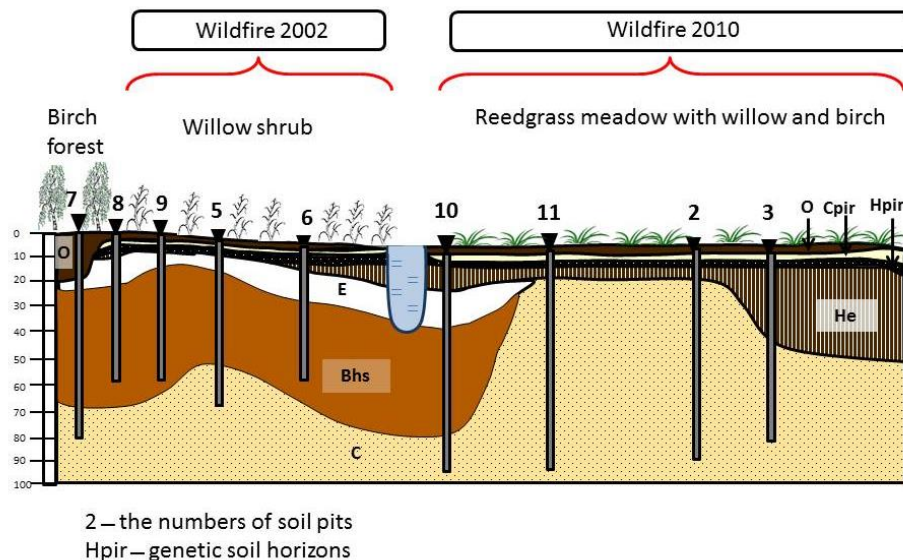


Fig. 3. The profile characteristics of investigated soils.

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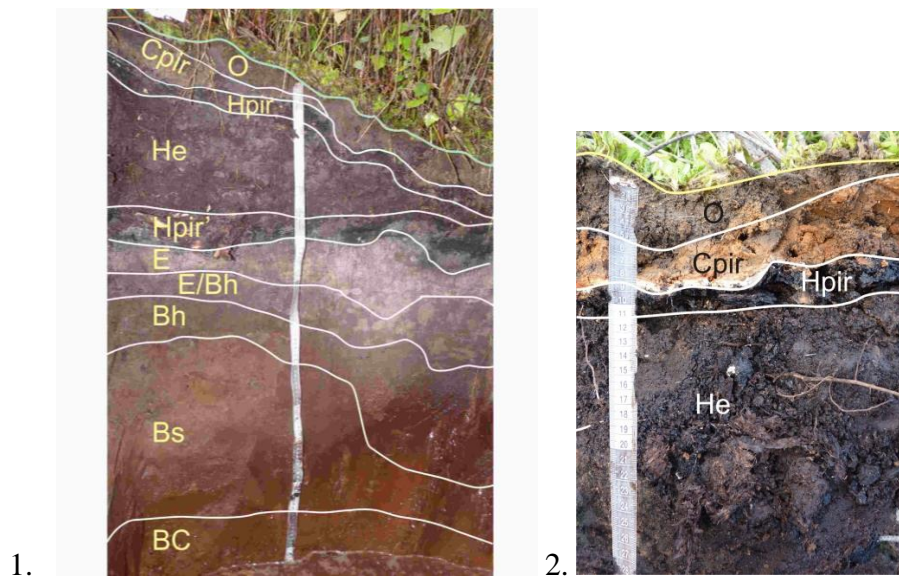


Fig. 4. Soil profiles investigated. 1 – post-pyrogenic histic podzol (pit 10), 2 – post-pyrogenic histosol (pit 3).

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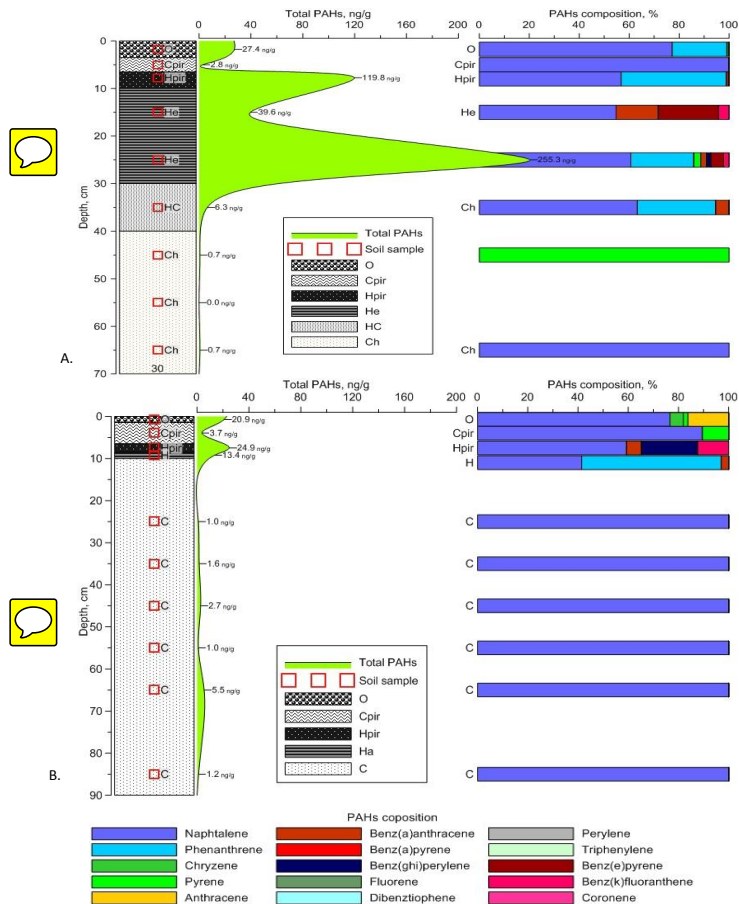


Fig. 5. The profile distribution and composition of PAHs in post-pyrogenic histosols. **(A)** In case of thick organogenic horizon (pit 3), **(B)** in case of almost complete burning out of organic layer (pit 2).

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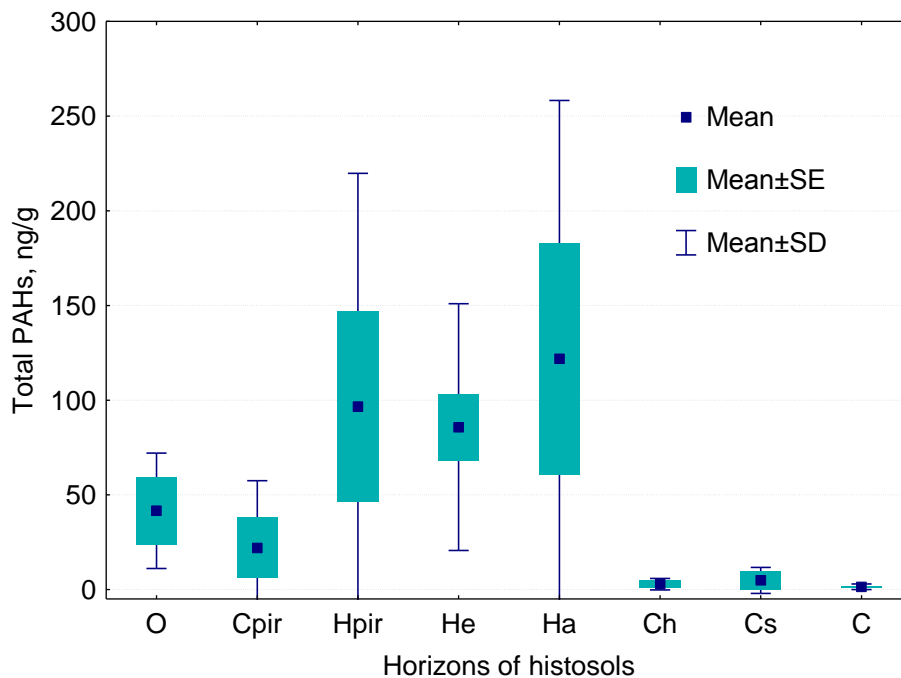


Fig. 6. The ANOVA analysis for total PAHs in different horizons of histosols.

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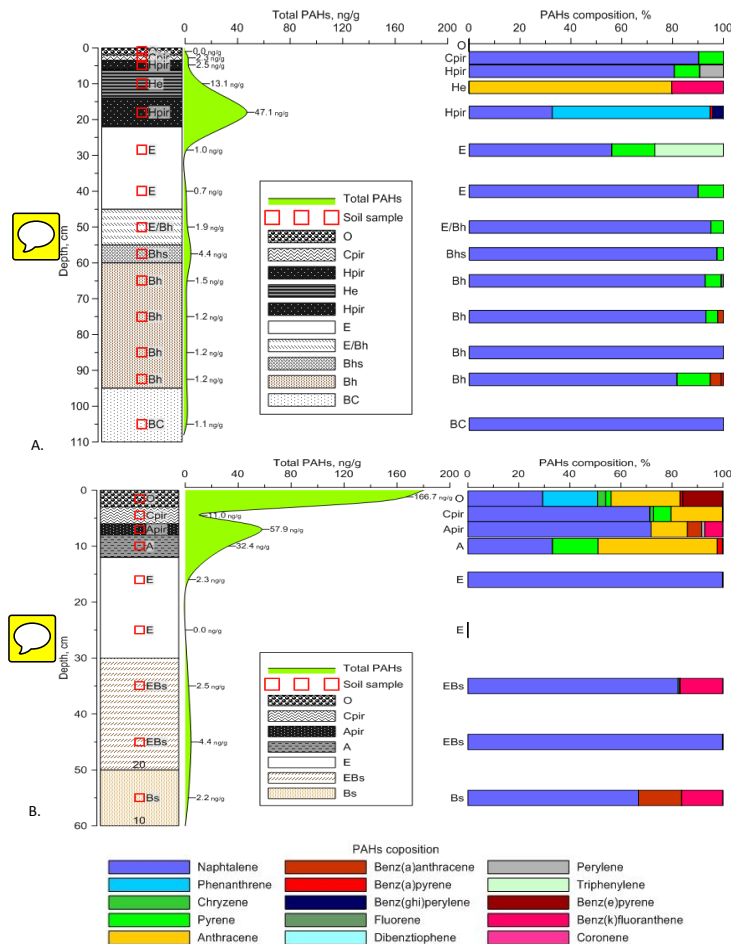


Fig. 7. The profile distribution and PAHs composition in post-pyrogenic histic podzols: **(A)** wild-fire 2010 (pit 10), **(B)** wildfire 2002 (pit 6).

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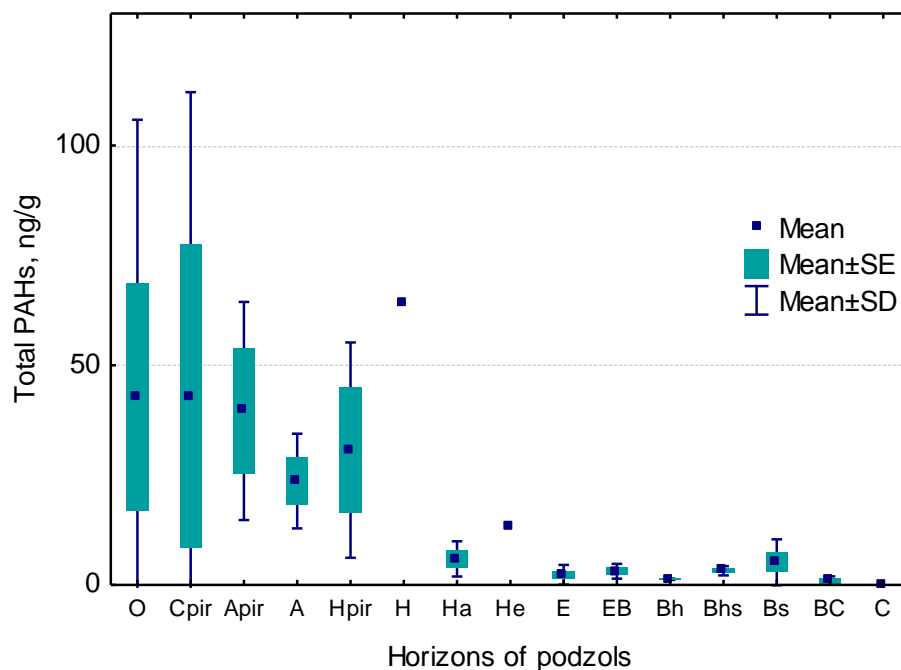


Fig. 8. The ANOVA analysis for total PAHs in different horizons of histic podzols and sod-podzols.

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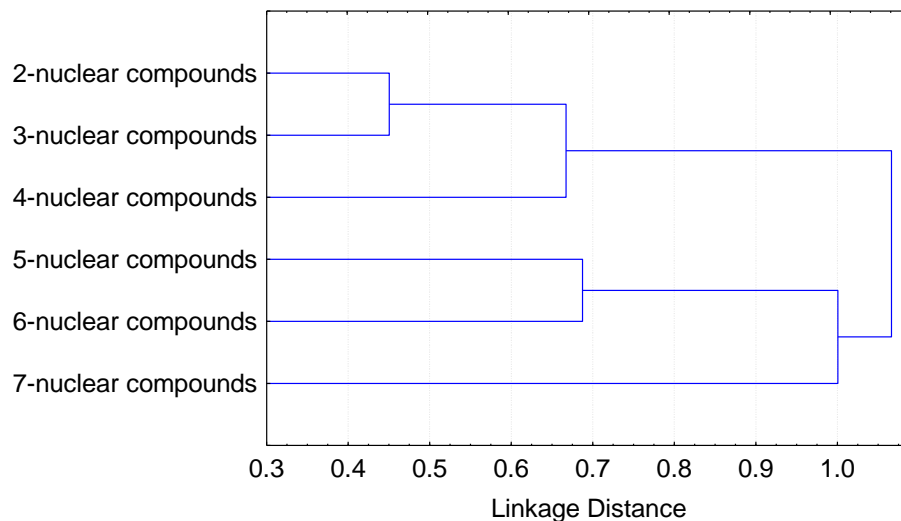


Fig. 9. The cluster analysis (complete linkage; $1 - \text{Pearson } r$) for PAHs groups in investigated soil samples.

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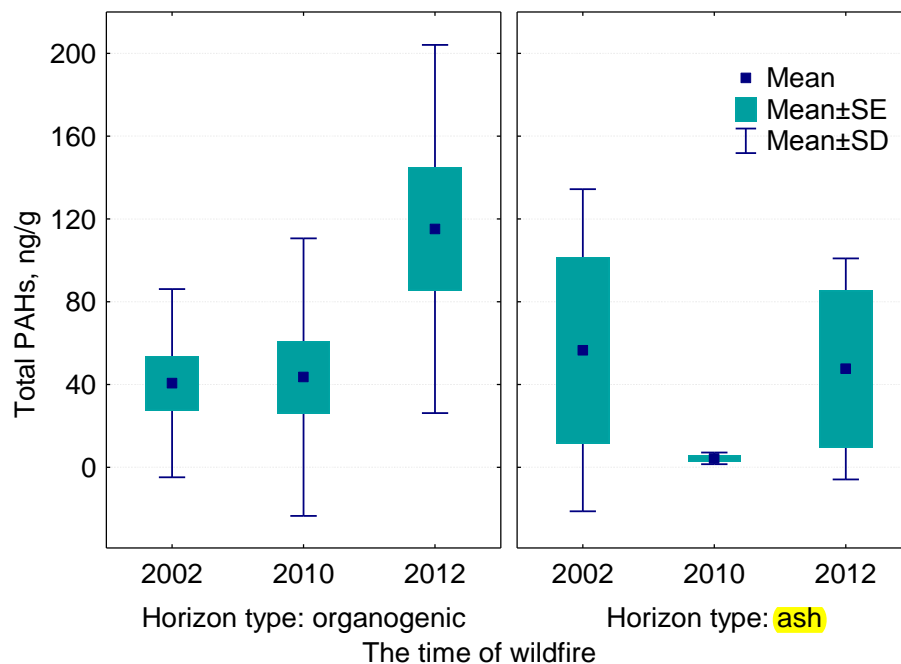


Fig. 10. The ANOVA analysis for total PAHs in different horizon types (organogenic and ash) of soils affected with fires of 2002, 2010, 2012.

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