

1 **Polycyclic aromatic hydrocarbons in post-fire soils of**  
2 **drained peatlands in West Meshchera (Moscow Region,**  
3 **Russia)**

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11 **Abstract**

12  
13 Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants that arrive to the  
14 environment from numerous anthropogenic and natural sources, but the data on their natural  
15 sources including wildfires remains insufficient. The level of contamination and the composition  
16 of PAHs in soils of the areas affected by wildfires were studied in this work. The study was  
17 conducted in Moscow Region (Russia) in areas occupied by drained peatland and strongly  
18 damaged by fires in 2002, 2010 and 2012. The features of PAH accumulation and profile  
19 distribution in histosols and histic podzols after the fires of different time were analyzed. It was  
20 shown that new soil horizons formed after the fires – C<sub>pir</sub>, H<sub>pir</sub> and incipient O horizons—and  
21 that these horizons differ in PAH accumulation rate. Maximal total concentrations of 14 PAHs  
22 were detected in charred peat horizons H<sub>pir</sub> (up to 330 ng/g) and in post-fire incipient O  
23 horizons (up to 180 ng/g), but the high-molecular weight PAHs (benz(ghi)perylene,  
24 benz(a)pyrene, benz(k)fluoranthene) were revealed only in charry peat horizons. The trends of  
25 higher PAH concentrations were found in cases when smouldering combustion was resulted in  
26 rather thick residual peat horizons. In cases of almost complete pyrogenic destruction of He  
27 horizons, total PAHs concentration were no more than 50 ng/g. Also PAH accumulation in upper  
28 horizons of soils near the sites of latest fires was observed.

1

## 2 **1. Introduction**

3 Polycyclic aromatic hydrocarbons (PAHs) are group of high molecular weight organic  
4 compounds, which include carcinogens and mutagens. PAHs are formed in natural and  
5 technogenic processes and are ubiquitous in different landscape components. Scientific interest  
6 in PAHs remains high during recent decades (Wilcke, 2000; Haritash and Kaushik, 2009; Cai et  
7 al., 2008; Geochemistry, 1996; Bandowe et al., 2014, Maisto et al., 2006, Baek et al., 1991).  
8 Most PAHs in the environment arrive from pyrogenic sources. So far pyrogenic anthropogenic  
9 sources of PAHs (automobile exhaust, various industrial and power plants emissions) are well  
10 studied (Khan et al., 2008; Mastral and Callen, 2000; Tsibart and Gennadiev, 2013; Wilcke,  
11 2000, 2007; Agarwal, 2009; Kwon, 2014; Mu et al., 2013). And nowadays in developed  
12 countries there is a trend of reducing environmental contamination with PAHs because of  
13 improvement in technologies (Guo et al., 2011).

14 The amount of PAHs arriving into the environment from natural pyrogenic sources  
15 (wildfires, volcanism) remains uncertain. Numerous works are devoted to PAH formation from  
16 vegetation components influenced by flaming and smouldering combustion. Burning conditions  
17 (the amount of available oxygen, the duration of heating, the temperature) and the type of  
18 vegetation define the amount and composition of PAHs (Ramdahl and Bechler, 1982; Jenkins,  
19 1996; Nussbaumer, 2003; Medeiros and Simoneit, 2008; Simoneit, 1999; Schauer et al., 2001;  
20 Nakajima et al., 2007; Fitzpatrick et al., 2008; Kakareka et al., 2004).

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

32 Peat fires differ from other fire types, because the burning material in this case is not only  
33 the vegetation, but also the soil organic matter. The conditions present in peat smouldering favor  
34 PAH formation because fires propagate slowly and deep soil horizons are affected by high

1 temperature (Rein et al., 2008; Hartford and Frandsen, 1992). Moreover, in comparison with  
2 flaming fire smouldering consume most of the peat. Also, smouldering drives the spread of the  
3 pyrolysis front where PAH are produced, and the smouldering process occurs under the  
4 conditions of low oxygen and temperature (500-700°C) comparing with flaming fire (Rein,  
5 2013). These conditions favour the processes of organic radicals recombination and PAH  
6 forming.

7 It is worth noting that the combustion products differ depending on the peat type, moisture  
8 and the completeness of combustion. Products of pyrolysis are gaseous mixture of organic  
9 species released to the air. They include volatile organic compounds, hydrocarbons (CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>,  
10 CH<sub>3</sub>OH) and particulate matter. During the oxidation stage of combustion, CO and CO<sub>2</sub> are  
11 produced (Rein, 2013). Peat smoke also contains sulphur, potassium, oxides of nitrogen (Blake  
12 et al., 2009) and metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn) (Betha et al., 2013).  
13 PAHs are part of the peat combustion products in most cases and after the fires they generally  
14 accumulate across the whole soil profile (Vane et al., 2013; Kakareka et al., 2004; Blake et al.,  
15 2009). So, PAHs can accumulate in-situ in char and ash layers before they are released into the  
16 atmosphere (Rein, 2013). Moreover below the fire front higher production of aromatic and  
17 condensed molecules takes place (Zaccone et al., 2014). And also gaseous PAHs after releasing  
18 to the atmosphere can be transported and accumulate in other sites (Rein, 2013).

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

26 The aim of this study was to reveal the features of PAH accumulation in podzols and  
27 histosols of drained peatlands affected by wildfires. Study objectives included: 1) the comparison  
28 of PAH distribution and levels of accumulation in different post-fire soils – histosols and  
29 podzols; 2) the identification the parts of post-fire soil profiles with maximal PAH accumulation;  
30 3) the detection of the trends of different PAH groups accumulation; and 4) the comparison of  
31 PAH accumulation in soils after fires of different time.

32

33

## 2. Materials and methods

### 2.1. Study area

This 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. The investigated site is situated 15 km to the North of Shatura (Fig. 1) and 200 m to the west of the village of Dolgusha (Fig. 2).

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

The investigated area is covered with peatlands overlying ancient alluvial deposits, which are located above the confining clay layer. The development of these wetlands is caused by flattened relief and shallow horizon of waterproof clay. The area covered in peat bogs 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 era of peat extraction the thickness of peat layer reached 7,5 m and its average thickness was 2,5-4 m (Zonov and Konstantinovich, 1932).

These large areas were transformed during the drainage and peat mining. Beginning at the end of the 18th century the peat bogs of Moscow Region were used as peat fields. The demand for peat increased in the 1920s, when peat-burning power stations including Shaturskaya station were constructed (Wetlands of Moscow Region, 2008; Simakin, 1958). The peat deposits in Shatura district were mined beginning in the 1920s (Timashev, 1932). Now mining no longer occurs, and most of peat-bogs in Meshchera bog province are in a stage of recovery (Wetlands of Moscow Region, 2008).

As a result of peat mining, natural bog complexes were changed to large open pits, connected with systems of channels and distributaries and with fields of peat mining at different stages of recovery, with birch–aspen forests occurring on their banks. On the plots with flooded peat pits the process of bog restoration has started, but it will take several centuries before peat deposits will start to accumulate (Sushkova, 2008).

1 Because of changes in hydrological regime, the number and areas of peat fires has  
2 increased dramatically in this region (Wetlands of Moscow Region, 2008). According to  
3 Zaidel'man (2003) there is a repeating pattern of the fires in drained peatlands. Almost every 10  
4 years large fires occur (1972, 1982, 1992, 2002). In 2010, wildfires in Russia damaged large  
5 areas and in Moscow region they caused significant air pollution, degradation of ecosystems and  
6 health impacts for the population (Donkelaar et al., 2011; Shvidenko et al., 2011).

7 The soil cover of the area is presented by gleyic histosols, histic podzols and sod podzols  
8 (WRB, 2006) variously altered by the wildfires. Podzols are formed under forest vegetation on  
9 sandy parent material in terms of water percolation. These soils have eluvio-illuvial distribution  
10 of organo-mineral complexes within the profile. Histosols are characterized by the accumulation  
11 of organic matter and various compounds in thick peat horizons, and they contain more material  
12 available for burning. One important goal of our study was to establish the patterns of PAH  
13 accumulation in different soil types and to check if post-fire PAH distribution follows general  
14 soil forming processes.

15 Background soils are represented by histosols and histic podzols. The histosols have the  
16 following horizons O-H-Hp-He-Ha-C and typical profile of histic podzols has – O-A-E-EBhs-  
17 Bhs-Cs horizons. After the smouldering fire and burning out of the peat layer, the new ash  
18 horizons (Cpir) up to 5 cm depth form; they are underlaid by *peat charry horizons* (Hpir) with 2-  
19 3 cm and *pyrogenic muck peat horizons* (Ha,pir) with 2-3 cm thickness.

20 Post-pyrogenic histic podzols are confined to the peripheral part of peatlands; the parent  
21 material for them is bare quartz sands, and typically their profile has the following horizons O-  
22 Cpir-Hpir-He-Ha-E-EBhs-Bhs-Bh-BC-C. Post-pyrogenic gleyic histosols occupy large areas and  
23 form in the central parts of peatlands; their profile consists of O-Cpir-Hpir-He-Ha-Ch-Cs-Cg  
24 (Fig. 3, 4).

25 It should be pointed out that the thickness of horizons in soils affected by the fire varies  
26 depending on the intensity of pyrogenic impact. The depth of organogenic horizons in soil pits  
27 ranges from 10 to 30 cm at a distance of several meters.

## 28 29 **2.2. Soil sampling and laboratory analysis**

30 In order to study PAH accumulation in post-fire soils of different types the areas covered  
31 with histosols (pits 7, 8, 9, 11, 12) and sod podzols (pits 2, 3, 4, 5, 6) were sampled as well as  
32 areas with analogous background soils (pits 1, 10).

1 For the comparison of PAH accumulation in soils after fires of different time the areas  
2 affected by fires of 2002, 2010 and 2012 were studied. The field work and sampling were  
3 conducted in 2012, and in total we studied 12 soil pits (Fig. 2).

4 Soil pits were excavated to a depth of 50-100 cm depending on the depth of parent  
5 material. Detailed morphological descriptions of soil profiles were taken.

6 For the identification the parts of post-fire soil profiles with maximal PAH accumulation  
7 the samples were collected from each genetic horizon and in cases of thick horizons (more than  
8 10 cm) samples were taken at 10-cm intervals. Samples were stored in plastic bags and taken to  
9 the laboratory, where they were air-dried, homogenized and sieved through 0,25 mm sieve.

10 The target PAHs in this study were: naphthalene, pheanthrene, chrysene, pyrene,  
11 anthracene, benz(a)anthracene, benz(a)pyrene, benz(ghi)perylene, fluorene, dibenztiophene,  
12 triphenylene, benz(e)pyrene, benz(k)fluorantene, coronene. This group of compounds includes  
13 PAHs from low-molecular weight to high molecular-weight compounds (2 - 7 benzene rings in  
14 their structure), which are widespread in the environment.

15 The quantitative analysis was conducted with spectrofluorometry method at the  
16 temperature of liquid nitrogen (Spolskii spectroscopy) (Alexeeva and Teplitskaya, 1988; Gooijer  
17 et al., 2000; Personov, 1981; Gennadiev et al., 1996).

18 Liquid extraction was used in the analysis. 3 g of air-dried soil samples were extracted with  
19 n-hexane (5 ml) at room temperature. The degree of extraction was controlled by the absence of  
20 extract luminescence under UV light. In cases of the presence of extract luminescence the  
21 extraction was continued with 5 ml of n-hexane. This method of extraction excluded an  
22 alteration of matter as is possible by thermal, or acoustic effects and other kinds of intensive  
23 extractions.

24 The measurements were done on a Jobin Yvon Fluorolog-3-22 spectrofluorimeter. The  
25 extract was frozen in liquid nitrogen (77 K). Then, the mixture of PAHs in the frozen extract was  
26 irradiated by light with optimum wavelengths for each compound, and the PAH luminescence  
27 spectra were recorded (Fig. 5).

28 The wavelengths of the excitation and emissions of luminescence used for the PAH  
29 identifications are given in Table 1. Spectral fractionation (identification of each hydrocarbon by  
30 the most optimum excitation and luminescence wavelengths) was used. High selectivity of the  
31 method is obtained by using a spectra selection of PAHs in multicomponent solutions by  
32 scanning the narrow excitation wave band (Alekseeva and Teplitskaya, 1981). Identification and  
33 quantitative estimations of PAHs were made by comparison of fluorescence and excitation

1 spectra with the reference standard solution SRM NIST 2250a (36 PAHs mixture). Limits of  
2 detection (LOD) for each PAH were  $\leq 0,1$  ng/g. The limits of quantification (LOQ) for each PAH  
3 were  $\leq 0,5$  ng/g. In total 109 soil samples were analyzed for PAH concentration. The analysis  
4 was done in one replicate.

### 5 **2.3. Statistical analyses**

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

9

## 10 **3. Results**

11 The studied soils varied highly in PAH concentrations; their total content changed from 5  
12 to 330 ng/g. In the histosols not affected by fire (pit 10), the total PAH concentrations ranged  
13 from 20 to 100 ng/g within the profile; their composition included naphthalene, benz(a)anthracene  
14 and phenanthrene. In the histic podzols not affected by fire (pit 1) the total PAH concentration  
15 varied from 32 ng/g in A horizon to 0,2 ng/g in BC horizon. Naphthalene and pyrene prevailed in  
16 this profile. In mineral horizons Bhs only naphthalene and sporadically pyrene occurred.  
17 Phenanthrene and benz(a)anthracene were found only in organic horizons (table 2).

18

### 19 **3.1. Profile distribution of PAHs in soils of different types**

20 The common features of PAH distribution in *post-fire histosols* (pits 7, 8, 9) were the  
21 following (Fig. 6, 7, table 3). These soils had the ash horizon Cpir at depth 2-5 cm, and typically  
22 at these sites they had low PAH concentrations (5-8 ng/g). Below and above Cpir horizon there  
23 were two maxima of PAH concentration. The first maximum of PAH concentration was detected  
24 in surface incipient horizons O (20-70 ng/g), where mainly 2-3-nuclear compounds (naphthalene,  
25 phenanthrene, anthracene) occurred. The second maximum was below Cpir in pyrogenic charry peat  
26 horizons (Hpir). In these horizons total PAH concentration reached 255 ng/g. The PAH  
27 composition in these horizons was also different. Cpir horizons had predominantly low-  
28 molecular weight compounds: 2-nuclear naphthalene and 4-nuclear pyrene. In Hpir horizons 5-6-  
29 nuclear compounds prevailed: benz(ghi)perylene, benz(e)pyrene, benz(k)fluoranthene and  
30 naphthalene occurred in a lower concentrations. In underlying organic horizons, He and Ha  
31 benz(a)anthracene occurred. In humic-infiltrated horizon Ch, low PAH concentrations (up to 5-10  
32 ng/g, coefficient of variation for total PAHs 106 %) were registered and hydrocarbons were  
33 presented only by naphthalene.

1 Post-fire histosols had various differences in PAH distribution. In pit 9 the thickness of  
2 undestroyed peat horizons were greatest among the investigated soils (approximately 30 cm),  
3 and PAH concentrations were also highest in this case – up to 255 ng/g; moreover PAH  
4 concentrations were relatively high within the entire depth of the organic layer. PAH  
5 composition was presented by a wide range of compounds – from low-molecular weight to 5-6-  
6 nuclear compounds – benz(ghi)perylene, benz(e)pyrene and benz(k)fluoranthene. In cases of more  
7 complete combustion of peat (pits 8 and 7), where mineral material was present from 10-14 cm  
8 depth, the total PAH concentrations were much lower – from 5 to 25 ng/g (Fig. 7).

9 It may be noted that total PAH concentrations in residual peat horizons of post-fire  
10 histosols changed from 10 to 255 ng/g, with coefficients of variation in He horizon of 118 % and  
11 155% in the. In sites with more complete combustion of peat, PAH molecules accumulated in  
12 smaller amounts (10-20 ng/g). In cases of incomplete burning, their concentrations in peat  
13 horizons were > 200 ng/g.

14 The analysis of variances indicated significant difference in total PAH concentration  
15 between different horizon types of histosols (ANOVA:  $F=3,6$ ;  $p<0,01$ ) (Fig. 8). Mineral horizons  
16 (Ch, Cs, C) had the smallest ranges and mean values and organogenic horizons (Hpir, He, Ha)  
17 had the greatest ranges and mean values.

18 *Sod-podzols and histic podzols* (pits 4, 5, 2, 3, 6) subjected to wildfires were slightly  
19 different in levels of PAH accumulation. Also there were two maxima of total PAH  
20 concentrations in these soils. The first maximum was most frequently confined to pyrogenic  
21 organogenic soil horizons (He,pir, Ha,pir, Apir, He, Ha); these contained up to 40-60 ng/g. The  
22 composition of hydrocarbons in these horizons and the contribution of separate components to  
23 PAH associations differed slightly. In most cases PAH were presented by naphthalene,  
24 anthracene, and pyrene. In particular cases high-molecular weight PAH (perylene,  
25 benz(ghi)perylene, benz(k)fluoranthene, benz(a)anthracene) appeared (Fig. 9, 10, table 3).

26 Furthermore, occasionally Cpir and post-pyrogenic O horizons of pits 4 and 5, closer (50  
27 m) to the burnt area of 2010, contained up to 150 ng/g PAH. These sites were affected by fire  
28 2002, perhaps because they were directly nearby the site of recent burnt area (Fig. 3).

29 At a distance from the site of the last fire the Cpir horizons (pits 2 and 3) (table 3), formed  
30 in the fire of 2002, contain PAHs in low amounts – up to 2-3 ng/g, in some cases – to 10-12  
31 ng/g. Naphthalene prevailed among hydrocarbons, while in soil pit 3 3-4-nuclear PAHs –  
32 chrysene, pyrene, anthracene – were added. The post-fire surface incipient O horizons in these  
33 soils contained from 3 to 40 ng/g PAHs. PAH composition was comprised of naphthalenes and  
34 traces of benz(a)anthracene, perylene, and benz(ghi)perylene.



1 In contrast with histosols, the sod-podzols are characterized by eluvio-illuvial translocation  
2 of hydrocarbons. For instance, eluvial horizons E contained from 0,7 to 5 ng/g PAHs with  
3 coefficient of variation 98%, and in some cases hydrocarbons were not detected. The PAHs were  
4 represented in these horizons only by naphthalene and trace amounts of phenanthrene and  
5 pyrene. The upper parts of illuvial Bhs horizons had total concentrations in amounts up to 12  
6 ng/g, PAH composition included mainly naphthalene, but benz(a)anthracene, fluorene,  
7 benz(e)pyrene and benz(k)fluorantene occurred in some cases (Fig. 10). So in contrast with  
8 background sod-podzols, the post-fire soils tended to have some migration of high-molecular  
9 weight compounds to illuvial soil horizons (Fig. 10).

10 As opposed to histosols (upper O), Cpir, Apir horizons of histic and sod-podzols had high  
11 levels of PAHs, which exceeded the range in pyrogenic organogenic horizons (Fig. 11). In the  
12 group of podzols significant differences between PAH concentrations in different horizons were  
13 identified (ANOVA:  $F=2,12; p<0,05$ ).

14 In the investigated soils, PAHs tended to form groups different in their distribution, which  
15 was confirmed by cluster analysis (Fig. 12). Low-molecular weight 2- and 3-nuclear compounds  
16 had similar distribution in both histosols and podzols throughout the whole profile. The 5-6-  
17 nuclear compounds had similar distribution and were detected only in organogenic horizons  
18 Hpir, Ha, He.

19 Among the samples, the coefficient of variation was high for high-molecular weight  
20 compounds, especially in Hpir horizons, for benz(a)pyrene (283%), benz(ghi)perylene (283%),  
21 benz(k)fluorantene (437%), and chrysene (195%). The variation of low-molecular weight  
22 compounds was lower; in H horizons coefficients of variation for naphthalene were 131% and  
23 126% for phenanthrene.

### 24 25 **3.2. The PAH accumulation in soils of burnt sites of different time**

26 Certain differences in the intensity of PAH accumulation could be noted in soils of  
27 different age burnt sites. On the site burned in 2012, the post-fire histosol within the burnt area  
28 (pit 12) and histosol situated nearby the burnt site and containing charred peat layers from  
29 previous fires (pit 11) were studied. In the soil of this most recently-burned site the total PAH  
30 concentrations were highest among all sites studied. Here PAH concentrations were 330 ng/g  
31 and were confined to charry peat horizon Hpir (table 4). The PAH composition was represented  
32 by naphthalene and anthracene. In a deeper horizon He of post-fire histosol without charry  
33 material high-molecular weight compounds benz(ghi)perylene and benz(e)pyrene occurred. The

1 same compounds were detected in soil, adjacent to the burnt area, but in a lesser amount; the  
2 total PAH concentration did not exceed 140 ng/g. In comparison with the histosols of the 2-year  
3 post-burn area (pits 8, 9) this site is characterized by higher PAH concentration.

4 In the case of sod-podzols affected by the fires of 2002 and 2010 (pits 5 and 6) the  
5 pyrogenic organogenic horizons had similar PAH concentrations (Fig. 9, 10). The differences in  
6 the intensity of eluvio-illuvial process were not detected.

7 The ANOVA indicated significant differences in PAH concentrations depending on number  
8 of years following the fire (Fig. 13; ANOVA:  $F=4,09$ ;  $p<0,05$ ). The organogenic horizons from  
9 the fire in 2012 had higher PAH concentrations. In the surface ash horizons C<sub>pir</sub> of burned areas  
10 from 2002, the tendencies of PAH concentration decreasing were not detected.

## 11 12 **4. Discussion**

### 13 14 **4.1. Profile distribution of PAHs in soils of different types**

15 These data on PAH concentration and composition in soils not affected by fires  
16 corresponded with results obtained for soils of other territories distant from PAH sources  
17 (Gennadiev and Tsibart, 2013; Wilcke, 2007; Rovinskii, 1988, Gabov et al., 2007; Krasnopeeveva,  
18 2008).

19 The production of PAHs in H<sub>pir</sub> horizons of *histosols* could be result of the structure of the  
20 smouldering front. These horizons correspond to the pyrolysis front, where wide various volatile  
21 compounds and hydrocarbons, including PAHs are formed. Above this horizons oxidation and  
22 ash formation processes take place with no PAHs formation (Rein, 2013). Under the conditions  
23 of smouldering and low oxygen access PAHs may actively form in combustion zone (Blomqvist  
24 et al., 2006., Jenkins et al., 1996; Mastral et al., 1999). Moreover the intense PAH formation  
25 during the long-duration heating has been shown in literature (Gonzalez-Vila et al., 1991), so in  
26 cases of incomplete burning of peat horizons the conditions for high PAH production tend to be  
27 present. Also, possibly, during the fire not only H<sub>pir</sub> horizon, but the entire peat layer was  
28 subjected to heating, and PAH formation could take place in organogenic horizons at all depths.

29 In addition, the possible factor causing different PAH concentrations in peat horizons, was  
30 amount of peat remained after the burning. The greater the residual mass of peat, the greater the  
31 sorption of PAHs that were observed to take place. At the same time, allowing for the high  
32 variability of absolute PAH concentrations in residual peat horizons, it could be surmised that  
33 they tend to accumulate 5-6-nuclear compounds, which could indicate processes of peat  
34 combustion. Vane et al. (2013) also pointed out the presence of low- and high-molecular PAHs

1 in soils after peat fire. However, 5-6-nuclear compounds (benz(ghi)perylene, benz(a)pyrene,  
2 benz(e)pyrene, benz(k)fluoranthene) could be considered as the indication group, marking the  
3 peat combustion.

4 The soils with very shallow (up to several cm) peat horizons remaining following fire had  
5 low PAH concentrations due to the fact that almost all organic matter is totally burned out. High  
6 coefficients of variation of PAHs in residual peat horizons could be caused by different duration  
7 and depth of heating of these horizons at different sites. The depth of changes in soils differs  
8 depending on the fire intensity and location characteristics (various moisture content, microrelief  
9 and peat thickness) (Efremova and Efremov, 2006; Grishin et al., 2013).

10 In the surface incipient horizon O (20-70 ng/g), where mainly 2-3-nuclear compounds  
11 (naphthalene, phenanthrene, anthracene) occurred, these compounds were presumably sorbed by  
12 new organogenic horizons from the atmosphere. Sorption is one of the leading process in soil  
13 involving PAHs (Trapido, 1999; Wicke, 2000), and the factors determining the rate of sorption  
14 are the content of organic matter and the presence of clay minerals (Maliszewska-Kordybach,  
15 2005; Maliszewska-Kordybach et al., 2010). These were quite high in the newly-formed organic  
16 horizons.

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

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

26 Also probably, as the accumulation of heavy PAHs takes place in-situ in char and ash  
27 horizons, PAHs are translocated across them to the atmosphere, because these horizons act as  
28 filters of gases. The accumulation of low-molecular weight PAHs could be explained by  
29 atmospheric input, these compounds release to the atmosphere with other combustion products,  
30 where they are translocated and then deposited at other plots (Rein, 2013).

31 In contrast with histosols, the sod-*podzols* were characterized by eluvio-illuvial  
32 translocation of hydrocarbons, which was also found in study of Gabov (2007), so PAH  
33 distribution follows the soil-forming processes typical to the wet climate of taiga biomes. The

1 increased migration of PAHs after the fire was, probably, caused by vegetation destruction  
2 during the fire and following intense percolation through the soil profile.

#### 4 **4.2. The PAH accumulation in soils of burnt sites of different time**

5 The histosols affected by the fire in 2012 had higher PAH concentration in comparison  
6 with the histosols after the fire of 2010. On the one hand it is caused that arriving PAHs,  
7 especially low-molecular weight compounds, may degrade after the fire. On the other hand, in  
8 the present case, the organic horizons of the most recently-burned site were not completely burnt  
9 out, which favours the intense sorption and accumulation of polycyclic aromatic hydrocarbons in  
10 these soils. But it is worth mentioning that the time of pyrogenic PAH presence in soil could  
11 differ depending on the conditions. Thus, even on a geological scale the elevated PAH  
12 concentration in the deposits of Cretaceous and Jurassic periods could be explained by  
13 ubiquitous occurrence of wildfire (Killops and Massourd, 1992; Marynowski et al., 2011.;  
14 Belcher, 2006). However, according to Garcia-Falcoan (2006) the concentrations in burned  
15 organo-mineral soils remained high only during the first three months after fire and then PAHs  
16 were reduced by soil processes including degradation and migration.

17 In the case of sod-podzols from the 2002 fire, the concentrations of PAHs could be  
18 influenced also by the 2010 fires; therefore, trends of PAH degradation with the time were not so  
19 prominent.

20 Considering the soils of drained peatlands, it is necessary to emphasize that in both post-  
21 fire sod-podzols and histosols, the total PAH concentrations could be rather high – up to  
22 hundreds of ng/g. These peculiarities differ from the features founded in our previous researches  
23 – in Polistovo natural Reserve (Pskov Region, Russia), where post-fire organogenic peat soils  
24 have higher PAH concentrations in comparison with sod-podzol soils (Gennadiev and Tsibart,  
25 2013). Moreover, in the undrained soils the total PAH concentrations did not exceed 150 ng/g.  
26 Presumably, in Shatura district the deep changes in the hydrologic regime occurred after the  
27 drainage and the level of groundwater decreased. In these cases fire affected the soil cover of the  
28 area to a great extent and new horizons having different capacity for PAH accumulation formed.  
29 Also, after the catastrophic influence of the fire the heterogeneity of soil cover increased,  
30 resulting in highly contrasting soil profiles and spatial PAH distribution.

31 However it should be noted that even under conditions of catastrophic fires on the drained  
32 peatlands in the studied cases, the PAH concentrations, especially high-molecular weight  
33 compounds, were relatively low: for example benz(a)pyrene concentrations did not exceed 3  
34 ng/g.

1 The findings from this study correspond to some previously-reported results in the  
2 literature. Vane and al. (2013) note that PAH concentrations in peat soils after fire are lower than  
3 the amount dangerous for biota. Also there is no evidence that amounts of PAHs accumulated  
4 after the fire are dangerous for humans, as they are lower than hazardous levels determined for  
5 soils. But the variation of high-molecular weight PAHs in soil horizons was high as these  
6 compounds occur not in all horizons, and their formation is a more complicated process in  
7 comparison with low-molecular PAHs.

## 8

## 9 **5. Conclusions**

10 The conclusions of our study are the following:

11 1. The wildfires on the drained peatlands caused the change of morphological properties of  
12 soils; new soil horizons C<sub>pir</sub>, O, H<sub>pir</sub>, Ha<sub>pir</sub> were formed with different accumulation rates of  
13 PAHs. Highest PAHs concentrations were seen in charr peat H<sub>pir</sub> horizons and in post-fire  
14 incipient O horizons.

15 2. Post-fire histosols and histic podzols differed in their PAH distribution. In both cases,  
16 highest PAH concentrations occurred in the organogenic post-fire horizons; but in cases of histic  
17 podzols their slight accumulation of PAHs in illuvial horizons was possible.

18 3. 5-6-nuclear compounds were formed in pyrogenic horizons Ha<sub>pir</sub> and He<sub>pir</sub>. Their  
19 production was facilitated in smouldering processes due to lack of oxygen; this group could be  
20 considered as an indicator group of peat combustion. 2-3-nuclear PAHs occurred within the  
21 whole profile; in sod-podzols and histic podzols their migration to illuvial horizons was  
22 observed. In the cases we studied, PAH composition in pyrogenic horizons did not change in  
23 different soil types.

24 4. The trends of higher PAH accumulation in soils were observed in cases of incomplete  
25 burning out of peat horizons. PAH sorption in upper horizons of soils near the sites of the most  
26 recent fires was observed.

## 27

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## References

- 1                   **References**
- 2   Agarwal, T.: Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi,  
3   India, *Journal of Hazardous Materials*, 171, 894–900, 2009.
- 4   Alexeeva, T. A., Teplitskaya, T. A.: Spectrofluorometric methods of polycyclic aromatic  
5   analysis in natural and technogenic medias, Leningrad, 215 pp., 1981.
- 6   Baek, S. O., Field, R. A., Goldstone, M. E., Kirk, P. W., Lester, J. N., Perry, R.: A review of  
7   atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior, *Water Air Soil*  
8   *Pollut.*, 60, 279–300, 1991.
- 9   Bandowe, B., Meusela, H., Huang, R., Hod, K., Cao, J., Hoffmann, T., Wilcke, W.: PM2.5-  
10   bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese  
11   megacity: Seasonal variation, sources and cancer risk assessment, *Science of The Total*  
12   *Environment*, 473–474, 77–87, 2014.
- 13   Belcher, C. M.: Impacts and wildfires - an analysis of the K-T event, *Biological processes*  
14   *associated with impact events*, 221-243, 2006.
- 15   Belis, C. A., Offenthaler, I., Weiss, P.: Semivolatiles in the forest environment: the case of  
16   PAHs, *Plant Ecophysiology, Organic Xenobiotics and Plants, Part 1*, 47-73, 2001.
- 17   Betha, R., Pradani, M., Lestari, P., Joshi, U., Reid, J., Balasubramanian, R.: Chemical speciation  
18   of trace metals emitted from Indonesian peat fires for health risk assessment, *Atmospheric*  
19   *Research*, 122, 571–578, 2013.
- 20   Blake, D., Hinwood, A.L., Horwitz P.: Peat fires and air quality: Volatile organic compounds  
21   and particulates, *Chemosphere*, 76, 419–423, 2009.
- 22   Blomqvist, P., Persson, B., Simonson, M.: Fire emissions of organics into the atmosphere, *Fire*  
23   *Technology*, 43, 213-231, 2007.
- 24   Bojakowska, I. and Sokołowska, G.: Polycyclic aromatic hydrocarbons in materials of burned  
25   peatlands, *Polish Journal of Environmental Studies*, 12, 401-408, 2003.
- 26   Cai, Q., Mo, C., Wu, Q., Katsoyiannis, A., Zeng, Q.: The status of soil contamination by  
27   semivolatile organic chemicals (SVOCs) in China: A review, *Science of The Total Environment*,  
28   389, 209–224, 2008.
- 29   Cooijer, C., Ariese F., Hofstraat, J. W.: *Shpol'skii Spectroscopy and Other Site-Selection*  
30   *Methods, Applications in Environmental Analysis, Bioanalytical Chemistry and Chemical*  
31   *Physics*, John Wiley & Sons, N.Y, 552 pp., 2000.
- 32   di Folco, M. and Kirkpatrick, J.: Topographic variation in burning-induced loss of carbon from  
33   organic soils in Tasmanian moorlands, *Catena*, 87, 216–225, 2011.
- 34   Donkelaar, A., Martin, R., Levy, R., da Silva, A., Krzyzanowski, M., Chubarova, N.,  
35   Semutnikova, E., Cohen, A.: Satellite-based estimates of ground-level fine particulate matter

1 during extreme events: A case study of the Moscow fires in 2010, *Atmospheric Environment*, 45,  
2 6225-6232, 2011.

3 Dymov, A. A., Dubrovsky, Yu. A., Gabov, D. N.: Pyrogenic changes in iron-illuvial podzols in  
4 the middle taiga of the Komi Republic, *Eurasian Soil Science*, 47, 47–56, 2014.

5 Efremova, T. T., Efremov, S. P.: Pyrogenic transformation of organic matter in soils of forest  
6 bogs, *Eurasian Soil Science*, 39, 1297-1305, 2006.

7 Fitzpatrick, E. M., Jones, J. M., Pourkashanian, M., Ross, A. B., Williams, A., Bartle, K.D.:  
8 Mechanistic aspects of soot formation from the combustion of pine wood, *Energy and Fuels*, 22,  
9 3771-3778, 2008.

10 Freeman, D. J. and Cattell, F. C. R.: Woodburning as a source of atmospheric polycyclic  
11 aromatic hydrocarbons, *Environmental Science and Technology*, 24, 1581–1585, 1990.

12 Gabov, D. N., Beznosikov, V. A., Kondratenok, B. M.: Polycyclic aromatic hydrocarbons in  
13 background podzolic and gleyic peat-podzolic soils. *Eurasian Soil Science*, 40, 256–264, 2007.

14 Garcia-Falcoan, M. S., Soto-Gonzaalez, B., Simal-Gaandara, J.: Evolution of the concentrations  
15 of polycyclic aromatic hydrocarbons in burnt woodland soils, *Environmental Science and*  
16 *Technology*, 40, 759–763, 2006.

17 Gennadiev, A. N. and Tsibart, A. S.: Pyrogenic polycyclic aromatic hydrocarbons in soils of  
18 reserved and anthropogenically modified areas: factors and features of accumulation, *Eurasian*  
19 *Soil Science*, 46, 28–36, 2013.

20 Gennadiev, A. N., Pikovskii, Yu. I., Florovskaya, V. N., Alexeeva T. A., Kozin, I. S., Ogloblina,  
21 A. I., Ramenskaya, M. E., Teplitskaya, T. A., and Shurubor, E. I: *Geochemistry of Polycyclic*  
22 *Aromatic Hydrocarbons in Rocks in Soils*, Moscow University publ., Moscow, 188 pp., 1996.

23 Gonzalez-Vila, F., Lopez, J., Martin, F., del Rio, J.: Determination in soils of PAH produced by  
24 combustion of biomass under different conditions, *Fresenius J. Anal Chem.*, 339, 750–753, 1991.

25 Grishin, A. M., Zima, V. P., Kasymov, D. P.: On the deepening mechanism of the site of peat  
26 combustion, *Journal of Engineering Physics and Thermophysics*, 86, 996-1001, 2013.

27 Guo, W., Pei, Y, Yang, Z., Chen, H.: Historical changes in polycyclic aromatic hydrocarbons  
28 (PAHs) input in Lake Baiyangdian related to regional socio-economic development, *Journal of*  
29 *Hazardous Materials*, 187, 441–449, 2011.

30 Haritash, A. K., Kaushik, C. P.: Biodegradation aspects of Polycyclic Aromatic Hydrocarbons  
31 (PAHs): A review, *Journal of Hazardous Materials*, 169, 1–15, 2009.

32 Hartford, R. A., Frandsen, W. H.: When It's Hot, It's Hot... Or Maybe It's Not! (Surface Flaming  
33 May Not Portend Extensive Soil Heating), *International Journal of Wildland Fire*, 2(3), 139–144,  
34 1992.

1 Jenkins, B., Jones, A. D., Turn, S. Q., Williams, R. B.: Emission factors for polycyclic aromatic  
2 hydrocarbons from biomass burning, *Environmental Science and Technology*, 30., 2462–2469,  
3 1996.

4 Kakareka, S. V., Kukharchic, T. I., Zanevslaya, L. A., Kurman, P. V., Chuduk, V. N., Chomich,  
5 V. S.: Modeling and assessment of PAHs emissions during wildfires in peatlands, in: *Natural*  
6 *resources*, 10, The institute on natural resources usage and ecology of Belorussian National  
7 Academy, Belorussia, 58-62, 2004.

8 Khan, A., Ishaq, M., Khan, M.: Effect of vehicle exhaust on the quantity of polycyclic aromatic  
9 hydrocarbons (PAHs) in soil, *Environ Monit Assess*, 137, 363–369, 2008.

10 Killops, S. D., Massourd, M. S.: Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient  
11 sediments: evidence for Jurassic vegetation fires, *Org. Geochem.*, 1, 1-7, 1992.

12 Krasnopeeva, A.: Natural bituminoids in soils of the forest zone: Luminescence diagnostics and  
13 content levels (Satino Research Station, Moscow State University). *Eurasian Soil Science*, 41,  
14 1282–1293, 2008.

15 Kudravtseva, N. L.: Geostructural location and conditions of peat bogs and deep lakes  
16 nourishment in Meshchera downfold and on the Oka-Tsna bar, in: *The Aspects of ground water*  
17 *and engineer-geological processes studying*, Russia, Moscow, 74-84, 1973.

18 Kwon, H. and Choi, S.: Polycyclic aromatic hydrocarbons (PAHs) in soils from a multi-  
19 industrial city, South Korea, *Science of the Total Environment*, 470–471, 1494–1501, 2014.

20 Maioli, O. L., Knoppers, B. A., Azevedo, D. A.: Sources, distribution and variability of  
21 hydrocarbons in total atmospheric suspended particulates of two Brazilian areas influenced by  
22 sugarcane burning, *J. Atmos. Chem.*, 2009, 64, 159–178, 2009.

23 Maisto, G., Nicola, F., Iovieno, P., Prati, M. V., Alfani, A.: PAHs and trace elements in volcanic  
24 urban and natural soils, *Geoderma*, 136, 20–27, 2006.

25 Maliszewska-Kordybach, B., Klimkowicz-Pawlas, A., Smreczak, B., Stuczyński, T.:  
26 Relationship between soil concentrations of PAHs and their regional emission indices, *Water Air*  
27 *Soil Pollution*, 213, 319-330, 2010.

28 Maliszewska-Kordybach, B.: Dissipation of polycyclic aromatic hydrocarbons in freshly  
29 contaminated soils – the effect of soil physicochemical properties and aging, *Water, Air, and Soil*  
30 *Pollution*, 168, 113-128, 2005.

31 Marynowski, L., Scott, A. C., Zatoń, M., Parent, H., Garrido, A. C: First multi-proxy record of  
32 Jurassic wildfires from Gondwana: Evidence from the Middle Jurassic of the Neuquén Basin,  
33 Argentina, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 299, 129-136, 2011.

34 Masclet, P., Cachier, H., Lioussse, C., Wortham, H.: Emissions of polycyclic aromatic  
35 hydrocarbons by savanna fires, *J. of Atmospheric Chemistry*, 22, 41–54, 1995.



1 Mastral, A, Callean, M., Garcia T.: Polycyclic aromatic hydrocarbons and organic matter  
2 associated to particulate matter emitted from atmospheric fluidized bed coal combustion.  
3 Environmental Science and Technology, 33, 3177-3184, 1999.

4 Mastral, A. and Callen, M.: A Review on Polycyclic Aromatic Hydrocarbon (PAH) Emissions  
5 from Energy Generation, Environmental Science and Technology, 34, 3051-3057, 2000.

6 Medeiros, P. and Simoneit, B.: Source profiles of organic compounds emitted upon combustion  
7 of green vegetation from temperate climate forests, Environmental Science and Technology, 42,  
8 8310–8316, 2008.

9 Mu, L., Peng, L., Cao, J., He, Q., Li, F., Zhang, J., Liu, X., Bai, H.: Emissions of polycyclic  
10 aromatic hydrocarbons from coking industries in China, Particuology, 11, 86–93, 2013.

11 Nakajima, D., Nagame, S., Kuramochi, H., Sugita, K., Kageyama, S., Shiozaki, T., Takemura,  
12 T., Shiraishi, F., Goto, S.: Polycyclic aromatic hydrocarbon generation behavior in the process of  
13 carbonization of wood, Bull Environ Contam Toxicol., 79, 221-225, 2007.

14 Nussbaumer, T.: Combustion and co-combustion of biomass: fundamentals, technologies, and  
15 primary measures for emission reduction, Energy and Fuels, 17, 1510–1521, 2003.

16 Personov, R. I.: Site Selection Spectroscopy of Organic Molecules in Solutions and its  
17 Application, J. Luminescence, 24/25, 475, 1981.

18 Radojevic, M.: Chemistry of forest fires and regional haze with emphasis on Southeast Asia,  
19 Pure appl. Geophys, 160, 157–187, 2003.

20 Ramdahl, T. and Bechler, G.: Characterization of polynuclear aromatic hydrocarbon derivatives  
21 in emissions from wood and cereal straw combustion, Analytica Chimica Acta, 1982, 144, 83–  
22 91, 1982.

23 Rein, G., Cleaver, N., Ashton, C., Pironi, P., Torero, J. L.: The severity of smouldering peat fires  
24 and damage to the forest soil, Catena, 74, 304–309, 2008.

25 Rein, G.: Smouldering Fires and Natural Fuels, Fire Phenomena and the Earth System: An  
26 Interdisciplinary Guide to Fire Science, Chapter 2, 15-34, 2013.

27 Rovinskii F. Ya., Teplitskaya T. A., Alexeeva T. A.: Background monitoring of polycyclic  
28 aromatic hydrocarbons, Leningrad, 224 pp., 1988.

29 Schauer, J., Kleeman, M., Cass, G., Simoneit, B.: Measurement of emissions from air pollution  
30 sources. 3. C1-C29 organic compounds from fireplace combustion of wood, Environmental  
31 Science and Technology, 35, 1716-1728, 2001.

32 Shvidenko, A. Z., Shchepashchenko, D. G., Vaganov, E. A., Sukhinin, A. I., Maksyutov, Sh. Sh.,  
33 McCallum, I., Lakyda, I. P.: Impact of Wildfire in Russia between 1998–2010 on Ecosystems  
34 and the Global Carbon Budget, Doklady Earth Sciences, 441, Part 2, 1678–1682, 2011.

35 Simakin, G. Ya.: Peat resources of Moscow Region, Moscow, Russia, 74 pp., 1958.

- 1 Simoneit, B.: A review of biomarker compounds as source indicators and tracers for air  
2 pollution, *Environ. Sci. and Pollut. Res.*, 6 (3), 159-169, 1999.
- 3 Sushkova, I. V.: The description of the cover disturbances taken place on the former peat-mining  
4 territories in Shaturskiy district of Moscow region and further development prognosis of  
5 vegetation in the area, *Bulletin of Moscow State Regional University. Series "Natural sciences"*,  
6 №2, 43-46, 2008.
- 7 Timashev, A.: Shatura power plant, Moscow-Leningrad, Russia, 128 pp., 1932.
- 8 Trapido, M.: Polycyclic aromatic hydrocarbons in Estonian soil: contamination and profiles,  
9 *Environmental Pollution*, 105, 67-74, 1999.
- 10 Tsibart, A. S. and Gennadiev, A. N.: Polycyclic Aromatic Hydrocarbons in Soils: Sources,  
11 behavior, and Indication Significance (A Review), *Eurasian Soil Science*, 46, 728–741, 2013.
- 12 Vane, C. H., Rawlins, B. G., Kim, A. W., Moss-Hayes, V., Kendrick, C. P., Leng, M. J.:  
13 Sedimentary transport and fate of polycyclic aromatic hydrocarbons (PAH) from managed  
14 burning of moorland vegetation on a blanket peat, South Yorkshire, UK, *Science of the Total  
15 Environment*, 449, 81–94, 2013.
- 16 Vergnoux, A., Malleret, L., Asia, L., Doumenq, P., Theraulaz, F.: Impact of forest fires on PAH  
17 level and distribution in soils, *Environmental Research*, 111, 193–198, 2011.
- 18 Wetlands of Moscow Region. Natural, economic and historical-cultural aspects, *Wetland  
19 International-Russia Programme, KMK, Scientific press, Moscow, Russia*, 89 pp., 2008.
- 20 Wilcke, W.: Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil, *Geoderma*,  
21 141, 157–166, 2007.
- 22 Wilcke, W.: Polycyclic aromatic hydrocarbons (PAHs) in soil — a review, *J Plant Nutr Soil Sci*,  
23 163, 229–248, 2000.
- 24 WRB: World Reference base for soil resources 2006, 2nd edition, *World Soil Resources  
25 Reports*, No 103, Food and Agriculture Organization of the United Nations, Rome, 2006
- 26 Yuan, H., Tao, S., Li, B., Lang, C., Cao, J., Coveney, R. M.: Emission and outflow of polycyclic  
27 aromatic hydrocarbons from wildfires in China, *Atmospheric Environment*, 42, 6828–6835,  
28 2008.
- 29 Zaccone, C., Rein, G., D’Orazio, V., Hadden, R. M., Belcher, C. M., Miano, T. M.: Smouldering  
30 fire signatures in peat and their implications for palaeoenvironmental reconstructions,  
31 *Geochimica et Cosmochimica Acta*, 137, 134–146, 2014.
- 32 Zaidel’man, F. R., Morozova, D. I., Shvarov, A. P., Batrak, M. V.: Vegetation and pedogenesis  
33 on pyrogenic substrates of former peat soils, *Eurasian Soil Science*, 39,12-20, 2006.
- 34 Zaidel’man, F. R. and Romanov, S. V.: Ecological-hydrothermal assessment of pyrogenic soils  
35 of cutover peatlands, *Eurasian Soil Science*, 40, 82-92, 2007.

1 Zaidel'man, F. R., Bannikov, M. V., Shvarov, A. P.: Properties and fertility of pyrogenic  
2 formations on burnt drained peaty soils, Eurasian Soil Science, 32, 1032-1039, 1999.

3 Zaidel'man, F. R., Morozova, D. I., Shvarov, A. P.: Changes in the properties of pyrogenic  
4 formations and vegetation on burnt previously drained peat soils of poles'ie landscapes,  
5 Eurasian Soil Science, 36, 1159-1167, 2003.

6 Zonov, N. T. and Konstantinovitch, A. E.: Geologic structure, mineral resources and ground  
7 waters of Egorievskii, Shaturskii, Korobovskii and Kurovskii Districts of Moscow Region,  
8 Transactions of Moscow geological survey bureau, 11, Moscow, Russia, 1932.

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Table 1. The wavelengths of the excitation and emissions of luminescence used for the

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## PAH identifications

| PAH                | Excitation ( $\lambda$ , nm) | Emission ( $\lambda$ , nm) |
|--------------------|------------------------------|----------------------------|
| Naphthalene        | 290                          | 322                        |
| Pheanthrene        | 293                          | 346                        |
| Chrysene           | 269                          | 361                        |
| Pyrene             | 352                          | 372                        |
| Anthracene         | 253                          | 378                        |
| Benz(a)anthracene  | 290                          | 384                        |
| Benz(a)pyrene      | 367                          | 402                        |
| Benz(ghi)perylene  | 367                          | 419                        |
| Fluorene           | 288                          | 302                        |
| Dibenztiophene     | 286                          | 425                        |
| Triphenylene       | 287                          | 462                        |
| Benz(e)pyrene      | 333                          | 388                        |
| Benz(k)fluorantene | 310                          | 401                        |
| Coronene           | 300                          | 445                        |

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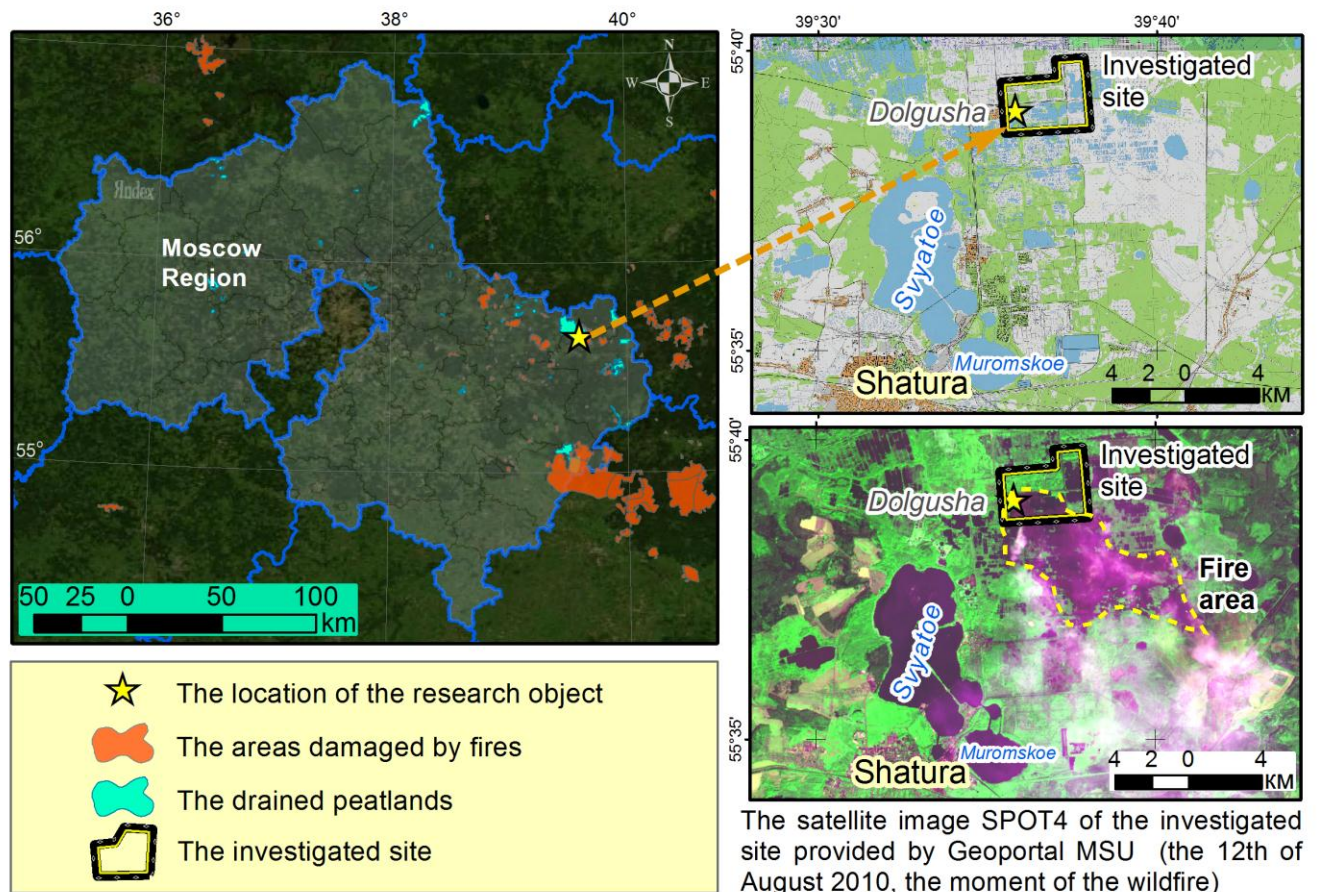
Table 2. PAHs concentrations in soils of unburnt area

| Horizon depth, cm            | Horizon | Naphthalene | Phenanthrene | Chrysene | Pyrene | Anthracene | Benz(a)anthracene | Benz(a)pyrene | Benz(ghi)perylene | Fluorene | Dibenztiophene | Perylene | Triphenylene | Benz(e)pyrene | Benz(k)fluoranthene | Coronene | Total PAHs   |
|------------------------------|---------|-------------|--------------|----------|--------|------------|-------------------|---------------|-------------------|----------|----------------|----------|--------------|---------------|---------------------|----------|--------------|
| <b>Histic podzol (pit 1)</b> |         |             |              |          |        |            |                   |               |                   |          |                |          |              |               |                     |          |              |
| 0-1                          | O       | 8,7         | 26,7         | <LOD     | <LOD   | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>35,4</b>  |
| 1-10                         | A       | 2,7         | 6,3          | <LOD     | <LOD   | 0,3        | 0,9               | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>10,2</b>  |
| 10-18(21)                    | A       | 6,9         | 11,8         | <LOD     | <LOD   | <LOD       | 12,1              | <LOD          | <LOD              | <LOD     | <LOD           | 0,1      | <LOD         | <LOD          | 1,3                 | <LOD     | <b>32,3</b>  |
| 18(21)-26                    | E       | 3,3         | 2,3          | <LOD     | <LOD   | <LOD       | 0,1               | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>5,6</b>   |
| 26-37(40)                    | E/Bhs   | 5,3         | <LOD         | <LOD     | 0,1    | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>5,4</b>   |
| 37(40)-55(57)                | Bhs     | 3,0         | <LOD         | <LOD     | <LOD   | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>3,0</b>   |
| 55(57)-65                    | Cs      | <LOD        | <LOD         | <LOD     | <LOD   | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD           | 0,2      | <LOD         | <LOD          | <LOD                | <LOD     | <b>0,2</b>   |
| <b>Histosol (pit 10)</b>     |         |             |              |          |        |            |                   |               |                   |          |                |          |              |               |                     |          |              |
| 0-5                          | He      | 11,0        | <LOD         | <LOD     | <LOD   | <LOD       | 8,6               | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>19,6</b>  |
| 5-10                         | He      | 29,1        | 36,1         | <LOD     | <LOD   | 3,4        | 11,6              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>80,2</b>  |
| 10-15                        | He      | 40,6        | 49,3         | <LOD     | <LOD   | <LOD       | 19,7              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>109,6</b> |
| 15-20                        | He      | 34,7        | 38,0         | <LOD     | <LOD   | <LOD       | 9,6               | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>82,3</b>  |
| 20-30                        | Ha      | 32,5        | <LOD         | <LOD     | <LOD   | <LOD       | 16,2              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>48,7</b>  |
| 30-40                        | Ha      | 45,9        | <LOD         | <LOD     | <LOD   | <LOD       | 12,0              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>57,9</b>  |
| 40-50                        | Ha      | 63,5        | 27,2         | <LOD     | <LOD   | <LOD       | 46,5              | <LOD          | <LOD              | <LOD     | <LOD           | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>137,2</b> |



Table 4. PAHs concentrations in soils of recent burnt area (2012)

| Horizon depth, cm                                       | Horizon | Naphthalene | Phenanthrene | Chrysene | Pyrene | Anthracene | Benz(a)anthracene | Benz(a)pyrene | Benz(ghi)perylene | Fluorene | Dibenzthiophene | Perylene | Triphenylene | Benz(e)pyrene | Benz(k)fluoranthene | Coronene | Total PAHs   |
|---|---------|-------------|--------------|----------|--------|------------|-------------------|---------------|-------------------|----------|-----------------|----------|--------------|---------------|---------------------|----------|--------------|
| Histosol, the plot of recent burn area 2012 (pit 12)    |         |             |              |          |        |            |                   |               |                   |          |                 |          |              |               |                     |          |              |
| 0-3   | O       | 9,2         | <LOD         | 0,2      | 0,3    | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | 0,2                 | <LOD     | <b>9,8</b>   |
| 3-5(6)  | Hpir    | 285,8       | <LOD         | <LOD     | <LOD   | 46,8       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>332,6</b> |
| 7(9)-16   | He      | 68,5        | 21,3         | <LOD     | <LOD   | <LOD       | <LOD              | <LOD          | 6,2               | <LOD     | <LOD            | <LOD     | <LOD         | 10,0          | <LOD                | <LOD     | <b>106,0</b> |
| Histosol, the plot adjacent to burnt area 2012 (pit 11) |         |             |              |          |        |            |                   |               |                   |          |                 |          |              |               |                     |          |              |
| 0-1   | Hpir    | 31,4        | 21,0         | <LOD     | 8,3    | <LOD       | 12,5              | 3,1           | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>76,3</b>  |
| 1-10  | He      | 39,8        | <LOD         | <LOD     | <LOD   | <LOD       | 77,9              | <LOD          | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>117,6</b> |
| 10-11   | Cpir    | 70,3        | 8,5          | <LOD     | 2,8    | <LOD       | 3,5               | <LOD          | 0,2               | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>85,3</b>  |
| 11-11,5   | Hpir    | 15,2        | <LOD         | 0,1      | <LOD   | <LOD       | <LOD              | <LOD          | 3,7               | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>19,0</b>  |
| 11,5-20   | He      | 120,5       | <LOD         | <LOD     | <LOD   | 15,6       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>136,0</b> |
| 20-30   | He      | 66,6        | <LOD         | <LOD     | <LOD   | <LOD       | <LOD              | <LOD          | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>66,6</b>  |
| 30-40   | He      | 60,1        | <LOD         | <LOD     | 1,9    | <LOD       | 3,1               | <LOD          | 1,3               | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>66,3</b>  |
| 40-45   | He      | 114,3       | <LOD         | <LOD     | <LOD   | <LOD       | 1,3               | 0,2           | <LOD              | <LOD     | <LOD            | <LOD     | <LOD         | <LOD          | <LOD                | <LOD     | <b>115,8</b> |



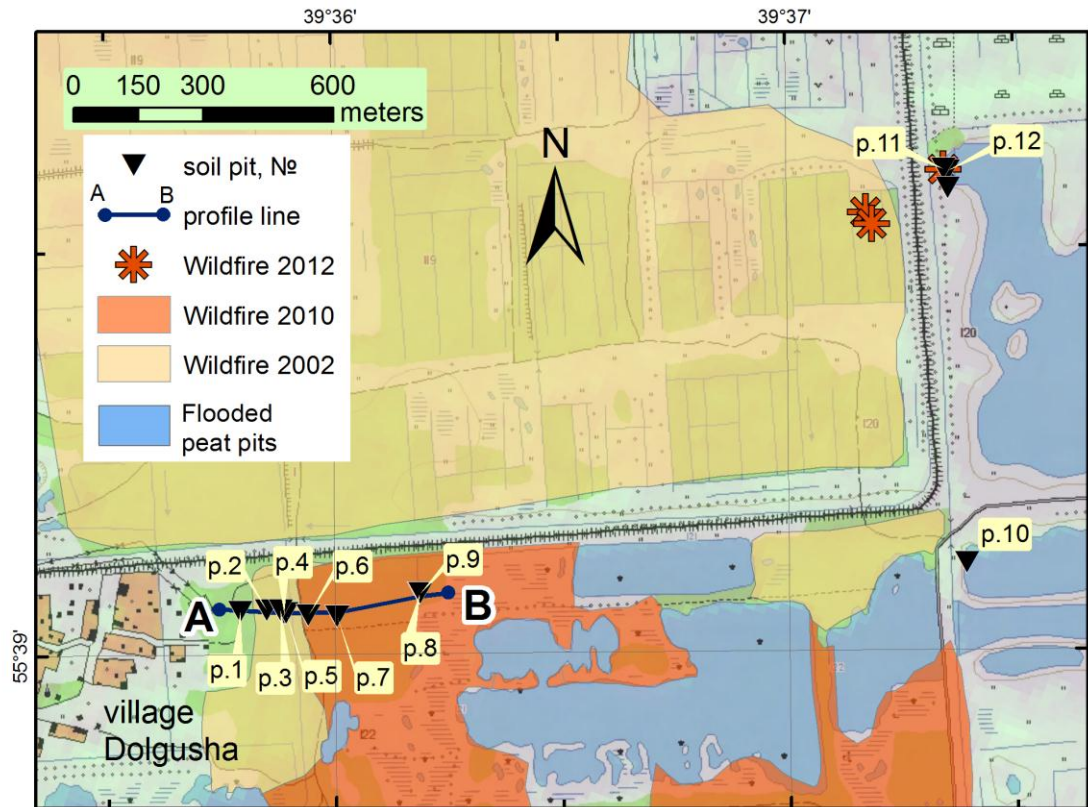
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2 Fig. 1. The location of the research site.

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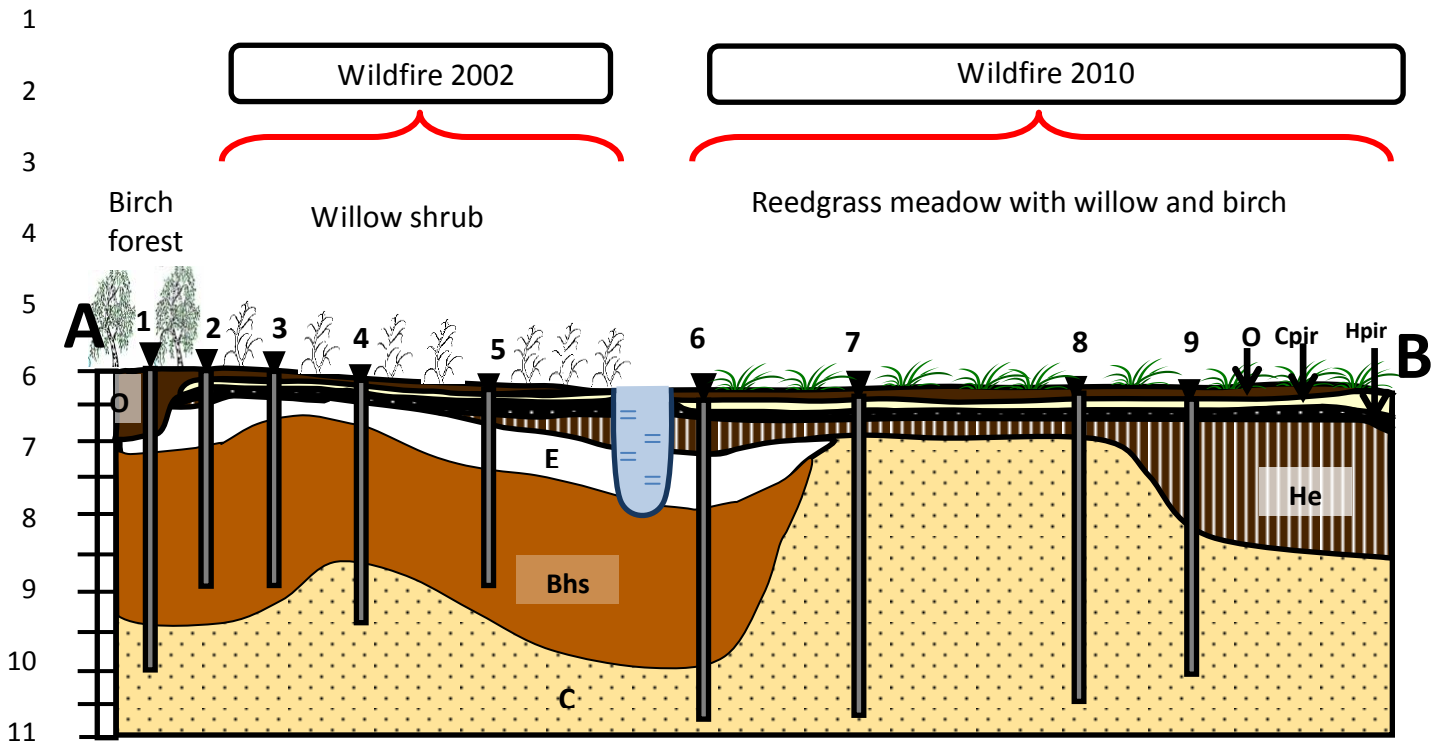


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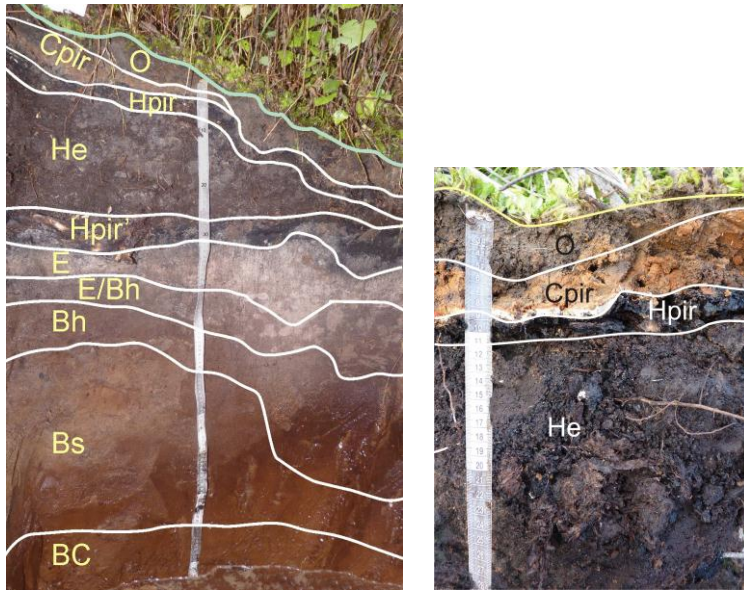
Fig. 2. The location of the investigated soil pits.

4



2 – the numbers of soil pits  
**Hpir** – genetic soil horizons

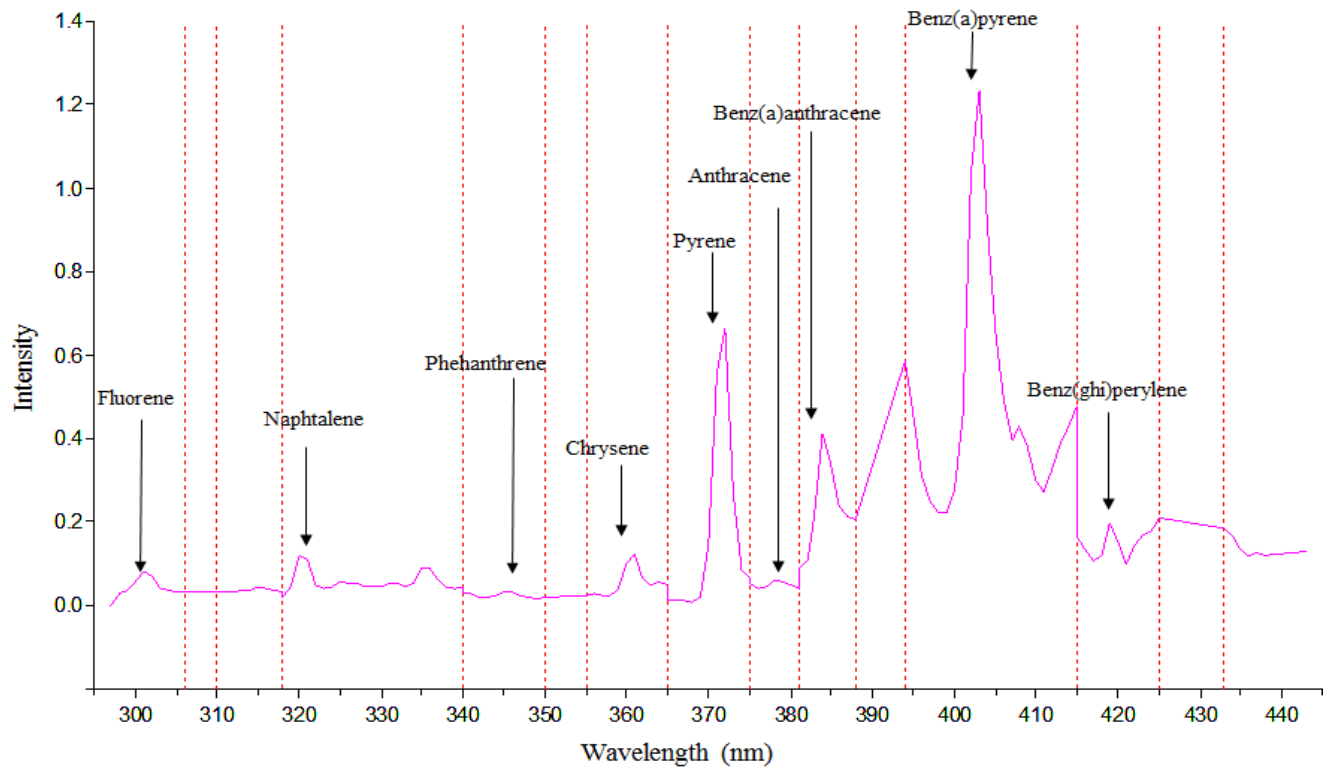
Fig. 3. The profile characteristics of the investigated soils.



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Fig. 4. Soil profiles investigated. 1- post-pyrogenic histic podzol (pit 6), 2-post-pyrogenic histosol (pit 8).

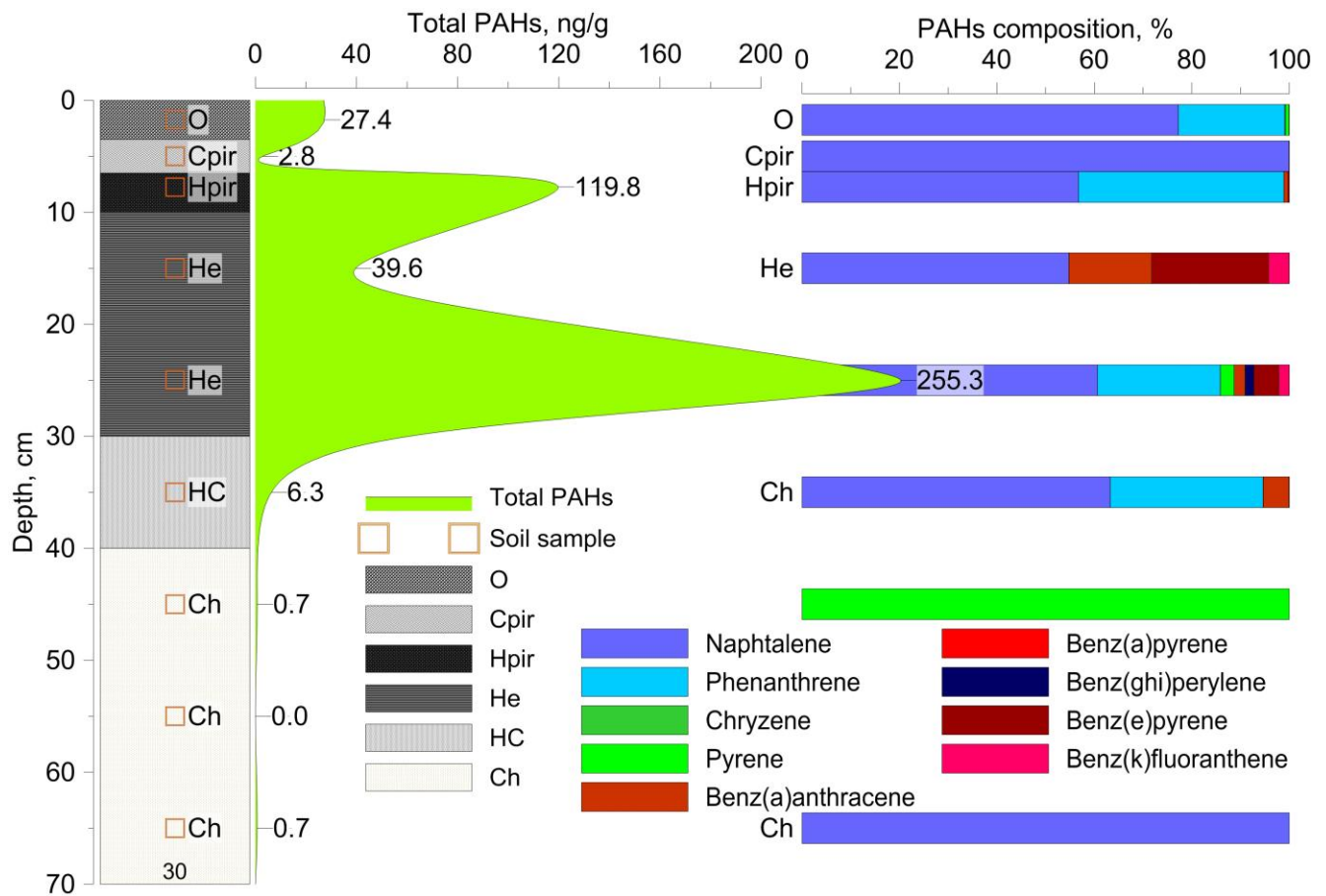
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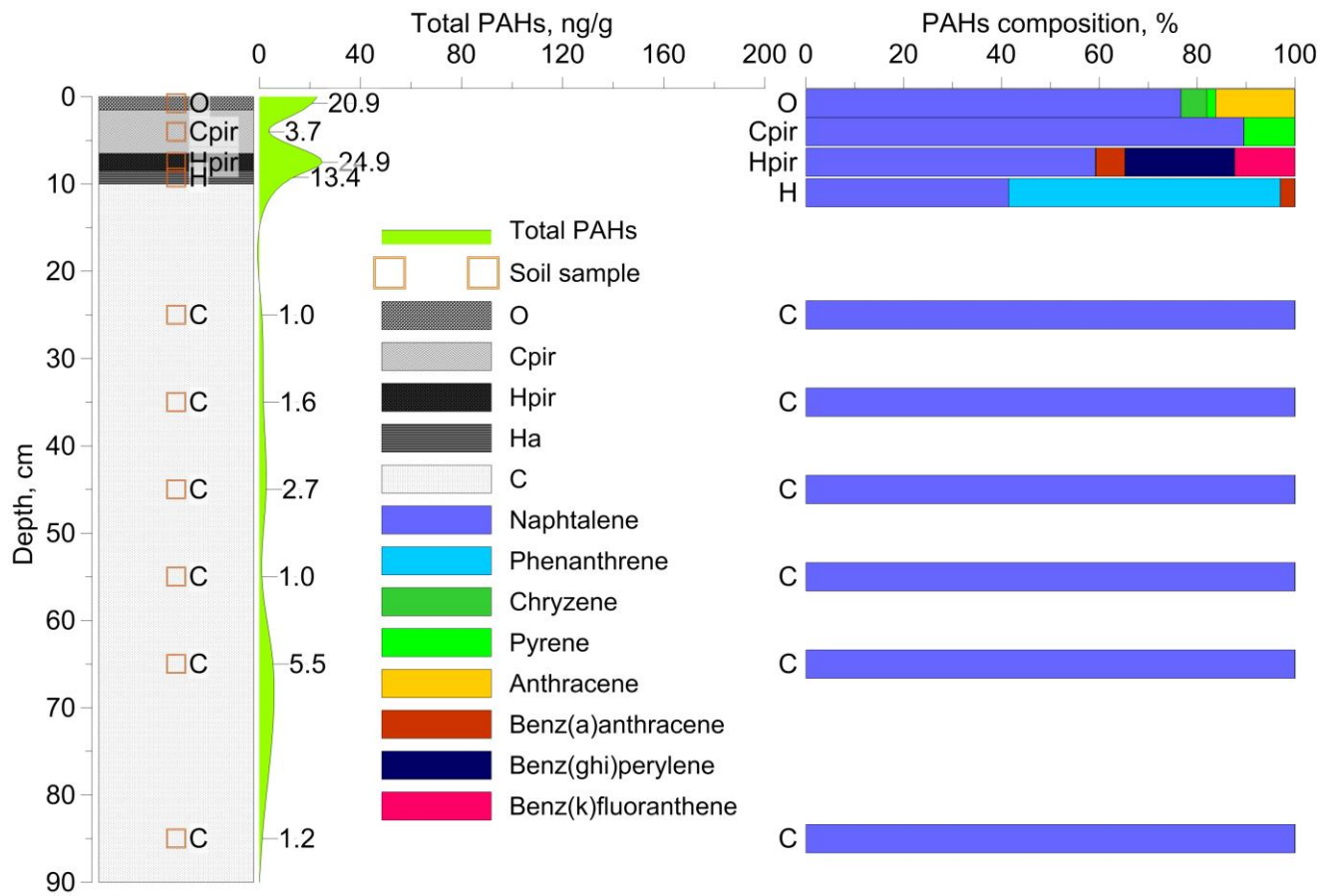
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3 Fig 5. PAH luminescence spectra for SRM NIST 2250a.

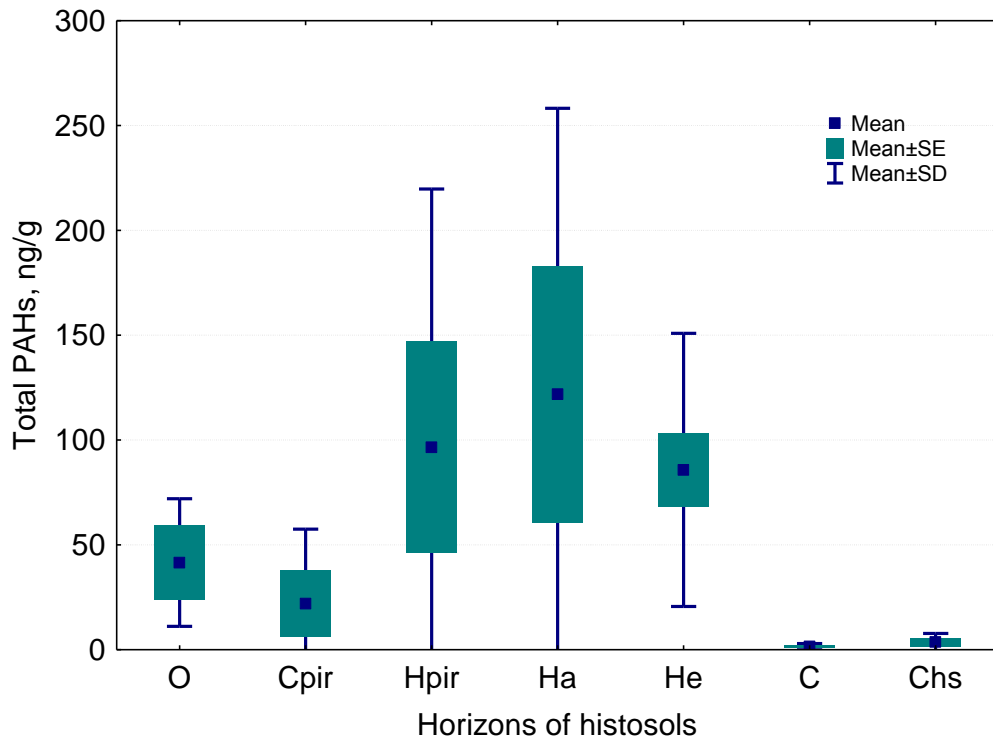
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2 Fig. 6. The profile distribution and composition of PAHs in post-fire histosol in case of  
3 thick organogenic horizon (pit 9).  
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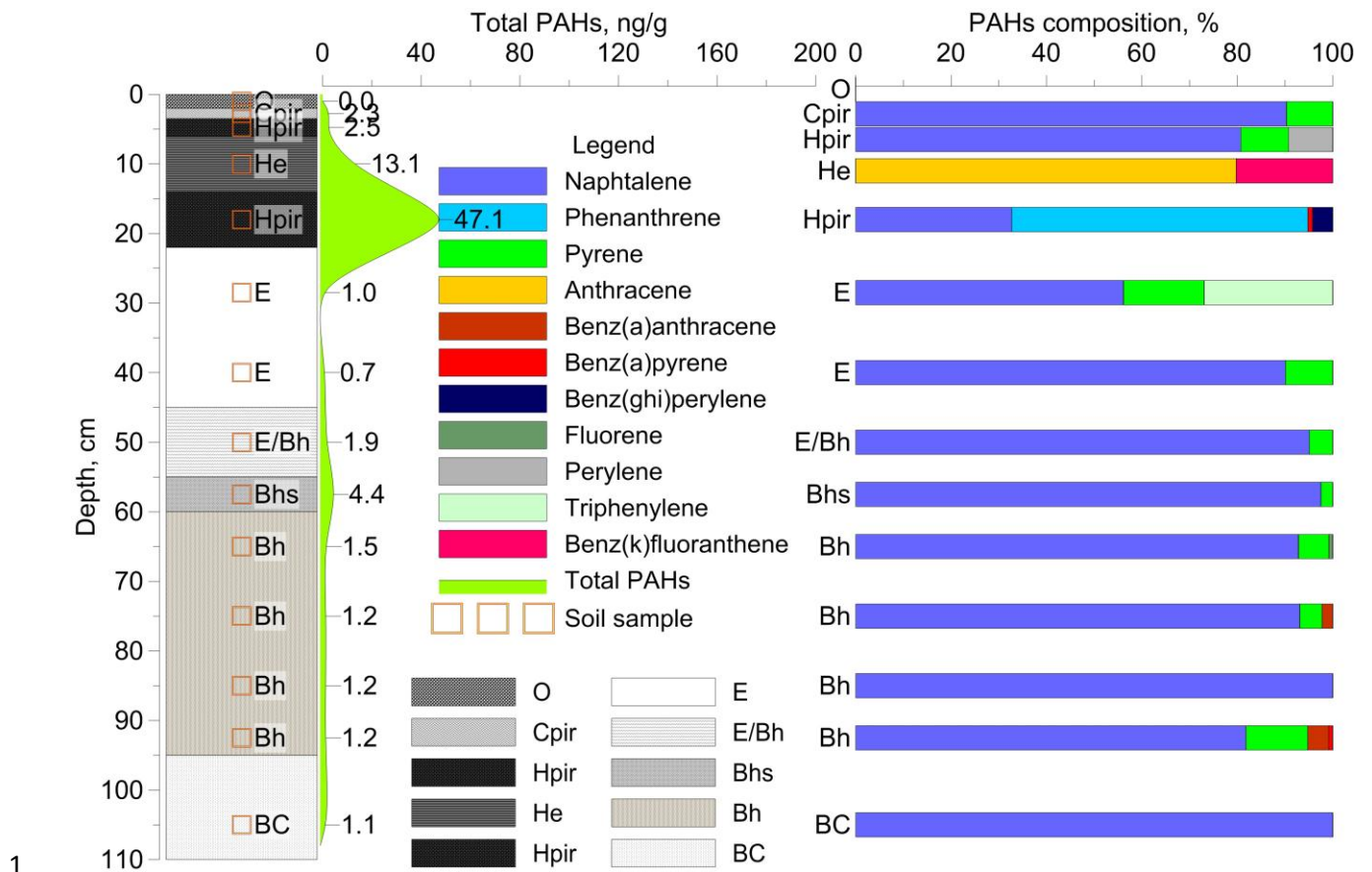


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2 Fig. 7. The profile distribution and composition of PAHs in post-fire histosol in case of  
3 almost complete burning out of organic layer (pit 8).  
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Fig. 8. The categorized box and whisker plot for total PAHs in different horizons of histosols (pits 7, 8, 9). The number of sample replicates (O-3, Cpir-5, Hpir-6, He-14, Ha-5, Chs-5, C-12). Horizons Cs and Ch were combined for this analysis, indicated by Chs.

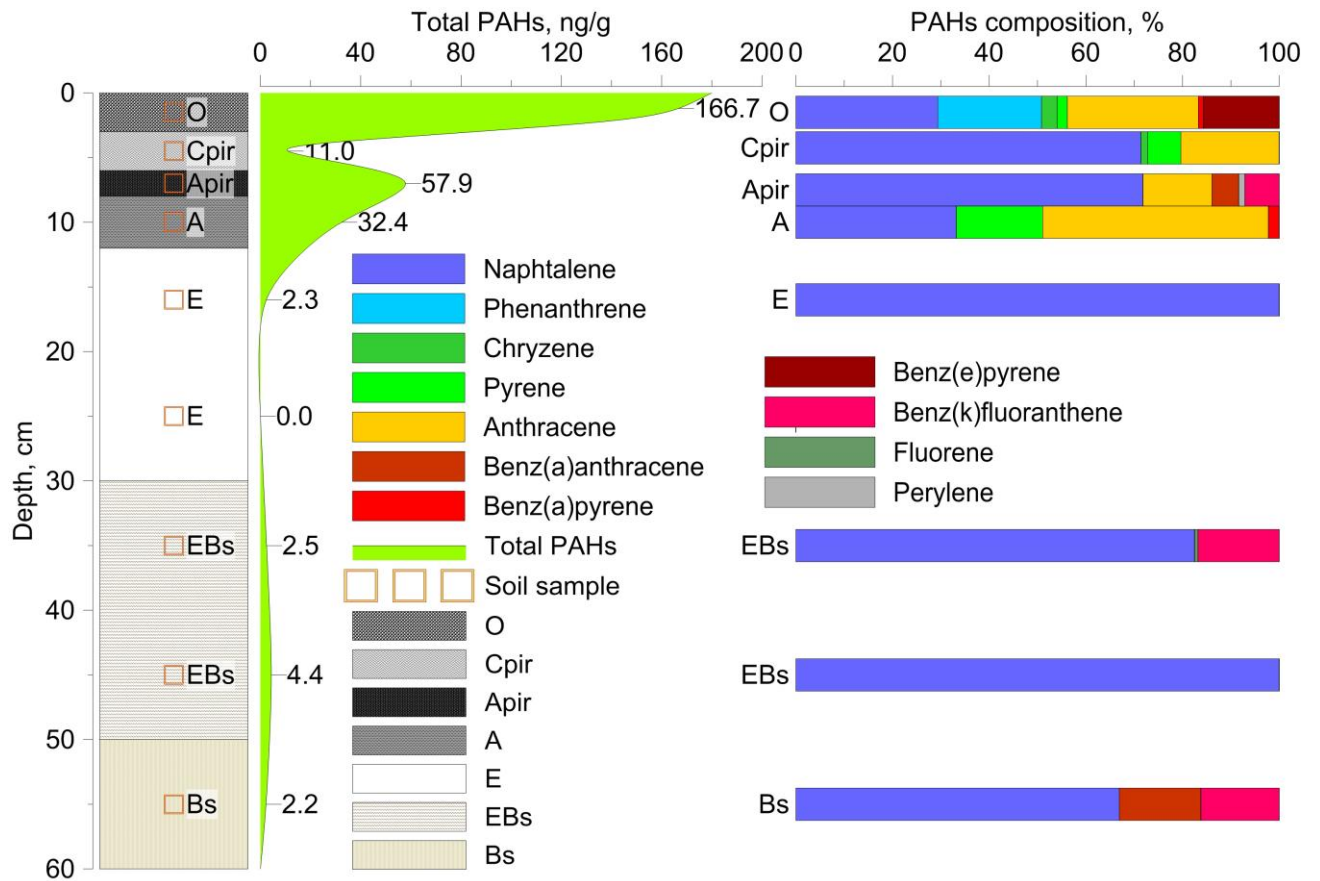


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2 Fig. 9. The profile distribution and PAHs composition in post-pyrogenic histic podzols,  
3 wildfire 2010 (pit 6).

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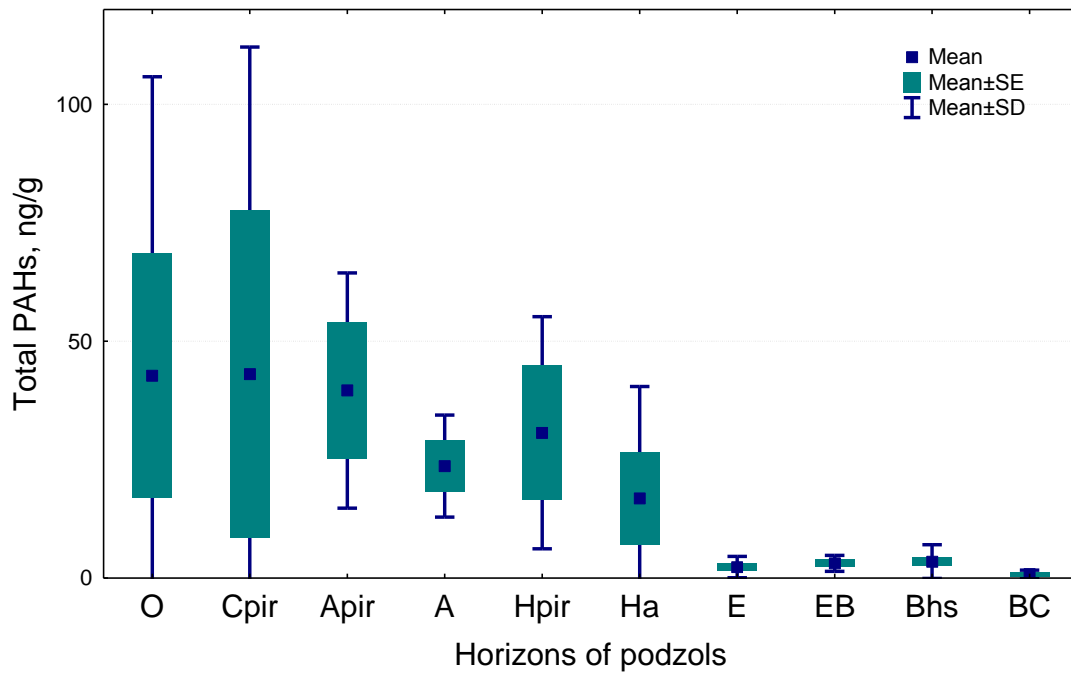


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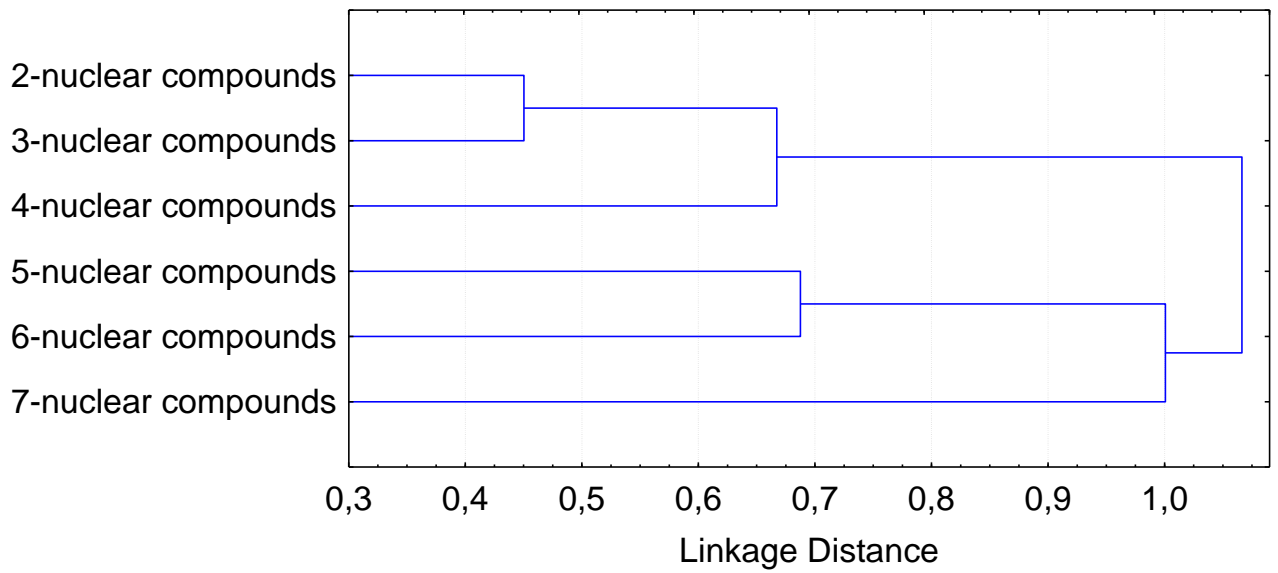
4 Fig. 10. The profile distribution and PAHs composition in post-pyrogenic histic podzols  
5 from the wildfire of 2002 (pit 5).

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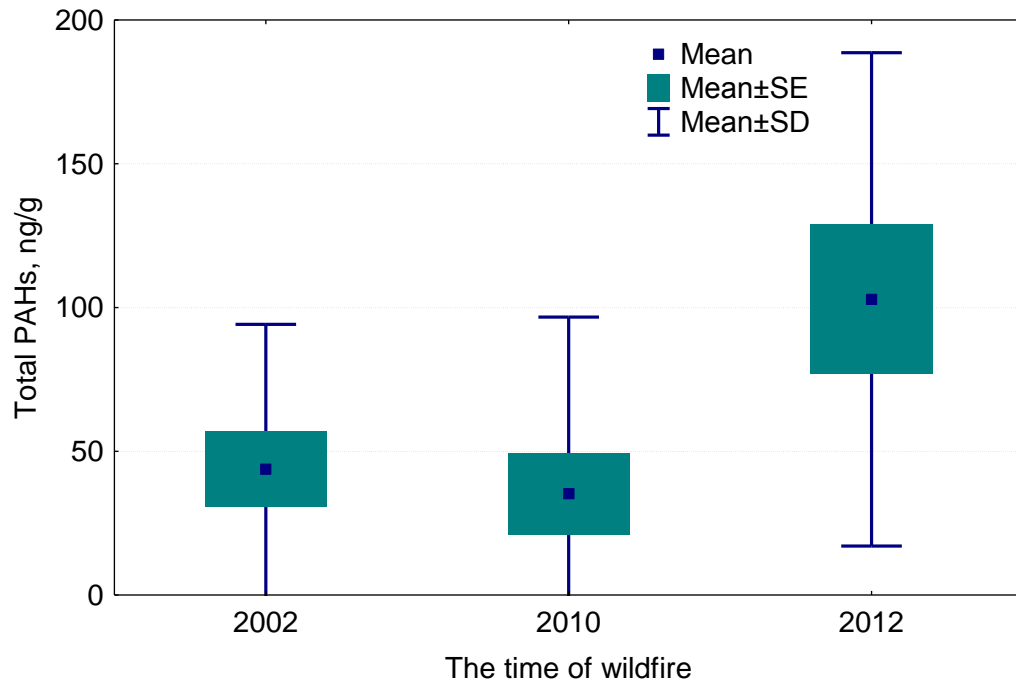
Fig. 11. The categorized box and whisker plot for total PAHs in different horizons of podzols (pits 2, 3, 4, 5, 6). The number of sample replicates is as follows: O:6; Cpir:4 Apir:3; A:3; Hpir:3; Ha:6; E:9; EB:5; Bhs:15; BC:4. Horizons Bh, Bs, and Bhs were combined for this analysis into Bhs.



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Fig. 12. The cluster analysis (complete linkage; 1-Pearson  $r$ ) for PAHs groups in the investigated soil samples.

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4 Fig. 13. The categorized box and whisker plot for total PAHs in horizons Hpir, Apir, O and Cpir  
5 of soils affected by fires of 2002, 2010, 2012 (pits 2, 3, 4, 5, 6, 7, 8, 9, 11, 12). The number of  
6 sample replicates: 2002– 15, 2010 – 19, 2012 – 11.

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