Artículo de investigación

THE BIOGENIC AND PYROGENIC FACTORS OF HEAVY METAL AND RADIONUCLIDE ACCUMULATION IN THE PEAT SOIL OF THE CENTRAL PART OF THE EAST EUROPEAN PLAIN

БИОГЕННЫЙ И ПИРОГЕННЫЙ ФАКТОРЫ АККУМУЛЯЦИИ ТЯЖЕЛЫХ МЕТАЛЛОВ И РАДИОНУКЛИДОВ В ТОРФЯНИКАХ ЦЕНТРА ВОСТОЧНО-ЕВРОПЕЙСКОЙ РАВНИНЫ

FACTORES DE ACUMULACIÓN BIOGÉNICA Y PYROGÉNICA PARA METALES PESADOS Y RADIONÚLIDOS EN LAS PIEDRAS DE LA LLANURA DEL ESTE EUROPEO

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Abstract

The article deals with the evaluation of the contribution of peat deposition (a natural process causing long-term removal of toxic elements from the migration streams) to the natural capability of the Meshchera lowland landscapes to act as the buffer with respect to the anthropogenic input of heavy metals (HM). It was found that even despite the prevalence of peat soil, it plays a minor role in the heavy metal assimilation capacity of the landscapes, compared to the accumulation of heavy metals by wood and bark, which is 5 to 9 times higher, and to the involvement of heavy metals in the recyclic flows, which is 70 to 150 times higher. In the conditions of the low trophic level of sandy substrates in Meshchera, the mobile forms of heavy metals are extensively involved in the biogenic migration, and peat accumulates them residually, in small amounts. The highest probability of accumulation in peat is typical of slow-moving toxic agents (Pb), while the lowest one is typical of highly mobile biophiles (Zn). The main factors of the vertical distribution of heavy metals in peat strata are their accumulation in the boundary layers, i.e. pyrogenic and tree-stump horizons (2010, the Early Subatlantic, the Subboreal, and more ancient ones), including that in the course of vertical water migration. All of the above factors significantly impede the use of

Аннотация

Статья посвящена оценке вклада торфяных аккумуляций (природного процесса, обеспечивающего удаление токсичных элементов из миграционных потоков на длительное время) в естественный ассимиляционный потенциал ландшафтов Мещерской низменности по отношению к антропогенному поступлению тяжелых металлов (ТМ). Установлено, что даже несмотря на широкое распространения болотных ландшафтных комплексов в Мещере, торфяные почвы играют незначительную роль в ассимиляции тяжелых металлов по сравнению с накоплением ТМ древесиной и корой (в 5-9 раз выше накопления в ежегодно нарастающем слое торфа) и с вовлечением ТМ в рециркуляционные потоки (в 70-150 раз выше). В условиях низкой трофности песчаных субстратов в Мещере подвижные формы тяжелых металлов активно участвуют в биогенной миграции, а их накопление в торфе идет «по остаточному принципу» и в целом невелико. Наибольшей вероятностью накопления в торфяниках отличаются малоподвижные токсиканты (Pb), наименьшей – подвижные биофилы (Zn). Основные факторы вертикального распределения ТМ в торфяных толщах –

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peat deposits in the Polesye-type landscapes as the natural site for studying aerial technogenic pollution. Fires in forest and peat areas release up to 43% of radiocesium deposited in peat into the atmosphere along with the combustion gases, while natural radionuclides remain relatively stable.

Keywords: biogenic, pyrogenic, contribution, peat deposition, landscapes, soil

накопление на пограничных горизонтах, пирогенных и пнёвых (2010 г., раннесубатлантических, суббореальных и более древних), в том числе в процессе вертикальной водной миграции. Все это существенно осложняет использование торфяников Мещеры в качестве природного планшета при изучении аэротехногенного загрязнения. При лесо-торфяных пожарах в атмосферу с продуктами горения улетучивается до 43% накопленного в торфе радиоцезия при относительно стабильности естественных радионуклидов.

Ключевые слова: торф, тяжелые металлы, радиоцезий, естественные радионуклиды, пирогенные горизонты, аэротехногенное загрязнение, критические нагрузки, Восточно-Европейская равнина.

Resumen

El artículo trata sobre la evaluación de la contribución de la deposición de turba (un proceso natural que causa la remoción a largo plazo de elementos tóxicos de las corrientes migratorias) a la capacidad natural de los paisajes de las tierras bajas de Meshchera para actuar como amortiguador con respecto a la contribución antropogénica de Metales pesados (HM). Se encontró que incluso a pesar de la prevalencia del suelo de turba, desempeña un papel menor en la capacidad de asimilación de los metales pesados de los paisajes, en comparación con la acumulación de metales pesados por la madera y la corteza, que es de 5 a 9 veces mayor, y para la participación de metales pesados en los flujos de reciclaje, que es de 70 a 150 veces mayor. En las condiciones del bajo nivel trófico de sustratos arenosos en Meshchera, las formas móviles de los metales pesados están ampliamente involucradas en la migración biogénica, y la turba las acumula de forma residual, en pequeñas cantidades. La mayor probabilidad de acumulación en turba es típica de los agentes tóxicos de movimiento lento (Pb), mientras que la más baja es típica de biófilos altamente móviles (Zn). Los principales factores de la distribución vertical de los metales pesados en los estratos de turba son su acumulación en las capas límite, es decir, los horizontes pirogénicos y de tocón de árbol (2010, el Subatlántico Temprano, el Subboreal y los más antiguos), incluso en el curso de Migración vertical de agua. Todos los factores anteriores impiden significativamente el uso de depósitos de turba en los paisajes de tipo Polesye como el sitio natural para estudiar la contaminación tecnogénica aérea. Los incendios en áreas de bosques y turba liberan hasta el 43% del radiocesio depositado en turba en la atmósfera junto con los gases de combustión, mientras que los radionúclidos naturales permanecen relativamente estables.

Palabras clave: biogénico, pirogénico, contribución, deposición de turba, paisajes, suelo.

Introduction

The study of peat deposition areas is of scientific and practical interest due to the capability of peat to deposit atmospheric fallouts, including the fallouts of technogenic pollutants (Mezhibor, 2009). Of particular importance is the capability of peat deposits to remove large amounts of toxic agents from the biological cycles, thus improving the natural capacity of landscapes to act as the buffer against pollution and save nature protection resources to a certain degree. This aspect is being elaborated as part of the critical loads methodology (UNECE Convention on Long-Range Transboundary Air Pollution, 2004). Besides, a number of studies have considered peat as a natural site allowing to estimate the rate and volume of atmospheric fallouts and their change proportionally to the growth of the anthropogenic burden in the twentieth century (Badenkova, 1982). At the same time, some authors often proceed from the possibility of long-term preservation of the dust particles that came into peat from the atmosphere (Boyarkina et al., 1993; Shotyk, 1996).

The main objectives of this research were:

- to study the peculiar features of the accumulation of low-clarke elements, heavy metals and radionuclides, in peat deposits surrounded by substrates with a low trophic level (mostly quartz sand);
- to determine the contribution of peat depositions in the natural geochemical resistance of landscapes to the anthropogenic chemical pollution;
- to evaluate the factors of vertical distribution of elements in peat strata under the influence of biogenic migration, radial water removal, technogenic pollution, and fires during the arid periods of the Holocene;
- to evaluate the conditions of accumulation of toxic and radioactive elements with different geochemical and landscape properties in peat deposits.

Objects and methods

The study was carried out in the landscapes of the Meshchera natural province of the mixed forest area, located in the center of the East European Plain (Fig. 1). This area has some peculiar natural features. The originally low altitude and tendency to the contemporary tectonic subsidence have determined the accumulation of the re-washing out and re-sedimentation of the Eurasian glacial sediments within the Meshchera lowland, mostly during the Moscow glacial stage (alternative names in other regions – Riss II period, Saale glaciation, Wolstonian stage, Illinoian stage). The landscapes of the research area are of the so-called “Polesye-type”, widely spread on the lowland plains of Europe (former periglacial lowlands), from the north of Germany to the Cis-Ural region.

The Quaternary deposits in Meshchera are 15 to 60 m thick and are mostly represented by quartz sand and large-size aleurites. They have a very poor capacity of cation exchange and low reserves of weatherable minerals. As a result, these subtaiga ecosystems of the Meshchera lowland exist in the conditions of a permanent lack of mineral nutrition elements. Inevitably, this causes rather specific conditions for the formation of the chemical composition of the peat deposits.

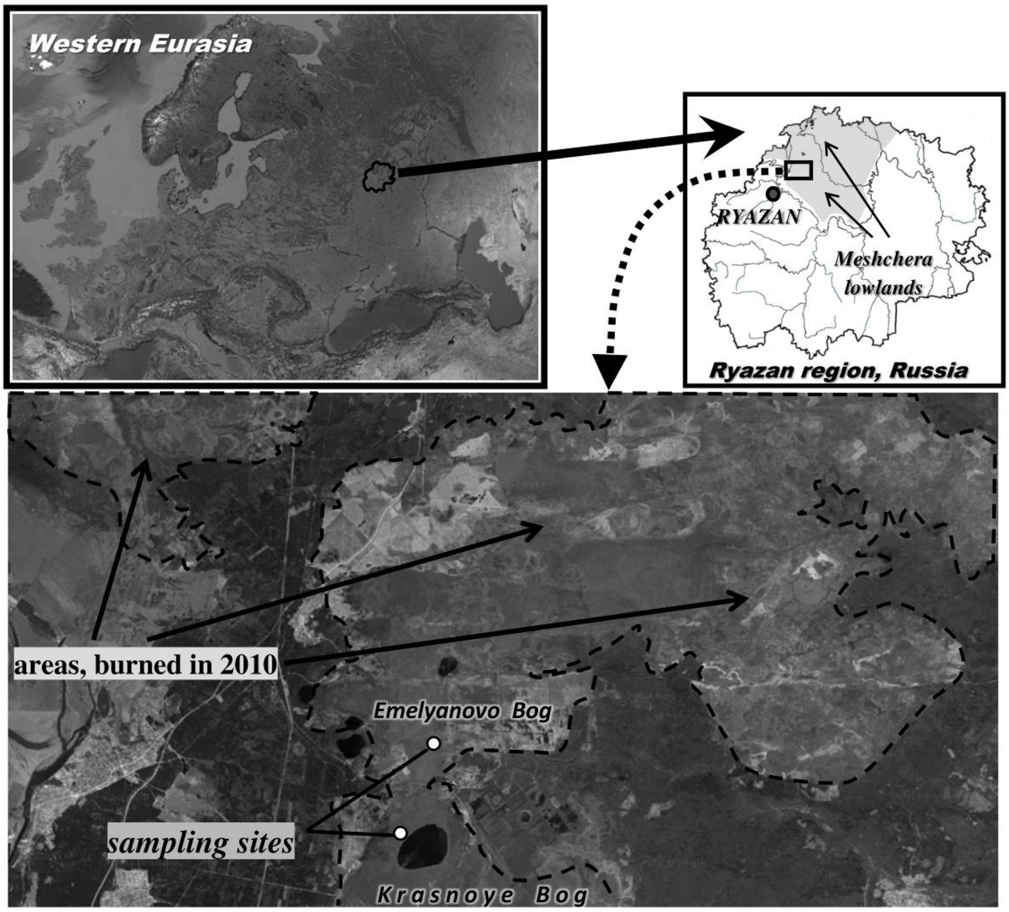

Fig. 1. Localization of the study área

The deposition of fluvioglacial and alluvial sand deposits leveled out the inhomogeneity of the pre-Quaternary period, and for this reason the Meshchera lowland has a non-contrasting relief profile. This circumstance, aggravated by the tectonic subsidence and the physical properties of sand determined the poor water exchange and wide propagation of wetland landscapes. The localization of the largest lakes and peatlands is due to the geological structure (because of the low-contrast profile of the modern relief, mainly due to the configuration of the buried pre-Quaternary erosion cuts and buttes). The Krasnoye bog, being one of the main objects of our study, can serve as an example.

The study area was severely affected by large-scale forest and peat fires in 2010 (Fig. 1 and 2) and is currently undergoing early stages of post-fire succession (Fig. 3).

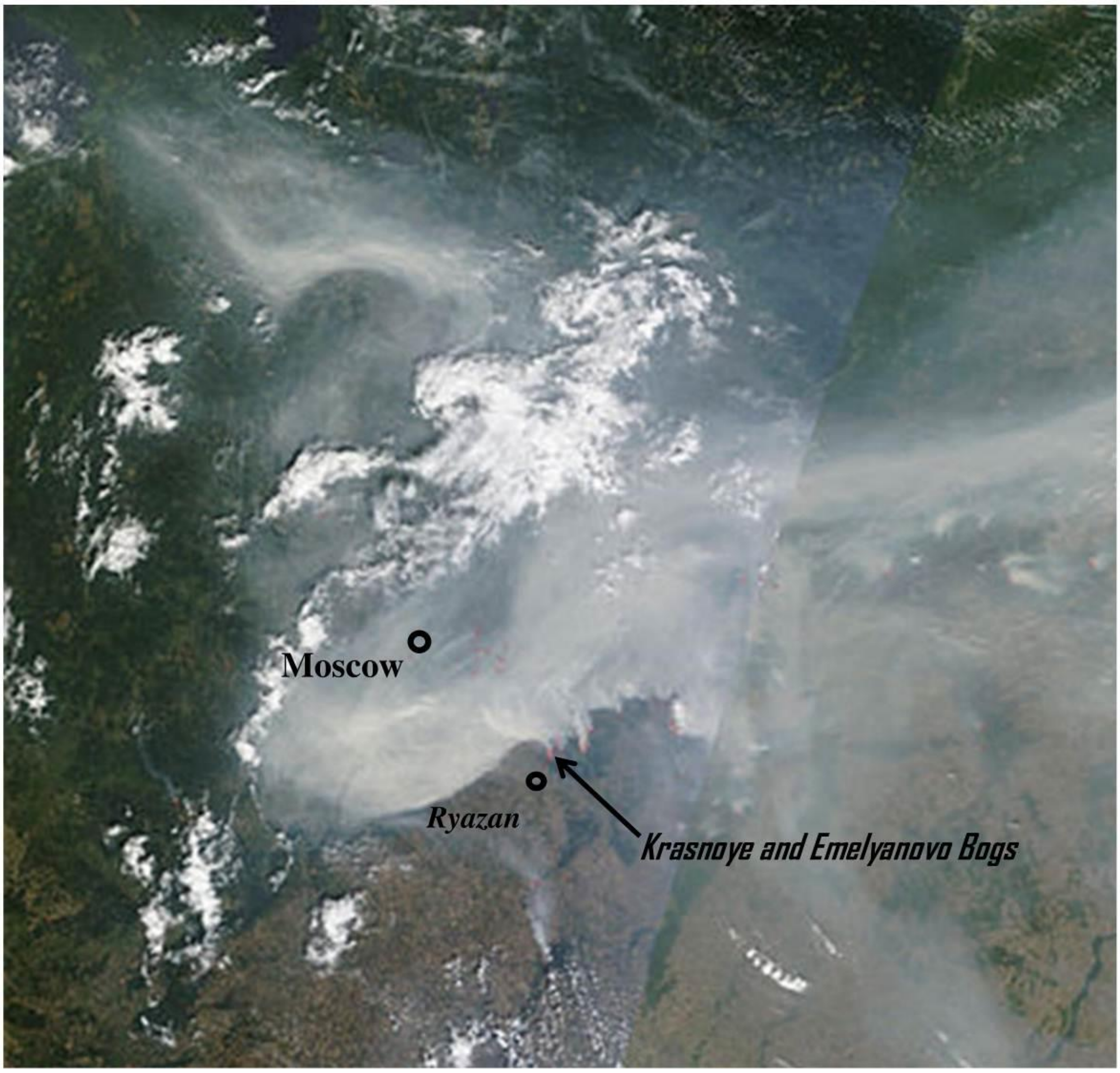

Fig. 2. Smoke plumes and pyrocumulus clouds from intense wildfires, raged in Central Russia (especially in Meshchera lowlands), seen from NASA’s Terra satellite on August 4, 2010

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Fig. 3. Recovery succession in the ecosystems of Krasnoye bog after the wildfire of 2010 (in the foreground there is a part of the peatland drilling core, divided into fragments of 10 cm)

Peat deposition, being a component of the ecological-geochemical potential of the subtaiga landscapes of Meshchera, was evaluated based on the methodology of critical loads (CL). CL is the highest possible input of a pollutant into the ecosystem that does not violate its structure or reduce its performance over a long period (at least 100 years) (Krivtsov, 2011; UNECE Convention on Long-Range Transboundary Air Pollution, 2004). In this case, the main receptor is the state of the ecosystem, rather than human health. When calculating the critical burden of heavy metals, we used the mass-balance equation, which despite its apparent simplicity fully complies with the basic principles of this methodological approach:

$$CL = Mupt + Mleach + MSD(acc) + MDGP, \qquad (1)$$

where Mupt is the adsorption of a certain element M by vegetation, Mleach is the leaching out with the surface or subsurface runoffs, MSD(acc) is the accumulation in soil in the immobilized forms, MDGP is the absorption by the yearly growing peat (only for hydromorphic ecosystems).

As is seen from the equation (1), the aggregate input of the exogenous toxic agent must be compensated by the natural mechanisms of its remediation, which would remove the excess of the element from the functioning processes. There are four of such processes in the forest ecosystems of Meshchera: the long-term accumulation in the increment of wood and bark; the leaching out by the surface and sub-surface runoff; and the allowable accumulation in soil, as well as the process of accumulation in the yearly incrementing peat layer for wetland ecosystems (for a number of reasons, the latter process should be considered separately from MSD(acc)). The main objective of our research was to evaluate the possible scope of such accumulation.

We used the drilling data (the archived materials of the Ryazan branch of the Regional Geological Information Foundation) and topographic maps of the 1:25,000 scale. The share of heavy metals in the peat deposits, biological objects and natural water reservoirs was determined by the atom absorption method (flame version) using the microwave system of acidic mineralization of samples. The specific activity of 137Cs and natural radionuclides was determined with a gamma-ray scintillation spectrometer MKC-01A MULTIRAD-gamma and the Progress software suite. We determined the weight percentage of the mineral components in organic soil and biological objects by ashing in a muffle furnace at a temperature of 4500C (in several steps where necessary).

Results and discussion

As seen in Fig. 4, the Krasnoye bog, as a local ecosystem, was formed in the top part of the Belsky buried butte massif comprised of limestone, with numerous erosion cuts of lower order that were formed before the Jurassic (Zheleznova, Tobratov, 2017). After the regression of the Mesozoic seas, these cuts recovered in general. The existence of erosion cuts buried under the layer of the Early Quaternary sand, was the original cause of the developed waterlogging and formation of thermokarst basins in the Valdai (alternative names in other regions – Würm, Weichselian, Devensian and Midlandian, Wisconsin glaciations). Later, in the Holocene, these basins, originally occupied by lakes, turned into wetlands, mostly bogs, due to the near-top location with respect to the roof of the Belsky butte. For this reason, the Krasnoye bog's peat has a low content of ash: 2.5–3.0%.

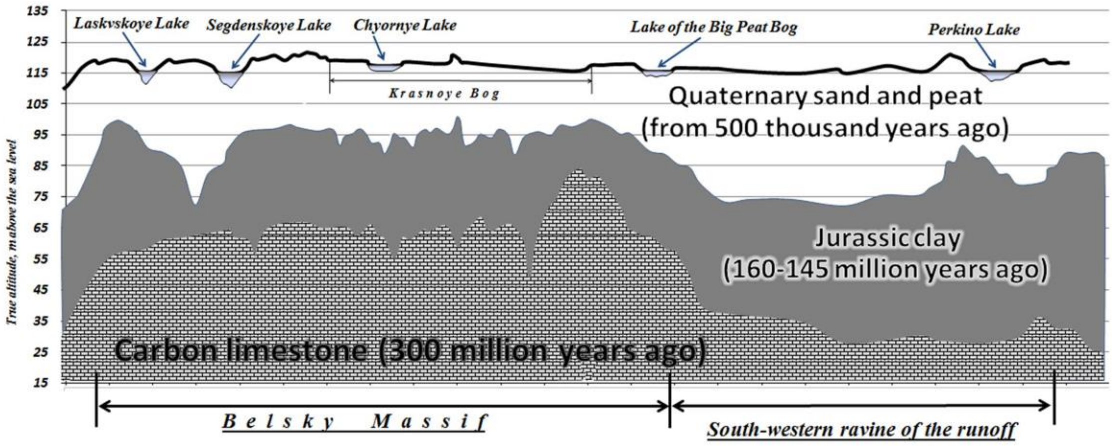

Fig. 4. The geological structure of the exploration área

We estimated the peat growth rate by means of radiocarbon dating of the Emelyanovo bog peatland (1.7 km to the north from the Krasnoye bog). According to the dating results, the age of the peat at the depth of 45.5 cm is 2085±51 years (IGAN-3877, calibrated data). This testifies to the medium rate of peat accumulation during the Subatlantic period of the Holocene, about 0.218 mm per year. These data are rather consistent with the research results of earlier studies of Moscow state University's landscape laboratory (Abramova, 1999). This rate is just 40% of the rate in the bogs of Belarus (Kozlov, 2011) due to the more expressed continental climate in Meshchera. For example, in the south of West Siberia, the rate does not exceed 0.16 mm per year, decreasing to 0.10 mm per year in the north-taiga area (Moskovchenko, 2006). Thus the peatland growth rate is predictably dependent on the continentality of the climate. Therefore, the center of the East European Plain has a unique status in the system of climatic gradients in these terms (Fig. 5). In our opinion, the main factor limiting the growth of peat in Meshchera, is not the lack of climatic thermal resources (as in Western Siberia), but the high probability of advection from the arid subtropics, which significantly increases the risk of wildfires (Fig. 2).

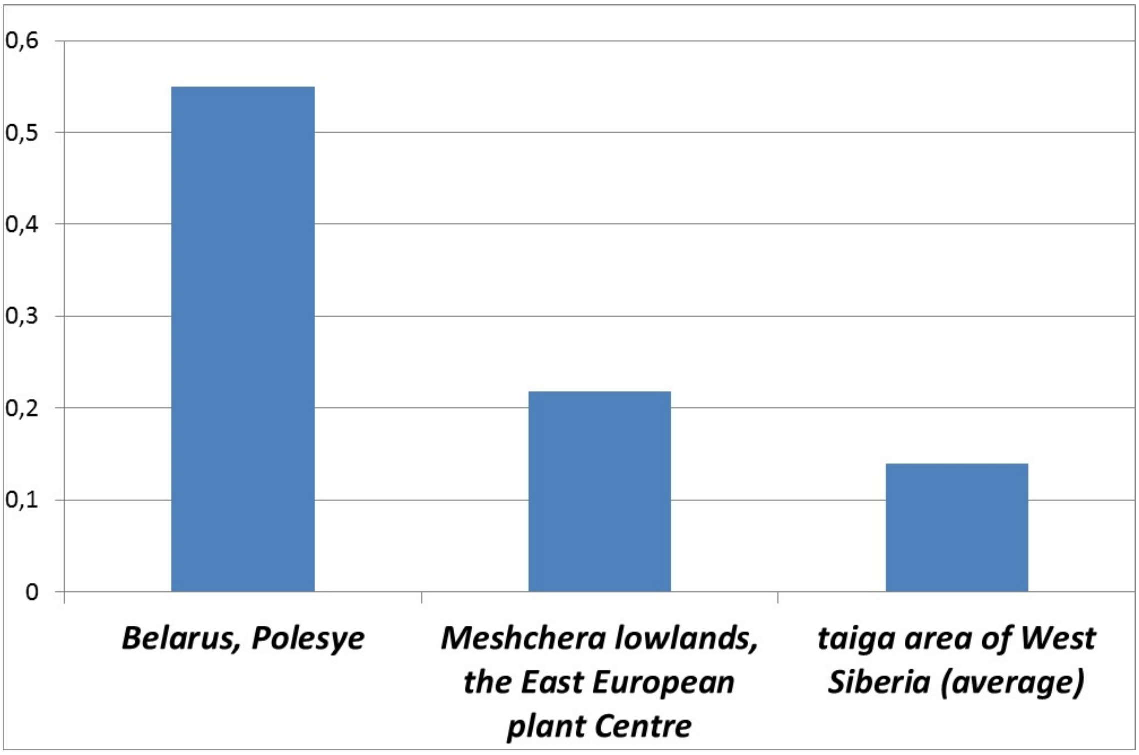

Fig. 5. The current average peatland growth rates depending on the continentality of the climate (mm per year)

The indicated rate was taken as the same for all bogs and wetlands in the exploration area. Using the taxation data, we determined the area of hydromorphic types of forest site conditions (according to P.S. Pogrebnyak's methodology (1968)) with peat soils. The contribution of peat deposition into the biogeochemical processes in the ecosystems of South Meshchera was estimated for each forest compartment by the following formula:

$$DGP = CHMg.n\text{-}s \times IP \times \rho P \times 10; \quad (2)$$

where DGP is the heavy metal deposition in the growing peat of the bog soil, g/ha*year, CHMg.n-s is the average concentration of gross non-silicate (extractable by aqua regia) forms of heavy metals in the surface layers of the bog soil in the exploration area, mg/kg (determined experimentally, and for Cu, Zn, and Cd equal to 4.64; 23.17 and 0.38 mg/kg, accordingly); IP is the layer of yearly increment of peat (0.218 mm); ρP is the density of the peat skeleton, kg/dm3 (determined experimentally, and equal to 0.182 kg/dm3 on the average, ranging between 0.060 and 0.350 kg/dm3); 10 is the conversion factor for the given area.

Table 1 shows the results of calculation compared to the biogeochemical parameters of the forest ecosystems of Meshchera. Its analysis allowed us to make two important conclusions. Firstly, the weight of the organic matter yearly deposited in the growing peat deposits is insignificant compared to the biological production of the tree layer and underwood: it makes only 1.5% of these products and 1/12 of the yearly increment of stemwood with bark, to which it can be compared by their contribution to the geochemical buffering capacity of the landscapes.

Table 1. The biological productivity of forest ecosystems of South Meshchera, the involvement of heavy metals in the productive processes and long-term immobilizatio

	Layers, fractions of the phytomass	Increment, m/ha×year (1) and % (2)		Heavy metals in the products, g/ha×year (1) and % (2)					
				Cu		Zn		Cd	
		1	2	1	2	1	2	1	2
Tree layer	**Aboveground part**	**3.740**	**44.9**	**18.382**	40.4	**208.084**	**46.5**	**1.148**	**29.6**
Tree layer	*including in stem wood and bark*	1.451	17.5	2.762	6.1	24.916	5.5	0.287	7.4
Tree layer	*including in needles and leaves*	1.606	19.3	11.769	25.9	165.927	37.0	0.591	15.2
Tree layer	**Underground part**	**2.374**	**28.5**	**11.328**	**24.7**	**121.662**	**27.2**	**1.407**	**36.3**
Tree layer	*including in tender roots*	2.152	25.9	10.683	23.5	116.476	26.0	1.347	34.7
Underwood, the grass-bush and moss-lichen layers		2.086	25.1	15.288	33.6	115.354	25.8	1.279	33.0
Average deposition in the yearly incremented peat layer (0.218 mm)		**0.121**	**1.5**	**0.563**	**1.2**	**2.811**	**0.6**	**0.046**	**1.2**
Total for phytocenosis		**8.320**	**100**	**45.471**	**100**	**447.911**	**100**	**3.880**	**100**

Secondly, the idea for the relative share of bioproduct fractions in the migration streams of heavy metals allows comparing their contribution to the biological productivity per cent on the one hand, and to the metal accumulation rate on the other hand (these data are provided in columns 2). If the percentage of contribution to the overall biological productivity is greater than that to the migration streams of a certain metal, such a fraction does not specialize in depositing the metal. And on the contrary, with an inverse ratio of percentage, the fraction is the biological accumulator of the element. In case of a relative percentage equality, the corresponding fraction accumulates the element passively in general, without any efforts to diffuse it, or, on the contrary, selectively accumulates it.

A typical example is the fraction of photosynthetic organs: as shown in Table 1, its share in the total yearly product makes less than 20%, while the percentage of heavy metal deposition is significantly higher. For example, biophile copper and zinc are typically selectively deposited in needles and leaves (26–37% of the total amount involved in the production processes), and toxic cadmium is diffused (15%, compared to 19.3%). In the tender root fraction, the biophiles, copper and zinc, on the contrary are deposited passively in general, while cadmium, being a toxic element, is selectively deposited on the root barrier (Zheleznova et al., 2017).

Table 1 makes it evident that due to the low ash content, wood accumulates smaller amounts of elements: the percentage of accumulation of all the mentioned heavy metals, despite their biophile or toxic nature, by the diametrical increment of stems was only about one third or even less of the total amount of products of the given fraction (5.5–7.4% vs. 17.5%). Consequently, the actual contribution of stemwood increment into the natural geochemical buffering capacity of the landscapes is, unfortunately, a fraction of the values we could expect if we knew just the general productivity. This is due to the low ash content in the wood. However, different elements display their geochemical features even with this negative background: wood ash accumulates the least amount of zinc, the highest amount of cadmium, and the average amount of copper. This is due to the features of transport of these elements in the conductive tissues of stems (Zheleznova et al., 2017).

A similar comparison of the percentage for peat depositions testifies to the fact that their contribution to the rate of heavy metal

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immobilization is below the expected one (despite the fact that the expected value is already negligibly small). Thus, the amount of elements deposited in the ash part of peat is smaller than could be expected based on the scope of yearly deposition, which results in the even smaller contribution of peat deposition in the assimilative capacity of the landscapes. This contribution is just 11 to 20 % of the immobilizing capacity of wood stems despite the above-mentioned low capacity of metal deposition. We should also note that the observed differences between the elements under study, related to their affinity to peat deposition (1.2% at maximum for copper and cadmium and 0.6% at minimum for zinc) are also not accidental, similarly to stem wood.

As follows from Fig. 6, the role of peat accumulations as components of HM's critical loads on Meschera ecosystems is extremely insignificant, the contribution of accumulation in stem tissues and removal with surface waters are many times greater. Only for copper the contribution of peat accumulation in sanation capability of the ecosystems reaches any noticeable values and is comparable with immobilization in bark, the reasons for this are discussed below. It should be noted that there is an excess of Cd (the imbalance is equal to +55.7%) that is due to the high level of its anthropogenic supply in Central Russia, and its deposition in the growing peat is not able to reduce the above excess.

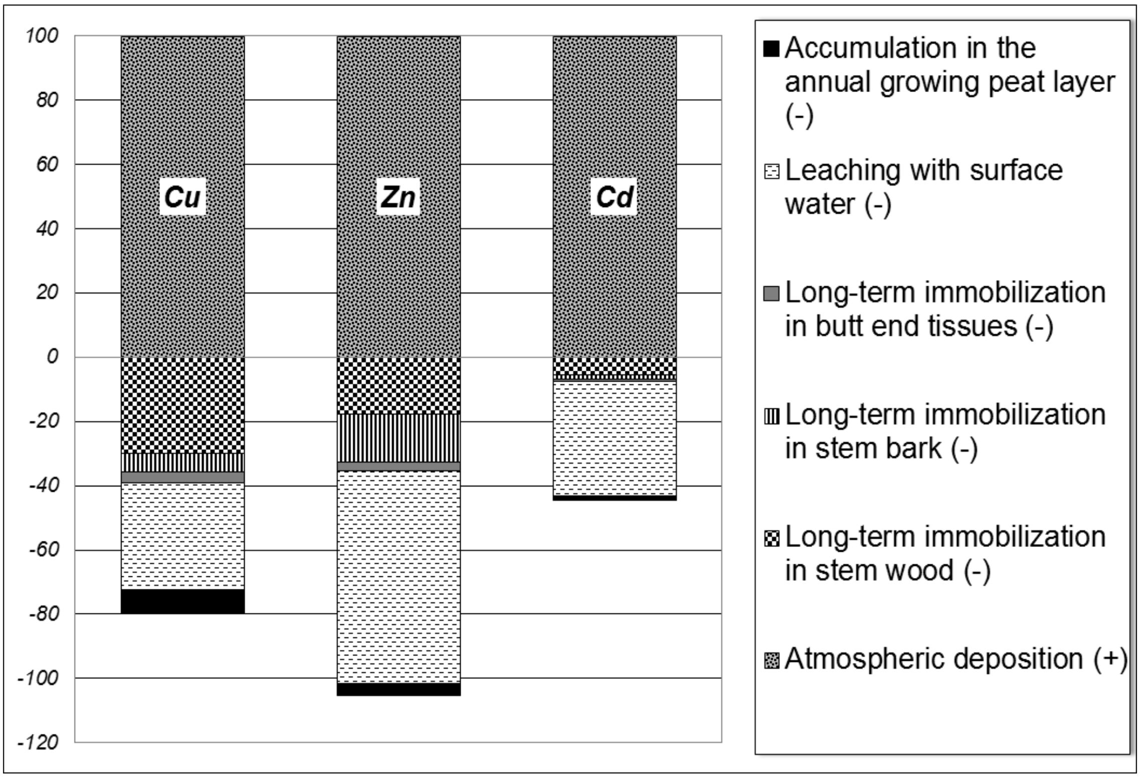

Fig. 6. Balance of heavy metals in forest ecosystems of southern Meshchera (percentage of income balance sheet item – annual atmospheric deposition)

The cause of a much lower deposition of heavy metals in peat ash and the cause of different affinity of the metals to peat accumulation are clarified in Figure 7, showing the regional average concentrations of elements in the mineral state of two genetically interrelated biological objects: yearly incrementing peat and peat-forming vegetation (mostly trees).

As displayed by the provided data, the maximum, nine-fold difference in the concentration of the ash part of plants and peat are typical of zinc, being a typomorphic element of zonal humid landscapes. The great demand of the subtaiga ecosystem plants in this particular biophile element results in its extraction from any deposition and migration environments of the landscape and its deposition in the biomass. The high mobility of zinc in natural solutions, its affinity to forming complexes with highly-molecular organic matter and to the specific absorption by minerals contribute to this phenomenon (Ladonin, Margolin, 1997).

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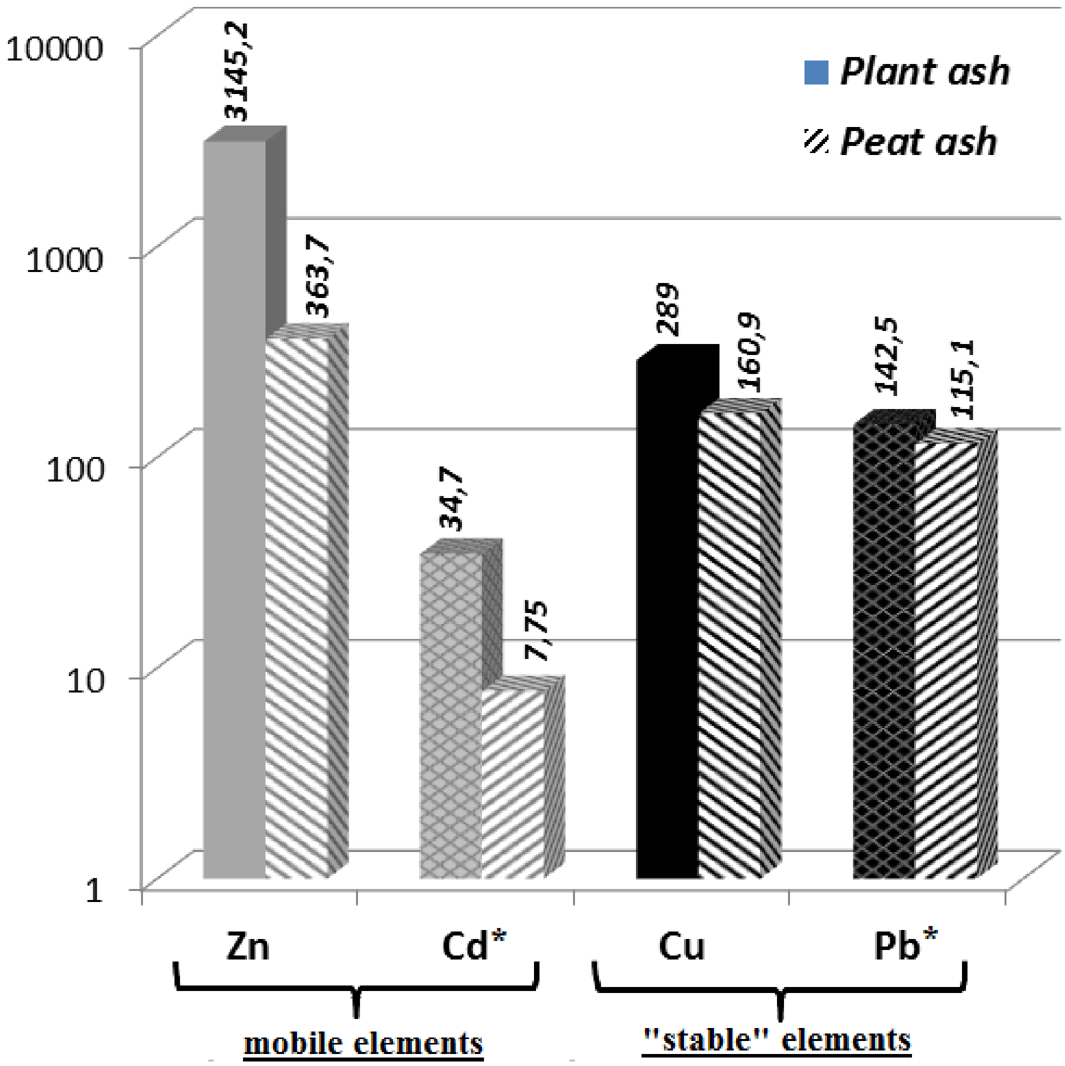

**toxic elements with an almost complete lack of biological functions*

Fig. 7. The differences in the concentrations of heavy metals in the ash of peat-forming plants and peat ash (mg/kg)

Cadmium is a geochemical analog of zinc. It is similar to zinc not only by its valence shell, but also by its high mobility and proneness to the ionic form of migration. However, there are significant differences between these elements: cadmium is much more mobile than zinc and has almost zero biophile property, unlike zinc. In case of biological absorption, cadmium often follows the same path as zinc, but it is absorbed passively (Zheleznova et al., 2017). This is why, similarly to zinc, the cadmium content in the ash of peat and peat-forming plants also has noticeable differences: this element is deposited in the incrementing part of plants more intensely than in growing peat. However, these differences are just half of those of zinc. Even despite the high hydrochemical mobility of cadmium, the difference is just 4.4-fold (compared to the 9-fold difference of zinc). Consequently, the overall mobility is not the only factor of metal migration and deposition: the less biophile elements deposit less intensely in plants and relatively more intensely in peat.

Copper and lead comprise a special group of elements, as they are fixed more stably by mineral and organic substrates due to the high affinity to specific absorption. These elements are especially efficiently immobilized by highly-molecular organic matter (Ladonin, Margolin, 1997). For this reason, peat soil has the conditions for their efficient fixation, which allows us to expect the least possible difference between their concentrations in the ash of peat and plants. However, one should take into account that the biophile properties of copper and lead are rather different. As a result, the difference between Cu and Pb deposition in ash is only a fraction of the difference between Zn and Cd, but copper demonstrates its specific properties as a biophile element in such an environment. For copper, there persists a noticeable difference between its deposition in peat and plants, being up to 1.8 times higher in plants. For Pb, which is not biophile, like Cd, the said difference decreases, but does not disappear completely, and is 1.25 times higher in plants.

Thus, the deposition of elements in peat ash is a probabilistic process and is determined by the degree of the hydrothermal mobility of the element on the one hand, and by the plant's demand for the element on the other hand. The higher the mobility and the biophile property of the element, the lower the probability that it will be exposed to long-term removal from the biogeochemical processes and be preserved in the mineral state of the incrementing layer of peat for decades. A typical example of such an element is biophile and typomorphic (in subtaiga landscapes) zinc. Zinc typically demonstrates intense deposition in the biotic block to the detriment of deposition in peat. On the other hand, the low migration capability and non-biophile nature of the element on the contrary contribute to its deposition in peat. Lead is the most indicative of this phenomenon. In this case, the factor of hydrochemical mobility and the biophile nature equally impact the element accumulation in peat ash.

It is interesting to note that even toxic and slow-moving lead has been observed in higher concentration in plant ash compared to peat ash. For other elements, the difference is even larger as they are more biophile and/or mobile. Consequently, in the conditions of extremely scarce natural substrates of Meshchera in terms of nutrient elements, plants seek these elements intensively, thus significantly hindering their burial in the deposit substrates, including peat. In these conditions, the chemical composition of peat ash is formed residually: it is saturated with the most stable and least biophile elements, while the mobile biophiles are selectively deposited in the incrementing vegetation. The reserve of the latter for a long period remains suspended in the biological cycles and is not removed from the landscape functioning processes. For slow-moving toxic agents, such as lead, the process of removal and long-term deposition in the peat layer is more probable. But even in this case, the process of biological absorption turns out to be more intensive, compared to immobilization in the peat substrate.

Consequently, the peat deposits of Meshchera accumulate only an insignificant part of the elements that have not been involved in the biogeochemical processes and vertical water migration. Deposition in peat is a considerably less significant process than the selective activity of organic matters and leaching. The root cause of this phenomenon is the extreme leanness of the soil and soil-forming rocks in Meshchera in terms of the migrating forms of the elements, as well as the weatherable minerals. In these conditions, any mineral component of the peat strata is exposed to active transformation and loses a major part of elements, in case they are capable of biogenic and water migration. Only the least mobile and biophile exogenous elements can be deposited, but even they are mostly passively involved in biological absorption. Consequently, the high extent of preservation of the exogenous dust particles in the peat of the Meshchera lowland is highly unlikely: they are most probably exposed to intensive geochemical transformation resulting in the removal of the migrating form of the elements. Due to this, the role of the peat in Meshchera as a natural site, where it is possible to study the time dynamics of atmospheric fallouts, is also quite theoretical. In other natural areas with higher trophicity of substrates and higher ash content of peat deposits, the situation can be completely different.

We considered the patterns of vertical distribution of elements in Meshchera peat deposits. The main object of the study was the drill core in the center of the Krasnoye bog: the maximum drilling depth was 1.7 m. The structure and chemical composition of the peat layer are rather inhomogeneous and have a complicated history of development during the Holocene. The main factors disturbing the homogeneity of the peat deposits are the surfaces of relapsing development (the boundary horizons) that mark the arid periods of the Holocene, when the growth of peat deposits was suspended. In Meshchera, there are two types of such layers: the pyrogenic and tree-stump layers.

The upper part of the peat deposits that can be studied by manual drilling and profiling, is dominated by the pyrogenic horizons, the layers of ash and coal buried under the latest peat deposits and emerged as the result of large-scale fires. We studied and dated the best morphologically defined horizons, as well as determined their typical deposition depth (Fig.

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8). We discovered that all of them were confined to the xerothermic climatic phases of the Holocene. Consequently, pyrogenic destruction of Meshchera peatlands is a phenomenon quite typical for this region, occurred repeatedly, and the 2010 wildfires are not a unique event.

Their most significant horizon is located at a depth of 127 cm (this depth reduced to 98 cm after a fire in 2010). It was formed during the xerothermic stage of the Subboreal period (4600 years ago). At that time, a natural fire destroyed the layer of peat that had been forming for a thousand years before the cataclysm happened. The event is evidenced by the differences in the radiocarbon dates below and above the said horizon (Fig. 8).

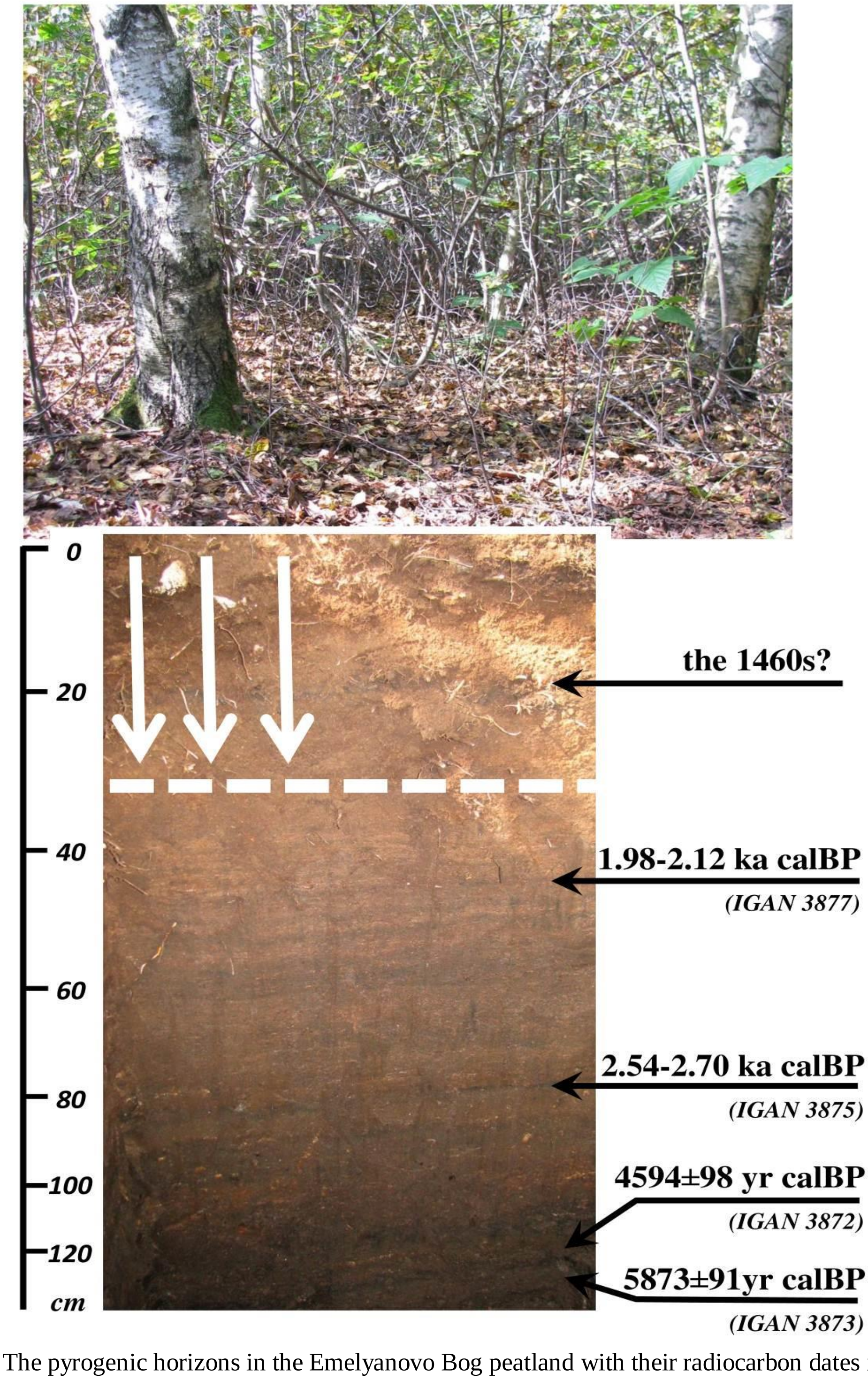

Fig. 8. The pyrogenic horizons in the Emelyanovo Bog peatland with their radiocarbon dates indicated (the picture was taken in 2009)

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Note: the dashed line indicates the current surface of the peat deposit after the large-scale fires of 2010 (the pyrogenic decrease of the peatland was 35 cm; the layers of peat that had accumulated for the previous 1200 years were destroyed).

The depth and age of the pyrogenic horizons in Meshchera determined by us are consistent with the data of other researchers (Aleksandrovskiy, Aleksandrovskaya, 2005) and do not contain any information contradicting the known facts. However, we believed it to be essential to answer another question: What is the specific geochemical feature of these horizons, what is the scope of inhomogeneity that they cause in the chemical composition of the peat strata, and what are the factors of such inhomogeneity?

The largest tree-stump horizon is located at a depth of 1.7–2.3 m beneath the surface of the Krasnoye bog peatland (Fig. 9). This horizon prevented us from a deeper manual drilling and limited us to the above-mentioned depth. A radiocarbon dating and micromorphological study of vegetation tissues showed that this horizon was represented only by roots and basis of common pines, and was formed during the chilly but dry Late Boreal era (9200–9300 years ago). A similar, but less significant and less extended horizon is confined to the depth range of 55–70 cm and corresponds to the warming in the beginning of the Subatlantic period of the Holocene (about 2300 years ago).

Fig. 9. The tree-stump horizon at the Krasnoye bog was formed during the era of the Late Boreal warming, 9230±110 years ago (IGAN 3878)

It should be mentioned that in 2010, the modern pyrogenic horizon was formed on the surface of most explored peatlands, and that it undergoes intensive geochemical transformation currently. As evidenced by the data of Table 2, the microelement composition of ash and coal of the modern pyrogenic horizon is not unique and is mostly similar to the composition of the more ancient horizons, particularly of the Subboreal ones. The most typical example in this case is copper, which is highly stable in organic soil. As shown in Table 2, several deposition maximums are noticed on the vertical profile of the copper concentrations in peat ash, with a double concentration of Cu, compared to the average values. The most pronounced maximums are typical of the modern surface of the peatland and to the depth of 120 cm, which corresponds to the Subboreal boundary horizon. The less pronounced maximums of the copper concentrations are located at the typical depths of the tree-stump horizon propagation. Consequently, pyrogenic concentration is the main factor of deposition in peatlands for slow-moving copper, while biogenic deposition is a more intense process compared to it.

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At the same time, zinc, being a biophile typomorphic element of acidic humid landscapes, is the most intensively accumulated in the tree-stump horizons, unlike copper. Among the pyrogenic deposits, the most considerable ones are the horizons of 2010 and of the Subboreal xerothermic era. Similarly to copper, they are rather comparable by the concentration of zinc.

The regularities of vertical distribution of lead are more sophisticated. In particular, it is being actively leached out from the pyrogenic-peat horizon of 2010 currently, as a result of which the more ancient pyrogenic deposits, especially the Early Subatlantic ones, are more expressed. The biogenic depositions of lead in the tree-stump horizons are noticeable in the lower and middle parts of the peatland; while the pyrogenic depositions are more pronounced in the upper part. Analyzing the vertical distribution of lead in the Krasnoye bog peatland, one can assume that this element is capable of more noticeable intraprofile migration (apparently, in the composition of highly molecular organo-mineral complexes (Ladonin, Margolin, 1997)), while the ancient pyrogenic formations, particularly the ones close to the surface, can act as the absorbent of the lead leached out from the ash-coal sediments of 2010. Allegedly, due to the high affinity to complex formation, lead is potentially more mobile in peat soil than its partial geochemical analog, copper, and even zinc. On the contrary, a more stable state and preservation in the ancient boundary horizons without any noticeable loss are more typical of copper.

Table 2. The vertical distribution of heavy metal concentrations in the peat strata of the Krasnoye bog

Sampling depth (cm)	Concentrations in peat ash (mg/kg)			Notes
	Cu	Zn	Pb	
0-10	97,5	443,4	69,3	pyrogenic horizon (2010)
10-20	289,2	397,5	89,5	
20-30	140,8	374,1	97,7	
30-40	104,6	406,3	63,0	
40-50	126,2	393,5	142,2	
50-60	149,5	508,0	160,1	stump-folded horizon (about 2.3 ka calBP)
60-70	128,6	412,4	142,2	
70-80	206,8	369,2	182,0	pyrogenic horizon (about 2.6 ka calBP)
80-90	190,4	286,7	60,8	
90-100	163,4	296,3	96,3	
100-110	83,9	236,6	59,1	
110-120	297,9	459,2	134,7	pyrogenic horizon (about 4.5 ka calBP)
120-130	125,5	319,8	120,2	
130-140	119,9	317,9	157,2	
140-150	275,2	398,8	113,4	pyrogenic horizon (probably 7.0-7.5 ka calBP)
150-160	143,5	354,0	133,4	
160-170	166,2	470,8	156,5	stump-folded horizon (over 9.0 ka calBP)

170-210	98,0	255,0	79,8
210-245	149,6	211,0	129,6

The data represented in Table 2 also allow estimating the complexity and multifactor pattern of the vertical element distribution in the peat strata. In the conditions of the Meshchera lowland, it is impossible to accurately reveal the classical pattern of the exponential growth of element accumulation from the ancient layers of peatlands to the contemporary ones under the impact of technogenesis (Badenkova, 1982; Boyarkina, 1993; Mezhibor, 2009; Shotyk, 1996), as has been described in numerous publications. The patterns revealed by us testify to the fact that there are natural factors (mostly, the climate dynamics and its consequences) that result in equally significant deposition of elements and rather comparable to technogenesis in terms of the scope.

The above assumptions with respect to the element deposition in the boundary horizons under the effect of two factors of different nature, both passive concentration and radial redistribution, are absolutely confirmed by the analysis of the vertical regularity of the specific radionuclide activity. A marker of the process of passive pyrogenic (or any other) concentration can be the isotope of the natural radionuclide 232Th. According to literature (Kuznetsov, 2008), thorium is one of the elements that are most stable in the landscape, and does not produce any migration forms in natural environments. Radiocesium (137Cs), being a fully technogenic element and by its nature unable to be present in any layers of peat beneath the depth of 1.5–2.0 cm provided no hydrochemical migration is involved, can be considered to be an indicator of the vertical migration process.

As is seen in Fig. 10, the vertical distribution of these two completely different radionuclides is virtually the same by its main features and resembles the above patterns of the vertical distribution of Cu. In particular, the deposition of both ^{232}Th and radiocesium in the pyrogenic horizons of 2010, the Subboreal, and Late Atlantic eras is very distinct. Their Early Subatlantic pyrogenic depositions are also rather distinct, with a noticeable accumulation of the elements even in the upper tree-stump horizon (about 60 cm).

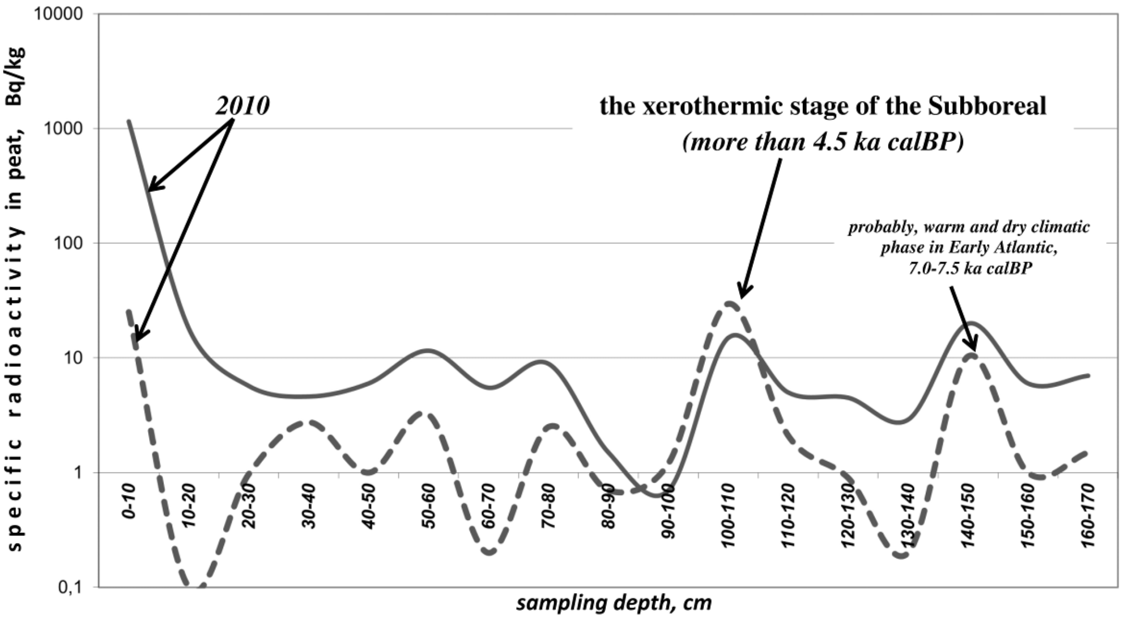

Fig. 10. The vertical distribution of the specific activity of radiocesium 137Cs (solid line) and thorium 232Th (dashed line)

Consequently, both the pyrogenic concentration (the passive factor, indicated by 232Th), and the vertical water migration (the active factor, indicated by 137Cs) are the comparably important factors of element accumulation in the boundary peat horizons. For various elements, the contribution of each of them is different, depending on their geochemical mobility, but it is unlikely to be equal to zero for any of them. The fact of detecting 137Cs in a detectable amount even at a depth of about 2 m testifies to the fact that the influence of the vertical water migration on the redistribution of elements can be significant even in the conditions of peat soil with high absorbing capacity.

In conclusion, we would like to review in detail the geochemical consequences of the fires of 2010. Trying to solve a side scientific problem (obtain the sufficient amount of peat ash for an experiment in vegetative containers), we burned a considerable amount of peat and thus simulated the conditions of a peat fire. Before the burning, we selected mixed samples of peat, consisting of 8 to 12 individual specimens, determined the specific activity of 137Cs and natural radionuclides (NRN) in the samples, and then determined the ash content. The specific activity and ash content obtained in different batches of the burnt peat (of the same weight) were averaged. Knowing the average specific activity and ash content of the burnt peat, we defined the expected values of the radionuclide content in peat ash and compared them to the actual values measured in the ash specimens immediately after burning.

Table 3. The scope of pyrogenic transformation of radionuclides in peat ash during a fire (results of a model experiment)

Indicator	Cs-137	Ra-226	Th-232	K-40
expected values, *Bq/kg*	2254.12	26.1	37.68	615.3
actual values, *Bq/kg*	1276.9	30.9	41.8	527.2
difference, %	-43%	+18%	+11%	-14%

It turned out that the burning process has a noticeable effect on the specific activity of radionuclides (Table 3). In particular, the content of geochemically stable natural radionuclides 226Ra and 232Th even increased to a certain extent (apparently, due to the removal of other elements). We recorded the tendency of removal of the more mobile radionuclide 40K along with the combustion products. But the most significant fact is that almost half of the original content of technogenic radiocesium migrated to the atmosphere in the course of peat combustion. The results of the experiment again demonstrate how dangerous can be the consequences of forest and peatland fires within the contour of the Chernobyl radioactive trace. Even 30 years after the disaster at the Chernobyl NPP, 137Cs remains the most mobile radionuclide, weakly associated with the soil absorbing complex, and in unfavorable conditions, especially in case of fires.

Conclusion

Thus, in the conditions of the Meshchera natural province, peat soil (even the one of the bog-type) cannot be treated as the natural sites ensuring long-term accumulation of aerial technogenic pollutants, unlike other regions (Badenkova et al., 1982; Boyarkina et al., 1993; Shotyk, 1996). This is due to the high deficiency of nutrient elements in the conditions of the prevailing low trophic level of substrates and the selective geochemical activity of the biological block of forest landscapes, which keeps elements within the cycles of biogenic migration and hinders their long-term deposition in the incrementing layer of peat. As a result, the microelement compositions of the ash of peat and peat-forming plants become very distinctively different. The accumulation of heavy metals in the Meshchera peatlands is a probabilistic process, completely controlled by the biogenic migration. In this situation, the highest probability of accumulation in peat is typical of slow-moving toxic agents (Pb), while the lowest one is typical of highly mobile biophiles (Zn). The main factors of the vertical distribution of heavy metals in peat strata are their accumulation in the boundary layers, i.e. pyrogenic and tree-stump horizons (formed in 2010, the Early Subatlantic, the Subboreal, and more ancient ones), including that in the course of vertical water migration. It was found that fires are not only the factor of pyrogenic concentration of elements, but also a stimulus for water and aerial migration of the most mobile ones. In particular, forest and peat fires release up to 43% of deposited radiocesium along with the combustion products (while the natural radionuclides remain relatively stable), which evidences the relevance of the problem of secondary radioactive pollution of the Chernobyl trace landscapes even 30 years after the Chernobyl disaster.

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