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Assessment of Fe, Cr and Pb concentration changes depending on the age of peat core layers

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Abstract. In the Arctic and subarctic regions peat soils are widespread. They serve as an indicator of anthropogenic pollution in different historical periods. Samples of peat of different ages were studied – layer of vegetation 0 cm, 0-5 cm, 5-35 cm, 85-140 cm. The age of the layers was defined on the basis of the lead-lead dating method. The elements were identified by inductively coupled plasma mass spectrometry. It was determined that the highest concentration of all three elements is observed in peats aged 2-29 years. This is due to both anthropogenic and groundwater effects. In areas that are below the maximum level of groundwater, a portion of the elements associated with readily soluble organic matter in the water is washed out and transported to the rivers with groundwater. Iron concentrations are observed in peat, regardless of anthropogenic activity, which is less characteristic of lead. This is also evidenced by large concentrations of chromium in younger layers. Lead and chromium are not nutrients. Such significant changes in lead and chromium concentrations may indicate air pollution due to the widespread development of industry and the transboundary transport of pollutants to the subarctic zone.

1. Introduction

Industrial and other anthropogenic activities cause heavy metals and other pollutants to penetrate into the atmosphere. Once pollutants are in the air, they get transferred over long distances and fall out with precipitation. In the Arctic and subarctic regions, peat soils are widespread and can serve as indicators of such type of pollution. Soils of ombrotrophic bogs accumulate pollution only due to precipitation. As a result, peat, being a deposit accumulating contaminants from the atmosphere, can serve as an indicator of pollution levels in the Arctic region [1].

A product of decomposition of the biological materials, such as mosses, grass, shrubs, trees and other living organisms in wetlands, peat can effectively accumulate pollutants through chemical and physical sorption. Due to its origin, peat has a high content of organic substances such as lignin, humic acids and peat bitumen which contain in their chemical structure a large number of oxygen and nitrogen-containing groups. These groups are negatively charged and have very high affinity to the heavy metals which allows them to form different bonds between organic molecules and metals and therefore accumulate heavy metals in their structure [2]. At the same time, peat has a porous structure and due to that a physical sorption may occur.

The formation of ombrotrophic bogs begins with the upper layers and then during the humification of organic matter bottom layers of peat produces. So, the bottommost level are the oldest layers. Due to such type of the peat formation ombrotrophic swamps accumulate anthropogenic pollutants from the atmosphere during the existence of all human civilization. Peat absorbs heavy metals and reduces



their mobility. Thus, the profiles of such bogs, selected from different depths, can serve as an indicator of atmospheric pollution in various historical periods [3].

2. Methods

The Ilas bog located near the city of Arkhangelsk ($64^{\circ} 20' 2.75''$ N, $40^{\circ} 36' 33.75''$ E) was chosen as the research site. This bog is a typical representative of high-moor bogs [4], which receive nutrients and potential pollutants only from precipitation. In this work, we selected samples of peat from different depths. Four layers were selected: a layer of vegetation (0 cm), 0–5 cm, 5–35 cm, 85–140 cm.

The age of the layers was characterized on the basis of the lead-lead dating method. All samples were air dried, crushed, averaged and mineralized with concentrated nitric acid (doubly distilled) in the TOPWave microwave decomposition system (Analytik Jena, Germany) using at 200°C for 45 minutes. The internal standard, which contained 6Li, Sc, Y, In, Tb and Bi was added to each sample prior to the decomposition step. The prepared samples were analyzed using the Aurora Elite inductively coupled plasma mass spectrometer (Bruker, Germany) with the following parameters: first extraction lens -1 B, second extraction lens -150 B, third extraction lens -200B, corner lens -210 B, eft mirror lens 38 B, right mirror lens 26 B, bottom mirror lens 32 B. Doubly charged ions level of $^{138}\text{Ba}^{++}/^{138}\text{Ba}^{+}$ and oxide level $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ was less than 3%. Argon plasma gas flow was 18 L/min, auxiliary gas flow 1,8 L/min, sheath gas flow 0,15 L/min, nebulizer gas flow 1,00 L/min, RF generator power 1,45 KW, stabilization delay 15 s, torch depth 6,5 mm. Cr abalysis was provided using the CRI interface with H_2 as a reaction gas at flow rate 105 ml/min.

3. Results and discussion

Out analysis has found that the highest concentration of iron is observed in peat aged 2–29 years (Figure 1). As can be seen from the presented data, the maximum concentration of iron is observed in the layer with an age of 2–29 years. This can be due to the anthropogenic and groundwater effects. It should be noted that the extraction of iron ore and the use of iron for economic purposes has been showing an exponential growth since the discovery of iron by man. In global metallurgical production, iron accounts for up to 95%; in 2011 global iron ore mining exceeded 2.8 billion tons, and in 2017 it grew by another 7%.

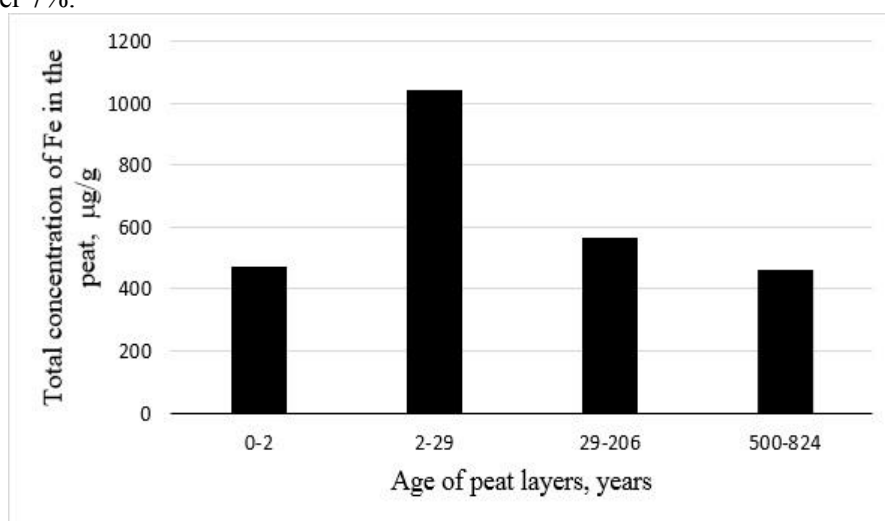


Figure 1. Concentration of Fe in peat layers, $\mu\text{g/kg}$.

However, there exists a threshold for iron content in peat layers, which is not characterized by exponential dependence. A conclusion can therefore be made that the maximum iron content is associated with the action of groundwater and the specific sorption properties of a given peat layer with respect to iron ions. This may occur due to different ratios in the composition of peat humic substances and other components of peat. In the northern part of the Arkhangelsk region where the

study was conducted, the groundwater levels ranged from 0.5 m to 1.7 m. For a given bog, the groundwater level varies seasonally from 5 cm to 50 cm. Groundwater can affect iron content. In the peat layers that are below the maximum groundwater level – layers 3 and 4 which correspond to the time range of more than 29 years – the readily soluble organic substances of peat components that had adsorbed iron ions, tend to be washing out. Because of this, these easily soluble organic substances (fulvic acids, sugars, peptides, etc.) flushing with groundwater in rivers. The levels of organic matter and of iron in the rivers of the north-west of Russia is stably high. A similar dependence is observed in the distribution of lead content (Figure 2). The highest lead content is observed in the layer aged of 2-29 years and is almost 4 times higher than the content in the younger peat layer. In the layers older than 29 years, lead concentration can be 20 times lower. Comparing the change in the content of lead and iron, we can conclude that the same mechanisms affects the concentration of these elements in peat. It should be noted that the concentration of lead in the first layer is two times higher than in layers 3 and 4. It is obvious that groundwaters, too, produce, via the easily soluble peat components capable of binding the ions of metal, a major effect on the concentrations of lead.

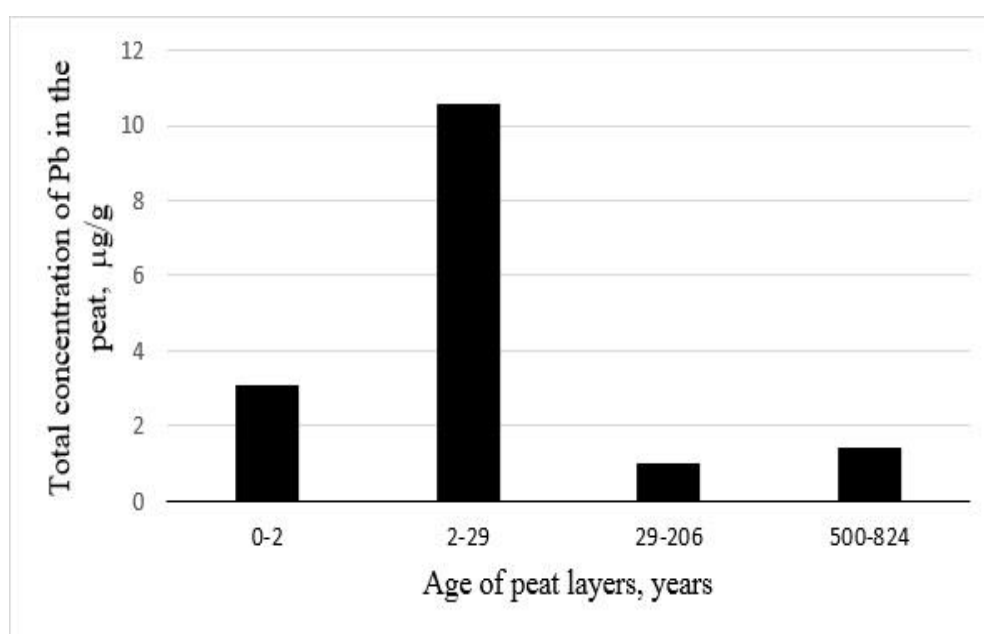


Figure 2. Concentration of Pb in peat layers, µg/kg.

The chromium distribution pattern in peat layers (Figure 3) is less pronounced than that of lead. Chromium content is predominantly higher in the second layer, while in the first layer its content is one quarter lower. In the deeper, older peat layers, its content tends to decrease 3- or 4-fold. We associate maximum concentrations of chromium with the same reasons as for lead and iron. At the same time, chromium concentration in the upper layers differs greatly from its concentration in the lower ones. Comparing the variation in layers of the concentrations lead, iron and chromium, it can be noted that the variation in lead concentration is much more manifest than the that in the concentrations of iron and chromium. The maximum variation between the layers for iron is 2 times, chromium - 4 times, and lead - 11 times. This can be explained by the fact that certain concentrations of iron occur in peat naturally, regardless of anthropogenic impact, whereas lead and chromium are mainly 'anthropogenic' elements. This is also evidenced by large concentrations of chromium in the young layers.

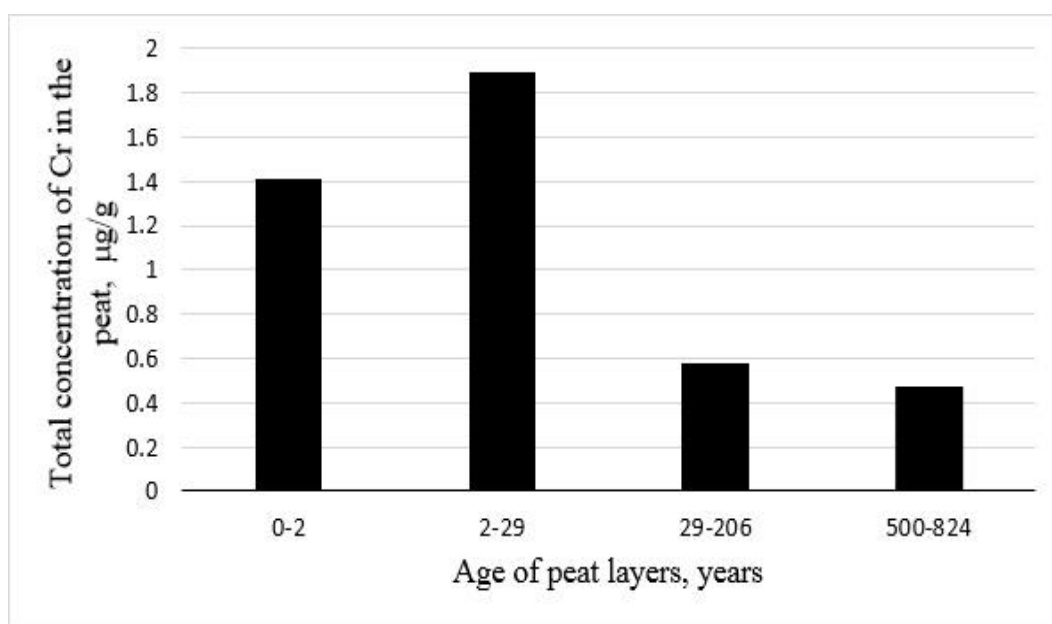


Figure 3. Concentration of Cr in peat layers, µg/kg.

Thus, summing up all the data obtained, it can be concluded that once the metal ions enter the upper soil levels with precipitation and through decomposing vegetation they tend to accumulate during the first thirty years, reaching their maximum concentration levels as the peat layers thicken. It is known that dense moss cover makes a perfect trap for metals contained in precipitation and aerosol particles. Therefore, the high concentration of lead and chromium in the first layer (0 cm) can be explained by the ability of the vegetation cover, especially mosses, to accumulate them. Subsequently, peat layers experience a significant effect from groundwater. Groundwater washes out the readily soluble substances containing a certain amount of absorbed metals, and the concentration of metals stabilizes. Given this external effect, estimating the levels of anthropogenic impact on environment based on the content of these elements in the peat layers becomes very challenging and requires additional research. Nevertheless, the change in lead and chromium concentrations as high as this points at industrial development and the transboundary transfers as causes of the air pollution in the subarctic zone.

4. Conclusion

The maximum concentration of iron, lead and chromium is observed in peat layers aged 2-29, equaling 1000 µg / kg, 10 µg / kg, 1.9 µg / kg, respectively.

The fact that the elements under study tend to accumulate in the peat layers of 2-29 years is explained by the fact that it is during this time interval that peat thickens, as well as by the composition of peat.

The decrease in concentrations of the elements under study in the peat layers aged 29-824 years is associated with groundwater, which flushes the readily soluble substances with certain amount of absorbed metal, thereby stabilizing concentrations of these metals.

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