

Short communication

**Estimation of heavy metals content and regularities of its migration within a soil profile during pyrogenic soil formation in the context of the Scotch pine forest in Togliatty city**

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**Abstract**

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Forest fires are among the most significant disturbances on a global scale. Affecting biodiversity and biogeochemical cycles, forest fires play an important role in atmospheric chemical processes and the global carbon cycle. Using the example of the pyrogenic landscapes of the Samara region, this article reviews changes in the accumulation regularity of heavy metal content and its migration within a soil profile during pyrogenic soil formation. In the case of surface forest fires, the studied postpyrogenic soils are characterized by increased cadmium, nickel and zinc content in the Opyr pyrogenic horizon. In contrast, the content of all analyzed heavy metals decreases compared to the control for crown forest fires, indicating active element emissions into the atmosphere.

**Keywords**

contamination index, demutation changes, heavy metal, postfire succession, postpyrogenic soil, total soil, Zc

**Introduction**

As primary factors in the functioning of geochemical flows in landscapes, soils accumulate, redistribute and transform chemical elements (ALEKSEEV et al., 2016; ZADOROZHNYAYA et al., 2018). These three processes occur during the interaction of soil components with groups of pollutants such as heavy metals (GULINSKA et al., 2003; TOMASHUNAS and ABAKUMOV, 2014). The nature of this interaction (accumulation or removal) depends on the soil's properties and genetic horizons. For example, soil organic

matter and clay minerals sorb metals such as lead, zinc and copper. The environmental conditions favor the accumulation of elements along the profile and the organic matter's properties determine the strength of heavy metal bonds (POKROVSKY et al., 2006; ANTCIBOR et al., 2014).

Forest fires are currently recognized as fundamental factors determining element migration on the soil surface. The annual dust and aerosol emissions from forest fires are quantitatively comparable to those from volcanoes. Prior studies estimated that aerosols remain in the troposphere for up to 28 days (DOBROVOL'SKIĬ, 1983). Larg-

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er dust particles settle much faster, an important consideration related to the geochemical problems caused by forest fires (SHULMAN et al., 2017). New sedimentation undoubtedly alters the geochemical background of the soil and of the vegetation cover (GAŠOVÁ et al., 2017), as the elements deposited were not present before the forest fire.

Forest burning is accompanied by the atmospheric emission of heavy metals and radionuclides and the passive accumulation of metals at fire sites (MICHOPoulos, 2021a, 2021b). Substances belonging to the first hazard class, such as mercury, cadmium, arsenic, radioactive cesium and strontium, actively migrate through the atmosphere during forest fires. Lead, plutonium and some other elements migrate with a lesser extent of activity than the least dangerous elements, such as zinc, manganese and antimony (IMESON et al., 1992; BENTO-GONCALVES et al., 2012; SANTIN et al., 2016). Element emission during a strong forest fire can amount to half of their initial content (Bi et al., 2006). The information presented above suggest that element behavior during forest fires depends on several factors, including fire type, the state of combustible materials, weather conditions, the distribution of elements in the forest ecosystem and the geochemical characteristics of the elements themselves (ROBICHAUD, 2000; DOERR and SANTIN, 2016; DYMOV et al., 2018).

A substantial number of publications have addressed the department of heavy metals in soils and their interaction and antagonistic reactions with plant organisms (IL'IN, 1973; KLOKE, 1979; YAGODIN et al., 1998; KABATA-PENDIAS, 2010). The soil content of heavy metals in soluble form is higher in technogenic landscapes (VASIL'EVA and KADATSKIĬ, 1998; ABAKUMOV and KOPTSEVA, 2022).

Information regarding the transformation of heavy metal forms in forest pyrogenic areas is scarce, it has not

been thoroughly studied. Heavy metals have been detected in all components of forest biogeocenosis. Their inclusion in various biogeochemical processes affects the transformation of heavy metal forms under the influence of high forest fire temperatures. This is especially true for the forest floor. As the location for various biogeochemical processes, the forest floor serves as the most capacious and significant geochemical barrier against atmospheric emission and migration of chemical elements into deeper soil layers.

This study aims to characterize heavy metal concentrations in postpyrogenic soils and to assess the regularity of their migration throughout the soil profile during pyrogenic soil formation. Postpyrogenic ecosystems require a comprehensive study to understand the role of soil cover in the functioning and restoration of terrestrial ecosystems in the context of the catastrophic consequences of forest fires on a national scale. While this problem is neither unusual nor regional, a deeper understanding is critical to developing effective environmental management strategies for forest ecosystems in the Russian Federation.

## Materials and methods

Post-fire plots located in the city of Togliatti, Samara region in southwestern Russia, were studied to assess heavy metal content and the regularity of heavy metal migration in postpyrogenic soils. In 2010, Togliatti experienced 35 catastrophic forest fires during the fire hazard period. The area impacted by fires was 2,087 hectares, including 1,037 hectares affected by a crown forest fire (FLORA FOLIUMII, 2010; DAVYDOVA and MOROV, 2011). Unfortunately, Togliatti's forests burned again in 2021. The fire affected Scotch pine forests formed on sandy and sandy loam sediments

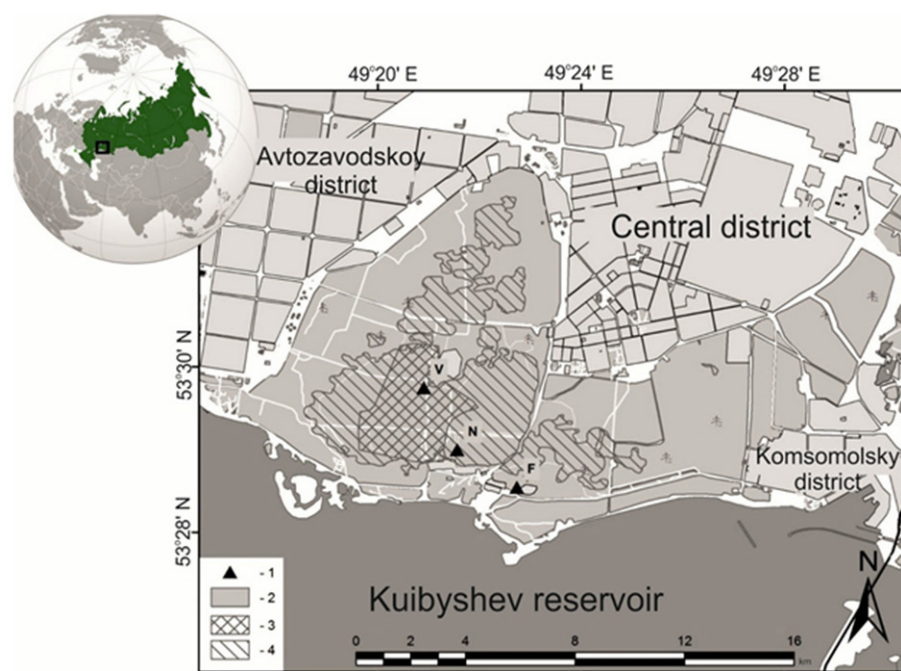


Fig. 1. Study plots in Stavropol pine forest damaged by forest fires in 2010. Symbols: ▲ – areas of soil profiles (V, crown fire area; N, surface fire area; F, control plot); 2 – forested areas (before the fire in 2010); 3 – areas affected by the crown fire; 4 – areas affected by the surface fire.

of aeolian or alluvial origin in a subboreal climate. The territory of the Stavropol pine forest impacted by the fires is a former park zone between the Komsomolsk, Central and Avtozavodsk districts of Togliatti, near the Institute of Ecology of the Volga Basin RAS, located at coordinates 53°29'43.80"N, 49°20'56.44"E, 179 m above sea level (MAKSIMOVA et al., 2014) (Fig. 1).

Soil cover post-fire dynamics studies were conducted at two plots affected by surface and crown forest fires, respectively, and at a control site that was not exposed to fire. Site No. 1, located in a middle-aged pine forest in Togliatti, experienced a surface fire in late July 2010 that resulted in the burnout of the lower layers with partial damage to the forest stand. Site No. 2, also located in a middle-aged pine forest in Togliatti, was affected by a crown fire in late July 2010, causing the complete burnout of the vegetation cover. For the control (site No. 3), we selected a similar forest area with an identical soil type located about 1 km from the postpyrogenic plots and unaffected by combustion. A transect consisting of at least three soil pits was laid out within each site, crossing a forest stand of similar age and species, as well as micro- and mesorelief and a shrub layer. Postpyrogenic surveys were carried out from 2010 until 2019; heavy metal analysis of soil samples began in 2012.

This study examined 48 soil samples taken in various areas of sites No. 1, 2 and 3. Samples were taken from all genetic soil horizons to a depth of about 50 cm. The content of heavy metals (Cu, Pb, Cd, Zn, Ni) in soil samples was determined via atomic absorption spectrometry. The values thus obtained were compared to the available approximate permissible concentrations (APC) and maximum permissible concentrations (MPC) specified in sanitary regulations and standards 1.2.3685-21 "Hygienic standards and requirements for ensuring the safety and (or) harmlessness of habitat factors to humans" (*Sanitarnye pravila i normy SanPiN 1.2.3685-21...*, 2021) and methodology instructions 2.1.7.730-99 "Hygienic assessment of soil quality in populated areas" (*Metodicheskie ukazaniya 2.1.7.730-99...*, 1999). Regulatory limiting indexes are used when calculating the soil pollution index (SPI), an integrated indicator of MPC. If the SPI is above 1, the soil is considered contaminated.

Soil and soil horizons names were assigned according to the classification and diagnostics of soils in Russia (SHISHOV et al., 2004). The content of heavy metals was determined using an atomic absorption spectrophotometer Kvant 2M (Moscow, Russia), following the "Soil quality – determination of cadmium (Cd), cobalt (Co), copper (Cu), lead (Pb), manganese (Mg), nickel (Ni) and zinc (Zn) in aqua regia extracts of soil – flame and electrothermal atomic absorption spectrometric" method (ISO 11047:1998).

Total soil contamination indexes ( $Z_c$ ) were calculated for each soil sample. The technogenic element concentration coefficient ( $K_c$ ) was calculated to assess the degree of soil contamination:  $K_c = K_{tot} / K_{back}$ , where  $K_{tot}$  is the element content in the studied soil and  $K_{back}$  is the element content in the background soil. When the soil is contaminated with two or more elements, we calculate the total contamination index ( $Z_c$ ) as follows:  $Z_c = \sum K_c - (n - i)$ , where  $K_c$  is the technogenic element concentration

efficient ( $K_c > 1$ ) and  $n$  is the number of elements with  $K_c > 1$ . The heavy metal concentrations in soils of the Samara region obtained by PROKHOROVA and MATVEEVA (2000) were used as background concentrations.

The normal distribution of the data was verified. A variance analysis (ANOVA) and a post hoc test (Fisher's least significant difference) were performed. The differences between control, surface forest fires and crown forest fires were considered significant at  $p < 0.05$ . The statistical data processing and analysis were conducted using standard methods in MS Excel 2016, Past (version 3.20) and Statistica (version 10).

## Results and discussion

The soil concentrations of heavy metals were analyzed and compared to the APC and MPC for soil samples from surface and crown forest fires areas, as well as for the control site for the period 2012–2019 (Table 1). At site No. 1 (surface forest fire), cadmium clearly exceeded the APC in the upper pyrogenic horizon in 2012 and 2019. The values for cadmium content at site No. 3 (control) and site No. 2 (crown forest fire) after nine years were borderline. Nickel also exceeded the APC at the Opyr horizon on site No. 1 in 2012. In the same sample, zinc concentrations were slightly above the APC ( $55 \text{ mg kg}^{-1}$ ). Copper and lead concentrations did not exceed the APC or MPC in any of the studied samples. Results indicate that excess heavy metal content was only detected in the upper pyrogenic horizon, which was directly exposed to heating and burnout during forest fires.

The soil contamination index ( $Z_c$ ) revealed that most samples exhibit an un Hazardous level of total pollution ( $Z_c < 16$ ). Only one sample, the pyrogenic horizon Opyr after a surface fire, displayed a moderately hazardous level of contamination ( $16 < Z_c < 32$ ). All studied soil samples had SPI values below one, indicating unpolluted soils.

Results suggested that the amount of elements involved in intensive migration is proportional to the strength of the forest fire. Heavy metal elements are actively emitted from the soil into the atmosphere during intense crown fires, contributing to soil surface denudation. The deeper burnout of main heavy metal deposits, primarily in the middle and lower layers of the forest floor and secondarily as mosses and lichens, is responsible for the active emissions. In contrast, surface fires lead to the accumulation of heavy metals in the surface horizons of postpyrogenic soils.

Statistical processing of the obtained data revealed a statistically significant differentiation in the average content of all studied heavy metals in the studied soil samples.

Heavy metals are removed from the burned material in postpyrogenic areas, lowering forest fires' adverse effect on soils (BOGORODSKAYA et al., 2010). The behavior of heavy metals during forest fires in the studied area is characterized by atmospheric migration, passive accumulation in the fire area, redeposition on the leeward side of the fire with the enrichment of all components of forest biogeocenosis, and long-range transport (SHCHERBOV et al., 2015). Therefore, wildfires contribute to the uncontrolled migration of pollutants, resulting in the contamination of

Table 1. Average content of heavy metals in studied soil

Horizon Depth (cm)	Cu (mg kg <sup>-1</sup> )		Pb (mg kg <sup>-1</sup> )		Zn (mg kg <sup>-1</sup> )		Ni (mg kg <sup>-1</sup> )		Cd (mg kg <sup>-1</sup> )		Zc	Soil pollution index					
	2012	2017	2012	2017	2012	2017	2012	2017	2012	2017							
	2019	2019	2019	2019	2019	2019	2019	2019	2019	2019							
Surface fire																	
Opyr / 0-4	9.04	2.96	7.63	19.70	2.13	11.00	55.00	9.90	37.40	20.90	9.61	17.70	0.75	0.10	0.57	31.9	0.7
AY / 4-15	5.19	4.04	5.27	4.20	5.22	4.13	16.60	17.10	16.40	11.80	11.20	12.10	0.21	0.19	0.27	2.8	0.3
AC1 / 15-25	3.64	2.60	2.59	2.70	1.54	1.50	9.69	7.91	7.00	9.61	9.97	9.80	0.13	0.07	0.07	7.2	0.1
AC2 / 25-35	3.27	nd	nd	2.51	nd	nd	9.10	nd	nd	9.79	nd	nd	0.12	nd	nd	10.4	0.1
C / 35-50	3.21	nd	nd	2.38	nd	nd	9.05	nd	nd	10.40	nd	nd	0.09	nd	nd	11.1	0.1
Crown fire																	
Opyr / 0-8	3.21	6.72	4.76	6.82	7.99	12.30	19.70	30.50	33.40	10.60	15.30	13.80	0.22	0.39	0.44	7.1	0.4
AY / 8-14	2.32	4.12	3.25	2.97	2.03	2.66	9.52	12.30	11.40	9.05	10.50	10.30	0.12	0.12	0.08	2.5	0.2
AC1 / 14-20	2.10	3.53	3.49	2.84	3.37	3.50	8.72	9.24	9.30	9.26	11.00	10.50	0.14	0.10	0.09	8.0	0.1
AC2 / 20-30	2.09	nd	nd	2.54	nd	nd	7.65	nd	nd	9.60	nd	nd	0.12	nd	nd	10.6	0.1
C / 30-45	2.38	nd	nd	2.66	nd	nd	7.18	nd	nd	10.50	nd	nd	0.13	nd	nd	10.4	0.1
Control																	
O / 0-10	6.35	7.39	7.01	16.50	16.70	16.56	41.10	36.30	38.42	11.30	12.60	12.40	0.42	0.48	0.47	11.7	0.4
AY / 10-15	2.80	2.43	2.50	5.61	2.01	2.50	17.50	8.05	12.40	8.20	7.72	7.90	0.21	0.12	0.11	4.8	0.2
AC1 / 15-23	1.59	2.13	2.01	2.78	1.85	1.96	8.25	6.88	7.02	6.49	6.84	6.56	0.13	0.11	0.11	7.4	0.1
AC2 / 23-35	1.15	nd	nd	2.67	nd	nd	6.07	nd	nd	6.02	nd	nd	0.14	nd	nd	10.3	0.0
C / 35-45	1.26	nd	nd	2.62	nd	nd	5.15	nd	nd	6.29	nd	nd	0.15	nd	nd	10.1	0.0
MPC	32																
APC	33											55	20	0.5			

nd, no data; MPC, maximum permissible concentration; APC, approximate permissible concentration.

new areas. Considering the landscape-geochemical positions, results revealed the migration pattern of all heavy metals along the catena. The heavy metal content was minimal at the slope position and maximal at the accumulative position, confirming that erosion processes activate after fires. In addition, the data presented in Table 1 suggest that heavy metals previously sorbed by organic matter leach into the depth of the soil profile after rains. After fires, the relative increase in all analyzed heavy metals compared with the control samples ranged from 2.7 times for cadmium to 20.5 times for lead.

## Conclusions

This study helped determine the heavy metal content of soils in postfire areas in Togliatti, Samara Region, after the catastrophic fires of 2010. These soils are primarily characterized by increased cadmium, nickel and zinc content in the pyrogenic horizon O<sub>pyr</sub> in areas that experienced a surface forest fire. In contrast, the contents of all analyzed heavy metals decreased after crown forest fires, indicating that elements were actively emitted into the atmosphere.

For effective environmental monitoring, the soil and vegetation cover of post-fire areas should be examined closely. The soil cover can receive natural and technogenic flows of chemical substances from autonomous landscapes. Vegetation absorbs and neutralizes a significant amount of chemical substances. Plants and soils can therefore serve as an informative indicator of the environmental state. To mitigate the catastrophic consequences of forest fires on a national scale and understand the role of the soil cover in the functioning and restoration of terrestrial ecosystems, further comprehensive studies of postpyrogenic ecosystems are required.

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