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Effect of forest fire on changes in the content of total and available forms of selected heavy metals and catalase activity in soil

Abstract: The aim of the paper was to assess the effect of forest fire on the content of total and available forms of zinc, copper, lead, nickel and cadmium, as well as the activity of catalase in soil. The study was performed directly (2012) and a year after the fire (2013). The fire had a significant effect on the content of those heavy metals in surface horizons, however, it did not result in their rapid growth. The concentrations of total forms of metals did not exceed the norms provided for in Regulation of the Polish Minister of the Environment. The soil samples analysed can be considered unpolluted with those metals. The availability coefficients calculated showed an unfavourable higher availability of lead and cadmium over zinc and copper. The statistical analysis showed a significant effect of fire on the activity of catalase. Resistance of soil (*RS*) for catalase demonstrated lower values in the year 2012 as compared with 2013 (except for B soil). The calculated values of time index (*TI*) pointed to the activation of the enzyme a year after the fire. The Ward clustering method facilitated determining similarities between the sites in two research years (2012 and 2013) with the selected soil parameters. With the PCA method a negative effect of fire was identified.

Keywords: catalase, fire forest, heavy metals, resistance of soil

INTRODUCTION

Forest fire is a disaster phenomenon with a destructive effect on the functioning of forest ecosystems. It causes death to many plant and animal species as well as affects soil properties. During fire soil is exposed to varied thermal conditions and the depth of changes caused by fire is determined by three major factors: types of fire (at the ground – lower or at the top-upper), its duration and intensity (Iglesias et al. 1997). Immediately after fire a short-term increase in soil fertility can occur, however, after some time, nutrients, released by the effect of fire, get leached from it and this is how fire makes its fertility exhausted (Brais et al. 2000). A destructive impact of fire results in a decrease in the number and diversity of soil micro- and macrofauna and in weakening the enzymatic activity of soils (Prędecka et al. 2010). Fire also affects physical and chemical soil properties; a decrease in structure, porosity, organic matter content, pH increase (Iglesias et al. 1997, Januszek et al. 2001, Carter and Foster 2004, Certini 2005, Ekinci 2006, Gonet et al. 2009, Miesel et al. 2012). The changes can lead to a number of disturbances in the ecosystems flora and fauna dynamics development (DeBano 2000, Clark 2001, Bogacz et al. 2013). During fire temperature deep down the soil increases. If temperature on the surface is about 438°C, then 3 cm deep temperature is 25.6°C, and 7 cm deep – 17°C; such a rapid change in temperature can destroy microorganisms, a source of enzymes. One of the key enzymes defending organisms from negative effects of oxidative stress is catalase. In soil environment catalase is present in microorganisms cells using oxygen for respiration processes (Brzezińska 2006). According to Wang et al. (2012), the activity of catalase plays an important role in soil solution chemistry and can change oxidation-reduction reaction of soil. There are many reports on the effect of fires mostly on biological soil properties (Hamman et al. 2008, Olszowska 2009, Lemanowicz and Bartkowiak 2015), however, few papers cover the content of microelements.

The aim of the paper has been to evaluate the effect of forest fire on the contents of total and available forms of zinc, copper, lead nickel and cadmium as well as the activity of catalase in soil immediately and a year after the fire.

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MATERIAL AND METHODS

The research area covered the site after fire found in the Fordon forest (53°07'N, 18°06'E) in Bydgoszcz. The Fordon forest is a pine forest, the composition of which is dominated by Scots pine (*Pinus sylvestris*), on sandy and sandy-loamy soils.

The site after fire occurred in March 2012 and it covered the area of about 10 ha. Fire lasted about 6 hours. Soil was sampled right after fire in the spring of 2012 and a year after fire (May 2013). After the organic layers removal soil samples was from 2 mineral horizons: 0–15 cm (surface horizon) and 15–30 cm (subsurface horizon). Four sampling locations were defined: stand not caught by fire – control area (C), border area (E ecotone) and soils caught by fire, 150 m (point A) and 200 m (point B) away from the border area. The control area was defined in pine tree stands neighbouring with the site after fire.

The soil sampling locations were determined with the scattered points method, made up of a few individual samplings from 27 points (PN-ISO 10381-2:2007P).

In the air-dried soil samples with disturbed structure, sieved through ∅ 2 mm, some physiochemical properties: percent of clay fraction; total organic carbon (TOC); pH were presented in earlier research (Lemanowicz and Bartkowiak 2015). The total content of selected heavy metals was assayed with Crock and Severson's (1980) method and its available forms were extracted with 1M HCl – Rinkis method. The total contents and available forms were determined applying the method of atomic absorption spectroscopy with the PU 9100X spectrometer (Philips).

The activity of catalase [E.C. 1.11.1.6] (CAT) in soil was determined with the Johnson and Temple method (1964) with 0.3% hydrogen peroxide solution as a substrate. The residual H_2O_2 was determined by titration with 0.02 M $KMnO_4$ under acidic conditions.

The results facilitated a calculation of the availability factor (*AF*) as suggested by Obrador et al. (2007), expressed as follows:

$$AF = \left(\frac{Available\ content}{Total\ content}\right) \times 100$$

where *AF* – availability factor (%).

To assay the percentage changes in the activity of catalase, as compared with the control soil, the coefficient of relative change (*RCh*) was calculated compliant with the formula provided by Chaer et al. (2009):

$$RCh = \left(\frac{T}{C} - 1\right) \times 100$$

where: *T* – mean activity of catalase in the treated soil sample, *C* – mean value obtained for the control.

Resistance of soil (*RS*) determined according to the activity of catalase in soil was calculated using the formula proposed by Orwin and Wardle (2004):

$$RS = 1 - \left[\frac{2|D_0|}{C_0 + |D_0|}\right]$$

where: $D_0 = C_0 - P_0$, C_0 – parameter value in control soil over time t_0, P_0 – parameter value in disturbed (burnt) soil over time t_0. The value of the resistance and resilience index is bounded by –1 and +1.

Based on the results, the time index was calculated:

$$\frac{t2}{t1}$$

where t1– content of the element in 2012; t2– content of the element in 2013. *TI*>1 means an increase, *TI*<1 means a decrease in content of some heavy metals and activity of catalase (Lemanowicz and Krzyżaniak 2015).

Two-way analysis of variance (ANOVA) was used to determine the effects of samples of burnt soil and soil depth. The study was carried out in a randomized design.

Pearson linear correlation coefficients analysis was used to estimate the relationships between the content of total and available heavy metals, TOC, pH_{KCl}, clay, the activity of the catalase.

Principal component analysis (PCA) was applied using data for soil catalase activities, content TOC and heavy metals and soil physiochemical properties. The first two principal components (PC1 and PC2) were selected for a further interpretation of the results. Hierarchical cluster analysis (CA) with Ward's method (1963) was used to identify the similarity groups between sampling.

All analytical measurements were performed with three replications. Arithmetic mean values are shown in tables. Differences among mean values of content of the selected chemical and biochemical properties were analyzed using a factorialdesign analysis of variance (ANOVA). In these analyses, the least significant difference (LSD) was calculated using the Student's t-test at 0.05 probability. The SD value is given only in comparison in individual years.

RESULTS AND DISCUSSION

Table 1 presents the results of selected physiochemical properties. In the soils covered by fire an inconsiderable increase in pH value, a decrease in the content of clay fraction and an increase in organic carbon were identified (Lemanowicz and Bartkowiak 2015). Literature reports on a high forest fire intensity resulting in an increase in the soil pH value in surface horizons, accompanied by a decrease in the content

TABLE 1. The content of clay fraction, pH and total organic carbon (TOC) in soils

Objects*	Depth (cm)	Clay (%)		pH_{KCl}		TOC ($g \cdot kg^{-1}$)	
		2012	2013	2012	2013	2012	2013
C	0–15	1.02	0.94	4.01	3.86	9.23	17.29
	15–30	1.08	0.77	4.22	4.30	3.90	4.42
E	0–15	0.50	1.25	4.78	4.56	16.77	23.11
	15–30	1.06	0.75	4.37	4.52	4.55	11.44
A	0–15	1.03	0.72	4.96	5.25	13.39	16.89
	15–30	1.29	0.14	4.54	4.75	5.72	7.15
B	0–15	0.83	0.54	4.99	4.38	12.22	14.56
	15–30	1.53	0.52	4.68	4.36	7.54	3.25
SD		0.30	0.31	0.35	0.40	4.61	6.96

*C – control, E – ecoton, A – burned forest 150 m away from ecatone, B – burnt forest 200 m away from ecatone.

of organic carbon and nitrogen (Schafer and Mack 2010, Aref et al. 2011, Verma and Jayakumar 2012).

The analysis of variance has shown that the content of total and available forms of heavy metals was significantly modified both by the site and the soil sampling depth (Tables 2 and 3). There was found the definitely highest content of total forms of zinc (38.78 $mg \cdot kg^{-1}$), copper (13.80 $mg \cdot kg^{-1}$), lead (47.38 $mg \cdot kg^{-1}$), nickel (64.53 $mg \cdot kg^{-1}$) and cadmium (3.08 $mg\ kg^{-1}$) as well as available forms (14.09 $mg\ kg^{-1}$ Zn, 3.15 $mg \cdot kg^{-1}$ Cu, 16.43 $mg \cdot kg^{-1}$ Pb and 11.57 $mg \cdot kg^{-1}$ Ni) in surface horizons of the sites. The highest values for total forms Zn, Cu and Pb were noted in the surface horisons at stand B in year 2012 while for Ni in stand A only in year 2013. The highest values

TABLE 2. Total content of heavy metals ($mg \cdot kg^{-1}$)

Objects I factor	Depth (cm) II factor	Zn		Cu		Pb		Ni		Cd	
		2012	2013	2012	2013	2012	2013	2012	2013	2012	2013
C	0–15	12.75	12.40	6.25	5.73	16.85	19.85	13.75	12.98	2.78	1.63
	15–30	11.60	10.53	6.63	5.50	14.00	15.28	11.50	12.05	2.78	1.30
E	0–15	26.25	16.38	8.85	7.25	21.15	16.58	13.90	15.48	3.08	1.68
	15–30	12.75	12.43	6.43	5.95	12.85	13.85	11.90	12.43	2.78	1.40
A	0–15	21.38	26.43	8.28	6.63	19.58	35.69	13.50	64.53	0.94	1.90
	15–30	15.20	12.93	5.95	5.95	12.28	14.73	11.65	22.35	0.93	1.73
B	0–15	18.40	38.78	7.40	13.80	17.00	47.38	13.23	35.8	1.29	2.08
	15–30	11.43	11.85	6.75	4.75	17.00	14.43	12.05	7.68	1.07	1.98
Mean		16.22	17.10	7.06	6.95	16.37	22.25	12.72	22.99	1.96	1.75
$LSD_{0.05}$	I factor	0.082	5.656	0.058	0.058	0.139	0.245	0.192	0.158	0.101	0.165
	II factor	0.042	2.880	0.030	0.029	0.071	0.125	0.098	0.080	0.051	0.084
Interaction	I / II	0.115	7.999	0.082	0.082	0.197	0.346	0.271	0.223	0.142	n.s.
	II / I	0.083	5.759	0.059	0.059	0.142	0.249	0.195	0.161	0.102	n.s.
SD		5.36	9.90	1.03	2.87	3.14	12.46	1.00	18.94	0.97	0.27

n.s. – not significant.

TABLE 3. Available forms of heavy metals ($mg \cdot kg^{-1}$)

Objects I factor	Depth (cm) II factor	Zn		Cu		Pb		Ni		Cd	
		2012	2013	2012	2013	2012	2013	2012	2013	2012	2013
C	0–15	2.56	3.16	1.53	1.24	0.46	0.55	9.14	9.82	0.81	1.07
	15–30	2.40	2.27	1.33	1.12	0.55	0.31	6.73	8.09	0.78	1.18
E	0–15	10.3	6.09	2.33	1.62	0.91	0.87	12.06	8.09	0.89	1.17
	15–30	3.93	3.04	1.29	0.98	0.59	0.69	7.70	7.05	0.84	1.27
A	0–15	7.59	11.53	2.29	1.92	1.10	16.43	11.57	9.56	0.63	1.29
	15–30	3.68	3.46	1.33	1.45	0.64	7.26	6.82	7.27	0.60	1.39
B	0–15	5.37	14.09	1.57	3.15	0.82	1.05	9.36	10.48	0.83	1.37
	15–30	2.67	2.80	1.65	1.24	0.64	0.73	10.89	5.58	0.98	1.45
Mean		4.82	5.83	1.61	1.60	0.73	3.50	9.30	8.25	0.80	1.29
$LSD_{0.05}$	I factor	0.032	0.202	n.s.	0.075	0.070	0.060	0.145	0.067	0.062	0.047
	II factor	0.016	0.103	0.281	0.038	0.036	0.031	0.074	0.034	n.s.	0.024
Interaction	I / II	0.045	0.286	n.s.	0.106	0.100	0.085	0.205	0.095	0.087	n.s.
	II / I	0.033	0.206	n.s.	0.076	0.072	0.061	0.148	0.068	0.063	n.s.
SD		2.82	4.52	0.42	0.70	0.21	5.71	2.18	1.64	0.13	0.13

n.s. – not significant.

of total Cd were also found in the surface horisons were noted in the soil sampled from the border area (E) but only in 2012. Bogacz et al. (2011), in the post-fire areas used as forests and meadows, found a varied effect of fire on the content of some heavy metals. The contents of Zn, Pb and Cd increased due to fire, while the content of Cu did not change. The concentration of metals was observed mostly in surface horizons. The pools of those metals in forest soils were lower than in meadow soils and soil reaction was favourable to metal concentration. In the present study the relation with the soil pH was found only for the content of total forms of nickel a year after the fire ($r = 0.748$, $p < 0.05$) (Table 7). The analysis of correlation, however, confirmed a significant positive dependence between the content of total forms of Zn, Cu, Pb and Ni and total organic carbon in the soil sampled in 2012 (Table 7), which can be due to the accumulation of metals related to the amount of carbon in ashes produced during fire. Over the first months after the fire the concentrations of heavy metals in soil can exceed the permitted content limits. In this study the concentration of metals did not exceed the norms provided for in Regulation of the Minister Polish of the Environment (Dz.U. No. 165, item. 1359. 2002, Dz. U. item. 1395. 2016). The soil samples analysed can be thus considered unpolluted.

Mobility and availability of metals is controlled by many chemical and biochemical processes which occur in soils. Not all of them are of the same importance for each metal. Soil reaction is a decisive parameter. The analysis of correlation identified only significant positive dependencies between soil reaction and the content of available lead forms in both years of analysis ($r = 0.871$, $p < 0.05$ and $r = 0.855$, $p < 0.05$, respectively) (Table 7). Garcia-Marco and Gonzalez-Prieto (2008), investigating short- and medium-term effects of fire in terms of the availability of microelements in soil, have identified that even an inconsiderable soil pH increase due to fire was enough to decrease the availability of some microelements. In 2012 an increase in soil pH at the sites caught by fire was related, as for some metals analysed, to a decrease in the content of their available forms. However, it was not confirmed by the analysis of of correlation. Yet the analysis of correlation demonstrated, similarly as for total forms, significant positive dependencies between the content of available forms of Zn, Cu, Pb and Ni, and the content of organic carbon (Table 7). Determining the admissible limits of the content of available forms in terms of their phytotoxicity, it was found that for Zn, Cu and Ni, they were not exceeded (Korzeniowska and Stanisławska-Glubiak 2003). To evaluate the availability of heavy metals, availability factor (*AF*) was applied.

TABLE 4. Available factors (*AF %*)

Objects	Depth (cm)	Zn		Cu		Pb		Ni		Cd	
		2012	2013	2012	2013	2012	2013	2012	2013	2012	2013
C	0–15	20.08	25.48	24.48	21.66	54.24	50.15	3.35	4.24	29.19	65.85
	15–30	20.69	21.57	20.08	20.36	48.07	52.96	4.78	2.57	28.11	90.77
E	0–15	39.24	37.19	26.33	22.34	57.02	48.81	6.55	5.62	28.94	69.85
	15–30	30.82	24.47	20.08	16.47	54.47	50.90	4.96	5.55	30.27	90.71
A	0–15	35.51	43.63	27.67	28.98	59.11	26.79	8.15	25.46	66.49	67.89
	15–30	24.21	26.77	22.35	24.37	55.56	49.37	5.49	32.48	64.52	80.58
B	0–15	29.18	36.34	21.22	22.83	55.06	75.57	6.20	2.93	63.95	66.02
	15–30	23.37	23.63	24.44	26.11	64.06	53.24	5.31	9.51	91.12	73.42

TABLE 5. Index of changes in time (*TI*) for heavy metals

Objects	Depth (cm)	Zn		Cu		Pb		Ni		Cd	
		Tot.	Av.	Tot.	Av.	Tot.	Av.	Tot.	Av.	Tot.	Av.
C	0–15	0.97	1.23	0.92	0.81	1.18	1.07	0.94	1.20	0.59	1.32
	15–30	0.91	0.95	0.83	0.84	1.09	1.20	1.05	0.56	0.47	1.51
E	0–15	0.62	0.59	0.82	0.70	0.78	0.67	1.11	0.96	0.54	1.31
	15–30	0.97	0.77	0.93	0.76	1.08	0.92	1.30	1.17	0.50	1.51
A	0–15	1.24	1.52	0.80	0.84	1.82	0.83	4.78	14.93	2.02	1.37
	15–30	0.85	0.94	1.00	1.09	1.20	1.07	1.92	11.34	1.85	1.49
B	0–15	2.11	2.62	1.86	2.01	2.79	1.12	2.71	1.28	1.61	1.06
	15–30	1.04	1.05	0.70	0.75	0.85	0.51	2.97	1.14	1.85	1.36

Tot. – total forms, Av. – available forms.

As for lead and cadmium, the factor values were very high, irrespective of the soil sampling location and the year of analysis (Table 4). The calculated values of the coefficient of availability for the metals analysed were as follows: Pb >Cd>Zn>Cu> Ni and pointed to a greater availability of nickel and cadmium than that of zinc and copper. An unfavourable behaviour of the metals analysed is related to soil reaction and the content of organic carbon. Those two parameters are essential for the control of the availability of micro-elements, directly affecting their solubility (Obrador et al. 2007, Diatta et al. 2014).

Time index (index of changes in time – *TI)* presents changes in the content of the metals analysed in soil throughout the year. The highest values for most metals analysed were reported in surface horizons of site B (Table 5). Literature reports confirm a slight increase in the content of total and bioavailable forms of heavy metals in soils exposed to fires (Stancov Jovanovic et al. 2011, Mitic et al. 2015).

One of the most important enzymes defending organisms against negative effects of oxidative stress is catalase. According to Brzezińska (2006), catalase released from cells shows a considerable stability thanks to sorption by clay minerals and organic substance thus reducing its activity. The results of the ANOVA (Table 6) showed a significant effect of both sites and depth on the changes in activity of catalase in the soil. The highest activity of CAT 0.402 mg H_2O_2 g^{-1} min^{-1} for 15–30 cm was obtained in the soil collected from the site (A) (2012) while in 2013 in site B (0.431 mg H_2O_2 g^{-1} min^{-1} for 15–30 cm). Gömöryová et al. (2008) also report on a variation in the activity of the enzyme (cellulase) depending on how far the location was from fire. There was shown no effect of heavy metals on the activity of soil catalase, which must have been related to non-exceeding the norms of their concentration.

With the positive values of *TI* index (except for the soil sampled from location A 0–15 cm) an increase in activity a year after fire was found, which shows that soil of both layers received the state of relative dynamic biological equilibrium, indispensable for the right operation of forest ecosystem.

The activity of catalase in the soil sampled in 2012 from horizon 0–15 cm of point B got most inhibited (*RCh* -12.71%), as compared with the control, similarly as a year after fire (*RCh* –13.24%).

TABLE 6. The activity of catalase (mg H_2O_2 g^{-1} min^{-1}) and index of changes in time (*TI*), resistance (*RS*) and relative changes (*RCh*) of activity the catalase in soil

Objects I factor	Depth (cm) II factor	2012	2013	TI	*RS*		*RCh* [%]	
					2012	2013	2012	2013
C	0–15	0.346	0.385	1.10	–	–	–	–
	15–30	0.334	0.368	1.19	–	–	–	–
E	0–15	0.310	0.368	1.28	0.81	0.93	-10.41	-4.42
	15–30	0.295	0.376	1.20	0.79	0.96	-11.67	2.17
A	0–15	0.328	0.394	0.99	0.90	0.95	-5.20	2.34
	15–30	0.402	0.397	1.11	0.66	0.85	20.36	7.88
B	0–15	0.302	0.334	1.21	0.77	0.77	-12.71	-13.24
	15–30	0.356	0.431	1.14	0.87	0.71	6.59	17.12
Mean		0.335	0.382					
$LSD_{0.05}$	I factor	0.006	0.006					
	II factor	0.003	0.003					
Interaction	I/II	0.009	0.009					
	II/I	0.006	0.006					
SD		0.034	0.028					

TABLE 7. Pearson's correlation coefficients ($p<0.05$)

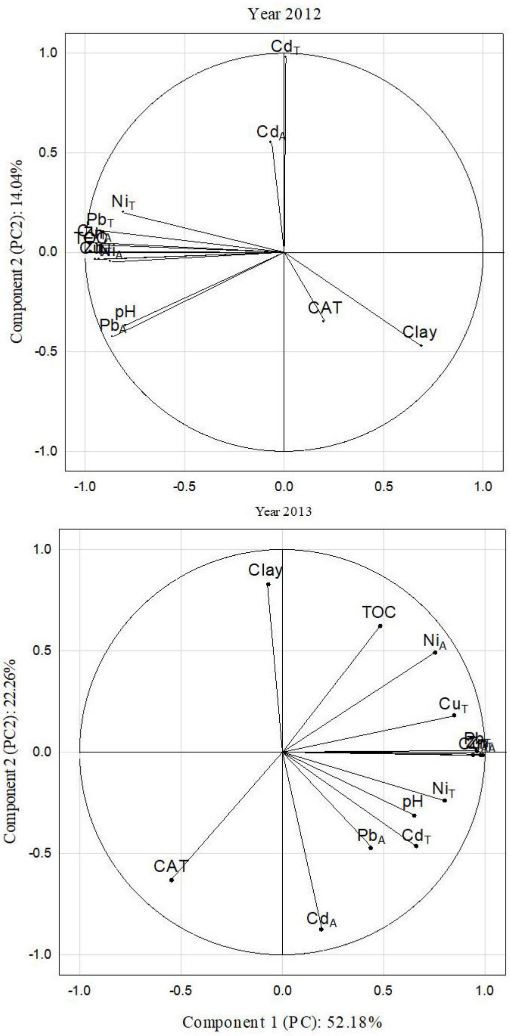
Parameters	Zn		Cu		Pb		Ni	
	Tot.	Av.	Tot.	Av.	Tot.	Av.	Tot.	Av.
Year 2012								
TOC	0.902	0.871	0.885	0.897	0.926	0.764	0.891	0.865
pH_{KCl}	n.s.	n.s.	n.s.	n.s.	n.s.	0.871	n.s.	n.s.
Year 2013								
pH_{KCl}	n.s.	n.s.	n.s.	n.s.	n.s.	0.855	0.748	n.s.

Tot. – total forms, Av. – available forms, n.s. – not significant.

Resistance of soil (*RS*) is an effective measure of activity of some enzymes responses to environmental stress (Orwin and Wardle 2004, Borowik et. al 2014). The values of resistance of soil for the activity of catalase were positive throughout the study. However they differed depending on the place of sampling, depth as well as the years in which the research was conducted (Table 6). The authors of the index (Orwin and Wardle 2004) report on the *RS* values falling within the range from -1 to 1, where 1 stands for a lack of the effect of human impact on the environment. Lower *RS* values in 2012, as compared to 2013, point to a negative effect of fire on selected parameters (this does not apply to point B).

To determine the nature and strength of dependencies between the parameters in 2012 and 2013, the method of principal component analysis (PCA) was applied. A projection of the variables on the factor-plane clearly demonstrated correlations between some soil properties and catalase activity (Fig. 1). In 2012 two principal factors had a significant total impact (75.9%) on the variance of the variables. It was found that most variance was included in the first principal component (PC1). Component 1 (PC1) accounted for 61.9% of the variance of the properties. Both TOC, total content of Zn, Cu, Pb and available form of Zn and Cu content had a major negative effect on PC1 (> -0.900) (Table 8). Moreover, total content of nickel and available forms of lead and nickel had a major negative effect on PC1 (>-0.800). In the soils sampled right after fire an immobilization of almost all heavy metals (except for total and available forms of Cd) was identified. Negative values had a negative effect on the source of variation in parameters. That dependence strongly suggests that the variables have a similar source (fire). Most heavy metals were strongly positively correlated with the content of TOC. The share of the second principal component (PC2) (14.04%) showed only a positive correlation (0.977) with the total cadmium form. In 2013 there were found positive correlations with total forms of most metals analysed (Zn, Cu, Pb, Ni) and available form of Zn and Cu with the first principal component (PC1) which accounted for 52.17% of variation, while the second principal component (PC2) revealed a positive correlation with clay fraction (0.831), and a negative correlation for available forms Cd (-0.878).

To determine the similarities between soils sampled from 4 sites (2 depths) in two research years (2012 and 2013), Ward's method (1963) was applied, based on soil properties (clay, pH_{KCl}, TOC), the contents of total and available heavy metals (Zn, Cu, Pb, Ni, Cd) and the activity of catalase (CAT). In 2012 the clustering procedure facilitated differentiating three



a

b

FIGURE 1. Projection of the variables on the factor-plane in soils

TABLE 8. Values of the two extracted factor loadings for 14 elements

Parameters	Year 2012		Year 2013	
	PC1	PC2	PC1	PC2
Clay	0.688	-0.470	-0.074	0.831*
TOC	-0.967*	0.001	0.481	0.622
pH	-0.794*	-0.365	0.647	-0.309
$Zn_{Tot.}$	-0.933*	-0.034	0.975*	0.009
$Cu_{Tot.}$	-0.965*	0.049	0.847*	0.178
$Pb_{Tot.}$	-0.921*	0.109	0.963*	0.008
$Ni_{Tot.}$	-0.806*	0.197	0.799*	-0.239
$Cd_{Tot.}$	0.008	0.977*	0.663	0.467
$Zn_{Av.}$	-0.937*	0.037	0.987*	0.014
$Cu_{Av.}$	-0.952*	-0.036	0.944*	0.015
$Pb_{Av.}$	-0.859*	-0.423	0.439	0.468
$Ni_{Av.}$	-0.867*	-0.048	0.753	0.493
$Cd_{Av.}$	0.061	0.546	0.196	-0.878*
CAT	0.203	-0.345	-0.551	0.632
Variation (%)	61.90	14.04	52.17	14.13
Eigenvalue	8.667	1.965	7.304	1.978

Tot. – total forms, Av. – available forms, * statistically significant.

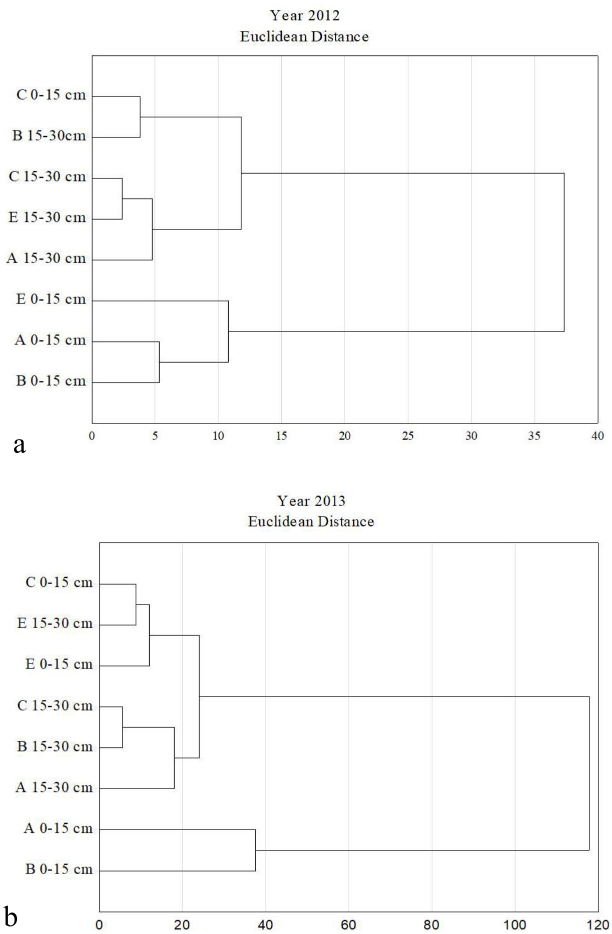


FIGURE 2. Dendrogram analysis of some physicochemical parameters (clay fraction, TOC, pH, ZnTot. CuTot., PbTot., NiTot., CdTot., ZnAv., CuAv., PbAv., NiAv., CdAv., CAT) in soil

clusters of soils with similar properties, content of heavy metals and CAT (Fig. 2a). Cluster 1 groups soils from site $C_{0–15cm}$ and $B_{15–30cm}$. Cluster 2 groups soils from C, E and A from the depth of 0–15 cm, while cluster 3 includes soils E, A and B from the depth of 0–15 cm. In 2013 also 3 clusters were separated; however, they were differently clustered than in 2012 (Fig. 2b). Cluster 1 consisted of soils from site $C_{0–15cm}$, $E_{0–15cm}$, $E_{15–30cm}$ and cluster 2 – soils from sites C, A and B from the depth of 15–30 cm, whereas cluster 3 – soils A and B from the depth of 0–15 cm. The clustering analysis demonstrated similarities of soils of the forest ecosystem sites under study. Differences in clustering the sites in years were identified, which was related to the effect of fire on the soil parameters.

CONCLUSION

The research has shown a significant effect of fire on the contents of the heavy metals under study. Both the distance from ecotone and soil sampling depth had a significant on changes of the parameters. Fire did not cause a rapid increase in the content of heavy metals. The concentrations of total metal forms did not exceed the norms provided for in Regulation of the Minister of the Environment. The soil analysed can be considered unpolluted with those metals. The calculated availability factor (*AF*) showed an unfavourable higher availability of lead and cadmium than zinc and copper. With the calculated values of time index (*TI*), no unambiguous changes in the content of heavy metals were identified. Fire changed the activity of catalase significantly. Only in surface horisons of soil the *RCh* index value showed the highest inhibition of catalase in soil from the site 200 m away from the ecotone (only in surface layers of soil). In the soil a year after fire the enzyme got activated, which was confirmed by a positive *TI* value.

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Oddziaływanie pożaru lasu na zmiany zawartości form całkowitych i przyswajalnych wybranych metali ciężkich oraz aktywności katalazy w glebie

Streszczenie: Celem pracy była ocena wpływu pożaru lasu na zawartość form całkowitych i przyswajalnych cynku, miedzi, ołowiu, niklu i kadmu oraz aktywności katalazy w glebie. Badania przeprowadzono bezpośrednio (2012 rok) i rok po pożarze (2013 rok). Pożar wpłynął istotnie na zawartość analizowanych metali ciężkich w poziomach powierzchniowych, ale nie spowodował gwałtownego ich wzrostu. Odnotowane stężenia form całkowitych metali nie przekroczyły norm przyjętych w Rozporządzeniu Ministra Środowiska. Analizowane próbki glebowe można zaliczyć do niezanieczyszczonych tym metalami. Wyliczone współczynniki przyswajalności wykazały niekorzystną wyższą dostępność ołowiu i kadmu nad cynkiem i miedzią. Analiza statystyczna wykazała istotny wpływ pożaru na kształtowanie się aktywności katalazy. Wskaźnik oporności (*RS*) dla katalazy wykazał niższe wartości w roku 2012 w porównaniu do roku 2013 (za wyjątkiem gleb ze stanowiska B). Obliczone wartości współczynnika zmienności w czasie (*TI*) świadczyły o aktywacji badanego enzymu rok po pożarze. Metoda grupowania Warda pozwoliła na określenie podobieństw między badanymi stanowiskami w dwóch latach badań (2012 i 2013 rok) na podstawie wybranych parametrów glebowych. Na podstawie metody PCA stwierdzono negatywny wpływ pożaru.

Słowa kluczowe: katalaza, metale ciężkie, pożar lasu