

Continuous and Periodical Effects of Smoke from Crop Residue Combustion on Soil Enzymatic Activity

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Abstract—Wildfires result in the emission of large volumes of toxic smoke, which is transported hundreds of kilometers away from the fires and can have an adverse impact on soil, biota, and humans. A series of modelling experiments on pyrogenic fumigation of soil has been carried out to assess the effects of gaseous products of wildfires on soil biochemical parameters. The effects of continuous exposure to gaseous substances and periodical, repetitive effects of smoke exposure on soil have been determined. The results have been compared with a single intense smoke exposure. It was found that pyrogenic impact significantly affected the enzymatic activity of ordinary chernozem. The degree of influence depended on the duration and periodicity of smoke exposure. In all experiments, enzymes of oxidoreductase class (catalase, peroxidase, polyphenol oxidase) were more sensitive to fumigation than invertase from hydrolase class. High concentrations of toxic gases were the cause of suppressed enzymatic activity of soils. The following concentrations exceeded the maximum permissible concentrations for atmospheric air: CO 714 times, phenol (hydroxybenzene) 441 times, acetaldehyde 24100 times, formaldehyde 190 times. Accumulation of polycyclic aromatic hydrocarbons (PAHs) in soil after fumigation was revealed, the total content of PAHs was 377 ng/g. The highest values were recorded for naphthalene, where the concentration was 4.4 times higher than the maximum permissible concentration and phenanthrene, 2.8 times higher than the maximum permissible concentration. It has been found that 60-min intensive smoke affects the soil to a lesser extent than continuous and periodical ones. Indices of enzymatic activity of chernozem after such fumigation decreased by 15–33% depending on the enzyme, and after continuous and periodical by 41–84 and 31–78%, respectively. The obtained data indicated a significant effect of smoke on the enzymatic activity of soils under continuous and periodical exposure to gaseous products of combustion.

Keywords: fumigation, enzymes, ordinary chernozem, toxicity, bioindicators

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INTRODUCTION

The interest to the study of pyrogenic factors (fire and smoke) effects on natural ecosystems grew in last decades. Fires play a specific role; they can have a pernicious influence on forests - burning vegetation completely or partly. The trend is observed in many regions of the world towards the increase of areas, subjected to fire, and fumigation of adjacent territories, and this is connected not only with anthropogenic activity, but also with climate change [31, 40]. About 7 million hectares of forest burned out in Australia in 2019–2020. The number of large forest fires and annual area of fires increased in south-eastern Australia beginning from the 1950s [48, 63] due to dangerous fire situation and drought. Similar changes were found in the countries of Europe, Asia, and North and South America [33, 40, 65]. Soils on the slopes lose their water retention capacity owing to fires, and this can be the cause of other natural phenomena such as draughts and

landslides, similar to those occurred in California (USA) in 2007 [62]. There is some available information by now about the influence of fire and high temperature on soil properties [44, 58] and soil biota [3, 34]. More than 90% of inflammations in forests are directly connected with human activity, determined largely by intended arsons and incorrect behavior [41, 61]. This increases significantly the possibility of forest fires in remote areas visited by humans and threatens animal habitats because of vegetation burning and changes in soil properties [42].

It should be noted that additionally to high temperatures and direct flame, ecosystems can be affected by smoke resulting of thermal destruction of plant materials in forest fires. It is known that smoke can content different compounds, which are highly toxic and hazardous [1, 2]. Smoke contains many phenolic compounds, which are commonly known to possess mutagenic carcinogenic properties [2, 15]; oxides of

carbon and nitrogen and other substances are emitted as well. It is found that burning process by itself affects the composition of gaseous substances. If there is an incomplete burning of materials, so carbon monoxide, hydrogen cyanide, hydrocarbons and other gases are mostly emitted [51]. It should be taken into account that aerosols are formed in the course of biomass burning. They represent largely fine particles (PM 2.5—particles of up to 2.5 μm in diameter) [22, 59], and it is known that these particles are mostly composed of organic substances [38]. All gaseous substances formed in the result of burning can be transported for hundreds of kilometers from the epicenter of inflammation and settle down with atmospheric precipitations. The volume of CO, CO₂, and particles <2.5 μm emissions caused by burning of forest biomass in the territories of Siberian and Far Eastern Federal Districts accounted for more than 80% of all-Russian emissions in 2016 and 2021 [24]. The territory of Siberia is one of most destroyed by fire among the areas of boreal ecosystems of the world [54], and smoke due to a long-distant transport from subjected to wildfires caused smoke pollution not only of adjacent regions, but was recorded in Moscow and some other regions of the European Russia [14]. The influence of wildfire smoke has negative effects on the population health [27, 55], and pulmonary and cardiovascular system diseases are recorded. Negative effects of smoke on animals were also studied and described [5, 66].

However, the influence of chronic effect of smoke on soil properties developed under the conditions of long-lasting smoke pollution remains to be unstudied at present time. There were no such researches earlier. The effect was not studied of regularly repeated influence of gaseous substances on soil, though it is known that smoke can remain in the atmosphere for a relatively long time [59]. This process is repeated very often in many regions of the world due to highly dangerous fire situation. The process of dispersion and transportation of pollutants was already studied in wildfires in Southeast Asia. This region together with Siberia and Far East is one of the most fire-dangerous in the world; Smoke pollution was often occurred here [30, 36], and transportation of smoke for long distances by winds was recorded [35, 37]. Significant emissions of toxic smoke to the atmospheric air from forest combustion were reported [43, 47].

The effect of smoke pollution of soil produced by short (15 min) and longer (60 min) influence of smoke on soil enzymes, pH, and concentrations of salts was studied earlier. It was found that the depth of gaseous substances penetration into the soil is limited by the upper 0–5 cm layer [58], and time of inhibition plays an important role in the decrease of enzyme activity of soil. Soil enzymes are formed mostly from soil microorganisms and decomposed animal and plant residues. They are the key biocatalysts participating in the destruction of organic substances [26]. Enzymes play an important role in biogeochemical cycles of soil car-

bon and nitrogen [70]. Enzyme activity is an important metabolic driving force of soil ecosystems reflected the intensity and direction of soil elements cycling and transformation [32]. They are sensitive early indicators of changes in soil ecosystems [72].

The aim of our work was to study the influence of smoke from burning plant material (pine sawdust) on enzyme activity of ordinary chernozem, modelling chronic effect of smoke under conditions of long fire period. The effect was studied of gaseous products of combustion on enzyme activity of soil under periodical influence of smoke: modelling of regularly repeated inflammations. The most sensitive soil enzyme, which responded to smoke in different ways, were found, and the results of current study were compared with one-time (60 min) effect of fumigation. Concentrations of certain chemical substances of smoke were determined in order to find the causes of changes in soil enzymes activity. Concentrations were determined of polycyclic aromatic hydrocarbons (PAHs) in soil as possible cause of the changes in the activity of soil enzymes.

OBJECTS AND METHODS

Studied object was the soil of an arable plot in the Botanical Garden, Southern Federal University (0–10 cm); it was calcareous light clayey ordinary chernozem of Southern Europe facies (Haplic Chernozem (Aric, Loamic, Pachic). Soil of experimental plot had the following properties: horizon thickness (A + AB) 80 cm, organic carbon content in the plow horizon 2.0%, heavy loamy particle-size composition, Physical clay content is 53%, concentrations of mobile phosphorus 3.3 mg P₂O₅/100 g, exchangeable potassium K₂O 341 mg/kg, nitrates N–NO₃ 8.4 mg/kg.

Model experiments were carried out under the laboratory conditions with the help of smoke generator Merkel Standard (Helicon, Russia). Air temperature was 21°C; relative humidity, 54–58%; atmospheric pressure, 755–757 mm Hg (100.67–100.93 kPa). Parameters of aerial medium were determined with the help of meteorological meter MES-200A (ZAO NPP Elektronstandart, Russia). Pine sawdust was the object of burning. Transparent container as gas chamber for fumigation has the volume of 50 L in all experiments. Air delivery to the chamber was carried out with reciprocating compressor Hailia Aco 208 (Haili Group Co. Ltd, Chine) with flow rate production 17.5 L/min.

Only the influence of smoke was studied in experiments, heat influence measurement was excluded by the construction features of smoke generator. The temperature of gaseous products of burning was higher than that of atmospheric air and accounted for 25.8°C; it was determined with the help of the laboratory thermometer TL-2 (OAO Termopribor, Russia). Air-dry soil of mass 40 g was placed as a layer 0.6 cm thick into polypropylene vessels of 200 mL in volume in triplicate for every sample. Then all samples with

soil were placed into gas chamber for treatment with smoke. The conditions of all experiments were similar: smoke temperature, soil mass in vessels, gas chamber for fumigation, parameters of aerial medium.

Time of soil fumigation in the first experiment with one-time effect was 60 min of an uninterrupted fumigation. However, time of fumigation under real conditions can be much longer, up to several days. So, time of soil fumigation in the second experiment accounted for 12, 24, and 36 h, during which smoke came into gas chamber during 3 min every hour to maintain the smoke concentration during the experiment. Hence, continuous effect of smoke was modelled, i.e. the effect developed under long-lasting influence of the destructive factor. The integrated effect of smoke entering the gas chamber in this experiment accounted for 36, 72, and 108 min. The influence of the periodical effect of fumigation was studied in the third experiment, when soil was treated with smoke for 10 min every 7 days during 42 days, and this was sum total the same time of influence as in the first experiment with one-time effect of smoke. The modelling was carried out of regularly repeated effect of smoke on soils in the fires, because periodical fires can appear in fire-dangerous regions during a rather short time.

Enzyme activity of chernozem was determined after completing the fumigation [7]. Enzymes of oxidoreductase class (catalase, peroxidase, polyphenol oxidase) and invertase from hydrolase class were taken as indicators. Selection of enzymes for analysis was determined by their information value and high sensitivity to anthropogenic changes [6, 7]. Catalase activity was determined by Galstyan volumetric method by the rate of H_2O_2 decomposition. Catalase decomposes H_2O_2 to water and molecular oxygen, which is formed in the respiration process of living organisms and other biochemical reactions [12]. Activities of polyphenol oxidase and peroxidase were determined by Karyagina and Mikhailova method with hydroquinone as substrate. These enzymes play an important role in the processes of humus formation. Polyphenol oxidase catalyzes oxidizing of polyphenols to quinones in the presence of free aerial oxygen. Peroxidase catalyzes oxidation of polyphenols in the presence of H_2O_2 or organic peroxides [12]. Invertase was determined with modified colorimetric method, based on determination of copper reduced by glucose with Fehling's solution [7]. Invertase activity characterizes better the level of fertility and biological activity of soil [19]. Concentrations of solutions with reaction products were determined at spectrophotometer PE 5300VI (OOO Ekokhim, Russia). Obtained results for experimental samples were compared with the control ones (taken as 100%).

The influence of combustion products on pH of soil suspension was determined for experiments 1 and 2 with potentiometric method with the help of unit Hanna HI-98128-pHep-5 (HANNA, Germany) at

soil: water proportion 1 : 2.5. Analysis for concentrations of soluble salts in suspension was carried out in similar way using the HI-9034 conductivity meter (Hanna, Germany).

Concentrations of gases from burning of pine sawdust were determined. The smoke was analyzed with the help of gas analyzer DAG-16 (OOO Ditgaz, Russia), recommended for gas sampling. After sampling of gaseous substances, the following units were used to determine the concentrations: gas chromatograph Kristall 2000M (ZAO SKB Khromatek, Russia), chromatograph FGH-01 (OOO NPF Anatek, Russia), photometer KFK-3-01-ZOMZ (AOOT Zagorsk Optical-Mechanical Plant, Russia), spectrophotometer UV-1800 (Shimadzu Corporation, Japan).

Concentrations of PAHs in soil were determined according to the registered methods [9–11] in triplicate with the help of Agilent Technologies 1260 chromatograph (Agilent Technologies Inc, USA) with fluorescence detector. Soil before analysis was fumigated during 30 min, and after that, PAHs from the list of priority pollutants were determined in the samples. The obtained results were compared with Canadian standards [28] for soils of agricultural territories, because there are the data for Russia only on benzo(a)pyrene.

Our experiments with smoke were close to real conditions, when fires produce strong and intense smoke pollution, which can have negative effects on soil, biota, and humans. Smoke by itself can move for great distances, far from the epicenter of inflammation, and remain in the bottom layer during long time, forming smog.

Statistical treatment of results was carried out with the help of one-way ANOVA at the level of statistical significance $p < 0.05$ in the programs Microsoft Excel and Statistica 12.0. Volume of samples, which were used for the analysis of variance, was $n = 9$ for both control and experimental samples.

RESULTS

Enzyme activity in control variants was within typical limits for this soil type. Activities of all enzymes according to the scales of enrichment [6, 7] were at the medium levels. The decrease of activities of soil enzymes by 15–33% was observed in the case of 60-min influence of smoke from burning of plant materials (Fig. 1). However, time of fumigation in the continuous experiment was longer, and greater suppression of enzyme activity was found. For example, the values of catalase activity decreased by 84% after 36 h of soil fumigation in gas chamber, whereas it decreased by 25% after 60-min—long fumigation (first experiment). Similar changes were observed for all studied enzymes (Fig. 2). In a similar way, the activities of enzymes decreased in the third experiment, where the effect of periodical fumigation on soil was evaluated (Fig. 3). Catalase, peroxidase, and polyphen-

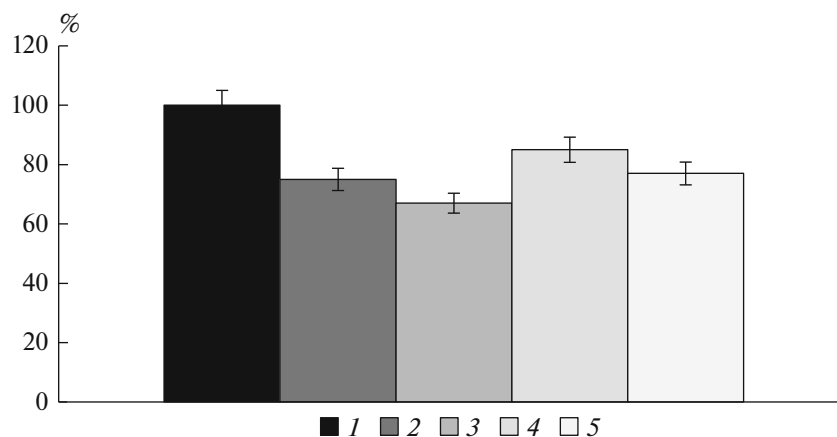


Fig. 1. Decrease of enzyme activity of soil after single 60-minute fumigation: (1) control; (2) catalase; (3) polyphenol oxidase; (4) peroxidase; (5) invertase (difference is significant at $p < 0.05$).

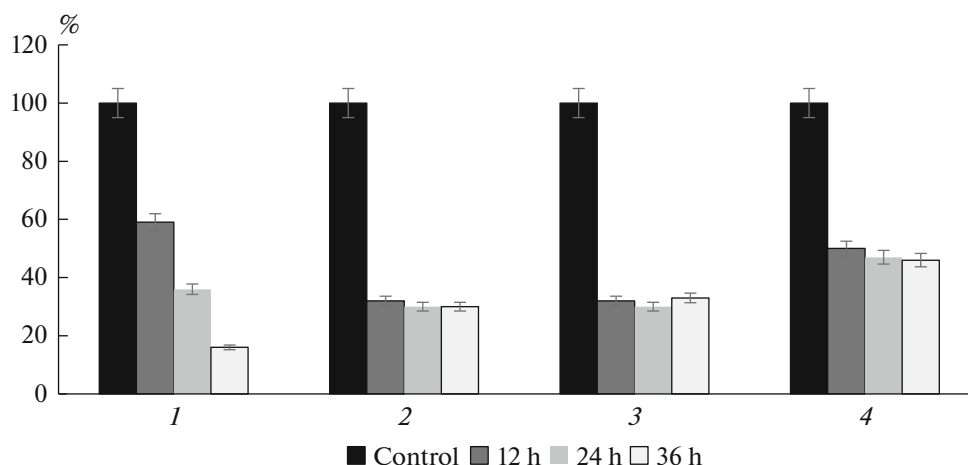


Fig. 2. The change of enzyme activity in ordinary chernozem after chronic influence of smoke: (1) catalase; (2) polyphenol oxidase; (3) peroxidase; (4) invertase (difference is significant at $p < 0.05$).

nol oxidase from oxidoreductase class appeared to be the most sensitive to gaseous substances after all three experiments, invertase was less sensitive.

The pH values of soil suspension and concentrations of soluble salts undergo a change in the course of continuous experiment. The pH value decreased from 7.8 to 5.5 (Table 1). In experiment with 60-min influence of smoke on chernozem, the pH value decreased from 7.8 (control variant) to 6.3. Mineralization increased after prolonged effect from 9.2 mg/L in control to 183–248 mg/L after 12–36 h of fumigation, whereas concentration of salts accounted for 210 mg/L after the first experiment (60 min of fumigation).

The analysis of smoke demonstrated significant exceedance of limits for pollutants in the atmospheric air SanPiN 1.2.3685-21 for some chemical compounds. The values of maximum single MPC for carbon monoxide must not exceed 5 mg/m³, daily average and

annual average values must not exceed 3 mg/m³. However, we observed in our study a pronounced increase of concentration of carbon monoxide, 3570 mg/m³, which was 714 times higher than maximum single and 1190 times higher than daily average and annual average MPSs (Table 2). One can see that the concentration of acetaldehyde (C₂H₄O) was 24100 times higher than the values of SanPiN 1.2.3685-21 on maximum permissible concentrations of pollutants in the atmospheric air of urban and rural settlements. Of all studied substances, C₂H₄O underwent maximum changes. Additionally to acetaldehyde, exceedance of limits was recorded for nitrogen oxides, formaldehyde, hydroxybenzene, saturated hydrocarbons C₆H₁₄–C₁₀H₂₂, and sulfur dioxide (only for average daily MPC).

Concentrations of PAHs in soil were taken into account, some of which exceeded the background concentrations provided by Canadian regulatory doc-

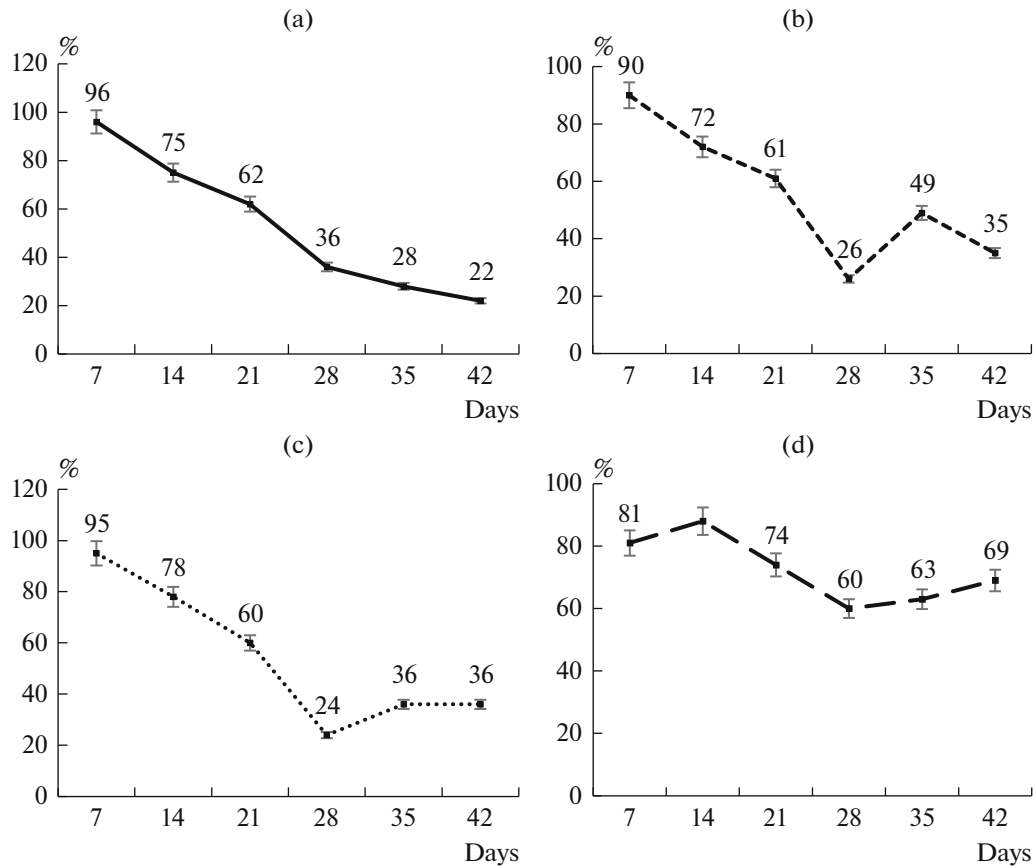


Fig. 3. Decrease of enzyme activity in ordinary chernozem in experiment with periodic influence of smoke: (a) catalase, (b) peroxidase, (c) polyphenol oxidase, (d) invertase (difference is significant at $p < 0.05$).

uments [28] on regulation of soils of agricultural territories. Concentration of naphthalene in soil was higher than the permissible value 4.4 times and accounted for 57.3 ng/g. Concentration of phenanthrene was higher than the permissible value 2.8 times (132.3 ng/g). The total content of PAHs from the list of priority pollutants accounted for 377 ng/g in experimental samples and 277 ng/g in control (reference) samples.

DISCUSSION

The results obtained on continuous (experiment 2) effect were compared with single 60-min impact (experiment 1). The decrease of enzyme activity in the

first experiment was less pronounced, if comparing it with 12-h-long impact. The duration of smoke introduction to the gas chamber with soil was greater than in the experiment 1 (60 min), whereas summary duration of fumigation in continuous 12-h experiment accounted for 36 min (3-min fumigation every hour). For example, catalase activity decreased by 41%, and in the first experiment by 25%. Similar results were obtained for other enzymes. Hence, the effect of continuous influence on biochemical parameters was more pronounced than the that of single 60-minute-long fumigation. The data of this model study are close to real conditions, when smoke can be for a long time in the bottom layer, not mixing with more dense and cold air. Thus, the medium becomes immobile, and

Table 1. The change of pH of soil suspension after continuous experiment (12–36 h)

Variant of soil fumigation	pH	Mineralization, mg/L
Control (without fumigation)	7.8	9.2
12 h	7.0	183
24 h	6.3	224
36 h	5.5	248

Table 2. Concentrations of gaseous substances in smoke in comparison with hygienic standards of concentrations of pollutant substances in atmospheric air in urban and rural settlements (SanPiN 1.2.3685-21)

Substance	Concentration in experiment, mg/m ³	MPC in atmospheric air, mg/m ³		
		maximum single	daily average	annual average
Sulfur dioxide (SO ₂)	0.28	0.5	0.05	–
Carbon monoxide (CO)	3570	5	3	3
Nitrogen dioxide (NO ₂)	60	0.2	0.1	0.04
Nitrogen monoxide (NO)	40	0.4	–	0.06
Acetaldehyde (C ₂ H ₄ O)	241	0.01	–	0.005
Formaldehyde (CH ₂ O)	9.53	0.05	0.01	0.003
Phenol hydroxybenzene (C ₆ H ₆ O)	4.41	0.01	0.006	0.003
Mixture of saturated hydrocarbons C ₆ H ₁₄ –C ₁₀ H ₂₂	312.69	50	5	–
Hexane C ₆ H ₁₄	238	60	7	0.7

concentration of pollutants increases with time and forms smog.

The third experiment on periodical influence of smoke similar to the second experiment can be close to real conditions, because the frequency of repeated fires is high in fire-dangerous regions of the world. The results of this experiment differed significantly from those of the first experiment, because the effect of fumigation was more pronounced. The total time of fumigation in this case was the same as in the first experiment with single effect and accounted for 60 min. However, the treatment of chernozem with smoke was increased to 42 days (10 min of fumigation every 7 days). Obtained results attested a strong effect of such influence. This was connected with peculiarities of enzymes, which responded differently to pyrogenic factor. It is known that biological systems can adapt to most unfavorable environmental factors, avoiding or decreasing the adverse effect [3, 7].

Catalase was the most sensitive enzyme in all experiments. It is the most sensitive parameter and responds even in the case of insignificant influence of different stress events [4, 6–8]. Peroxidase and polyphenol oxidase also appeared to be sensitive and underwent significant changes. These enzymes are sensitive to the effects of different types, and the levels of their activities can serve as important diagnostic criteria [6, 7, 64, 71].

It should be noted that researches of fumigation influence on soil and plants were carried out earlier [45, 57, 79, 80]. However, only fumigation of soil or plants was described in these studies with special preparations such as dazomet, methyl boride, etc. The composition of such preparations differs of the composition of smoke. Using such substances resulted in insignificant stimulation of plant seedlings and biological activity of soil. The changes were observed earlier in enzyme activity after straw burning [44], and the

results of this study demonstrated that enzymes of hydrolase class were more resistant to pyrogenic effects than oxidoreductases. It was found that temperature factor (hot smoke), ashes, and flame impact contributed to the change of enzyme parameters. Similar results on different sensitivity of enzymes were obtained in our work. The values of invertase decreased to lesser extent than the values of catalase, peroxidase, polyphenol oxidase. However, temperature factor was excluded in our work, because there were not ash input to the soil and no flame impact. Hence, only the influence of smoke on the activity of soil enzymes without additional factors was studied.

Enzymes are the products of metabolism of microorganisms. Enzyme activity arises in the result of the totality of processes of input of enzymes from living organisms, their stabilization, and activity in soil [18]. Microorganisms are extremely sensitive to different factors. Fumigation from the burning sawdust was no exception. Gaseous substances of smoke had apparently negative effect on microorganisms, and, hence, on the change of soil enzymes activity. Some chemical compounds were found in smoke. For example, carbon monoxide CO, which is qualified as one of priority environmental pollutant. The level of CO accounted for 3570 mg/m³. Increased concentrations of toxicant and substitution of a part of air by CO apparently caused the decrease of concentration of oxygen, which is required by many organisms for life activity. Carbon monoxide was presented in great concentrations, and this apparently changed significantly the pH values in the medium inhabited by microbiota, and, as a result, some microorganisms died.

Increased concentrations were recorded for phenol C₆H₆O and formaldehyde CH₂O. Similar to the case with CO, this caused the suppression of microflora and, therefore, the decrease of enzyme activity. The exceedance was recorded in our work of maximum

Table 3. Concentrations of priority polycyclic aromatic hydrocarbons in soil in experimental and control (background) samples

Substance	Concentrations of PAHs in experimental samples, ng/g	Concentrations of PAHs in background (control) samples, ng/g
Naphthalene	57.3	8.2
Fluorene	28.5	13.3
Phenanthrene	132.3	69.5
Anthracene	14.5	8.1
Fluoranthene	37	32.4
Pyrene	43.2	39
Benz(a)anthracene	12.7	13
Benz(b)fluorantene	21.1	16.8
Benz(k)fluorantene	6.9	8.3
Benzo(a)pyrene	15.6	15.7
Dibenz(a,h)anthracene	7.9	4.1
Total PAHs	377	228.4

single concentration of formaldehyde by 190.6 times, daily maximum concentration by 953 times, and annual maximum concentration by 3176 times. Phenol (C_6H_6O) concentration was exceeded by 441 (maximum single permissible concentration) times, 735 (maximum daily concentration) times, and 1470 (maximum annual concentration) times. This could have negative effect on soil microbiota. Presented data can be compared with work [17], where suppressing action was described in details of phenol and formaldehyde in high concentrations (100 and 1000 MPC) on composition and viability of soil microorganisms in leached chernozem. Hence, we can conclude that CO , C_6H_6O , and CH_2O made maximal contributions to the decrease of enzyme activity in our study.

The decrease of pH value and increase of soluble salts content in soil suspension occurred in the result of high concentrations of gaseous chemical compounds, which were well dissolved in this suspension. Dissolving of carbon monoxide resulted in formation of carbonic acid H_2CO_3 in the suspension, and interaction of suspension with C_2H_4O resulted in the formation of acetic acid. This apparently resulted in the displacement of pH towards acidification. It should be taken into account that sulfur dioxide in concentration 0.28 mg/m^3 was found in smoke. This concentration was 5.6 times higher than maximum daily concentration, but almost two times lower than maximal single value. This was enough to obtain diluted sulfuric acid produced by dissolving of SO_2 in soil suspension.

It is supposed that the decrease of enzyme activity could be connected also with PAHs. It was found in the course of analysis that concentrations of naphthalene (57.3 ng/g, exceedance by 4.4 times) and phenanthrene (132.3 ng/g, exceedance by 2.8 times) in soil samples of experiment exceeded Canadian standards.

The sum of all studied in experimental samples PAHs from the list of priority pollutants accounted for 377 ng/g (Table 3) and 228.4 ng/g in control samples.

Such results were apparently connected with the burning material (pine sawdust). Obtained data on the exceedance of background values of naphthalene and phenanthrene agree with the results of other researches [39, 56], in which the exceedance was found of these substances, when burning pine needles and other material of plant origin. The exceedance of background (control) values of these substances was recorded in our study too. Emission of these polycyclic aromatic hydrocarbons could be promoted by temperature of burning. It is known that alkylated derivatives of naphthalene are the most distributed substances in the case of burning in the middle range of temperatures. Phenanthrene derivatives dominated after relatively high temperatures [39]. However, concentration of phenanthrene in our study accounted for 69.5 ng/g in control samples, and this was higher than the value (46 ng/g) adopted in Canada. This can be explained by the fact that PAHs can be transported in the aerosol emissions for tens of kilometers from different sources and gradually settle down on soil surface. Moreover, selected for our experiment soil (ordinary chernozem) is located within the city boundaries, and this increases the probability of finding low concentrations of hazardous substances. It is known that urban soils are the most contaminated, and emissions of coal-fired thermal power plants and burning of biomass are the main sources of contamination of adjacent territories. When analyzing control samples of chernozem, insignificant exceedance of phenanthrene concentrations was found. In general, such trend was observed in many cities of the world, and was described in detail by researchers from different countries [23, 52, 73]. When analyzing fumigated soil samples, concentrations sig-

nificantly increased from 69.5 (control) to 132.3 ng/g (exceedance by 1.9 times of control values from the place of soil sampling and by 2.9 times of Canadian standards). More condensed PAHs included to the lists of priority pollutants were found in insignificant concentrations.

The exceedance of concentrations of PAHs in soils had direct influence on their biological (enzyme) activity. Oxidoreductases such as dehydrogenases and catalases contribute directly to the degradation of PAHs by cleavage of benzene ring. Hydrolases (invertase) had indirect effects on the destruction of organic pollutants, changing metabolic activity of destructors via limitation of nutrition or supply [67, 75]. Phenanthrene and naphthalene as those with highest contents had pronounced effect on metabolism of biological systems, because their concentrations in pyrogenically contaminated soils had direct effects on the work of enzyme systems.

Catalase is an antioxidant enzyme, indicator of soil ecotoxicity [46, 76]. Microbial cells have protective mechanisms, which improve their survival under the conditions of oxidative stress, such as increased activity of catalase [20]. Metabolism of PAHs causes the formation of reactive electrophilic metabolites, which are in actual fact the carcinogenic compounds responsible for DNA damage [20]. Microbiological destruction of hydrocarbons in microorganisms promotes formation of H_2O_2 as a by-product within cells, and this results in cell damage. Catalase is an enzyme metabolizing H_2O_2 . It protects cells from damage by active forms of oxygen [60]. The level of catalase activity changes owing to fuel contamination of soil [50, 76] and contamination with polyarenes [25, 68].

Dehydrogenase is one of the main agents, decomposing soil pollutants containing hydrocarbons. This enzyme transports electrons and hydrogen through the chain of intermediate carriers of electrons to the final acceptor of electrons (oxygen), being thus a catalyst of PAH destruction [29, 60]. This index is the most sensitive under the conditions of soil contamination with polyarenes [25], where enzyme activity decreases significantly in the presence of pollutants [21, 49, 60, 77].

One more important agent of the biological destruction of PAHs is invertase. Despite this fact, polyarenes as in the case with dehydrogenases, inhibit the activity of invertases [21, 53, 74, 78].

There are data on the results of long-term soil monitoring, which confirm the change of enzyme activity in soils under the influence of large industrial facility, for example, Novocherkassk GRES power plant, emissions of which are also pyrogenic. As total content of PAHs increased from 2012 to 2019, the trend was observed towards the change of catalase activity and activities of dehydrogenases and invertases [16]. Calculation of Spearman rank correlation coefficient demonstrated the presence of weak and medium

interactions between the activities of catalases, dehydrogenases, and invertases under the conditions of increased concentrations of PAHs in soils over the studied period.

CONCLUSIONS

The difference was found as the result of chernozem fumigation in model experiments in the decrease of enzyme activity, which was caused by time of stress action and by chemical composition of smoke. Gaseous substances had pronounced negative effect due to their high toxicity. An experiment on modeling the periodical and continuous effects of smoke on soil demonstrated much greater decrease of enzyme activity than in the case of single 60-min fumigation. Catalase demonstrated greater sensitivity to smoke in all experiments, and its values decreased by 84% in the experiment with continuous influence and by 78% in the experiment with periodical fumigation of chernozem.

Carbon monoxide, nitrogen monoxide and dioxide, sulfur dioxide, phenols, acetaldehyde, formaldehyde, and hydroxybenzene were the main chemical compounds that affected the soil. Significant exceedance of MPC was observed for most compounds. The decrease of pH of soil suspension and increase of mineralization was observed after fumigation and was connected with the interaction between toxic substances of smoke and suspension.

The decrease of enzyme activity of chernozem could be connected with PAHs either. The exceedance of background concentrations of naphthalene and phenanthrene in soil was found. In general, the increase of concentrations of polyarenes in our study, and especially the increase of concentrations of naphthalene and phenanthrene, was connected with the pyrogenic origin of these substances. The increase of concentrations of these PAHs was connected with materials (pine sawdust) and temperature of burning.

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ETHICS APPROVAL AND CONSENT TO PARTICIPATE

This work does not contain any studies involving human and animal subjects.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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