Firewater Toxicity after Extinguishing Natural-Based Insulation Materials

Helena Hybská,[a] Linda Makovická Osvaldová,[b,]* Michaela Horvathová,[b]
Tatiana Hýrošová,[c] and Ágoston Restás [d]

Water is the most widely used fire extinguishing agent. It is used to eliminate a wide range of fires, often occurring in ecologically sensitive areas. There is little information on the toxicity of the fire-fighting substances in connection with aquatic and terrestrial organisms. Toxic substances often present in fire waters slow down life processes. As a result, some organisms die. This study deals with the extinguishing of burning solids (fiberboard, cannabis, straw, cork) with extinguishing water and assessment of its effects on the aquatic and terrestrial environment. The following test organisms were selected to test the effects of the extinguishing water: *Daphnia magna* – consumer; and *Sinapis alba* and *Lemna minor* – producers. A preliminary test was carried out on all the samples to evaluate the (positive / negative) effects of the fire water on the test organisms. Specific conductivity, pH, and chemical oxygen demand were also determined. The results of this study call attention to negative impacts of extinguishing water on the environment. It is necessary to pay attention to prevention and thus eliminate potential risks. If environmental contamination can no longer be prevented, the spread of contaminated water must at least be reduced.

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Contact information: a: Faculty of Ecology and Environmental Sciences, Technical University in Zvolen, T.G. Masaryka 24, 960 53 Zvolen, Slovakia; b: Faculty of Security Engineering, University of Zilina, Univerzitna 8215/1, 010 26 Zilina, Slovakia; c: Faculty of Wood Sciences and Technology, Technical University in Zvolen, T.G. Masaryka 24, 960 53 Zvolen, Slovakia; d: Institute of Disaster Management, National University of Public Service, Hungaria krt. 9-11, H-1101Budapest, Hungary;
** Corresponding author: linda.makovicka@fbi.uniza.sk*

INTRODUCTION

To adapt to the challenges posed by climate change, the construction industry is focusing on building sustainable, energy, resource-efficient, and cost-effective structures by increasing the use of biologically based construction materials. However, fire safety has always been crucial in wood construction (Zima and Kasymov 2016; Wang 2018). Every year, various types of fire extinguishing substances are used for a wide range of fires. These fire extinguishing substances are often used in ecologically sensitive areas where these fire-fighting substances are toxic to aquatic and terrestrial animals (Wang 2018). Even less information is available on the effects on the community and ecosystem levels. Due to the wide incidence and variety of fire-extinguishing effects, water is the most widely used extinguishing agent. For fire-fighting purposes, it is used either in a pure form (without any additives) or in a mixture with different chemicals that improve its fire-fighting performance. Water is a polar solvent of inorganic and organic compounds. The most important water extinguishing effect is the cooling effect. Water cools down the burning substances below their flashpoint and interrupts the burning process. In addition to the cooling effect, water acts as a fire extinguishing agent with its smothering effect (Kererekes *et al.* 2018; Zima and Kasymov 2018; Mensah *et al.* 2019, 2020).

Toxicity is the effect of extraneous substances on aquatic organisms (plants and animals). Extinguishing water can contain toxic substances and affect the environment as well as the health of aquatic and terrestrial organisms. The significance of our study lies in the idea of proving the effect of burning of the selected materials used in the exterior on changes in water quality using test organisms (a form of biomonitoring). A study by Ferraz *et al.* (2021) stressed that the assessment of the toxic impact of the water from firefighting (both natural and industrial) on aquatic (freshwater and marine) organisms was poorly investigated, so more studies in this area should be carried out. Silva *et al.* (2015) detected up to 16 polycyclic aromatic hydrocarbons in the fire-extinguishing water. Ecotoxicologic screening with four standard aquatic species from different functional groups and trophic levels found significant immobilization of *Daphnia magna* and a decrease in the growth rate of *Pseudokirchneriella subcapitata* and *Lemna minor*. This study also highlighted the need for further research into the complexity of the potentially harmful environmental effects of fires on water communities, with a focus on cascading effects along the trophic network. Fire toxicity is the biggest cause of death and injuries due to unwanted fires, yet it is the least well-studied area of fire science and technology. Clear correlations were observed between the stoichiometric equivalence ratio and major asphyxiant extracts. However, long-term toxic substances present in wastewater, such as carcinogenic polycyclic aromatic hydrocarbons and microscopic particles that arise from their agglomeration, are likely to be responsible for hundreds or thousands of additional deaths due to acute asphyxiants and irritants. The toxic substances in wastewater can also cause damage to the environmental components (Kärrman *et al.* 2016; Stec 2017; Graetz *et al.* 2021). The influence of fire fighting in the forest environment on the dynamics of the freshwater basins was addressed by the Harper *et al.* (2019), who found a significant immobilizing impact on *D. magna*.

Much attention is paid to the use of flame retardants in fire-extinguishing water in terms of their effects on the aquatic environment (Wang *et al.* 2014; Binio and Kieliszek 2018; Wang 2018; Plomp *et al.* 2020). This study investigated the extinguishing of solid substances of organic origin (fiberboard, straw, cork, and hemp) with fire-fighting water and assessed its impact on the aquatic and terrestrial environment. The reason for choosing these test materials is that they are of ecological (natural) character, have good thermal insulation properties and are starting to be applied more often in wooden buildings within the European region.

EXPERIMENTAL

A round-shaped sheet vessel with a diameter of 500 mm was used for the fire. Five pieces of spruce wood kindling sticks (200x10x15 mm) were placed on its bottom. A gas tank with a burner was used as the initiator. The insulation material samples were weighed to be approximately 300 g. At the time of the greatest burning rate of the spills, the insulation materials were put into the fire (Fig. 1). The burning intensity was determined based on the size of the flame and its radiant heat. The samples started to burn gradually, and the fire was extinguished the moment the samples were sufficiently burned (after 3 minutes), and a charred layer was formed. Drinking water from a public water supply was used to extinguish the fire. The water was collected into a container, filtered, and poured into a glass sample tube. These fire extinguishing samples of individual materials were then used for toxicity testing and for the determination of selected physicochemical parameters.

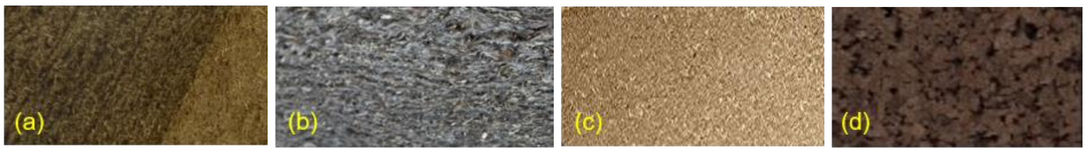

Fig. 1. a) Fiberboard, b) cannabis panel, c) straw panel, and d) cork insulation material

Fiberboard

Fiberboard is an insulation material made from wood fibers that is mainly used for structural sheathing insulation in buildings. Fiberboard slows heat transfer in the winter and summer seasons. Fiberboard is also used in the dry construction of internal parts of buildings, such as walls and floors (Antov *et al.* 2021). Fiber insulation boards are usually comprised of wood fibers (85%), which are obtained from sawdust and chips of coniferous trees. Coniferous trees are preferred because of their high fiber quality.

Cannabis Panel

Cannabis insulation panel is one of the most environmentally friendly insulation materials (Ninikas *et al.* 2019). Cannabis comes from a fast-growing annual plant called *Cannabis sativa*. Cannabis insulation panels are pleasant to the touch, have a pleasant scent, and have excellent thermal insulation parameters. They are also highly vapor-permeable (diffusely open), provide high protection against cold in the winter, and prevent overheating in the summer. Cannabis insulation panels also have good sound-insulation parameters. Cannabis insulation panels can perfectly regulate moisture without modification to its thermal and technical properties.

Straw Panel

Lignocellulose fibers present in annual grain plants are the natural raw material used to produce straw panels. Straw panels have a similar structure to wood fibers, and a high natural lignin content contributes to strong inter-fiber bonding. Straw panels also utilize a formaldehyde-free resin that provides a hydrophobic coating and solidifies the board (Hýsková *et al.* 2020).

Cork

Cork is a natural material with a specific cell structure that allows its use in the production of insulation against noise, heat leakage, and vibration (Gil 2015). Cork is used in the construction industry for exterior thermal insulation of facades, insulation of roofs, and for interior sound and heat insulation. Cork is obtained by peeling the bark from cork oak, which can regenerate the bark and allow its peeling without damaging the tree itself. The characteristics of cork are attributed to its structure and chemical composition. Cork mesh contains 89.7% gaseous substances, so its density is low. The gas element located in the cork allows hardly any conductivity in terms of thermal, acoustic, or vibration effects.

Cork's physical structure also provides strong compressibility and flexibility. Cork insulation is produced in the form of a pulp or boards. Cork boards are made without the use of external binders. At elevated temperatures in combination with high pressure, a resin is squeezed out of the cork granules, thereby allowing the compression of the granules into a plate form of 1000 mm × 500 mm. Cork boards keep their dimension after the compression. This method produces plates with the required thickness and density. Cork has long-lasting technical characteristics that facilitate its use in environmentally friendly, low-energy buildings where a healthy environment needs to be created.

Physicochemical Indicators

The chemical oxygen demand (COD)

Chemical oxygen demand (COD) is defined as the mass of oxygen equivalents that are consumed under well-defined conditions during processing of a liter of aqueous sample for the oxidation of the substances. The oxygen equivalents are provided by a strong oxidizing agent. In accordance with the ISO standard 8467 (2000), potassium dichromate ($K_2Cr_2O_7$) is used as a reagent to determine the COD.

Determination of the pH

The pH value significantly affects the chemical and biochemical reactions in water. A SenTix 81 electrode pH meter (WTW GmbH, Weilheim, Germany, InoLab pH Level 3) was used to determine the pH, in accordance with the ISO standard 10523 (2008).

Conductivity determination

Conductivity is a basic criterion for assessing the number of electrolytes present in water. The determination of conductivity reflects the concentration of dissolved substances in the form of ions as well as water mineralization. A WTW LF 318 conductometer (WTW GmbH, Weilheim, Germany) was used to determine the conductivity in accordance with the STN EN standard 27888 (1998).

Determination of dissolved oxygen content

Oxygen is the most important of the dissolved gases in water. The dissolved oxygen content in the water is expressed in mg/L and in % of the saturation of the water with oxygen related to the solubility of oxygen in the water at a given water temperature and atmospheric pressure. The dissolved oxygen was determined by the electrochemical method with a membrane probe. A WTW Oxi 340i oximeter type with a Stirrox G probe (WTW GmbH, Weilheim, Germany) was used to measure the dissolved oxygen content in accordance with the STN EN standard 25814 (2013).

Ecotoxicological tests

Two test organisms were selected to test the effect of the extinguishing water. *D. magna* (Fig. 2a) was used for the consumer, while *Sinapis alba* (Fig. 2b) and *L. minor* were used for the producers. Static tests and acute toxicity tests were performed according to the duration of the test. In all the tests, a preliminary test was performed to evaluate the positivity or negativity of the effect of the extinguishing water on the tested organisms in the aquatic environment (*D. magna* and *L. minor*) and the terrestrial environment (*S. alba*) (Hybská and Samešová 2015).

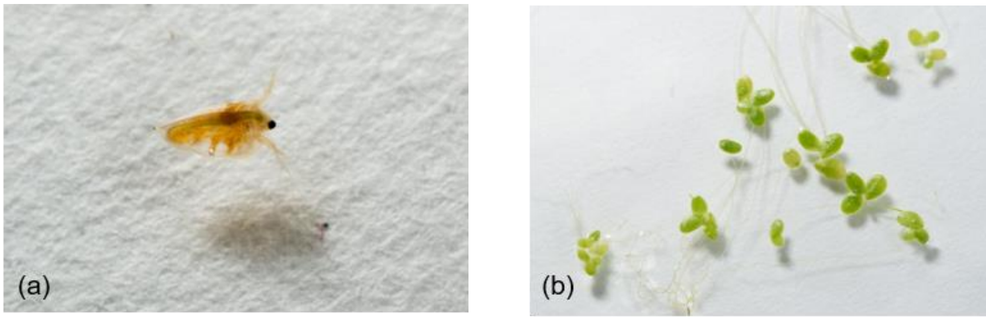

Fig. 2. a) Test organism of *Daphnia magna*, b) *Lemna minor* (laboratory breeding)

The test organisms used were classified with regard to the capacity of our research laboratory into at least two trophic levels. All three test organisms are generally used to assess possible toxic effects on the environment. Each test was repeated at least 12 times.

The test procedures and conditions, including inspection of the accuracy of the experiment, are shown in Table 1(STN EN ISO 6341, OECD 202 I), Table 2 (STN EN ISO 20079, OECD 221), and Table 3 (STN 83 8303).

Figure 3 shows the design of the *Daphnia magna* immobilization assay and Fig. 4 shows the design of the *Lemna minor* growth inhibition assay. Figure 5a shows the design of *Sinapis alba* root inhibition assay (after 72 hours of incubation) and Fig. 5b shows *Sinapis alba* seeds (germination capacity of 98%, determination of seed germination capacity in an accredited laboratory of the Central Control and Testing Institute in Agriculture, Seed Testing Laboratory in Vígľaš, Slovakia)

Data Analysis

The analysis of variance (ANOVA) method (Box *et al.* 2005; Triola 2010) was used to test and compare the measured data of the selected samples. The data analysis and presentation of results were processed in the MATLAB system (MathWorks, Natick, MA, USA). The results of ANOVA method can be considered reliable as long as the following assumptions are met: independence of observations, homogeneity of variance, and normal data distribution. The assumptions were verified before the results were processed in the method.

Table 1. Preliminary Test Conditions for *D. magna*

Test Organism	*D. magna* Straus (more than the third generation, obtained by acyclic parthenogenesis under the conditions of healthy breeding), individuals younger than 24 h since birth (no feeding)
Biotest Conditions	Temperature: 20 °C ± 2 °C; pH = 7.8 ± 0.2; laboratory conditions
Control Sample	Diluting water prepared from the solutions of $CaCl_2.2H_2O$ (1), p.a., $MgSO_4.7H_2O$ (2), p.a., $NaHCO_3$ (3), p.a., KCl (4), p.a. by the addition of solutions (1)- (4) per 10 mL and adding demineralised water into a volume of 1 L
Reference Substance	$K_2Cr_2O_7$, EC_{50}=0.95 mg/L (limit 0.3 to 1.5 mg/L)
Test Duration	48 h
Preliminary Test	20 *D. magna* /undiluted sample (10 mL), same conditions for a control
Validity of the Test	Immobilization ≤ 10%, change of concentration of dissolved oxygen O_2 ≤ 2 mg/L
Monitored Response	% of immobilized individuals

Fig. 3. *Daphnia magna* immobilization test design

Table 2. Conditions for the Test of Growth Inhibition of *L. minor*

Test Organism	*L. minor*; 12 to 15 leaves at the beginning
Incubation Temperature	Temperature: 25 °C ± 2 °C – thermostatic cabinets ST FOT (Eko Pol Poland) with simulation of day and night; lighting continually, min. intensity of 6,500 lux
Control Sample	Z-medium (was used as the nutrient solution and prepared in accordance with the instructions from its supplier - Culture Collection of Autotrophic Organisms - CCALA, Třeboň, the Czech Republic
Reference Substance	3,5dichlorophenol, EC_{50} = 3.05 mg/L (limit 2.2 to 3.8 mg/L)
Exposure	7 d
Preliminary Test	Volume 50 mL sample
Criterion of Validity	Average number of leaves in the control after the termination of the test > than eight times as large at the beginning of the test, pH at the end of the test < than 1.5 in comparison with initial pH
Biomass Determination	Whole plants of *L. minor*, including root, used for determination; biomass determined gravimetrically by drying into a constant weight at 105 °C (POL-EKO SL, Poland)
Monitored Parameters	Number of leaves counted, and appearance of the leaves evaluated (chlorosis, necrosis) at least three times during the test; growth inhibition (IC) in %

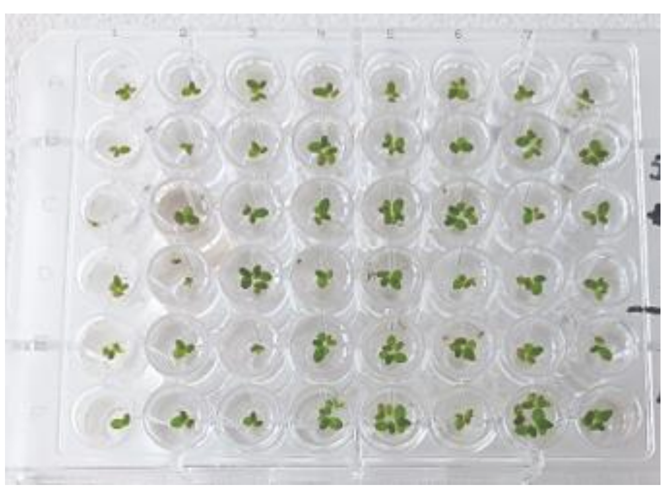

Fig. 4. *Lemna minor* growth inhibition assay design

Table 3. Conditions for the Test of Inhibition of Growth of Root of *S. alba*

Testing Organism	*S. alba*, per 30 seeds of *S. alba* L. in Petri dishes (diameter of 100 mm)
Sample Volume	10 mL
Temperature	20 °C ± 1 °C, thermostat TS 606 CZ/2-Var (WTW, Germany).
Control	Reconstituted water
Validity of the Test	Germination in control sample = 99.8 % (limit ≥ 90%)
Reference Substance	$K_2Cr_2O_7$, IC_{50}, 72 h = 28.5 mg/L (limit 4.1 to 85 mg/L)
Measuring Root Length	Steel calibrated measuring instrument
Exposure Time	72 h
The Response Monitored	Inhibition of growth of root from *S. alba* compared with the control

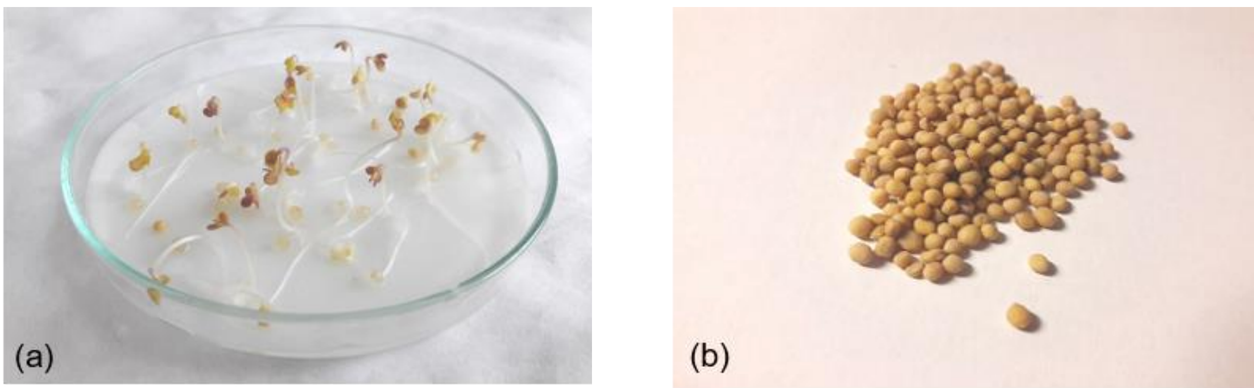

Fig. 5. a) Determination of *Sinapis alba* root growth inhibition (after 72 hours of incubation), b) *Sinapis alba* seeds (germination capacity of 98%, determination of seed germination capacity in an accredited laboratory of the Central Control and Testing Institute in Agriculture, Seed Testing Laboratory in Vígľaš, Slovakia)

RESULTS AND DISCUSSION

Physicochemical Indicators

The established values of indicators were evaluated based on the Government of the Slovak Republic Regulation No. 269/2010 Coll., which lays down requirements for the achievement of good water status, Annex No. 1, Part A Water quality indicators (general indicators) (Regulation of Slovak republic No. 269/2010). By determining the specific conductivity, the overall mineralization of the water was estimated. The recommended conductivity value is 110 mS/m. The highest conductivity value from the extinguishing was in samples of the hemp material. The pH of the fire water samples was between 6 and 8.5 (Table 4). Organic water pollution from the extinguishing process affected the pH of the samples and made it slightly more alkaline. The main group of oxidizable substances in water are organic substances. Therefore, this study estimated and demonstrated the pollution of water by organic substances that entered the firewater during the extinguishing of the samples. The specified values are recorded in Fig. 6. According to the above legislation, only the firewater from the cork complied with the maximum permissible values (35 mg/L).

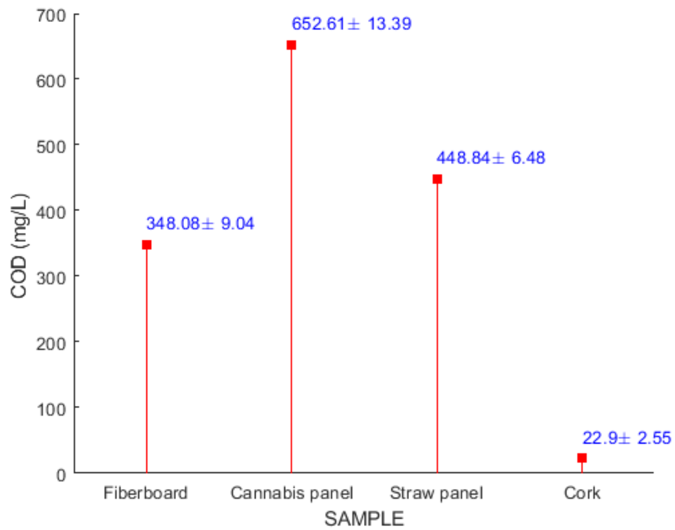

Fig. 6. Average values and the standard deviations of the COD measurements for the tested substances

Table 4. Determination of the pH and Conductivity Values

Sample	Fiberboard	Cannabis Panel	Straw Panel	Cork	Drinking Water
pH	7.10	7.54	6.88	10.64	6.90
Conductivity (mS/m)	54.50	105.30	10.64	62.40	42.10

Ecotoxicological Tests

The actual evaluation of the results obtained by the *S. alba* root growth inhibition test and the *L. minor* growth rate inhibition test was preceded by pre-processing the measured data and checking the assumptions necessary for the selected analysis. The data analysis and the presentation of the results were processed in MATLAB.

The influence of the selected material samples on the stated values for inhibition of S. alba was evaluated by the parametric ANOVA test at the level of significance of α = 0.05 (Table 5). The results of the test confirmed the significance of this effect on the experimental values.

Table 5. ANOVA Table

Source	SS	df	MS	F	p
Groups	8338.04	3	2779.35	108.55	0
Error	307.26	12	25.61	-	-
Total	8645.3	15	-	-	-

Note: Source of variation, SS-sum of squares, df-degrees of freedom, MS-mean square, F-test statistic, and *p*-value

To compare the average values of the inhibition of root growth of the individual materials, multiple comparison tests called post-hoc tests were used. The post-hoc tests (Fig. 7) showed significant differences between the fiberboard and the straw panel (p=0.000), the cannabis and the straw panel (p=0.000), and the cork and the straw panel (p=0.000). Figure 7 shows the average values of inhibition of growth of the roots of *S. alba* in experimental samples with 95% confidence intervals. The blue interval is the sample that was compared with the other samples. The red intervals did not overlap with the blue ones, which indicated that the inhibition values of the compared test sample straw differed significantly from the inhibition values of other materials.

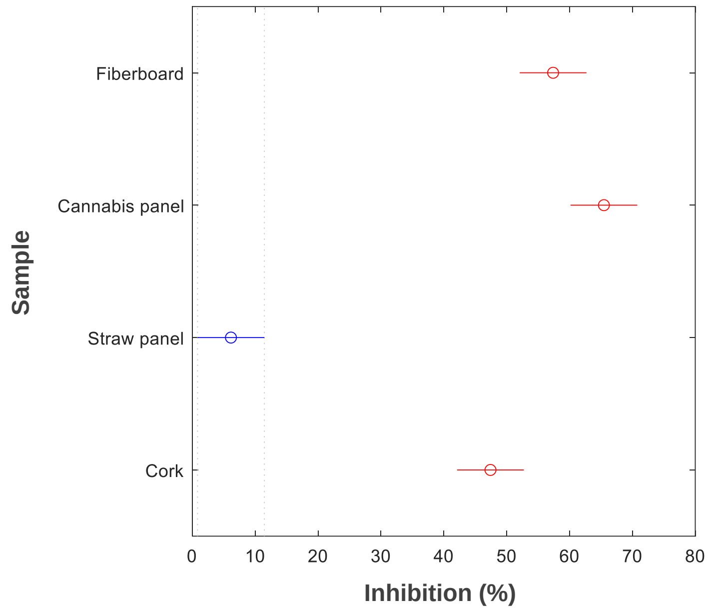

Fig. 7. Graphical representation of multiple comparison tests (3 material samples have means significantly different from the straw panel)

The post-hoc tests (Fig. 8) also showed a significant difference in the inhibition values for the cannabis and cork samples (p=0.001).

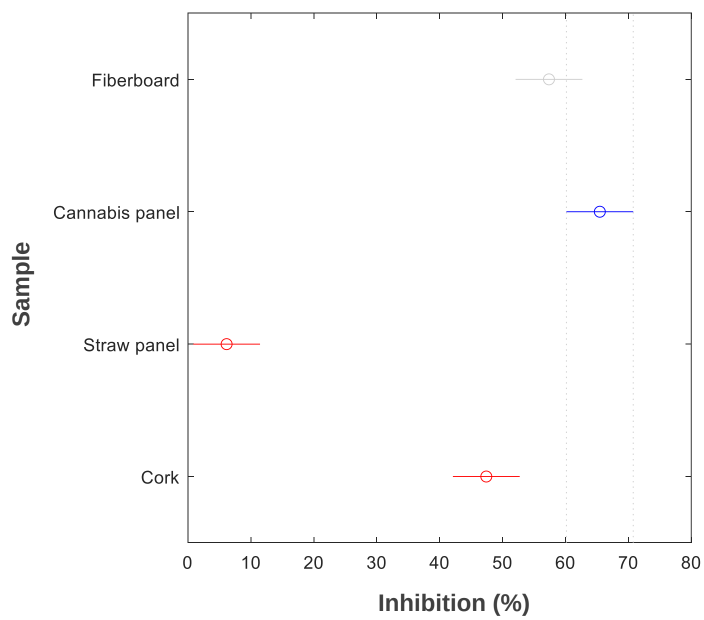

Fig. 8. Graphical representation of multiple comparison tests (2 material samples have means significantly different from the cannabis panel)

In the acute toxicity test of *L. minor*, the ANOVA test at the significance level α = 0.05 (Table 6) confirmed the significant influence of selected material samples on the inhibition values of *L. minor* (*p*=0.004).

Table 6. ANOVA Table

Source	SS	df	MS	F	*p*
Groups	1187.65	3	395.884	7.58	0.004
Error	626.95	12	52.245	-	-
Total	1814.6	15	-	-	-

Note: Source of variation, SS-sum of squares, df-degrees of freedom, MS-mean square, F-test statistic, and *p*-value

The post-hoc tests (Fig. 9) showed significant differences between the fiberboard and the straw panel (*p*=0.038), the cannabis and the straw panel (*p*=0.005), and the cork and the straw panel (*p*=0.012). Similar results were also observed for the *S. alba*. The inhibition of the *L. minor* growth rate for the other pairs of samples did not show significant differences.

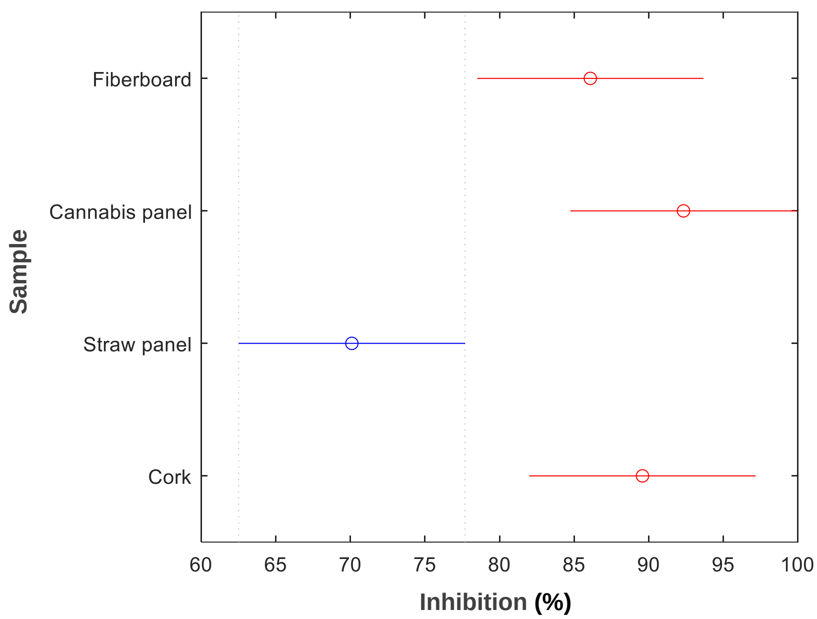

Fig. 9. Graphical representation of multiple comparison tests (3 material samples have means significantly different from the straw panel)

Sinapis alba root growth inhibition is a shortening of the average root length in the sample and the growth rate inhibition consists in monitoring the reduction in the number of *Lemna minor* leaves compared to the control solution (Diluting water and Z-medium are described in Tables 1 and 2.)

The determined results (the inhibition in %) of the acute toxicity preliminary tests performed on the *S. alba* (in the early phases of root growth) and the *L. minor* are shown in Fig. 10. During the 7 days exposure of *L. minor*, dead leaf tissue instances of necrosis and chlorosis (white or light yellow leaves) were also recorded. The validity of the test results was confirmed by the fact that the average number of leaves during checking increased eightfold during the test (the number of leaves during the inspection was 76) and the pH in the control sample did not change (the values at the end of the test were the same as shown in Table 4). The experimental samples had an inhibitory effect on the test organisms of *L. minor* (OECD Test No. 221 2006; ISO 20079 2008) with the significant differences described above. In a sample of extinguishing water used to extinguish the burning of wheatgrass, a comparable inhibition of growth rate of 69.90% was established (Veľková *et al.* 2019). The preliminary test with the test organism *S. alba* was positive, as it found an inhibition of root growth greater than or equal to 30% compared to the control sample (STN 83 303 1999). Based on the results obtained in the experiment, all the samples were positive except for the straw extinguishing water. In addition, the pollution of the extinguishing water had a strong inhibitory effect on the growth of the *S. alba* root. Negative effects on the root growth of *S. alba* compared to checking were also detected in the studies conducted in fire-extinguishing water from the extinguishing of wheatgrass and spruce wood (Veľková *et al.* 2019; Hybská *et al.* 2020).

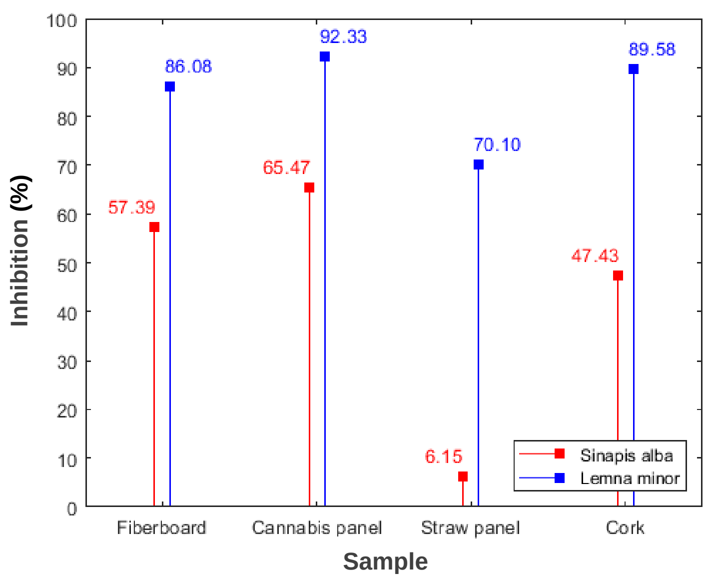

Fig. 10. Average inhibition values of the *S. alba* and *L. minor*

Table 7. Results of the Acute Toxicity Test on *D. magna*

Sample	**Immobilization (%)**	
	After 24 h	After 48 h
Fiberboard	95	95
Cannabis panel	100	100
Straw panel	100	100
Cork	100	100

The test organism of the water flea (*D. magna* Straus) used in the tests was obtained from laboratory breeding by acyclic parthenogenesis under specified breeding conditions. Immobilisation was defined as a macroscopically comparable inability of the self-reliant spatial motion of *Daphnias* up to 15 seconds after circular mixing of the sample. The individuals moving with the 2nd pair of antennae but unable of the given motion are considered to be immobilised as well. The preliminary test was performed on experimental samples (Table 7), in which the *D. magna* content that was released was positive because more than 50% of the water fleas were immobilized during the test (OECD Test No. 202 2004; ISO 6341 2013). The samples were aerated prior to the test. The dissolved oxygen content in the samples was greater than 8 mg/L, and there was no change in the pH of the test samples during the test. The strong inhibitory effect was confirmed by Harper *et al.* (2019), Veľková *et al.* (2019), and Hybská *et al.* (2020).

The inhibitory effect on the samples was confirmed by the high COD values in the samples. Based on this indicator, it is possible to conclude that the firewater was polluted by substances of organic origin. Although these are natural raw materials that can be used in the exterior, they pose an environmental risk. The obtained results showed that extinguishing water, which escapes into surface and groundwater after extinguishing the fire of natural substances, also has toxic effects on the environment.

The pH and conductivity indicators were determined to detect changes in the water after extinguishing. If the pH becomes more acidic, then there could be an increased solubility of hitherto insoluble substances. An increased conductivity value would demonstrate an increased concentration of ionized components in the water. This could also affect the condition of the test organisms. As was explained earlier in this article, these changes were not significant compared to the values determined in the drinking water used for extinguishing. The effect of high COD values manifested itself by high growth inhibition of test organisms (*Lemna minor* and *Sinapis alba*) and almost 100% immobilization of *Daphnia magna*. These values were used as an indicator of the determination of organic substances dissolved in water, which come mainly from the organic matter forming the tissues of the natural materials used for construction purposes.

CONCLUSIONS

1. The tests performed on samples of extinguishing water from different extinguishing materials (cork, straw, fiberboard, and cannabis) indicated a significant problem of environmental impact on aquatic and terrestrial environments.
2. Sufficient attention should be paid to the prevention of fires, which can eliminate potential risks. If the fire can no longer be prevented, the spread of contaminated water must be mitigated. Unfortunately, legislation in support for this issue is sparce.
3. The accidental entry of xenobiotics from fire extinguishing into the aquatic environment could adversely affect the aquatic ecosystem and thus disrupt its proper functioning.
4. From the firefighting point of view, cork is the best. On the other hand, from the ecotoxicological point of view, all results showed adverse effects, except for the water from the cork, which did not inhibit the growth of the *Sinapis alba* root.

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