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Bio-based wood preservatives: Their efficiency, leaching and ecotoxicity compared to a commercial wood preservative.

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Abstract

Companies in the wood industry are constantly developing their outdoor products. The possibility of using bio-based chemicals as an alternative to traditional wood preservatives—regulated in Europe by The Biocidal Products Regulation No 528/2012—has been considered, but chemical leaching from the wood decreases its effectiveness and may negatively affect the environment. This study aims to compare the effectiveness of bio-based chemicals with potential use in wood preservation to commercially available preservatives, to investigate their fixation to wood and their ecotoxicity and to quantify the potentially toxic elements leached from the wood. Pyrolysis distillates of tree bark, organic acids found in distillates, Colatan GT10 tannin extract and log soaking liquid as a hardwood veneer process residue were tested and compared with commercial pine oil and a copper-based wood preservative. In the wood decay test of impregnated pine sapwood specimens, Colatan GT10 extract performed as well as the commercial wood preservatives. The same decay trial with leached specimens significantly reduced the performance of the bio-based chemicals. The results of the ecotoxicity test with photoluminescent *Aliivibrio fischeri* bacteria showed that many bio-based chemicals with potential use in wood preservation have markedly lower ecotoxicity than commercially available wood preservatives, but the ecotoxicity of some bio-based chemicals is higher, as in the case of some of the pyrolysis distillates. The wood preservation efficiency and the ecotoxicity of the studied chemicals had a poor correlation, implying that other factors besides treatment agent toxicity play a role in deterring fungal growth on treated wood. The amount of elemental toxins in the leachates was low. These results emphasize the importance of the chemical ecotoxicity of bio-based preservative compounds, as their detrimental effect on the

environment can be higher than that of the traditional preservatives unless effectively linked to wood to prevent leaching.

Keywords: wood degradation, wood preservation, side-streams, fungistatic, antifungal chemicals, ecotoxicity

1. Introduction

Due to environmental concern about toxic chemicals, stricter political pressure and efforts to mitigate climate change and other global sustainability issues, chemicals legislation is gradually limiting the use of traditional wood preservatives — typically based on formulations containing heavy metals — in Europe and North America (Gerengi et al., 2014). In Europe, the use of wood preservatives are regulated by the Biocidal Product Regulation (EU 528/2012). Human health issues or ecological risks may lead to restrictions in use or banning, which may cause a deficiency in the number of available products in this field. This deficiency could potentially be overcome by increasing the use of natural chemicals that exhibit antifungal activity, such as essential oils (Moutaouafiq et al., 2019) and stilbenes (Lu et al., 2016).

Due to the foreseeable need, many researchers are studying, with some success, the inhibitory effects on fungal growth of different bio-based chemicals, such as mistletoe and lichen extracts (Yildiz et al., 2020), coffee-related waste extracts (Barbero-López et al., 2020; Barbero-López et al., 2018), metanolic extracts from beech wound-wood (Vek et al., 2013), monoterpenes (Zhang et al., 2016), propolis extracts (Woźniak et al., 2020) and vegetable and fruit peel extracts (Barbero-López, 2020). Different kinds of tannins have already been proven to successfully inhibit wood-decaying fungi (Anttila et al., 2013; Da Silveira et al., 2017; Tomak & Gonultas, 2018). As such, tests on tannin-based formulations as wood treatments have been underway for a number of years (Tondi et al., 2015). Pyrolysis distillates from different residues, such as bark distillates (Mourant et al., 2005; Mohan et al., 2008; Barbero-López et al., 2019) and coconut shell distillates (Shiny et al., 2017), are also able to inhibit wood-decaying fungi. The inhibitory effects of pyrolysis distillates on wood-decaying fungi are often attributed to their phenolic content (Mourant et al., 2005; Temiz et al., 2010) and their organic acids (Barbero-López et al., 2019). Bahmani et al. (2016) recently concluded that acetic and propionic acids, which are commonly found in pyrolysis distillates, can be used in palm wood protection. While the effectiveness at inhibiting wood-decaying fungi and the wood decay of many extractives has been proven, their leaching from wood into the environment remains a challenge.

The leaching of preservatives from wood usually causes a reduction in the wood's life-span as well as adverse effects on the environment and humans. Despite several studies on natural preservation chemicals, leaching remains an issue for pyrolysis distillates (Temiz et al., 2010; Mohan et al., 2008), tannins (Sommerauer et al., 2019) and chitosan (Alfredsen et al., 2004). Additionally, little attention is paid to the effects of the leachates on the environment despite the fact that many natural chemicals are toxic to living organisms, including some tannins (Libralato et al., 2011) and pyrolysis distillate compounds (Cordella et al., 2012). Thus, high concentrations of natural wood preservative compounds in soil or water can have undesired effects on the environment that need to be further studied and controlled.

The aim of this study was to test and compare natural chemicals as possible wood preservatives and to assess their leaching and acute ecotoxicity. A leaching test (EN 84), a wood mini block decay test (EN 113) and an acute ecotoxicity test using photoluminescent *Aliivibrio fischeri* bacteria (ISO 21338:2010) were performed. The results were compared to a commercial, copper-based wood preservative for above ground use and pine tall oil (used for centuries as a wood preservative) to understand the impact of the new wood preservatives on the environment compared with traditional treatments.

2. Materials and Methods

2.1 Chemicals used in this study

The chemicals tested in this experiment are summarised in table 1. MäntyEko® pine tall oil was also used as a commercial green wood preservative in the wood leaching and decay test but not in the acute ecotoxicity test. All the chosen chemicals except the log soaking liquid have been previously identified as possible wood preservatives due to their antifungal activity. Spruce log soaking liquids were included as it was suspected that they may contain extractives — with antifungal activity — leached out from the logs.

Table 1: Chemicals tested in this experiment, their origin and a brief description about them

Chemical	Origin	Brief description
Distillate 1	*Populus tremula* slow pyrolysis, drying phase	Water-like liquid with an smell similar to tar. Collected from drying phase (up to 135°C) when pyrolyzing *Populus tremula*.
Distillate 2	*Populus tremula* slow pyrolysis, torrefaction phase	Dark liquid with an strong tar-like smell. Collected from torrefaction phase (up to 275°C, condensed at 70 °C) when pyrolyzing *Populus tremula*.
Distillate 3	*Populus tremula* slow pyrolysis pyrolysis phase	Very dark liquid, and very strong tar-like smell. Collected from pyrolysis phase (up to 350°C, condensed at 70 °C) when pyrolyzing *Populus tremula.*
Propionic acid	Purchased: 99%; Merck KGaA, Darmstadt, Germany	An organic acid present in pyrolysis distillates. Based on literature, it could play a role in wood preservation.
Acetic acid	Purchased: 100%; Merck KGaA, Darmstadt, Germany	An organic acid present in pyrolysis distillates. Based on literature, it could play a role in wood preservation.
Formic acid	Purchased: 85%; Merck KGaA, Darmstadt, Germany	An organic acid present in pyrolysis distillates. Based on literature, it could play a role in wood preservation.
Colatan GT10	Provided by: Haarla, Tampere, Finland	Trademark product of UNITAN SAICA. It is a tannin-rich Colorado Quebracho (*Schinopsis Lorenzii*) bark extract. Presented as a brown-red powder, it is used as a substitute of phenol in resins phenol-formaldehyde.
Spruce	plywood mill site,	The water from soaking spruce logs in veneer or plywood

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log soaking liquids	Finland	industry. It is considered a residue.
Celcure C4	Koppers Inc., Pittsburgh, USA	Used as an industrial reference. It's a copper-based wood preservative that contains copper (II) carbonate (17%), ethanolamine (< 35%), benzalkonium chloride (4.75%), cyproconazol (0.096%), sodium nitrite (< 5%) and polyethoxylated tallow amine (< 5%)
MäntyEko® pine tall oil	EkoPine Ltd, Oulu, Finland	A commercial green wood preservative refined from crude tall oil (fatty and resin acids, sterols, waxes and short-chained carbohydrates,) that in turn is a by-product of Kraft pulping.

2.2. Wood leaching and decay test

Scots pine (*Pinus sylvestris*) sapwood from commercial timber from the Kerimäki sawmill, Finland, was cut into small specimens of 5 × 40 × 10 mm^3 (radial x longitudinal x tangential). The dry mass of the sapwood specimens at 50 °C was recorded.

The chemicals to be studied were then diluted in MilliQ water (Merck KGaA, Darmstadt, Germany). Acetic, propionic and formic acid, the three pyrolysis distillates and Colatan GT10 were diluted to 5% concentration (w/w). Celcure C4 was used at 1.6% concentration, the standard concentration used in the European wood industry for outdoor—above ground—applications. The spruce soaking liquid and pine oil were used without dilution. Each of these chemicals was then used to impregnate 20 pine sapwood specimens following a modified full-cell process, a common impregnation process used in wood industry for water-borne preservatives. In this process the wood specimens were submerged in the solutions and kept in a vacuum phase of 0.1 bar for 20 min followed by a pressure phase of 10 bars for 45 minutes. The wet mass of the specimens was measured right after finishing the impregnation process, and their dry mass was measured after oven drying them at 50 °C until constant mass was reached. The samples treated with pine oil were cured at 100 °C prior to drying and weighing at 50 °C. A batch of 20 wood specimens was kept untreated to be used as a control.

Half of the specimens treated with each chemical were then exposed to a leaching test according to the European norm EN 84. In brief, these wood specimens were submerged in 5:1 (v/v) of Milli-Q water to wood, and the water was changed first after 24 and 48 hours and then additional 7 times within the remaining 12 days, resulting in a total elution time of 14 days in water. After each water changes, the used water was collected and kept frozen (-15°C) for the elemental analyses. After the leaching test, the dry mass of the sapwood specimens at 50 °C was recorded to measure the mass loss caused by the leaching process.

The decay test was performed using the brown rot fungus *Coniophora puteana* (strain BAM 112), purchased from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany). Petri dishes (Ø 90 mm and 15 mm height) were prepared with 30 ml of 4% malt powder and 2% agar growth media. The petri dishes were inoculated under sterile conditions with one plug (Ø 5.5 mm) of an actively growing *C. puteana* in the centre of each dish. The petri dishes were parafilm sealed and kept in a growth chamber at 20 ± 2 °C and 65 ± 5% relative humidity. When the colonies reached the edge of the petri dish, the decay test was started.

The decay test was performed following a modified mini block procedure of EN 113 (Lu et al., 2016). Four wood specimens impregnated with the same chemical — two leached and two unleached — were placed in each petri dish, as shown in Figure 1. A mesh slightly larger than the wood specimens was used to avoid direct contact between the sapwood and the growth media. The petri dishes were sealed with parafilm™ and kept in a growth chamber at 20 ± 2 °C and 65 ± 5% relative humidity for 16 weeks. Afterwards, the dry mass of the sapwood specimens at 50 °C was recorded to measure the mass loss caused by *C. puteana*. A minimum mass loss of 20% should happen in the control specimens to consider the test valid, while adequate wood protection will be considered when the mean dry mass loss of impregnated wood specimens is less than 3% (EN 113).

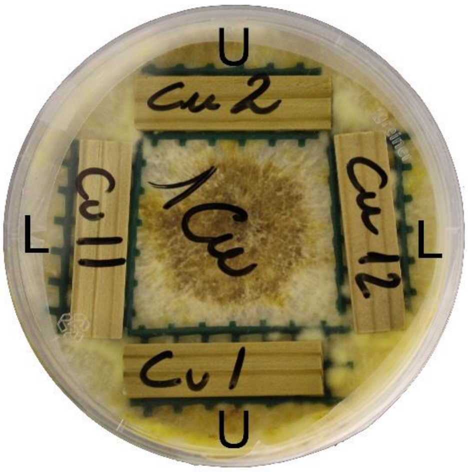

Figure 1: Configuration of sapwood specimens in the petri dish over the colony of *C. puteana*. The letter U next to the sapwood specimen indicates an unleached specimen, while L indicates a leached specimen.

2.3. Acute ecotoxicity test

The acute toxicity test of the chemicals was performed according to ISO 21338:2010. This acute ecotoxicity test was selected as it is ideal for screening, because of its easiness and short duration, even if it does not show all the effects on the environment. The luminescence reduction caused by the chemicals in the *Aliivibrio fischeri* photoluminescent bacteria was measured with a BioTox™ test kit (ISO 2010) purchased from Aboatox Inc. (Masku, Finland). A cold 2% NaCl solution was added to the bacterial solution and, after mixing, the solution incubated for 30 minutes at 4 °C and then for 30 minutes at 15 °C. A 5% (w/w) solution of the chemicals in 2% NaCl was prepared except in the case of the log soaking liquid, in which a 5% v/v solution in 2% NaCl was prepared. For the commercial copper-based preservative, a solution of 0.08% w/w was used due to its expected higher toxicity. MäntyEko® pine tall oil was not included in this test due to its low solubility in water. The pH of the test solutions was adjusted to 6–8.5 using 0.1 M NaOH. From each of these solutions, two dilutions of 1:1 and 2:3 in 2% NaCl were prepared, and from each of these two dilutions, a series of four more 1:1

dilutions in 2% NaCl were prepared. Two replicates of 300 µl were prepared for the experiment from every dilution, and they were kept at 15 °C for 15 minutes. Then, using the luminometer (Berthold Sirius 1, Pforzheim, Germany) and Sirius Software (Berthold, Pforzheim, Germany), 300 µl of the previously prepared bacterial suspension was injected into the dilutions, and the luminescence of the bacterial suspension was measured right after the injection and exactly 30 minutes after the injection. As a control, 2% NaCl solution with no other chemical was used.

The photoluminescence reduction was measured by comparing the reduction in bioluminescence after 30 minutes in all dilutions and the control. The results were reported as effective chemical concentrations that reduced bioluminescence by 20% (IC_{20}) and 50% (IC_{50}).

2.4. Elemental analysis of the preservatives and leachates

In order to understand which potentially eco-toxic elements are present in preservatives and the wood leachates, their compositions were analysed for 23 metals and metalloids using solution-based, inductively coupled plasma mass-spectrometry (ICP-MS). The leachate samples collected after 1, 3, 7, 10 and 14 days were used for the elemental analyses. Preservatives were tested in the concentration used for wood impregnation.

Element B and P concentrations were determined using inductively coupled plasma mass-spectrometry (ICP-MS). Analysis was performed using a NexION 350D ICP-MS (PerkinElmer Inc., Waltham, MA, USA) and ESI PrepFAST autosampler (Elemental Scientific, Omaha, NE, USA). The instrument was operated with an RF power of 1.6 kW and with nebuliser gas, auxiliary gas and plasma gas flows of 0.92, 18 and 1.2 $L \cdot min^{-1}$, respectively. Element isotopes without known spectral interferences were preferentially selected for analysis. A triple-quadrupole reaction system was used to remove polyatomic interferences in collision mode with kinetic energy discrimination (KED) using helium as the cell gas (3.7 $mL \cdot min^{-1}$). Two internal standards, scandium-45 and lutetium-175, were mixed online with the samples to compensate for matrix effects and instrument drift. Scandium-45 was used to correct measurements of analytes which have an atomic weight below 89 amu and lutetium-175 above 110 amu. Analytes were determined against certified multi-element calibration standards (TraceCERT® Periodic table mix 1 for ICP, Sigma-Aldrich) spiked with titanium (TraceCERT®, Ti single element standard for ICP, Sigma-Aldrich). Separate calibration ranges were used for different analytes: 4.0–400 $\mu g \cdot L^{-1}$ was used for Na, Mg, K, Ca, Al, Si and Fe, and 1.0–100 $\mu g \cdot L^{-1}$ was used for other elements. The stock calibration solution was diluted with HNO_3 (TraceMetalTM grade, Fisher Chemical) and de-ionized water (USF Elga Maxima) in such a way as to achieve 2.5% HNO_3 concentration. The samples were diluted within calibration ranges with HNO_3-solution (final acid concentration 2.5%) before ICP-MS-measurements. The sample uptake rate was 3.5 $mL \cdot min^{-1}$, and dwell times were set to 100 ms per amu. Three replicates were obtained for each sample. The data was processed using PerkinElmer Syngistix Data Analysis Software™.

2.5. Statistical analysis

The statistical analyses for the wood decay test were performed in IBM SPSS Statistics 25 (IBM, New York, USA). A Tamhane posthoc test was performed for the wood decay test specimens because the mass loss variance was not constant for all the treatments.

3. Results

3.1. Wood leaching and decay test

All the water-soluble chemicals successfully penetrated the wood, as indicated by the fact that the wet retention of the specimens was between 130–190% of the mass of the dry specimens (Table 1). The insoluble pine oil had a wet retention of 32%. Dry retentions varied across different treatments. About 80 $kg \cdot m^{-3}$ of pine oil stayed in the sapwood specimens after the sapwood specimens were cured in the oven. Colatan GT10 and propionic acid also successfully stayed in the sapwood specimens after drying, in amounts of about 21 $kg \cdot m^{-3}$ and 12 $kg \cdot m^{-3}$, respectively. Acetic acid was the only organic acid able to stay in sapwood in higher concentrations than the copper-based preservative. Distillates 1 and 2 caused a mass loss in the sapwood specimens. The rest of the chemicals were retained in the sapwood specimens in very low concentrations.

The chemical treatments and leaching had a very significant effect on the mass loss caused by *C. puteana* in the sapwood specimens: p = 0.000 and p = 0.003, respectively. In unleached specimens, pine oil, Colatan GT10 and the copper-based preservative differed significantly from the controls, while only the copper-based preservative differed significantly from the controls and the rest of the chemicals after leaching (Table 2). The mass loss caused by the wood-decaying fungus *C. puteana* was about 20% in both unleached and leached controls.

Both references – the copper-based preservative and the pine oil – had the lowest mass loss of all the studied chemicals, with no mass loss for the copper-based preservative in both unleached and leached specimens and with a mass loss of 1.5% in unleached specimens and 9% in leached specimens for the sapwood specimens treated with pine oil. Colatan GT10 prevented the mass loss of the unleached sapwood specimens but did not prevent the mass loss of the sapwood specimens after leaching. The acetic and formic acids did not cause any difference in the mass loss of the wood specimens when compared to the controls for both unleached and leached specimens, while propionic acid caused a higher mass loss than the controls, although the difference was not significant. Similarly, distillates 1 and 2 did not affect the mass loss caused by *C. puteana*, whereas distillate 3 slightly increased the mass loss of leached specimens, although the result cannot be considered statistically significant (p = 0.081). The log soaking liquids did not affect the mass loss caused by the fungal decay in either the unleached or leached specimens.

Table 2: Wet retention (%), dry retention (kg·m^{-3}) and mass loss (%) caused by *C. puteana* in leached and unleached sapwood specimens. An asterisk in the results of the mass loss indicate significant differences caused by the treatments within each leaching treatment

	Retention		Mass loss caused by *C. puteana* (%)	
	Wet retention (%)	Dry retention (kg·m^{-3})	Unleached	Leached
Acetic acid	190.1 ± 3.0	6.2 ± 0.1	16.5 ± 3.3	19.7 ± 4.3
Formic acid	187.8 ± 2.8	1.9 ± 0.1	24.6 ± 5.9	19.7 ± 3.5
Propionic acid	185.1 ± 2.4	12.2 ± 0.2	36.3 ± 4.6	40.2 ± 5.0
Distillate 1	184.0 ± 2.5	-3.7 ± 0.1	27.2 ± 4.9	29.7 ± 4.3
Distillate 2	188.4 ± 3.9	-2 ± 0.1	24.4 ± 5.6	22.5 ± 6.2
Distillate 3	184.7 ± 2.8	1.1 ± 0.1	35.6 ± 7.5	50.3 ± 6.0
Log soaking liquid	176.3 ± 2.4	2.7 ± 0.1	27.0 ± 5.0	31.8 ± 4.4
Colatan GT10	131.0 ± 2.4	20.8 ± 0.5	0.1 ± 0.2*	31.1 ± 3.3
Cu preservative	178.5 ± 3.1	3 ± 0.1	0.1 ± 0.2*	0.3 ± 0.4*
Pine oil	32.0 ± 0.9	80.4 ± 3.0	1.4 ± 1.0*	8.7 ± 3.5
Controls	-	-	20.5 ± 3.8	21.6 ± 2.6

3.2. Acute ecotoxicity of the test substances

The IC_{20} and IC_{50} values of the studied chemicals are shown in Table 3. The IC_{20} of the copper-based preservative was around 12 mg/L, and the corresponding IC_{50} value was 19 mg/L. Distillate 3 had very low IC_{20} and IC_{50} values – 0.02 mg/L and 0.19 mg/L. Based on Table 3, distillates 1 and 2 had IC_{20} values of over 560 mg/L. IC_{50} values were over 1000 mg/L for distillate 2 and over 1500 mg/L for distillate 1. Colatan GT10 and the log soaking liquids had IC_{20} values of 22 mg/L and 27 mg/L, respectively, while their IC_{50} values were 145 mg/L and 178 mg/L, respectively. Propionic acid was the chemical with the highest IC_{20} value, 15600 mg/L, while the IC_{20} value of formic acid was 662 mg/L and the IC_{20} value of acetic acid was 65 mg/L. The highest IC_{50} value was found in formic acid, with 23000 mg/L, very similar to the 21836 mg/L value of propionic acid. The IC_{50} value of acetic acid was 4051 mg/L.

Table 3: IC_{20} and IC_{50} values (mg/L) of the studied chemicals. The lower the IC_{20} and IC_{50} value, the higher the ecotoxicity of the chemical

Chemical	pH	Modified pH	IC_{20} (mg/L)	IC_{50} (mg/L)
Acetic acid	1.9	7.7	65	4052
Formic acid	1.3	6.3	662	23003
Propionic acid	2.2	7.1	15653	21836
Distillate 1	3.6	7.1	570	1589
Distillate 2	3.0	7.2	567	1085
Distillate 3	3.8	7.3	0.02	0.2
Log soaking liquid	4.0	6.7	27	178
Colatan GT10	7.7	-	22	145
Cu	9.5	8.4	12	19

No correlation was found between IC_{20} value and the mass loss (wt-%) of the sapwood specimens compared with control specimens (R^2 = 0.305). Similarly, no correlation was found between IC_{50} value and the mass loss (wt-%) of the sapwood specimens compared with controls (R^2 = 0.312).

3.3. Elemental composition of the preservatives and leachates

The chemical preservatives with which the wood was impregnated contained a wide array of elemental metals that were also present in leachates. Lead was found in high concentration in the leachates of all of the tested bio-based chemicals, while copper and zinc were found in the copper-based preservative leachates (Table 4). Some elemental metal leaching was also noted in the leaching of untreated wood. The concentration of lead decreased in Colatan GT10 and propionic acid leachates as the test progressed, while its concentration in the pyrolysis distillate leachates stayed more or less constant. Most of the elements in the leachates were found in their highest concentrations on the first leaching day following an expected decreasing trend of concentration, being in good agreement with Tao et al. (2013). Copper presented a high peak after the first leaching day in the copper-based preservative, while on the third day the concentration of this element in leachates was over 2 µg/L. Other elements found in concentrations over 1 mg/L after the first leaching day in the bio-based chemicals were potassium, calcium and magnesium, while 10 mg/L sodium was found in the first day leachate of Colatan GT10.

The original solutions used to impregnate the wood had the following concentrations of the analysed elements: the copper-based wood preservative had 1490 mg/L of Cu and a low concentration of chromium, zinc, strontium, barium and lead; the 5% Colatan GT10 solution had markedly higher concentrations of strontium, barium and lead, while the pyrolysis distillate at 5% concentration contained rather low quantities of elemental metals; the 5% propionic acid solution contained a substantial amount of copper but only a limited content of other elemental toxins.

Table 4. Elemental concentration (Cu, Zn, Sr, Ba and Pb) in µg/L of the leachates of the untreated pine wood, copper-based wood preservative, pyrolysis distillate from the operating temperature of 350°C, propionic acid and Colatan GT10. The Cu content was measured as mg/L

Sample	**Leachate day**	**Cu (mg/L)**	**Zn (µg/L)**	**Sr (µg/L)**	**Ba (µg/L)**	**Pb (µg/L)**
Untreated pine wood	1	0.16	34.4	12.2	8.5	7.0
	2	0.10	12.8	5.7	7.7	2.8
	3	0.08	8.0	3.0	2.1	6.7
	7	0.07	5.2	2.0	1.3	9.3
	10	0.05		5.2	2.0	11.8
	14	0.04	1.4	1.6	1.2	2.1
Cu-based preservative	Original solution (1.6%)	1490	61.4	38.6	12.3	2.3
	1	9.10	11.4	7.1	6.1	0.1
	2	4.86	7.0	3.6	2.9	0.4
	3	2.24	2.4	1.1	0.8	<0.1
	7	1.08	8.8	0.3	0.2	0.2
	10	0.90	0.5	0.3	0.2	0.2
	14	0.31	0.5	0.3	0.1	<0.1
Colatan GT10	Original solution (5%)	0.34	45.7	2270	830	52.9
	1	0.01	18.6	20.4	12.4	41.5
	2	-	2.6	8.4	6.3	29.7
	3	0.00	3.0	3.1	1.9	23.5
	7	0.00	1.5	1.0	0.5	23.2
	10	0.00	-	1.1	0.5	33.7
	14	0.00	1	0.3	0.2	12.9
Pyrolysis distillate	Original solution (5%)	0.51	87.7	19.7	21.8	1.7
	1	0.01	28.0	15.0	10.0	7
	2	-	25.0	10.7	7.6	25.7
	3	0.00	8.3	4.0	3.0	27.1
	7	0.00	3.8	1.7	1.3	27.0
	10	0.00	6.0	1.4	1.1	22.9
	14	0.00	7.1	0.8	0.6	25.0
Propionic acid	Original solution (5%)	3.15	0.2	9.3	5.1	1.0
	1	0.01	0.3	31.4	29.2	126.7
	2	-	-	18.8	18.0	88.6
	3	0.00	<0.1	10.0	8.9	74.9
	7	0.00	0.2	2.4	2.2	54.5

	10	0.00	<0.1	1.4	1.3	58.8
	14	0.00	<0.1	0.4	0.4	22.7

4. Discussion

The dynamics of the biocide release from a given piece of wood are determined by the diffusion processes in the porous structure. Once the biocides reach the external surface of the wood, their dispersion in the environment is ensured by the water circulation in soils and surface and ground waters, potentially affecting the quality of environmental compartments (including water resources for human consumption) and the integrity of living targets (Schiopu & Tiruta-Barna, 2012). The dispersion of the released pollutants into the surrounding water and soils dilutes the initial leachate.

Of all the tested chemicals, only the unleached Colatan GT10, the copper-based preservative and the pine oil reduced the mass loss caused by *C. puteana* below 3% and can be considered as adequate wood preservatives based on the EN 113. However, after leaching, Colatan GT10 induced a slight increase in the mass loss. Despite the copper-based preservative's similar growth inhibition of *C. puteana* in unleached specimens, the acute toxicity of Colatan GT10 was clearly lower. Tannins are known to inhibit the wood-decaying fungi (Anttila et al., 2013), but they leach from wood as easily as other compounds that have been suggested as preservatives, such as wood extracts (González-Laredo et al., 2015) and caffeine (Kwaśniewska-Sip et al., 2019). The lower toxicity of Colatan GT10 compared to the copper-based preservative highlights that tannins can be a green solution to wood preservative formulations for above ground applications if their fixation to wood can be significantly improved. Colatan GT10 could also be used in indoors applications due to its high efficiency prior to leaching.

Pyrolysis distillates 1 and 2 did not affect the mass loss caused by *C. puteana*. Distillate 3 caused a slight increase in the mass of unleached specimens and a larger increase in leached specimens. Pyrolysis distillates have lately gained attention, and thus they have been studied as possible wood preservatives over the last decade. They are known to be effective against wood-decaying fungi (e.g. Temiz et al., 2010; Kim et al., 2012; Shiny et al., 2017), though their effectiveness and composition varies depending on the pyrolyzed material and the processing conditions (Barbero-López et al., 2019; Zhao et al., 2020). Similar results were found by Mourant et al. (2005), who found variable results depending on the different fractions and the fungi against which they were tested. Thus, our results may differ from previous studies if the feedstock used for the pyrolysis was not conducive to the development of wood preservatives or if the fungus was not sensitive to them.

The ecotoxicity values for the pyrolysis distillates varied greatly. The pH level of ecotoxicity analysis may underestimate the role of heavy metal cations due to elevated pH required by the measurement protocol, which may have deprotonated some metals into complexes that have lower bioavailability during the test. Nevertheless, the differences between the different chemicals were clear. While distillates 1 and 2 showed lower ecotoxicity than the copper-based preservative and some of the other natural chemicals, distillate 3 had the highest toxicity of all the studied chemicals. Indeed, distillate 3 is from the pyrolysis phase (up to 350 °C) water soluble (70 °C) phase and contains the highest concentration of bioactive compounds. A previous study carried out by Cordella et al. (2012) found that slow pyrolysis distillates could have acute toxic effects on humans and aquatic organisms. A study performed by de Lima (2019) found that fast pyrolysis distillates from wood were also toxic to *Daphnia magna*, presenting an EC_{50} value of 26 mg/L. A recent study concluded that distillates produced from fast pyrolysis have low toxicity in aquatic environments (Campisi et al., 2016). Our study found that distillates from the same feedstock can vary in their ecotoxicity depending on the processing temperature, which must be taken into consideration prior to using them as a possible antifungal agent or wood preservative. This is most likely due to the significantly different chemical composition of distillate fractions, as shown by Zhao et al. (2020) in processing birch bark and Salami et al. (2020) in some African hardwoods. In this study, distillate treatments had no additional heat treatment, nor were any binding agents used. However, proper polymerization and effective binding of bioactive molecules could possibly reduce the component leaching.

The organic acids studied in this experiment had the lowest toxicity values of all the studied chemicals. Furthermore, none of the organic acids were effective against the mass loss caused by *C. puteana*. A previous experiment found that propionic acid was able to inhibit several wood-decaying fungi, including *C. puteana*, in a malt agar media (Barbero-López et al., 2019), a conclusion which differs from the results of the present experiment, performed in wood. Bahmani et al. (2016) proved that acetic and propionic acid at 5% concentration can act as a short-term wood protector against moulds and decay fungi – this does not agree with our findings either. More research is needed in this field to gain a better understanding of the effects of the organic acids and their synergy in wood.

The log soaking liquid containing some water-soluble compounds from spruce bark had no effect on the mass loss of the sapwood caused by *C. puteana*, and its toxicity was slightly lower than that of Colatan GT10. This liquid needs to be studied further as it might be rich in different extractives, although it has no effect on the wood's resistance to decay.

The elements found in the leachates indicated that most of the toxic elements impregnated in the wood leach out in the first days when exposed to leaching. The wood treated with copper-based wood preservatives showed the lowest concentration of elemental heavy metals in the leachates of all the treated and untreated wood. In the past, chromium compounds were incorporated to reduce copper leaching, but a recent generation of copper-based preservatives uses ethanolamine as a fixative. However, their efficiency is still not as good (Thaler & Humar, 2014). About 8 µg/L of copper leached out from the copper-based preservative-treated wood after one day of being exposed to leaching, while the leached copper concentration decreased to about 2 µg/L after 3 days. The other elements studied showed a similar trend, with the exception of lead (Pb), a systemic toxicant which can cause several kinds of harm to humans and the environment, even at low doses (Tchounwou et al., 2012; Jaishankar et al. 2014). The concentration of lead did not decrease significantly during the leaching days. Leaching from wood is a continuous process, affected by the exposure of the wood to water and acidity of media (Hasan et al., 2010; Tao et al., 2013). In this test, the leaching of metals from the treated wood was influenced by the constant exposure of the wood to water – the wood specimens were underwater for 14 days, which allowed the water to penetrate deeper into the wood and solubilise the metals (Taylor & Cooper 2005). Other severely toxic elements, such as cadmium, were not present in the leachates, or their concentration was below the detection levels. Both copper and lead are harmful to the environment and to humans (He et al., 2005; Brito et al., 2020), and their synergies might also increase the ecotoxicity of these leachates (Jung et al., 2014). Wood specimens treated with propionic acid showed the highest leaching of metals of all the checked wood specimens, possibly due to the higher solubility of metals in the propionic acid. The presence of elements, such as lead, might be responsible for the antifungal activity found in some bio-based chemicals (Barbero-López et al. 2019), and their leaching to the environment may cause very negative effects. Additionally, larger specimens are usually better for more accurate results in leaching tests (Bahmani et al., 2016), which highlights the need for further investigation with industrial-size wood specimens in long-term weather testing.

It is important to consider that the degradation products of the bio-based chemicals used to preserve wood may perform differently from the original chemicals. Due to their degradation, the effectiveness as wood preservatives may vary. Additionally, the degradation products resulting in the environment due to leaching may also have an ecotoxic effect and influence the condition of water or soil ecosystems (Boxall et al. 2004), but their effects are not fully understood yet. Similarly, the commercial wood preservatives contain several chemicals in their formulations in addition to their main reagent. While the negative effects of treated wood into the environment are known (Xing et al. 2020) and the leachability of the commercial wood preservatives and their main reagent in contact with water are also known (Humar et al. 2007), the effects of the co-formulants have not been broadly studied and need further attention. These co-formulants may be non-toxic when tested in lab scale, but they may create degradation products or create synergies with other chemicals in the environment with high ecotoxicity. Future studies should focus in understanding the degradation and synergies of the leachates from treated wood, as well as their effects into the water and soil ecosystems.

The impregnation process used in this experiment was a modified full-cell (Bethel) process, as it is a common practice in wood industry to use this method for water soluble wood preservatives. The different chemicals tested in this experiment may perform better if optimized protocols for their use in wood is followed. Bio-based chemicals are promising wood preservatives as they are effective fungal inhibitors, but they present high heterogeneity depending on the feedstock and they leach out from wood (Teacă et al. 2019, Broda 2020). Testing of different methods to treat wood would provide useful knowledge about the performance of bio-based chemicals in wood, such as coating them together with film-formers, or doing an *in situ* polymerization of the chemical in wood (Teacă et al. 2019).

It is important to highlight that ecotoxicity tests should be performed for all the chemicals used for wood preservation, as many chemicals that look similar can have very different effects on the environment, as their constitution varies depending on the feedstock and processing temperature (Zhao et al. 2020). For example, pyrolysis distillates were very different in their toxicity to the photoluminescent bacteria, even if their only difference was their processing temperature.

5. Conclusion

Colatan GT10 looks to be the most promising wood preservative of all the studied chemicals, and the ecotoxicity of this Quebracho tannin mix is lower than the toxicity of the copper-based wood preservatives. Its fixation to wood needs to be further addressed to make its use feasible in this application. The results of only one type of test do not offer a complete picture of the ecological risks of these compounds. The toxicity of some natural chemicals can be higher than the toxicity of the commercial wood preservatives, which highlights the need for more systematic ecotoxicity tests in this field. If the ecotoxicity of the bio-based wood preservatives is ignored, the effects on the environment may be worse than those of traditional wood preservatives.

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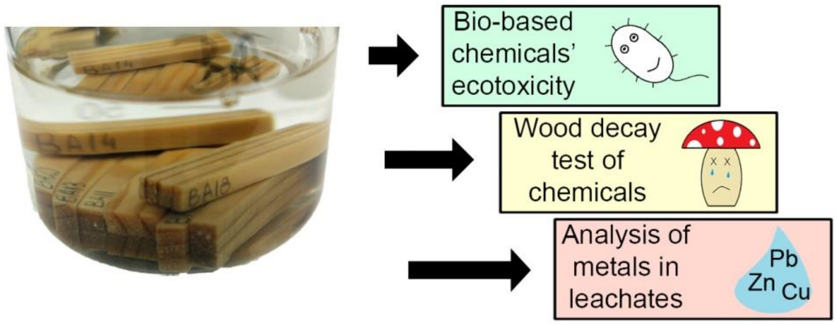
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Highlights

- Antifungal activity of bio-based preservatives decreased significantly after leaching
- Bio-based chemicals had generally lower ecotoxicity than the commercial products
- Some bio-based chemicals had higher ecotoxicity than the commercial products
- Fixation of preservative components to wood is needed to reduce their ecotoxicity