Fate of triazoles in softwood upon environmental exposure

Klara Kukowskia, Veronika Martinská, Carl A. Sedgeman, Paige Kuplic, Evguenii I. Kozliak, Stephen Fisher, Alena Kubatová

Chemistry Department, University of North Dakota, Grand Forks, ND, 58202, USA
Marvin Windows and Doors, Warroad, MN, 56763, USA

 highlights

- Wood treated with tebuconazole was exposed to outdoor conditions for six months.
- ~80% of tebuconazole (TAZ) remained in wood despite the exposure.
- Wood-sorbed tebuconazole remained intact (no bio-, photo- or thermal degradation).
- Leaching accounted for TAZ losses from cross-sectional surfaces.
- Propiconazole behavior in wood was similar to that of tebuconazole.

abstract

Determining the fate of preservatives in commercial wood products is essential to minimize their losses and improve protective impregnation techniques. The fate of triazole fungicides in ponderosa pine wood was investigated in both outdoor and controlled-environment experiments using a representative triazole, tebuconazole (TAZ), which was accompanied by propiconazole (PAZ) in selected experiments. The study was designed to mimic industrial settings used in window frame manufacturing. To investigate the TAZ fate in detail, loosely and strongly bound fractions were differentiated using a multi-step extraction. The loosely bound TAZ fraction extracted through two sonications accounted for 85 ± 5% of the total TAZ, while the strongly bound TAZ was extracted only with an exhaustive Soxhlet extraction and corresponded to the remaining 15 ± 5%.

A significant fraction (~80%) of the original TAZ remained in the wood despite a six-month exposure to harsh environmental conditions, maintaining wood preservation and assuring minimal environmental impact. Depletion of loosely bound TAZ was observed from cross-sectional surfaces when exposed to rain, high humidity and sunlight. Water leaching was deemed to be the major route leading to triazole losses from wood. Leaching rate was found to be slightly higher for TAZ than for PAZ. The contribution of bio-, photo- and thermal degradation of triazoles was negligible as both PAZ and TAZ sorbed in wood remained intact. Triazole evaporation was also found to be minor at the moderate temperature (20 – 25 ºC) recorded throughout the outdoor study.

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1. Introduction

Wood matrix is known to be susceptible to biological attacks from microorganisms, e.g., fungi and bacteria. The resulting gradual
wood decay contributes to natural recycling but also leads to deterioration of wood products while still in service (Satapute and Kaliwal, 2016). To ensure the resistance to decay, wood is commonly impregnated with various biocides that are designed to penetrate well into the matrix and remain in place. However, upon harsh environmental conditions, preservatives can undergo biological, thermal and photo-degradation or be lost through vaporization and water leaching. Therefore, determining the fate of wood-sorbed preservatives is crucial to evaluate the extent of wood protection.

Inorganic preservatives had been widely used for wood impregnation in the last century, however metal leaching (Dubey et al., 2010; Waldron and Cooper, 2010; Mercer and Frostic, 2012) and problematic combustion of the impregnated wood (Tame et al., 2007) triggered health and environmental concerns (Katz and Salem, 2005). As a result, alternative organic biocides (metal-free or copper containing) have been introduced exhibiting lower mammalian toxicity and possessing lesser harm to the environment (Schmidt-Sonnenschein, 2005). The main classes of metal-free fungicides include carbamates, creosotes, iso-thiazolones, quaternary ammonium compounds, sulfamides and triazoles (Reiprecht, 2010). Triazoles (e.g., tebuconazole and propiconazole) are among the most commonly used in commercial formulations for wood impregnation due to their efficient protection against sapstain and mold (Barnes, 2001; Morrell, 2012; Schiopu and Tiruta-Barna, 2012). Tebuconazole (TAZ) accounts for the largest share of global triazole demand with 16,000 tons (FrontResearch, 2016). Triazoles are highly soluble in organic solvents (Cherepinisoff and Rosenfeld, 2009) with a lower water solubility (0.032 g L\(^{-1}\) for TAZ at 25 °C); nevertheless, they exhibit high antifungal activity in both solvent-borne paints and water-based coatings (Brus et al., 2005).

The preservative’s retention is essential not only for the impregnation efficacy but also for reduction of the environmental pollution resulting from its release into water (Papa et al., 2004; Bollmann et al., 2014a, 2014b). Several outdoor (Kennedy, 2004; Woo, 2010; Bollmann et al., 2014b) and laboratory-simulated wood leaching studies (Li et al., 2009; Lupsea et al., 2012, 2013; Schoknecht et al., 2014) were performed, of which many used metal complexes along with triazoles. Metals have been shown to significantly influence the triazole behavior in wood by reducing their leaching rates through formation of metal-triazole complexes (Evans et al., 2007; Norková et al., 2012; Jaklova-Dytr'ova et al., 2014). For example, the natural depletion of TAZ from pine decks co-impregnated with copper preservatives during a six-month outdoor exposure to urban rain was found to be only 0.8% of the original amount present in decks (Kennedy, 2004). In contrast, a year-long outdoor leaching study on impregnated spruce (not containing metals) showed the percentages of leached TAZ to be 21.0–25.5% in the first 7 months and 22.5–30.3% in 12 months, depending on the initial TAZ concentration in the impregnation solution (Woo, 2010). Unexpectedly, the TAZ concentrations in the collected leachate samples were greater than could be explained by solubility alone, thus suggesting that TAZ was physically dislodged from the wood surface by rain instead of simple dissolution in water.

In addition to leaching, vaporization may also decrease the amount of biocide and affect the product’s service life. Even though vaporization of triazoles is not expected, as the corresponding Henry’s constants suggest their non-volatility (e.g., TAZ has a Henry’s constant of 1 × 10\(^{-5}\) Pa m\(^3\) mol\(^{-1}\)), low yet detectable emission rates were reported in several studies (Horn et al., 2003; Clausen and Kofod-Swensen, 2009; Yu et al., 2009; Bollmann et al., 2014a). A two-year indoor cabin study on impregnated timber (using a water-based formulation containing TAZ, propiconazole, and other preservatives) showed the concentration of airborne triazoles between 3 and 10 ng m\(^{-3}\) (Yu et al., 2009). Horn et al. (2003) also reported low TAZ emission rates of 0.5 μg m\(^{-2}\) h\(^{-1}\) for wood impregnated with an organic solvent.

Past studies described both biotransformation and biodegradation of TAZ and propiconazole (PAZ) by the surrounding microbial species (fungi, bacteria) in liquid media (Obanda, 2008; Obanda et al., 2008; Obanda and Shupe, 2009), soil (Potter et al., 2005; White et al., 2010), and wood matrix (Woo et al., 2010). As reported earlier, cleavage of the triazole ring is one of the major pathways for TAZ degradation by bacteria, mold, and soft and brown rot fungi (Obanda, 2008; Obanda and Shupe, 2009). Once the azole ring is cleaved, TAZ loses its fungicidal activity. Another common detoxification path is TAZ oxidation leading to hydroxy-substituted products (Obanda and Shupe, 2009). The hydroxyl group can be further acetylated or oxidized to form and ester or carboxyl group. Acetylation causes the deactivation of TAZ by decreasing its hydrophilicity. Aside from triazole ring cleavage and alkyl chain oxidation, PAZ was also found to undergo degradation of the dioxygen ring (Kim et al., 2003) and yield breakdown products such as 1,2,4-triazole, 2,4-dichlorobenzoic acid, and 1-chlorohydrocinnamic (Satapute and Kaliwal, 2016).

Even though previous studies identified the presence of triazoles in leachate water and indoor air, they only focused on one of the depletion scenarios as opposed to their combination. Also, as discussed above, metals were often added to the impregnation solution, thus these studies cannot be used to assess triazole behavior when formulations without metal additives are used. Herein, a three-part study investigating the environmental fate of triazole fungicides in ponderosa pine corner pieces (representing window frame corners) is presented. Leaching, vaporization and degradation of triazoles were examined to determine their potential removal paths. First, the impact of environmental exposure on wood impregnated with a representative triazole, TAZ, was studied upon harsh outdoor conditions. Then, smaller-scale indoor experiments enabled an assessment of the effects of light, humidity, temperature, and time on TAZ and PAZ behavior in wood. Finally, the contribution of leaching to triazole depletion from wood was evaluated by determining TAZ and PAZ water leaching rates in laboratory settings. Throughout this study, both 14C-labeled and non-labeled TAZ were employed with the goal of achieving quantitative measurements using a radiolabeled tracer along with a detailed characterization of potential degradation products using the non-labeled fungicide.

2. Experimental

2.1. Chemicals

Analytical standards, TAZ, PAZ, iodopropynyl butylcarbamate (IPBC) and an internal standard, hexaconazole (HAZ), were of >99% purity and purchased from Sigma-Aldrich (St. Louis, MO, USA), as was sodium azide. Acetone and acetonitrile (LCMS or GC grade) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Water was purified using a DirectQ Millipore system (Billerica, MA, USA).

Woodlife 111 RTU from Kop-Coat, Inc. (Pittsburgh, PA, USA) was used as a common nonpolar solvent with 0.22% of dissolved fungicides (TAZ, PAZ, and IPBC). For the analysis of fungicide distribution, uniformly 14C-labeled TAZ obtained from Commerce Institute of Isotopes Co., Ltd. (Budapest, Hungary) with a radioactivity of 7.4 MBq mL\(^{-1}\) was spiked as a tracer to Woodlife resulting in a radioactivity of 0.74 MBq L\(^{-1}\) of the impregnation solution. A scintillation cocktail, Betamax, was obtained from MP Biomedical, LLC (Solon, OH, USA).
2.2. Outdoor exposure study

The exposure study was performed on ponderosa pine frame corner sections (41.2 cm x 3.6 cm x 3.6 cm). Ponderosa pine is found in abundance in North America and thus dominantly used in window manufacturing (Western Wood Products Association, accessed July 2016). Each section consisted of two wood blocks, which were ultimately assembled together to comprise a corner piece (Fig. 1). For the impregnation, conditioned unassembled blocks were fully submerged into the radiolabeled Woodlife solution for 3.0 min. Impregnation by full submersion is commonly used in the US as it is an effective and cost-efficient technique. Radiolabeled tracer was used to determine the total TAZ amount in wood including the original TAZ molecule but also its potential degradation products without the need of knowing their structure. Wood blocks were then dried for one week before they were assembled together and shipped to a Marvin Windows and Doors facility (Warroad, MN, USA) where they were painted white using aqueous based paint to mimic the routine industrial handling. After the paint application, selected wood sections were shipped to Hilo, Hawaii in January 2014 and underwent a six-month outdoor study whose detailed experimental layout is described in Table S1. During the exposure, all wood blocks remained assembled.

Exposures included wood section storage under direct sun, in shade (no sun), and under direct sun with an additional treatment applied before the exposure and each month afterwards. This treatment consisted of a sodium azide (NaN₃) aqueous solution (10 g L⁻¹) applied on the wood surface using a synthetic paint brush to prevent microbial TAZ biodegradation. Exposure to direct sunlight causes wood to dry out fast and shrink. Repeating cycles of wetting and drying (i.e., swelling and shrinking) may cause cracking and checking of the wood surface, which would ultimately decrease wood resistance towards microbial attack. Therefore, the sodium azide treatment was used in combination with direct sun exposure.

After six months, “T” shaped wood blocks were cut with a band saw followed by extraction and analysis of selected 2-mm wide wood slices (#1, 2, 4, 6, 8, 10, 12, 14, and 16) using either liquid scintillation counting (wood blocks impregnated with radiolabeled Woodlife solution) or gas chromatography-mass spectrometry (GC-MS) for wood blocks impregnated with non-labeled Woodlife. For the GC-MS analyses, three slices were analyzed (#1, 12, and 14) per each wood block. “U” shaped wood blocks were only used for the assembly of a corner piece of window frames. They were not analyzed as the results from “T” shaped wood blocks were considered to be representative of both assembly parts.

The TAZ amounts in wider wood slices #13 and #15 were approximated by breaking them into 2-mm units for the purpose of calculation and fitting an exponential function between them. The two boundary slices were analyzed and thus the TAZ amounts were known. An exponential relationship was observed for slices #1–11 shown in Fig. 3 (only the first two surface slices had higher amounts of TAZ which then plateaued at a lower value for the distal slices) and was thus used for the calculation of TAZ in wood slices #13 and #15. The total TAZ amount in the entire “T” shaped wood block was then calculated as a sum of TAZ recovered from analyzed slices and the estimated TAZ from slices that were not analyzed (#13 and #15). Comparing the total TAZ amounts in exposed and control wood allowed for TAZ recovery calculations.

2.3. Controlled-environment study

Smaller-sized wood blocks (30.5 cm x 3.8 cm x 3.8 cm) were used for the experiments conducted in laboratory settings. Even though the wood size was decreased for practical reasons, the impregnation technique remained identical - wood blocks were impregnated using the procedure described in Section 2.2 but with a non-labeled Woodlife solution (containing the same amount of fungicides as radioactive Woodlife). In addition to TAZ and PAZ, the used Woodlife solution contained IPBC, a carbamate fungicide, which is often combined with triazoles to enhance the efficiency of wood impregnation (Uhr et al., 2011). IPBC was previously reported to undergo both thermal and photo-degradation (Lee et al., 1991; Kositchaiyong et al., 2014) and was used in this study as a negative control confirming that the experimental conditions were severe enough to cause its degradation.

Controlled-environment experiments were performed in smaller-scale glass chambers (Fig. S1). Each impregnated wood block was air dried after impregnation and cut in half, then one half was introduced upright into a chamber (with the freshly cut surface facing downward) while the other half was stored in a freezer (used as a control).

Using a fractional factorial design of experiments, i.e., Taguchi design, the individual impact of 4 factors (temperature, light, relative humidity, and time) on triazole behavior was evaluated. Each factor was studied on three levels - low, medium, and high. For each wood sample, the non-exposed control was available allowing the analysis of results as paired data (i.e., changes in the control and desorption experiments). Detailed experimental layout is provided in Table S2 and the method is further discussed in Section 2.7.

After exposure for the allotted time, wood blocks were air dried and the upper portion of the wood was cut with a band saw so the

Fig. 1. Wood corner section (41.2 cm x 3.6 cm x 3.6 cm, when assembled together) cutting scheme. Each “T” shaped wood block was cut into 2-mm wide wood slices (#1–11, 12, 14, 16) that were subjected to analysis by either liquid scintillation counting or GC-MS.
surface 2-mm slice could be analyzed. Prior to the GC-MS analysis, wood was extracted with acetone using Soxhlet.

2.4. Wood leaching experiments

To investigate triazole leaching rates, wood corner sections identical to those in the outdoor study were used since the kinetics may be affected by the wood geometry and assembly. The sections were conditioned, impregnated with a non-labeled Woodlife solution using the same technique as described above, dried and painted white.

Ten assembled wood sections were placed on a raised platform in Rubbermaid roughneck totes (18-gallon volume) under a flowing, recirculating water irrigation system. The sections were laid horizontally on the platform and water was sprayed in a 90° angle (exposing the radial and tangential wood surface). Wood sections in one tote were exposed to 11.3 L of water per week for a total of four weeks. Since the leaching experiments were conducted within a shorter time period than the outdoor study, an excessive amount of water was used to approximate the leaching potential of triazoles.

A 1.0 L sample from each tote was collected weekly to be analyzed by high performance liquid chromatography–mass spectrometry (HPLC-MS). The control experiment involved the same setup using wood sections that were not impregnated (1 tote with 10 wood sections). Along with the leachate water samples, 1.0 L of setup using wood sections that were not impregnated (1 tote with 10 wood sections). Along with the leachate water samples, 1.0 L of water was analyzed as a blank experiment.

2.5. Wood cutting & extraction

Wood blocks were cut into slices using a Craftsman 22.9 cm band saw purchased from Sears Brands Management Corporation (Hoffman Estates, IL, USA) in a ventilated laminar hood. The blade used was a Powertec saw blade (157.5 cm (Hoffman Estates, IL, USA) in a ventilated laminar hood. The blade had 10 teeth per 10 cm, 10 teeth per 2.5 cm).

The extraction method employed was designed to exhaustively extract TAZ from wood as well as to assess the extent of TAZ sorption. Wood slices were further cut into smaller pieces using a razor blade and extracted by an exhaustive three-step extraction protocol. The first and second extraction steps were sonication in acetone (3.5 mL, volume adjusted to cover the wood surface) to extract loosely bound TAZ that is either weakly interacting with the wood matrix or sorbed near the wood surface. Extracts from each sonication were collected and analyzed separately. The third step was an overnight Soxhlet extraction with 120 mL of acetone to recover strongly bound TAZ, which remained sorbed within the wood after the two sonication steps. To validate that all extractable TAZ was released with the three-step protocol, an additional Soxhlet extraction in acetone was performed yielding no TAZ.

2.6. Analysis & instrumentation

For the liquid scintillation counting analysis, 1.0 mL of a wood extract in acetone was vortexed with 4.0 mL of the scintillation cocktail and analyzed after an overnight equilibration in a scintillation counter, Beckman Coulter LS 6500, purchased from Beckman Coulter, Inc. (Fullerton, CA, USA). The analysis was run for 30 min in a DPM calculation mode (disintegrations per minute, which is directly proportional to the tracer concentration).

GC–MS protocol was adapted from Stavova et al. (2011). Analyses were performed using a 6890 Series II Plus GC coupled to a 5975C MS detector (Agilent, Santa Clara, CA). Separations were carried out using a 22 m-long DB-5MS column with 0.25 mm internal diameter and 0.25 μm film thickness (J&W Scientific, Rancho Cordova, CA, USA).

HPLC-MS analyses were conducted on an Agilent 1100 HPLC coupled to a high resolution Time of Flight MS G1689A Series 6200. All HPLC separations were performed using an Agilent Eclipse Plus C18 150 mm × 2.1 mm reverse phase HPLC column with 3.5 μm particle size. A binary solvent system consisting of A: 5% acetonitrile in water with 2.5 mM ammonium acetate and B: acetonitrile with 2.5 mM ammonium acetate was used. A gradient program starting with 40% B and ending with 90% B was run at a flow rate of 0.2 mL min⁻¹. The total analysis time was 35 min. The column oven temperature was set to 30 °C and injection volume was 20 μL. Electrospray ionization was performed in a positive mode with drying gas (N₂) set to 350 °C at a flow rate of 12 L min⁻¹ and the nebulizer gas (N₂) pressure set to 25 psi. The electrospray and fragmentor voltages were 4350 V and 125 V, respectively.

2.7. Statistical data processing

All experiments were performed in quadruplicate and the results were reported as mean values. Comparison of data sets was done using a two-sample t-test at 95% confidence level.

The controlled-environment study was designed using a fractional factorial design of experiments, the Taguchi design, which is commonly used in industry for its robustness (Schmidt and Launsby, 1992). The use of a fractional factorial design was a necessity due to a large number of variables prohibiting the use of a one-variable-at-a-time approach. The Taguchi design uses orthogonal arrays, which estimate the effects of factors on the response mean and variation (Minitab, accessed June 2016). The design is thus balanced so that factor levels are weighted equally. As a result, each factor can be assessed independently of all the other factors, so the effect of one factor does not affect the estimation of a different factor. Taguchi design evaluates the individual impact of main factors as opposed to their interactions, which are generally less significant. Minitab statistical software was used to design the experimental setup and analyze the results. Four factors (%RH, temperature, light and time) were studied on 3 levels (low, medium, and high). Results were reported as p-values where factors with p < 0.05 were considered to be statistically significant.

3. Results and discussion

3.1. Loosely and strongly bound tebuconazole

TAZ loss from wood due to environmental exposure was apparent from the first and second sonication steps (Fig. 2). This loss was attributed to the loosely bound TAZ, which may be either weakly interacting with the wood matrix or sorbed near the wood surface (more accessible by the solvent), and consequently readily removed during exposure. The TAZ amount recovered through the third step, Soxhlet extraction, was similar for the exposed and control wood and is referred to as strongly bound TAZ. Loosely bound TAZ accounted for 85± 5% of the total TAZ while strongly bound TAZ represented the remaining 15± 5%, and this distribution remained constant for both surface and distal slices. Therefore, evaluation of the TAZ loss during the outdoor study was based only on the loosely bound TAZ fraction that was prone to be removed from the wood.

3.2. TAZ loss upon environmental exposure

The outdoor exposure of impregnated wood led to a TAZ loss from the surface slices (e.g., wood frame corner) accompanied by minor losses from the nearest subsurface slices. The spatial distribution of loosely bound TAZ in a “T” shaped wood block for various environmental exposures was based on 14C-labeled TAZ.
determination and is shown in Fig. 3. A depletion of loosely bound TAZ was observed from surface wood slices #12 and 1, and sub-surface slice #2. The losses in slices #1 and #2 were not as significant as for slice #12, the full-size surface slice. Based on the loss observed from slice #2, further minor losses may be expected in the wood slice adjacent to slice #12.

The depletion of loosely bound TAZ did not appear to affect wood preservation. Since the wood surface (slices #1, and 12) contained the highest amount of sorbed TAZ, a significant amount remained in this region despite the exposure to harsh conditions. The quality of wood seemed to remain intact as long as the active fungicide was present in all wood slices in sufficient amounts. So even though surface slices #1 and #12 lost up to 75% of the originally present loosely bound TAZ, the remaining \( \mu g \cdot g^{-1} \) concentration was still more than twice the concentration present in inner slices. Additionally, each slice contained the strongly bound TAZ (15\(^\pm\) 5\% of total TAZ), which is not accounted for in Fig. 3. Strongly bound TAZ was not affected by outdoor conditions and thus remained sorbed in wood increasing the amount of total TAZ in each slice.

The recoveries of loosely bound TAZ from the entire wood block were -80\% of the initially sorbed amount and seemed to be unaffected by the exposure type (Fig. 4). TAZ recoveries from wood exposed to direct sunlight were comparable to recoveries from wood stored in the shade (no sun exposure). Also, the sodium azide treatment did not appear to impact the TAZ loss. Since sodium azide was applied to prevent biodegradation and protect the wood from deterioration, its negligible effect on TAZ retention may be interpreted as indirect evidence of biodegradation being insignificant compared to the evaporation and leaching. This preliminary conclusion was further confirmed in the next section by comparing TAZ amounts quantified by GC-MS to the scintillation data to verify that all carbon-14 was present in the non-degraded TAZ molecule.

### 3.3. Evaluation of triazole degradation

The outdoor study conducted in the previous section monitored carbon-14 originally present in a TAZ molecule. However, upon the environmental exposure, TAZ may undergo degradation or transformation yielding still radiolabeled but inactive products (Obanda and Shupe, 2009). Therefore, TAZ potential degradation products were investigated by GC-MS using exposed wood impregnated with non-labeled Woodlife.

The close match of GC-MS results with scintillation counting indicated that the majority of carbon-14 remained present in the non-degraded TAZ structure (Fig. 5). Comparison of the loosely bound TAZ amounts recovered in selected wood slices as quantified by either liquid scintillation counting (detecting carbon-14) or GC-MS (quantifying TAZ) showed no statistical difference between these amounts. Results from a two-sample \( t \)-test are provided in Table S4. Considering the higher standard deviations, degradation could not be completely ruled out, however it would represent only a minor contribution to the depletion of loosely bound TAZ. Also, additional MS screening for potential degradation products containing chlorine molecules (showing a distinct chlorine isotopic pattern in the obtained mass spectra) did not reveal their presence, thus the TAZ thermal, photo- or biological degradation was deemed to be negligible.

PAZ degradation was also considered negligible as PAZ recoveries from control and sun-exposed wood were similar to TAZ recoveries (Fig. S2). Due to this similarity of PAZ and TAZ behavior in wood, the same conclusions as for TAZ can be drawn. Also, GC-MS was used to screen for previously published PAZ degradation products (Kim et al., 2003; Satapute and Kaliwal, 2016) and other compounds containing chlorine atoms, though none were found.

### 3.4. Environmental factors contributing to triazole loss

A controlled-environment study using the Taguchi design of experiments was carried out to further investigate the cause of fungicides’ depletion from the wood surface. The aging conditions targeted were temperature, light, relative humidity and exposure time. The study monitored both triazoles, TAZ and PAZ in the surface layer of wood over the period of 21 weeks. Additionally, the Woodlife solution contained IPBC, which was used as a control chemical to compare our findings to the reported thermal and photo-degradation data.

Judging based on \( p \)-values, temperature followed by the
exposure time appeared to be the most strongly contributing factors for both TAZ and PAZ (Table S3). Assuming no degradation of triazoles (as inferred in the previous section), evaporation can be viewed as an important path of their depletion from wood. The emission rate of triazoles was found to be ~1 μg m⁻² h⁻¹ for exposure at 25 °C, which is similar to the rate of 0.5 μg m⁻² h⁻¹ reported by Horn et al. (2003). With increasing temperature, the emission rates increased exponentially to 55 μg m⁻² h⁻¹ at 55 °C and 200 μg m⁻² h⁻¹ at 80 °C, which are the upper bounds of effective temperatures on the wood surface during summers in temperate and hot climates, respectively. However, considering the moderate temperatures in Hilo during the outdoor study (21–26 °C), evaporation could have accounted for a TAZ loss of 5–10 μg g⁻¹ of wood, which would represent a negligible contribution to the total observed TAZ loss (~600 μg g⁻¹ of wood). Therefore, evaporation could not be attributed to the TAZ loss from wood exposed to ambient temperatures.

For IPBC control, light factor was shown to significantly affect its loss, thus photo-degradation of IPBC during the exposure was likely. Vaporization and thermal degradation of IPBC could not be ruled out since the temperature and time were also among the significant factors. These findings agreed with previously reported thermal and photo-degradation of IPBC (Lee et al., 1991; Kositchaiyong et al., 2014) and thus confirmed that the effect of experimental conditions was observable via the Taguchi design. Contrary to the expectations based on the published data on leaching experiments (Lupsea et al., 2012, 2013), the air humidity did not affect the fungicide loss. The reason could be the lack of wood saturation with water (water-filled pores), which was previously reported to be essential for fungicide leaching (Styszko et al., 2015).

3.5. Triazole leaching

To ascertain the contribution of leaching to the triazoles loss from environmentally exposed wood, kinetic data for TAZ and PAZ leaching were obtained. The triazole loss from wood was virtually independent of time, i.e., yielding a constant amount every week, but dependent on the amount of applied water (Fig. 6). The TAZ and PAZ leaching rates related to the amount of water were approximated using linear functions, but with increasing amounts of applied water, the leaching curves would eventually level off (Ho et al., 2005) due to the inability of water to access and dissolve the sorbed triazole from either distinctly located or poorly accessible sites within the wood matrix. The TAZ leaching rate was slightly higher than that for PAZ, even though the TAZ solubility in water is three times lower at room temperature. The observed higher TAZ leaching rate may be due to the different interactions of each fungicide with the wood matrix.

The use of identical wood sections as in the outdoor study allowed for an approximation of triazole amounts that could have leached during the six-month exposure. Based on the on-site measurements in Hilo, Hawaii, the precipitation in 2014 was 63% per six months (1.6 m). Considering the surface area of each wood section exposed to rain (0.02 m²), the amount of water fallen on each section over six months was estimated as being as high as 32 L. Using the leaching kinetic data shown in Fig. 6, approximately 32% of TAZ and 26% of PAZ could have leached into water, if all this estimated amount of rain actually fell on the given wood sections. Since the TAZ loss during the outdoor study was ~20% (Fig. 2), leaching would represent a major path of its removal. This finding agrees with previously reported 21.0–25.5% of leached TAZ from wood upon seven months of outdoor exposure (Woo, 2010).

The observed six-month losses represent the upper boundary of TAZ depletion due to the high amount of rains in Hawaii during this season. The amount of retained fungicide in wood may be further increased by triazole chemical modification that will decrease its polarity, thus rendering it less water-soluble and more wood-bound.

4. Conclusions

A six-month outdoor study exposing impregnated wood corner
sections (representing window frame corners) to harass environmental conditions revealed TAZ losses from the 2-mm wide cross-sectional surface followed by minor losses from the nearest sub-surface. The total depletion of loosely bound TAZ was not affected by the type of exposure and amounted to ~20% of the originally sorbed TAZ in wood exposed to rain, wind and sunlight. Since the total TAZ amount in wood remained high, the depletion of loosely bound fungicide did not seem to affect the product preservation. Using a fractional factorial design (Taguchi design), significant factors contributing to TAZ and PAZ losses were found to be temperature and time of exposure. Therefore, evaporation of triazoles appeared to be a significant path of their removal. However, considering the moderate temperature during the outdoor study, evaporation could only account for a minor portion of the observed TAZ loss. Additionally, bio-, photo- and thermal degradation were negligible since no degradation products were found and light was not among the significant factors affecting triazole loss.

Controlled experiments revealed that up to 32% of TAZ (and 26% of PAZ) could have leached from the exposed wood during the six-month exposure suggesting water leaching to be the major route of triazole losses from wood. Leaching rate was found to be slightly higher for TAZ than for PAZ.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.05.168.

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