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Fate of triazoles in softwood upon environmental exposure

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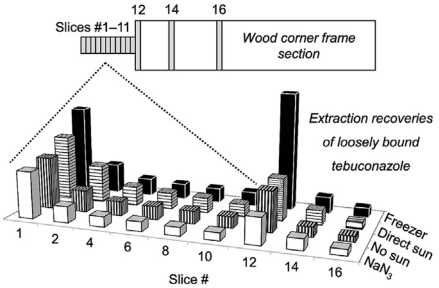
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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 °C) recorded throughout the outdoor study.

1. Introduction

Wood matrix is known to be susceptible to biological attacks from microorganisms, e.g., fungi and bacteria. The resulting gradual

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wood decay contributes to natural recycling but also leads to deterioration of wood products while still in service (Sathre and González-García, 2014). 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 Frostick, 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, isothiazolones, quaternary ammonium compounds, sulfamides and triazoles (Reinprecht, 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 consumed per year and a global market of $600 million in 2015 (FrontResearch, 2016). Triazoles are highly soluble in organic solvents (Cheremisinoff 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 (Bruns 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; Jaklová-Dytrtová 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, evaporation 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 Kofoed-Sørensen, 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 dioxolane ring (Kim et al., 2003) and yield breakdown products such as 1,2,4-triazole, 2,4-dichlorobenzoic acid, and 1-chlorobenzene (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 ^{14}C-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 ^{14}C-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 Biomedicals, LLC (Solon, OH, USA).