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Degradation and sorption of the fungicide tebuconazole in soils from golf greens☆

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ABSTRACT

The fungicide tebuconazole (TBZ) is used to repress fungal growth in golf greens and ensure their playability. This study determined the degradation and sorption of TBZ applied as an analytical grade compound, a commercial fungicide formulation or in combination with a surfactant product in thatch and soils below two types of greens (USGA and push-up greens) in 12-cm vertical profiles covered by three different types of turf grass. Only minor TBZ degradation was observed and it was most pronounced in treatments with the commercial fungicide product or in combination with the surfactant compared to the analytical grade compound alone. A tendency for higher TBZ sorption when applied as the formulated product and lowest sorption when applied as a formulated product in combination with the surfactant was observed, with this effect being most distinct on USGA greens. No correlation between occurrence of degradation and soil depth, green type or grass type was observed. Sorption seemed to be the main process governing the leaching risk of TBZ from the greens and a positive correlation to the organic matter content was shown. In light of these findings, organic matter content should be taken into consideration during the construction of golf courses, especially when following USGA guidelines.

1. Introduction

The sport of golf is growing in popularity worldwide. Environmental concerns about course construction and management have been raised with regard to the impact of golf courses on nearby water resources (Baris et al., 2010; Cohen et al., 1999; Magri and Haith, 2009). These constructed landscape elements are composed of different playing zones, including roughs, tees, fairways and greens. One of the design challenges, especially with greens, is to ensure efficient drainage to protect the turf grass cover from becoming moist or flooded due to heavy rain events or intensive irrigation, for example, which may encourage fungal diseases (Baris et al., 2010). This is achieved by a construction using mostly permeable materials, facilitating efficient removal of excess water from golf courses. The most common way of constructing golf greens worldwide follows the US Golf Association (USGA) guidelines (Larsbo et al., 2008). USGA greens are characterized by the excavation of the original top soil and the addition of a sandy layer (called a “root zone mixture”) followed by a drainage layer consisting of coarse gravel (USGA, 2004) (Fig. 1A). Another popular construction is what is known as the “push-up” green, which in contrast to USGA greens uses the native soil material (Fig. 1B) and therefore generally has a relatively high organic matter content (Oppold, 1997). Most push-up greens have lower porosity and hydraulic conductivity than USGA greens and therefore drain to a lesser extent (Oppold, 1997).

Due to the dense structure of and stress (mowing nearly every day to 3–5 mm length) applied to turf grass on golf greens, fungicides are used extensively to prevent fungal growth. The frequency of pesticide application may be higher in these areas compared to agricultural land, for example (Magri and Haith, 2009), and combined with the intensive irrigation on golf greens presents possibilities for the leaching of fungicides from golf greens to drainage and groundwater. Water quality data with pesticide concentrations exceeding drinking water threshold limits have recently been reported in Europe and across the United States in connection with golf courses (Baris et al., 2010; Cohen et al., 1999; Magri and Haith, 2009; Wu et al., 2002). The degradation and sorption processes occurring within and below the green thatch layer (Fig. 1) are major parameters that determine leaching potential once the fungicides leave the foliage cover (Magri and Haith,

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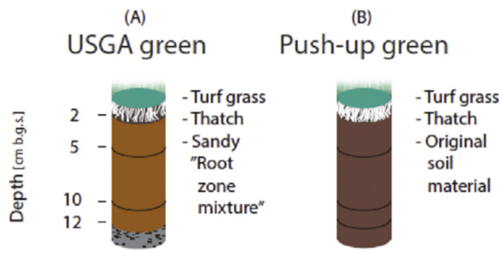

Fig. 1. Vertical soil profiles of golf green constructions: (A) USGA green and (B) push-up green. Depth is given in centimeters below ground surface (cm b.g.s.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2009). Generally, however, the extent and rate of these processes and the soil parameters controlling them are unknown for many of the fungicides used on golf greens.

Tebuconazole ((*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-1(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol) (TBZ) is a broad-spectrum benzotriazole fungicide used in the management of greens to repress fungal growth which negatively affects the turf grass cover and thereby the quality of the golf course. TBZ is also used in the agricultural production of different cereal crops, for example, and is reported to be moderate to highly persistent in different soils, with the time taken for 50% dissipation ranging from 49 to 610 days, and no or very limited mineralization of either the chlorophenyl or triazole rings (a maximum of 0.4% of the added ^{14}C-labeled TBZ mineralized after 112 days of incubation) (Bending et al., 2007; Conclusion on the Peer Review, 2014; Strickland et al., 2004). The sorption of TBZ in these soils is primarily controlled by the organic matter and mineral contents (Conclusion on the Peer Review, 2014; Cadkova et al., 2012) and TBZ as part of a commercial product has generally been observed to have a higher soil sorption compared to analytical grade TBZ alone (Cadkova et al., 2013a). In parallel to the fungicides, surfactant products are also used on greens to reduce hydrophobicity in the turf and underlying sandy root zone, and thereby provide better drainage from the surface and improved water access for grass roots (Larsbo et al., 2008; Aamlid et al., 2009).

The objectives of this study were therefore to estimate the degradation and sorption of the fungicide TBZ in soils below two types of greens (USGA and push-up) in 12-cm vertical profiles covered by three different types of turf grass. The effect of additives in a commercial fungicide formulation and the addition of a commonly used surfactant product on the sorption and degradation of TBZ were elucidated and an attempt made to correlate this to simple soil parameters.

2. Materials and methods

2.1. Chemicals

Analytical grade tebuconazole (TBZ; (RS)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentan-3-ol; CAS RN 107,534-96-3, > 99.3% purity) was purchased from Sigma Aldrich and [phenyl ring-*U*-^{14}C]-TBZ (5.225 MBq mg^{-1}, purity > 98%) from IZOTOP (Budapest, Hungary). The commercial TBZ product, Orius 200 EW® (Orius; 200 g TBZ L^{-1}), was purchased from ADAMA Northern Europe B.V. (formerly Makhteshim-Agan). The surfactant Revolution® was purchased from Aquatrols Corporation, (NJ, USA) (diluted 20 L Revolution to 800 L water^{-1} ha^{-1}).

2.2. Golf course description and sampling for soil water properties

The focus in this study was on two green types: USGA greens and push-up greens. USGA greens are constructed as specified by the US Golf Association (USGA, 2004), and characterized by the excavation of the original soil material and the addition of specified sandy soil layers used as the growth layer. Push-up greens are constructed using native materials, usually from a local sand pit (often with unknown particle size distribution) and are a cheaper alternative to USGA greens (Fig. 1).

For each type of green, golf courses with a dominance of red fescue [*Festuca rubra* (L.)], colonial bent [*Agrostis capillaris* (L.)] or annual bluegrass [*Poa annua* (L.)] were investigated. Red fescue and colonial bent grass tend to create thatch layers a couple of centimeters thick connected to a deeper root system going down to at least 15–20 cm depth. In comparison, annual bluegrass grows without a distinct thatch layer and is characterized by a superficial root system. The grass type and spraying history for each golf course are listed in Table 1.

Large sample cores (diameter 10.8 cm) were sampled to a depth of 12–15 cm and used to determine texture, porosity and water saturation. Two large soil cores from each golf course representing each green type were sampled using a green hole cutter. The initial, saturated and dry weights (105 °C) of the two cores of known volume were measured. Based on this, bulk density, porosity and water saturation were estimated, as described in the standards "Recommended Practices for Core Analysis" (API RP 40, 1998), "Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass" (ASTM D2216-10, 2010), and "Standard Test Method for Determination of Vibrated Bulk Density of Calcined Petroleum Coke" (ASTM, 2010). After this the samples were re-saturated and frozen. The frozen samples were cut into at least five slides, representing the five depths below ground surface (b.g.s.): 0–2 cm (Depth 1), 2–5 cm (Depth 2), 5–10 cm (Depth 3), 10–12 cm (Depth 4) and 12–15 cm (Depth 5; not available at Push-up Course 2) and the textural analysis of each depth was performed in accordance with the standard "Test for Geometrical Properties of Aggregates – Part 1: Determination of Particle Size Distribution – Sieving Method" (DS/EN, 2004) except for Depth 1 due to the dense structure of the thatch which made it impossible to sieve the samples. It was assumed that it was texturally similar to Depth 2 (Table 2).

2.3. Sampling for degradation, sorption, soil texture and inorganic studies

The six different golf courses representing three USGA greens and three push-up greens (Table 1) were sampled using a tubular soil sampler (diameter 2.0 cm). Nine to 15 greens were sampled per golf course and from each green a minimum of seven small soil cores were sampled from the turf (red fescue, annual bluegrass or colonial bentgrass) and 12 cm b.g.s. Each soil core was divided *in situ* into the four fractions representing the four depths b.g.s. 0–2 cm (Depth 1), 2–5 cm (Depth 2), 5–10 cm (Depth 3) and 10–12 cm (Depth 4). All the fractions from each depth and green were pooled in plastic bags and transported back to the laboratory and stored in the dark at −20 °C. Prior to the experimental set-up, all fractions were acclimated for one week at 10 °C. For each golf course, one composite sample per depth representing all the greens from one golf course was prepared by pooling each fraction from all the sampled greens, resulting in four composite samples per golf course. Each composite sample was homogenized by sieving and further mass reduction for laboratory subsampling was performed by bed blending, as described in the representative sampling standard "Representative Sampling – Horizontal Standard" (DS3077, 2013) and by Kardanpour et al., 2015. Turf grass was cut from the turf layer (Depth 1) before fractions were homogenized in a coffee grinder prior to sieving.