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Rainfastness of mancozeb on apple seedlings determined through deposition quantification of mancozeb residue and a fluorescent pigment

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ABSTRACT

Mancozeb spray deposition and the persistence thereof to rainfall are important factors influencing the efficacy of apple scab control caused by *Venturia inaequalis*. Fungicide deposition can be assessed through quantification of fungicide residue, or fluorescent pigment quantification. Fluorescent pigment quantification is a more cost effective and less labour intensive method, since it is assessed using only photomacrography and image analyses. The yellow fluorescent pigment used in this study was shown to be a suitable tracer for five different mancozeb formulations on apple leaves when evaluated at different concentrations (0.5, 1.0, 1.5 and 2.0). Pearson's correlation was significant ($P < 0.001$) and high ($r = 0.896$) between fluorescent particle coverage (FPC%) and mancozeb residue (mg/kg$_{Dry\ Weight}$) for all five formulations. The particle size ranges of two wettable powder (WP) formulations were significantly smaller than those of the other WP formulations, but this did not result in differences in mancozeb residue on apple leaves. The persistence of mancozeb to different rain volumes applied to apple leaves was determined for three mancozeb formulation treatments: Dithane M-45 800 WP NT, Ventum 800 WP, and Ventum 800 WP combined with the sticker-spreader adjuvant Nu-Film P. There were no significant differences ($P > 0.495$) between the three treatments based on FPC% and mancozeb residue quantity when simulated rain was applied to apple seedlings at a constant rainfall intensity of 5 mm/h at five different rainfall volumes (0, 1, 5, 10 and 15 mm). A fair to good correlation ($r = 0.697$ and 0.995) existed between FPC% and mancozeb residue, and their percentage loss at different rainfall volumes. However, the response of FPC% and mancozeb residue differed based on exponential regression curves. This was due to a markedly larger predicted loss by each model's asymptote, 51.67% for FPC% and 40.76% for mancozeb residue. Based on actual mancozeb residue values, a significant percentage loss in residue already occurred after applying 1 mm (32.90%) rain. When rain volumes were increased to 5 and 10 mm rain, the percentage losses (37.88 and 41.08%) did not differ significantly from 1 mm rain. The same was true for percentage loss in FPC%, except that a significant higher loss occurred at 10 mm (52.36%) than at 1 mm rain (41.13%).

1. Introduction

In South Africa, regular fungicide applications are used to control apple scab caused by *Venturia inaequalis* (Cooke) G. Wint., an economically important disease of apples world-wide. A key fungicide used in apple scab management is mancozeb (Schwabe, 1980), a broad-spectrum contact fungicide containing a mixture of manganese (manganese ethylene bis-dithio-carbamate) and zinc ions (Crnogorac and Schwack, 2009; Gullino et al., 2010). A typical scab spray program in South Africa consists of weekly mancozeb sprays starting at green tip. Depending on cultivar differences, green tip can be as early as the first week in August, but seldom later than the second week of September. Weekly sprays continue until petal fall, and then bi-weekly sprays are applied until the beginning of December. From December onwards, sprays are applied every 4 weeks, until 3–4 weeks before harvest. This can result in a total of 12–14 mancozeb sprays applied per season in South Africa (personal communication, J.P.B. Wessels, ProCrop Trust Consult, South Africa). Regular weekly mancozeb applications at the start of the season are essential since new shoots and flowers develop continuously, which is highly susceptible to scab (Schwabe, 1979; MacHardy, 1996).

Rainfall can influence the persistence and efficacy of mancozeb

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sprays (Kudsk et al., 1991; Hunsche et al., 2007). On apple seedlings, the amount of mancozeb washed off from leaves has been shown to increase as the volume and intensity of simulated rain increase. Mancozeb has been reported as having relatively poor rainfastness on apple seedling leaves, with 55–80% loss occurring after 1–5 mm of heavy rain (5 mm/h) (Hunsche et al., 2007). In contrast, mancozeb is perceived as having relative good rainfastness in South Africa, based on unpublished data (personal communication W.F.S. Schwabe, The Fruit Doctor, Somerset West, South Africa). Growers will often only reapply mancozeb after 5–10 mm of heavy, or 20 mm of soft rain (personal communication J.P.B. Wessels). In the United States of America, reapplications are made after 25 mm of rain has fallen (Ellis et al., 1984). Similar to the South African perception, mancozeb was shown to be more persistent on grape, pea, bean and potato leaves (Kudsk et al., 1991; Cabras et al., 2001; Hunsche et al., 2006) than on apple seedlings (Hunsche et al., 2007). Differences in rainfastness between different crops can be due to differences in leaf surface characteristics (Hunsche et al., 2006).

In South Africa, the Western Cape region is the most important apple producing region (Department Agriculture: Forestry and Fisheries Republic of South Africa, 2011, 2012) and it is classified as a winter rainfall area. Frequent rains and temperatures conducive to scab development continue as late as November in this region. Rainfall during the mancozeb spray window range from approximately 100 mm–200 mm in the Ceres and Grabouw/Elgin regions respectively (www.capefarmmapper.com; sdwebx.worldbank.org/climateportal). Rain will sometimes fall twice within the same week early in the season, causing growers to reapply mancozeb-based on the amount of rain fallen, in order to protect new shoots and flowers.

Adjuvants can be combined with fungicide sprays to reduce weathering, extend the efficacy and improve the distribution, adherence and rainfastness of pesticides (Hunsche et al., 2006; Percival and Boyle, 2009). Only two studies have investigated the effect of adjuvants on the rainfastness of mancozeb. Rapeseed oil ethoxylates improved the rainfastness of mancozeb on apple, bean and kohlrabi seedlings (Hunsche et al., 2006). The addition of various sticker adjuvants also improved mancozeb rainfastness on pea and potato (Kudsk et al., 1991).

The effect of rainfall on the persistence of fungicides can be determined using natural rainfall occurring in orchards during the growing season (Schutte et al., 2012), or simulated rain (Cabras et al., 2001; Hunsche et al., 2007). Evaluating the effect of simulated rain has the advantage that a range of specific rain volumes and intensities can be investigated. Over the past 62 years many different rain simulators have been built and used for various purposes including the assessment of soil erosion, soil water infiltration and chemical wash-off (Grierson and Oades, 1977; Hunsche et al., 2007; Arnaez et al., 2007; Iserloh et al., 2012, 2013). There is no standard rainfall simulator design, and therefore simulators differ in rainfall intensities and distribution, drop sizes and drop velocities (Iserloh et al., 2012, 2013).

Disease control is directly dependent on effective fungicide deposition quantification. Therefore, the quantity (the amount of active ingredient on a target surface) of contact fungicide deposition realised on target surfaces (leaves, twigs, and fruit) is important (Fourie et al., 2009; Van Zyl et al., 2010a, b; Van Zyl et al., 2013). Fungicide deposition quantity can be investigated cost effectively using a yellow fluorescent pigment in combination with photomicrographic (small target area) or photomacrographic (larger target area) image analyses (Brink et al., 2016a, b; Graham, 2010; Van Zyl et al., 2010a, b; Van Zyl et al., 2013, 2014). The deposition of fungicide can also be determined through quantification of fungicide residues, although this is expensive (Van Bruggen et al., 1986; Hwang et al., 2001; Hamm et al., 2006; Hunsche et al., 2006, 2007; Bringe et al., 2007). For mancozeb, the main methods used for quantification of mancozeb residues are the measurement of carbon disulphide (CS_2) (Hwang et al., 2001; Crnogorac and Schwack, 2009) or manganese (Mn)-ion concentrations (Van Bruggen et al., 1986; Hamm et al., 2006; Hunsche et al., 2006; 2007; Bringe et al., 2007).

Different fungicide formulations and particle size can have an effect on the rainfastness and tenacity of fungicide sprays. The effect of particle size on the tenacity of different fungicides may vary and is somewhat controversial. For example, the tenacity of copper oxychloride and copper carbonate has respectively been reported by Somers and Thomas (1956) and Hyre (1942) to increase with decreasing particle size. However, Somers and Thomas (1956) reported that the tenacity of copper carbonate was not influenced by particle size, nor that of cuprous oxide. Schutte et al. (2012) compared copper hydroxide, copper oxychloride and cuprous oxide with each other and found that particle size differences between these products did not affect rainfastness or weathering. For mancozeb, only Kudsk et al. (1991) have reported that the rainfastness of mancozeb WP formulations improved with a decrease in particle size (Kudsk et al., 1991). The controversial reports on the effect of particle size on the tenacity of copper may in part be due to the fact that surface active compounds, such as wetting and sticking agents, are added to commercial fungicide formulations, which might also influence tenacity (Somers and Thomas, 1956). This has been reported for mancozeb where mancozeb SC formulations had a higher rainfastness than WP formulations on pea and potato (Kudsk et al., 1991).

In South Africa, approximately 22 different mancozeb formulations are registered on apple (Agritel, www.agritel.co.za). It is unknown whether these formulations, which mostly include low-cost generic formulations, differ in rainfastness, particle size, and whether the addition of adjuvants can improve rainfastness on apple leaves. Mancozeb rainfastness is especially important in the later part of the growing season where bi-weekly sprays are applied, and where maximum residue values must not be exceeded. It is also important early in the season since rain often occurs over a 7-day period. If the current perception of mancozeb rainfastness in South Africa is overestimated, it can lead to reduced control following rain events, or if it is underestimated it can result in over application, and increased costs to the producer. Superior rainfastness of specific mancozeb formulations, or improvement of persistence through the addition of adjuvants, can improve scab control on leaves early in the season when continuous rain often occurs over 7-day periods and wet orchards conditions or limitations in available sprayers on a farm prevent re-applications.

The aims of the study were to use a yellow fluorescent pigment as a tool to (i) investigate the deposition of five commercially available mancozeb formulations (Dithane M-45 800 WP NT, Ventum 800 WP, Mancozeb 800 WP, Pennfluid and Vondozeb), which differ in particle size and (ii) the rainfastness (persistence) of two mancozeb formulations with or without an adjuvant on apple seedling leaves. The persistence of the formulations to five different rain volumes at a moderate rain intensity (5 mm/h) was assessed. The utility of the yellow fluorescent pigment was assessed in all experiments by comparing its deposition to mancozeb residue deposition.

2. Materials and methods

2.1. Plant material

Golden Delicious apple seedlings (*Malus domestica* Bork h.) (18–24-month old) were used in all experiments. The seedlings were produced by first extracting apple seeds from fruit and placing it in water containing 2 g/L captan (Captab WP, Universal Crop Protection (Pty) Ltd., South Africa) for one day. After drying, the seeds were stratified in perlite moistened with captan water (2 g/L) at 4 °C for 3 months until germination. Germinated seeds were placed in crates with perlite and incubated at 25 °C. After 2–3 weeks when seedlings emerged, the seedlings were planted into seedling trays. The seedlings were transplanted after 3 weeks into 1 L plastic bags containing a sterile sand and bark (2:1 v/v) growth medium. Seedlings were grown in a glasshouse at