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Copper Losses in Surface Runoff from Flatwoods Citrus Production Areas

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Abstract Crop production in areas with a high water table and poorly drained soils requires special drainage infrastructure to allow adequate rooting depth. In addition to facilitating drainage, this infrastructure also facilitates discharge of agrichemicals dissolved in drainage and runoff water. Copper export from bedded citrus production areas was evaluated using simulated rainfall events following application of copper. Copper concentrations in runoff water from individual water furrows ranged from 13 to 223 μg/L during the staged events, while copper loadings ranged from 32 to 302 g/water furrow.

Keywords Pesticide · Water quality · Runoff · Citrus production

The Indian River (IR) citrus production region is an intensively managed agricultural production area where concerns over pesticide export to surface water have been raised. Intensive pest management programs are necessary for producing marketable crops due to the sub-tropical nature of the Indian River region. This region, which produces 75 % of the grapefruit grown in the state of Florida (http://Indian-river.fl.us/citrus/district.html, accessed 1/15/2012), is located along the east coast of Florida from Volusia to Palm Beach County and includes land adjacent to the Indian River Lagoon (IRL), one of the most biodiverse estuaries in the US (http://www.sms.si.edu/IRLFieldGuide/IRLBiodiv.htm, accessed 2/15/2012). Citrus production within this region is unique in that it often occurs on beds due to the high water table level in this historically wetland area. These beds drain by shallow water furrows between beds into lateral ditches that are connected to larger canals and ultimately into the IRL (Fig. 1). Beds may be designed to support a single row of trees along the top, or two or more rows on either side of the middle of the bed (closer to the edges). Large volumes of surface runoff and associated agrichemicals may leave the production areas in a short period of time due to these drainage features (Wilson et al. 2007a, b; Miles and Pfeuffer 1997). Survival, health, and/or reproduction of non-target organisms exposed to these pesticides may be compromised depending on the pesticides' chemical and physical properties, concentrations, and exposure durations.

One pesticide of concern within the region is copper. Copper is a fungicide/bacteriocide commonly used in citrus production pest management programs for controlling citrus scab, melanose, greasy spot, and all fungal diseases of the rind (Stover et al. 2004; Rogers et al. 2010). Copper can be especially toxic to gill-breathing aquatic organisms, where it acts primarily as an ionoregulatory toxicant. In this case, Cu^{2+} as well as some copper hydroxide complexes bind to and inactivate transport proteins on the gill surface that are responsible for ionoregulatory processes (Wood 2001). Exposure to copper concentrations less than 100 μg/L induces large losses of Na^{+} and Cl^{-} across the gills, causing declining osmolality, fluid volume disturbances, and cardiovascular collapse (Wood 2001).

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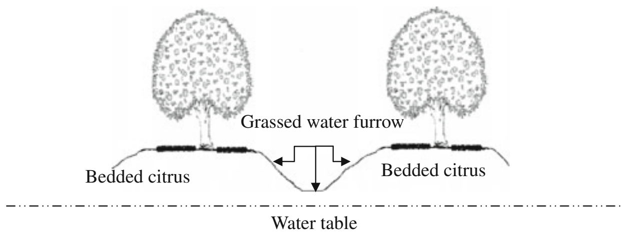

Fig. 1 Cross-sectional diagram of typical bedded citrus production system with maintenance of vegetated water furrows and weed-free zones underneath the trees

Given the potential toxicity of copper fungicides to non-target aquatic organisms, its dominant use in citrus production, and the efficient and effective drainage provided under the bedded citrus production systems within the IR region, identification of possible losses and concentrations in runoff water is needed to assess potential ecological risks to aquatic receiving water bodies and to determine if mitigation strategies need to be developed and implemented. This study evaluated losses of copper in runoff water at the tree-row/water furrow level during simulated rainfall events.

Materials and Methods

This study was conducted in a citrus grove located at the UF/IFAS Indian River Research and Education Center, Fort Pierce, FL. Trees in the grove were 48-year-old 'Temple' orange trees grafted onto Cleopatra mandarin rootstocks that were planted on single-row beds. Trees were 4.9–6.1 m tall and approximately 6.1 m wide. The tree rows and water furrows were 156.7 m long, with a tree spacing of 9.1 m across-row and 6.9 m within-row (160 trees/ha). There were approximately 22 mature trees per bed, with 2–3 younger trees at the water furrow outlet end. The soil type was Wabasso, which is classified as a sandy, siliceous, hyperthermic Alfic Haplaqualf (Watts and Stankey 1980). This soil is poorly drained (Watts and Stankey 1980). Tree rows were planted in an East–West orientation.

Twelve-replicate water furrows (copper applied to trees on each side) were evaluated. In order to measure the volume of water discharged out of each water furrow, small 60° V-notch weirs were constructed and placed at the upstream end of each furrow discharge pipe (Department of the Interior 1975). Water depth measurements were taken at 10 min intervals from the time that water began flowing through the weir.

Copper (Kocide 2000, DuPont, Wilmington, DE) was applied to the site at a rate of 3.4 kg/ha using a PTO-driven radial-fan airblast sprayer (Air-O-Fan GBC-10) operated with ALBUZ ATR-80 nozzles (Saint-Gobain Ceramiques Avancees Desmar Quest), and calibrated to deliver 2,339 L/ha (250 gal/acre). The temperature, dew point, relative humidity, wind speed, and wind direction recorded during the application were 26°C, 23°C, 81 %, and 13.8 kph towards the southwest (270°), respectively.

Senninger Model 4023-1-3/4 impact sprinklers (Senninger Irrigation Inc., Clermont, FL) mounted on 6.1 m risers were installed in portable, concrete base units. The base units were installed in the test blocks on an 18.3 × 18.3 m spacing (every other bed), with 6 units per row (91.4 m from first to last riser). Sprinklers were fitted with No. 12 nozzles and discharged at a rate of approximately 28.4 L/min. The sprinkler heads were positioned above the treetops and discharged water in a 360° pattern, 23° trajectory. This configuration delivered a precipitation rate of approximately 0.46 cm/h and a wetted diameter of 36.6 m. The water source for the overhead system was surface water from a North St. Lucie River Water Control District canal that was pumped into the IRREC grove irrigation/drainage infrastructure. A 7.5 KW gasoline powered pump was connected to the irrigation system risers near the blocks studied to boost the grove mainline pressure from 276 kPa to approximately 414 kPa, a level suitable for the impact sprinklers. Monitored runoff events were conducted over two, 2-day periods due to infrastructure limitations with water being applied only to the furrows/tree rows being monitored on each respective date. Eight replicates were sampled 1 day after treatment (DAT) and the other four 2 DAT. Likewise, runoff events were staged and the same replicates were sampled again 12 and 13 DAT. No rainfall occurred during the periods between sampling.

Water samples were collected in polyethylene bottles at the discharge end of each of the 12 water furrows. Samples were preserved by addition of 15 % nitric acid to lower the pH to less than 2. All samples were placed in an ice cooler immediately after collection, and were stored in the lab at room temperature until digestion and analysis. The first sample in each furrow was collected when water began flowing through the weir. Subsequent samples were collected at 20 min intervals for the first hour, 30 min intervals for the second and third hours and at 1 h intervals thereafter.

It was not possible to monitor the entire runoff event (from start to end of flow) due to limited personnel, non-uniform flows in some furrows, and analytical capacity. Samples were collected for the first 3.0–9.3 h (mean: 6.5 h, standard deviation: 2.1 h, median: 5.4 h) during the first event and 3.6–10.9 h (mean: 7.2 h, standard deviation: 2.3 h, median: 7.8) during the second. The differences in length of time monitored reflect differences in the amount of time that it took for runoff to begin in each water furrow. Fewer samples were collected from furrows where runoff began later in the day. Some ponding of water was noticeable in some furrows, which is typical in older groves. Samples of the irrigation water were also collected at the pump intake throughout the simulated rainfall period.

Samples were analyzed using a ThermoElemental Iris 1000 (ThermoFisher Scientific, Waltha, MA, US) inductively coupled plasma with atomic emission spectroscopy (ICP-AES) detection. The analytical method followed the recommendation of EPA method 6010B. Unfiltered samples were acid digested (EPA 3052) before analysis. The detection limit for the method was 9 ng/mL. Percent recoveries from copper-fortified water samples ranged from 80 % to 92 %. Field blanks and irrigation water background concentration check samples were also collected and analyzed to confirm lack of contamination in the system.

The mass of copper discharged during the monitored portion of each event was estimated by multiplying the concentration measured by the volume of water that passed through the weir during the sampled interval of time. This load estimation method assumed that the concentration was constant during each time interval where volume was measured.

Summary statistics (mean, standard deviation, median, maximum, and minimum) were calculated for concentrations and runoff volumes relative to each treatment. Due to the dependence of cumulative copper discharges on cumulative water volume discharges, masses discharged were normalized to the mean discharge volume for all 12 water furrows.

Results and Discussion

A summary of the runoff volumes discharged from water furrows is shown in Fig. 2a. Runoff volume ranged from 5,038 to 28,537 L during the first runoff events (1–2 DAT) and 8,167–23,293 L during the second events (12–13 DAT).

Copper concentrations were detected in runoff water during both sets of runoff events (Table 1). During the 1–2 DAT event, concentrations ranged from 43 to 233 µg/L. The mean and median concentrations were 94 and 87 µg/L, respectively. Concentrations were slightly skewed towards higher concentrations as indicated by the greater mean relative to median values. The 25th, 50th, 75th, 90th, and 95th centiles were: 79, 87, 96, 141, and 152 µg/L, respectively. During the second events (12–13 DAT), concentrations ranged from 13 to 66 µg/L, with mean and median concentrations of 40 and 37 µg/L, respectively, indicating slight skewness towards higher concentrations. The 25th, 50th, 75th, 90th, and 95th centiles were: 32, 37, 55, 62, and 63 µg/L, respectively.

To estimate copper loadings, the mean discharge volume for all of the replicate water furrows combined was selected for normalization. Mean discharge volumes were 16,281 ± 2,481 L (±standard error) and 14,707 ± 1,474 L for the first and second set of events, respectively. Copper losses ranged from 0.93–2.68 g/furrow (1–2 DAT) to 0.29–0.91 g/furrow (12–13 DAT).

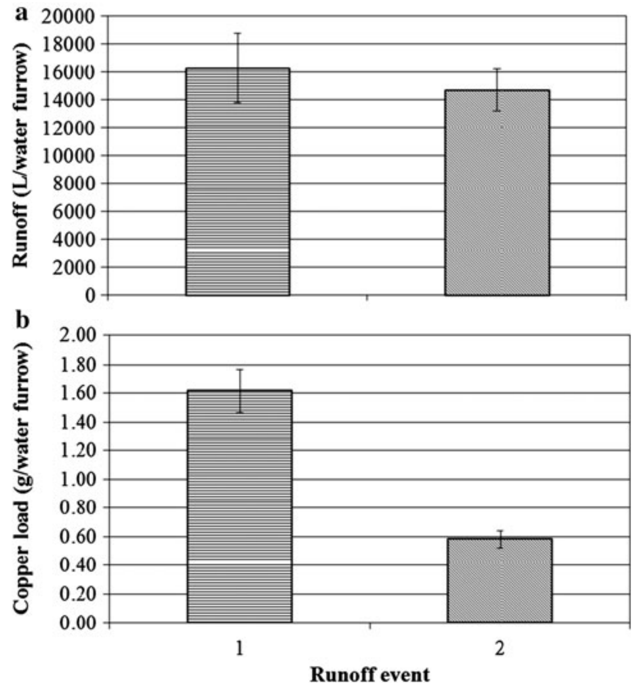

Fig. 2 Summary of cumulative **a** water discharge volumes (L) and **b** copper loadings (g) from water furrows within a bedded citrus production system

Table 1 Summary of copper concentrations (µg/L) detected in runoff water following copper application (3.4 kg/ha)

Summary statistic	Copper (µg/L)		
	Event 1[a]	Event 2[b]	Combined[c]
N	101	96	197
Mean	94	40	68
Standard error	3	1	3
Median	87	37	63
Minimum	43	13	13
Maximum	223	66	223
Centiles			
25th	79	32	38
50th	87	37	63
75th	96	55	87
90th	141	62	106
95th	152	63	141

[a] 1–2 days after copper application

[b] 12–13 days after copper application

[c] Events 1 and 2 combined

These results indicate that significant amounts of runoff water and copper may be discharged from production areas following application. A typical 16.2 ha citrus production area with the same row dimensions in this study would contain approximately 113 water furrows. Assuming that a typical rainfall event discharges 16,281 L of water per furrow, this translates to a discharge volume of 1,839,753 L of surface runoff water per 7 h/0.46 cm/h rainfall event. Likewise, copper discharges ranging from 105.1 to 302.8 g would be expected 1 DAT, and 32.7–102.8 g during the second runoff event from a 16.2 ha production area. Total potential losses would be expected to be greater since detectable concentrations were still present at the end of the second runoff events.

While total copper was found in the surface runoff water, some uncertainty exists regarding the actual form of the copper. Cu^{2+} and CuOH are generally considered to be the bioactive forms of copper, and are the forms applied for pest control. However, Cu^{2+} is transformed to other, non-bioactive and less bioavailable forms in the soil environment (Ma et al. 2006; Cavallaro and McBride 1978; Williams and McLaren 1982; Brennan et al. 1980; Brennan et al. 1986; McLaren and Ritchie 1993). It may be retained in the soil by sorption to organic carbon, cation exchange, or it may be precipitated in soils with high pH (Bertling et al. 2006). Concentrations and loadings were generally reduced by more than 50 % during the second set of runoff events relative to the first. This reduction was likely due to aging of the copper residues on the soil since no rainfall or irrigation events occurred between the sampling periods and copper does not degrade. Likewise, copper may have also been sorbed to dissolved organic carbon (DOC) in the simulated rain water since it has a high affinity for DOC (Ponizovsky et al. 2006; Suave et al. 1997). Water within the irrigation water supply canal has a brown color due to DOC from abundant plant growth and senescence within the watershed. Unfortunately DOC was not measured in this study.

Results from this study indicate that copper can leave the site of application in surface runoff water following applications to citrus production areas. However, the form of copper in the runoff water is not known, which is important for determining ecological risks. Further studies are needed to determine the actual copper forms and transformation kinetics. Similar losses should be expected in other areas where high water tables and poorly drained, sandy soils require production on beds.

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