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Efficacy and environmental fate of copper sulphate applied to Australian rice fields for control of the aquatic snail *Isidorella newcombi*

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ABSTRACT

Copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) is widely used for controlling *Isidorella newcombi*, an aquatic snail that causes substantial damage to rice crops in southeastern Australia. We conducted field trials on a Birganbigil clay loam soil that demonstrate high levels of efficacy against adult *I. newcombi* (95% mortality at 6.38 kg ha^{-1} $CuSO_4 \cdot 5H_2O$ (1.14 mg Cu L^{-1})). Dissolved copper fell below the detection limit (0.02 mg Cu L^{-1}) between 7 and 20 d after spraying at application rates up to 2.16 mg Cu L^{-1} (12 kg ha^{-1} $CuSO_4 \cdot 5H_2O$). Total copper concentrations in the water column fell below the detection limit (0.007 mg Cu L^{-1}) 7–12 d after spraying at initially applied concentrations of 0.52–1.12 mg Cu L^{-1}, but remained detectable (0.01–0.02 mg Cu L^{-1}) until 30 days after spraying (the conclusion of monitoring) when applied at higher initial concentrations (1.18–2.16 mg Cu L^{-1}). There was a strong positive correlation ($r^2 = 0.90$, $P < 0.001$) between copper application rate and copper concentrations in surface sediments 30 d after spraying. Bioassays with immature snails using three different test soils beneath irrigation water showed that underlying soil type strongly influenced the response of snails to applied copper, with significant ($P < 0.05$) differences between LC_{90} values which ranged from 0.41 to 1.04 mg applied Cu L^{-1}. Laboratory studies showed that dissolved copper concentrations remained significantly higher ($P < 0.05$) in the water column above the soil that had the most deleterious effect on copper toxicity. Dissolved organic carbon concentrations were significantly ($P < 0.05$) higher in both this soil and in the overlying water in the corresponding bioassay system, and correlated more closely with LC_{90} values than other water chemistry parameters such as total hardness. Our results support the ongoing use of a variable copper application rate of 6–12 kg ha^{-1} $CuSO_4 \cdot 5H_2O$ to allow for site-specific variations in efficacy, and suggest that variations in the release of dissolved organic carbon compounds from flooded soils may be a key factor moderating copper toxicity to *I. newcombi* in rice fields.

1. Introduction

Isidorella newcombi (A. Adams & Angas) *sens. lat.* is a native Australian freshwater snail that causes extensive damage to irrigated rice crops in southern New South Wales (NSW) each year. The snails feed on the roots of the rice plants at or near the junction with the stem, leading to reduced tillering and delayed plant maturity. Damage in the early stages of crop growth can lead to substantially reduced plant establishment if the seedlings are completely severed or the damaged root systems become detached from the soil (Stevens, 2002). *I. newcombi* is not acutely affected by the majority of conventional pesticides applied at realistic operational concentrations (Stevens et al., 1996), and although some synthetic compounds such as niclosamide offer considerable potential for *I. newcombi* control, none of these have yet been commercialised in Australia.

Climatic factors constrain rice production in NSW to one crop per year, which is typically sown in October and harvested in March or April. Soil dormancy is a key factor driving the pest status of *I. newcombi*, as snails can enter dormancy in the soil when a rice crop is drained prior to harvest, and over 40% of dormant snails will survive until flooding of a consecutive crop in the following spring

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(Stevens, 2002). Snails cannot survive the longer period of dormancy necessary if rice crops are rotated between paddocks to provide a summer fallow, and this has allowed some farmers to implement a cultural approach to snail control. The use of crop rotations for snail management is however currently declining, since minimising water use has become a priority for the industry and consecutive cropping, which exacerbates the snail problem, allows water savings of around 10% in the second and subsequent consecutive rice crops. This is due to residual water in the soil profile reducing the amount of water necessary for initial bay filling. This movement away from rotation-based snail management in order to reduce water usage has led to an increase in snail problems, coupled with a greater dependence on chemical control.

Grist and Lever (1969) were the first authors to report *Isidorella* sp. as a pest of rice in NSW, however it did not become a highly significant pest for the rice industry until 1973 (Stevens, 2002). Copper sulphate has been the only chemical control agent used against *I. newcombi* since that time, and has been applied at rates of 6–12 kg ha^{-1} (for copper sulphate pentahydrate). Experience has shown that the efficacy of copper for *I. newcombi* control is variable between sites, and also, to some extent, between seasons at individual sites. This variability is to be expected, since the biological activity of copper as a toxicant when applied to aquatic systems is influenced by a large number of environmental factors including water hardness, turbidity, pH, and dissolved organic matter (DOC) (Erickson et al., 1996; Sciera et al., 2004; Rogevich et al., 2008; Constantino et al., 2011).

The use of copper sulphate as a molluscicide in Australian rice crops has been authorised through a series of permits issued by the Australian Pesticides and Veterinary Medicines Authority (APVMA) or its predecessor agencies. The APVMA is a federal agency responsible for the regulation of agricultural and veterinary chemicals throughout Australia. The permit system is designed to authorise the use of agrochemicals on a short-term basis whilst full chemical registration is sought, and in 2006 the APVMA declined to issue further permits for copper usage as a molluscicide in rice, requiring the material to be formally registered. This necessitated the generation of efficacy and environmental fate data and provided the initial stimulus for this study. There was, however, also a need to develop a better understanding of how environmental conditions within rice fields affect the performance of copper sulphate as a molluscicide, with a particular view towards assisting farmers to optimise control whilst minimising the amount of copper entering the environment. In order to achieve these objectives, we conducted two field evaluations of copper efficacy and environmental fate to determine the optimal application rate for the control of adult *I. newcombi*, determine how long total and dissolved (0.45 μm filtered) copper persisted in the water column, and quantify what proportion of the applied copper could be detected in surface sediments. We then conducted a series of laboratory bioassays on immature *I. newcombi* using a number of different soil/water systems to determine what role the underlying soil type might have on copper efficacy. We assessed persistence of dissolved copper in the water column of these systems, and also analysed soil and water column dissolved organic carbon (DOC) levels in order to explain the variations in applied copper toxicity.

2. Materials and methods

2.1. Evaluation of container suitability

Since dissolved copper has the potential to adsorb to surfaces, we conducted an initial evaluation of the storage and experimental containers chosen for use throughout this study to ensure they would not compromise our results. Polycarbonate containers with polyvinylchloride screw lids were obtained from Techno-Plas Pty Ltd, St Marys, South Australia. The smaller size containers (model C5744UU) were 70 mL in capacity, while the larger containers (model C10065UU) were 250 mL in capacity with an internal diameter of approximately 60 mm at their mid point. The small containers were used as ‘dippers’ for subsample collection in the field trials and to store water samples prior to chemical analysis. The larger containers were used for the storage of composite water samples from the field trials, and also as experimental containers for both the bioassays and laboratory adsorption studies. Dissolved copper is defined here as being the copper present in a water sample after it has been passed through a 0.45 μm filter (Deaver and Rodgers, 1996; Eaton et al., 2005; Rogevich et al., 2008) and includes ionic copper, copper bound to particles less than 0.45 μm in diameter, and also copper bound to dissolved organic compounds.

To determine whether these containers were appropriate for handling water samples to be analysed for dissolved copper, we prepared a 2 mg L^{-1} copper solution using copper sulphate pentahydrate (AnalaR® analytical grade, ≥ 99.5% purity, BDH Chemicals (Australia) Pty Ltd, Port Fairy, Victoria) and metal-free water, and added 160 mL to each of five of the 250 mL polycarbonate containers. The containers were capped and maintained at 25 ± 1 °C with a 15L:9D lighting cycle for 7 days. Two 50 mL aliquots were then taken from each container. One aliquot was passed through a 30 mm diameter 0.45 μm pore size PTFE membrane syringe filter (Chromacol Ltd, Welwyn Garden City, Herts, UK) using a 20 mL disposable plastic syringe without rubber gasket (Lomb Scientific Pty Ltd, Taren Point, NSW) and into a 70 mL capacity polycarbonate container. The other aliquot was poured directly into a second 70 mL container without filtration. All subsamples (5 × filtered and 5 × unfiltered) were acidified to pH < 2 using 1 mL of 70% HNO_3 (Univar® analytical grade, assay 68–70%, Ajax Finechem Pty Ltd, Taren Point, NSW) and maintained at 25 ± 1 °C (15L:9D) for a further week before analysis of copper concentrations. Syringes, syringe filters and containers had all been acid-washed for 1 h in 10% nitric acid and air dried before use. The copper concentration in the initial copper solution was also analysed for comparative purposes. Dissolved copper concentrations in water samples were determined using a SpectraAA 10 Plus atomic absorption spectrometer (AAS) (Varian Inc., Palo Alto, CA) with air/acetylene flame, a wavelength of 324.8 nM and a 0.5 nm slit width. Calibrations were made using acidified copper standards and were checked regularly during each session.

After 7 d exposure in the bioassay containers, filtration, acidification, and storage for a further 7 d, the dissolved copper concentration in unfiltered samples had declined by only 1.13% (from 2 mg L^{-1} to 1.977 ± 0.002 (SE) mg L^{-1}) whilst in the filtered samples the decline was 1.65% (from 2 mg L^{-1} to 1.967 ± 0.004 (SE) mg L^{-1}), indicating that our exposure, filtration and storage protocols had minimal effect on the recovery of dissolved copper.

2.2. Characteristics of soils, water, and the water from soil/water bioassay systems

Three soil types were chosen for use in the laboratory experiments, selected on the basis of their anticipated variability in physical and chemical characteristics. The Yanco soil, a Birganbigil clay-loam (van Dijk, 1961) classified as brown chromosol (Isbell, 1996) used in the laboratory studies was taken from the site used for the two field trials prior to those trials being initiated. Soil collection details are provided in Table 1, along with data on soil physical and chemical properties. All soil analyses were undertaken by accredited laboratories at the NSW Office of Environment and Heritage (OEH). Electrical conductivity, pH ($CaCl_2$) and total organic carbon were assessed using the methods of Rayment and Lyons