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Evaluation of copper toxicity using site specific algae and water chemistry: Field validation of laboratory bioassays

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ABSTRACT

Studies of metal toxicity to microalgae have predominantly been conducted using single non-target algae species and without due regard for the chemistry of the treated waters, leading to ineffective or excessive algaecide treatments. In this study, indigenous multi-algal species (*Scenedesmus quadricauda*, *and Scenedesmus subspicatus* and *Oscillatoria agardhii*) were used in laboratory toxicity bioassays under simulated field water chemistry (pH = 7.2, hardness = 196 mg L^{-1} as $CaCO_3$, and alkalinity = 222 mg L^{-1} as $CaCO_3$) to determine the optimum copper sulfate treatment dose to control algae growth in an irrigation canal. Toxicity bioassays were conducted using copper sulfate in chelated (with EDTA) and non-chelated (without EDTA) forms to assess the influence of the use of synthetic chelators in toxicity studies. Also, copper toxicity to the indigenous algae species was measured in the non-modified EPA test medium (pH = 7.5, hardness = 92 mg L^{-1} as $CaCO_3$, alkalinity = 10 mg L^{-1} as $CaCO_3$ and EDTA = 300 μg L^{-1}) to assess the impact of the water chemistry on algae inhibitory algal dosages. Under simulated water chemistry conditions, lower toxicity was measured in the test flasks with the chelated form of copper (96 h- EC_{50} = 386.67 μg L^{-1} as Cu) as compared to those with the non-chelated metal (96 h-EC_{50} = 217.17 μg L^{-1} as Cu). In addition, higher copper toxicity was measured in the test flasks prepared with the non-modified EPA medium using chelated copper (96 h-EC_{50} = 65.93 μg L^{-1} as Cu) as compared to their analogous microcosms with modified water chemistry (96 h-EC_{50} = 386.67 μg L^{-1} as Cu), the increased water hardness and alkalinity in the latter case contributing to the decrease of the metal bioavailability. Results from laboratory experiments showed good correlation with copper dosages used in a small scale field testing to control algae growth, increasing confidence in laboratory bioassays.

1. Introduction

Studies on the toxicity of copper based algaecides to microalgae have mostly used commercial species laboratory bioassays in prepared test media to determine the effective metal inhibitory dose to cultured organisms (Araújo et al., 2010; Contreras et al., 2010; Hochmuth et al., 2014). Fast growing species, easily cultured and enumerated in the laboratory have been the organisms of choice in algal inhibition tests and are usually obtained from commercial sources. These bioassays, though sensitive and highly reproducible, lack the environmental realism in using indigenous algae species of the affected water body which may have different sensitivity to the algaecide than the test organism. Also, they do not reproduce the algal-algal interactions occurring in natural ecosystems and which often affect the toxicity of the used algaecide. Single-species bioassays may over- or underestimate copper toxicity in natural waters. Franklin et al. (2004) demonstrated that the toxicity of copper to *Trachelomonas* sp. was greater in the presence of other species, with copper concentrations required to inhibit growth rate by 50% decreasing from 9.8 to 2.8 μg Cu L^{-1} in single and multi-species freshwater bioassays, respectively. In contrast, the authors reported a reduction in copper toxicity to the diatom *P. tricornutum* in marine multispecies bioassays, with an increase in the 72-h EC_{50} value from 13 μg Cu L^{-1} in single-species bioassays to 24 μg Cu L^{-1}. In their experiments on the assessment of copper toxicity to the algal species *M. Aeruginousa* in the presence and absence of *C. pyrenoidosa* and *S. obliquus*, Yu et al. (2007) found that the 24-h EC_{50} value of *M. aeruginousa* in the multispecies populations was significantly higher than those in the single species populations. Compared with *S. obliquus*, the effect of *C. pyrenoidosa* on *M. aeruginousa* was found to be more noticeable. In addition, toxicity bioassays are mostly conducted without due regard for the chemistry of the treated waters, a major factor affecting the availability of copper to biota and, consequently, the required dose of

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the used algaecide for controlling algal blooms.

Algae susceptibility to copper varies widely between species. Blue-green algae are the most sensitive to the effect of copper, whereas in other algae groups copper toxicity is reduced through a decrease in the bioavailability of the metal caused by algal excretion of metal-binding compounds or the production of intercellular metal-binding peptides (Huff and Angel, 1989; Cooke et al., 1993; Hullebusch et al., 2002; Bossuyt and Janssen, 2004; Wang et al., 2017). Hence, laboratory toxicity testing using commercial algae species, reflect the susceptibility of the monitored species to direct chemical effects and exclude potential effects of the algaecide on indigenous coexisting algal organisms in the affected water body (Franklin et al., 2004; De Laender et al., 2009).

In addition, the chemistry of the treated water plays a major role in defining copper speciation in natural ecosystems and consequently its algaecidal effect. Copper is less toxic in waters with high pH, hardness, and alkalinity due to its precipitation into insoluble forms and to competition with calcium and magnesium for binding sites on the algal cells membrane (Button and Hostetter, 1977; Cook et al., 1997; Hullebusch et al., 2002). Also, adsorption of copper on colloid and particulate components within the treated water body, and its complexation by natural dissolved organic carbon (DOC) reduces in general its availability for biological uptake (Cook et al., 1997; Hullebusch et al., 2002). Synthetic chelators such as ethylenediaminetetraacetic acid (EDTA) and citrate commonly used in toxicity bioassays to prevent the precipitation of ions in the test media, could thus underestimate copper toxicity in field waters.

The determination of correct copper dosages for a given lake or water supply reservoir is a key factor in ensuring success in controlling undesirable algae growth. In this study, it is our purpose to define optimum copper dosages for the treatment of an irrigation canal suffering from excessive algae proliferation with consequent negative impact on the irrigation scheme, mainly the obstruction of drip irrigation systems and sprinkler nozzles. For this aim, algal toxicity bioassays using indigenous algal species representative of the natural algal community and accounting for the site specific water characteristics were conducted in laboratory microcosms. Copper sulfate in chelated and non-chelated forms was used to account for the effect of synthetic chelators in toxicity bioassays. In addition, toxicity bioassays were conducted in the standard non-modified EPA test medium to account for the effect of water chemistry, namely pH, hardness and alkalinity, on the copper speciation and toxicity. The results from laboratory experiments were compared to copper dosages used in small scale field testing to assess the accuracy of laboratory predictions of responses of algae in site waters.

2. Materials and methods

2.1. Water sampling and testing

Water samples were collected from Canal 900, an open concrete-lined irrigation channel that extends over 18.5 km of the south central portion of Lebanon's Bekaa Valley. The Canal extracts water from Lake Qaraoun in the Litani River Basin and serves the surrounding agricultural lands through distribution reservoirs and irrigation networks (Litani River Authority, 2018). The Canal is subject to algae proliferation during the summer causing water flow retardation, clogging of irrigation drippers, and foul odors. As a result, the Canal is operating at around 30% of its capacity, serving 1900 ha out of the originally planned 7000 ha of irrigated land (BAMAS, 2005). Algae proliferation in the Canal is essentially due to agricultural runoff and domestic wastewater discharge in the upper Litani Basin leading to water quality degradation in the River and the built up of nutrients in the Qaraoun Lake (LRBMS, 2011). The high temperature, long daylight duration, low flow rate and closed end of the Canal are further contributing to algae growth. A total of eight water samples were collected along the water stretch in 1 L polyethylene bottles and transported to the laboratory in a portable cooler (4 °C) for subsequent analysis and algae identification. Fig. 1 shows the study area along with the field sampling and testing sites, and exact coordinates are provided in Supplementary information, SI (Table S1). Aliquots of 50 mL of the collected samples were acidified using nitric acid (HNO_3) to pH < 2 and stored at 4 °C for subsequent copper analysis. Samples were analyzed, and exhibited, pH 7.14 (sd = 0.097), alkalinity 221 mg L^{-1} as $CaCO_3$ (sd = 13.82), hardness 198 mg L^{-1} as $CaCO_3$ (sd = 8.91), total phosphorous 85 µg L^{-1} (sd = 18), total nitrogen 3.94 mg L^{-1} (sd = 0.43), DOC < 0.5 mg L^{-1}, and background copper concentration 4.65 µg Cu L^{-1} (sd = 3.65). The measurements were respectively performed according to the following standard methods: SM 4500-H^+ B, SM 2320B, SM 2340C,

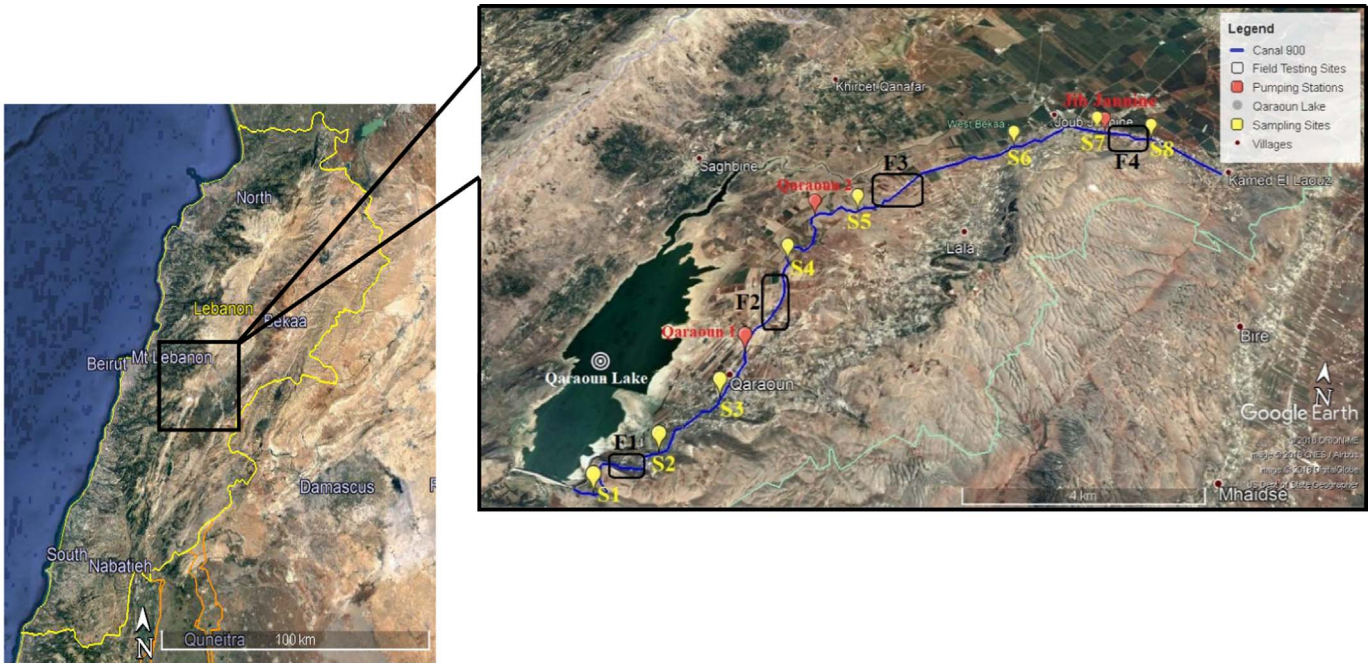

Fig. 1. Study area including field sampling and testing sites along Canal 900.