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Ecotoxicology of bromoacetic acid on estuarine phytoplankton

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ABSTRACT

Bromoacetic acid is formed when effluent containing chlorine residuals react with humics in natural waters containing bromide. The objective of this research was to quantify the effects of bromoacetic acid on estuarine phytoplankton as a proxy for ecosystem productivity. Bioassays were used to measure the EC_{50} for growth in cultured species and natural marine communities. Growth inhibition was estimated by changes in chlorophyll *a* concentrations measured by fluorometry and HPLC. The EC_{50}s for cultured *Thalassiosira pseudonana* were 194 mg L^{-1}, 240 mg L^{-1} for *Dunaliella tertiolecta* and 209 mg L^{-1} for *Rhodomonas salina*. Natural phytoplankton communities were more sensitive to contamination with an EC_{50} of 80 mg L^{-1}. Discriminant analysis suggested that bromoacetic acid additions cause an alteration of phytoplankton community structure with implications for higher trophic levels. A two-fold EC_{50} decrease in mixed natural phytoplankton populations affirms the importance of field confirmation for establishing water quality criteria.

1. Introduction

When a disinfectant such as sodium hypochlorite (NaClO) is added to wastewater, it hydrolyses to form hypochlorous acid (HClO). Hypochlorous acid is a weak acid and will undergo partial dissociation between pH 6.5 and 8.5 (Albert and Serjeant, 1984). Aqueous bromine and aqueous chlorine species compete to react with the humic matter. Aqueous chlorine will oxidize bromide to form hypobromous acid (HBrO), which will also undergo a partial dissociation (Abarnou and Miossec, 1992; Allonier et al., 1999; Agus et al., 2009). Hypochlorous acid and hypobromous acid can then react with organic compounds in aqueous solution to produce non-volatile halogenated aliphatic acids including haloacetic acids (HAAs) which may then be discharged into marine waters (Masters and Ela, 2008; Plewa et al., 2010; Ding et al., 2013). Current literature-reported environmental concentrations of bromoacetic acid in surface waters are predominately <0.1 μg L^{-1} (LeBel et al., 1997; Hashimoto et al., 1998; Williams et al., 1997; Dojlido et al., 1999; Scott et al., 2000, 2002).

HAAs readily partition in water because of high Henry's Law constants ($1.08 * 10^5$ to $2.26 * 10^5$), low pK_as (~1.39) and high water solubility, and rarely volatize back into the atmosphere because complete ionization occurs (Dean and Lange, 1992; Bowden et al., 1998; Hanson and Solomon, 2004; Taylor, 2006). Aquatic environments are particularly vulnerable to HAA contamination because HAAs are unlikely to adsorb onto suspended solids or sediments, but instead will remain dissolved in the water column for exposure to aquatic plants and phytoplankton (Hanson and Solomon, 2004). Free residual chlorine in seawater oxidizes bromide into bromine, making the bromine species of HAAs likely compounds in coastal cities and estuarine ecosystems where salt-water intrusion into the surface waters may cause high bromide levels (Abarnou and Miossec, 1992; Agus et al., 2009; Richardson and Ternes, 2011). Brominated disinfection by-products are typically less volatile and more toxic than their chlorinated analogs (Yang and Zhang, 2013; Liu and Zhang, 2014). Bromoacetic acid (BAA) is of particular interest because mono-HAAs have been shown to be more cytotoxic than their di- and tri-analogs (Giller et al., 1997; Plewa et al., 2010).

Phytoplankton can be used as a proxy for estuarine health and productivity to understand the lethal effects and cytotoxicity of BAA. Algae are a particularly good early indicator of pollutant toxicity in an ecosystem because of their high capacity for chemical uptake (due to a high surface area to volume ratio), widespread prevalence, and high turnover rate (DeLorenzo, 2009). Phytoplankton are also a key functional group in estuaries and changes in community abundance or composition may affect ecosystem structure and function (Bougis, 1976; Sournia, 1978; Nyholm and Källqvist, 1989).

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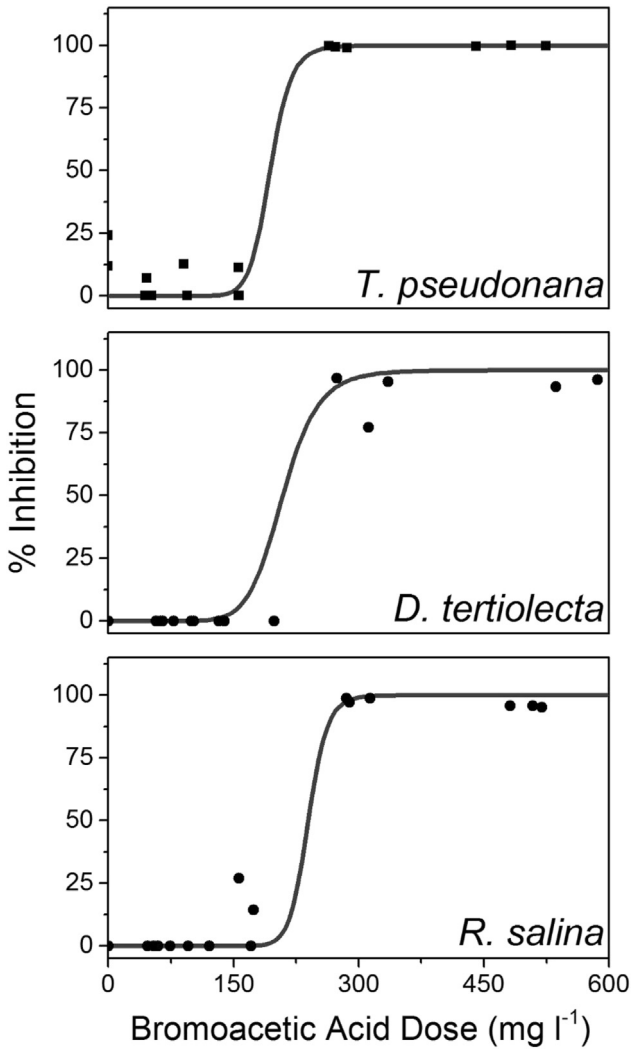

Fig. 1. Concentration-response curves of cultured phytoplankton to bromoacetic acid, shown by growth measured as fluorometric extracted chlorophyll *a* inhibition in treated incubations relative to controls. Circles indicate experimental data points used to interpolate curves.

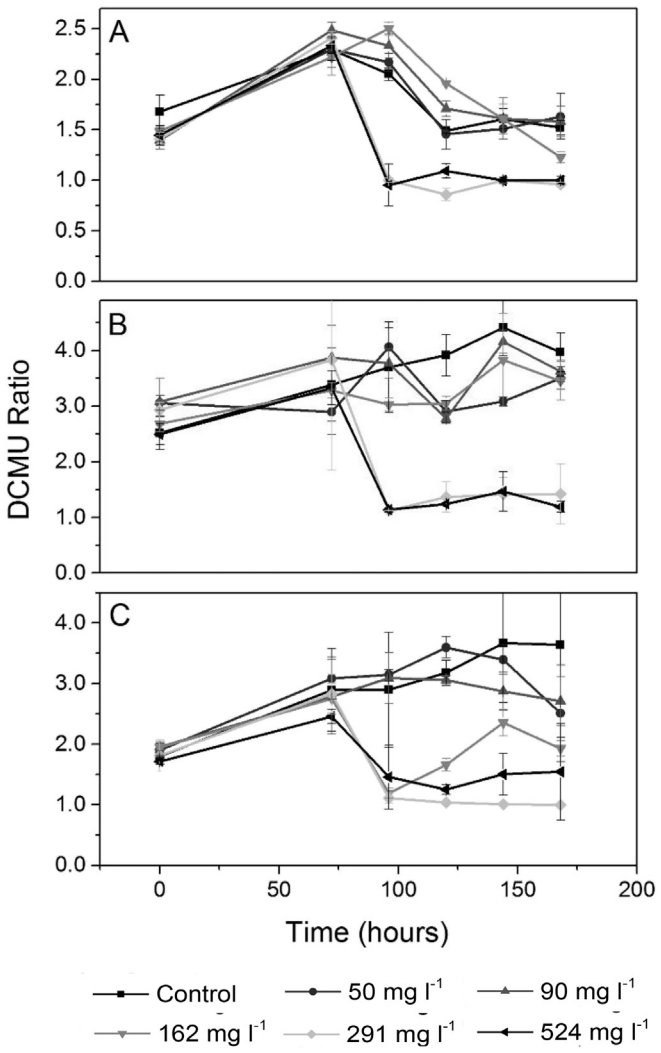

Fig. 2. DCMU ratios of cultured phytoplankton exposed to bromoacetic acid. Experimental treatments were applied at 72 h to ensure that the phytoplankton were in exponential growth. Error bars are standard deviations of treatment replications. A: *Thalassiosira pseudonana*; B: *Dunaliella tertiolecta*; C: *Rhodomonas salina*.

The objective of this research was to characterize the ecotoxicology of BAA in the coastal zone, using marine phytoplankton as an indicator of estuarine health. Phytoplankton have been shown to be particularly sensitive to HAA contamination (Hanson and Solomon, 2004; Agus et al., 2009). To investigate this relationship, both cultured single-algal species and natural communities were exposed to varying concentrations of BAA. Single-species toxicity tests are often conservative estimates of true community response because environmental stressors, inter-species competition, and nutrient availability may make natural phytoplankton communities more sensitive to toxicant exposure (Cairns, 1992; De Laender et al., 2009).

2. Materials and methods

2.1. Lab experiments

Due to the difficultly in predicting the variability of toxicity thresholds between species, multiple phytoplankton groups were represented in the experimental design. Unialgal cultures of the diatom *Thalassiosira pseudonana* (NCMA 1335), the chlorophyte *Dunaliella tertiolecta* (NCMA 1320) and the cryptophyte *Rhodomonas salina* (NCMA 1319) were obtained from the Provasoli–Guillard National Center for Marine Algae and Microbiota and used for static case-control toxicity assessments. These phytoplankton were

Table 1
Concentration–response equations for cultured phytoplankton growth inhibition in response to bromoacetic acid (BAA) exposure measured as the change in concentration of extracted chlorophyll *a* in treated incubations relative to controls.

Phytoplankton species	Concentration–response curve equation	R^2	EC_{50}
Thalassiosira pseudonana	$\%Inhibition = 0 + (100\text{-}0)/(1 + (193.769/[BAA])^{15.310}$	0.990	194 mg L^{-1}
Dunaliella tertiolecta	$\%Inhibition = 0 + (100\text{-}0)/(1 + (209.011/[BAA])^{21.078}$	0.979	209 mg L^{-1}
Rhodomonas salina	$\%Inihibition = 0 + (100\text{-}0)/(1 + (239.569/[BAA])^{9.799}$	0.978	240 mg L^{-1}