

# Effects of metal pollution and macronutrient enrichment on the photoproduction of hydroxyl radicals in seawater by the alga *Dunaliella salina*

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## Abstract

The marine microalga *Dunaliella salina* was used as a model organism in this study. Hydroxyl radicals ( $\cdot\text{OH}$ ) were determined using HPLC with sodium benzoate as a probe, and the photochemical activity of marine alga in the formation of  $\cdot\text{OH}$  was confirmed for the first time. Coastal organisms are often exposed to both metal pollution and macronutrient enrichment, and so the effects of algal concentration, exposure time, macronutrient (nitrate and phosphate) additions and metal pollution (5.0  $\mu\text{g/L}$  Pb(II) and 0.1  $\mu\text{g/L}$  methylmercury) on the photoproduction of  $\cdot\text{OH}$  were examined. Photoproduction was increased with increasing algal concentration and with exposure time. It could be increased greatly, with or without the presence of *D. salina*, by the addition of Pb(II), or Pb(II) and methylmercury, but was decreased by the addition of methylmercury only. Photoproduction of  $\cdot\text{OH}$  was positively correlated with the amount of basic functional groups on the cell's surface and also with the chlorophyll a content per cell. The influence of macronutrient additions on the photoproduction of  $\cdot\text{OH}$  resulted from the photolysis of nitrate and their effects on the photochemical activity of *D. salina*.

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## 1. Introduction

There is growing interest in the photochemical production of the highly reactive  $\cdot\text{OH}$  radical in terms of: (a) the degradation of natural organic nutrients and organic pollutants; and (b) the biogeochemistry of trace metals,

that is, the species and their bioavailability, together with species transport and the transformation of trace metals. Both the Joint Global Ocean Flux Study (JGOFS) and the Land–Ocean Interactions in the Coastal Zone Project (LOICZ), the core projects of the International Geosphere–Biosphere Program (IGBP), are focused on the biogeochemical processes involved in the cycles and fluxes of macronutrients, and on the distribution, transport, transformation, and cycling, and also the end-result, production and consumption of trace metals. The  $\cdot\text{OH}$  radical has become a good tool to: (a) elucidate the fate of

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inorganic and organic chemical species in oceanic surface waters; (b) provide an understanding of the role that the limiting of micronutrients might play in regulating ecosystem structure and oceanic production; and (c) elucidate the mechanisms controlling the fate of contaminants added to the ocean by human activities.

Numerous studies over the last 20 years have provided unequivocal evidence that the  $\cdot\text{OH}$  radical is generated in natural waters by the photolysis of dissolved organic matter (DOM), nitrite and nitrate; and by the ligand-to-metal charge-transfer reactions or photo-Fenton chemical reactions of metal ions at sufficiently high concentration (Vaughan and Blough, 1998; Qian et al., 2001; Grannas et al., 2006). However, Mopper and Zhou (Zhou and Mopper, 1990) report that the total  $\cdot\text{OH}$  production rate in seawater is significantly larger than that expected from the sum of these processes. They conclude that there is a “missing source” of  $\cdot\text{OH}$  radical production. This source, we thought for four reasons, was most likely to be due to photochemical behavior driven by marine algae: (a) in our previous study, the photo-oxidation of Sb(III) (Li et al., 2006a,b) was observed in seawater and could be accelerated by marine algae; (b) the effects of some freshwater green and blue algae on the formation and decay of  $\cdot\text{OH}$  radicals have been detected (Zepp and Schlotzhauer, 1983; Liu et al., 2004); (c) the source of DOM is believed to be marine organisms, such as algae and bacteria (Hirose, 2006); and (d) algal cells (dead or alive) can easily be light-induced to produce hydrogen peroxide (Petasne and Zika, 1997; Mopper and Zhou, 1990), a source of  $\cdot\text{OH}$  radicals. Such an explanation has not been mentioned previously. *Dunaliella salina* is a unicellular green marine microalga that lacks a rigid cell wall, and can be used as a model marine organism (Su et al., 2003), and so we chose it for our investigations.

Metal (such as mercury and Pb(II)), pollution, especially in harbors, enclosed bays, and typhoon shelters, has been relatively well documented in many coastal marine waters (Centineo et al., 2004; Bravo-Sánchez et al., 2001; Liu et al., 1999). The input of metals into the coastal environments is often accompanied by other environmental pollutants such as macronutrients. There is a great deal of evidence suggesting a global increase in nutrient levels of coastal waters through riverine and sewage inputs (Smith et al., 1999; Rydberg et al., 1996). Coastal eutrophication has become worldwide, and consequently, coastal organisms are frequently exposed to both metal pollution and macronutrient enrichment (Kucuksezgin et al., 2006). The growth, biomass, mean diameter, and the biochemical composition of marine

algae is affected by these two types of coastal contamination (Skei et al., 2000; Li et al., 2005).

We performed experiments to address the following questions for the first time: (a) is the photochemical production of  $\cdot\text{OH}$  radicals influenced by the presence of marine algae (*D. salina*)?; (b) is the concentration of  $\cdot\text{OH}$  radicals in seawater affected by coastal contamination, including metal (methylmercury and Pb(II)) pollution and macronutrient (nitrate and phosphate) enrichment?; and (c) does the coexistence of marine algal and coastal contamination have a combined effect on the photoproduction of  $\cdot\text{OH}$  radicals in coastal waters? Answers to none of these questions have been reported previously.

The  $\cdot\text{OH}$  radical in seawater can be determined using HPLC with sodium benzoate as a probe (Qian et al., 2001), and we used this method to investigate both the photoproduction of  $\cdot\text{OH}$  radicals in coastal waters using the marine alga *D. salina*, and also the influence of metal pollution and macronutrient enrichment on the photoproduction of  $\cdot\text{OH}$ .

## 2. Materials and methods

### 2.1. Chemicals and reagents

All reagent and buffer solutions were prepared in low carbon deionized water obtained from a Nanopure system with a UV organic oxidation attachment (Barnstead, Pittsburgh, PA). The carbon content of this water was less than  $2 \mu\text{mol L}^{-1}\text{-C}$ . Sodium benzoate (Sigma Chemical Co.) was recrystallized three times from low carbon deionized water. Methanol (HPLC grade, Aldrich Chemical Co.) was distilled in glass. All other chemicals were of analysis grade (Shanghai Experiment Reagent Co., China).

### 2.2. Marine alga culture

Axenic culture of a coastal green alga *D. salina* was obtained from the State Key Laboratory for Marine Environmental Science, Xiamen University. It was maintained in seawater (with *f*/10 levels of Si and vitamins added, but without trace metals) at different N (added as  $\text{NaNO}_3$ ) and P (added as  $\text{Na}_2\text{HPO}_4$ ) concentrations at  $19^\circ\text{C}$ , under a light illumination of  $140 \mu\text{mol photons m}^{-2} \text{S}^{-1}$  with a 14/10 h light/dark cycle. Exponentially growing cells were used for the experiments.

The seawater used in all experiments was collected 10 km offshore in Zhangzhou Bay, Fujian State, China. It was filtered with  $0.2 \mu\text{m}$  membrane filters, and then stored at  $4^\circ\text{C}$  for about 6 months before the experiments began. The background concentrations of Fe, Mn, and Cu in the seawater were measured using graphite furnace atomic absorption spectrometry (GFAAS) with a GBC 932AA spectrometer (GBC Co., Australia), and they were 6.26, 1.23, 0.55 nmol/L, respec-

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