THE PHOTODEGRADATION OF DOMOIC ACID AND THE EFFECTS OF METAL CHELATION

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ABSTRACT

Domoic acid added to 0.2 μm-filtered Wrightsville Beach, NC seawater (WBSW) to a final concentration of 100 nM rapidly photodegraded to 75% of its initial concentration under simulated sunlight after ten hours of irradiation. The average first order rate constant of domoic acid photodegradation at 24ºC was 0.14 ± 0.01 h^{-1}. When domoic acid was added to deionized water to a final concentration of 100 nM and irradiated in a fashion analogous to the WBSW experiments, there was no significant change in the rate constant (t-test, 95% confidence level) indicating components of the natural seawater matrix such as DOC, ionic strength, and pH do not affect the rate of domoic acid photodegradation.

Fe(III) and Cu(II) were added to a 100 nM domoic acid sample in WBSW to a final concentration of 100 nM and irradiated in a fashion analogous to the WBSW experiments without added metals. After irradiation, no significant change in the domoic acid photodegradation rate constant was observed (t-test, 95% confidence level) in the presence of the metals suggesting that complexation of domoic acid by Fe(III) and Cu(II) does not affect the rate of photodegradation of domoic acid.

Upon irradiation of domoic acid under simulated sunlight, a series of three photoproducts are formed which are believed to be geometrical isomers of domoic acid. The mechanism of photoisomerization of domoic acid most likely results from the cis-trans isomerization of the conjugated diene. Upon the absorption of a photon, a π electron is excited to the lowest unoccupied molecular orbital to form a diradical intermediate (triplet excited state) or a polar zwitterion intermediate (singlet excited state). Either way, the double bonds are essentially broken allowing the molecule to

twist. Upon the return of the electron to ground state, any of the three geometrical isomers of domoic acid can be formed.

The efficiency of domoic acid photodegradation rapidly decreases as the irradiance wavelength increases, particularly between 280 and 315 nm. There is a slight increase in the efficiency of degradation from 315 nm to 335 nm, but beyond 335 nm the efficiency of photodegradation drops off rapidly, most likely because the energy of the incoming radiation decreases with higher wavelengths.

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DEDICATION

I would like to dedicate this thesis to my family. Mom and Dad, you two have always believed in me, and you have always told me that I could achieve anything that I set out to do. I still don't know if that's entirely true, but without you guys I wouldn't be where I am today. Thank you for everything that you have done for me! And Adam, believe it or not, you are my inspiration! I have looked up to you since we were in grade school, and I still do to this day. I admire your energy and ambition, and I strive to make you proud of me. I just want to thank all of you for being there when I need you most. I love you guys!

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