TABLE OF CONTENTS

ABSTRACT iv

ACKNOWLEDGMENTS vi

LIST OF TABLES vii

LIST OF FIGURES viii

INTRODUCTION 1

EXPERIMENTAL 3

Sample Collection 3

Reagents and Standards 5

Hydrophobic DOM Extraction 5

Inorganic Ion Analysis 6

Dissolved Organic Carbon and Total Dissolved Nitrogen 7

Optical Analysis 9

EEM Precision Analysis 11

Nuclear Magnetic Resonance 11

Supporting Data 14

Photochemical Experiments 14

Quantum Efficiency Experiments 15

RESULTS AND DISCUSSION 19

Correlation Analysis 24

Seasonality 25

Impact of Storm Origin 25

Diurnal Variations 26

Photochemical Studies 26

C/N Ratios 36

Quantum Efficiency Studies 38

Nuclear Magnetic Resonance Studies 45

REFERENCES 56

APPENDIX 60

ABSTRACT

The quantity of chromophoric dissolved organic matter (CDOM) was measured in 125 rain events in Wilmington, NC between February 21, 2002 and August 11, 2003. All rain events had measurable CDOM, although there was much variability between events. The amount of fluorescent CDOM was affected by season and storm origin. There was significantly more fluorescent CDOM in winter and continental rain, relative to summer and coastal events. Diurnal variations were also seen where the amount of fluorescent CDOM decreased gradually from the morning through the afternoon and evening hours.

In addition to measuring the quantity, the photolabilty of rainwater CDOM was also studied and compared to the photodegradation of CDOM in natural waters. There was significant photodegradation of CDOM in all events studied after 12hour exposure to simulated sunlight. Approximately half the fluorescence was lost upon irradiation of rainwater CDOM, which was similar to the amount of fluorescence loss of the Cape Fear River (CFR) CDOM. Maximum loss of CDOM absorbance in rainwater was in the UV-A region, while maximum loss shifted to the lower end of the UV-B region for the CFR. Monochromatic and filtered sunlight experiments demonstrated that the degree of photobleaching of rainwater CDOM was directly related to the amount of UV-A and UV-B irradiation present.

The structural characteristics of the rainwater CDOM were also examined. The carbon to nitrogen ratio of extracted rainwater CDOM was 24, which is approximately half the CFR CDOM C/N ratio. The C/N ratio increased in rainwater while it decreased in CFR after irradiation, suggesting different mechanisms of photodegradation. The extracted fluorescent CDOM was also examined via ^{1}H NMR. The fluorescent CDOM

had primarily aliphatic character, while the CFR CDOM had relatively more aromatic character. Upon photolysis, rain CDOM lost primarily aliphatic moieties. In summary, rainwater contains significant amounts of photodegradable chromophoric dissolved organic matter. This has important ramifications with respect to the wavelength dependent spectral attenuation of solar radiation in atmospheric waters.

ACKNOWLEDGMENTS

I would like to thank my research committee Dr. Robert Kieber, Dr. Joan Willey, Dr. Pam Seaton, and Dr. Rob Whitehead for their patience, support and guidance. Special thanks go to Sue Zvalaren, Rance Hardison, and Jason Smith for their friendship and always being there in the early mornings to help with rain collection when I needed them for a ride. I appreciate the opportunity to work with a wide variety of members of MACRL and the UNCW staff. To my wife Molly, I could not have completed this project without her unconditional love, support, patience, and understanding.

LIST OF TABLES

Table Page

1. 3D Fluoromax precision test with two different rain samples. Relative standard deviations were calculated for each integrated region. Samples were irradiated for 7 hours under a solar simulator. The irradiated samples were tested again after 13 hours in a controlled dark area. The initial samples were kept in a controlled dark area for 24 hours and then retested, SS = solar simulator, dark = controlled dark storage.....12

2. Volume weighted averages from surface volume values from polydata5 fluorescent integrations under each observed peak maxima. The maxima A, M, C, T, and entire scan (scatter reducing) were measured for all rain events collected at Wilmington, NC between February 21, 2002 and August 11, 2003. Average year data represent rain events between February 21, 2002 and February 28, 2003. The A, C, M, T, and entire scan peaks are all relative to the polygon integration program designed by Coble (1996), n = number of samples and amt = rain amount in mm.....21

3. Simple average spectral slopes with standard deviations and absorbance coefficients with standard deviations for all rain events and for events broken down by season and storm type. 23

4. Percentage of fluorescence loss after 12 hours irradiation. CFR = Cape Fear River. 30

5. Percentages of absorbance coefficients and spectral slopes lost after 12 hours of irradiation. CFR = Cape Fear River.....33

6. Rain event data for photochemical experiments. N/A = not applicable, cont. = continental.....34

7. Carbon/Nitrogen ratios from before/after C_{18} solid phase extraction cartridge experiments. CFR = Cape Fear River. 37

8. Quantum efficiency absorbance lost for E417 after single wavelength irradiation. Examples of λ maximum Abs. loss shown in Figure 11.....47

9. Integrated regions (ppm) from before and after irradiation experiments of rain events and a surface water sample. CFR = Cape Fear River.....57

10. Rain data analytes for the events studied in detail. N/A = not applicable, CFR = Cape Fear River, NSS = Non Seasalt Sulfate 59

LIST OF FIGURES

Figure Page

1. Intensity of the solar spectrum at summer solstice, calculated solar spectrum at solar solstice, and the solar simulator spectrum over wavelengths 280-800nm 16

2. Typical EEMs spectra of rainwater. The A, M, C, and T labels are based upon the work of Coble (1996): where A and C indicate terrestrial humic-like substances, M is marine humic-like material and T indicates the presence of protein-like substances....20

3. a and b. Typical graphs of winter/summer and coastal/continental rainwater plotted by absorbance coefficient (Abs. Coeff.) and wavelength 22

4. Average surface volumes from EEMs entire scan regions plotted by time of day, n varies from 30 to 35 in each time period 27

5. a, b, c, and d. Typical rain event and CFR EEMs before/after 12 hour irradiation under the solar simulator. CFR = Cape Fear River 29

6. a and b. Typical absorption spectra and difference in absorption spectra before and after irradiation of rain event E413, plotted by absorbance coefficient (Abs. Coeff.) and wavelength 31

7. a and b. Absorption spectra and difference in absorption spectra before and after irradiation of Cape Fear River water, plotted by absorbance coefficient (Abs. Coeff.) and wavelength. Note differences in scales compared to Figure 5 35

8. a and b. Percentages of initial fluorescence remaining after 12 hour irradiation using various cut-off filters 39

   c and d. Percentages of initial fluorescence remaining after 12 hour and 36 hour irradiation using various cut-off filters....40

9. a and b. Quantum efficiency results for A and C peaks....42

   c and d. Quantum efficiency results for entire scan and M peaks 43

10. a and b. Quantum efficiency results for the single wavelength experiments. The A, C, M, and entire scan peak regions were plotted at 265.2, 300, 313, 365, 404.5, and 435nm....44

11. a, b, and c. Difference in absorption spectra before and after monochromatic irradiation at 265.2, 300, and 313nm 46

12. a, b, and c. ^{1}H NMR presaturation spectra of the internal standard, blank extraction and extraction of CDOM from rain event E414 48

13. a, b, and c. ^{1}H NMR presaturation spectra of extractions from two different rain events and a Cape Fear River sample before irradiation 50

14. a, b, and c. Before and after irradiation ^{1}H-NMR integrated regions for two rain events and a natural water sample. CFR = Cape Fear River 51

15. a, b, and c. ^{1}H NMR presaturation spectra of rain event E451 before/after 12 hour irradiation and the difference between the two....53

16. a, b, and c. ^{1}H NMR presaturation spectra of a Cape Fear River water sample before/after 12 hour irradiation and the difference between the two 54

17. a, b, and c. Correlation figures with rain events highlighted that were studied in detail. E411=lime green, E413=red, E414=light blue, E417=orange, and E451=pink 58

18. a, b, and c. ^{1}H NMR presaturation spectra of rain event E413 before/after 12 hour irradiation and the difference between the two 60

19. a, b, and c. EEMs and absorption spectra before and after irradiation of rain event E413 61

20. a, b, and c. ^{1}H NMR presaturation spectra of rain event E414 before/after 12 hour irradiation and the difference between the two 62

21. a, b, and c. EEMs and absorption spectra before and after irradiation of rain event E414 63

22. a and b. EEM and absorption spectra before irradiation of rain event E417 64

23. a, b, and c. EEMs and absorption spectra before and after irradiation of rain event E411 65

24. a and b. ^{1}H NMR presaturation spectra of rain event E417 and E411....66

25. a, b, and c. EEMs and absorption spectra before and after irradiation of rain event E451 67

26. a, b, and c. EEMs and absorption spectra before and after irradiation of Cape Fear River water 68