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DISSOLVED ORGANIC CARBON FLUXES FROM A NEW ENGLAND SALT MARSH

A Dissertation Presented

by

Hayley Nicole Schiebel

Submitted to the Office of Graduate Studies,
University of Massachusetts Boston,
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2016

School for the Environment

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DISSOLVED ORGANIC CARBON FLUXES FROM A
NEW ENGLAND SALT MARSH

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by
Hayley Nicole Schiebel

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ABSTRACT

DISSOLVED ORGANIC CARBON FLUXES FROM A
NEW ENGLAND SALT MARSH

May 2016

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Blue carbon systems (mangroves, salt marshes, and seagrass beds) sequester large amounts of carbon via primary productivity and sedimentation. Sequestered carbon can be respired back to the atmosphere, buried for long time periods, or exported ("outwelled") to adjacent ecosystems. This study estimates the total outwelling of dissolved organic carbon (DOC) from the Neponset Salt Marsh (Boston, Massachusetts) as well as the major plant and sediment processes contributing to the overall flux. The total export was quantified via high-resolution *in situ* chromophoric dissolved organic matter (CDOM) measurements as a proxy for DOC using 12 years of transect data. Seasonal trends, alternate sources of fresh water, and long-term trends in DOC export will be discussed. To characterize the percentage of this flux attributable to marsh vegetation, the effects of sunlight, anoxia, plant species, biomass type, and microbes on plant leaching were studied using incubations of above- and belowground biomass over four seasons. Seasonal comparisons led to

the “Fall Dump” hypothesis in which higher DOC concentrations are leached during the fall when marsh plants senesce for winter. In summing seasonal fluxes from vegetation, approximately 46% of the total DOC export from the marsh may be attributed to leaching from the three dominant plant species in the Neponset Salt Marsh. The influence of seasonality and climate change (e.g., drought) on both overland flow and deep sediment pore water leaching were also investigated. Depending on season and marsh condition, overland flow and sediment pore water leaching combined could contribute 8-16% of the total export from the marsh. Finally, the influence of natural sunlight irradiation and microbes on the release of dissolved organic matter (DOM) from resuspended surface sediments was studied and approximately 11-22% of the total export could be attributable to this flux. Approximately 49 mol C m^{-2} yr^{-1} are outwelled from the Neponset Salt Marsh and, using net primary productivity estimates from the literature, 16 ± 12 mol C m^{-2} yr^{-1} are buried in the Neponset Salt Marsh.

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DEDICATION

To the strongest and smartest women I know,
Mom, Amy, Annie Pannie, and Nina

TABLE OF CONTENTS

CHAPTER Page

ABSTRACT iv

ACKNOWLEDGEMENTS vi

DEDICATION viii

LIST OF FIGURES xiii

LIST OF TABLES xvii

CHAPTER 1: INTRODUCTION 1

Carbon Cycle and Blue Carbon 1

Carbon Burial and Outwelling 5

Dissolved Organic Carbon 8

Chromophoric Dissolved Organic Matter 9

Neponset Salt Marsh 12

Chapter Summaries 14

CHAPTER 2: ESTIMATING TOTAL DISSOLVED ORGANIC CARBON EXPORT FROM A NEW ENGLAND SALT MARSH 17

Abstract 17

Introduction 20

Methods 23

Study site 23

Transects 25

Buoy data 31

Watershed sampling 33

Sample analysis 34

Results and Discussion 35

Outwelling fluxes 35

Alternate freshwater inputs 44

Long-term trends 45

Conclusions 48

CHAPTER Page

CHAPTER 3: DISSOLVED ORGANIC MATTER EXPORT FROM NEPONSET SALT MARSH GRASSES 49

Abstract 49
Introduction 52
Methods 54
Study site 54
Sunlight irradiation incubations 55
Anoxia incubation 56
Sample analysis 57
Results 59
Composition 62
Anoxia 64
Species 64
Sunlight 64
Biomass type 65
Microbial contribution 65
Seasonal leaching fluxes 66
Discussion 68
Anoxia 68
Species 69
Sunlight 70
Biomass type 71
Microbial contribution 72
Seasonal leaching fluxes 73
Conclusions 80

CHAPTER 4: NEPONSET SALT MARSH SEDIMENT SOURCES OF DISSOLVED ORGANIC MATTER 82

Abstract 82

CHAPTER Page

Introduction 84
Methods 88
Study site 88
Experiment 1: surface sediment/overland flow 88
Experiment 2: deep sediment pore water leaching 92
Sample analysis 95
Results and Discussion 96
Seasonality 96
Marsh health 98
Core location 101
CDOM/DOC relationship 107
Sediment DOC fluxes 109
Conclusions 114

CHAPTER 5: PHOTOCHEMICAL RELEASE OF DISSOLVED ORGANIC MATTER FROM RESUSPENDED SALT MARSH SEDIMENTS 116
Abstract 116
Introduction 119
Methods 121
Study site 121
Sunlight irradiation experiments 122
Chemical and fluorescence measurements 126
Results 128
Release of DOC and DN from Florida Salt Marsh sediments 128
Release of DOC and DN from Neponset Salt Marsh sediments 131
CDOM Optical measurements 133
Discussion 138
Release of DOC and DN due to sunlight irradiation 138
Microbial degradation of photo-released DOM 144
Characterization of photo-released CDOM 146

CHAPTER Page

Resuspended sediment contribution....151
Conclusions 152
CHAPTER 6: SUMMARY 154
Neponset Salt Marsh Outwelling Budget 154
Total export 155
Plant matter leaching fluxes 156
Surface sediment/overland flow and sediment leaching fluxes 156
Resuspended sediment leaching fluxes 157
Neponset Salt Marsh Carbon Burial 159
Future Work 161
Comprehensive Neponset Salt Marsh profile 161
Climate change impacts in the Neponset Salt Marsh 162
Comparative outwelling budget 163
Broader Impacts 163
Salt marsh significance 163
Salt marsh carbon burial 164
Conclusions 167
APPENDIX A 168
APPENDIX B 185
REFERENCES 201

LIST OF FIGURES

FIGURE Page

Figure 1.1. Simplified schematic of the global carbon cycle.. 2

Figure 1.2. Global distribution of blue carbon ecosystems (Murray et al., 2011).....3

Figure 1.3. Carbon burial rate by area for three terrestrial forests compared to blue carbon systems (McLeod et al., 2011).....4

Figure 1.4. CDOM/DOC relationship for an estuary (shown here for the Neponset River in Boston, Massachusetts). 11

Figure 1.5. Neponset Salt Marsh. 13

Figure 1.6. Conceptual model of processes contributing to DOC outwelling in the Neponset Salt Marsh.....14

Figure 2.1. Deviations from a conservative CDOM/salinity relationship in an estuary: (a) concave up indicates CDOM removal while (b) concave down indicates CDOM production (Sholkovitz et al., 1978; Peterson et al., 1994; Gardner et al., 2005). 23

Figure 2.2. Neponset River and Neponset Salt Marsh maps showing the location of Lower Mills Dam (freshwater endmember) and Neponset Salt Marsh……...24

Figure 2.3. (a) Conceptual diagram showing actual and apparent endmembers (*in situ* CDOM concentration). The solid line represents a non-conservative mixing line and the dashed line shows the tangent to the data at the mouth of the estuary, representing the CDOM exported from the mouth of the estuary. The difference between these two values represents the export derived *in situ*. (b) November 2012 cruise data with *in situ* CDOM sources accounting for approximately 35% of the total export. 27

Figure 2.4. Plot of *in situ* CDOM concentrations versus discrete DOC samples for a cruise completed on August 25, 2013. 31

Figure 2.5. (a) Buoy data from a location near the mid-marsh point in the Neponset Estuary. (b) 24-hour data from September 27, 2012 at the same location. 32

Figure 2.6. *In situ* CDOM concentration and water temperature from a buoy at the mouth of the Neponset River.....33

FIGURE Page

Figure 2.7. Neponset watershed sampling site endmembers (F-forest; R- residential; I-industrial; G-golf course; W-wetland; PP – pour point, which is a mixture of any other land use types). 34

Figure 2.8. Average Boston temperatures throughout the year with the seasons as delineated for this study (Blue Hills Observatory, 2015). 36

Figure 2.9. Median daily discharge rates by month from the Neponset River (USGS, 2002). 38

Figure 2.10. Linear regression of marsh export and temperature with outliers circled in red (2003) and blue (2009-2010) as well as regression with outliers removed (inset). 42

Figure 2.11. December 2013 cruise showing evidence of a small pulse contributing to the overall export near Gulliver Creek (shown in red/green). 44

Figure 2.12. September CDOM/salinity curves for 2001, 2009, 2010, 2012, and 2013 46

Figure 3.1. Treatments that yielded no significant difference in plant DOC leaching rates. 60

Figure 3.2. Treatments that yielded a significant difference in plant DOC leaching rates. 62

Figure 3.3. CDOM/DOC relationships for four seasonal sunlight irradiation incubations and the Neponset Estuary. 63

Figure 3.4. Concentration of DOC leached at the end of the incubation (per g dry weight original plant material) for *S. alterniflora* and *S. patens* AGB and BGB by season (standard error plotted at 95% confidence intervals). 66

Figure 4.1. Blue carbon systems sequester a large amount of carbon in sediment with a smaller sequestration potential in biomass (Murray et al., 2011). 84

Figure 4.2. Sensor locations with wells installed at 1, 6, and 10-m distances perpendicular from the Neponset River creek bank. 89

Figure 4.3. Sediment core extracted 10 m from the Neponset River creek bank during the July 2014 incubation. 90

FIGURE Page

Figure 4.4. Overland flow experimental setup. 91

Figure 4.5. Core locations for pore water incubation (not drawn to scale) with cores removed in duplicate at 60 cm (orange arrow), 120 cm (white arrow), and 180 cm (red arrow) from the top of the marsh flats. 93

Figure 4.6. Pore water leaching experimental setup.....94

Figure 4.7. July and October 2014 overland flow leaching concentrations. 97

Figure 4.8. July 2014 overland flow incubation data comparing healthy and drought marsh conditions for the 10-m core location (dominated by *S. patens*). 99

Figure 4.9. October 2014 overland flow incubation comparing leaching patterns between *S. alterniflora* and *S. patens*. 103

Figure 4.10. Pore water DOC leaching concentrations for cores taken at three different depths. 106

Figure 4.11. Cross section of typical New England marsh sediment where MHW^1 is mean high water level when marsh development began, MHW^2 is mean high water at present and MLW is mean low water at present (Niering and Warren, 1980). 107

Figure 4.12. CDOM/DOC relationship for each incubation (healthy and drought conditions where applicable) compared to the 2013 CDOM/DOC relationship for the Neponset Estuary. 108

Figure 5.1. Concentration changes of DOC (a, b) and DN (c, d) with time during the direct sunlight incubation experiments from the resuspended Florida salt marsh sediments in the (a, c) non-poisoned and (b, d) poisoned light and dark control bottles.. 129

Figure 5.2. Concentration changes of DOC (a, b) and DN (c, d) with time during the direct sunlight incubation experiments from the resuspended clay fraction of Neponset salt marsh sediments in the (a, c) non-poisoned and (b, d) poisoned light and dark control bottles. 132

FIGURE Page

Figure 5.3. Photo-released CDOM fluorescence (QSU) vs. DOC (μM) from the resuspended (a, b) Florida salt marsh sediments and (c, d) clay fraction of Neponset salt marsh sediments during the direct sunlight incubation in the non-poisoned and poisoned light and dark control bottles. 134

Figure 5.4. Changes of CDOM absorbance coefficient a_{337} (a, b) and absorbance slope ratio SR (c, d) with incubation time for the resuspended sediments in the light and dark control bottles. 135

Figure 5.5. EEMs for CDOM of seawater (as background) and in the sunlight irradiated seawater with resuspended Florida and Neponset salt marsh sediments (light-medium and light-high poisoned samples only). 137

Figure 5.6. Percent organic carbon and nitrogen photo-released from the sediment solid phases and respired at end of the sunlight irradiation incubation. 143

Figure 5.7. DOC (μM) vs. DN (μM) photo-released during the sunlight irradiation experiments compared with the water samples collected from Florida salt marsh (a) and Neponset salt marsh and estuary (b) The linear regression of the field samples generated an overall C/N ratio. 150

Figure 6.1. Contribution of major processes in the Neponset Salt Marsh to the overall DOC export 158

LIST OF TABLES

TABLE Page

Table 2.1. Dates and accompanying data for all cruises.. 25

Table 2.2. Seasonal outwelling fluxes from the Neponset Salt Marsh (mean ± SE) where [AEM] is the apparent endmember concentration, [FEM] is the freshwater endmember concentration, and discharge is the three-day average before each cruise extrapolated to a year.....37

Table 3.1. Leaching concentrations at the end of the sunlight irradiation incubations (normalized by biomass) per experiment (8 days) as evidence for Fall Dump hypothesis in the Neponset Salt Marsh by species for non-poisoned AGB and BGB samples exposed to sunlight (mean ± SE).....67

Table 3.2. Four growth phases over one year for *Spartina spp*. in New England based upon first and last frost days of the year in 2012 and vegetation observations. 74

Table 3.3. Biomass decay equations (where D = decay concentration and t = time) and leaching rates for both AGB and BGB using data for non-poisoned samples exposed to sunlight. 75

Table 3.4. Net primary productivity (NPP) estimates by species across all seasons, percent carbon by species, and root:shoot ratios (R:S) by species.....77

Table 3.5. Leaching flux and percentage of total yearly outwelling by species across all seasons for non-poisoned samples exposed to sunlight. 78

Table 4.1. Inundation scheme for pore water leaching incubation.....94

Table 4.2. Data comparing fall and summer overland flow leaching for different marsh condition, tidal regimes, and vegetation patterns (mean ± SE). 96

Table 4.3. Data comparing drought and healthy overland flow leaching rates for different seasons, tidal regimes, and vegetation patterns (mean ± SE). 98

Table 4.4. Data comparing the effect of vegetation pattern/distance from the creek bank on overland flow leaching concentrations for different seasons, marsh conditions, and tidal regimes (mean ± SE).....102

Table 4.5. Overland flow incubation fluxes. 110

TABLE Page

Table 4.6. Data used for pore water leaching flux calculation. 112

Table 5.1. Chemical compositions and weight of salt marsh sediments added to the irradiation experiments regardless of poisoned/non-poisoned or light/dark conditions within each marsh. 122

Table 6.1. Neponset Salt Marsh burial estimates compared to New England burial rates from the literature 160

CHAPTER 1

INTRODUCTION

Carbon Cycle and Blue Carbon

Over the past two hundred years, human activities have significantly altered the global carbon cycle. Global carbon emissions have increased by approximately 90% since 1970 with a consensus among climate scientists that the anthropogenic use of fossil fuels, cement production, and land use change are the major causes of these increased emissions in the atmosphere (Figure 1.1; Caldeira and Wickett, 2003; Solomon et al., 2009; IPCC, 2014).

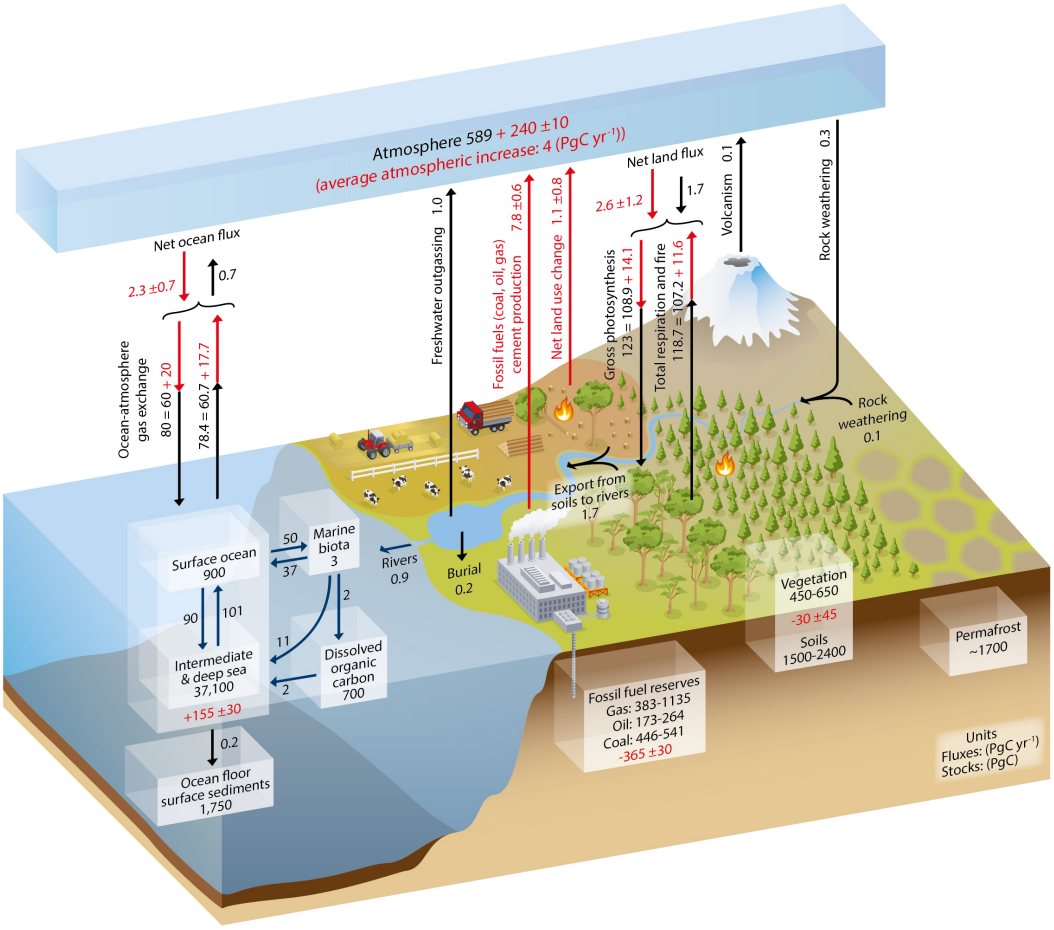


Figure 1.1. Simplified schematic of the global carbon cycle. Black numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the Industrial Era. Red numbers and arrows indicate annual anthropogenic fluxes averaged over the 2000–2009 time period and represent a perturbation of the carbon cycle post-1750 (IPCC, 2014).

Proposed engineered carbon sequestration techniques have focused on lowering atmospheric carbon dioxide (CO_2) concentrations as it is the most abundant greenhouse gas. However, natural ecosystems that remove excess CO_2 from the atmosphere also have a role in climate change mitigation. At the interface between aquatic and terrestrial environments, blue carbon systems (mangroves, salt marshes, and seagrass beds) sequester large amounts of carbon in via primary productivity and sedimentation, so these

systems are prime candidates for conservation (Figure 1.2; Chmura et al., 2003; McLeod et al., 2011; Duarte et al., 2014; Artigas et al., 2014).

Figure1.2. Global distribution of blue carbon ecosystems (Murray et al., 2011).

It is estimated that while blue carbon systems comprise less than 1% of the Earth's surface (Duarte, et al., 2005; Nellemann et al., 2009; Kulawardhana et al., 2014), they represent approximately 25% of the global soil carbon sink (Chmura et al., 2003). When compared to terrestrial ecosystems that sequester carbon (i.e., forests), blue carbon systems sequester more carbon per unit area than any other habitat on Earth with sequestration rates ranging from 4.8 to 87.2 Tg C yr^{-1} (Figure 1.3; Chmura, 2013).

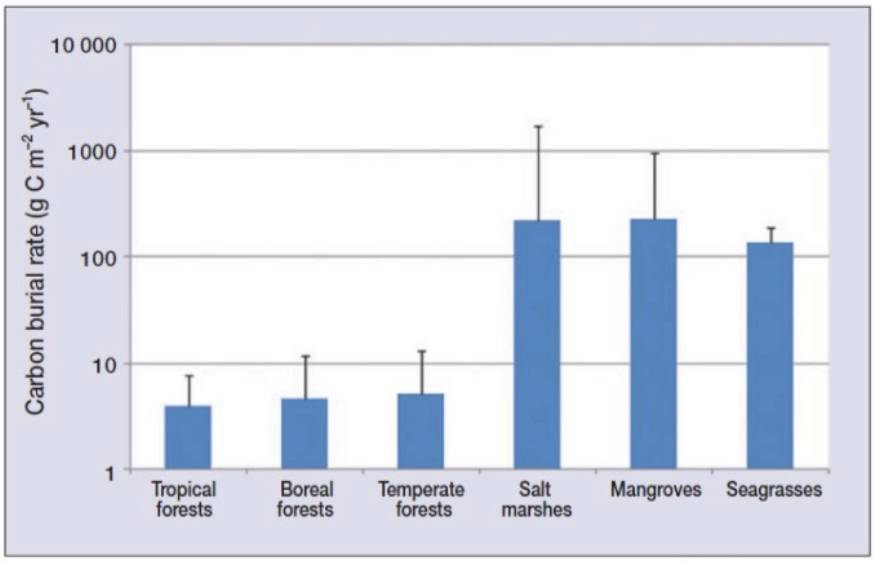


Figure 1.3. Carbon burial rate by area for three terrestrial forests compared to blue carbon systems (McLeod et al., 2011).

Within blue carbon ecosystems, approximately 5.1 million hectares of global coastlines are salt marshes (Pendleton et al., 2012), which protect shorelines from erosion by both trapping sediments and buffering wave action as well as filtering runoff from land systems (Pendleton et al., 2012). Salt marshes also provide 75% of commercial fishery habitats for species such as shrimp and blue crab (Pendleton et al., 2012). These ecosystem services, in addition to sequestering up to 7.7 tons of CO_2 globally per hectare, have led to salt marshes being valued at up to U.S. $10,000/hectare (Barbier, 2012; Burdick and Roman, 2012).

Even with all of these ecosystem services, New England salt marshes have undergone a multitude anthropogenic disturbances in the last century including nutrient loading, ditches for mosquito control, filling, draining, habitat fragmentation, and invasive species introductions (Gedan et al., 2009; Bernhard et al., 2015). A sampling of salt marsh habitats along the New England coast estimated that approximately 40% of

these habitats have been lost due to anthropogenic influences since the European settlement (Bromberg and Bertness, 2005). On a global scale, more than 65% of wetland habitat has already been lost due to physical anthropogenic disturbances, which directly correlates to a loss in ecosystem services (Lotze et al., 2006).

The sustainability of salt marshes and, by extension, their effectiveness in sequestering atmospheric CO_2 will also be affected by global climate change. The IPCC estimates that emissions from CO_2 and other greenhouse gases could lead to a 2-6°C increase in global temperatures and a 0.8-2.0 m increase in sea level by the year 2100 (IPCC, 2014). Plot-level experiments have shown that increased CO_2 concentrations, warmer temperatures, and minimal sea-level rise (up to 1 cm above mean high water) could actually increase primary productivity and marsh accretion (Kirwan et al., 2009; Charles and Dukes, 2009; Kirwan et al., 2014). However, coastal wetland loss from climate-driven changes (e.g., increased drought conditions or increased inundation with sea-level rise, depending on location) is predicted to cause an additional 20–45% loss of salt marsh habitat by the end of this century (Craft *et al*., 2008). Through land use conversion and other human activities, the release of stored carbon from blue carbon systems to atmospheric CO_2 currently represents a substantial economic burden, ranging in annual damages up to U.S. $42 billion (Pendleton et al., 2012).

Carbon Burial and Outwelling

To determine whether a salt marsh is a source or sink of carbon, an equation representing the amount of carbon buried in salt marshes must consider all fluxes of carbon in and out of the system:

$$C_B = (GPP - R) - L = NPP - L \qquad \text{Equation 1.1}$$

Where:

C_B = Carbon burial

GPP = Gross primary productivity

R = Respiration

L = Lateral Flux

Net primary productivity and respiration rates are documented in the literature for New England salt marshes. Steever et al. (1976) estimated productivity in the Cottrell Marsh in Connecticut to be 51 mol C m^{-2} yr^{-1} while a Rhode Island marsh was estimated to produce 36-70 mol C m^{-2} yr^{-1} (Nixon and Oviatt, 1973). Forbrich and Giblin (2015) studied ecosystem dynamics in Plum Island marsh in Massachusetts and found that from May to October 2012, primary productivity averaged -72 mol C m^{-2}, respiration averaged 49 mol C m^{-2}, and net ecosystem exchange was approximately -24 mol C m^{-2}. In terms of burial rates, Howes et al. (1985) estimated that 10% of the carbon fixed through photosynthesis in salt marshes was buried in Great Sippewissett Salt Marsh (Cape Cod, MA). Houghton and Woodwell (1980) found annual burial rates of 25 mol C m^{-2} yr^{-1} in a Long Island, New York marsh. Artigas et al. (2015) estimated an annual burial rate of 16 mol C m^{-2} yr^{-1} for a salt marsh in New Jersey, and noted that 22% of the total fixed carbon remained as biomass or within the sediments. Artigas et al. (2014) found an average sedimentation rate of 1.4 mm yr^{-1} using cesium-137 dating. Ignoring the lateral flux of carbon to other systems, they surmised that the marsh had a carbon accumulation rate of 16 mol C m^{-2} yr^{-1}.

The lateral flux of carbon from salt marshes is less agreed upon. Teal (1962) noted that approximately 45% of the primary production in a salt marsh in Georgia was removed with the tides from the marsh. Conversely, a Long Island, New York salt marsh was found to have a net flux of carbon into the marsh at rates of 4.4 mol C m^{-2} yr^{-1} (Woodwell and Whitney, 1977). Odum (1980) then expressed the notion that the productivity of nearshore waters can be enhanced not only by the upwelling of nutrients from the bottom of the water column, but also from the outwelling of nutrients, organic matter, and organisms from fertile estuaries. A large number of estuarine flux studies have been conducted since the "Outwelling Hypothesis" was introduced. Nixon (1980) conducted a meta-analysis of estuarine and coastal productivity from 12 salt marshes and concluded that it was unclear whether these systems were sources or sinks of carbon. In two decades alone, outwelling research was conducted at 41 sites and presented in 42 publications (Childers et al., 2000). However, very few of these studies have quantified estuary-coastal ocean exchanges (Valiela et al., 1978; Valiela and Teal, 1979).

While more studies are beginning to quantify estuary-coastal ocean exchange (inclusive of not only salt marsh ecosystems; Tzortziou et al., 2011; Duarte et al., 2014; Schiebel et al., 2014; Wang et al., 2014; Moyer et al., 2015), there are numerous reasons why directly testing the outwelling hypothesis has proven difficult. Sampling water flow and constituent concentrations in tidal channels connecting estuaries to the coastal ocean is complicated if the estuary is large, has multiple tidal channels, or is remotely located (Childers et al., 2000). As previously mentioned, there is a high rate of spatial and temporal variability within estuaries. Flux quantification precision, accuracy, and error

are also highly variable (Childers et al., 1993; Deegan and Garritt, 1997; Childers et al., 2000; Pendleton et al., 2012).

Coastal outwelling is different in several aspects from riverine transport. River mouths often act as a point source for continental materials delivered to the shelf and intertidal zones generally accommodate highly productive ecosystems covering broad geographic areas. Transport mechanisms and water sources may facilitate coastal outwelling via precipitation, surface water runoff/marsh overland flow, groundwater discharge, tidal recharge/discharge through marsh and creek sediments, and bi-directional tidal currents linking the marsh to the ocean (Valiela et al., 1978; Harvey et al., 1987; Childers et al., 1993; Troccaz et al., 1994; Krest et al., 2000; Tobias et al., 2001; Dittmar and Lara 2001).

Dissolved Organic Carbon

Dissolved organic matter (DOM) includes dissolved forms of carbon, nitrogen and phosphorus (Qualls et al., 1991; Hedin et al., 1998; Kalbitz et al., 2000; Cialino, 2015). DOM represents an important source of nutrients for the aquatic world (Jackson and Williams, 1985; Gomi et al., 2002; Aller and Blair, 2006), enhances primary productivity (Rabalais et al., 2002), and absorbs harmful ultraviolet (UV) radiation (Green and Blough, 1994; Morris et al., 1995).

Marine dissolved organic carbon (DOC) is one of the largest reservoirs of organic carbon at the Earth's surface. However, significant gaps in understanding both transport and biogeochemical cycling of DOC at the land-sea interface remain (Childers et al., 2002; Chavez et al., 2007) as this area is characterized by high spatial and temporal

variability. While the role of salt marshes in nutrient and carbon turnover is poorly constrained, it is clear that a high proportion of net primary production in coastal wetlands is introduced to the ocean as DOC (Gallagher et al., 1976; Charles and Dukes, 2009; Fagherazzi et al., 2012).

Because DOC is operationally defined as organic molecules that pass through a filter (0.7 μm), this is the major form of carbon transported in soil pore water and streams (Kolka et al., 2008). This allows DOC to hydrologically transport carbon between different pools in a salt marsh ecosystem (e.g., deep sediment pore water to the adjacent estuary). DOC concentration in runoff increases with increasing wetland area. This is particularly true in New England, where wetlands are characterized as peatlands with high organic soil concentrations (Aitkenhead et al., 1999). DOC exiting peatlands can be upwards of 4-8% of annual net primary productivity and fluxes of DOC from watersheds with wetlands typically range from 2-10 g C m^{-2} yr^{-1} (Kolka et al., 1999; Elder et al., 2000; Kolka et al., 2008). Conversely, in watersheds with little to no wetland soils, the loss of DOC is minimal with respect to other carbon pools and fluxes (Kolka et al., 2008).

Chromophoric Dissolved Organic Matter

DOM is an amalgamation of thousands of compounds and chromophoric dissolved organic matter (CDOM) is the optically measureable component of DOM (Coble, 2007; Kowalczuk et al., 2009). CDOM absorbs light over a broad range of wavelengths, both visible and UV. CDOM is typically yellow in color and fluoresces blue when irradiated with UV light (Coble, 2007). Due to its light absorbing properties,

CDOM is believed to be important for most photochemically-mediated processes in surface waters and a source of reactive oxygen species in marine waters (Cooper et al., 1989; Del Veechio and Blough, 2002). CDOM is becoming more prevalent in the literature for applications such as remote sensing of ocean color related to organic carbon cycling, remote sensing of chlorophyll as an indicator of primary production, carbon cycling in coastal waters, and as a tracer of riverine input of organic carbon to the ocean (Kowalczuk et al., 2009).

CDOM is composed of a mixture of humic substances, amino acids, and pigments from various sources (Cialino, 2015). The primary source of CDOM in coastal waters is from rivers and groundwater transporting terrestrially derived CDOM from soils. CDOM can be produced *in situ* by plankton and bacteria (Cialino, 2015). Upwelling, pore water advection, sediment resuspension, and anthropogenic sources (e.g., sewage effluent) also provide CDOM contributions to an ecosystem (Coble, 2007). CDOM sinks include photodegradation and microbial decomposition. The major products of degradation and decomposition are dissolved inorganic carbon (DIC) and (not colored) low molecular weight organic compounds (Cialino, 2015). Photodegradation results in the release of labile, biologically available compounds (Del Vecchio and Blough, 2004; Yamashita and Jaffe, 2008). In estuaries, it is possible for a surface layer of low salinity, high CDOM riverine water to remain on top of higher salinity estuarine water, although this will vary by river system, tide, season, and discharge rates (Cialino, 2015). CDOM photodegradation is also enhanced in this layer due to sunlight exposure (Wang *et al*., 2014). Phytoplankton and bacteria can rapidly consume the nutrient flux within this freshwater layer, including labile CDOM. CDOM in coastal waters can also be affected

by dilution, physical mixing, biological degradation, and *in situ* production (Coble, 2007), making the measurement of both CDOM and DOC fluxes in coastal environments more difficult.

In terrestrially influenced areas such as salt marshes, when the CDOM/DOC relationship is known, CDOM can be used as a proxy for DOC concentrations. CDOM is easily measured *in situ* (allows for high-resolution sampling with sensors) and DOC concentrations can be obtained via discrete sample collection and laboratory analysis (Green and Blough, 1994; Coble, 2007). Plotting the concentrations of CDOM against the concentrations of DOC for a sample yields a correlation and also relates to the quality of DOC in a system (Figure 1.4).

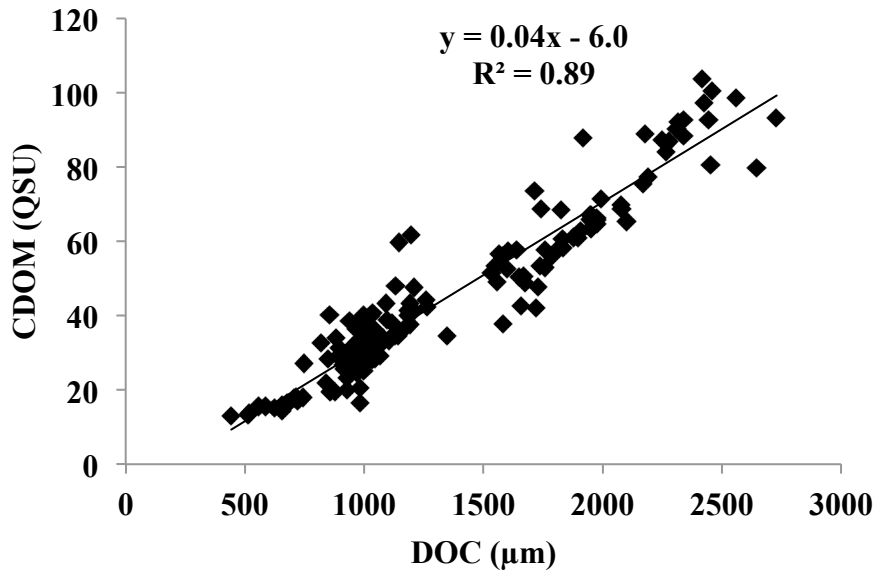


Figure 1.4. CDOM/DOC relationship for an estuary (shown here for the Neponset River in Boston, Massachusetts).

DOM that is fresher, more pigment-like, and more aromatic has a higher CDOM/DOC ratio. Carbohydrates, saturated hydrocarbons, cellulose, and photodegraded

DOM have lower CDOM/DOC ratios. The CDOM/DOC ratio can get higher as material becomes more humified and marine bacteria can make more CDOM as the degrade particles (Harvey et al., 2015).

Neponset Salt Marsh

The Neponset River is located in Boston, Massachusetts. The watershed draining into the Neponset River covers approximately 300 hectares and watershed contributions originate from areas within 14 cities and towns populated by roughly 330,000 people. The Neponset River is the second largest river entering into Boston Harbor after the Charles River and flows. The depth of the main channel at the mouth is approximately 4 m with a tidal range of 3 m and a large portion of water is exchanged during each (semi-diurnal) tidal cycle. The tidal volume and depth contribute to a short time scale of mixing within the estuary (~3-5 days). The estuary is fringed by the 110 hectare Neponset Salt Marsh (Figure 1.5).

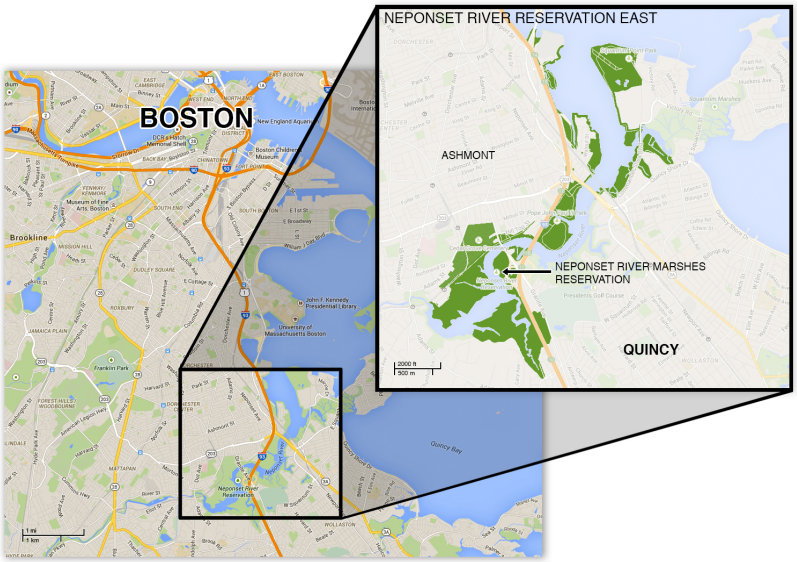


Figure 1.5. Neponset Salt Marsh.

The marsh is predominantly covered by an invasive reed, *Phragmites australis,* and two species of *Spartina*: *S. alterniflora* (low marsh, inundated twice daily) and *S. patens* (high marsh, inundated during spring tides). The marsh is bordered by the Lower Mills Dam at the landward extent of the estuarine portion of the Neponset River with the flow gauged by the United States Geological Survey (USGS) at a location just downstream from the dam. This measurement provides a critical scale for estimated export from the estuary and the dam marks the freshwater end of the estuary with approximately 5-10 PSU salinity.

There are several components to consider when constructing a DOC outwelling budget for the Neponset Salt Marsh and this study will aim to quantify the total and seasonal outwelling variation as well as the sub-fluxes of DOC outwelling from plants and sediment in the marsh (Figure 1.6).

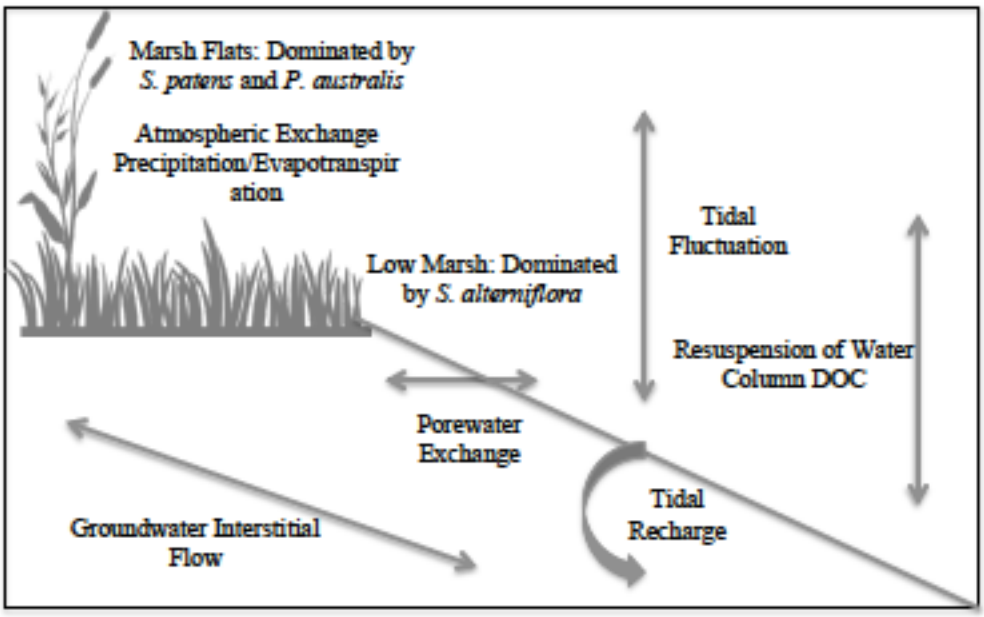


Figure 1.6. Conceptual model of processes contributing to DOC outwelling in the Neponset Salt Marsh.

Chapter Summaries

Chapter 2 will quantify the total DOC export from the Neponset Salt Marsh. From 2001 through 2013, transects of the Neponset River from Boston Harbor to the freshwater endmember at the Lower Mills Dam were conducted using high-resolution measurements to distinguish CDOM sources by comparing the actual and apparent endmembers of the data. Seasonality, sources of freshwater inputs, and long-term export trends will be discussed. Most importantly, an average annual and seasonal DOC export rates from the marsh will be quantified and used in subsequent chapters to characterize the contributions from major processes to the total export.

Chapter 3 will investigate the role of plant matter DOC leaching in the overall export from the Neponset Salt Marsh. The focus of this chapter will be the seasonal DOC flux variation as marsh grasses enter senescence for the winter, e.g., the Fall Dump. The

three major plant species in the Neponset Salt Marsh are compared in terms of leaching rates: *S. patens* and *S. alterniflora*, and *P. australis*. Variables believed to affect DOC leaching will be examined including: sunlight, microbes, plant species, above- versus belowground biomass, and anoxia. Using transect data from Chapter 2, the total DOC leaching flux as well as the seasonal contribution attributed to the dominant plant species in the Neponset Salt Marsh will be described.

Chapter 4 will explore two separate sediment processes and their contribution to the overall DOC outwelling in the Neponset Salt Marsh: surface sediment/overland flow and deep sediment pore water leaching. Surface sediment/overland flow represents the DOC leached from the surface sediment and vegetation on the marsh flats only during high tides while the other process described in this chapter is the leaching from deeper sediment on the marsh flats throughout the full range of a tidal cycle. In addition to seasonality, marsh health (e.g., drought versus healthy conditions), sediment core distance from the main creek bank, and sediment depth will be investigated for their roles in DOC leaching from marsh sediment. Using transect data from Chapter 2, the total DOC leaching flux as well as the seasonal contribution attributed to these two processes in the Neponset Salt Marsh will be described.

Finally, chapter 5 will describe incubation experiments used to determine the influence of natural sunlight irradiation on the release of DOM from resuspended surface sediments. Sediment export will be compared between the Neponset Salt Marsh and a salt marsh in Florida under different sunlight and bacterial conditions. Photo-released CDOM will be characterized by fluorescence and excitation-emission matrix (EEM) spectroscopy.

Upon determining the percentage of the overall outwelling that can be attributed to plant and sediment processes in the Neponset Salt Marsh, a DOC outwelling budget will be constructed and other possible contributions not studied here will be discussed. Additionally, literature values for respiration and primary productivity for similar salt marshes in New England will be utilized to assess the possible carbon burial potential of the Neponset Salt Marsh.

CHAPTER 2

ESTIMATING TOTAL DISSOLVED ORGANIC CARBON EXPORT FROM A NEW ENGLAND SALT MARSH

Abstract

At the interface between oceanic and terrestrial environments, blue carbon systems sequester large amounts of carbon via productivity and sedimentation. In addition to ecosystem services such as climate change mitigation and fish nursery habitats, salt marshes also export organic matter and nutrients to adjacent estuaries and coastal oceans. While the outwelling of organic matter has been difficult to quantify due to steep gradients, irregular geomorphologies, and rapidly changing conditions, this study combines ship transects using high-resolution *in situ* chromophoric dissolved organic matter (CDOM) sensors, seasonal monitoring, buoy data, and discrete samples to estimate dissolved organic carbon (DOC) export over various spatial and temporal scales. From 2001 through 2013, 35 transects of the Neponset River Estuary in Boston,

Massachusetts were completed with a small research vessel towing an instrument package called the Mini-Shuttle. The total export of DOC from the Neponset Salt Marsh was estimated inter-annually and seasonally. Estimates ranged from $1.2 \pm 0.2 \times 10^7$ mol C yr^{-1} for summer months to $14 \pm 21 \times 10^7$ mol C yr^{-1} for spring months with a high relative contribution from the salt marsh plants in the fall. The total annual average DOC export from the Neponset Salt Marsh is $5.4 \pm 8.6 \times 10^7$ mol C yr^{-1} or approximately 49 mol C m^{-2} yr^{-1}. Using multiple linear regression analysis, it was found that temperature, day length, and river discharge significantly affect the export of DOC from the Neponset Salt Marsh into the estuary. High-resolution measurements allowed secondary sources of fresh water from Gulliver Creek and a Massachusetts Water Resources Authority standpipe to be identified. Over decadal timescales, the Neponset Salt Marsh was found to export significantly lower DOC concentrations over time due to a combination of anthropogenic disturbances including a salt marsh restoration, mosquito ditching, and the invasion of the common reed *Phragmites australis*.

This chapter is an extension of a publication currently in preparation:

Schiebel, H.N., Gardner, G.B., Peri, F., Cialino, K.T. and R.F. Chen. Estimating total dissolved organic carbon export from a New England salt marsh.

Author contributions to this dissertation chapter:

1. H. Schiebel collected and analyzed DOC samples from cruise conducted in 2012 and 2013, collected watershed samples from 2012 through 2015, wrote the majority of the chapter, created figures 2.1, 2.2, 2.3a, 2.4, 2.8, 2.9, and 2.10, and compiled all tables in the chapter.
2. G. Gardner attended all cruises, created and implemented the MatLab program to calculate endmembers, wrote the section of the chapter outlining equations 2.1 through 2.4, and created figures 2.3b, 2.11, and 2.12 as well as all figures in Appendix A.
3. F. Peri attended all cruises, built the Mini-Shuttle, and contributed to chapter edits.
4. K. Cialino collected watershed samples from 2006 through 2012 and contributed the watershed portions of the chapter results.
5. R. Chen contributed to the chapter results.

Introduction

As climate change is now unequivocal, the Intergovernmental Panel for Climate Change (IPCC) recommends reducing carbon dioxide (CO_2) emissions by 85% by 2050 to prevent a mean temperature increase of 2°C (IPCC, 2014). Switching to low carbon emission energy sources and adopting proposed engineered carbon sequestration techniques are current solutions to limit climate change. However, storage using natural systems that remove CO_2 can also play a role in climate change mitigation. Salt marshes sequester a large amount of CO_2 via both vegetation and sedimentation, and assessment of the response of salt marsh carbon sequestration to climate change and sea-level rise has become an active area of research (Chen et al., 2015). For example, models of organic matter accumulation have been used to estimate carbon pool dynamics in response to sea-level rise and a warming climate (Kirwan and Mudd, 2012).

The amount of carbon buried in a salt marsh is a result of the net productivity of the salt marsh plants, the remineralization of organic matter over various timescales, and the export of organic matter. Salt marshes export a significant amount of their primary productivity to adjacent ecosystems via outwelling (Odum, 1980; Snedaker, 1978; Duarte et al., 2010; Duarte et al., 2014). The outwelling of both particulate organic matter (POM) and dissolved organic matter (DOM) supports offshore consumers and serves as an important functional role of salt marshes (Snedaker, 1982; Macintosh, 1982; Cacador et al., 2009; Duarte et al., 2014). Junk et al. (1989) coined the term “flood pulse” to describe the flushing of organic matter from salt marshes to other systems via tidal exchange. Bouchard (2007) noted that estuaries and their adjacent ecosystems are “coupled systems” that are strongly interconnected by both biotic and abiotic interactions

(nutrients, organic matter, species). Duarte et al. (2014) observed that carbon export is strongly influenced by the salt marsh dieback phenomenon in which an increase in the amount of litter is generated within the marsh due to increased senescence unrelated to seasonality. In the face of both warming temperatures associated with climate change as well as land use change, it was noted that wetland deterioration could actually enhance outwelling (Duarte et al., 2014).

While few studies have investigated seasonal outwelling fluxes for salt marsh systems, seasonality is well-understood for terrestrial systems. Temperate deciduous leaves senesce during fall with nearly zero biomass production in winter (Kaiser et al., 2010). Over a two-year study, dissolved organic carbon (DOC) content in temperate forest soil water in Austria was shown to increase in late autumn and decrease to low values for winter and early spring (Kaiser et al., 2010).

Marine DOC represents a large reservoir of organic carbon at the Earth's surface. It has traditionally been difficult to estimate the outwelling of DOC in estuaries due to steep gradients, irregular geomorphologies, and rapidly changing conditions as both biogeochemical and transport processes in salt marshes are characterized by high spatial and temporal variability. Although nutrient and carbon turnover in salt marsh systems has been difficult to quantify, it is clear that a comparatively high proportion of net primary production in coastal wetlands is introduced to the ocean as DOM (Gallagher et al., 1976; Charles and Dukes, 2009; Fagherazzi et al., 2013).

Chromophoric dissolved organic matter (CDOM) is the optically measureable component of DOM and may be used as a proxy for DOC under certain conditions (Coble, 2007; Kowalczuk et al., 2009). Due to its light absorbing properties, CDOM is

believed to be important for most photochemically-mediated processes in surface waters and to be a source of reactive oxygen species in marine waters (Cooper et al., 1989; Del Veechio and Blough, 2002). The primary source of CDOM in coastal waters is from rivers and groundwater transporting terrestrially derived CDOM from soils. CDOM can also be produced *in situ* by phytoplankton (Gali et al., 2013, Figueroa et al., 2015) or removed by photodegradation or microbes (Coble, 2007).

The main mechanisms for DOC/CDOM outwelling from salt marshes to adjacent estuaries are river flow and tidal exchange. DOC in many estuarine systems can be conservative (Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998), while in some systems, processes such as phytoplankton and salt marsh grass production or anthropogenic inputs have been observed to be large DOC contributors (Aminot et al., 1990; Peterson et al., 1994; Gardner et al., 2005). CDOM is easily measured based on its fluorescent and/or absorption characteristics (Chen, 1999; Chen and Gardner; 2004; Gardner et al., 2005) and high-resolution CDOM-salinity plots are possible with optical CDOM sensors, ship transects, or long-term buoy deployments. CDOM is relatively conservative over estuarine timescales with fresh water being a major CDOM source, so any deviation from a linear relationship between CDOM and salinity should be indicative of mid-estuary production (concave down) or removal (concave up; Figure 2.1).

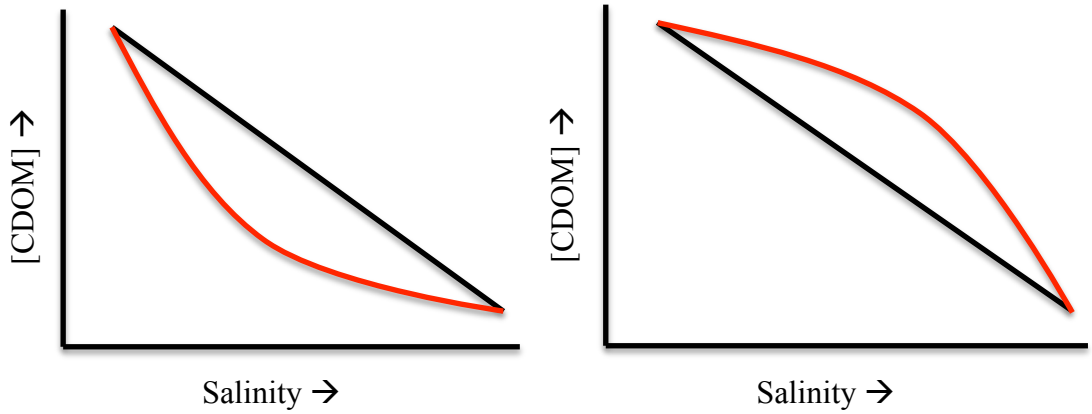


Figure 2.1. Deviations from a conservative CDOM/salinity relationship in an estuary: (a) concave up indicates CDOM removal while (b) concave down indicates CDOM production (Sholkovitz et al., 1978; Peterson et al., 1994; Gardner et al., 2005).

Methods

Study site

The Neponset River Estuary is approximately 7 km long and varies in width from 25 to 250 m at low water. The river is the second largest entering into Boston Harbor (Gardner et al., 2005). The depth of the main channel at the mouth is approximately 4 meters with a semi-diurnal tidal excursion of 3 meters. The tidal volume and depth contribute to a short time scale of mixing within the estuary of ~3-5 days (Figure 2.2).

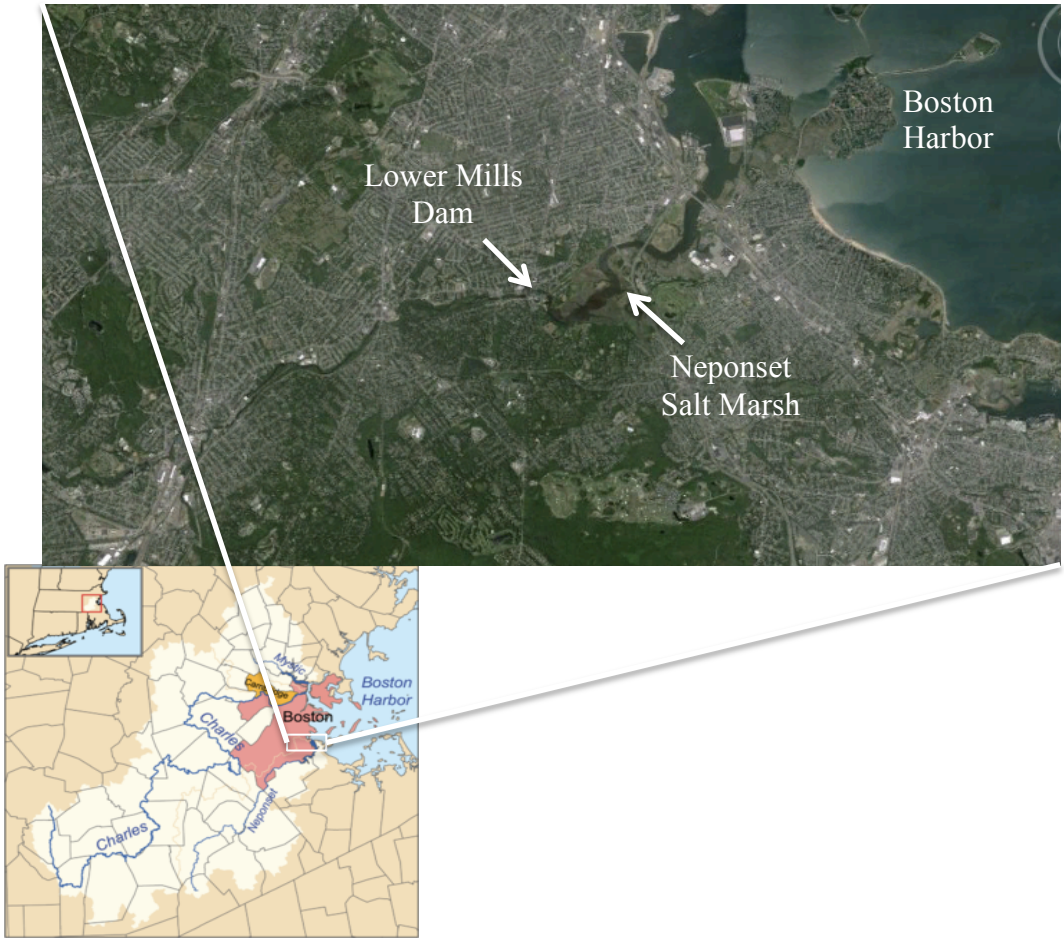


Figure 2.2. Neponset River and Neponset Salt Marsh maps showing the location of Lower Mills Dam (freshwater endmember) and Neponset Salt Marsh.

The Neponset Salt Marsh is 110 hectares and comprised of three plant species: *Spartina alterniflora* (*S. alterniflora*) dominates in the low marsh while *Spartina patens* (*S. patens*) and the invasive reed *Phragmites australis* (*P. australis*) dominate the marsh flats. Approximately 29% of the intertidal surface area is open water (Gardner et al., 2005). The marsh is bordered by the Lower Mills Dam at the landward extent of the Neponset River Estuary with the flow gauged by the United States Geological Survey (USGS, 2002). The dam marks the end of the freshwater endmember of the estuary with salinity ranging from 5-10 PSU.

Transects

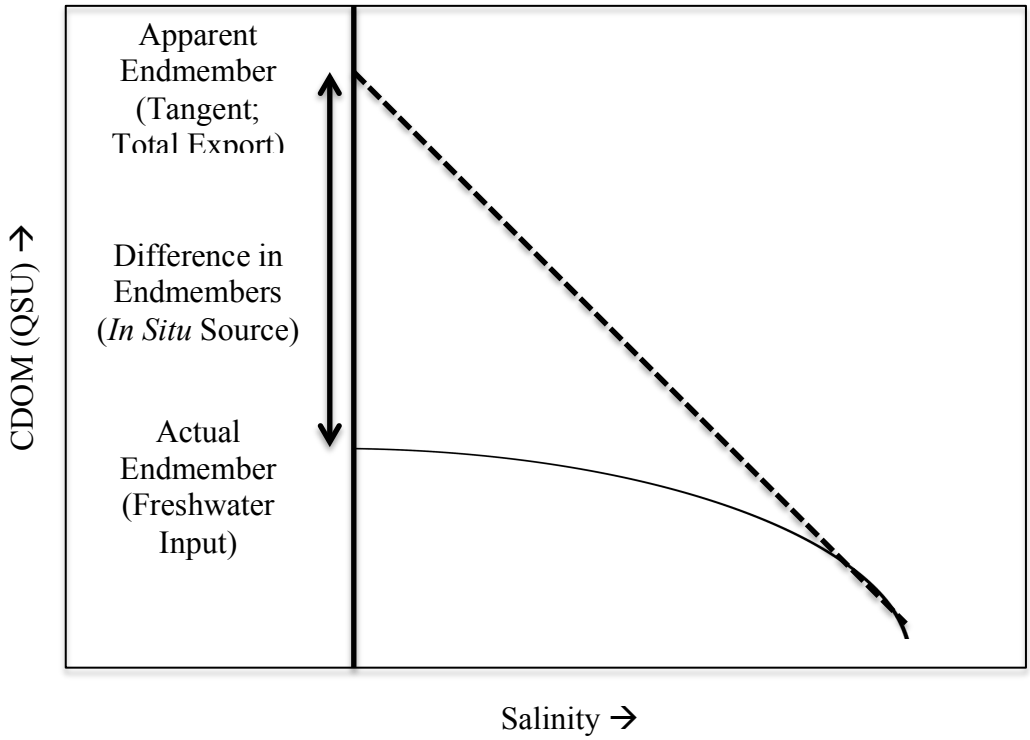
From 2001 through 2013, 35 transects of the Neponset River Estuary were conducted with a small research vessel (RV Neritic) from the mouth to the navigable head of the estuary (Table 2.1; Appendix A).

Table 2.1. Dates and accompanying data for all cruises. Total rain and total snow were totaled for three days prior to each cruise date. Air temperature was averaged for three days prior to each cruise date. Numbers in parentheses indicate multiple cruises conducted on a certain day.

Date	Julian Day	Days After Neap Tide	Total Rain (cm)	Total Snow (cm)	Avg. Temp. (°C)
September 14, 2001	257	5	0.127	0	26
November 6, 2001	310	15	0.762	0	14
August 21, 2002	233	7	0.864	0	29
August 21, 2002 (2)	233	7	0.864	0	29
August 21, 2002 (3)	233	7	0.864	0	29
August 22, 2002	234	8	2.06	0	31
August 22, 2002 (2)	234	8	2.06	0	31
August 22, 2002 (3)	234	8	2.06	0	31
August 22, 2002 (4)	234	8	2.06	0	31
August 22, 2002 (5)	234	8	2.06	0	31
August 22, 2002 (6)	234	8	2.06	0	31
August 23, 2002	235	9	1.24	0	27
August 23, 2002 (2)	235	9	1,24	0	27
August 30, 2002	243	0	2.13	0	21
August 31, 2002	243	1	2.26	0	20
April 3, 2003	93	11	1.32	0	5.7
September 25, 2009	268	15	0	0	26
November 4, 2009	308	11	0	0	14
December 9, 2009	343	2	0.051	1.27	3.9
January 21, 2010	21	15	27.9	17.8	2
September 22, 2010	265	8	0	0	22
December 11, 2010	345	14	0	0	-0.9
June 22, 2012	174	12	0	0	32
September 11, 2012	256	4	1.80	0	24
October 5, 2012	279	14	0.336	0	19
October 16, 2012	290	9	0.533	0	18

October 23, 2012	297	3	0.559	0	20
November 14, 2012	319	9	0.737	0	17
November 30, 2012	335	11	0.381	0	4
January 13, 2013	13	10	0.330	0	6.5
August 25, 2013	237	12	0	0	27
September 23, 2013	256	12	0.940	0	23
October 20, 2013	293	10	0	0	17
November 20, 2013	324	11	0.483	0	12
December 11, 2013	345	3	1.27	1.78	3

The Mini-Shuttle, a depressor wing outfitted with a Teledyne RDI Citadel conductivity, temperature and depth (CTD)-NV instrument, and a Turner Cyclops-7 CDOM/FDOM fluorometer was utilized in tow-yo mode on transects of the Neponset Estuary. The Mini-Shuttle was kept at the surface when traveling upstream and was undulated throughout the water column (from 25 cm from the bottom to 10 cm from the surface in water depths from 5 meters to < 1meter) when traveling downstream to obtain both a full two-dimensional cross-section as well as a high-resolution surface transect for each cruise. With a custom-built winch and the ship traveling at 4 knots, *in situ* measurements allowed high-resolution distributions to be mapped. High-resolution CDOM data plotted against salinity yielded *in situ* sources of CDOM and, by proxy, DOC. The importance of *in situ* sources was estimated by comparing the actual and apparent freshwater endmembers determined by extending different sections of the CDOM-salinity curve to zero (Figure 2.3a).



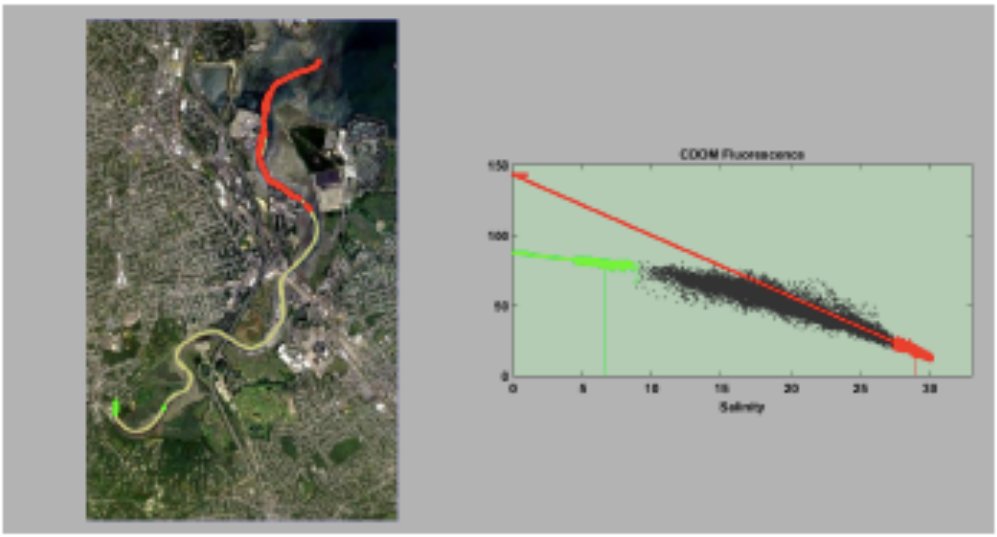


Figure 2.3. (a) Conceptual diagram showing actual and apparent endmembers (*in situ* CDOM concentration). The solid line represents a non-conservative mixing line and the dashed line shows the tangent to the data at the mouth of the estuary, representing the CDOM exported from the mouth of the estuary. The difference between these two values represents the export derived *in situ*. (b) November 2012 cruise data with *in situ* CDOM sources accounting for approximately 35% of the total export.

To estimate the marine (apparent) and freshwater (actual) endmembers for each survey, an interactive Matlab program was written by Dr. Bernie Gardner that presents a plot of the mixing curve and associated cruise track and allows the user to select regions of either plot. The program selects the data in the chosen region and differentiates them by color (Figure 2.3b). It then uses the Matlab polyfit function to estimate the endmembers (zero intercept of the fitted linear function). The endmembers presented here were generated by selecting the highest (generally >25 PSU) and lowest (generally <10 PSU) salinity regions of the mixing curves. The selected regions depend on available data, which depends on hydrographic conditions and navigation restrictions. The data at either end of the mixing curve is generally linear and so the fitted results closely match the tangent to the mixing curve. In general, a sufficiently small salinity range may be selected such that the result is a reasonable approximation to the tangent. Extreme curvature at either end of the mixing curve implies dynamic fluctuation of the endmembers and introduces greater uncertainty in the use of this method for estimating export.

The export of any dissolved constituent in an estuary may be estimated from the freshwater input into the estuary and the relationship between the concentration of the constituent (e.g., CDOM) and salinity. The apparent end member (AEM) can be defined as the zero intercept of a tangent to the CDOM/salinity mixing curve:

$$AEM = C - S\frac{\partial C}{\partial S} \qquad \text{Equation 2.1}$$

Where:

C = [CDOM]

S = Salinity

Assuming that the estuary can be regarded as steady state and well-mixed, CDOM is exported by a combination of advection (which, in steady state, is controlled by the fresh water entering the estuary since that volume must also leave) and longitudinal dispersion, which can be modeled as the product of a diffusion coefficient and the longitudinal gradient of CDOM:

$$Q_C = RC + D_x \frac{\partial C}{\partial x} = RC + D_x \frac{\partial C}{\partial S}\frac{\partial S}{\partial x} \qquad \text{Equation 2.2}$$

Where:

Q_c = Export flux of CDOM

R = River input

D_x = Dispersion coefficient

The chain rule is used to express the CDOM gradient in terms of the salinity gradient and the CDOM-salinity curve slope. To estimate the dispersion coefficient, the flux of salt past any section in the estuary is simply the river input multiplied by salinity. Since the salinity of the river input is 0, the flux of salt past any section in the estuary must be balanced by an upstream diffusive flux:

$$-RS = D_x \frac{\partial S}{\partial x} \Rightarrow D_x = -\frac{RS}{\partial S / \partial x} \qquad \text{Equation 2.3}$$

Combining Equations 2.2 and 2.3 results in:

$$Q_C = R\left(C - S\frac{\partial C}{\partial S}\right) = R * AEM \qquad \text{Equation 2.4}$$

While this is most applicable to a well-mixed estuary, it is reasonably applicable to any estuary if the constituent concentration and salinity are regarded as sectional

averages. In this case, the dispersion coefficient incorporates not only diffusion, but also estuarine circulation.

For the Neponset Salt Marsh, assuming a constant freshwater endmember and a well-mixed estuary where tidal influence is stronger than riverine influence, the AEM multiplied by the freshwater discharge to the estuary provides an estimate of the flux of that constituent leaving the estuary, in this case CDOM export to Boston Harbor (Figure 2.3). The AEM does not represent a geographical boundary, but rather a high salinity endmember that can vary by cruise. The product of the tangent to the AEM at the high salinity end of the curve and the freshwater discharge represents the total export from the estuary and incorporates any *in situ* CDOM inputs along the cruise transect. The product of the AEM at the low salinity end of the curve and the freshwater discharge represents the riverine input. The difference between the two endmembers multiplied by the freshwater discharge, therefore, represents the total of *in situ* sources of CDOM within the estuarine system. Since the Neponset Estuary is dominated by marsh inputs, it is assumed that the *in situ* source is also dominated by marsh DOM inputs (versus phytoplankton or any additional CDOM source). In this way, the Mini-Shuttle data was used to compare total CDOM export fluxes at different times of year and across different years from the Neponset Salt Marsh.

An all-Teflon pumping system or hand-dipped bottles were used to gather discrete samples at set points along the transect that yielded cruise-specific correlations between CDOM and DOC as well as provided calibration data for the CDOM fluorometer. Using these conversion factors, CDOM source and export data can be converted into DOC source and export estimates given R^2 values greater than 0.90. Discrete DOC

concentrations were compared to *in situ* CDOM concentrations for each cruise (e.g., Figure 2.4).

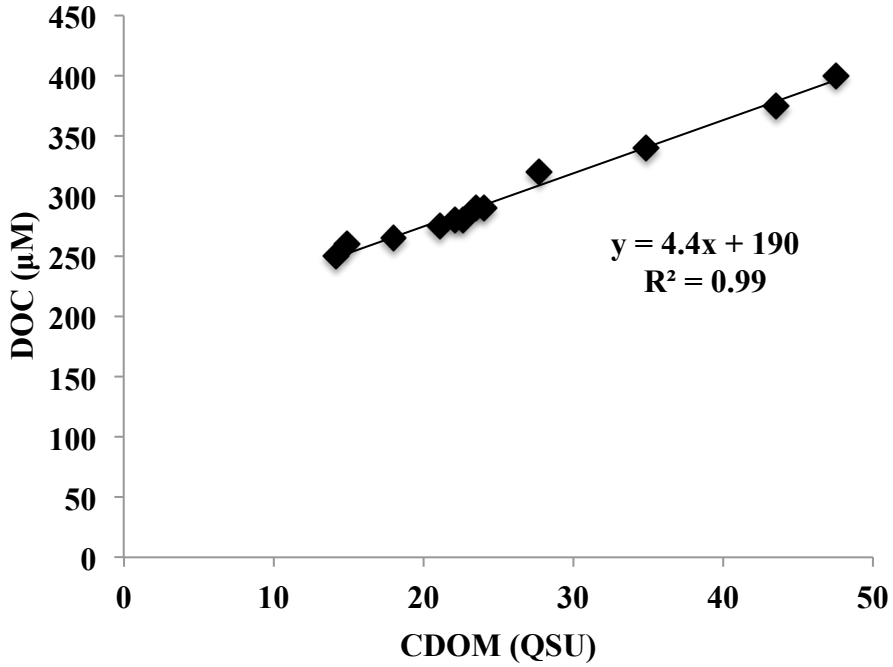


Figure 2.4. Plot of *in situ* CDOM concentrations versus discrete DOC samples for a cruise completed on August 25, 2013.

Buoy data

Environmental monitoring buoys consisting of a meteorological sensor package and an *in situ* water quality sensor package were deployed to obtain CDOM values from December through May when cruises were difficult to complete due to weather and other operational issues (i.e., bridge maintenance to allow the boat upriver; Figure 2.5).

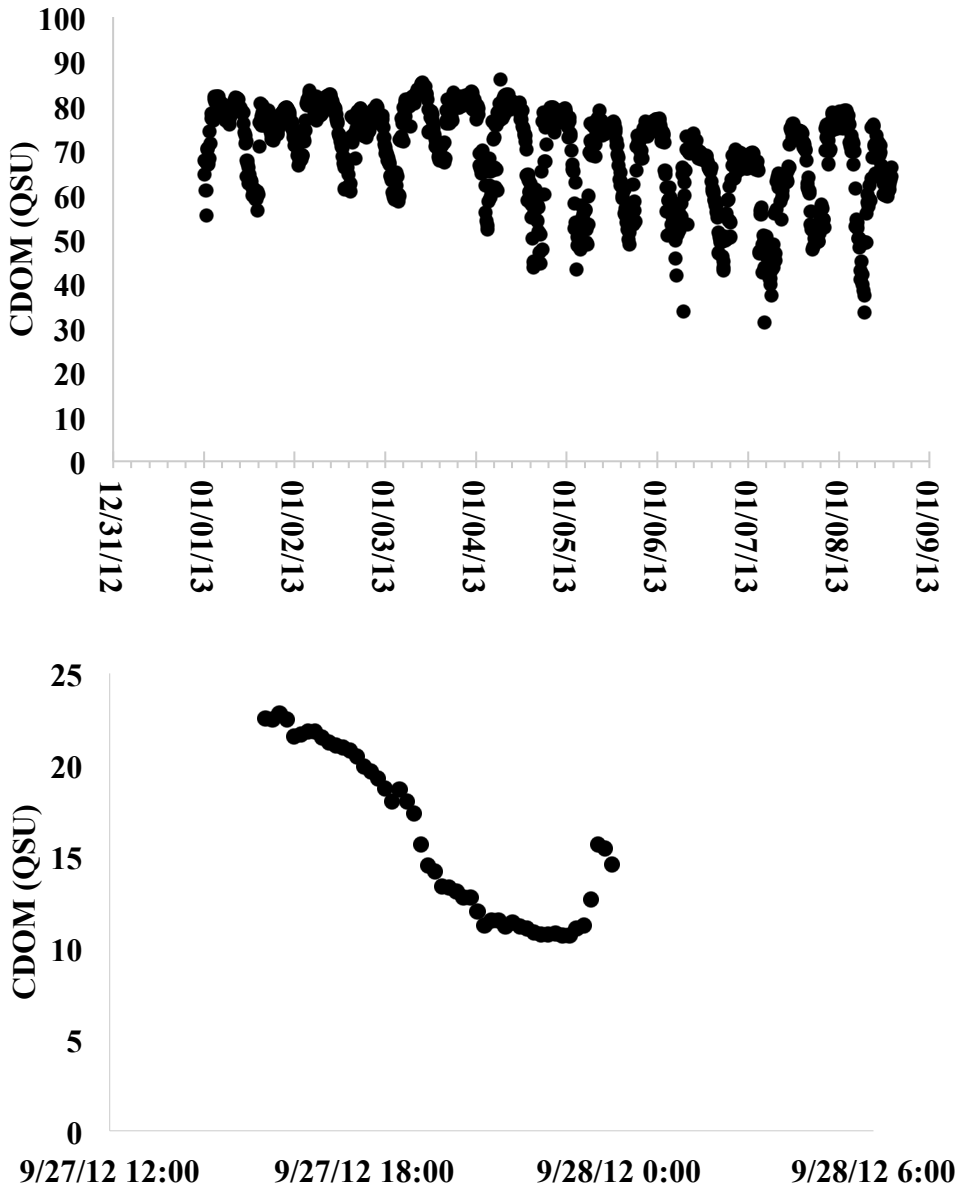


Figure 2.5. (a) Buoy data from a location near the mid-marsh point in the Neponset Estuary. (b) 24-hour data from September 27, 2012 at the same location.

The *in situ* assembly consisted of an Onset Computers 12-bit temperature sensor, an In-Situ Aqua Troll 200 salinity sensor, and a Wet-Labs ECO FL CDOM fluorometer with a wiper to protect against biofouling. All data were acquired at ten-minute intervals and telemetered over a GSM-cellular network at 30-minute intervals. The CDOM voltage

reading from each fluorometer was converted to CDOM concentration in quinine sulfate units (QSU) by using factory calibrations provided by gain setting and instrument range. The buoy data enhanced Mini-Shuttle data with temporally continuous CDOM-salinity mapping at 3 locations in the Neponset River (e.g. Figure 2.6).

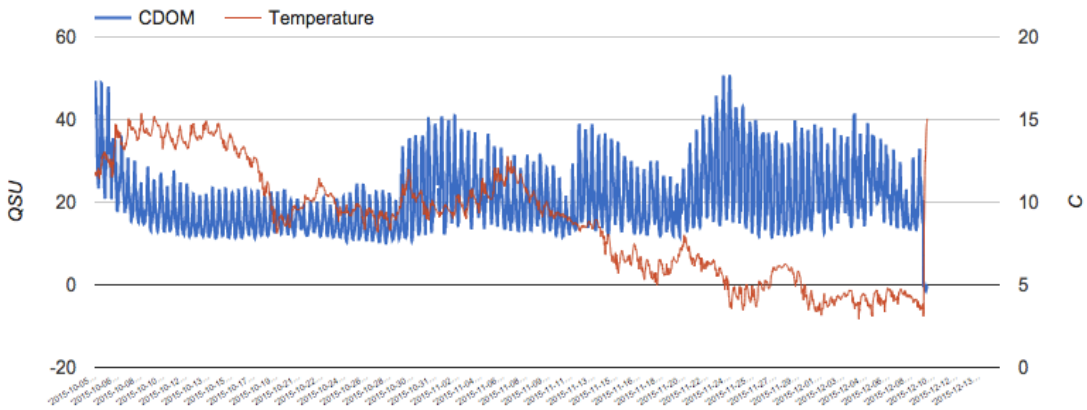


Figure 2.6. *In situ* CDOM concentration and water temperature from a buoy at the mouth of the Neponset River.

Watershed sampling

In order to examine terrestrial inputs into the Neponset River, monthly watershed sampling was conducted beginning in March 2006 through present for thirty sites throughout the Neponset watershed (Huang and Chen, 2009; Cialino, 2015). MassGIS was utilized to create land cover maps in order to determine dominant land use types in the watershed and delineated the following five most prevalent types: residential (38%), forest (34%), industrial (5%), wetland (4%), and golf course (2%) with the rest of the watershed considered mixed-use land types (Figure 2.7).

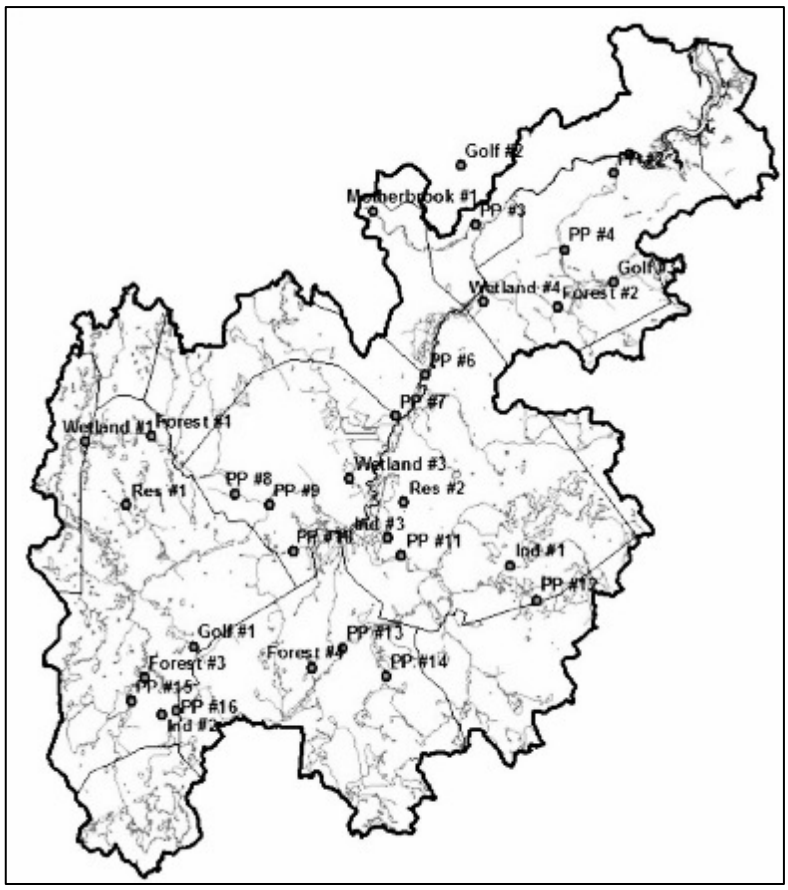


Figure 2.7. Neponset watershed sampling site endmembers (F-forest; R- residential; I-industrial; G-golf course; W-wetland; PP – pour point, which is a mixture of any other land use types). Endmember sites' subwatersheds are >80% of the stated land use/land cover (Huang and Chen, 2009).

All samples throughout the watershed (salinity = 0) were collected within 12 hours using a cleaned stainless steel bucket and transported in 250-ml pre-combusted (4 hours at 500°C) glass bottles.

Sample analysis

After collection (for discrete transect and watershed samples), each sample was filtered through a pre-combusted 0.7 μm glass fiber filter (Whatman GF/F). DOC samples were filtered into pre-combusted (4 hours at 500°C) 40-mL borosilicate glass

vials with Teflon-lined screw caps, acidified to pH < 2 using phosphoric acid, and refrigerated until analysis. DOC concentrations were measured using a Shimadzu TOC-V analyzer equipped with an autosampler. The instrument was calibrated using 5-point carbon calibration curves. Carbon standards were prepared using potassium hydrogen phthalate (KHP). All standards and samples were injected in triplicate. Instrument blank and DOC values were checked against reference low carbon water and deep seawater (Consensus Reference Materials, University of Miami, Rosenstiel School of Marine and Atmospheric Sciences). Blank subtraction was conducted using Milli-Q water, which was analyzed at set intervals (every 10 samples) during sample analysis.

CDOM fluorescence was measured using a Photon Technologies International QM-1 spectrofluorometer. Single fluorescence emission scans from 350 to 650 nm were collected for an excitation wavelength of 337 nm. The fluorescence of Milli-Q water was determined as a blank on each day of analysis and subtracted from sample spectra prior to integration. Peak areas were integrated and converted to quinine sulfate units (QSU) where 1 QSU is equivalent to the fluorescence emission of 1 μg/l quinine sulfate solution (pH 2) integrated from 350 to 650 nm at an excitation wavelength of 337 nm (Chen and Gardner, 2004). All sample data were collected using a 1-cm quartz cuvette and expressed in quinine sulfate units (QSU).

Results and Discussion

Outwelling fluxes

For the purposes of this study, seasons were defined by temperature as it was found to be the major driver influencing estuary export. In Boston, the average

temperature varies from 2.2°C (January) to 27°C (July) with most months averaging well above freezing (Figure 2.8).

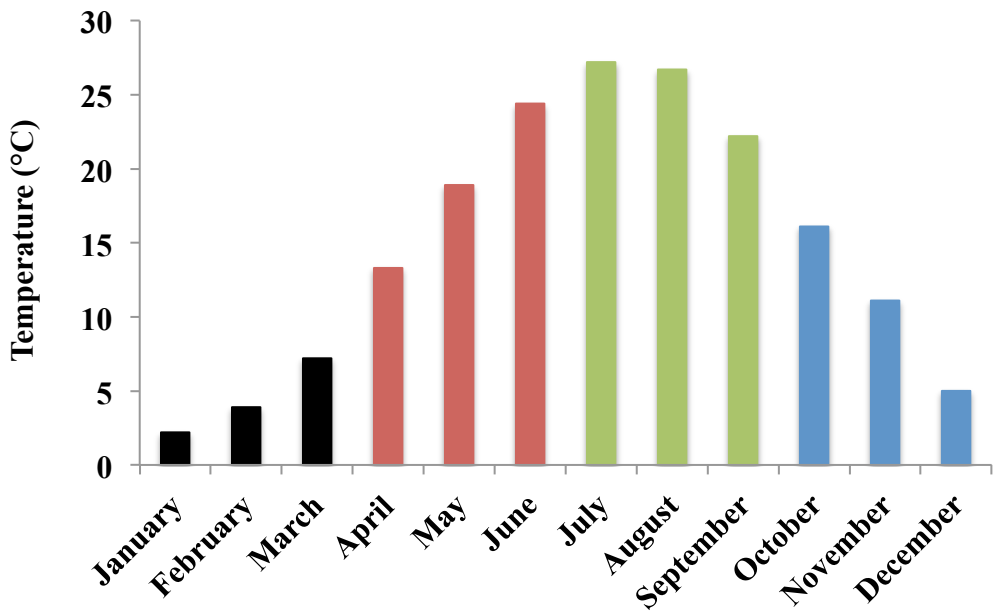


Figure 2.8. Average Boston temperatures throughout the year with the seasons as delineated for this study (Blue Hills Observatory, 2015).

Winter (January, February, March) in New England is generally accompanied by several days below freezing and high amounts of snowfall. The average temperature for the season is 4.5°C. The marsh is assumed to have little (if any) live plant biomass based upon observations. Two cruises (January 2010, January 2013) were conducted during the winter season for this study (Table 2.1). Spring (April, May, June) brings warmer temperatures (19°C average) and a combination of high rainfall and snowmelt creating a strong pulse of DOC into Boston Harbor and therefore increased outwelling. Because snowmelt is (mostly) watershed-derived, it is likely to increase freshwater export and total export but not marsh-derived export. Two cruises (April 2003, June 2012) were conducted during spring months (Table 2.1). Summer (July, August, September) is the

most productive season in the marsh with little of this productivity outwelling to Boston Harbor (based on transect data) and a high average temperature (26°C). There were nineteen cruises conducted during summer months for this study with a set of intensive cruises in August 2002 under different tidal regimes (Table 2.1). Fall (October, November, December) has a lower average temperature (11°C) and high *in situ* concentrations as marsh plants senesce for the winter (Schiebel et al., *in prep*). There were twelve cruises conducted during the fall months during this study (Table 2.1).

Two cruises during spring months (April 2003, June 2012) yielded an average difference in endmembers of 26 ±10 QSU, resulting in an average export of 14 ± 21 x 10^7 mol C yr^{-1} for spring, the highest export by season due to high discharge rates and high *in situ* CDOM production (Table 2.2).

Table 2.2. Seasonal outwelling fluxes from the Neponset Salt Marsh (mean ± SE) where [AEM] is the apparent endmember concentration, [FEM] is the freshwater endmember concentration, and discharge is the three-day average before each cruise extrapolated to a year.

Season	Sample Size	[AEM]-[FEM] (QSU)	[DOC] (10^{-4} mol C l^{-1})	Discharge (10^{11} l yr^{-1})	Export (10^7 mol C yr^{-1})
Spring	2	26 ±10	3.0 ± 0.4	5.1 ± 7.6	14 ± 21
Summer	19	65 ± 12	4.7 ± 0.5	0.3 ± 0.04	1.2 ± 0.2
Fall	12	45 ± 9	3.9 ± 0.4	0.5 ± 0.5	2.1 ± 1.9
Winter	2	16 ± 15	6 ± 0.6	2.0 ± 3.3	4.4 ± 7.1
Average					5.4 ± 8.6

As previously mentioned, the AEM concentration minus the freshwater endmember (FEM) concentration provides the *in situ* CDOM concentrations obtained from the Mini-Shuttle for each cruise. DOC concentrations were obtained from DOC/CDOM plots contracted for each cruise based on discrete hand samples of DOC

taken at set points on each transect. Three-day average discharge data prior to each cruise was obtained from the USGS flow gauge at the Lower Mills Dam and extrapolated to a year (Figure 2.9).

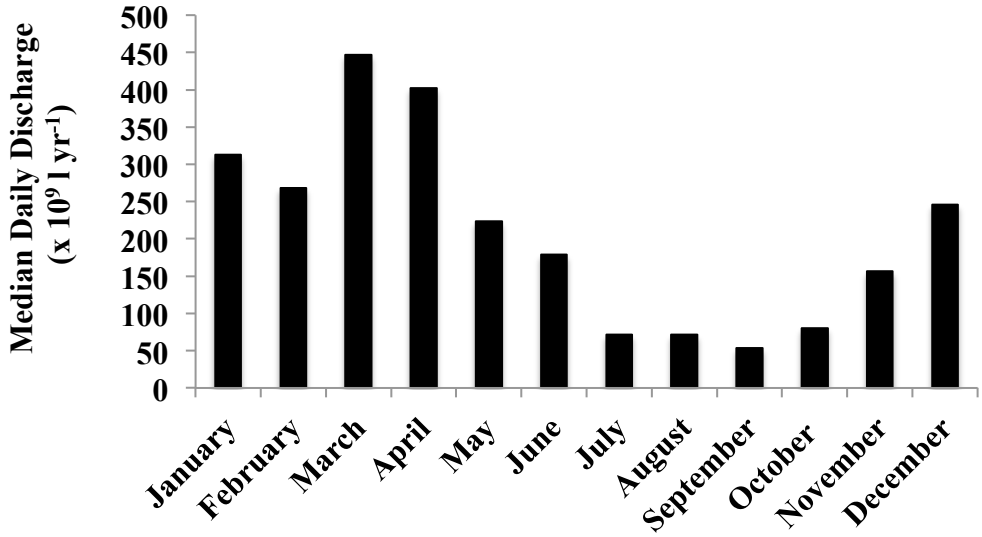


Figure 2.9. Median daily discharge rates by month from the Neponset River (USGS, 2002).

The DOC concentration multiplied by the flow data allowed for an export of DOC from the estuary for each cruise to be calculated and then averaged by season. Using a 90% confidence interval, a small sampling size, and wide range in discharge resulted in a large standard error for this season. An early spring flush in Boston would be driven by snowmelt as the watershed begins to thaw and there is a strong freshwater pulse into the marsh and, subsequently, Boston Harbor. For April 2003, there was a significant amount of snowfall (198 cm in total for the season) throughout the watershed that may have influenced the freshwater input to the Neponset River. In June 2012 the average temperature was 19°C with approximately 12 cm of rainfall throughout the month. While both cruises for spring had similar *in situ* CDOM production (20 QSU for April 2003 and

30 for June 2012), the discharge was higher in April 2003 (9.8×10^{11} l yr^{-1}) than in June 2012 (4.9×10^{10} l yr^{-1}), leading to a much higher total export (2.7×10^{8} mol C yr^{-1} for April 2003 versus 1.6×10^{7} mol C yr^{-1} for June 2012).

The spring snowmelt is known to cause a DOC pulse in freshwater systems, as seen in the Neponset Estuary. Khosh and McClelland (2014) observed peaks in both DOC concentrations and export fluxes during the spring snowmelt in the Arctic and noted that frozen ground and the snow matrix act to constrain melt-water to the soil surface. The restriction of flow could facilitate DOC export from senescent above ground vegetation and detritus contributing to a high export pulse. Singh et al. (2015) found higher concentrations of DOM during spring snowmelt season in terrestrial forests and attributed the pulse to an export in labile DOM associated with the hydrologic flushing of DOM that had accumulated in the soil over the dormant winter season. This phenomenon is also likely in the Neponset Estuary although possibly not captured by the small sampling size for the season.

Two cruises were conducted in winter: January 21, 2010 and January 13, 2013. The average CDOM concentration exported from the marsh during this season based upon these two cruises is 16 ± 15 QSU and approximately $4.4 \pm 7.1 \times 10^{7}$ mol C yr^{-1} are exported during the winter months alone from the Neponset Estuary (Table 2.2). Again, the error here is calculated with a 90% confidence interval and is large due to the low sampling size. In addition, the two cruises yielded a larger difference in *in situ* CDOM concentration production than during spring months (7 QSU in January 2010 versus 25 QSU in January 2013). For the 2010 cruise, CDOM production is near zero (7 QSU). This is expected as the plants have gone senescent for the winter. The average

temperature for January 2010 in Boston was -1.3°C, and 33.5 cm of snowfall fell during the month. However, for the 2013 cruise there is a strong CDOM production attributed to the salt marsh. January 2013 had an average temperature of -0.27°C and only 17 cm of snowfall (Blue Hills Observatory, 2015). The discharge rate in January 2010 was much higher due to the higher rates of both snowfall and rainfall (4.1×10^{11} l yr^{-1}) than in January 2013 (2.4×10^{9} l yr^{-1}), leading to a much higher total export (8.7×10^{7} mol C yr^{-1} for 2010 versus 7.0×10^{5} mol C yr^{-1} for 2013).

Through ten years of monthly watershed data, an overall trend was observed where winter months tended to have lower DOC concentrations throughout the watershed (Cialino, 2015). This is surmised to be for two reasons: (1) DOC concentration decreases due to lack of flow since a portion of the water is trapped in ice; and/or (2) DOC concentrations decreased with lower temperatures due to lower respiration rates. Even though watershed and salt marsh CDOM production is low in winter, export is high due to high discharges during the winter months.

Twelve cruises were conducted during the fall months (October, November, December). The average difference in endmembers over 12 cruises was found to be 45 ± 9 QSU (Table 2.2), resulting in an average export of $2.1 \pm 1.9 \times 10^{7}$ mol C yr^{-1}. Fall had the second highest contribution from the salt marsh and relatively low discharge in comparison to other seasons. During fall, marsh plants begin to senesce and "dump" a large proportion of DOC into the estuary, which then outwells to adjacent systems (Schiebel et al., *in prep*).

During summer months (July, August, September) and peak marsh plant growing season, relatively little DOC is being exported to adjacent estuaries. The average

difference in endmembers for the six cruises during this season is 65 ± 12 QSU (Table 2.2), resulting in an average DOC export of 1.2 ± 0.2 x 10^7 mol C yr^{-1}. Nineteen cruises with a smaller range in CDOM endmember concentrations and discharge rates provides less variability in the total export at the 90% confidence interval. While there was a large production of *in situ* CDOM, the discharge is the lowest for the summer months and so the smallest portion of carbon export for the year is also during this season.

The average export (considering all 35 cruises) from the Neponset Salt Marsh is 5.4 ± 8.6 x 10^7 mol C yr^{-1} or approximately 49 mol C m^{-2} yr^{-1} (Table 2.2). However, if the extreme outlier in April 2003 is removed the average export is 22 mol C m^{-2} yr^{-1}, which is within the range in the literature. Nixon (1980) reported the annual export of five marshes ranging from 0.7 – 11.7 mol C m^{-2} yr^{-1}. Dame et al. (1986) studied outwelling in a South Carolina inlet and found that DOC outwelling varied by season with highest outwelling in the summer (2.7 x 10^8 mol C yr^{-1}) and lowest outwelling in the spring (0.83 x 10^8 mol C yr^{-1}). The annual estimate of DOC flux in this inlet was 27 mol C m^{-2} yr^{-1}. Osburn et al. (2015) found rates of 11 mol C m^{-2} yr^{-1} for a North Carolina salt marsh.

A multiple linear regression showed that the two parameters that drive the marsh export (the difference between the actual and apparent endmember multiplied by the monthly discharge for each cruise) in the Neponset Estuary are temperature and day length (multiple R^2 = 0.43; p-value = 3.0 x 10^{-4}), both of which are major factors affecting plant senescence. Because temperature (p-value = 2.9 x 10^{-3}) had more of an impact on marsh export than day length (p-value = 0.27), a regression plot was created to analyze outliers (Figure 2.10).

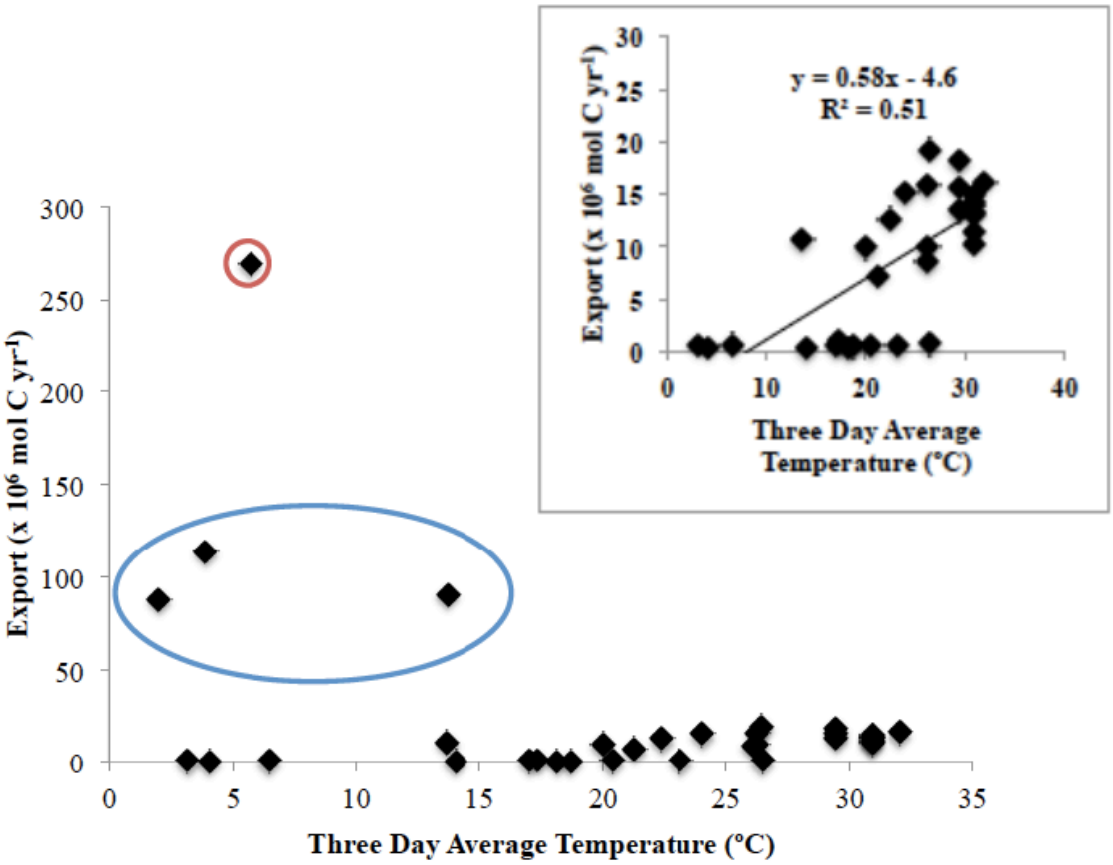


Figure 2.10. Linear regression of marsh export and temperature with outliers circled in red (2003) and blue (2009-2010) as well as regression with outliers removed (inset).

The four outliers identified all represented cruises with exceptionally high discharge rates. The 2003 cruise (Figure 2.10; circled in red) was conducted in April. The Blizzard of 2003 was in February of that year and it can be surmised that this was seen in the high discharge rate in April. With 70 cm of snowfall during the blizzard, it was the snowiest month in Boston's history to date. As temperatures rose in March and April, this snow melted and was released into the Neponset Estuary. The average discharge rate during April in the Neponset Estuary is 85 m/sec and in 2003 the discharge rate was 340 m/sec. This led to an exceptionally high marsh export rate and a high amount of

uncertainty in the cruises for spring since there were only two cruises conducted during that season. The other three cruises (Figure 2.10, circled in blue) were conducted between November 2009 and January 2010. The North American Blizzard of 2009 occurred in December 2009 with 28 cm of snowfall in Boston, contributing to a high discharge during this time and an unusually high export for this season. If these four outliers were removed from the regression, then the R^2 value increases to 0.51 (Figure 2.10, inset).

In the Neponset Estuary, as temperature and day length decrease, the export of DOC/CDOM from the marsh increases. This is consistent with the theory of the Fall Dump (Schiebel et al., *in prep*). As marsh plants begin to senesce in colder temperatures, they leach, or dump, a significant amount of DOC into the Neponset Estuary. Growing degree days (GDD) have been utilized extensively to predict the development phases of terrestrial plants and, more recently, some species of insects and zooplankton (Mackas et al., 1998; Gillooly, 2000; Neuheimer and Taggart, 2007). GDD are calculated as the integral over time (t) of temperature (T) above a threshold value (T_{Base}) that varies by species:

$$\mathrm{GDD} = \sum_{i-t_0}^{t} (T_i - T_{Base})\Delta t \qquad \text{Equation 2.5}$$

Where:

T = Temperature (°C)

T_{Base} = Temperature limit below which plant growth does not occur

T_{Base} has been shown to vary in perennial grasses from 4-10ºC, however no temperature thresholds have been yet identified in either *P. australis* (Bonhomme 2000; Moot 2010) or *Spartina spp.* (Lovat, 2013). Evidence suggests that T_{Base} in the Neponset River estuary is approximately 10ºC (Huang and Chen, 2009).

Alternate freshwater inputs

There are additional inputs of fresh water to the Neponset Estuary besides the Neponset River entering at Lower Mills Dam. Gulliver Creek is an ungauged source that provides a small addition of fresh water to the overall export. On several of the cruises, a small downturn in CDOM is observed when the mini-shuttle passes Gulliver Creek on an outgoing tide (Figure 2.11).

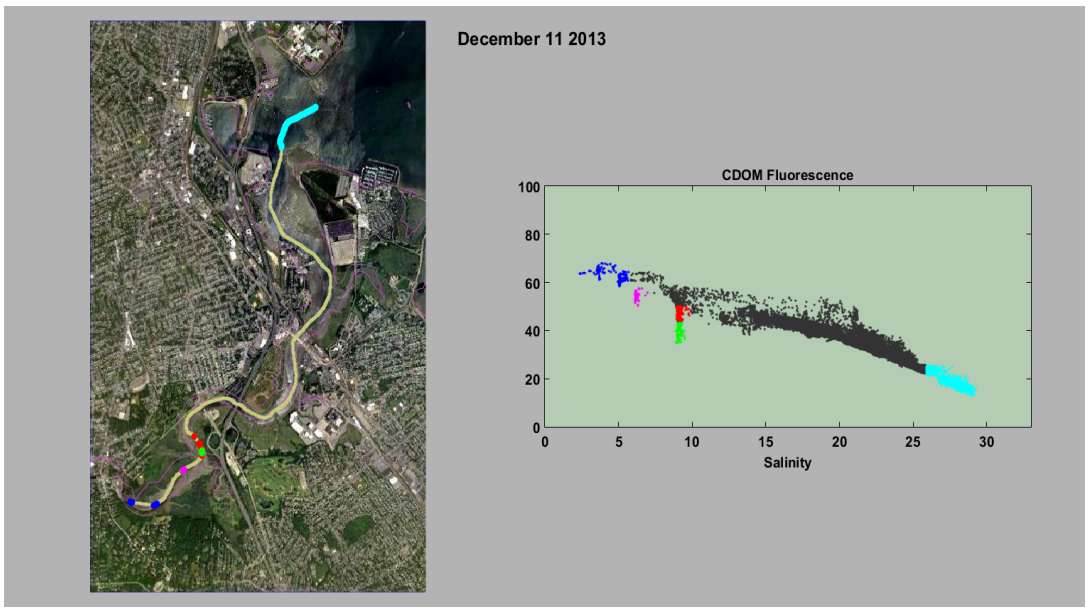


Figure 2.11. December 2013 cruise showing evidence of a small pulse contributing to the overall export near Gulliver Creek (shown in red/green).

Gulliver's Creek is mostly culverted, so does not acquire CDOM or DOC from any soils before it flows into the Neponset Estuary. If a water mass from Gulliver's Creek is seen by the Mini-Shuttle, it could have a different CDOM/salinity relationship, presumably with a lower CDOM at the same salinity. The rapid transition into this water mass would appear to connect the data from the mainstream Neponset to the Gulliver Creek water mass and could appear as a drop in CDOM at the same salinity (Figure

2.11). The Gulliver Creek water mass is rapidly tidally mixed into the background and would be observable only as a small deflection below the conservative mixing line of the tides and flows aren't conducive to maintaining the discrete water mass, so this distinct drop in CDOM/salinity is only seen on 4 of the 35 cruises. The significance of this observation, however, suggests that minor rivers and tributaries could affect CDOM and DOC distributions, but have only a minor effect on the overall export as estimated using differences in endmembers. In this instance, higher resolution observations allow discrimination between different freshwater inputs.

A second possible source of fresh water into the Neponset Estuary at nearly the same location is a Massachusetts Water Resources Authority (MWRA) standpipe on the opposite shore. Since its construction in 1975, the standpipe has steadily leaked fresh water into the Neponset River (Conuel, 1990). It has been estimated by the Department of Conservation and Recreation (DCR) that between one and two million gallons of fresh water are discharged daily into the Neponset Estuary from this standpipe (Conuel, 1990). The MWRA standpipe could contribute as little freshwater as 0.20% on a day with a high discharge rate (April 2003) or as much as 20% on a day with a low discharge rate (August 2002).

Long-term trends

The actual and apparent endmembers were calculated and plotted for each cruise to elucidate any long-term trends. September was the most often-surveyed month and so was the best choice to compare over time (Figure 2.12).

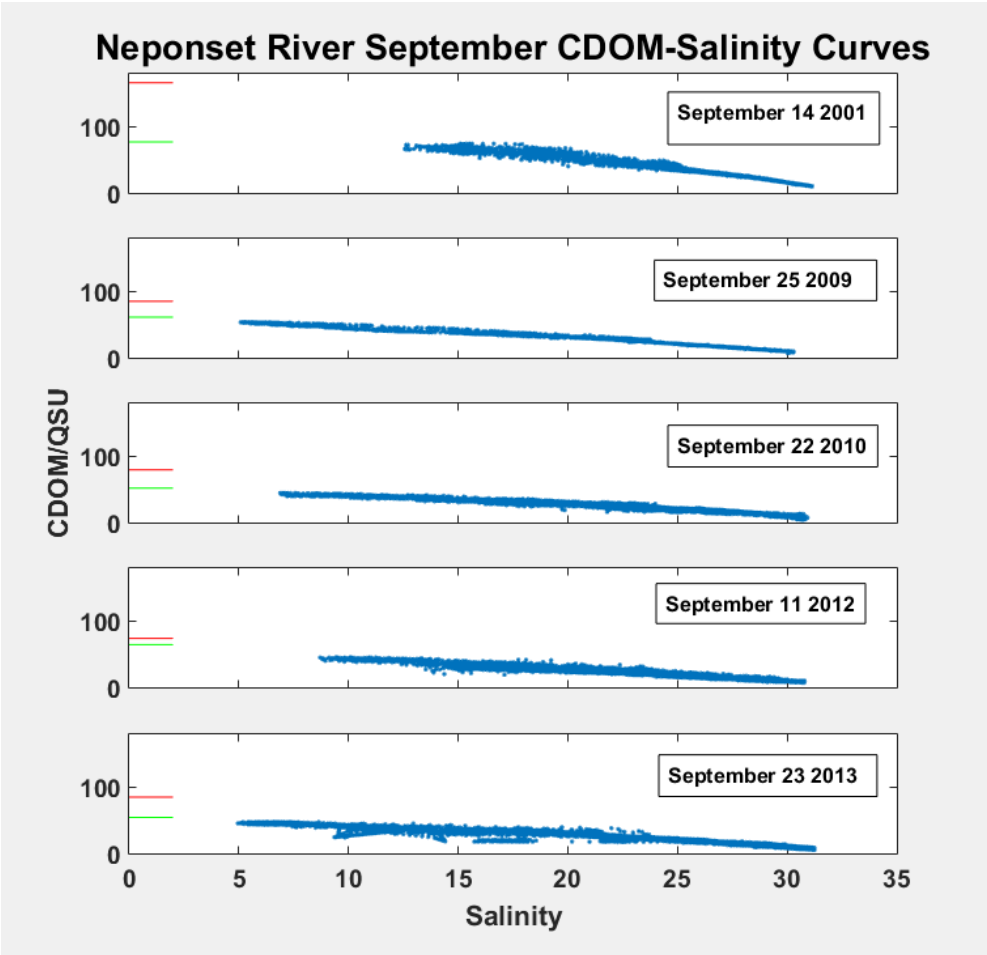


Figure 2.12. September CDOM/salinity curves for 2001, 2009, 2010, 2012, and 2013. CDOM values here are based on factory calibrations rather than discrete DOC samples (Seapoint CDOM fluorometer for 2001, 2009, and 2010; Turner CDOM fluorometer for 2012 and 2013).

Other than the first cruise (2001), all of the September cruises seem to follow the same general trend in CDOM concentrations and salt marsh inputs. It should be noted that the 2001, 2009 and 2010 cruises utilized a different CDOM sensor (Seapoint) than the 2012 and 2013 cruises (Turner) and this could account for a shift from 2010 to 2012. The largest difference between export, however, is from 2001 to 2009. In 2009, 2010, 2012, and 2013, the freshwater endmember was 86 ± 8.6 QSU, the apparent endmember

was 57 ± 13 QSU, and the salt marsh input was 29 ± 11 QSU. In 2001, the salt marsh input was 99 QSU, which is statistically higher.

There are a few reasons for this significant decrease in DOC export between 2001 and 2009. In the summer of 2005, the Great Meadows Farms contracting company, under the direction of the DCR restored 15 acres of the Neponset Salt Marsh (Perry, 2009). The dumping of creek sediments on the marsh due to dredging around 1960 had raised the height of the marsh by approximately 0.5 m such that salt water could no longer regularly flush the area, and the salt marsh environment was slowly dominated by the invasive *P. australis,* which prefers lower salinities (Perry, 2009). In 2005, several thousand cubic yards of the old dredge spoil deposits were removed from the marsh thus restoring salt water flushing tidally and eliminating *P. autralis* from this area. Preliminary data shows that the restoration exposed lower total organic carbon (TOC) concentrations in older sediments, which would explain the smaller carbon export as the restoration was completed on approximately 15% of the marsh flats (Bulpett, *unpublished data*). A similar mechanism could be occurring in the marsh over time that would lead to exposed sediments with lower TOC concentrations. Since the 1930s, mosquito ditches have been added to the Neponset Salt Marsh where ditches were dredged to lower mosquito populations (Perry, 2009). These ditches can erode away over time and it is possible that between 2001 and 2009 some of this erosion may have occurred. A final possibility for the lower export over time is the extensive proliferation of *P. australis*. The impacts associated with this invasion are an increase in sediment trapping and a decreased water flow due to its photosynthetic pathway (Gratton and Denno, 2005). Both of these processes could lead to less export from the marsh over time.

Conclusions

This study aimed to quantify the outwelling of DOC by way of high resolution *in situ* CDOM sensor observations in an effort to better understand the total carbon export from the Neponset Estuary. From 2001 through 2013, the seasonal export ranged from $1.2 \pm 0.2 \times 10^7$ mol C yr^{-1} for summer months to $14 \pm 21 \times 10^7$ mol C yr^{-1} in spring months with a total average export of $5.4 \pm 8.6 \times 10^7$ mol C yr^{-1} or approximately 49 mol C m^{-2} yr^{-1}. Temperature and day length along with freshwater discharge significantly affect the marsh DOC/CDOM export in the estuary. High-resolution observations reveal additional inputs of fresh water to the Neponset Estuary besides the Neponset River at Lower Mills Dam (Gulliver Creek, MWRA standpipe). The *in situ* CDOM production in the estuary has significantly decreased over time from 99 to 29 ± 11 QSU. This is attributed to several anthropogenic disturbances in the Neponset Salt Marsh, the dominant CDOM/DOC source in the Neponset Estuary. Additional CDOM transect measurements in winter and spring as well as observations over the course of a rapid change in hydrograph (i.e., storm) would help refine these export trends.

CHAPTER 3

DISSOLVED ORGANIC MATTER EXPORT FROM NEPONSET SALT MARSH GRASSES

Abstract

Salt marshes sequester large amounts of carbon via primary productivity and sedimentation. This study aimed to quantify and characterize the seasonal variation in chromophoric dissolved organic matter (CDOM) and dissolved organic carbon (DOC) leaching from plants in the Neponset Salt Marsh (Boston, Massachusetts). Incubations were conducted to monitor seasonal variation in CDOM/DOC leaching rates from *Spartina alterniflora*, *Spartina patens,* and *Phragmites australis*. Factors thought to affect carbon leaching from plant material were investigated. Sunlight, biomass type, and microbial treatments had significant effects on leaching rates, while anoxia and plant species treatments did not show consistent trends. Seasonal comparisons support the hypothesis of the "Fall Dump" in which higher DOC concentrations are leached during

the fall when marsh plants senesce for winter. Using experimental leaching rates, seasonal plant leaching fluxes ranged from 2.8-10 x 10^6 mol C $season^{-1}$ and an annual leaching rate of 25 x 10^6 mol C yr^{-1}. Using measurements for the total marsh export quantified from ship-based CDOM transects through the estuary, it is estimated that DOC leaching from the dominant plant species in the Neponset Salt Marsh may contribute approximately 45% of the total outwelling DOC flux.

This chapter is an extension of a publication currently in preparation for submission:

Schiebel, H.N., Wang, X., Peri, F., and R.F. Chen. Dissolved organic matter leaching from New England salt marsh grasses.

Author contributions to this dissertation chapter:

1. H. Schiebel collected and analyzed all samples, wrote the majority of the chapter, created all figures, and compiled all tables in the chapter.
2. X. Wang helped with experimental setup, and contributed to chapter edits.
3. F. Peri helped with experimental setup, and contributed to chapter edits.
4. R. Chen contributed to the chapter edits.

Introduction

Coastal blue carbon is a collective term for the climate change mitigation benefits provided by the biogeochemical processes naturally performed by salt marshes, mangroves, and seagrasses (Emmett-Mattox and Crooks, 2014). These systems sequester more carbon dioxide (CO_2) per area via primary productivity and sedimentation than their terrestrial counterparts (e.g., rainforests; McLeod et al., 2011). Salt marshes in particular have been estimated to bury 1.5-143 mol C m^{-2} yr^{-1} (McLeod et al., 2011). While other services provided by salt marshes have been known for quite some time in terms of valuation including habitats for biodiversity, storm and flood protection, and improved water quality (Pendleton et al., 2012), coastal blue carbon as an ecosystem service is more recently being quantified (Emmett-Mattox and Crooks, 2014). The loss of salt marshes from conversion and degradation has an estimated value of 3.6–19 billion $U.S. yr^{-1} on a global scale considering sequestration services alone (Pendleton et al., 2012).

Carbon burial in a salt marsh depends not only on primary productivity and respiration rates, but also the amount of carbon transported laterally from marshes to adjacent ecosystems. Odum (1980) noted that the productivity of nearshore waters can be enhanced not only by the upwelling of nutrients from bottom waters, but also from the outwelling of nutrients, organic matter, and organisms from fertile estuaries. In the two decades following the Outwelling Hypothesis, outwelling research was conducted at 41 sites and presented in 42 publications (Childers et al., 2000). However, out of these studies, very few have quantified estuary-coastal ocean exchanges (Valiela et al., 1978; Valiela and Teal, 1979).

While more studies are beginning to quantify estuary-coastal ocean exchange (inclusive of not only salt marsh ecosystems; Tzortziou et al., 2011; Duarte et al., 2014; Schiebel et al., 2014; Wang et al., 2014; Moyer et al., 2015), there are numerous reasons why directly testing the outwelling hypothesis has proven difficult. Sampling water flow and constituent concentrations in tidal channels connecting estuaries to the coastal ocean is complicated if the estuary is large, has multiple tidal channels, or is remotely located (Childers et al., 2000). As previously mentioned, there is a high rate of spatial and temporal variability within estuaries. Flux quantification precision, accuracy, and error are also highly variable (Childers et al., 1993; Deegan and Garritt, 1997; Childers et al., 2000; Pendleton et al., 2012).

Even fewer studies in the current body of literature have focused on the leaching flux from salt marsh grasses (versus the total flux; Wang et al., 2014). New England salt marshes are typically dominated by *Spartina alterniflora* (*S. alterniflora*) and *Spartina patens* (*S. patens*), but the invasion of *Phragmites australis* (*P. australis*) has proliferated in salt marshes along the east coast of the United States (Silliman and Bertness, 2004). *P. australis* has a different, less water-efficient photosynthetic pathway than *Spartina* species, has a higher aboveground biomass (AGB), and often results in less carbon within the sediment (Emery and Fulweiler, 2014). Its larger biomass also leads to a greater storage of carbon in AGB as well as altered litter dynamics (Windham, 2001).

Marine dissolved organic carbon (DOC) is one of the largest reservoirs of organic carbon at the Earth's surface (Hansell and Carlson, 2014). However, significant gaps in understanding both the transport and the biogeochemical cycling of DOC at the land-sea interface remain due to high spatial and temporal variability in this area (Alongi et al.,

2012; Wang et al., 2014). While their role in nutrient and carbon turnover is poorly constrained, it is clear that a high proportion of net primary production in coastal wetlands is introduced to the ocean as DOC (Fagherazzi et al., 2013; Barron et al., 2014).

Chromophoric dissolved organic matter (CDOM) is the optically measureable component of dissolved organic matter (DOM) and may be used as a proxy for DOC under certain conditions (Kowalczuk et al., 2003; Gardner et al., 2005). CDOM is believed to be important for most photochemically-mediated processes in surface waters and a major source of reactive oxygen species in marine waters (Del Vecchio and Blough, 2002; Chen and Jaffé, 2014). CDOM studies are becoming more prevalent in the field of remote sensing with algorithms that enable CDOM to be directly estimated from space (Aurin and Dierssen, 2012; Fan and Warner, 2014; Brezonik et al., 2015). CDOM interferes with the remote sensing of chlorophyll as an indicator of primary production (Aurin and Dierssen, 2012; Le et al., 2013) and can be used as a tracer of riverine organic carbon inputs to the ocean (Fichot and Benner, 2012; Granskog et al., 2012).

Methods

Study site

The Neponset River is located in Boston, Massachusetts. The watershed draining into the Neponset River covers approximately 3.0 x 10^6 m^2 and watershed contributions originate from areas within 14 cities and towns populated by roughly 330,000 people. The Neponset River is the second largest river entering into Boston Harbor after the Charles River. The estuary has a semi-diurnal tidal cycle with an average tidal excursion of approximately 3 m and is fringed by the 1.1 x 10^6 m^2 Neponset Salt Marsh. The

Neponset Salt Marsh is predominantly covered by the invasive reed, *P. australis,* and two native species of *Spartina*: *S. alterniflora* (low marsh, inundated twice daily) and *S. patens* (high marsh, inundated during spring tides).

Sunlight irradiation incubations

Four incubations were conducted in Summer 2012 (summer), Fall 2012 (fall), Winter 2013 (winter), and Spring 2013 (spring) to measure seasonal variation in CDOM and DOC leaching rates from *S. alterniflora* and *S. patens*. Plant biomass was collected at a designated site in the Neponset Salt Marsh so that collections for each season came from within the same 100 m^2 area for each experiment. Samples were collected by hand and taken back to the lab where they were cleaned to remove all sediment and then separated into either AGB or belowground biomass (BGB). Clean sample splits were dried so water content could be measured and wet weights could be converted to dry weights. Ten wet grams of wet, cleaned samples were placed directly into 1-liter Teflon bottles filled with one liter of Boston Harbor seawater with a relatively low CDOM (approximately 20 QSU) and DOC (approximately 250 μM) concentration to begin each incubation (Day 0). Samples were placed in either clear Teflon bottles (99% transmission of visible and UV light > 300 nm wavelength) or opaque Teflon bottles (0% transmission) to examine the effect of sunlight on carbon leaching. Half of all samples were poisoned by adding 2.0 ml of saturated $HgCl_2$ solution to determine the microbial effects (inclusive of bacteria and fungi) on carbon leaching.

Experiments were conducted for eight days. Plant decomposition generally occurs in three phases: rapid leaching, slow decomposition, and stabilization (Chapin et al.,

2011), and experiments were designed to encompass the initial release of carbon from plant matter (Chapin et al., 2011; Wang et al., 2014). Temperature and photosynthetically active radiation (PAR) were monitored continuously with sensors. All sample bottles were placed in a water bath to maintain a constant temperature of 26 ± 1^0C by running tap water through the water bath continuously. All samples received approximately 9 hours (08:00 to 17:00 EST) of full sunlight irradiation per day. Discrete duplicate samples were taken on Days 1, 2, 3, 4, 5, and 8. An additional incubation comparing the leaching rates of *S. patens* and *P. australis* was conducted in Summer 2014 using the same methods.

Anoxia incubation

Because BGB is often exposed to anoxic conditions while AGB is normally degraded under oxic conditions in blue carbon systems (Trevathan-Tackett et al., 2015), an incubation was conducted in Summer 2013 to analyze the impacts of anoxia on plant leaching. Approximately twenty-five grams of wet weight biomass (AGB and BGB was separated similarly to the sunlight irradiation incubations with sample splits taken for a wet-dry conversion) was added to 2 liters of Boston Harbor water with relatively low CDOM (approximately 20 QSU) and DOC (approximately 250 μM) concentrations to begin the incubation (Day 0). Two-liter Pyrex bottles were utilized for this experiment to eliminate oxygen permeability and to include more plant matter so that anoxia was induced more rapidly. Half of the samples were kept oxic by continuously bubbling oxygen through an all-Teflon tubing system. Half of all samples were poisoned by adding 2.0 ml of saturated $HgCl_2$ solution to determine microbial influences on plant matter

DOC leaching. This incubation was continued for twenty-one days with discrete sampling on Days 1, 2, 3, 4, 5, 8, 12, 15, 18, and 21, running longer than sunlight irradiation experiments to ensure rapid leaching was complete and slow decomposition of plant biomass had begun.

Sample analysis

After collection (for all incubation samples), each sample was filtered through a pre-combusted 0.7 μm glass fiber filter (Whatman GF/F). DOC samples were filtered into pre-combusted (4 hours at 500°C) 40 mL borosilicate glass vials with Teflon-lined screw caps, acidified to pH < 2 using phosphoric acid, and refrigerated until analysis. DOC concentrations were measured using a Shimadzu TOC-V analyzer equipped with an autosampler. The instrument was calibrated using 5-point carbon calibration curves and carbon standards were prepared using potassium hydrogen phthalate (KHP). All standards and samples were injected in triplicate. Injections were generally within 2% of each other and duplicate samples within 5%. Instrument blank and DOC values were checked against reference low carbon water and deep seawater (Carbon Reference Materials (CRM), University of Miami, Rosenstiel School of Marine and Atmospheric Sciences). Blank subtraction was conducted using Milli-Q water, which was analyzed at set intervals (every 10 samples) during sample analysis.

CDOM fluorescence was measured using a Photon Technologies International QM-1 spectrofluorometer. Single fluorescence emission scans from 350 to 650 nm were collected for an excitation wavelength of 337 nm. The fluorescence of Milli-Q water was determined as a blank on each day of analysis and subtracted from sample spectra prior to

integration. Peak areas were integrated and converted to quinine sulfate units (QSU) where 1 QSU is equivalent to the fluorescence emission of 1 μg/l quinine sulfate solution (pH 2) integrated from 350 to 650 nm at an excitation wavelength of 337 nm (Chen and Gardner, 2004). All sample data were collected using a 1-cm quartz cuvette and expressed in quinine sulfate units (QSU). Samples above 100 QSU were diluted with Milli-Q water prior to analysis (or re-analysis) to minimize internal quenching in the samples. All glassware used for sample collection, storage, and analysis was acid-cleaned and baked at 500°C for 4 hours. To confirm that CDOM could be used as a proxy for DOC here, a CDOM/DOC plot was constructed for each incubation.

Samples for all experiments were taken in duplicate and duplicates were statistically similar. All results reported are normalized by dry weight material taken at the beginning of each experiment with baseline water concentrations subtracted per gram dry weight plant material. Due to the small sampling size for each treatment, student t-tests were used to determine if different treatments were statistically significant with p-values included for either 1- or 2-tailed distributions depending on previous findings in the literature: if an outcome was expected, a 1-tailed distribution was used; if an outcome was unknown, a 2-tailed distribution was used. All standard errors and t-tests were completed assuming a 95% confidence interval. It should be noted that the leaching rates described below represent exponentially fitted rates found using experimental data while the term “leachate” represents the concentration in incubation bottles at the end of each experiment (8-21 days depending on treatment) and was used to compare experimental variables). Additionally, figures provided in this chapter represent overall trends:

additional figures from all treatments as well as statistical results can be found in Appendix B.

Results

Of the five treatments tested in this study, anoxia and species type yielded no consistent trends in plant leaching rates (Figure 3.1), while three treatments had significant effects on plant leaching rates: sunlight, type of plant matter, and microbes (Figure 3.2).

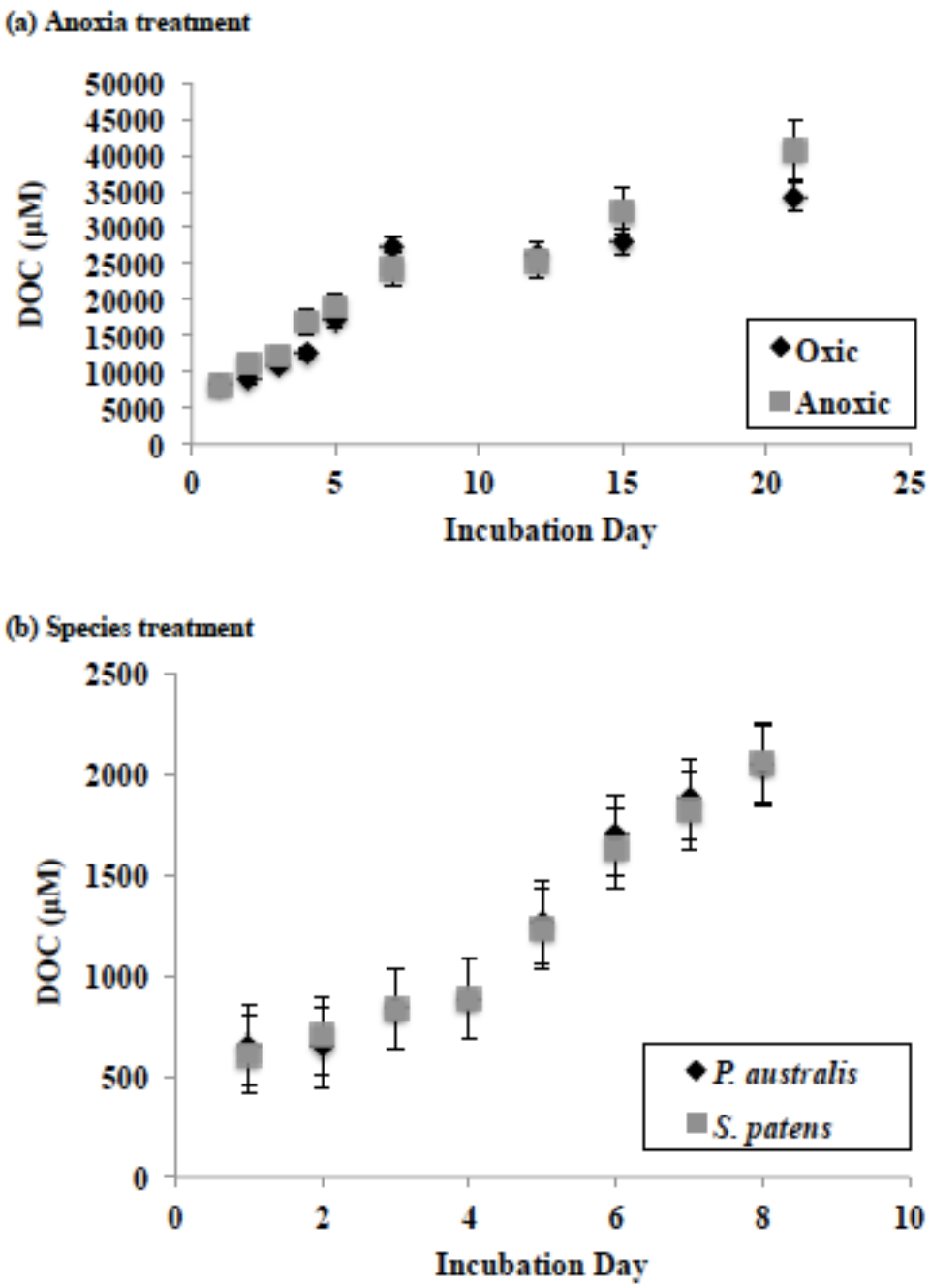
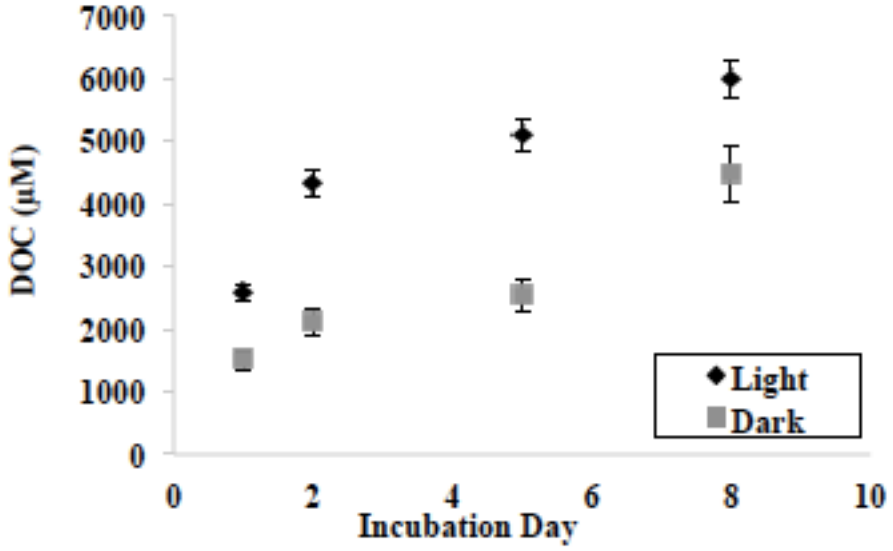
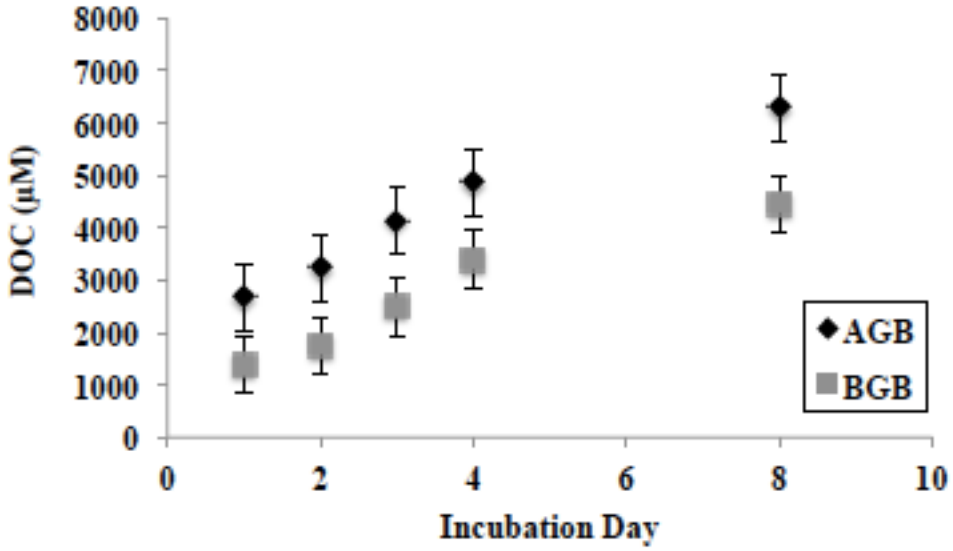


Figure 3.1. Treatments that yielded no significant difference in plant DOC leaching rates. (a) Oxic and anoxic non-poisoned *S. alterniflora* BGB not exposed to sunlight from summer 2013; (b) Non-poisoned *S. patens* and *P. australis* AGB not exposed to sunlight leaching concentrations from summer 2014.

(a) Sunlight treatment



(b) Biomass type treatment



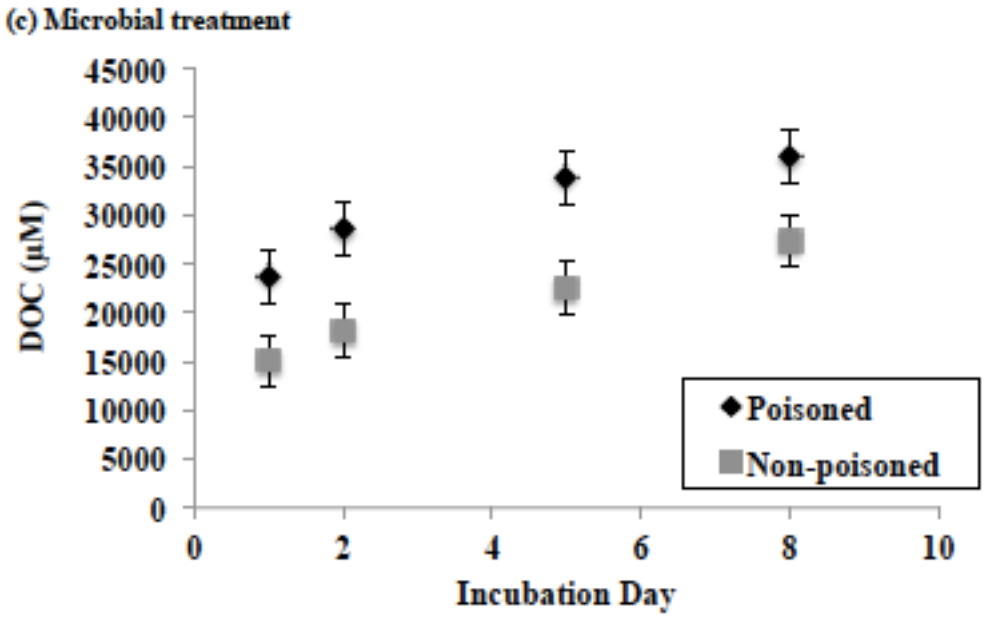


Figure 3.2. Treatments that yielded a significant difference in plant DOC leaching rates. (a) Poisoned *S. alterniflora* AGB exposed versus not exposed to sunlight from winter 2013; (b) Poisoned *S. patens* AGB and BGB not exposed to sunlight in spring 2013; (c) Poisoned and non-poisoned *S. alterniflora* AGB not exposed to sunlight during fall 2012.

Composition

CDOM/DOC relationships were compared among all non-poisoned samples exposed to sunlight during the four seasonal irradiation incubations to the background CDOM/DOC relationship in the Neponset Estuary from cruise transects completed in 2012 (Chapter 2; Figure 3.3).

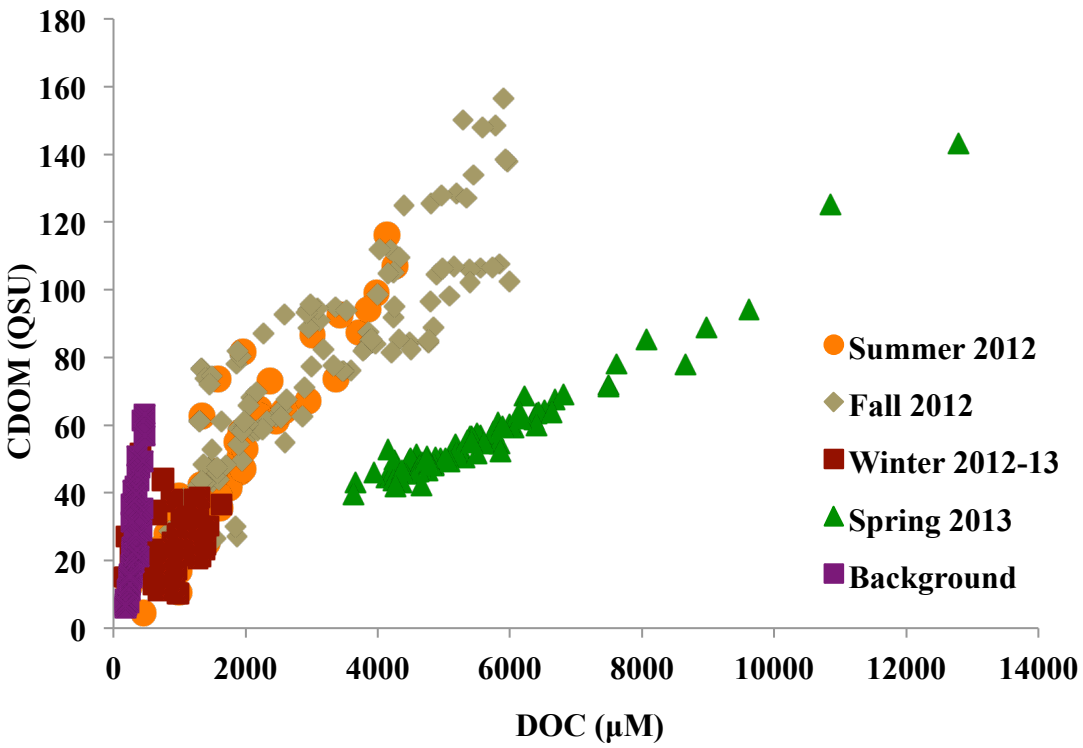


Figure 3.3. CDOM/DOC relationships for four seasonal sunlight irradiation incubations and the Neponset Estuary. Background represents the estuary CDOM/DOC ratio from 2012 cruise transects (Chapter 2). The incubation samples are all non-poisoned samples exposed to sunlight by season.

Plotting the concentrations of CDOM against the concentrations of DOC for a sample yields a correlation and also relates to the quality of DOC in a system. DOM that is fresher, more pigment-like, and more aromatic has a higher CDOM/DOC ratio. Carbohydrates, saturated hydrocarbons, cellulose, and photodegraded DOM have lower CDOM/DOC ratios. The CDOM/DOC ratio can get higher as material becomes more humified and marine bacteria can make more CDOM as the degrade particles (Harvey et al., 2015). For the plant experiments here, the spring incubation had the lowest CDOM/DOC ratio. During the growing season, marsh plants are releasing mostly cellulose and retaining nitrogen-containing molecules (i.e., pigments), leading to less colored material leaching from the plants. The background CDOM/DOC ratio in the

estuary is more colored than any of the incubations. This suggests that plant contributions are mostly carbohydrates and relatively low in color. Further, the background estuary water has different composition that the incubation samples. It can be surmised that the DOM leaching from plants is not the majority of the DOM in the estuary based on the CDOM/DOC relationships seen here.

Anoxia

The Summer 2013 incubation was conducted to compare the effect of anoxia on DOC leaching rate (Figure 3.1a; Appendix B). Bottles that were allowed to go anoxic (no bubbling) turned black and had a noticeable sulfide odor after Day 12. Due to variability across treatments and within species, it was deduced that there was no consistent trend regarding anoxia and carbon leaching rate for the species studied here.

Species

In comparing the seasons in both poisoned versus non-poisoned samples of *S. alterniflora* and *S. patens*, there was no significant trend across treatments by species (Figure 3.1b; Appendix B). Additionally, for every treatment during the Summer 2014 experiment, *S. patens* and *P. australis* did not leach significantly different amounts of DOC (p-values ranging from 0.32 to 0.87).

Sunlight

Across all seasons, species, and biomass type (AGB/BGB), samples exposed to sunlight leached more carbon than control samples (opaque Teflon bottles; Figure 3.2a; Appendix B). The influence of sunlight increasing leaching rates is consistent with

previous studies with salt marsh grass samples from the Neponset and Florida's Snipe Creek (Schiebel et al., 2014).

Biomass type

AGB leached significantly more carbon than BGB, suggesting lability is an important factor in DOC leaching from marsh grasses (Figure 3.2b; Appendix B). The two exceptions to this trend were Winter 2013 (88.9 ± 7.3 x 10^{-4} mol C versus 13.9 ± 2.4 x 10^{-4} mol C; p-value=0.0014) and Spring 2013 (75.2 ± 7.5 x 10^{-4} mol C versus 61.0 ± 2.2 x 10^{-4} mol C; p-value=0.035). Both poisoned and non-poisoned *S. alterniflora* biomass samples collected during the Summer 2012 experiment leached similar rates of carbon (p-value=0.38 for poisoned and 0.18 for non-poisoned).

Microbial contribution

It is important to note that direct microbial abundance measurements were not taken for this experiment. Rather, the effect of microbes on leaching rate was investigated for overall trends. Additionally, the process of microbial production of leachable DOM and the degradation of leached DOM are two different processes. The results here represent the sum of these processes (Figure 3.2c; Appendix B). For both *S. alterniflora* and *S. patens* across all seasons, poisoned samples without microbes leached significantly more carbon than non-poisoned samples where microbes were present in the incubation samples (p-values ranging from 0.0011 to 0.0094). These incubations were conducted in 1-liter Teflon bottles filled with unmixed seawater, thus natural salt marshes with frequent water exchange and turbulence might be expected to leach more carbon than under these experimental conditions. While this study revealed that the leachate here was

generally a more labile form of DOC, field-measured DOC concentrations are probably more refractory, and so the approximations presented herein could be overestimated. Additionally, the $HgCl_2$ utilized to kill microbes in poisoned samples could have two effects: (1) $HgCl_2$ could lyse bacterial cells and solubilize bacteria to DOM; and (2) $HgCl_2$ could degrade plant tissues in the bottles.

Seasonal leaching fluxes

A major goal of this study was to characterize the "Fall Dump" where salt marsh plants begin to senesce for winter and "dump" a large proportion of carbon into surrounding ecosystems (Figure 3.4).

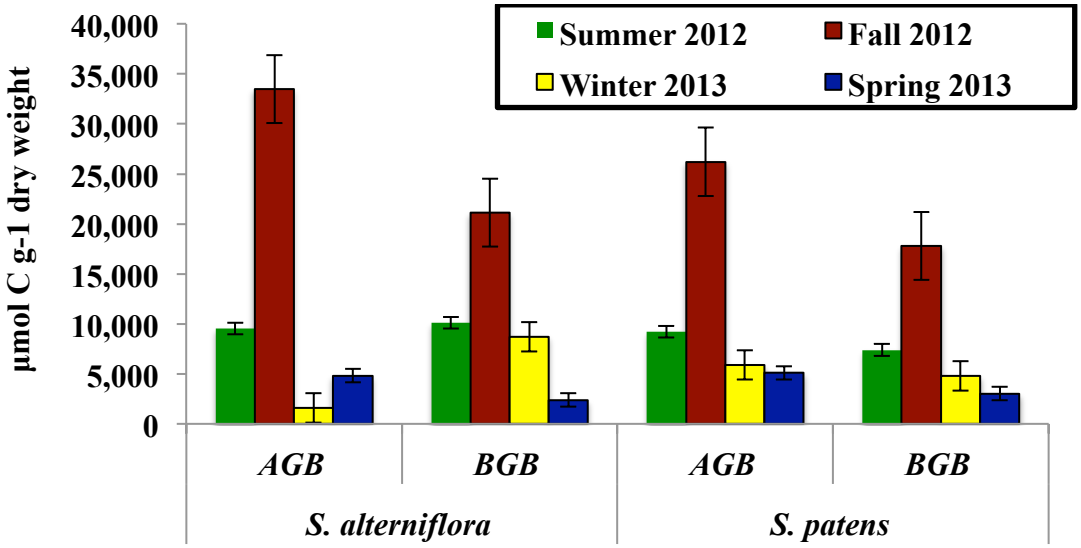


Figure 3.4. Concentration of DOC leached at the end of the incubation (per g dry weight original plant material) for *S. alterniflora* and *S. patens* AGB and BGB by season (standard error plotted at 95% confidence intervals). The samples used to characterize this trend were all non-poisoned samples exposed to sunlight to mimic realistic marsh conditions. *P. australis* was omitted since all four seasons were not studied.

While plants had the highest leaching concentrations during the fall, plants also leached a large concentration of DOC in the summer. The spring and winter incubation

samples provided a minimal pulse of DOC to adjacent systems. Upon comparing all treatments by season, the Fall Dump trend was found to be statistically significant in the Neponset Salt Marsh (Table 3.1).

Table 3.1. Leaching concentrations at the end of the sunlight irradiation incubations (normalized by biomass) per experiment (8 days) as evidence for Fall Dump hypothesis in the Neponset Salt Marsh by species for non-poisoned AGB and BGB samples exposed to sunlight (mean ± SE). P-values are reported from t-tests using one-tailed distributions.

Species	Biomass	Season	(x 10^{-4} mol C)	P-Value
S. alterniflora	BGB	Fall 2012	**211 ± 2**	N/A
		Summer 2012	101 ± 0	0.0001
		Spring 2013	23.7 ± 3.5	0.0001
		Winter 2013	87.2 ± 4.1	0.0002
	AGB	Fall 2012	**335 ± 40**	N/A
		Summer 2012	95.5 ± 1	0.0036
		Spring 2013	48.1 ± 8.6	0.0026
		Winter 2013	15.8 ± 0.02	0.0020
S. patens	BGB	Fall 2012	**178 ± 3**	N/A
		Summer 2012	73.8 ± 4.6	0.0004
		Spring 2013	30.2 ± 0.04	0.0001
		Winter 2013	47.7 ± 1.7	0.0001
	AGB	Fall 2012	**262 ± 4**	N/A
		Summer 2012	92.2 ± 2.7	0.0001
		Spring 2013	51 ± 2.4	0.0001
		Winter 2013	59.1 ± .09	0.0001

For the species studied here, the DOC leached during the fall was significantly higher than any other season (p-values ranging from 0.0001 to 0.0036). These leaching rates represent maximum rates for two reasons. First, the plants were cut in the marsh in order to fit into the incubation sample bottles, which could induce leaching from plant matter. Second, the temperature was controlled in all four seasonal incubations with the use of a water bath. If the temperature had been changed seasonally to represent that of the estuary throughout the year, then microbial activity would be different and lead to

different leaching rates. As such, these incubations investigated the seasonality in plant phenology, not microbial activity.

Discussion

Anoxia

Studies have found that organic matter degradation is more rapid under oxic conditions than under anoxic conditions (Harvey and Nuttle, 1995; Lehmann et al., 2002). Wang et al. (2007) found that CDOM produced from *S. patens* was degraded more rapidly in oxic waters than in anoxic waters. However, the results in the literature are mixed as to how much anoxia affects the release of DOM. Griffiths et al. (2000) investigated the release and bioavailability of DOM from terrestrial litter under different oxygen levels and found that the amount metabolized was independent from the amount of oxygen available (0.004 - 0.007 mol DOC g^{-1} for leaf matter). Moore and Dalva (2001) compared maple trees, *Sphagnum* moss, and different peat samples and elucidated that there was no significant difference between DOC release under oxic and anoxic conditions using a similar incubation technique. Because DOC is well correlated to microbial activity (Andersson and Nilsson, 2001; Moore and Dalva, 2001; Farjalla et al., 2006), lower DOC production should occur under anoxic conditions.

In the current experiment in the Neponset Salt Marsh, results for the effects of anoxia on leaching are mixed (Appendix B). As mentioned, decay of salt marsh grass litter occurs in three phases (Valiela et al., 1985). The first phase lasts les than ten where 5 to 40% of the litter is lost, and the rapid release of biomolecules occurs during microbial mediated hydrolysis (Valiela et al., 1985). The biomass lost in these

experiments was consistent with the first phase of decay (approximately 5% for sunlight and 10% for anoxia incubations). A second, slower phase lasts up to a year where microbial degradation of organic matter and subsequent leaching of hydrolyzed substances removes an additional 40 to 70% of the original material. Finally, a third phase may last an additional year or longer characterized by slow decay of only relatively refractory materials remaining. By this third stage as little as 10% of the original material may remain (Lee, 1980; Valiela et al., 1985; White and Howes, 1994). The incubations presented here examined only the first phase, as seasonal pulses reflect only short-term processes. DOC production might be higher under anoxic conditions, but would also likely be offset by less microbial degradation of DOM. The Neponset Salt Marsh experiments presented here measured only the net effect of microbial contributions to bio-production of DOM and bio-degradation of DOM (Appendix B).

Species

In New England salt marshes, the most noticeable plant zonation pattern occurs at the mean high water line, separating the low and high marsh habitats (Nixon, 1982). *S. alterniflora* is a cord grass exclusively dominating low marsh habitats, while the high marsh is dominated by dense growth of *S. patens*. Both *Spartina* species are C_4 plants, which have a more elaborate photosynthetic pathway than that of C_3 plants. This adaptation evolved in response to high light intensities, high temperatures, and dryness (Edwards et al., 2010). Most of the leaching and decomposition studies comparing marsh plants have implemented litter bags and investigated long-term decomposition rates. Gallagher et al. (1976) found that the carbon added to the DOC pool from *S. alterniflora*

leaves alone contributed up to 0.51 mol C m^{-2} yr^{-1}. Marinucci (1982) studied *Spartina* litter decomposition and found that 20-25% of the carbon was leached as DOC in the initial phase of decomposition with a steady loss of 2.1 x 10^{-4} mol C day^{-1}. *S. alterniflora* was studied in a Georgia salt marsh and found to leach 10-12% of its biomass over eight month incubations. The leaching concentrations found for the species studied in the Neponset Salt Marsh were consistent with those previously reported in the literature (1.8 - 45 x 10^{-4} mol C day^{-1}, depending on season and species) with higher leaching concentrations in autumn for *Spartina spp*. (Appendix B).

Sunlight

The influence of sunlight on DOM quantity and quality has been examined for many years with mixed conclusions (Arnon and Benner, 1996; Moran and Zepp, 1997; Benner and Biddanda, 1998; Zepp et al., 1998, 2002; Ziegler and Benner, 2000; Mayer et al., 2012). Photochemical reactions in aquatic systems induced by the absorption of solar radiation can alter the chemical structure and optical properties of DOM and thus play an important role in carbon and nutrient cycles in coastal waters (Zepp et al., 1998; Ziegler and Benner, 2000; Schiebel et al., 2014). Several studies have shown that exposure to sunlight degrades larger molecules into smaller products that can be removed either via direct volatilization of carbon gases or through rapid microbial degradation (Kieber et al., 1990; Mopper et al., 1991; Miller and Zepp, 1995; Wetzel et al., 1995; Graneli et al., 1996). CDOM can undergo important photo-induced processes such as photolysis of higher molecular weight into lower molecular weight compounds (Wang et al., 2009), generation of free radicals (Sandvik et al., 2000), photo-mineralization (Evans et al.,

2007), or photo-bleaching (Shank et al., 2010) as well as the formation of biologically labile compounds which are more readily usable for auto- and heterotrophic activity (Moran and Zepp, 1997).

Studies involving the photo-dissolution of particulate organic matter (POM) have also been documented. POM can absorb light at similar wavelengths as DOM, breaking down larger molecules into smaller molecules that allow for the transfer of POM into DOM (Mayer et al., 2006; Kieber et al., 2007). Shank et al. (2011) exposed suspended sediments from Florida to sunlight for 24 hours and found six-fold increase in DOC concentrations. Additionally, Pisani et al. (2011) quantified the amount of DOM that was photo-produced from flocculent material in the Florida Everglades. They found that under dark conditions, DOC increases were minimal while samples exposed to artificial sunlight leached up to 0.022 mol C g^{-1}. King et al. (2012) noted that increasing litter exposure to solar radiation increased mass loss by 23%. It was demonstrated in the current study that sunlight enhances the dissolution of organic carbon from vegetation by 6-50% depending on species and season, producing a larger amount of DOC for leaching in the Neponset Salt Marsh (Appendix B).

Biomass type

The decomposition of plant biomass is dependent upon the biomass composition (Enriquez et al., 1993) as well as environmental factors such as temperature, water availability, and nutrient availability. Kenworthy and Thayer (1984) found that during the early stages of decay, BGB leaches soluble organic matter that is readily usable by microbes. Griffiths et al. (2000) found that the amount of DOC leached after 29 days

from terrestrial leaf litter was much higher than any other portion of the plants investigated (bark, twigs, roots). Holmer and Olsen (2002) investigated the decomposition of seagrass and mangrove AGB and BGB. After 43 days, seagrass AGB was rapidly decomposed while no decomposition could be detected for seagrass rhizome detritus. Similarly, Fourqurean and Schrlau (2003) measured decomposition rates of mangroves and seagrasses using litterbags. Seagrass AGB had a higher percentage of biomass in the labile pool (57%) than did seagrass BGB (29%). Further, they noted that the decomposition rate of the starting material reflected the fractionation in labile and refractory components and that nutrient availability had no influence on the decomposition rates. In the Neponset Salt Marsh system, AGB leached more carbon than BGB, suggesting lability has a strong influence on DOC leaching (Appendix B).

Microbial contribution

In comparison with other ecosystems, salt marsh sediments have some of the highest rates of heterotrophic microbial activity, and it is documented that many microbial processes in the sediment are closely linked to the functioning of marsh plants (Howarth, 1993; Hemminga et al., 1996). Maie et al. (2007) found that up to 61% of the leached DOC from several different wetland and estuarine plant species was removed by microbes within the first three days of an incubation. Lignocellulose from aquatic vascular plants such as these is the most abundant accessible reservoir of organic material as it is indigestible to most invertebrate marsh species (Moran and Hodson, 1990), but is readily available to microbes. Buchan et al. (2003) studied the effects of both bacteria and fungi on *S. alterniflora* in a southeastern U.S. marsh and found that both played a critical

role in the decomposition process. During the first two decomposition phases (days to years), microbes were shown to rapidly degrade plant matter. Alkemade et al. (1993) studied *Spartina anglica* decomposition by bacteria and concluded that the majority of plant degradation occurred at the production site by bacteria. The population of bacteria on dead and dying plant matter was much higher (1400 individuals per gram of dry weight matter) than in green, photosynthesizing AGB (100 individuals per gram of dry weight matter). Implementing similar incubation techniques to determine the relative contributions of bacteria to degradation rates of *S. alterniflora*, Benner et al. (1984) found that after 23 days, 10% of the lignin component and 20% of the polysaccharide component of plant matter was degraded by bacteria. Similarly, Moran and Hodson (1990) found that up to 40% of the total lignocellulose was mineralized by bacteria in both marine and freshwater estuary systems. Wang et al. (2014) found a DOC leaching rate of 1,600-7,200 μM C per gram of dry weight per day in bacteria-inhibited samples and a much lower apparent rate of 800-1,200 μM C per gram of dry weight per day in bacteria-active samples, which is consistent with the findings here that bacteria can rapidly degrade labile leached DOM. This is also true in the Neponset Salt Marsh; microbes play a strong role in the amount of carbon leached for both *S. alterniflora* and *S. patens*, regardless of season (Appendix B).

Seasonal leaching fluxes

A seasonal leaching flux of DOC from salt marsh plants was estimated based on the growth phases of *Spartina spp*. in New England (Table 3.2).

Table 3.2. Four growth phases over one year for *Spartina spp*. in New England based upon first and last frost days of the year in 2012 and vegetation observations.

Growth Phase	Months	Incubation Month	Length (Days)
Pre-growth	April 26– June 30	June	65
Peak growth	July 1 – October 14	August	105
Senescence	October 15– December 30	November	76
Dead	January 1 – April 25	January	114

These values were derived from 2012 frost dates and marsh vegetation observations. Pre-growth (April 26 through June 30) comprised the June 2012 (spring) incubation and began from the date of the last freezing day in Boston through marsh observations of a significant increase in AGB. Peak growth (July 1 through October 14) contained the August 2012 (summer) incubation since October 14 was the first day of brown vegetation observations in the marsh. Senescence (October 15 through December 30) comprised the November 2012 (fall) incubation and was characterized as the time the marsh senesced through the first freeze of the year. Finally, the dead phase (December 31 through April 25) encompassed the January 2013 incubation (winter).

In order to estimate the leaching flux from salt marsh grasses in the Neponset Salt Marsh, the below equations were used:

$$PLF = \sum PLF_{Growth\ Phase} \qquad \text{Equation 3.1}$$

$$PLF_{Growth\ Phase} = L_{\%} * NPP * SAC * BR * I \qquad \text{Equation 3.2}$$

Where:

PLF = Plant leaching flux (mol C yr^{-1})

PLF_{Season} = Plant leaching flux (mol C growth $phase^{-1}$)

L_{RATE} = Experimental percent leached

NPP = Net primary productivity (mol C m^{-2} growth $phase^{-1}$)

SAC = Species area coverage (m^2)

BR = Biomass ratio (BGB or AGB/total biomass)

I = Inundation multiplier

Determining the seasonal experimental leaching rate was accomplished by using an exponential biomass decay fitted to the experimental biomass decay and extrapolated to the duration of the season/growth phase for each biomass type (AGB or BGB) for *S. alterniflora, S. patens*, and *P. australis*. Only non-poisoned samples exposed to sunlight were utilized to mimic realistic marsh conditions and thus leaching rates were calculated (Table 3.3).

Table 3.3. Biomass decay equations (where D = decay concentration and t = time) and leaching rates for both AGB and BGB using data for non-poisoned samples exposed to sunlight.

Species	Biomass Type	Season	Equation	R^2 Value	Leaching Rate
S. alterniflora	BGB	Peak Growth	$D = (2.0 \times 10^5)^{e-0.007t}$	0.91	0.52
		Senescence	$D = (2.0 \times 10^5)^{e-0.015t}$	0.86	0.68
		Dead	$D = (2.0 \times 10^5)^{e-0.002t}$	0.94	0.20
		Pre-growth	$D = (2.0 \times 10^5)^{e-0.0003}$	0.91	0.019
	AGB	Peak Growth	$D = (1.1 \times 10^5)^{e-0.007t}$	0.94	0.74
		Senescence	$D = (1.1 \times 10^5)^{e-0.037t}$	0.99	0.97
		Dead	$D = (1.2 \times 10^5)^{e-0.0004t}$	0.84	0.43
		Pre-growth	$D = (1.1 \times 10^5)^{e-0.002t}$	0.87	0.52
S. patens	BGB	Peak Growth	$D = (2.2 \times 10^5)^{e-0.001t}$	0.99	0.0096
		Senescence	$D = (2.3 \times 10^5)^{e-0.01t}$	0.89	0.46
		Dead	$D = (2.2 \times 10^5)^{e-0.0004t}$	0.74	0.051
		Pre-growth	$D = (2.3 \times 10^5)^{e-0.0009t}$	0.99	0.085
	AGB	Peak Growth	$D = (1.2 \times 10^5)^{e-0.01t}$	0.95	0.79
		Senescence	$D = (1.2 \times 10^5)^{e-0.029t}$	0.99	0.93
		Dead	$D = (1.2 \times 10^5)^{e-0.015t}$	0.84	0.89
		Pre-growth	$D = (1.2 \times 10^5)^{e-0.005t}$	0.98	0.57

For example, for *S. alterniflora* BGB in the summer (peak growth phase), approximately 2.0 x 10^5 mol C (dry weight) were placed into the incubation bottle on Day 0 of the incubation. After 8 days, 1.9 x 10^5 mol C remained in the bottle using experimental data. Using the exponential decay function with 65 days as the input yields 9.6 x 10^4 mol C remaining if the incubation was extrapolated to the entire growth phase (65 days). The leaching rate was obtained by using the below equation:

$$\text{Leaching Rate} = \frac{B_I - B_F}{B_I} \qquad \text{Equation 3.3}$$

Where:

B_I = Initial biomass (Day 0; mol C)

B_F = Final biomass (extrapolated to end of growth phase; mol C)

Implementing this equation for *S. alterniflora* BGB in the summer yielded:

$$(2.0 \times 10^5 \text{ mol C} - 9.6 \times 10^4 \text{ mol C}) / 2.0 \times 10^5 \text{ mol C} = 0.52$$

Because productivity estimates were not collected for this study, estimates from the literature were used as approximations for each plant species by growth phase/season (Table 3.4).

Table 3.4. Net primary productivity (NPP) estimates by species across all seasons, percent carbon by species, and root:shoot ratios (R:S) by species.

Species	Season	NPP (mol C m^{-2} $season^{-1}$)	Source	%C	Source	R:S	Source
S. alterniflora	Summer	308	Pezeshki and DeLaune, 1991	48	Rice, 1982	3.9 ± 0.9	Emery and Fulweiler, 2014
	Fall	283					
	Winter	183					
	Spring	213					
S. patens	Summer	829	Pezeshki and DeLaune, 1991	45	Curtis et al., 1990	1.1 ± 0.1	Windham, 2001
	Fall	667					
	Winter	375					
	Spring	500					
P. australis	Summer	375	Emery and Fulweiler, 2014	42	Eid et al., 2010	1.9 ± 0.5	Emery and Fulweiler, 2014
	Fall	62.5					
	Winter	125					
	Spring	250					

Since no seasonal net primary productivity estimates could be found for *P. australis*, the annual net primary productivity estimate found in the literature was divided by four. This would provide an underestimate of productivity for *P. australis* in the summer and spring, but an overestimate of productivity in the winter and fall.

The area of the Neponset Salt Marsh is 1.1 x 10^6 m^2 (Carlisle et al., 2005). Aerial observations using Google Earth indicated that ~10% of the Neponset Salt Marsh was covered by *S. alterniflora*, 30% was covered by *S. patens*, and *P. australis*, while invasive, covered 35% of the marsh flats with the remainder of the marsh being unvegetated or covered by less-dominant species.

Because each plant was separated into AGB or BGB, and the biomass types had significantly different leaching rates, a biomass ratio was factored into the equation using literature values by species (Table 3.4). The root:shoot ratio represented the ratio of the

BGB to AGB (Harris, 1992). While for terrestrial trees under normal conditions exhibit root:shoot ratios of around 1:18 (Harris, 1992), the marsh plants studied here had root:shoot ratios of 4 ± 1 (*S. alterniflora*), 1.1 ± 0.1 (*S. patens*), and 1.9 ± 0.51 (*P. australis*).

Lastly, samples were inundated for 24 hours in the incubations, which is not realistic of the marsh tidal regime. An inundation multiplier was calculated for each species and biomass type based on the amount of time it is inundated in the marsh. This multiplier was calculated based on a tidal regime study in the Neponset River Salt Marsh (Schiebel et al., *in prep*). Using Equation 3.3 and implementing all of the components for all three plant species in the marsh provided a seasonal leaching flux from the Neponset Salt Marsh vegetation (Table 3.5).

Table 3.5. Leaching flux and percentage of total yearly outwelling by species across all seasons for non-poisoned samples exposed to sunlight.

Season	Total Seasonal Leaching Flux (x 10^6 mol C $season^{-1}$)
Spring/Pre-growth	2.8
Summer/Peak Growth	8.3
Fall/Senescence	10
Winter/Dead	3.2
Total (x 10^6 mol C yr^{-1})	25

It should be noted that because seasonal incubations were not conducted for *P. australis* and the leaching rates for *P. australis* and *S. patens* were not significantly different for any treatment, the leaching rates for *S. patens* were used for *P. australis* throughout the calculations. Both biomass types for all three species were then summed by season to determine the total seasonal flux attributable to *S. alterniflora*, *S. patens,* and *P. australis* ranging from 2.8 x 10^6 mol C $season^{-1}$ in the spring to 10 x 10^6 mol C season^{-}

^{1} in fall. Summing these seasonal fluxes yields a total leaching flux from these plants of 25 x 10^{6} mol C yr^{-1}. The percentage of the total export attributed to these plants was also estimated. Using methods from Chapter 2, the annual total export from the Neponset Salt Marsh 5.4 x 10^{7} mol C yr^{-1}. Using this estimate, the percentage of the total outwelling that was leached from the three main marsh grasses *S. alterniflora*, *S. patens,* and *P. australis* was found to be approximately 45%.

While few studies have investigated seasonal leaching fluxes in the literature for salt marsh systems, seasonality is well-understood for terrestrial systems. Temperate deciduous leaves senesce during fall with nearly zero biomass production in winter (Kaiser et al., 2010). Goulden et al. (1996) found over a two-year study that DOC content in temperate forest soil water increased in late autumn and decreased to low values for winter and early spring in Austria (Kaiser et al., 2010). Because plant senescence is generally controlled by environmental cues such as length of day, nutrient fluxes, and air temperature (Thomas and Stoddart, 1980), here it is hypothesized that these same factors drive salt marsh senescence and lead to an increased leaching flux during autumn.

In terms of seasonality of Neponset Salt Marsh DOC fluxes, the residence time is approximately 3-5 days for this material to reach the mouth of the estuary (Boston Harbor). The three dominant plant species in the Neponset Salt Marsh (*S. patens, S. alterniflora, P. australis*) could contribute 46% of the total DOC export from the marsh. Estiarte and Penuelas (2015) found that leaf senescence signals the transition from the active to dormant stages for deciduous trees and that this is cued by photoperiod, temperature and, to a minor extent, water availability. Singh et al. (2014) investigated seasonal DOM patterns for multiple watershed sources (litter leachate, soil water,

groundwater) and found a strong increase in DOC concentrations in autumn and spring, as seen here. Wong and Williams (2010) showed that the leaching from fresh leaf litter provided a strong DOM signal in stream waters in Canada while Kang and Mitchell (2013) found a higher DOC concentration in stream runoff following autumn leaf-fall.

Temperature has also been shown to affect both the release and decomposition of DOC from plant matter (Christ and David, 1996; Gödde et al., 1996; Anderson and Nilsson, 2001). Neff and Hooper (2002) measured the release of DOC under different temperatures in Alaska and found that total DOC release was positively correlated with DOC leaching from soils. Kim et al. (2014) investigated the DOC leaching from mineral soil into the Canadian waters near Quebec and found a proportional increase in DOC with temperature. Baldwin et al. (2014) found that the DOC export from floodplain litter increased with temperature in southeastern Australia. Couto et al. (2013) studied three plant species in a temperate Atlantic salt marsh in Portugal and found higher biomass values in the summer equated to higher rates of carbon storage in the summer.

Conclusions

Salt marshes, in addition to other ecosystem services, can help offset carbon dioxide emissions and mitigate against climate change via primary productivity and sedimentation. An important component affecting the total carbon burial in a salt marsh is the lateral flux of DOC to adjacent ecosystems. Several factors can contribute to higher overall leaching rates of DOC from salt marsh plants including increased sunlight exposure, lower root:shoot ratios, and the absence of microbial degradation. DOC under anoxic conditions and plant species played both smaller and more variable roles in carbon

leaching. Most importantly, seasonal comparisons led to the hypothesis of the "Fall Dump" in which higher DOC concentrations are leached during the fall when marsh plants senesce for winter. Using experimental leaching rates, net primary productivity estimates, marsh area, and root:shoot ratios for each plant species, the seasonal leaching fluxes were determined for the Neponset Salt Marsh ranging from 2.8-10 x 10^6 mol C $season^{-1}$ with a total annual flux of 25 x 10^6 mol C yr^{-1} or 46% of the total export from the Neponset Salt Marsh.

CHAPTER 4

NEPONSET SALT MARSH SEDIMENT SOURCES OF DISSOLVED ORGANIC MATTER

Abstract

Coastal blue carbon refers to the climate change mitigation benefits provided by the biogeochemical processes naturally performed by salt marshes, mangroves, and seagrasses. While blue carbon systems sequester a small amount of carbon in their biomass, a much larger proportion of sequestration occurs via sedimentation. New England salt marshes have undergone several physical disturbances in the last century including nutrient loading, ditching for mosquito control, filling, draining, habitat fragmentation, and invasive species introductions, all of which could alter sequestration rates in marsh sediments. Climate change will also affect these ecosystems through increased temperature and extreme shifts in climate (e.g., droughts) with the impacts of

these phenomena on sediment geochemistry are poorly constrained. An additional factor that affects carbon burial in a salt marsh is carbon outwelling to adjacent systems. This study investigates the seasonal leaching of dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) for salt marsh sediment processes via incubation experiments to look separately at two dominant mechanisms in the Neponset Salt Marsh in Boston, Massachusetts: surface sediment/overland flow and creek bank sediment pore water leaching. Seasonality, marsh condition (healthy versus drought), and sediment location were investigated as factors affecting the rate of leaching. DOC leaching fluxes were significantly higher during fall (versus summer) and under drought (versus healthy) conditions. Sediment core distance from the main creek bank as well as sediment depth did not show consistent trends in DOC leaching. Optical properties suggest that the dissolved organic matter (DOM) leached from sediment is similar in composition to background estuary water. Calculations based on these experiments show that approximately ~2-10% of the total outwelling was attributed to overland flow from surface sediment and vegetation (1.0-5.6 x 10^6 mol C yr^{-1}) depending on season and marsh condition and that 6% (3.5 x 10^6 moles C yr^{-1}) can be attributed to creek bank sediment pore water leaching.

Introduction

Coastal blue carbon refers to the climate change mitigation benefits provided by the biogeochemical processes naturally performed by salt marshes, mangroves, and seagrasses (Emmett-Mattox and Crooks, 2014). Over long timescales, these systems sequester up to an order of magnitude more carbon dioxide (CO_2) per area than their terrestrial counterparts (e.g., rainforests; McLeod et al., 2011). While blue carbon systems sequester a small amount of carbon in their biomass, a much larger proportion of the sequestration in salt marshes occurs in marsh sediment (Figure 4.1).

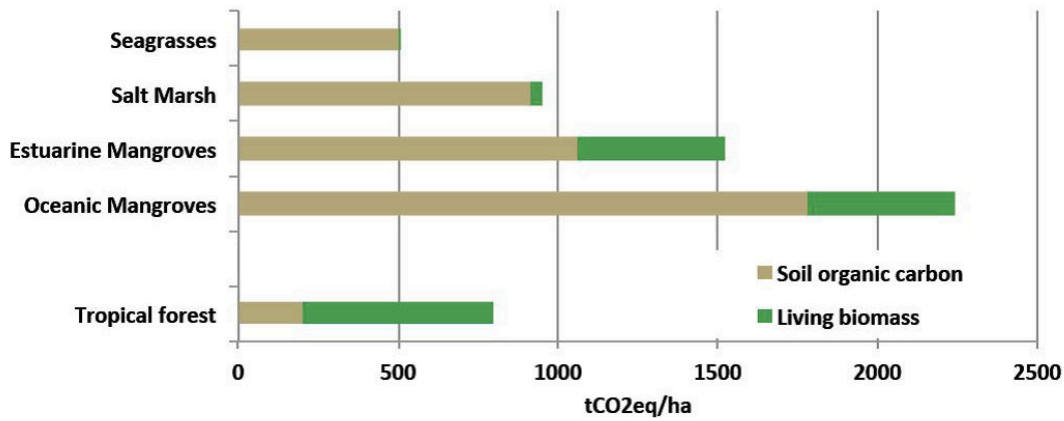


Figure 4.1. Blue carbon systems sequester a large amount of carbon in sediment with a smaller sequestration potential in biomass (Murray et al., 2011).

Salt marshes in particular have been estimated to bury from 1.5-143 mol C m^{-2} yr^{-1} (McLeod et al., 2011). Because organic matter is highly concentrated in marsh sediment (Chmura et al., 2003; Duarte et al., 2005; Donato et al., 2011; Breithaupt et al., 2012), the mineralization of this material can release large amounts of CO_2 and nutrients to the atmosphere, adjacent water ecosystems (Bouillon et al., 2008), and result in soil mass loss, which lowers marsh elevation (Kirwan and Mudd, 2012; Morris et al., 2012). However, organic matter mineralization is fundamental to both the structure and function

of salt marshes as it supplies energy to food webs (Teal, 1962), and provides nitrogen for primary productivity (Anderson et al., 1997).

Identifying sources that alter the mineralization of organic matter in salt marshes and their impacts is well-documented in the literature with mixed conclusions as to how these sources could affect mineralization. Examples of such processes include soil inundation, vegetation variation, and temperature. Increased rates of inundation that are expected with sea-level rise are predicted to increase rates of anoxia in the sediment, thereby decreasing mineralization rates (Miller et al., 2001; Gribsholt and Kristensen, 2003). However, in temperate salt marshes, experimental increases in tidal inundation had either no effect or slightly increased decomposition in litter bags (Kirwan et al., 2013). Vegetation composition impacts on organic matter mineralization in the literature also show mixed results. Some studies have indicated that salt marsh biogeochemistry differs with invasive species encroachment (i.e., higher soil organic matter; Osland et al., 2012). Other studies have found no difference in organic matter production with vegetation community shifts (Henry, 2012; Henry and Twilley, 2013).

Climate change will affect salt marshes through increased temperature and changes in precipitation patterns that could lead to more frequent droughts and/or flooding events in coastal areas (Findell and Delworth, 2005; Palomo et al., 2013). The literature has shown that hydrological shifts in wetland systems will influence plant communities (Hazeldon and Boorman, 1999; McKee et al., 2004; Laijo, 2006; Weston et al., 2006; Knorr and Blodau, 2009; Palomo et al., 2013). However, the impacts of extreme shifts in climate, such as droughts, on sediment geochemistry are not well-understood (Palomo et al., 2013). Drought has been identified as a factor promoting acute

salt marsh dieback along the United States East and Gulf coasts over the last decade (McKee et al., 2004). Marsh dieback could result from drought-derived changes in soil chemistry such as a decrease in pH (Palomo et al., 2013). Organic matter mineralization rates are higher with warmer temperatures and typically exhibit a seasonal pattern with higher rates during summer (Howarth and Teal, 1979; Alongi et al., 2005; Kirwin and Blum, 2011). Yet some studies have shown no seasonal patterns in mineralization (Alongi et al., 1999; Poungparn et al., 2009), experimental warming (Charles and Dukes, 2009), or spatial variation in temperature (Lovelock, 2008).

An additional factor that affects carbon burial in salt marsh sediment is carbon outwelling to adjacent systems. Odum (1980) expressed the notion that productivity of nearshore waters can be enhanced not only by the upwelling of nutrients from bottom waters, but also from the outwelling of organic matter from fertile estuaries. In two decades alone, outwelling research was conducted at 41 sites and presented in 42 publications (Childers et al., 2002). However, out of these studies very few have quantified estuary-coastal ocean exchanges (Valiela et al., 1978; Valiela and Teal, 1979; Duarte et al., 2014), and even fewer have investigated the leaching of organic matter from sediments to adjacent systems.

While more studies are beginning to quantify estuary-coastal ocean exchange (inclusive of not only salt marsh ecosystems) (Tzortziou et al., 2011; Duarte et al., 2014; Schiebel et al., 2014; Wang et al., 2014; Moyer et al., 2015), there are numerous reasons why directly testing the outwelling hypothesis has proven difficult. Sampling water flow and constituent concentrations in tidal channels connecting estuaries to the coastal ocean is complicated if the estuary is large, has multiple tidal channels, or is remotely located

(Childers et al., 2000). As previously mentioned, there is a high rate of spatial and temporal variability within estuaries. Flux quantification precision, accuracy, and error are also highly variable (Childers et al., 1993; Deegan and Garritt, 1997; Childers et al., 2000; Pendleton et al., 2012).

Dissolved organic carbon (DOC) represents the largest active reservoir of organic carbon on earth (Ludwig et al., 1996; Bates and Hansell, 1999; Hedges, 2002; Vantrepotte et al., 2015), and the understanding of DOC dynamics in coastal systems is imperative in order to characterize the role these systems play in the global carbon cycle. However, the large spatial and temporal variability in DOC concentrations within salt marshes adds limitations in characterizing the interactions and processes controlling this carbon reservoir both physically and biogeochemically (Vantrepotte et al., 2015).

A measurement that aids in the understanding of the carbon stock represented by salt marsh DOC as well as its outwelling fluxes to adjacent estuaries is chromophoric dissolved organic matter (CDOM) fluorescence. As the colored portion of dissolved organic matter (DOM), CDOM has been shown to be important in studying aquatic systems (Blough and Del Vecchio, 2002; Coble, 2007; Andrew et al., 2012). CDOM's optical properties have been extensively studied as it absorbs UV and visible light (Blough and Del Vecchio, 2002; Coble, 2007; Boyle et al., 2009; Andrew et al., 2012). CDOM optical properties in both fresh and marine water can be measured in a laboratory setting or *in situ* (Blough and Del Vecchio, 2002; Zepp et al., 2007; Andrew et al., 2012). Further, CDOM can be used as a proxy for DOC in certain scenarios (Ferrari, 2000; del Vecchio and Blough, 2004, Gardner et al., 2005; Fichot and Benner, 2012, Yang et al., 2013, Rochelle-Newall et al., 2014, Vantrepotte et al., 2015). Previous studies have

shown that CDOM and DOC behave consistently in coastal waters dominated by terrestrial discharges due to the conservative mixing of CDOM and DOC along a salinity gradient (Chapter 2; Vantrepotte et al., 2015).

This study will investigate the seasonal leaching of DOC and CDOM for salt marsh sediment processes obtained during two types of incubation experiments in the Neponset Salt Marsh in Boston, Massachusetts. Two different mechanisms will be investigated: sediment-water interaction (i.e., water flooding the sediments surface from above with plant matter included) and creek bank sediment pore water leaching.

Methods

Study site

The Neponset Salt Marsh is 1.1 x 10^6 m^2 and comprised of three plant species: *S. alterniflora* dominates the low marsh while *Spartina patens* (*S. patens*) and the invasive *Phragmites australis* dominate the marsh flats. The marsh is bordered by a dam at the landward extent of the Neponset Estuary with the flow gauged by the United States Geological Survey (USGS) at a location just downstream from the dam (USGS, 2002) that provides an indication of freshwater flow from the river, through the marsh, and into Boston Harbor.

Experiment 1: surface sediment/overland flow

The first process modeled in this study is overland flow, comprised of aboveground vegetation and surface sediment on the marsh flats that are inundated during high tide and leach DOC. Two weeks prior to the overland flow incubations, a preliminary study of tidal influence was conducted using Onset HOBO (Bourne, MA)

water level data loggers. Wells were installed at 1, 6, and 10-m distances perpendicular from the Neponset Estuary creek bank (Figure 4.2).

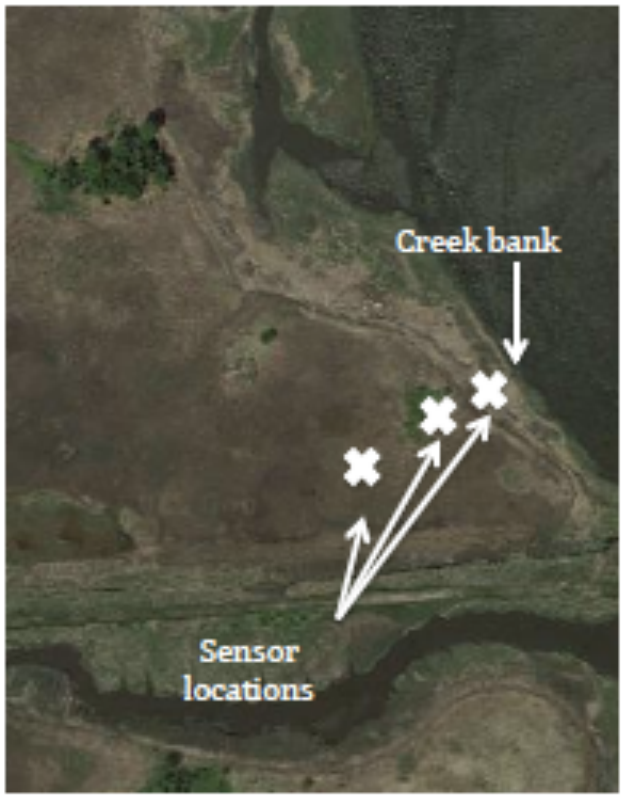


Figure 4.2. Sensor locations with wells installed at 1, 6, and 10-m distances perpendicular from the Neponset River creek bank.

Data loggers recorded absolute pressure to a depth of 2 m. Atmospheric pressure corrections were made in post-processing using an average barometric pressure of 14.73 PSI. Cores at 1- and 10-m distances from the creek bank were removed in replicate during a neap tidal cycle in July and October 2014 to observe both the growing and senescent seasons in the marsh. Core extraction sites were as close as possible to each other across seasons and cores were similar in composition between seasons. These core distances were chosen because they had a sharp delineation in vegetation coverage: cores located 1 m from the creek bank were dominated by *S. alterniflora* while cores located 10

m from the creek bank were dominated by *S. patens*. Plants were left in the cores for both experiments and cores were extracted using serrated polycarbonate tubes (Figure 4.3).

Figure 4.3. Sediment core extracted 10 m from the Neponset River creek bank during the July 2014 incubation.

Once cores were removed, the bottom of the core was covered with cheesecloth (400-mesh) to ensure particulate matter remained within the tube, capped at the bottom, and placed in a dark water bath in order to minimize sunlight penetration of the sediments in order to avoid any photo-degradation and to keep all cores at a constant temperature (Figure 4.4).

Figure 4.4. Overland flow experimental setup.

One liter of water was placed on the top of the core, left for the time indicated by the data logger sensors in preliminary tidal observations, and then manually drained off of the top of the core after the appropriate amount of time into sample bottles. Cores were inundated with one liter of Boston Harbor water with a relatively low (relative to marsh baseline concentration) CDOM (approximately 20 QSU) and DOC (approximately 250 μM) concentration to begin the incubation (Day 0) by manually mimicking the tides shown during the observation period for a period of one week. During the observation period, a strong diurnal inequality was shown and mimicked in these experiments ("Tide 1" and "Tide 2"). These same cores were then allowed to dry for one week with no water added in order to simulate drought conditions in the marsh, after which the experiment was conducted again for one week with the same tidal scheme. During both phases of the overland flow incubations ("healthy" and "drought"), photosynthetically active radiation

(PAR), water temperature, and sediment core temperature were continuously monitored and discrete samples were taken twice daily (once during each tidal cycle in replicate).

Experiment 2: deep sediment pore water leaching

One incubation was conducted in August 2015 to determine the DOC leaching from salt marsh creek bank sediment pore water with plant matter removed and to elucidate any differences in leaching at different depths. Cores of sediment were removed at three depths in duplicate (60 cm, 120 cm, and 180 cm from the top of the marsh flats) from the side of the marsh flats rather than via a core extractor from the top of the marsh flats (Figure 4.5).

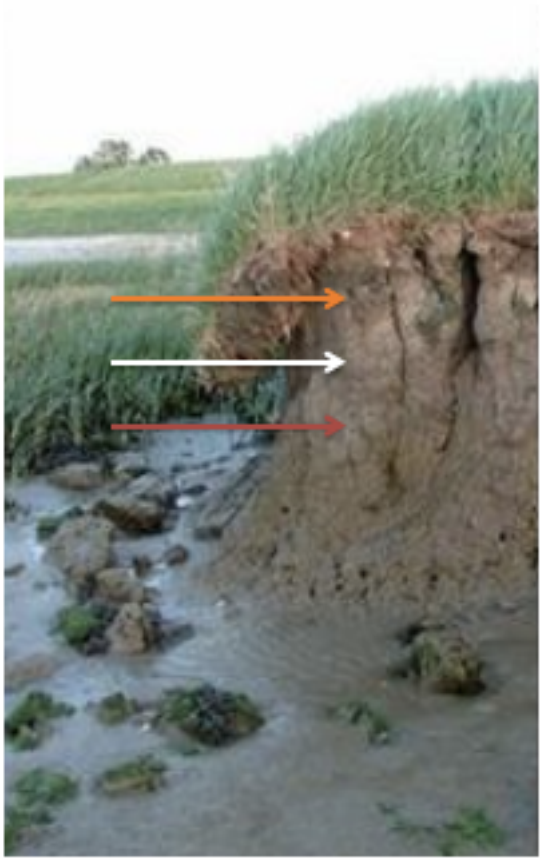


Figure 4.5. Core locations for pore water incubation (not drawn to scale) with cores removed in duplicate at 60 cm (orange arrow), 120 cm (white arrow), and 180 cm (red arrow) from the top of the marsh flats.

Using the same serrated polycarbonate tubes from the overland flow incubations lined with nylon mesh, cores removed from the side of the creek bank and then the core/core liner was removed from the polycarbonate tubes and sealed. Cores were completely encompassed by the nylon mesh and placed into a 2-gallon bucket. Tidal simulators were created based on the methods of MacTavish and Cohen (2014). Using two 2-gallon buckets for each core, one acted as the microcosm with mesh-enclosed sediment core and the other as a water storage reservoir with a lid to prevent evaporation and eliminate light. Water transfer between the reservoir and microcosm was accomplished using two Tom Aquatics Aqualifter (Placentia, CA) dosing pumps where

one pump transferred water into and the other withdrew water from the microcosm using aquarium tubing (0.65-cm diameter; Python Pro Quality Air Line Tubing). The pumps were then connected to programmable timers (GE 6-Outlet Heavy Duty Outdoor Timers) to simulate tides (Figure 4.6).

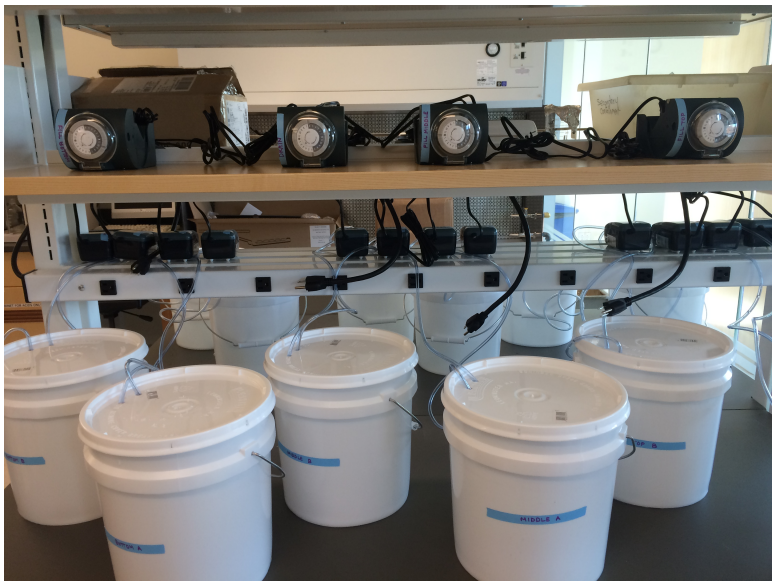


Figure 4.6. Pore water leaching experimental setup.

The result was one fixed high and low tide over a 24-h period with a simple inundation scheme designed to mimic the tide at the three different core depths based on the preliminary tidal regime study with no diurnal inequality (Table 4.1).

Table 4.1. Inundation scheme for pore water leaching incubation.

Time	Depth	Action
10:00 a.m.	180 cm (bottom of flats)	Core reservoir filled (3-L of harbor water)
12:00 p.m.	120 cm (middle of flats)	Core reservoir filled (3-L of harbor water)
2:00 p.m.	60 cm (top of flats)	Core reservoir filled (3-L of harbor water)
6:00 p.m.	All cores	Drained into storage reservoirs for sampling
10:00 p.m.	180 cm (bottom of flats)	Core reservoir filled (3-L of harbor water)
12:00 a.m.	120 cm (middle of flats)	Core reservoir filled (3-L of harbor water)
2:00 a.m.	60 cm (top of flats)	Core reservoir filled (3-L of harbor water)
6:00 a.m.	All cores	Drained into storage reservoirs for sampling

During inundation, 3 liters of Boston Harbor water was added to each bucket, allowed to soak cores in the bottom of the bucket, and then subsequently drained after the proper amount of time into the storage reservoir: 4 hours for 60-cm cores, 6 hours for 120-cm cores, and 8 hours for 180-cm cores. Once the water was in the storage reservoir after inundation, it was sampled and then new baseline water was added to the bucket for the next tidal cycle.

Sample analysis

After sample collection (for all three incubations), each sample was filtered through a pre-combusted 0.7 μm glass fiber filter (Whatman GF/F). DOC samples were filtered into pre-combusted (4 hours at 500°C) 40 mL borosilicate glass vials with Teflon-lined screw caps, acidified to pH < 2 using phosphoric acid, and refrigerated until analysis. DOC concentrations were measured using a Shimadzu TOC-V analyzer equipped with an autosampler. The instrument was calibrated using 5-point carbon calibration curves. Carbon standards were prepared using potassium hydrogen phthalate (KHP). All standards and samples were injected in triplicate. Instrument blank and DOC values were checked against reference low carbon water and deep seawater (CRM, University of Miami, Rosenstiel School of Marine and Atmospheric Sciences). Blank subtraction was conducted using Milli-Q water, which was analyzed at set intervals (every 10 samples) during sample analysis.

CDOM fluorescence was measured using a Photon Technologies International QM-1 spectrofluorometer. Single fluorescence emission scans from 350 to 650 nm were collected for an excitation wavelength of 337 nm. The fluorescence of Milli-Q water was

determined as a blank on each day of analysis and subtracted from sample spectra prior to integration. Peak areas were integrated and converted to quinine sulfate units (QSU) where 1 QSU is equivalent to the fluorescence emission of 1 μg/l quinine sulfate solution (pH 2) integrated from 350 to 650 nm at an excitation wavelength of 337 nm (Chen and Gardner, 2004). All sample data were collected using a 1-cm quartz cuvette and are expressed in quinine sulfate units (QSU). Samples above 100 QSU were diluted with Milli-Q water prior to analysis to minimize internal quenching in the samples and this process was completed for samples towards the end of incubations. All glassware used for sample collection, storage and analysis were acid cleaned and baked at 500°C for 4 hours. DOC results were compared to CDOM results to ensure a linear relationship for the period of study.

Results and Discussion

Seasonality

Based upon data from the overland flow incubations, surface marsh sediments consistently leached significantly more carbon during fall (October) than summer (July) regardless of marsh condition (healthy versus drought), tidal regime (diurnal inequality), or dominant vegetation pattern with p-values up to 0.012 (Table 4.2).

Table 4.2. Data comparing fall and summer overland flow leaching for different marsh condition, tidal regimes, and vegetation patterns (mean ± SE). P-values are reported from t-tests using 1-tailed distributions. Tide 2 indicates samples were inundated for twice as long as samples under the Tide 1 regime to mimic diurnal inequality.

Condition	Dominant Vegetation	Season	[DOC] (μM) Tide 1	P-value	[DOC] (μM) Tide 2	P-value
Healthy	*S. alterniflora*	October	315 ± 77	0.012	564 ± 22	0.00043
		July	58.9 ± 10.2		137 ± 9	

	S. patens	October	475 ± 2	0.00001	601 ± 31	0.00062
		July	91.2 ± 1.1		128 ± 3	
Drought	*S. alterniflora*	October	539 ± 42	0.0034	670 ± 6	0.00031
		July	231 ± 28		305 ± 17	
	S. patens	October	503 ± 1	0.0011	752 ± 82	0.0040
		July	228 ± 25		267 ± 27	

This result is consistent with Chapter 3, where a strong seasonal variation in plant matter DOC leaching was observed within the Neponset Salt Marsh (Figure 4.7).

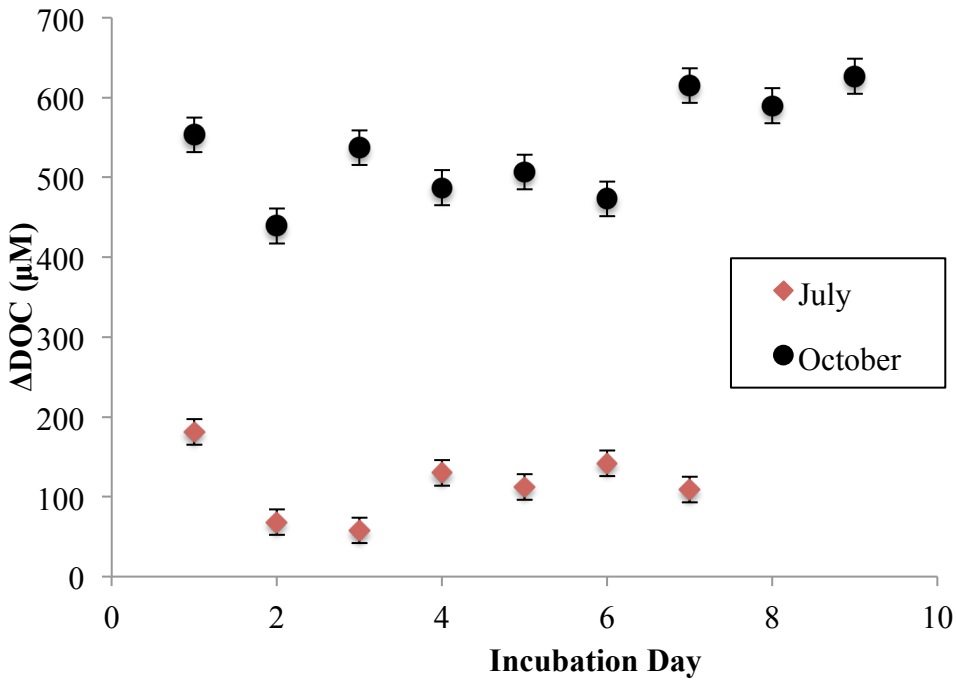


Figure 4.7. July and October 2014 overland flow leaching concentrations.

There have been studies observing the seasonal pulse in DOC from salt marshes, though not directly from sediment or overland flow. Gardner et al. (2005) originally discussed the importance of the seasonal DOC pulse in the Neponset Salt Marsh and concluded that degradation of organic matter derived from the mid-estuary salt marsh was an important seasonal source of DOC for the adjacent system during the fall months.

Yelverton and Hackney (1986) investigated a *S. alterniflora*-dominated salt marsh in North Carolina and found that DOC export concentrations ranged between 8.3 x 10^{-5} and 6.0 x 10^{-4} mol C l^{-1} and were the highest in the summer and lowest in the winter. Tzortiou et al. (2008) found that DOC concentrations in a Chesapeake marsh during the summer and early fall were the highest when looking at seasonal trends in export fluxes. Osburn et al. (2015) conducted a study in North Carolina and found a small seasonal variation in DOC export. DOC concentrations were observed to be 8.0 x 10^{-4} mol C l^{-1} during spring, 8.3 x 10^{-4} mol C l^{-1} in summer, and 8.7 x 10^{-4} mol l^{-1} in fall. The results for the Neponset Salt Marsh also show a strong seasonal difference in overland flow leaching rates in the Neponset Salt Marsh with fall leaching concentrations significantly higher than those observed in summer. Because plants were left in sediment cores for the overland flow incubations and these plants seasonally release a strong DOC pulse in the fall (Chapter 3), it can be surmised that marsh vegetation leaching strongly affects overland flow leaching.

Marsh health

For both overland flow incubations, surface sediment DOC leaching concentrations were significantly higher for drought conditions than healthy marsh conditions (p-values ranging from 9.5 x 10^{-4} to 0.038; Table 4.3; Figure 4.8).

Table 4.3. Data comparing drought and healthy overland flow leaching rates for different seasons, tidal regimes, and vegetation patterns (mean ± SE). P-values are reported from t-tests using 1-tailed distributions. Tide 2 indicates samples were inundated for twice as long as samples under the Tide 1 regime to mimic diurnal inequality.

Season	Dominant Vegetation	Condition	[DOC] (μM) Tide 1	P-value	[DOC] (μM) Tide 2	P-value
July	*S.*	Drought	231 ± 28	0.0038	305 ± 17	0.0017

2014	*alterniflora*	Healthy	58.9 ± 10.2		137 ± 9	
	S. patens	Drought	228 ± 25	0.0042	267 ± 27	0.0048
		Healthy	91.2 ± 1.1		128 ± 3	
October 2014	*S. alterniflora*	Drought	539 ± 42	0.019	670 ± 6	0.0057
		Healthy	315 ± 77		564 ± 22	
	S. patens	Drought	503 ± 1	0.00094	752 ± 82	0.038
		Healthy	475 ± 2		601 ± 31	

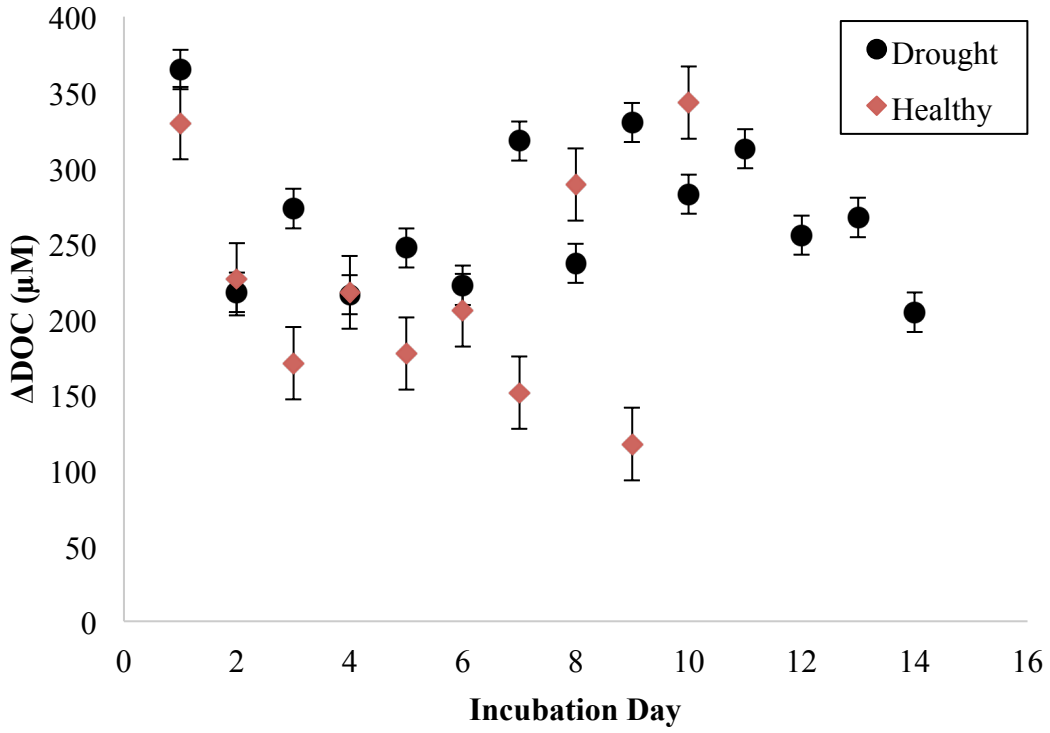


Figure 4.8. July 2014 overland flow incubation data comparing healthy and drought marsh conditions for the 10-m core location (dominated by *S. patens*).

There appears to be a small increase in DOC around day 10. The decay of salt marsh grass litter occurs in three phases (Valiela et al., 1985). The first phase lasts less than ten days where 5 to 40% of the litter is lost and the rapid release of biomolecules occurs during microbial mediated hydrolysis (Valiela et al., 1985). A second, slower phase lasts up to a year where microbial degradation of organic matter and subsequent leaching of hydrolyzed substances removes an additional 40 to 70% of the original

material. Finally, a third phase may last an additional year or longer that is characterized by slow decay of only relatively refractory materials remaining. By this third stage as little as 10% of the original material may remain (Lee, 1980; Valiela et al., 1985; White and Howes, 1994). The small increase seen here could be the transition from rapid leaching to the leaching of hydrolyzed substances in aboveground vegetation.

As climate change and water withdrawals become more pervasive in New England, possible drought conditions could occur under extended periods of no precipitation or decreased flow conditions in salt marshes. It is expected that by the end of this century, New England will experience a short seasonal drought each year with longer droughts every 6-10 years in certain areas under the current greenhouse gas emission scenario (Hayhoe et al., 2007). Medeiros et al. (2015) investigated drought-induced variability in DOM composition in a marsh-dominated estuary Brazil. Using a different experimental setup than the current study in the Neponset Salt Marsh (mass spectrometry and carbon isotope analyses), they found that during drought conditions the estuarine water had a stronger DOM pulse from the salt marsh than in non-drought conditions. Drought conditions have also been suggested as a factor promoting salt marsh vegetation dieback in the eastern United States (McKee et al., 2004; Palomo et al., 2013). This dieback could result from drought-derived changes in soil chemistry such as a decrease in pH and increased concentration of toxic metals from oxidative weathering of metal-sulfides to sulfuric acid (McKee et al., 2004; Palomo et al., 2013).

Additionally, *Spartina*-dominated marshes such as the one studied here are rich in organic matter due to high plant productivity and sediment trapping (Adam, 1990; Palomo et al., 2013). Oxygen is often lacking and the marsh sediment column is mostly

anoxic (Furukawa et al., 2004). During drought conditions, a decrease in sediment water content can lead to crack formation, thereby increasing oxygen concentration in the soil and promoting aerobic processes (Palomo et al., 2013). Because cores in the Neponset Salt Marsh were removed and exposed to oxygen, which would not occur normally, artificial promotion of aerobic processes could have occurred, causing a possible increase in leaching. Some studies have found that organic matter degradation is more rapid under oxic conditions than under anoxic conditions (Harvey and Nuttle, 1995; Lehmann et al., 2002; Wang et al., 2007). The current study in the Neponset Salt Marsh suggests that drought conditions could in fact lead to higher rates of DOC leaching from overland flow on the marsh flats (Figure 4.8).

Core location

The effect of core location was examined in terms of distance from the creek bank in the overland flow incubations as well as core depth in the marsh flats in the pore water incubation. There are two main differences between cores taken at 1 versus 10 m from the creek bank during the overland flow incubations: (a) the distance from the creek and so the amount of inundation during tidal exchange and (b) the dominant plant species. The cores dominated by *S. patens* were located ten m from the creek bank in the marsh while cores dominated by *S. alterniflora* were located one m from the creek bank. There was no consistent trend in leaching concentrations between the 1- and 10-m core distances from the creek bank for this study (Table 4.4).

Table 4.4. Data comparing the effect of vegetation pattern/distance from the creek bank on overland flow leaching concentrations for different seasons, marsh conditions, and tidal regimes (mean ± SE). P-values are reported from t-tests using 2-tailed distributions. Tide 2 indicates samples were inundated for twice as long as samples under the Tide 1 regime to mimic diurnal inequality.

Season	Condition	Dominant Vegetation	[DOC] (μM) Tide 1	P-value	[DOC] (μM) Tide 2	P-value
July 2014	Healthy	*S. alterniflora*	58.9 ± 10.2	0.025	137 ± 9	0.21
		S. patens	91.2 ± 1.1		128 ± 3	
	Drought	*S. alterniflora*	231 ± 28	0.91	305 ± 17	0.14
		S. patens	228 ± 25		267 ± 27	
October 2014	Healthy	*S. alterniflora*	315 ± 77	0.056	564 ± 22	0.20
		S. patens	475 ± 2		601 ± 31	
	Drought	*S. alterniflora*	539 ± 42	0.23	670 ± 6	0.19
		S. patens	503 ± 1		752 ± 82	

This is consistent with previous findings in the Neponset Salt Marsh where no significant difference in leaching concentrations was found between species when investigating *S. alterniflora* and *S. patens* under different seasonal conditions (Chapter 3; Figure 4.9).

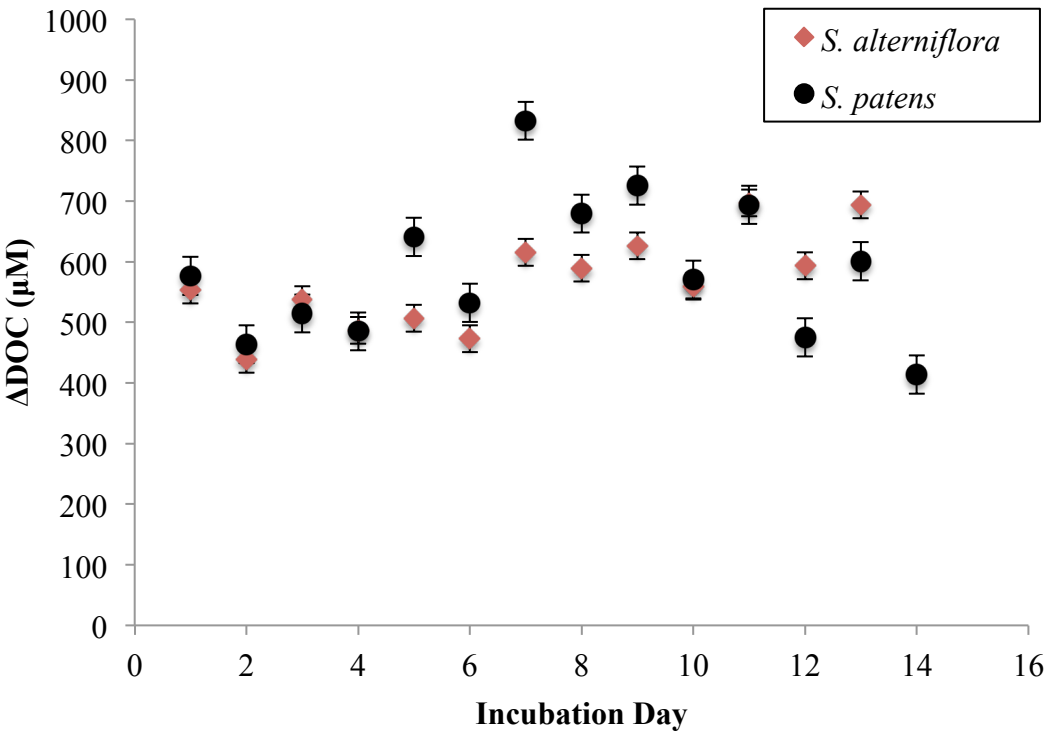


Figure 4.9. October 2014 overland flow incubation comparing leaching patterns between *S. alterniflora* and *S. patens*.

In comparing species under a range of conditions, *S. patens* and *S. alterniflora* appeared to have similar DOC export rates with respect to sunlight, bacteria levels, and above- versus belowground plant matter in the Neponset Salt Marsh (Chapter 3). In New England salt marshes, the most noticeable plant zonation pattern occurs at the mean high water line, separating the low and high marsh habitats (Nixon, 1982). *S. alterniflora* is a cordgrass exclusively dominating low marsh habitats while the high marsh is dominated by dense *S. patens*. Both *Spartina* species are C_4 plants, which have a more elaborate pathway than that of C_3 plants. This adaptation evolved in response to high light intensities, high temperatures and dryness (Edwards et al., 2010). Because both species

are C_4, the similarity in DOC export patterns is expected as they have compositional similarities.

While the dominant plant species in the overland flow incubations was not a significant factor affecting DOC leaching from surface sediments, the length of tidal inundation did make a difference in leaching concentrations (Table 4.4). The tidally mediated exchange of pore water between sediments and surface waters via the ebb and flow of tides is known in the literature as "tidal pumping" (Robinson et al., 2007; Gleeson et al., 2013). Call et al. (2015) examined the tidal pumping of DOC under a range of tidal regimes (neap, spring, ebbing) and found higher DOC export rates during neap tides than spring tides. Chambers et al. (2014) found that increased rates of inundation equated to higher rates of DOC production in mangrove peat soil in the Everglades. They surmised that this higher production was due to increased sea-level rise that increased the soil's probability of peat collapse and accelerated both nutrient and DOC export to the adjacent estuary. A similar phenomenon is possible the Neponset Salt Marsh. When sediments cores were inundated under the "Tide 2" regime for twice as long, the DOC leaching concentrations were consistently higher which could be due to peat collapse/cracking within the cores.

The rates of DOM utilization in *Spartina* detritus are highly variable with some components rapidly assimilated by microbes (hours to days) and some components have much longer turnover times (Moran and Hodson, 1994). Plant material leaches out of the sediment via belowground biomass (roots and rhizomes) as well as some detritus on the surface of the marsh flats. Older total organic carbon (TOC) that has been buried longer will slowly degrade and be made more soluble over time by both anaerobic and aerobic

bacterial processes. Conversely, older TOC could also aggregate and become less soluble over time. During each tidal cycle, overland flow would remove a portion of leachable DOM (e.g., labile material such as sugars, proteins, and compounds readily used by bacteria). The refractory components that remain over longer timescales are typically enriched in lignin byproducts and potential precursors of humic substances. The export of these components has been demonstrated using lignin biomarkers in several coastal systems (Meyers-Schulte and Hedges, 1986; Moran et al., 1991). The results from these experiments suggest that a longer inundation time correlates to more DOC removal and so over time this refractory material will also eventually leach from sediments (e.g., seasonally or annually).

In addition to the lateral core distance from the creek bank, the effects of sediment depth on sediment leaching were investigated through the pore water leaching incubation. There was no consistent trend in DOC leaching with varying depth (Figure 4.10).

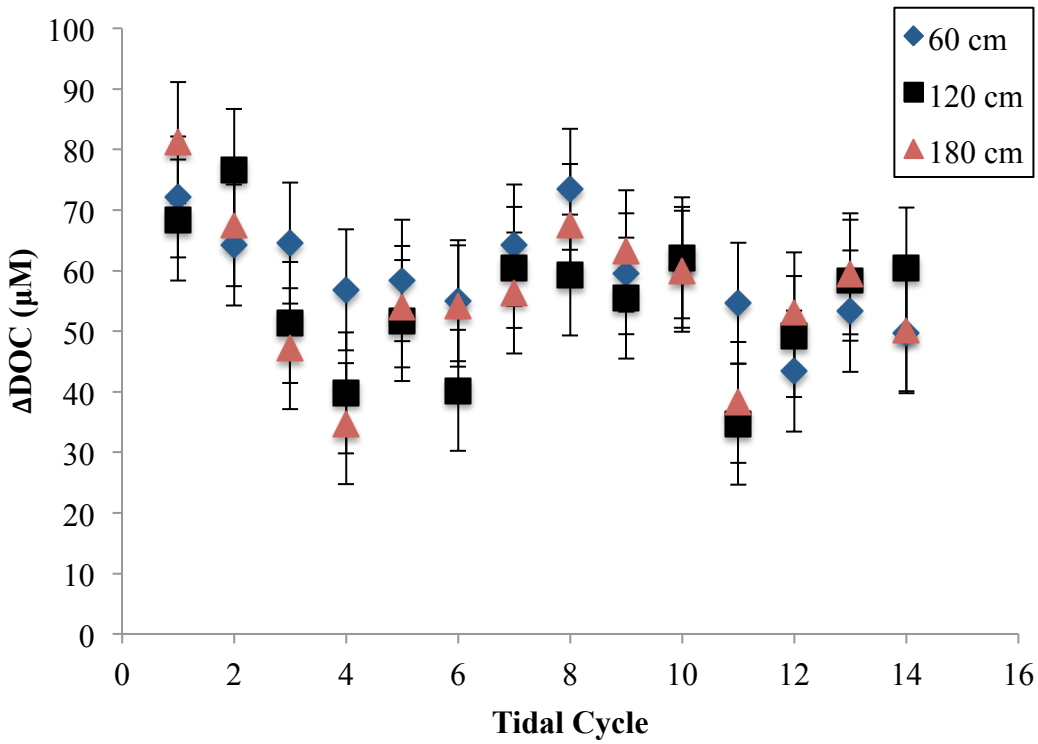


Figure 4.10. Pore water DOC leaching concentrations for cores taken at three different depths.

The cyclical pattern seen here is not associated with tides as cores for the pore water leaching incubation were inundated with the same tidal pattern over the entire incubation. Different water was obtained each tide as a baseline to add to the buckets and baseline DOC/CDOM concentrations were subtracted, so the variability is not accounted for in the background harbor water. There could be an induced priming effect by the addition of new baseline water where an acceleration of organic matter mineralization was caused by the addition of microbes in newly added water, causing an increase in decomposition and higher pulses of DOC export (Fontaine et al., 2003).

All cores were removed from the side of the marsh platform and from the same vertical column in the marsh (Figure 4.11).

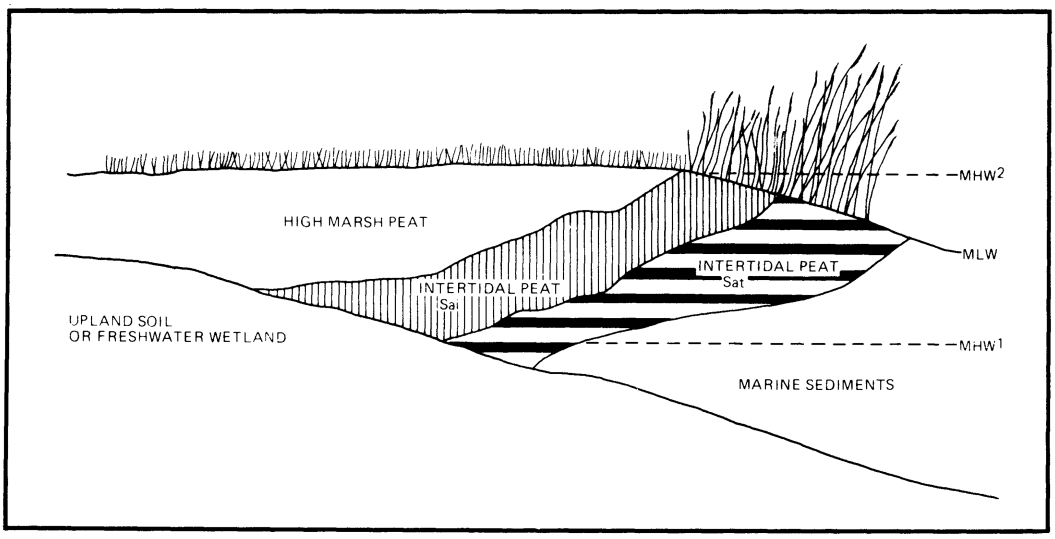


Figure 4.11. Cross section of typical New England marsh sediment where MHW^1 is mean high water level when marsh development began, MHW^2 is mean high water at present and MLW is mean low water at present (Niering and Warren, 1980).

While carbon:nitrogen ratios were not measured in this study, the cores were taken from the same column of sediment in the marsh and based on grain size were all the same type of sediment. Because all cores, regardless of depth, were extracted from the same intertidal peat sediment (based on observations), it is understandable that the leaching rates were not significantly different.

CDOM/DOC relationship

The CDOM/DOC relationship for each incubation was compared to the background CDOM/DOC relationship found the Neponset Estuary that was obtained during several cruises of the estuary in 2013 (Chapter 2; Figure 4.12).

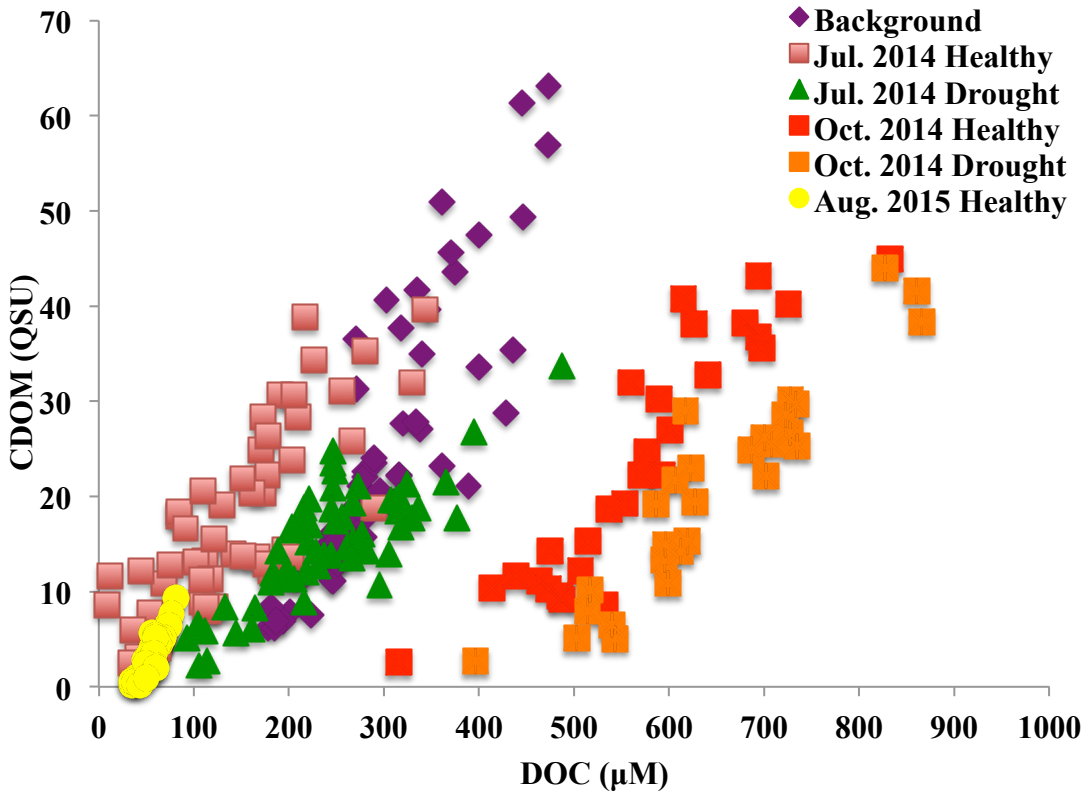


Figure 4.12. CDOM/DOC relationship for each incubation (healthy and drought conditions where applicable) compared to the 2013 CDOM/DOC relationship for the Neponset Estuary.

DOM that is fresher, more pigment-like, and more aromatic has a higher CDOM/DOC ratio. Carbohydrates, saturated hydrocarbons, cellulose, and photodegraded DOM have lower CDOM/DOC ratios. The CDOM/DOC ratio can get higher as material becomes more humified and marine bacteria can make more CDOM as the degrade particles (Harvey et al., 2015). All of the sediment-leached DOM from these experiments was similar in slope to the background in purple, suggesting that most of the estuarine background is of similar composition to the sediment-leached material and that sediments are the main contributor to outwelling in the Neponset estuary. There is little difference between seasons in terms of slope, which makes sense as sediments have longer

timescales for the movement of DOM. For both of the overland flow incubations, the healthy conditions had CDOM/DOC ratios for the drought conditions. This could be because drought causes more cracking and therefore more surface exchange with deeper (older) sediment that is less colored. The October overland flow incubation data has a higher x-axis than July overland flow incubations data. This suggests that during the fall, the leached DOC from sediment is colorless, which is consistent with some contribution from growing plant material (Chapter 3).

Sediment DOC fluxes

Two calculations were conducted to model sediment-water interactions in the Neponset Salt Marsh. Overland flow incubation data were used to model water flooding surface sediments above (with plants) at high tide. A second mechanism when water seeps in tidally to deeper creek bank sediments is represented by pore water leaching incubation data. Rather than normalizing by biomass (cores were not weighed for any incubations), the volume or area (where applicable) of the cores was implemented for calculations.

For the overland flow incubations, the DOC concentration multiplied by the surface area of the marsh provided an estimate for DOC fluxes from the sediment cores:

$$\mathrm{DOC_{OF}} = \sum \left(\frac{[\mathrm{DOC}]}{\mathrm{A_C}}\right) * \mathrm{A_M} \qquad \text{Equation 4.1}$$

Where:

$\mathrm{DOC_{OF}}$ = Total surface sediment/overland flow DOC flux (mol C yr^{-1})

[DOC] = Average daily core DOC leaching concentration extrapolated to a year (mol C yr^{-1})

A_C = Core area (1.3 x 10^{-2} m^2)

A_M = Area of marsh flats (400,000 m^2)

The DOC leaching concentration (μmoles l^{-1}) per liter of water (minus background estuary concentrations) for each tidal regime (diurnal inequality) was multiplied by 365 (therefore two tides per day), and summed to provide a total DOC leaching concentration per year (mol C yr^{-1}). The surface area of each core was 1.3 x 10^{-2} m^2 and the surface of the marsh flats was estimated from Google Earth and found to be approximately 400,000 m^2. An additional component of this equation is the percentage of the marsh flats dominated by each plant species where 10% of the marsh flats are dominated by *S. alterniflora* and 30% is dominated by *S. patens* (Chapter 3). This was accounted for in the marsh area (Table 4.5).

Table 4.5. Overland flow incubation fluxes.

Condition		Dominant Vegetation	DOC (mol C yr^{-1})	Leaching Flux by Area (mol C yr^{-1})	Total Leaching Flux (mol C yr^{-1})	% of Total Flux
July	Healthy	*S. alterniflora*	0.072	0.2 x 10^6	1.0 x 10^6	1.8
		S. patens	0.08	0.7 x 10^6		
	Drought	*S. alterniflora*	0.19	0.6 x 10^6	2.3 x 10^6	4.3
		S. patens	0.18	1.7 x 10^6		
October	Healthy	*S. alterniflora*	0.32	1 x 10^6	4.6 x 10^6	8.5
		S. patens	0.39	3.6 x 10^6		
	Drought	*S. alterniflora*	0.44	1.4 x 10^6	5.6 x 10^6	10

		S. patens	0.46	4.2×10^6		

The overland flow calculation assumes a diurnal inequality throughout the year. It was found in both overland flow incubations that a longer inundation time correlated to a higher flux of DOC. This would lead to an overestimate of the overland flow in this scenario. Rather than using the average of "Tide 1" and "Tide 2" regimes, they were separately calculated and summed for the total flux in this scenario to exhibit the difference that a strong diurnal inequality may have on marsh DOC fluxes. Based on the total outwelling found in the Neponset Salt Marsh (Chapter 2) of 5.4×10^7 mol C yr^{-1}, approximately 2-10% of the total outwelling was attributed to overland flow from surface sediment and vegetation depending on season and marsh conditions (healthy versus drought). This value is representative of surface sediments on the marsh flats and aboveground vegetation inundated at high tide. As such, these values should be slightly higher than those for the vegetation contributions (Chapter 3). In both the summer and fall experiments, the vegetation flux was higher than the overland flow flux by approximately 5%. The vegetation fluxes are probably an overestimate as several values such as net primary productivity were taken from the literature and artificial leaching was induced by cutting the plants when removing them from the marsh. The CDOM/DOC relationship seen for the vegetation (Chapter 3) also suggests that the plant fluxes are an overestimate as all of the incubations showed a lower CDOM/DOC ratio that the background estuary water.

The pore water leaching incubation was used to estimate the flux of DOC from Neponset Salt Marsh sediment as it was conducted with all plant matter removed:

$$DOC_{CBS} = \sum \left(\frac{[DOC]}{V_C} \right) * V_{IS} * 365 * 2$$ Equation 4.2

Where:

DOC_{CBS} = Annual DOC flux from creek bank sediment (mol C yr^{-1})

V_{IS} = Volume of interactive sediment (m^3)

V_C = Core volume (5.0×10^{-4} m^3)

[DOC] = Experimental concentration (μmoles l^{-1}) per 3 liters of water (minus background (mol C $tide^{-1}$)

The DOC concentration of all cores was averaged since no significant difference was observed among core location and found to be 1.7×10^{-4} mol C $tide^{-1}$ after accounting for the three liters used in the experiment. This was divided by the core volume (5.0×10^{-4} m^3) to obtain 0.34 mol C m^{-3}. The volume of "interactive" marsh sediment varied based on marsh creek bank height. Three heights were used in this calculation: mosquito ditches, creek banks along the main channel, and tributary creek banks (Table 4.6).

Table 4.6. Data used for pore water leaching flux calculation.

	Height (m)	Length (m)	Depth (m)	Volume (m^3)	Tidal Export (mol C $tide^{-1}$)	Annual Export (mol C yr^{-1})
Mosquito ditch	1	5,600	0.30	1,700	580	4.2×10^5
Tributary	1.5	8.400	0.30	3,800	1,300	9.4×10^5
Main channel	2	14,000	0.3	8,400	2,900	2.1×10^6
Total						3.5×10^6 (6%)

The surface length of all of the creek banks in the Neponset Salt Marsh is 28,000 m total (observations and GoogleEarth data) and the percentage of the surface length with each height was estimated using GoogleEarth. The depth of interactive sediment was

estimated to 30 cm based on sensor data from the tidal regime study as well as in the literature (Howes et al., 1984; Munson et al., 1997). Multiplying these three numbers per type of marsh height provided three different volumes of interactive sediment.

In multiplying each volume of interacting sediment that could be exporting the DOC concentration observed in the experiment (Table 4.6), an average annual flux from creek bank pore water leaching was obtained and summed for the three heights. Dividing the DOC flux found here for creek bank pore water leaching (3.5×10^6 moles C yr^{-1}) by the total export from the Neponset Salt Marsh (5.4×10^7 moles C yr^{-1}) showed that approximately 6% of the total marsh export can be attributed to creek bank pore water leaching. It is expected that if a fall incubation had been conducted for this type of incubation, it would have yielded a higher leaching percentage consistent with the seasonal trend seen in the overland flow incubations.

The literature is remiss in terms of leaching from salt marsh sediment or overland flow, but there have been studies that have quantified and qualified the export of DOC from salt marsh pore water. Yelverton and Hackney (1986) found that the DOC export from pore water was approximately 4.3 mol C m^{-2} yr^{-1} for an *S. alterniflora*-dominated salt marsh in North Carolina. For a salt marsh in Massachusetts, Howes and Goehringer (1994) directly measured interstitial water from creek banks vegetated with *S. alterniflora* using an *in situ* chamber technique over complete tidal cycles throughout the year. They found that the annually averaged creek bank seepage was 15.2 l m^{-2}. Sediments from the same salt marsh in Massachusetts were found to export 1.1 mol C m^{-2} yr^{-1} (Howes and Goehringer, 1994). For a salt marsh in Argentina with similar vegetation, the variability of the pore water composition in terms of particulate organic matter (POM) within the

marsh was found to be greater than the temporal variation, suggesting that both tidal flooding and vegetation are important factors in the dynamics of nutrients and organic matter in the sediment pore water (Negrin et al., 2011). More recently, Clark et al. (2014) characterized CDOM in marsh pore water and its contribution as a carbon source for a marsh in California dominated by *S. alternflora*. By observing pore water optical properties, they deduced that soil pore water is a reservoir of CDOM in the salt marsh and that organic material from terrestrial watershed inputs as well as *in situ* production from marsh vegetation was stored and processed in the sediments. The same is true for the Neponset Salt Marsh where a small contribution of the overall CDOM/DOC export is attributed to this creek bank pore water flux.

Conclusions

While blue carbon systems sequester a small amount of carbon in their biomass, a much larger proportion of the sequestration occurs via sedimentation. Climate change, specifically droughts, could alter the amount of carbon buried in salt marsh sediments. An additional factor that affects carbon burial in a salt marsh is carbon outwelling to adjacent systems. This study investigated the seasonal leaching of DOC and CDOM for salt marsh sediment via two types of incubation experiments in the Neponset Salt Marsh in Boston, Massachusetts. DOC leaching fluxes were higher during fall (versus summer), under drought (versus healthy) conditions, and with longer rates of tidal inundation. Optical properties suggest that the DOM leached from these experiments is similar in composition to the background water in the estuary. Calculations based on these experiments show that approximately ~2-10% of the total outwelling was attributed to

overland flow from surface sediment and vegetation (1.0-5.6 x 10^6 mol C yr^{-1}) depending on season and marsh condition and 6% (3.5 x 10^6 moles C yr^{-1}) can be attributed to deeper salt marsh sediment pore water leaching.

CHAPTER 5

PHOTOCHEMICAL RELEASE OF DISSOLVED ORGANIC MATTER FROM RESUSPENDED SALT MARSH SEDIMENTS

Abstract

Photochemical reactions in aquatic systems induced by the absorption of solar radiation can alter the chemical structure and optical properties of dissolved organic matter (DOM), and thus play an important role in carbon and nutrient cycles in coastal waters. Incubation experiments were conducted to determine the influence of natural sunlight irradiation on the release of DOM from resuspended surface sediments. The photo-release of dissolved organic carbon (DOC), dissolved nitrogen (DN), and chromophoric dissolved organic matter (CDOM) were quantified over time. During the 5-7 day incubations, 3.4-12.4 and 23-41% of the sedimentary organic carbon (TOC) and 2.8-10.2% and 25-46% of the solid phase nitrogen (TN) were released into DOC and DN

pools from Florida and Massachusetts salt marsh sediments, respectively. The suspended, fractionated, clay-size particles from Massachusetts released much higher DOC and DN than Florida bulk sediment. Up to 65% of the DOC and 100% of the DN photo-released from sediments were respired rapidly by bacteria indicating that microorganisms play an important role in regulating the concentration of DOC and DN. The bioavailability of photo-released DOC and DN also depends largely on the biochemical nature of the DOM released from different sediments. Optical measurements confirmed that significant CDOM production was associated with the sunlight-induced DOC release. Photo-released CDOM appeared to be marine and humic-like as characterized by fluorescence and excitation-emission matrix (EEM) spectroscopy. It is estimated that photo-production of DOC from resuspended sediments could account for 10-22% of the DOC measured in the coastal waters adjacent to the marsh systems studied. These results indicate that production of DOM from resuspended sediments due to direct sunlight irradiation could be an important source of DOC, CDOM, and secondary production in salt marshes and marsh-dominated coastal waters.

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Author contributions to this dissertation chapter:

1. H. Schiebel collected and analyzed DOC/CDOM samples from the Neponset Salt Marsh and wrote half of the chapter.
2. X. Wang collected and analyzed DOC/CDOM samples from the Snipe Creek Marsh, analyzed EEMs samples, made all figures and tables in the chapter, and wrote half of the chapter.
3. R. Chen contributed to chapter edits.
4. F. Peri built the shaking table utilized in the methods section and contributed to chapter edits.

Introduction

Photochemical reactions in aquatic systems induced by the absorption of solar radiation can alter the chemical structure and optical properties of dissolved organic matter (DOM), and thus play an important role in carbon and nutrient cycles in coastal waters (Zepp et al., 1998; Miller, 1999; Ziegler and Benner, 2000; Zepp, 2002; Kieber et al., 2006; Southwell et al., 2010, 2011; Helms et al., 2014). The photochemical influence on DOM quantity and quality has been examined for many years (Kieber et al., 1989; Moran and Zepp, 1997; Opsahl and Benner, 1998; Zepp et al., 2008), however photochemical influence on marine particles has only recently been investigated.

Several studies have indicated that photochemical reactions induced by light irradiation could enhance the dissolution of organic carbon from resuspended sediments, thus producing dissolved organic carbon (DOC), transferring organic matter from solid phases to solution (Kieber et al., 2006; Mayer et al., 2006, 2011, 2012; Shank et al., 2011; Southwell et al., 2011; Helms et al., 2014). Kieber et al. (2006) used sediments and water collected from two sites in the Cape Fear River Estuary in North Carolina and irradiated them with simulated sunlight at resuspended sediment concentrations of 1-2 g/L to find that 3 to 150 μM DOC were produced per gram of resuspended dry sediment by high energy ultraviolet light. Shank et al. (2011) studied artificial light irradiation on resuspended sediments collected from seven sites in Florida Bay and found similar production of DOC from solid phases, and that the DOC released was well correlated with the concentrations of the particulate organic carbon (POC) added. Further, it was estimated that 6-15% and 10-33% of the POC were released as DOC at high (1000 mg/l wet wt.) and low (100 mg/l wet wt.) sediment resuspension concentrations, respectively.

Mayer et al. conducted a series of comprehensive studies in recent years to investigate the photo-release of organic matter from various resuspended particles including marine sediments (Mayer et al., 2006, Mayer et al., 2009a; Estapa and Mayer, 2010), algal detritus (Mayer et al., 2009b) and soils (Mayer et al., 2012). These studies demonstrated that sunlight irradiation of suspended particles plays an important role in the transformation of POC to DOC in aquatic environments. Organic matter with relatively modern radiocarbon ages was released preferentially during the irradiation process (Mayer et al., 2009a), and DOC photo-released from resuspended coastal sediments was less bioavailable compared to the DOC photo-released from algal particulate detritus (Mayer et al., 2009b). Further they noted that photochemical reactions could shift POC to physical and chemical forms that were less available to metazoans and more available to osmotrophic microbes in coastal waters (Mayer et al., 2011). Southwell et al. investigated the influence of organic matter sources on the photochemical release of DOM in the Cape Fear River estuary and found that the photochemical release of DOC as well as phosphate was higher than dark controls at all study sites (2011). They additionally noted that the DOC release from fine sediments was ten times higher than bulk sediment suspensions.

These studies suggest that photo-dissolution of particulate organic matter could be not only an important source of DOC during carbon cycling and transfer in rivers, estuaries, and coastal waters where high concentrations of suspended sediment are often present, but also a complex process affecting the bioavailability of DOC in coastal waters. This potential source of DOC has not yet been thoroughly assessed under environmentally relevant sunlight conditions among a variety of sediment compositions. A meta-study of several fresh and salt water estuaries was compiled and found that fine-

grained, resuspended sediments from different basins exhibited a net photochemical DOC release ranging from 2 to 178 µmol/g/h (Helms et al., 2014). All the reported experiments to date have been conducted in the laboratory using simulated sunlight irradiation rather than natural sunlight so do not necessarily replicate the intensity, time duration, or periodicity of irradiation found naturally in coastal environments.

Salt marshes serve as an important interface between land and coastal ocean, and these systems often have relatively high and frequent sediment resuspension events due to tidal exchange and shallow water depths as well as storms and high river discharges. Two sets of incubation experiments were conducted to investigate the influence of direct sunlight irradiation on the release of DOM from sediment solid phases at environmentally relevant concentrations.

Methods

Study site

Sediments used for the irradiation experiments were collected from two salt marshes. The first sampling site is the Snipe Creek salt marsh (N 30º04.314; W 083º57.076) located in the Florida Big Bend region approximately 80 km south of Tallahassee. This salt marsh system is one of the largest in the United States, accounting for about two-thirds of Florida's Gulf of Mexico marshes (Montague and Odum, 1997). A small topographic slope (0.4 m/km) and a 1-m tidal range cause extensive surface water and material exchange, resulting in significant sediment resuspension in the shallow water of the marsh. As part of a joint project, carbon sources and DOM outwelling from this salt marsh system have been studied from October 2010 through

November 2012. The second site is the Neponset Salt Marsh (N 42º08.332; W 071º04.047), which is part of the urban Neponset watershed system that flows into Boston Harbor in Boston, Massachusetts. The Neponset watershed system covers an area of roughly 300 km^2 southwest of Boston, and contributes terrestrial organic carbon to Boston Harbor and Massachusetts Bay (Huang and Chen, 2009).

Sunlight irradiation experiments

Two irradiation experiments were conducted separately. The first experiment was conducted from April 10-15, 2011 using Florida salt marsh sediment. Surface sediments (~0.5 cm) were collected inside the Florida salt marsh creek along the creek bank during low tide on April 10, 2011. Water used for the incubation experiment was collected 1 km offshore (salinity ~25 PSU) where DOC concentrations are much lower (DOC ~300 μM) than in the marsh (DOC ~800 μM). After collection, sediment and water samples were transported back to a field lab near the Econfina River boat landing. Sediments were refrigerated for a few hours while water was filtered through pre-combusted 0.7 μm GF/F filters prior to the incubation experiment. Three concentration levels of sediment resuspension were prepared as low, medium and high concentrations (with duplicates) (Table 5.1).

Table 5.1. Chemical compositions and weight of salt marsh sediments added to the irradiation experiments regardless of poisoned/non-poisoned or light/dark conditions within each marsh.

Marsh	Sediment Load	Wet Weight (mg)	Dry Weight (mg)	C added (mg)	N added (mg)
Florida	Low	300	117	8.9 ± 0.8	0.56 ± 0.07

TOC: 7.6 ± 0.7%, TN: 0.48 ± 0.06% C/N: 15.8	Medium	1500	585	44.5 ± 4.0	2.81 ± 0.35
	High	2500	975	74.1 ± 6.7	4.68 ± 0.59
Neponset TOC: 3.3 ± 0.4%, TN: 0.39 ± 0.02% C/N: 8.5	Low	300	99	3.3 ± 0.4	0.39 ± 0.02
	Medium	1000	330	10.9 ± 1.3	1.29 ± 0.06
	High	1500	495	16.3 ± 2.0	1.93 ± 0.10

Three concentrations (300, 1,500 and 2,500 mg) representing low, medium, and high respectively) of well-homogenized wet sediment were added separately to three light and three dark one-liter Teflon bottles containing 1 liter of filtered seawater (all Teflon bottles were cleaned with 10% hydrochloric acid followed by Milli-Q water rinsing). The total suspended mater (TSM) concentrations measured during the field study were in the range of 100-300 mg/l (wet weight) in the marsh creek so the low resuspended sediment concentration used for the experiment was in the high range of the field TSM values. The medium and high-resuspended sediment concentrations were used to quantify the potential effects of direct natural sunlight irradiation on the release of DOC and CDOM under episodic storm or high wind conditions and to compare the results with the data reported from previous studies. For sunlight irradiation experiments, light Teflon bottles (99% transmission of visible and ultraviolet (UV) light above 300 nm wavelength) were used, and dark Teflon bottles (0% light transmission) were used as a control for non-irradiation. Immediately after the sediments were added to the bottles and samples were shaken well, a water sample was collected from each bottle as a time zero sample (to confirm if any solid phase organic matter was dissolved/desorbed as

DOC immediately upon sediment addition). At the same time, two sets (of 3 bottles) of medium and high sediment resuspension samples were poisoned by adding 2.0 ml saturated $HgCl_2$ solution to each bottle (this was not done for the low resuspension level in the first experiment. This treatment was used to eliminate bacterial activity and assess the influence of bacteria on the release of DOC from resuspended particles under both light irradiated and dark control conditions. All Teflon bottles (total 10 light and 10 dark) were capped and placed in a water bath (~ 30 cm depth) on a shaker, left outside in natural sunlight and shaken continuously to keep the sediment suspended. The temperature was kept at 26 ± 1^0C by running tap water through the water bath. During the five-day experiment, all samples were exposed to sunlight from 09:00 to 18:00 (9 hours). The samples experienced full sunlight irradiation on Days 1, 3, 4 and 5, and due to limited cloud cover, about 7 hours of full sunlight on Day 2. Direct UV levels were not measured during the experiment, but the average UV index from sunlight was 9.33 over the course of the experiment, within the very high range in April in Tallahassee, Florida as reported from the Climate Prediction Center of the National Weather Service (www.cpc.ncep.noaa.gov).

The second irradiation experiment was conducted from September 20 to October 2, 2012 with Neponset Salt Marsh sediments. Surface sediment (~0.5 cm) was collected in the marsh creek during low tide on September 20, 2012. Water used for the experiment was collected in Boston Harbor to ensure a lower DOC baseline and filtered after collection using baked 0.7 µm GF/F filters. Initial examination showed that some particles and clumps of the bulk sediment were large and were not able to be suspended in the water. Therefore surface sediments were wet sieved using a 65 µm screen sieve

and only the clay fraction < 65µm was used. The Neponset experiment was conducted under similar conditions to the Snipe Creek experiment (Table 5.1).

Three concentrations (300, 1,000 and 1,500 mg) of the wet clay fraction were added separately to three light and three dark one-liter Teflon bottles containing 1 liter of filtered seawater. TSM concentrations measured for the Neponset salt marsh ranged from 112-425 mg/l (wet weight) in the marsh creek so the suspended sediment concentrations added were similar and higher than the field TSM concentrations. Poisoned ($HgCl_2$) samples were prepared at the same time for the three concentrations in the light and dark bottles. Duplicates were run for each concentration of light and dark, poisoned and non-poisoned treatments. Immediately after the sediments were added to the bottles, all Teflon bottles were capped and placed in a water bath on a shaker, left outside in natural sunlight and shaken continuously to keep the sediment suspended for 12 days (the experiment ran longer due to some rainy and cloudy days). The temperature was kept at 20 ± 2°C by running tap water through the water bath. During the 12-day experiment, samples were only collected on the sunny days after days 2, 4, 5, 7 and 12 (average 8 full hours daily sunlight exposure). The rest of the days of the incubation were rainy or cloudy at least six hours of the day and so not used for sampling. The average UV index from the sunlight was 5.28, within the moderate level in late September in Boston (www.cpc.ncep.noaa.gov). Temperature and photosynthetically active radiation (PAR) were continuously monitored for this experiment. The average daily maximum photon flux was 1,842.3 µmol m^{-2} s^{-1}.

Chemical and fluorescence measurements

For the first irradiation experiment, water samples (30 ml) were collected from each bottle at 20:00 local time on days 1, 2, 3 and 5 and filtered through pre-combusted GF/F filters. Half of the filtered water was stored in 40-ml clear glass vials, acidified to pH 2 with HCl (2.0 N) and kept in a refrigerator ($4^{o}C$) for DOC and DN analysis. The other half of the filtered water was stored in 40-ml amber glass vials and kept frozen for CDOM fluorescence measurements. For the second irradiation experiment, water samples were collected at 17:00 local time on the 5 sunny days and processed for DOC, DN and CDOM measurements as described above.

Concentrations of DOC and DN were measured using a Shimadzu TOC-VCPN analyzer equipped with an autosampler. The instrument was calibrated using 5-point carbon and nitrogen calibration curves. Carbon standards were prepared using potassium hydrogen phthalate (KHP), and nitrogen standards were prepared with potassium nitrate (KNO_3). All standards and samples were injected in triplicate. Instrument blank and DOC values were checked against reference low carbon water and deep seawater (from D. Hansell's lab at the University of Miami). Blank subtraction was conducted using Milli-Q water, which was analyzed at set intervals (every 10 samples) during sample analysis. Sediment solid phase TOC and TN concentrations were analyzed using a Perkin-Elmer 2400 CHN Analyzer. CDOM fluorescence was measured using a Photon Technologies International QM-1 spectrofluorometer. Single fluorescence emission scans from 350 to 650 nm were collected for an excitation wavelength of 337 nm. The fluorescence of Milli-Q water was determined as a blank on each day of analysis and subtracted from sample spectra, thus eliminating the water Raman peak prior to integration. Peak areas

were integrated and converted to quinine sulfate units (QSU) where 1 QSU is equivalent to the fluorescence emission of 1 μg/l quinine sulfate solution (pH 2) integrated from 350 to 650 nm at an excitation wavelength of 337 nm (Chen and Gardner, 2004).

CDOM absorption was measured with a Cary 50 spectrophotometer after the thawed samples were re-filtered through pre-cleaned 0.2 μm Poretics polycarbonate filters to remove any glass fibers that may have resulted from GF/F filtration. Milli-Q water was used as a reference, and CDOM absorption spectra (200–800 nm) were baseline-corrected (Chen and Gardner, 2004). Absorption coefficients (*a*) at 337 nm were calculated based on Stedmon et al. (2000) using the equation: $a_{337} = 2.303A/L$ where A is the measured optical density at 337 nm, and L is the cuvette pathlength (m). In a recent study, Helms et al. (2008) suggested that the CDOM absorbance spectral slope ratio (S_R) calculated from two narrow wavelength ranges (275-295 nm and 350-400 nm) can be used as a good indicator of the sources and molecular weight of photo-bleached CDOM in coastal waters. This approach was applied to calculate $S_{275\text{-}295}$ and $S_{350\text{-}400}$ using a linear regression of the log-transformed absorbance coefficients between 275-295 nm and 350-400 nm. The slope ratio, S_R, was then obtained as $S_R = S_{275\text{-}295}/S_{350\text{-}400}$ (Helms et al., 2008).

In addition to single scan fluorescence data, excitation–emission matrix spectroscopy (EEMs) was used to examine selected samples on a Hitachi F4500 fluorescence spectrophotometer to further characterize CDOM fluorescence. Excitation wavelengths varied from 250 to 500 nm in 5 nm increments. Emission wavelength data were collected from 260 to 600 nm in 5 nm increments. A normalized Milli-Q EEM was collected and subtracted from sample data in order to remove the water Raman peak from

the resulting EEM. All fluorescence data were instrument-corrected based on factory-supplied correction factors (emission correction at the factory, excitation correction during laboratory installation). Data were converted to ASCII format and plotted using MATLAB. All sample data were collected using a 1-cm quartz cuvette and expressed in quinine sulfate units (QSU). An inner filter effect has been observed in samples above ~100 QSU (Gardner et al., 2005) and may affect interpretation of both single scan and EEMs results. Therefore, samples above 100 QSU were diluted with Milli-Q water prior to analysis to minimize this effect. All glassware used for sample collection, storage and analysis were acid cleaned and baked at 500°C for 6 hours.

Results

Release of DOC and DN from Florida Salt Marsh sediments

Direct irradiation from the natural sunlight of resuspended salt marsh sediments resulted in significant production of both DOC and DN (Figure 5.1).

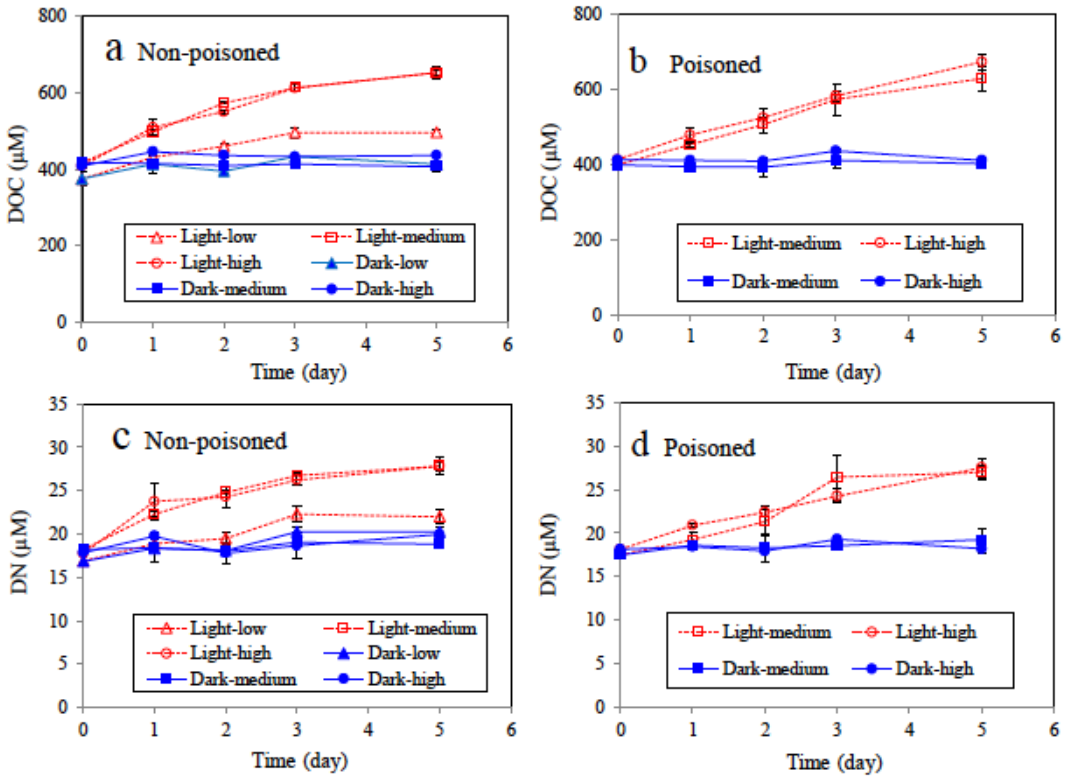


Figure 5.1. Concentration changes of DOC (a, b) and DN (c, d) with time during the direct sunlight incubation experiments from the resuspended Florida salt marsh sediments in the (a, c) non-poisoned and (b, d) poisoned light and dark control bottles. The error bars indicate the values of duplicate incubations.

The concentrations of DOC in the light bottles increased at all three particle concentrations (low, medium and high) (Figure 5.1a). At the low particle concentration, the average DOC concentration increased from the initial level (400 ±7 µM) to 500 ± 11 µM on Day 3 and remained relatively constant to Day 5, while DOC concentrations in the medium and high sediment resuspension levels increased continuously to Day 5. At the end of the experiment, 652 ± 6 µM and 652 ± 5 µM DOC were produced from the medium and high resuspended Florida salt marsh sediments, respectively, a 63% increase in DOC concentration. There were no significant differences in DOC production between the medium and high sediment resuspension levels (Figure 5.1a). In comparison to the

sunlight-irradiated samples, less than five percent DOC production was measured in the dark bottles for all of the particle concentrations (Figure 5.1a). At the end of the experiment, the average DOC concentration in the dark samples was 417 ± 4 μM, which was about the same as the initial seawater DOC concentration (400 ± 7 μM).

Sunlight irradiation of the $HgCl_2$-poisoned Florida salt marsh sediments showed similar patterns for DOC production (Figure 5.1b). DOC concentrations increased linearly with irradiation time in the light bottles. At the end of the experiment, production of DOC reached 677 ± 17 μM and 626 ± 28 μM for the medium and high resuspended sediment levels, representing 69% and 57% DOC concentration increases respectively. No statistically significant DOC release was found in the poisoned, dark bottles.

DN concentrations also increased for the sunlight irradiated Florida salt marsh sediments. In the non-poisoned light bottles (Figure 5.1c), concentrations of DN reached 22.0 ± 0.2 μM, 27.8 ± 0.5 μM and 27.9 ± 1 μM, respectively, for the low, medium and high suspended sediment levels at the end of the irradiation, indicating a 25%, 58% and 59% increase of DN from the initial seawater concentration (17.6 ± 0.7 μM). No significant differences of DN production were found between the medium and high-suspended sediment levels in the light bottles. In comparison to the sunlight-irradiated samples, concentrations of DN in the dark control bottles remained relatively constant. At the end of the experiment, the average DN concentration was 19.3 ± 0.5 μM, only a 10% increase from the initial seawater DN concentration. Similar patterns were found in the poisoned samples (Figure 5.1d). The concentration of DN increased to an average of 27.2 ± 1 μM, a 54% increase in the poisoned light bottles, and concentrations of DN remained constant in the poisoned dark bottles.

Release of DOC and DN from Neponset Salt Marsh sediments

In the non-poisoned incubation (Figure 5.2a), the concentrations of DOC increased in all three suspended particle concentration levels (low, medium and high) in the sunlight irradiated light bottles to 227 ± 12 μM, 260 ± 21 μM, and 260 ± 10 μM, corresponding to 62%, 86% and 86% increase in DOC concentrations from the initial 140 ± 2 μM. In comparison, the DOC concentrations measured in the non-poisoned dark bottles were consistent at 150 ± 3 μM at the end of the experiment, only a 7% increase (Figure 5.2a).

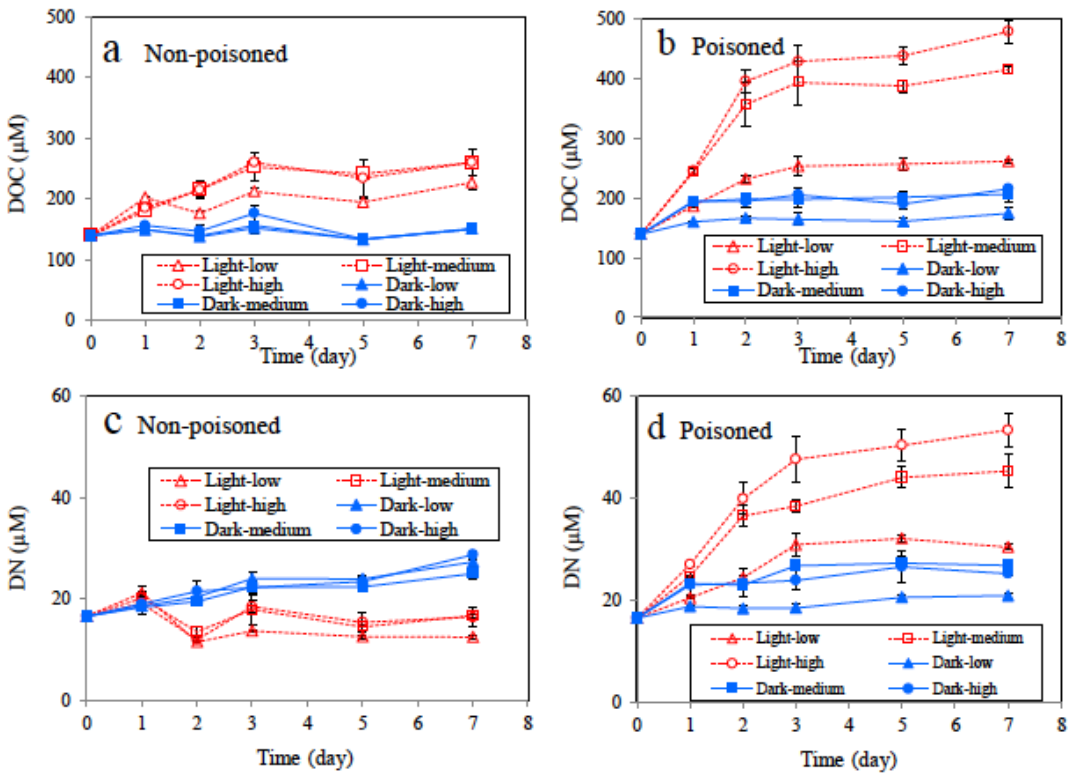


Figure 5.2. Concentration changes of DOC (a, b) and DN (c, d) with time during the direct sunlight incubation experiments from the resuspended clay fraction of Neponset salt marsh sediments in the (a, c) non-poisoned and (b, d) poisoned light and dark control bottles. The error bars indicate the values of duplicate incubations.

For the poisoned incubations using Neponset salt marsh sediments, the increase of DOC concentrations in the sunlight irradiated light bottles was much higher compared to the non-poisoned cases, especially for the medium and high-suspended sediment levels (Figure 5.2b). The DOC concentrations increased rapidly in the first three days and then remained relatively constant during the rest of the incubation period. At the end of the experiment, concentrations of DOC reached to 261 ± 2 μM, 414 ± 5 μM and 478 ± 20 μM for the low, medium and high suspended sediment levels, an 86%, 196% and 241% increase in DOC concentrations, respectively. In the poisoned dark bottles, the average

DOC concentration was 198 ± 24 μM, a 41% increase from the initial concentration at the end of the experiment.

The release of DN from the suspended Neponset salt marsh sediments in the non-poisoned case showed different patterns (Figure 5.2c). Unlike DOC, concentrations of DN in the light irradiated light bottles decreased on the second day and remained relatively constant through the end of the experiment. The average DN concentration was 15.2 ± 2.7 μM, an 8% decrease from the initial concentration of 16.6 ± 0.5 μM. DN concentrations in the non-poisoned dark bottle showed similarity for the three suspended sediment levels, with a slow increase over time. At the end of the experiment, the average DN concentration was 27.0 ± 2.0 μM, a 63% increase from the initial values.

Release of DN in the poisoned case for suspended Neponset salt marsh sediments is comparable to DOC (Figure 5.2d). Concentrations of DN increased rapidly in the sunlight irradiated light bottles in the first three days and remained constant for the rest of the incubation period. At the end of the experiment, concentrations of DN reached to 30.5 ± 0.5 μM, 45.4 ± 3.2 μM and 53.4 ± 3.4 μM in the low, medium and high suspended sediment levels, indicating 84%, 173% and 222% increase in DN concentration from the initial value. In the poisoned dark bottles, slow increases in DN concentrations were also observed. The average DN concentration was 24.4 ± 3.4 μM, a 47% increase from the initial concentration.

CDOM Optical measurements

CDOM fluorescence increased almost linearly with DOC concentration in the sunlight irradiated Florida salt marsh sediments in both treatments (Fig 5.3a,b).

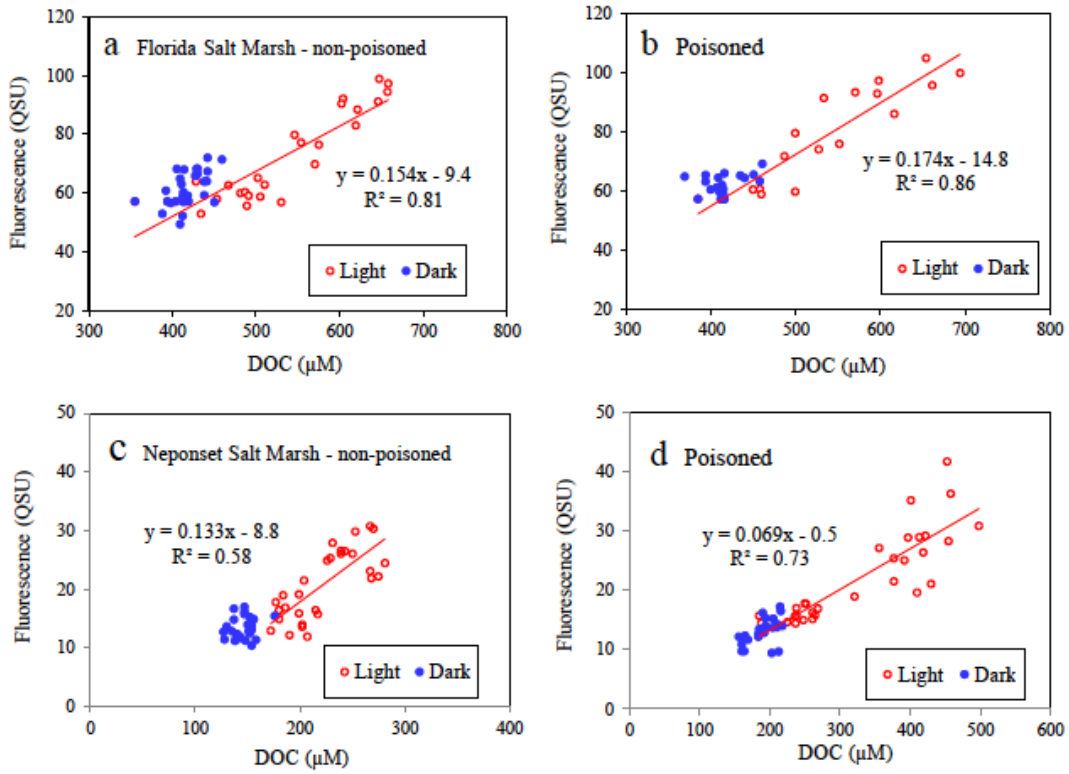


Figure 5.3. Photo-released CDOM fluorescence (QSU) vs. DOC (µM) from the resuspended (a, b) Florida salt marsh sediments and (c, d) clay fraction of Neponset salt marsh sediments during the direct sunlight incubation in the non-poisoned and poisoned light and dark control bottles. The line is a linear regression of the light bottle data.

No increase in CDOM fluorescence was measured in the dark control bottles. Neponset salt marsh sediments showed similar results. CDOM fluorescence increased in the sunlight irradiated light bottles and remained with no change in the dark bottles during the incubation (Figure 5.2c,d). Although the percentage release of DOC from the clay particles of Neponset marsh sediments was much higher than that of the Florida marsh sediments, CDOM fluorescence was much lower for organic matter released from the Neponset clay particles.

The absorbance coefficient a_{337} and the slope ratio S_R were plotted against irradiation time for CDOM measured in both light and dark bottles (Figure 5.4).

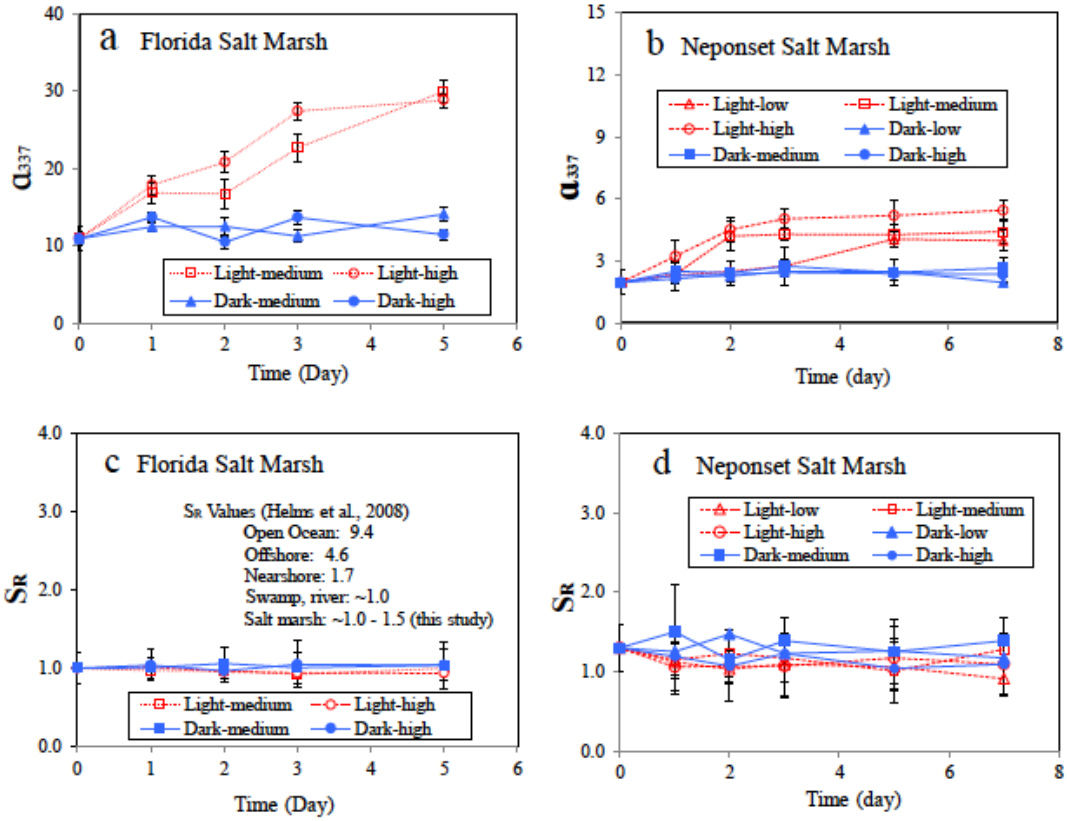


Figure 5.4. Changes of CDOM absorbance coefficient a_{337} (a, b) and absorbance slope ratio SR (c, d) with incubation time for the resuspended sediments in the light and dark control bottles. The error bars indicate the values of duplicate incubations.

For CDOM released from sunlight irradiated Florida salt marsh sediments, the absorbance coefficient a_{337} increased rapidly with the irradiation time (Figure 5.4a), and the values are much higher than the CDOM concentrations released from the sunlight irradiated Neponset salt marsh sediments (Figure 5.4b). The CDOM released from the Neponset salt marsh sediments also increased with irradiation time. Absorbance coefficient a_{337} measured for CDOM in the dark bottles remained constant over time for both sediments. The slope ratio S_R calculated for both light and dark bottles remained constant for both sediments during the experiment, close to the S_R value (10 and 1.30) of the initial seawater used for the experiment (Figure 5.4c,d).

The EEMs were measured for the sunlight irradiated samples (poisoned medium and high levels) and compared with the initial seawater as background. It can be seen that the intensity and characteristics of EEM spectra was different for CDOM released from the two site sediments during light irradiation (Figure 5.5).

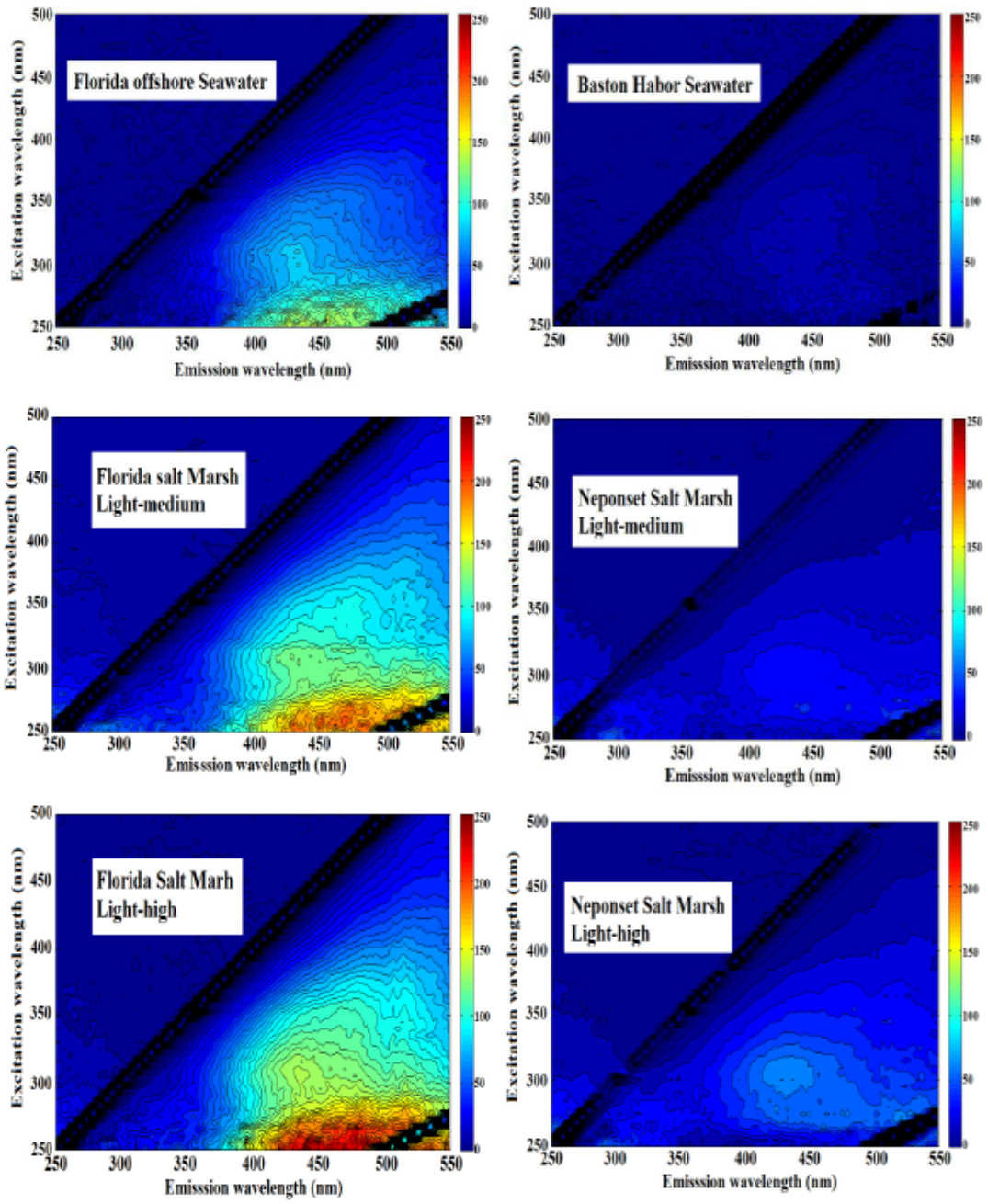


Figure 5.5. EEMs for CDOM of seawater (as background) and in the sunlight irradiated seawater with resuspended Florida and Neponset salt marsh sediments (light-medium and light-high poisoned samples only).

For Florida salt marsh sediments, the EEMs showed very strong peaks in the regions representative of UV humic-like substances as described previously by Coble

(1996) (Ex/Em 260/380-460 nm) and Stedmon et al. (2003) (Ex/Em 270 (360)/478 nm). There is also some indication of minor peaks or shoulders at 300/445 nm and 325/510 nm. This suggests that significant marine humic-like CDOM was produced with the DOC release from resuspended Florida marsh sediments during natural sunlight irradiation. This EEM signature of CDOM can also be seen in the Florida offshore waters where samples were collected for the incubation. Similarly, for Neponset marsh sediments, while values are lower, the EEMs suggest release of marine humic-like CDOM similar to what is found in Boston Harbor seawater.

Discussion

Release of DOC and DN due to sunlight irradiation

Many studies have investigated the effects of solar radiation on DOM in coastal environments (Arnon and Benner, 1996; Moran and Zepp, 1997; Benner and Biddanda, 1998; Zepp et al., 1998, 2002; Ziegler and Benner, 2000; Mayer et al., 2011). These studies demonstrated that solar radiation could not only degrade DOM in coastal waters but also alter the chemical structure and bioavailability of DOM. The mechanisms of solar irradiation to transfer resuspended POC to DOC, however, have been less documented. The results from these experiments provide strong evidence that the natural sunlight irradiation of resuspended salt marsh sediments plays an important role in the release of DOC and DN from the solid phase organic matter, supporting the conclusions derived from recent studies (Kieber et al., 2006; Mayer et al., 2009a, 2011, 2012 Riggsbee et al., 2008; Shank et al., 2011; Southwell et al., 2011; Helms et al., 2014). Mayer et al. (2006, 2009a) and Shank et al. (2011) referred to the production of DOC

during solar irradiation of resuspended sediments as photo-dissolution or a solar-enhanced dissolution process, while others considered it to be photo-production and photo-induced decomposition processes (Kieber et al., 2006; Maie et al., 2008; Riggsbee et al., 2008). Since organic matter of sediment solid phases contains a variety of organic compounds adsorbed onto particle surfaces, it is likely that the extensive sunlight irradiation of resuspended particles provides sufficient energy to enhance the chemical activity of particle-bound organic compounds, or break specific chemical bonds of the compounds and produce low molecular weight photoproducts, resulting in more organic compounds dissolved into solution (Wetzel et al., 1995; Opsahl and Benner, 1998; Kieber et al., 2006; Mayer et al., 2009, 2011). Since solar irradiation can change the chemical structure and activity of organic compounds, this will certainly affect the partitioning of different organic compounds between the solid phases and solution (Theng, 1974; Stumm and Morgan, 1996, Kieber et al., 2006). Although the dynamics and mechanisms of DOC production from resuspended sediment due to natural sunlight irradiation are still not fully understood, it is clear that this is a rapid process in which the majority of photo-released DOC and DN can be completed within three days of direct sunlight irradiation.

By comparing the two salt marsh sediments, two major differences can be emphasized. First, the release of DOC and DN from resuspended sediments was influenced by the intensity of exposure to UV and visible light, and the characteristics of the sediment solid phase. DOC photochemical degradation may be linked to variations in solar radiation and the depth of the water column. While the UV intensity was not directly measured at either site, the average UV index in the Snipe Creek area in Florida during this study is nine, while the average UV index for Boston, Massachusetts in

October is five. Based on observations, this varying intensity reaches the bottom of the water column (less than one m) at both sites. For Neponset salt marsh sediments, only the clay fraction (< 63μm) was used. The fine particles were fully suspended in seawater during shaking irradiation, and the photo-release of DOC (86-241%) and DN (84-222%) was much higher than that from the bulk Florida salt marsh sediments (DOC: 57-69% and DN: 54%). Even though the TOC and TN contents of Florida marsh sediments were higher than the clay fraction of Neponset marsh sediments (Table 2.1), these combined effects were more significant in determining the amount of DOM released. It should be noted that during an episodic storm event, very high re-suspension might lead total light and UV attenuation and stop photodissolution altogether. Photo-release values determined in this study should be representative of background conditions.

Second, the total percentage of sediment organic carbon released was higher for Neponset sediments. In order to quantitatively compare the dynamic processes of photo-release of DOC and DN from suspended sediments, DOC and DN released as a dry percentage of sediment TOC and TN added were calculated. The sunlight irradiation of Florida salt marsh sediment only released 3.4-12.4% and 2.8-10.2% of the solid phase TOC and TN into the dissolved phase, much less than the solid phase TOC (23-41%) and TN (25-46%) released from the clay particles of Neponset marsh sediments. This difference may be attributable to two factors. During the incubation, the bulk Florida salt marsh sediment contained significant decomposed small plant fragments, which contributed to a high TOC content of the sediment, but probably did not contribute to DOC released during light irradiation. Some of the bulk Florida marsh sediment large particles were not resuspended in seawater by gentle shaking during the experiments.

This difference, however, suggests an important possibility that in natural aquatic environments such as salt marshes, estuaries, and coastal waters where high turbidity resuspension events occur, it is mainly the clay particles which are suspended in the water column and transported offshore (Keil et al., 1994). These organic rich clay particles with high surface areas suspended in coastal waters could have sufficient residence times to receive sunlight irradiation and provide an important pathway of transforming solid phase TOC and TN into DOC and DN pools. It was also possible that the Florida salt marsh surface sediment was already "pre-exposed" to more sunlight than the Neponset surface sediment thus contributing to the observed differences.

The observed DOC release from the solid phases in these experiments was clearly not due to the simple dissolution and desorption of solid phase organic matter since DOC concentration increases were not observed after sediment addition in the light (time zero) or dark bottles for Florida sediments. For clay fraction Neponset sediments, a small amount of DOM desorption was seen over time in the dark bottles. Adsorption of organic compounds onto particle surfaces in aquatic systems is a dynamically rapid process in which equilibrium can be reached in less than one hour in most cases (Stumm and Morgan, 1996). Studies have shown that adsorption of organic compounds such as amino acids and glucose onto organic-rich marine and salt marsh sediments appeared to be a rapid and irreversible process, and these adsorbed organic compounds could not be desorbed back into solution easily due to sediment resuspension (Henrichs and Sugai, 1993; Wang and Lee, 1993). Both amino acids and glucose are labile compounds which can be utilized rapidly in water, and desorption cannot be accounted for during such rapid utilization. Amino acids and glucose could be protected on the surface and degraded

quickly when released. In other words, small compounds such as these can sorb irreversibly and then, when utilized, they are desorbed because their matrix protection breaks down. For some positively charged organic compounds such as aliphatic amines, which are widely distributed in salt marsh sediments at relatively high concentrations (Lee and Olson, 1984; Wang and Lee, 1994), their adsorption onto sediment particles is controlled mainly by ion exchange and the adsorption is a reversible process (Wang and Lee, 1993). Because these aliphatic amines are also major N-containing organic compounds, the observed DN increases in the dark control bottles were likely due to some desorption of aliphatic amines and ammonium adsorbed on to the salt marsh sediments by ion-exchange process. This could be particularly true for the clay fraction of Neponset sediments.

Although both DOC and DN concentrations increased with the amount of sediment added in both marsh sediment incubations (Figures 5.1-4), the percentages of solid phase TOC and TN photo-released as DOC and DN actually decreased with increasing concentrations of resuspended particles for both marsh sediments (Figure 5.6).

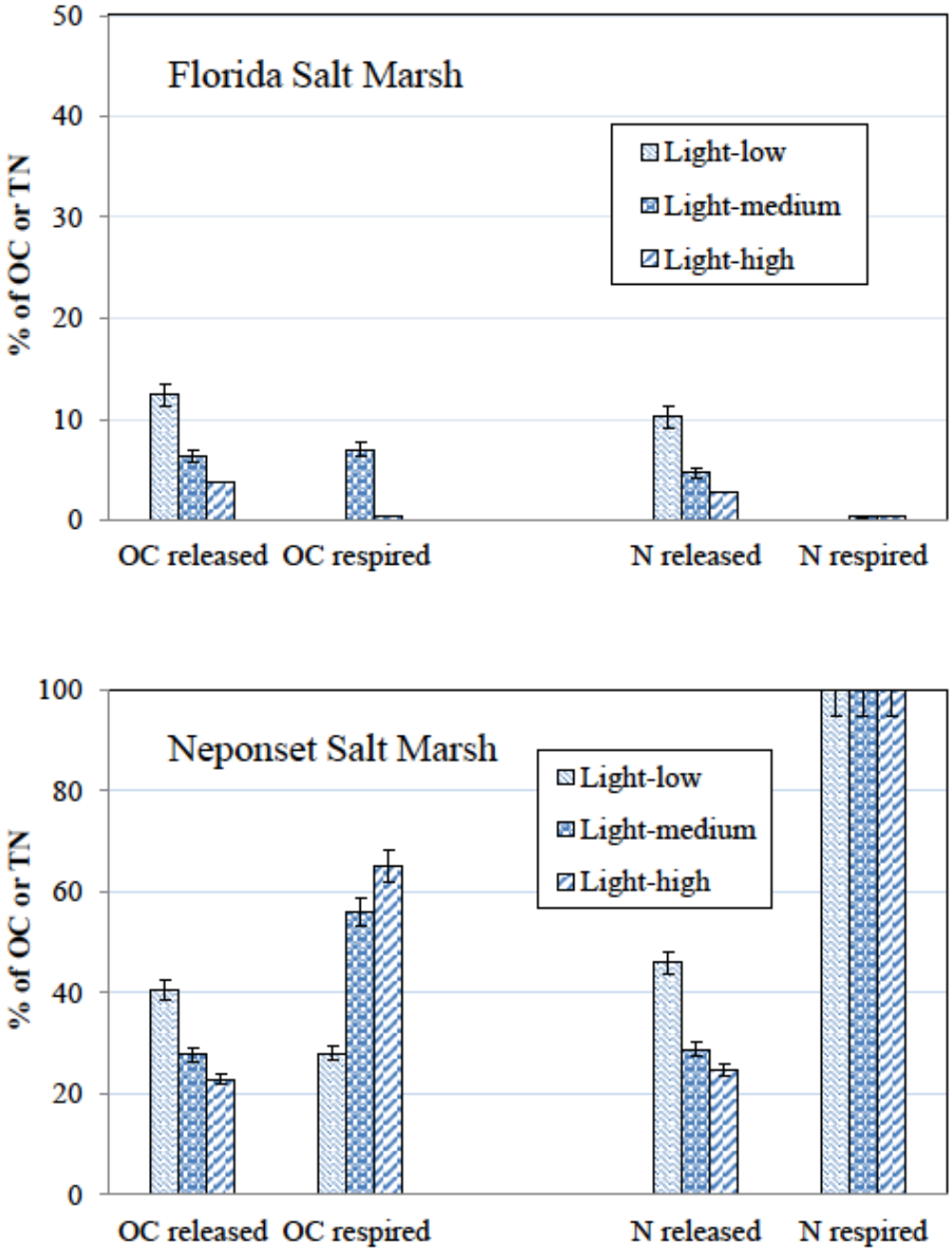


Figure 5.6. Percent organic carbon and nitrogen photo-released from the sediment solid phases and respired at end of the sunlight irradiation incubation. The percentage of respired OC and N were calculated as the differences between non-poisoned and poisoned samples.

The highest percentage of photo-release occurred at the low resuspended sediment levels. This observation is consistent with the results obtained in a recent study by Shank et al. (2011). Using sediments collected from 7 sites in Florida Bay, Shank et al. (2011) found that the fraction of POC that was photo-dissolved was larger (10-33%) at lower sediment additions (100 mg/l) than at the high sediment load (6-15%, 1000 mg/l). This difference is possibility due to increased exposure of particle surfaces to simulated solar radiation at the low suspended particle concentrations. In addition to this factor, certain chemical equilibrium/reactions or saturation balance between active particle surfaces and dissolved organic compounds in solution, which were independent of solid phase concentrations, could also play certain roles here. At high-suspended particle concentrations, the photoreaction and dissolution could be rate limited. In fact, the high percentage of photo-dissolution of DOC for the low suspended particle levels tested could be more realistic and significant in the natural coastal waters where the suspended particle concentrations are within the low ranges tested. This suggests that for the salt marsh systems studied, natural sunlight irradiation of resuspended particles is likely an important source of DOC production, considering the shallow water depth, the turbid conditions suggesting particle resuspension, and extended sunlight radiation.

Microbial degradation of photo-released DOM

Microbial activity played an important role in the degradation of DOC and DN during sunlight irradiation. Studies conducted in the field have demonstrated the importance of bacteria in regulating the production, degradation and distribution of DOC in salt marsh systems (Hopkinson et al., 1998; Moran et al., 1999). The Florida salt marsh

sediment incubation indicates that bacterial influence on the photo-release of DOC and DN is limited. In comparing the non-poisoned and poisoned incubations (Figure 5.1), no significant differences in concentration changes of DOC and DN were found between these two treatments. As calculated, bacteria in the non-poisoned incubation decomposed less than 7% of DOC photo-released from the solid phase and bacteria utilized no DN during the experiment (Figure 5.6). However, during a separate leaching experiment, we found that 56-90% DOC and 44-72% DN leached from the marsh plants and sea grasses in the same Florida salt marsh were respired (Wang et al., 2014), suggesting that the DOM released from marsh plants are much more labile than DOM photo-released from the sediments. During the Neponset salt marsh sediment incubation, however, the bacterial influence was significant. At the end of the experiment, 28-65% DOC and 100% DN photo-released from the clay particles were consumed by bacteria. While it is possible that during the Florida salt marsh sediment incubation, very strong UV irradiation generated an unfavorable environment in the tightly capped bottles for bacterial activities, it is more likely that the difference in the biochemical nature of the DOM photo-released from the two different sediments is the major explanation of the observed differences in bacterial utilization. A high percentage of photo-released DOM from the clay particles of Neponset salt marsh sediments was not optically active (as evidenced by CDOM and absorbance measurements) and was probably more labile so it could be consumed more readily by bacteria compared with the DOM photo-released from the Florida marsh sediments. This is supported by the EEMs results as discussed later.

Characterization of photo-released CDOM

In river and salt marsh-dominated coastal waters, CDOM comprises an important fraction of the DOM (Blough and Del Vecchio, 2002; Rochelle-Newall and Fisher, 2002; Chen et al., 2004). Possible sources of CDOM include river input, leaching from marsh plants, diffusion from sediments (Chen and Bada, 1989; Burdige et al., 1999; Wang et al., 2007), and in situ production by phytoplankton and zooplankton. The terrestrial-derived CDOM present in coastal waters is presumed to originate largely through the decomposition of vascular plant material in soil and sediment. Differences between the optical and physiochemical properties of these distinct CDOM types may result in distinct spectral properties that can be seen in EEM spectra (Coble, 1996; Chen et al., 2004). This experiment provides clear evidence that significant CDOM was released during the natural sunlight irradiation of resuspended salt marsh sediments (Figures 5.3-4). For CDOM photo-released from the suspended Florida salt marsh sediments, the fluorescence (QSU)/DOC ratio (as seen in the slope of the curve, Figure 5.3) was about the same in both non-poisoned and poisoned incubations. This suggests that CDOM photo-releases were in constant proportion to DOC releases, and the CDOM was not selectively released from sediments. Further, CDOM concentrations were not significantly photodegraded under the conditions of the experiment. This is also true for CDOM photo-released from the suspended clay particles of Neponset salt marsh sediments (Figure 5.3). However, the higher slope value (0.133) in the non-poisoned incubation versus the poisoned case (0.069) could suggest that bacteria preferably consumed DOC compared to CDOM.

It is also clear that while the absorbance intensity (a_{337}) of CDOM increased with time, the absorbance spectral slope ratio, S_R, indicated that the CDOM released from the sediment solid phase was comparable in quality to the CDOM dissolved in the marsh waters with similar optical properties (Figure 5.4). Helms et al. (2008) used the absorbance slope ratio S_R as an indicator of source and molecular weight of CDOM. They found that S_R varied significantly for CDOM from different waters. CDOM in swamp, river and estuarine waters had low S_R values (0.88-1.50) compared to CDOM (4.6-9.4) of the offshore (shelf break) and open ocean (Sargasso Sea) waters. A negative correlation between S_R and CDOM molecular weight was also found with low S_R generally correlated to a high molecular weight of CDOM. Here, the S_R values of CDOM released from both Florida and Neponset salt marsh suspended sediments are within the same range to the S_R values of CDOM of marsh waters (1-1.5). This suggests that this CDOM is likely from the same sources with similar molecular weight structures, most likely from the extensive degraded marsh plants and detritus which are the major organic matter inputs to both marsh water and sediments.

Using EEM analysis, the chemical properties of CDOM can be further examined. The CDOM photo-released from the resuspended Florida salt marsh sediments during sunlight irradiation was mainly composed of a large fraction of humic-like substances (Figure 5.5). This is consistent with the EEM properties of CDOM in coastal waters and marsh creek waters (*unpublished data*). These humic-like substances released from suspended sediment could comprise high molecular weight chemical structures (Repeta et al., 2002). These results are also consistent with Shank et al. (2011) where PARAFAC analysis was used to model the EEM data, and it was found that terrestrial and humic-like

components were the two major CDOM fractions photo-released from resuspended Florida Bay sediments. There were also indications of minor inputs of "marine humics" at 300/445 and 325/510 nm ex/em that are not present in background seawater (Figure 5.5). In the Florida experiment, it is clear that the photo-released CDOM had similar optical characteristics to the CDOM found in the water column supporting the hypothesis that much of the creek water DOM is ultimately derived from salt marsh plant material.

The very weak EEM spectra of CDOM released from the suspended clay particles of Neponset salt marsh sediment suggests a different proportion of CDOM released from the two different marsh sediments. This could explain why a large fraction of DOC photo-released from the Neponset salt marsh sediments is decomposed by bacteria. There were, however, no indications of tyrosine or tryptophan/like protein fluorescence released (280/320nm) in either experiment consistent with a lack of bacterial inputs of CDOM. Therefore, it can be concluded that irradiation of resuspended sediment from direct natural sunlight provides a potential source for CDOM to the coastal waters as well as for DOC.

The constant ratio of CDOM to DOC released suggests that CDOM can be used to track DOC released in this manner (Chen and Gardner, 2004). Considering the fact that DOM exposure to solar radiation can affect CDOM transformations through photochemical modification of its biological availability (Moran and Zepp, 1997, 2000; Zepp et al., 1998; Miller et al., 2002; Mayer et al., 2011), this certainly makes the DOC cycle more complicated in salt marsh dominated coastal waters than previously thought. Not only outwelling processes need to be quantified, but resuspension, photochemical

processes, and interactions with bacteria also need to be considered to determine the quality or bioavailability of outwelled DOM over time and space.

Both the Florida and Neponset salt marsh systems studied have a relatively shallow water depth (<1 m), and the water movement due to the tides can cause significant sediment resuspension in the marshes especially along the marsh banks (field observations). The TSM concentration ranged from 100-400 mg/l in the studied marsh waters. Extensive natural sunlight irradiation of resuspended sediments in the field thus could be an important DOC source to the marsh waters. To test this hypothesis, the DOC concentrations were plotted against DN concentrations for the sediment resuspension irradiation experiments and compared the results with the field measurements (Figure 5.7).

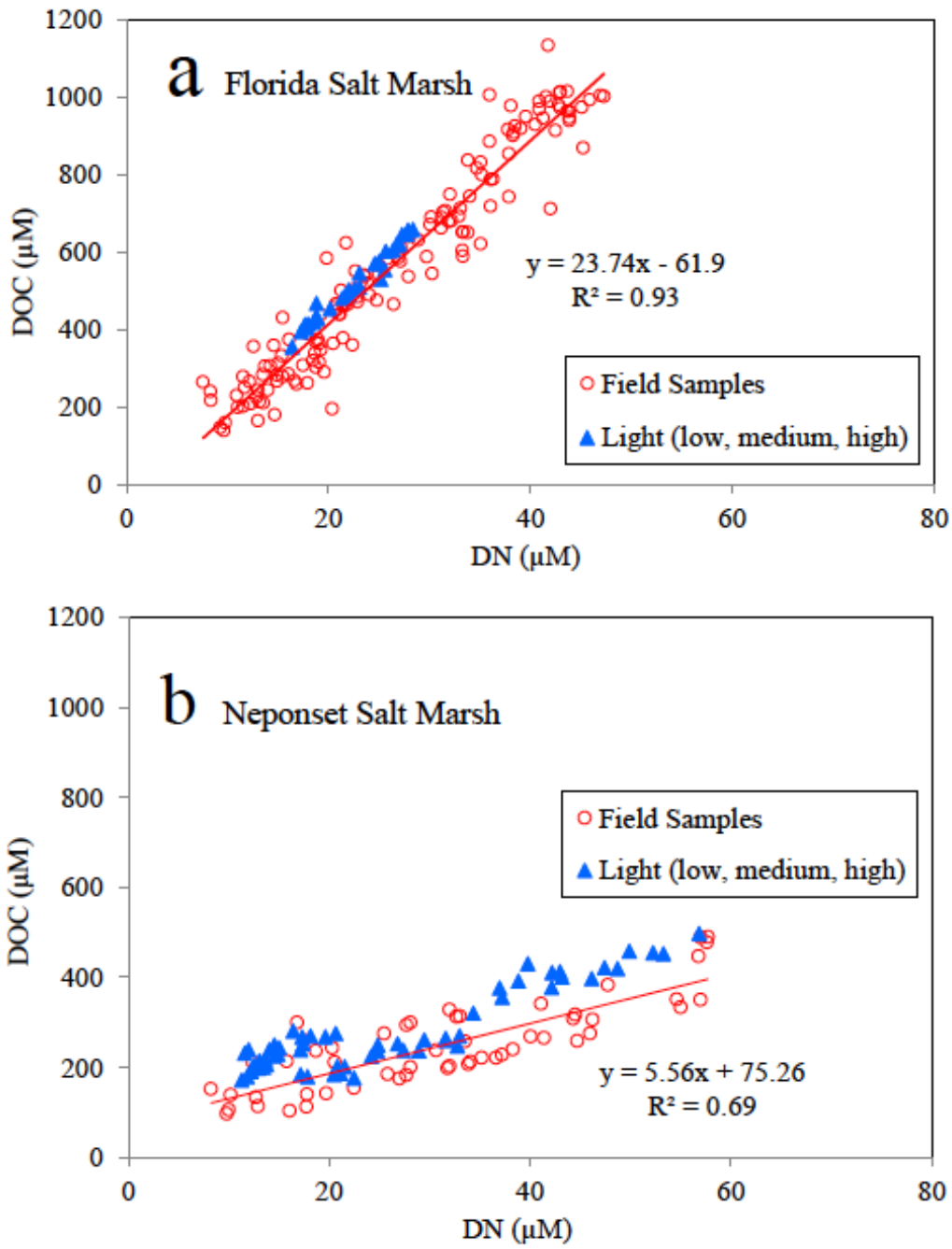


Figure 5.7. DOC (µM) vs. DN (µM) photo-released during the sunlight irradiation experiments compared with the water samples collected from Florida salt marsh (a) and Neponset salt marsh and estuary (b). The linear regression of the field samples generated an overall C/N ratio.

DOC concentration increased linearly with the increasing DN concentration in both marshes, and the overall slope generated a C/N ratio of 23.4 for the Florida salt marsh and 5.6 for the Neponset salt marsh. The experimental data fit with the field sample data in both cases, suggesting that the photo-released DOM had similar C/N ratios as the DOM present in the salt marsh waters, which was reworked extensively by bacteria. Significant photodissolution of DOM observed under environmentally-appropriate conditions along with the consistent composition of the DOM produced strongly suggests that the release of DOC and DN from resuspended sediments due to direct sunlight irradiation could be an important source of DOC and DN to the coastal waters in these systems.

Resuspended sediment contribution

In using the DOC production rate generated during the first two days from the non-poisoned low resuspended sediment load incubations (Florida salt marsh: 42 μM/day; Neponset salt marsh: 31 μM/day), and comparing them with the DOC concentration ranges measured in the field (Florida coastal waters outside the marsh: 200-400 μM; Neponset salt marsh: 140-230 μM), it is estimated that 10-22% of DOC in the coastal waters of Florida marsh system and Neponset marsh estuarine waters could be photo-released from sunlight irradiation of resuspended salt marsh sediments.

As discussed above, since humic-like substances appeared to be a major fraction of this photo-released DOC, which is significantly different from the protein-dominated, labile DOC leached from plants in these salt marshes (Wang et al., 2014), it may not be utilized rapidly by bacteria and could survive transport out of the marsh creek system to

accumulate in coastal waters. Also, by considering the chemical and optical similarities of DOM photo-released from resuspended sediments and that dissolved in the marsh waters, the estimate presented here could be reasonable reflecting the natural conditions in the system. Mayer et al. (2011) found that the DOC photo-released from resuspended Louisiana coastal sediments was less bioavailable; about 16-29% was respired by bacteria during a week long incubation period. They expected that the major fraction of photo-released DOC from resuspended sediments is likely transported offshore. Based on the simulated sunlight irradiation of resuspended sediment experiments, Kieber et al. (2006) estimated that the DOC produced by photochemical production from resuspended sediments might be significantly larger than the amount of DOC from either riverine input or sediment fluxes in the coastal waters (up to 1 m depth). This estimation was based on limited data with some uncertainties and assumptions. It appears that the results here support the conclusion of more recent studies (Kieber et al., 2006; Mayer et al., 2006, 2009a, 2011; Riggsbee et al., 2008; Shank et al., 2011), and further demonstrate that production of DOC as well as CDOM from resuspended sediments due to natural sunlight irradiation is an important source input of DOM in salt marsh-dominated coastal waters. The magnitude and threshold of photo-production of DOC and its fate and biogeochemical cycling in coastal waters, however, need to be further studied.

Conclusions

Photochemical reactions in aquatic systems play an important role in carbon and nutrient cycles in coastal waters. This study implemented incubation experiments to determine the influence of natural sunlight irradiation on the release of DOM from

resuspended surface sediments. During the 5-7 day incubations, 3.4-12.4 and 23-41% of the sedimentary organic carbon (TOC) and 2.8-10.2% and 25-46% of the solid phase nitrogen (TN) were released into DOC and DN pools from Florida and Massachusetts salt marsh sediments, respectively. The suspended, fractionated, clay-size particles from Massachusetts released much higher DOC and DN than Florida bulk sediment. Up to 65% of the DOC and 100% of the DN photo-released from sediments were respired rapidly by bacteria indicating that microorganisms play an important role in regulating the concentration of DOC and DN. The bioavailability of photo-released DOC and DN also depends largely on the biochemical nature of the DOM released from different sediments. Optical measurements confirmed that significant CDOM production was associated with the sunlight-induced DOC release. Photo-released CDOM appeared to be marine and humic-like as characterized by fluorescence and excitation-emission matrix (EEM) spectroscopy. It is estimated that photo-production of DOC from resuspended sediments could account for 10-22% of the DOC measured in the coastal waters adjacent to the marsh systems studied.

CHAPTER SIX

SUMMARY

Neponset Salt Marsh Outwelling Budget

The Neponset River is located in Boston, Massachusetts. The watershed draining into the Neponset River covers approximately 3.0 x 10^6 m^2 and watershed contributions originate from areas within 14 cities and towns populated by roughly 330,000 people. The Neponset River is the second largest river entering into Boston Harbor after the Charles River. The depth of the main channel at the mouth of the Neponset Estuary is approximately 4 m with a tidal range of 3 m and a large portion of water is exchanged during each (semi-diurnal) tidal cycle. The tidal volume and depth contribute to a short time scale of mixing within the estuary (~3-5 days).

The estuary is fringed by the 1.1 x 10^6 m^2 Neponset Salt Marsh. The marsh is predominantly covered by an invasive reed, *Phragmites australis,* and two species of

Spartina: *S. alterniflora* (low marsh, inundated twice daily) and *S. patens* (high marsh, inundated during spring tides). The marsh is bordered by the Lower Mills Dam at the landward extent of the Neponset Estuary with the flow gauged by the United States Geological Survey (USGS) at a location just downstream from the dam. This measurement provides a critical scale for estimated export from the estuary as well as marks the freshwater end of the estuary with salinity ranging from approximately 5-10 PSU.

Total export

Chapter 2 combined estimates the outwelling of dissolved organic carbon (DOC) using high-resolution *in situ* chromophoric dissolved organic matter (CDOM) sensors, seasonal monitoring, buoy data, and discrete samples of DOC. From 2001 through 2013, 35 transects of a portion of the Neponset River Estuary in Boston, Massachusetts were completed with a small research vessel towing an instrument called the Mini-Shuttle. The total export of DOC from the Neponset Salt Marsh was estimated inter-annually and seasonally. Export estimates ranged from $1.2 \pm 0.2 \times 10^{7}$ mol C yr^{-1} for summer months to $14 \pm 21 \times 10^{7}$ mol C yr^{-1} for spring months (small sampling size led to a large standard error for this season). The total average export from the Neponset Salt Marsh is $5.4 \pm 8.6 \times 10^{7}$ mol C yr^{-1} or approximately 49 mol C m^{-2} yr^{-1}. Because the major process driving this seasonality was hypothesized to be marsh plant senescence, factors affecting terrestrial plant senescence (e.g., air temperature, precipitation) and other physical factors (e.g., tides, river flow) were investigated and found to have no significant impact individually on the total *in situ* CDOM production in the Neponset Salt Marsh. It is

surmised that some set of parameters controls the marsh outwelling with high spatial and temporal variability over a short residence time in the estuary (3-5 days). High-resolution measurements allowed secondary sources of fresh water (Gulliver Greek, MWRA standpipe) to be identified. Over time, the Neponset Salt Marsh was found to export less overall DOC.

Plant matter leaching fluxes

Chapter 3 characterized the seasonal variation in DOC leaching from plants in the Neponset Salt Marsh in Boston, Massachusetts. Incubations were conducted to monitor seasonal variation in CDOM and DOC leaching rates from *S. alterniflora*, *S. patens,* and *P. australis*. While sunlight, bacteria, and biomass type all had significant effects on leaching rates, anoxia and plant species showed no consistent trend in leaching patterns. Most importantly, seasonal comparisons lead to hypothesis of the "Fall Dump" in which higher DOC concentrations are leached during the fall when marsh plants senesce for winter. Using experimental leaching rates and estimates for net primary productivity, marsh area, and root:shoot ratios for each plant species, seasonal plant leaching fluxes were quantified for the Neponset Salt Marsh ranging from 2.5-9.1 mol C m^{-2} $season^{-1}$. The annual flux of plant leaching was found to be 23 mol C m^{-2} yr^{-1}or approximately 46% of the total outwelling DOC flux.

Surface sediment/overland flow and sediment leaching fluxes

Chapter 4 investigated the seasonal leaching of DOC and CDOM for salt marsh sediment via two types of incubation experiments in the Neponset Salt Marsh. DOC leaching fluxes were significantly higher during fall (versus summer), under drought

(versus healthy) conditions, and with longer rates of inundation. Optical properties suggest that the composition of dissolved organic matter (DOM) leached from these sediment processes is compositionally similar to background estuary water. Calculations based on these experiments show that approximately ~2-10% of the total outwelling was attributed to overland flow from surface sediment and vegetation depending on season and marsh condition, and 6% can be attributed to deeper salt marsh sediment pore water leaching.

Resuspended sediment leaching fluxes

Incubation experiments were conducted to determine the influence of natural sunlight irradiation on the release of DOM from resuspended surface sediments (Chapter 5). The photo-release of DOC, DN, and CDOM were quantified over time. During the 5-7 day incubations, 3.4-12.4 and 23-41% of the sedimentary organic carbon (TOC) and 2.8-10.2% and 25-46% of the solid phase nitrogen (TN) were released into DOC and DN pools from Florida and Massachusetts salt marsh sediments, respectively. The suspended, fractionated, clay-size particles from Massachusetts released much higher DOC and DN than Florida bulk sediment. Up to 65% of the DOC and 100% of the DN photo-released from sediments were respired rapidly by bacteria indicating that microorganisms play an important role in regulating the concentration of DOC and DN. The bioavailability of photo-released DOC and DN also depends largely on the biochemical nature of the DOM released from different sediments. Optical measurements confirmed that significant CDOM production was associated with the sunlight-induced DOC release. Photo-released CDOM appeared to be marine and humic-like as characterized by fluorescence

and excitation-emission matrix (EEM) spectroscopy. It is estimated that photo-production of DOC from resuspended sediments could account for 10-22% of the DOC measured in the coastal waters adjacent to the marsh systems studied.

In summarizing all of the experiments in this study, the total outwelling can be compartmentalized based on the major processes contributing to the DOC export in the Neponset Salt Marsh (Figure 6.1).

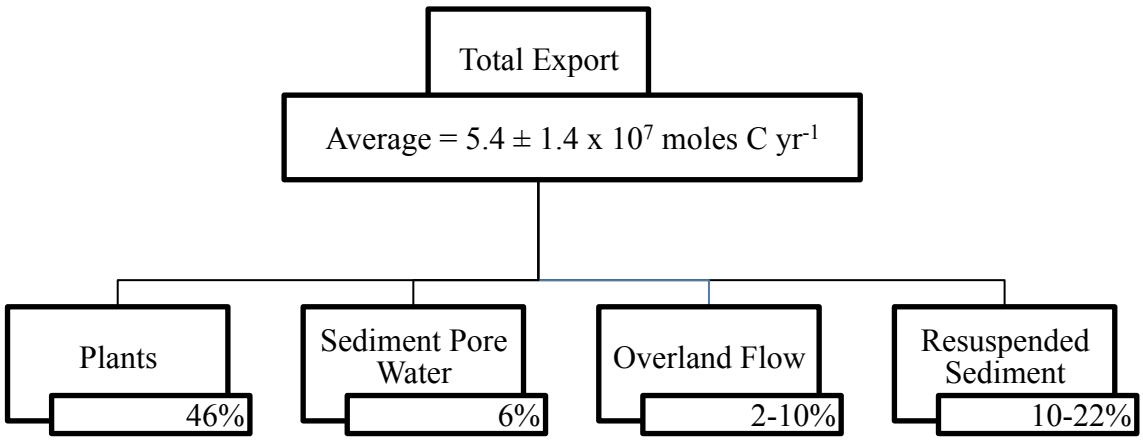


Figure 6.1. Contribution of major processes in the Neponset Salt Marsh to the overall DOC export.

It is expected that if a fall incubation had been conducted for the sediment pore water experiment, then a larger percentage could leach from this process consistent with the seasonal trend observed in other experiments. It should be noted that these processes do not work independently in the salt marsh. Incubations here attempted to isolate each component to determine a rough estimate for seasonal contributions from plants and sediment in the salt marsh. In compiling all of these numbers, it appears that the majority

of the DOC export (67-84%) can be accounted for by these major components. An additional factor that could contribute to the overall outwelling is benthic microalgae, which was not studied here.

The average export from the Neponset Salt Marsh is 5.4 ± 8.6 x 10^7 mol C yr^{-1} or approximately 49 mol C m^{-2} yr^{-1} (Chapter 2). However, if the extreme outlier in April 2003 is removed the average export is 22 mol C m^{-2} yr^{-1}, which is within the range in the literature. Nixon (1980) reported the annual export of five marshes ranging from 0.7 – 11.7 mol C m^{-2} yr^{-1}. Dame et al. (1986) studied outwelling in a South Carolina inlet and found that DOC outwelling varied by season with highest outwelling in the summer (2.7 x 10^8 mol C yr^{-1}) and lowest outwelling in the spring (0.83 x 10^8 mol C yr^{-1}). The annual estimate of DOC flux in this inlet was 27 mol C m^{-2} yr^{-1}. Osburn et al. (2015) found rates of 11 mol C m^{-2} yr^{-1} for a North Carolina salt marsh.

Neponset Salt Marsh Carbon Burial

Because the outwelling flux in the Neponset Salt Marsh has been estimated, it is possible to provide an approximation for the carbon burial potential of the system:

$$C_B = (GPP - R) - L = NPP - L \qquad \text{Equation 6.1}$$

Where:

C_B = Annual carbon burial

GPP = Gross primary productivity

R = Respiration

L = Lateral (outwelling) flux

While primary productivity and respiration were not measured in this study, there are estimates for New England salt marshes. Steever et al. (1976) estimated productivity

in the Cottrell Marsh in Connecticut to be 51 mol C m^{-2} yr^{-1} while a Rhode Island marsh was estimated to produce 36-70 mol C m^{-2} yr^{-1} (Nixon and Oviatt, 1973). Forbrich and Giblin (2015) studied ecosystem dynamics in Plum Island marsh in Massachusetts and found that from May to October 2012, primary productivity averaged -72 mol C m^{-2}, respiration averaged 49 mol C m^{-2}, and net ecosystem exchange was approximately -24 mol C m^{-2}. Niering and Warren (1980) conducted a thorough study of New England marshes and found an average net primary productivity rate of 65 ± 12 mol C m^{-2} yr^{-1}. Using this estimate and subtracting the outwelling flux found for the Neponset Salt Marsh in the current study (49 mol C m^{-2} yr^{-1}) yields 16 ± 12 mol C m^{-2} yr^{-1} sequestered by the Neponset Salt Marsh.

The burial rate found for the Neponset Salt Marsh (16 ± 12 mol C m^{-2} yr^{-1}) is within the range found in the literature (Table 6.1).

Table 6.1. Neponset Salt Marsh burial estimates compared to New England burial rates from the literature.

Site	Carbon Burial (mol C m^{-2} yr^{-1})	Reference
Neponset Salt Marsh	16	Schiebel, 2016
Long Island, NY	25	Houghton and Woodwell, 1980
Massachusetts	7.5-20	Roman et al., 1997
New Jersey	16	Artigas et al., 2015
Connecticut	13-16	Anisfeld et al., 1999

Howes et al. (1985) estimated that 10% of the carbon fixed through photosynthesis in salt marshes was buried in Great Sippewissett Salt Marsh (Cape Cod, MA). Houghton and Woodwell (1980) found annual burial rates of 25 mol C m^{-2} yr^{-1} in a Long Island, New York marsh. Artigas et al. (2015) estimated an annual burial rate of 16

mol C m^{-2} yr^{-1} for a salt marsh in New Jersey, and noted that 22% of the total fixed carbon remained as biomass or within the sediments. Artigas et al. (2014) found an average sedimentation rate of 1.4 mm yr^{-1} using cesium-137 dating. Ignoring the lateral flux of carbon to other systems, they surmised that the marsh had a carbon accumulation rate of 16 mol C m^{-2} yr^{-1}. While this is a back-of-the-envelope calculation for the rate of carbon burial in the Neponset Salt Marsh and net primary productivity measurements would help refine the burial estimate, preliminary analysis shows that the Neponset Salt Marsh burial rates are consistent with New England marsh burial rates.

Future Work

Comprehensive Neponset Salt Marsh profile

An important set of measurements could be completed to refine the current estimates of outwelling and burial rates for the Neponset Salt Marsh. Continuous photosynthetically active radiation (PAR) and temperature sensors at different points in the marsh (such as tributary entrances and the mouth of the river) would aid in understanding the cues affecting plant senescence, marsh export, and, by proxy, estuary export. Further, *in situ* CDOM and flow sensors could be deployed to monitor real-time changes on smaller scales in order to compare smaller outwelling fluxes with the overall outwelling. More detailed vegetation studies could also be conducted. Longer incubations to encompass all three phases of plant degradation and seasonal *P. australis* incubations would better characterize the leaching rates for the dominant plant species in the Neponset Salt Marsh. Productivity, root:shoot ratios, and respiration rates for the dominant vegetation in the marsh are necessary to have a better understanding of the

leaching flux. Additionally, elevation data and vegetation coverage surveys will aid in a better understanding of which species contribute most to leaching in the Neponset Salt Marsh. In terms of a sediment profile, CHN, grain size, and permeability measurements could be conducted to characterize the sediment.

Climate change impacts in the Neponset Salt Marsh

The sustainability of salt marshes and, by extension, their effectiveness in sequestering atmospheric CO_2 will also be affected by global climate change. The IPCC estimates that emissions from CO_2 and other greenhouse gases could lead to a 2-6°C increase in global temperatures and a 0.8-2.0 m increase in sea level by the year 2100 (IPCC, 2014). A suite of incubations investigating other possible climate change scenarios (e.g., warmer temperature, increased inundation due to sea level rise) would also be beneficial in understanding how both marsh vegetation and sediment may respond to a changing climate in the Neponset Salt Marsh. Plot-level experiments in the literature have shown that increased CO_2 concentrations, warmer temperatures, and minimal sea-level rise (up to 1 cm above mean high water) could actually increase primary productivity and marsh accretion (Kirwan et al., 2009; Charles and Dukes, 2009; Kirwan et al., 2014). However, coastal wetland loss from climate-driven changes (e.g., increased drought conditions or increased inundation with sea-level rise, depending on location) is predicted to cause an additional 20–45% loss of salt marsh habitat by the end of this century (Craft *et al*., 2008). Through land use conversion and other human activities, the release of stored carbon from blue carbon systems to atmospheric CO_2 currently represents a substantial economic burden, ranging in annual damages up to U.S. $42

billion (Pendleton et al., 2012). As such, understanding how marshes would be impacted by climate change would be cost-beneficial as well.

Comparative outwelling budget

Chapter 5 analyses of sediment from two different marsh systems highlighted the importance of comparing outwelling budgets between marshes. Preliminary data from Chapter 5 showed that the intensity and exposure to light affected the release of DOC and DN from resuspended sediments. Further, the sediment organic carbon released was higher for Neponset Salt Marsh sediments than sediments from a salt marsh in Florida. This suggests an important possibility that in natural aquatic environments such as salt marshes, estuaries, and coastal waters where high turbidity resuspension events occur, it is mainly the clay particles, which are suspended in the water column and transported offshore. Studying this hypothesis further would help better quantify the rate of DOC export from resuspended sediments.

Broader Impacts

Salt marsh significance

Over the past two hundred years, increased energy demands, fossil fuel reserves, and projected human population growth have altered the global carbon cycle. Until the past two centuries, the concentrations of carbon dioxide (CO_2) and and methane (CH_4) had never exceeded about 280 ppm and 790 ppb, respectively (IPCC, 2014). Current concentrations of CO_2 are approximately 390 ppm and CH_4 levels exceed 1,770 ppb (IPCC, 2014). The Intergovernmental Panel on Climate Change (IPCC) estimates

that global CO_2 emissions must be reduced by 85% from the 2000 levels by 2050 in order to prevent a mean temperature increase of 2°C (IPCC, 2014).

In addition to proposed engineered carbon sequestration techniques, recent approaches to lowering atmospheric CO_2 concentrations through carbon storage focus upon natural systems that remove excess CO_2 from the atmosphere. Blue carbon systems (mangroves, salt marshes, and seagrass beds) sequester more carbon per unit area than any other habitat on earth via primary productivity and sedimentation, making these systems an important tool in climate change mitigation (Chmura et al., 2003; McLeod et al., 2011; Duarte et al., 2014; Artigas et al., 2014).

Within blue carbon ecosystems, approximately 5.1 million hectares are salt marshes (Pendleton et al., 2012). In addition to climate mitigation (up to7.7 tons of carbon dioxide globally per hectare (Burdick and Roman, 2012)), salt marshes protect shorelines from erosion by both trapping sediments and buffering wave action as well as filtering runoff from land systems (Pendleton et al., 2012). Salt marshes provide 75% of commercial fishery habitats for species such as shrimp and blue crab (Pendleton et al., 2012). For these reasons, salt marshes have been valued at up to U.S. $10,000/hectare (Barbier, 2012; Burdick and Roman, 2012).

Salt marsh carbon burial

New England salt marshes have undergone several disturbances in the last century that could offset the amount of carbon sequestered in these systems. Examples of such disturbances include nutrient loading, ditches for mosquito control, filling, draining, habitat fragmentation, invasive species introductions, and modifications to normal tidal

flow for both recreational and commercial purposes (Gedan et al., 2009; Bernhard et al., 2015). A sampling of salt marsh habitats along the New England coast estimated that approximately 37% of these habitats have been lost due to anthropogenic influences since the European settlement (Bromberg and Bertness, 2005). This loss in habitats directly correlates to a huge loss in ecosystem services, including sequestration. On a global scale, more than 65% of wetland habitat has already been lost (Lotze et al., 2006).

Climate change will also affect salt marshes through increased temperature and changes in precipitation patterns that could lead to more frequent droughts and/or flooding events in coastal areas (Findell and Delworth, 2005; Palomo et al., 2013). The literature has shown that hydrological shifts in wetland systems will influence plant communities (Hazeldon and Boorman, 1999; McKee et al., 2004; Laijo, 2006; Weston et al., 2006; Knorr and Blodau, 2009; Palomo et al., 2013). Organic matter mineralization rates are higher with warmer temperatures and typically exhibit a seasonal pattern with higher rates during summer (Howarth and Teal, 1979; Alongi et al., 2005; Kirwin and Blum, 2011). Yet some studies have shown no seasonal patterns in mineralization (Alongi et al., 1999; Poungparn et al., 2009), experimental warming (Charles and Dukes, 2009), or spatial variation in temperature (Lovelock, 2008). Coastal wetland loss from climate-driven changes (e.g., increased drought conditions or increased inundation with sea-level rise depending on location) is predicted to cause an additional 20–45% loss of salt marsh habitat by the end of this century (Craft *et al*., 2008). Through land use conversion and other human activities, the release of stored carbon from blue carbon systems to atmospheric CO_2 currently represents a substantial economic burden, ranging in annual damages up to U.S. $42 billion (Pendleton et al., 2012).

In addition to climate change and anthropogenic disturbances to salt marshes, another component that can offset the carbon sequestered by salt marshes is outwelling. Teal (1962) noted that approximately 45% of the primary production in a salt marsh in Georgia was removed with the tides from the marsh. A salt marsh in Long Island, New York was found to have a net flux of carbon over one year into the marsh as particulate organic carbon (POC) sequestered (4.4 mol C m^{-2}), disputing the work of Teal (1962) (Woodwell and Whitney, 1977). Odum (1980) then expressed the notion that productivity of nearshore waters can be enhanced not only by the upwelling of nutrients from bottom waters, but also from the outwelling of nutrients, organic matter, and organisms from fertile estuaries.

A large number of estuarine flux studies have been conducted since the "Outwelling Hypothesis" was introduced. Nixon (1980) conducted a meta-analysis of estuarine and coastal productivity from 12 salt marshes and concluded that it was unclear whether these systems were sources or sinks of carbon. In two decades alone, outwelling research was conducted at 41 sites and presented in 42 publications (Childers et al., 2000). However, out of these studies, very few have quantified estuary-coastal ocean exchanges (Valiela et al., 1978; Valiela and Teal, 1979).

While more studies are beginning to quantify estuary-coastal ocean exchange (inclusive of not only salt marsh ecosystems) (Tzortziou et al., 2011; Duarte et al., 2014; Schiebel et al., 2014; Wang et al., 2014; Moyer et al., 2015), there are numerous reasons why directly testing the hypothesis has proven difficult. Sampling water flow and constituent concentrations in tidal channels connecting estuaries to the coastal ocean is complicated, especially if the estuary is large, has multiple tidal channels, or is remotely

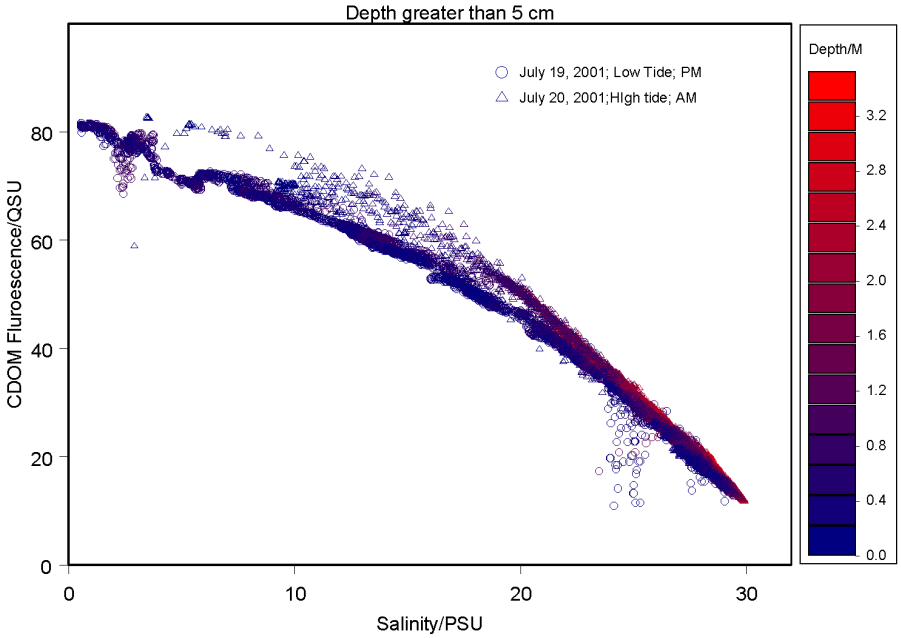
located (Childers et al., 2000). Even if all of these obstacles can be overcome, flux quantification precision, accuracy, and error is highly variable (Childers et al., 1993; Deegan and Garritt, 1997; Childers et al., 2000; Pendleton et al., 2012).

Conclusions

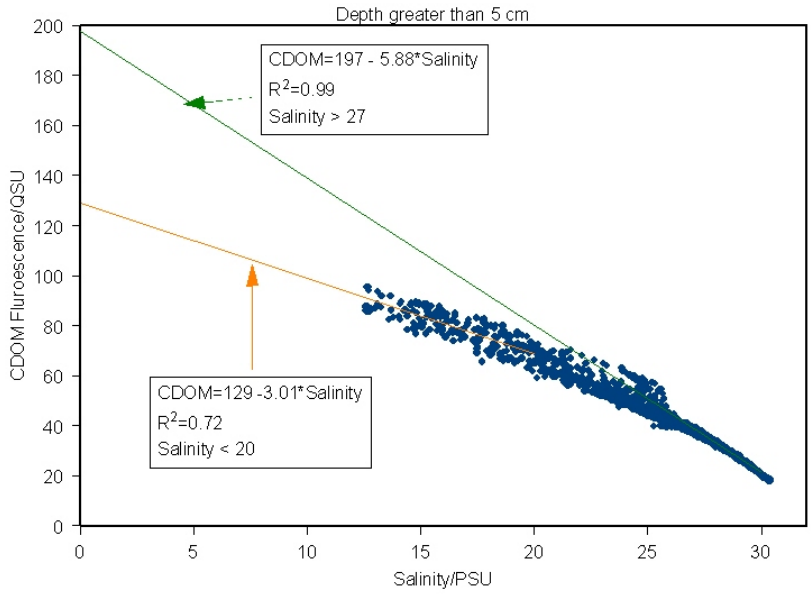
There are four important conclusions to be drawn from this work. First, this work represents the first complete DOC outwelling budget to date for a salt marsh with up to approximately 85% of the DOC exported from the Neponset Salt Marsh accounted for. Second, the Fall Dump hypothesis was confirmed where, in temperate salt marshes, plants "dump" a large proportion of carbon into estuary water in the fall as they begin to senesce for winter. This seasonal trend was seen in the total export (Chapter 2), vegetation leaching flux (Chapter 3), and overland flow sediment leaching flux (Chapter 4). Another consistent trend seen throughout this work was the importance of both sunlight and microbial processes in degrading DOM in salt marshes. This was observed in the total export where the length of day was a factor found to drive estuary export (Chapter 2). Additionally, both plant and sediment samples that were either exposed to sunlight or poisoned to remove microbes leached significantly more DOC (Chapter 3,5). Finally, climate change will be an important factor affecting New England salt marshes. Preliminary data show that sediment exposed to drought conditions will leach more DOC than healthy marshes (Chapter 4).

APPENDIX A

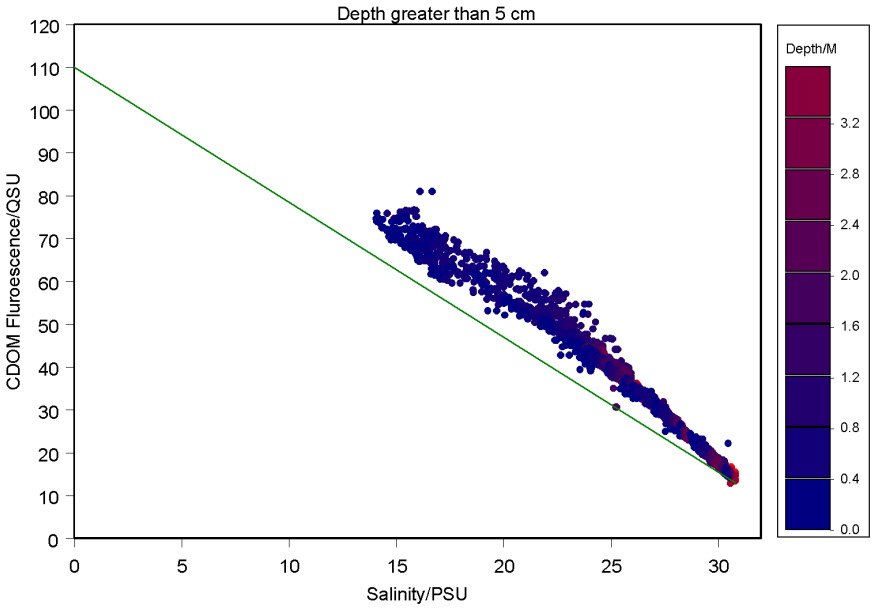
Appendix A1. CDOM-salinity relationship in the Neponset River from July 29 and 20, 2001.



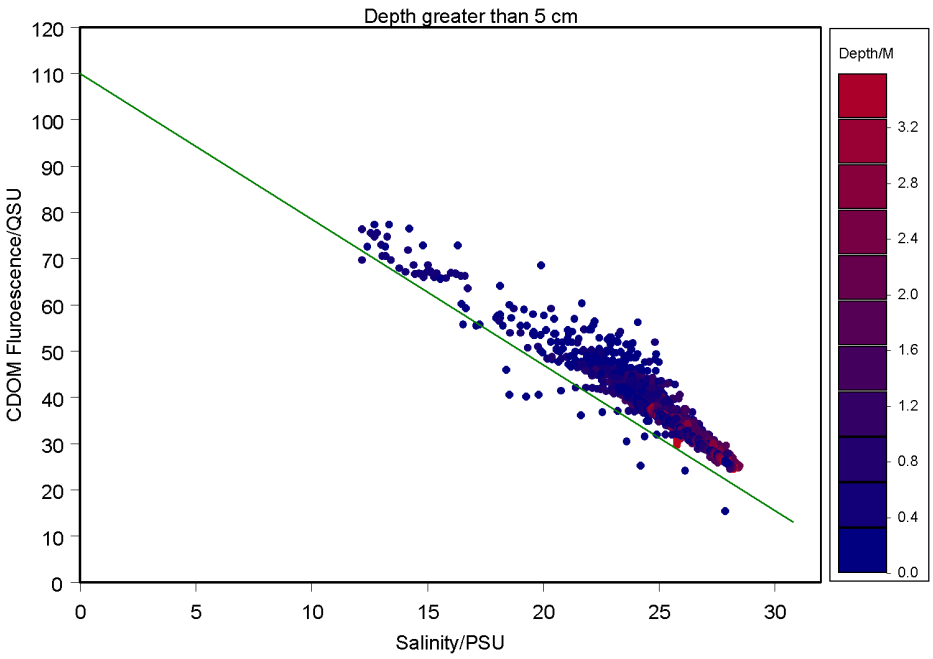
Appendix A2. CDOM-salinity relationship in the Neponset River from September 14, 2001.



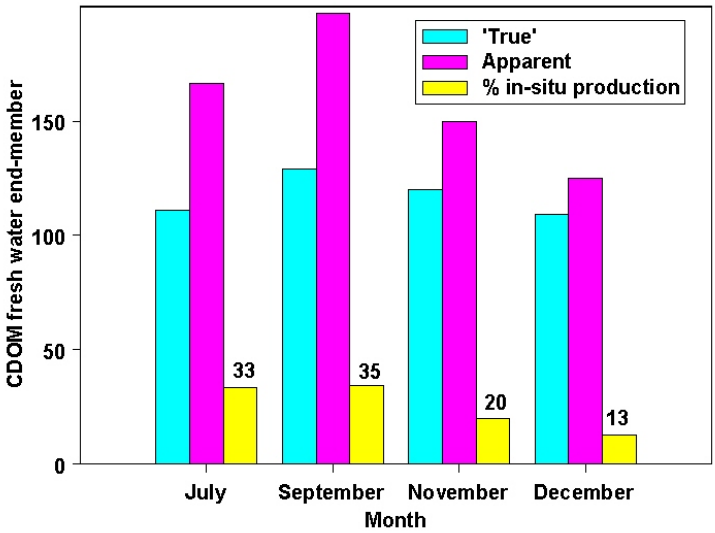
Appendix A3. CDOM-salinity relationship for the Neponset River from November 6, 2001.



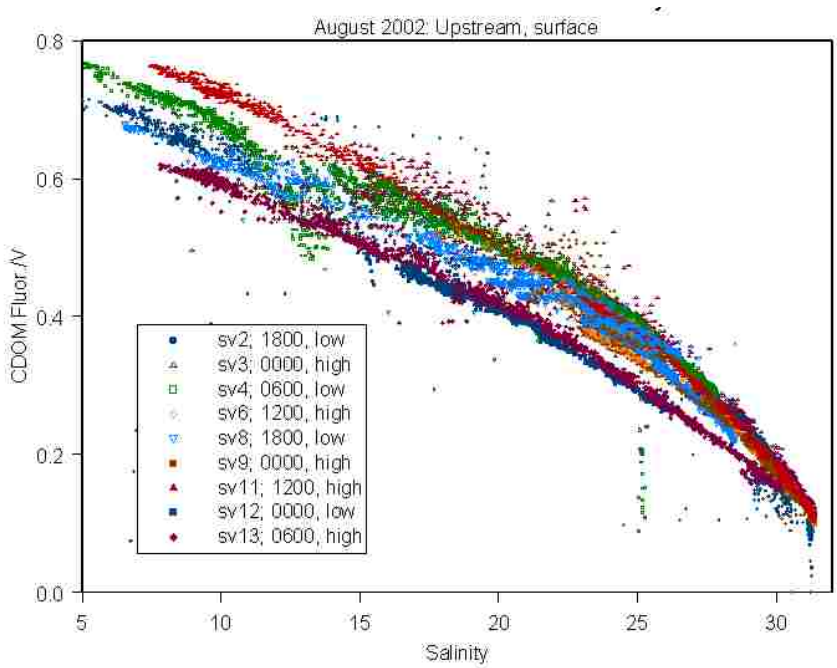
Appendix A4. CDOM-salinity relationship for the Neponset River from December 12, 2001.



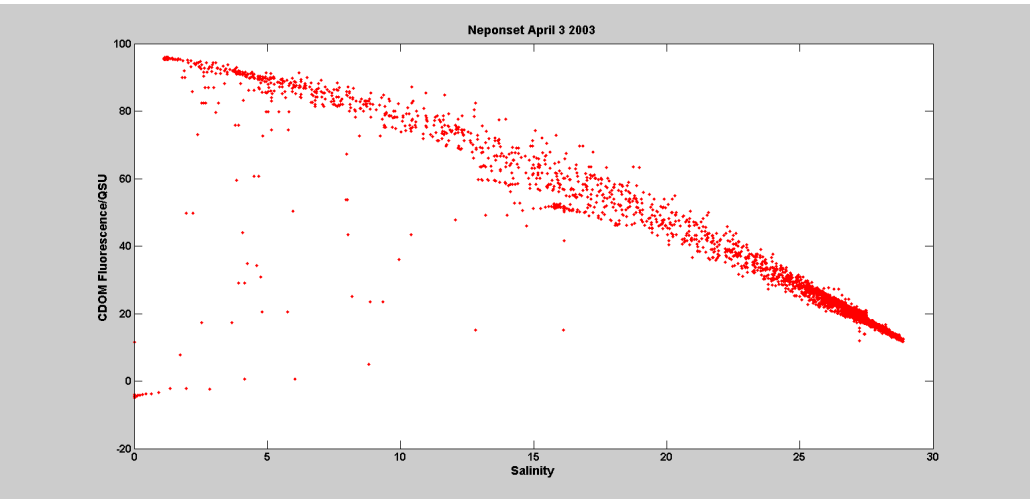
Appendix A5. CDOM freshwater endmembers for all 2001 transects in the Neponset River.



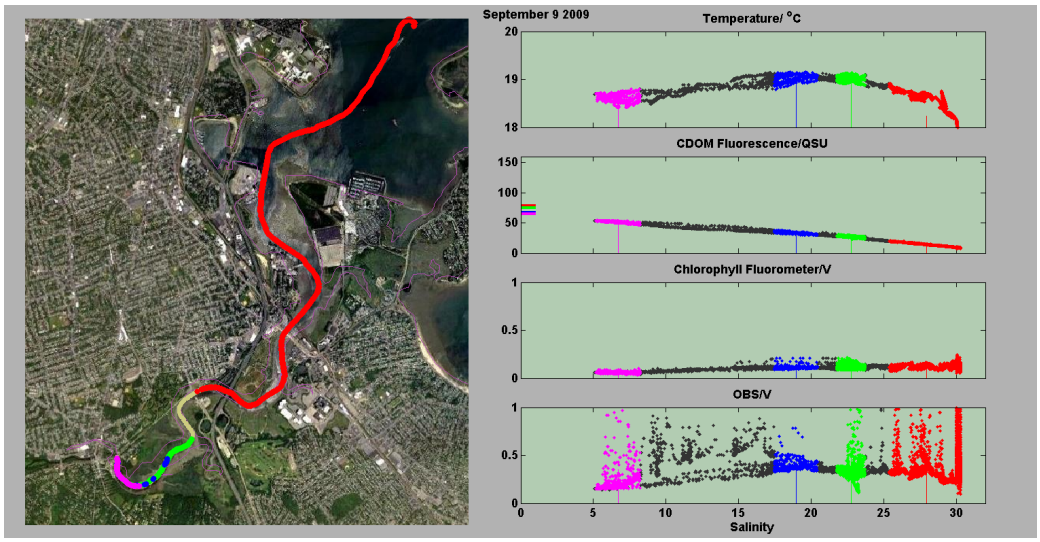
Appendix A6. CDOM-salinity relationship for the Neponset River from August 30 and 31, 2002.



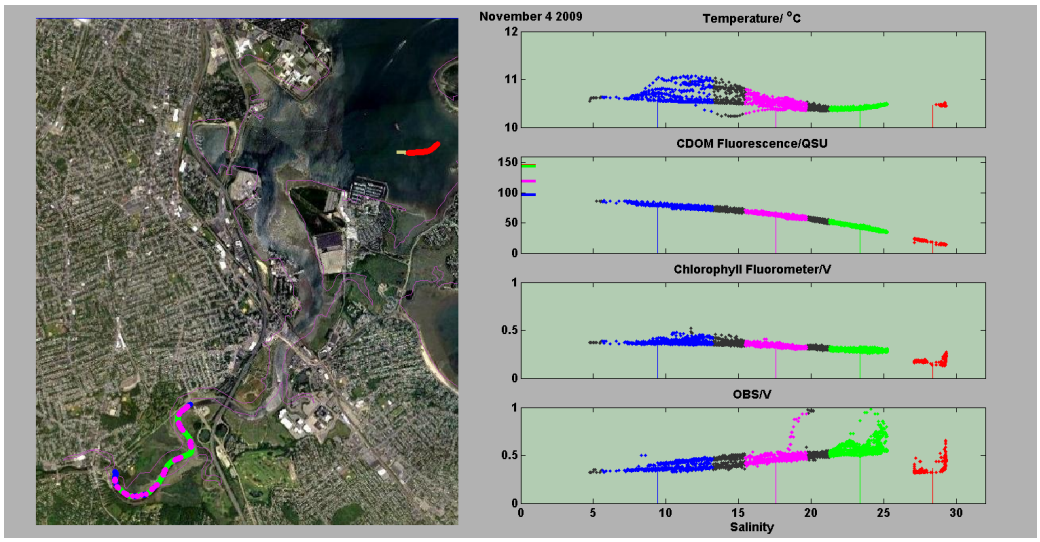
Appendix A7. CDOM-salinity relationship in the Neponset River from April 3, 2003.



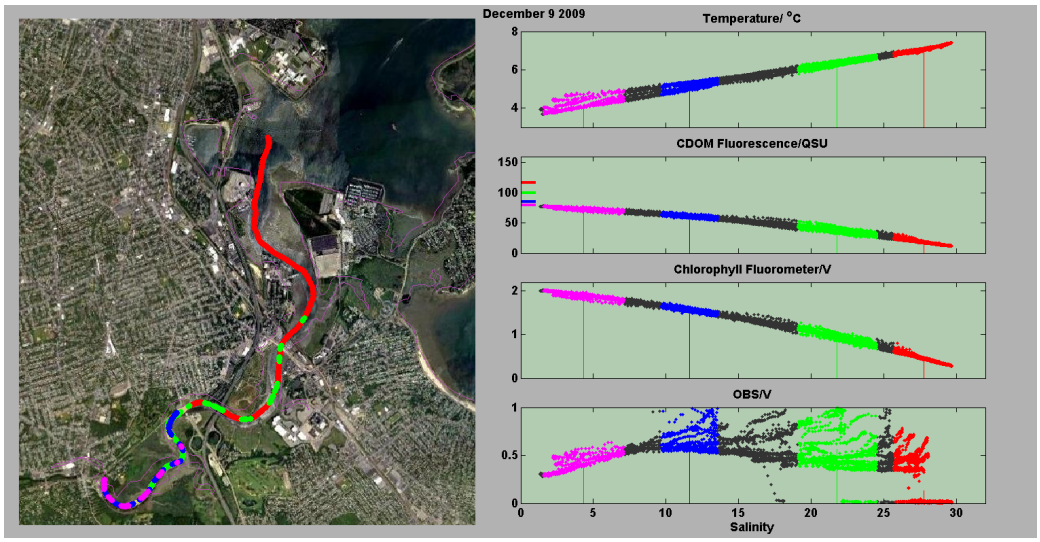
Appendix A8. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from September 9, 2009.



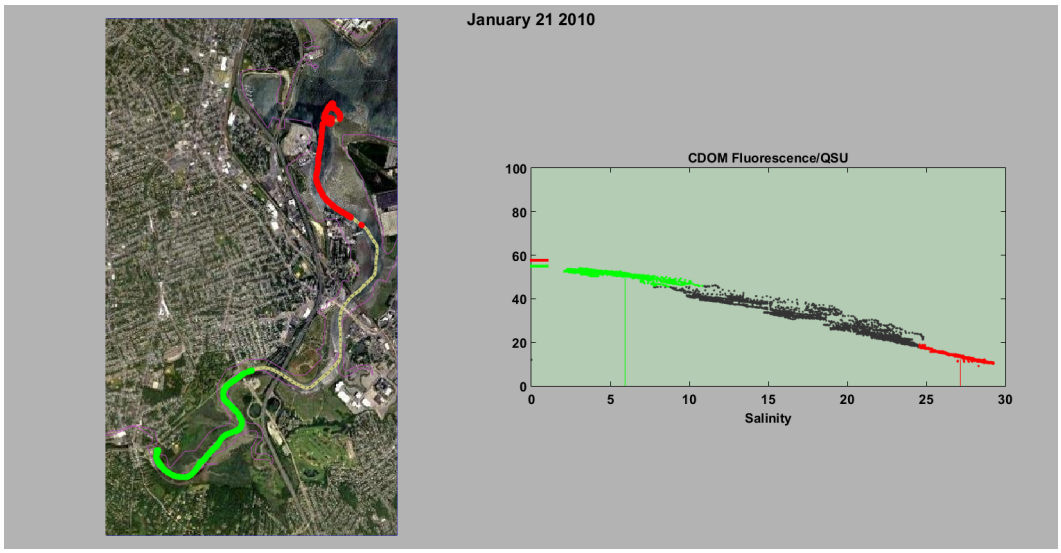
Appendix A9. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from November 4, 2009.



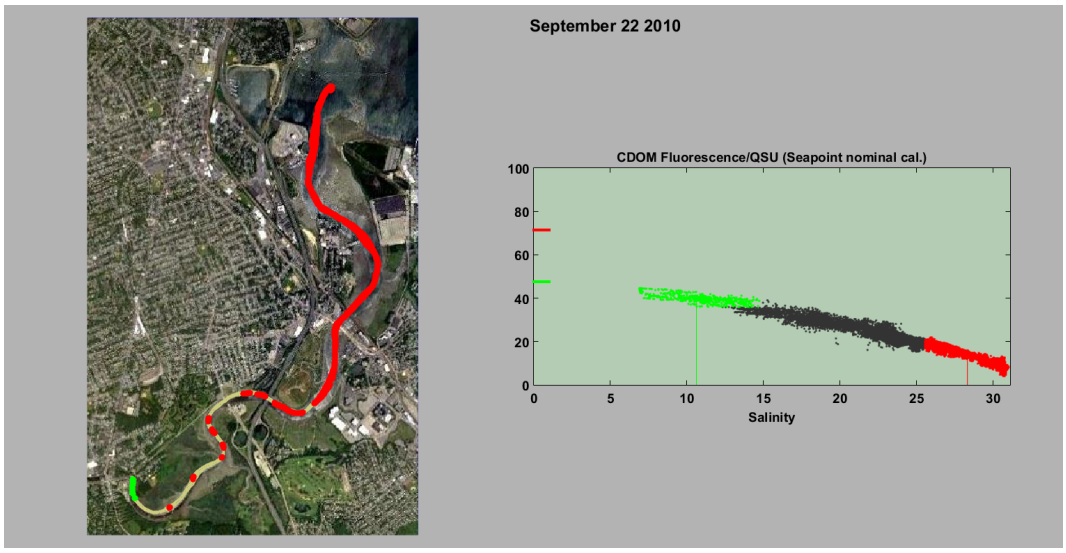
Appendix A10. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from December 9, 2009.



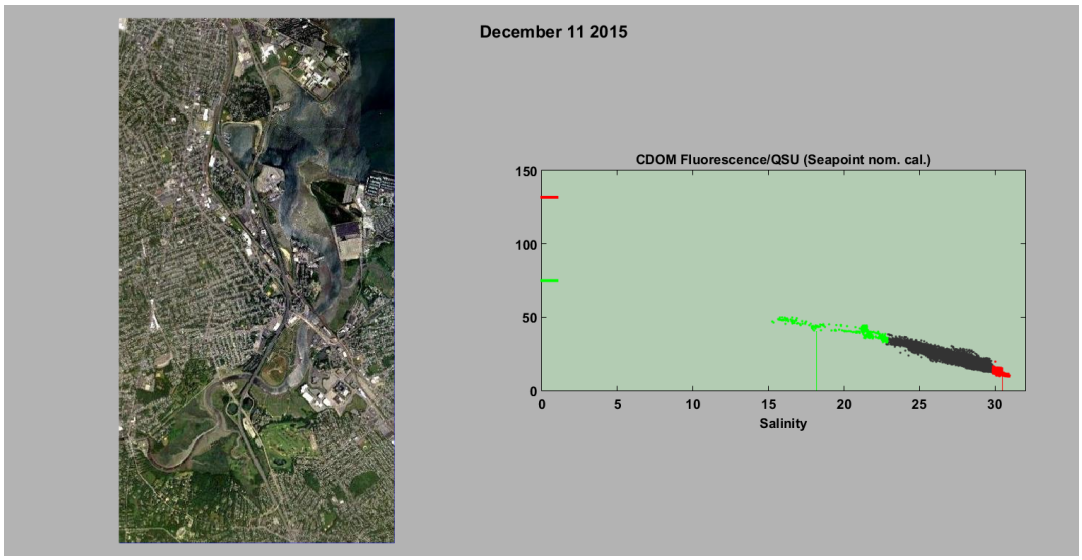
Appendix A11. CDOM-salinity relationship in the Neponset River from January 21, 2010.



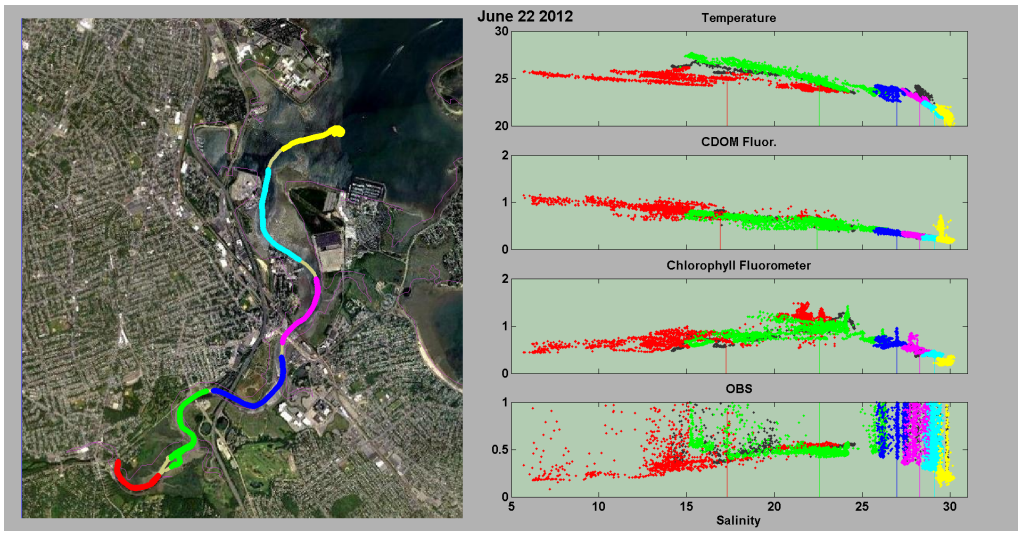
Appendix A12. CDOM-salinity relationship in the Neponset River from September 22, 2010.



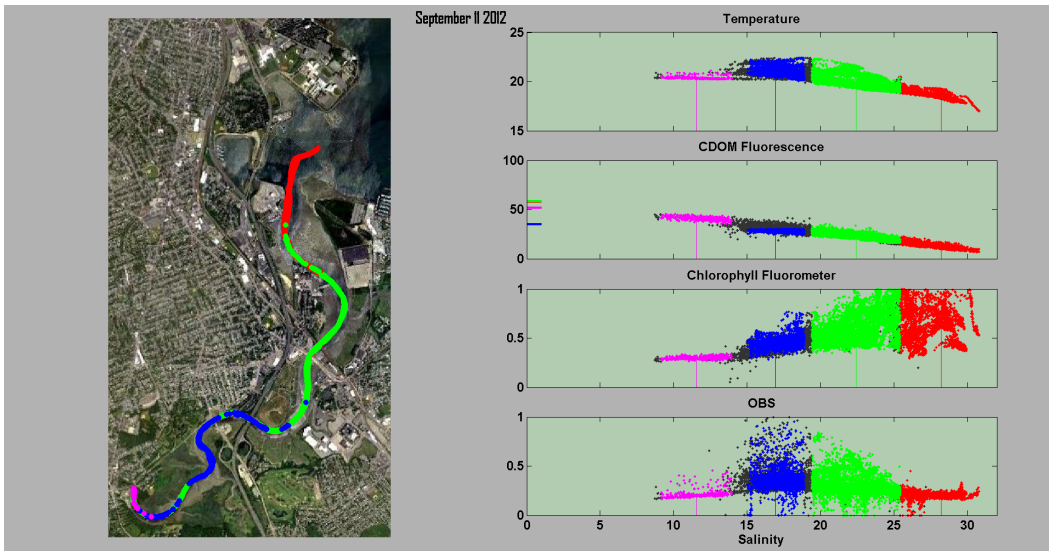
Appendix A13. CDOM-salinity relationship in the Neponset River from December 11, 2010.



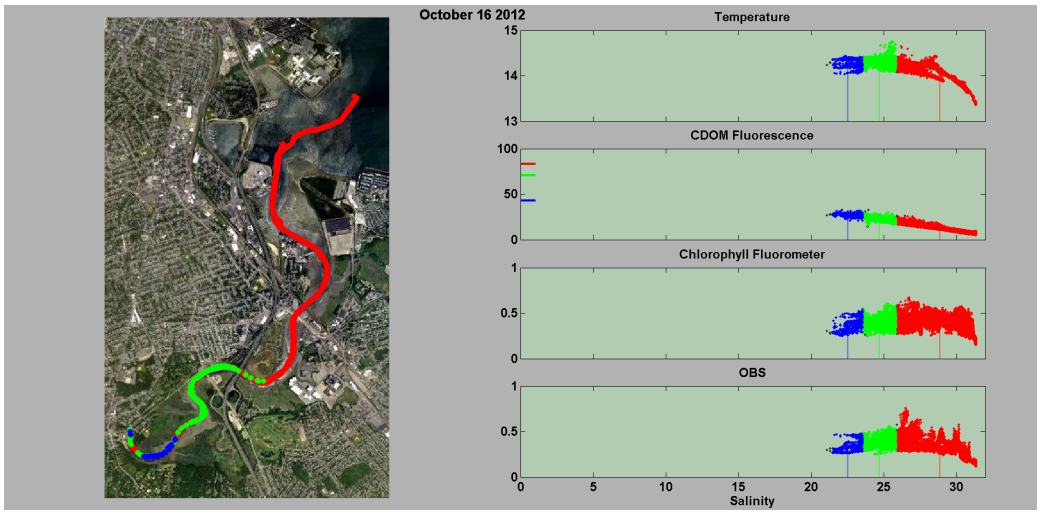
Appendix A14. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from June 22, 2012.



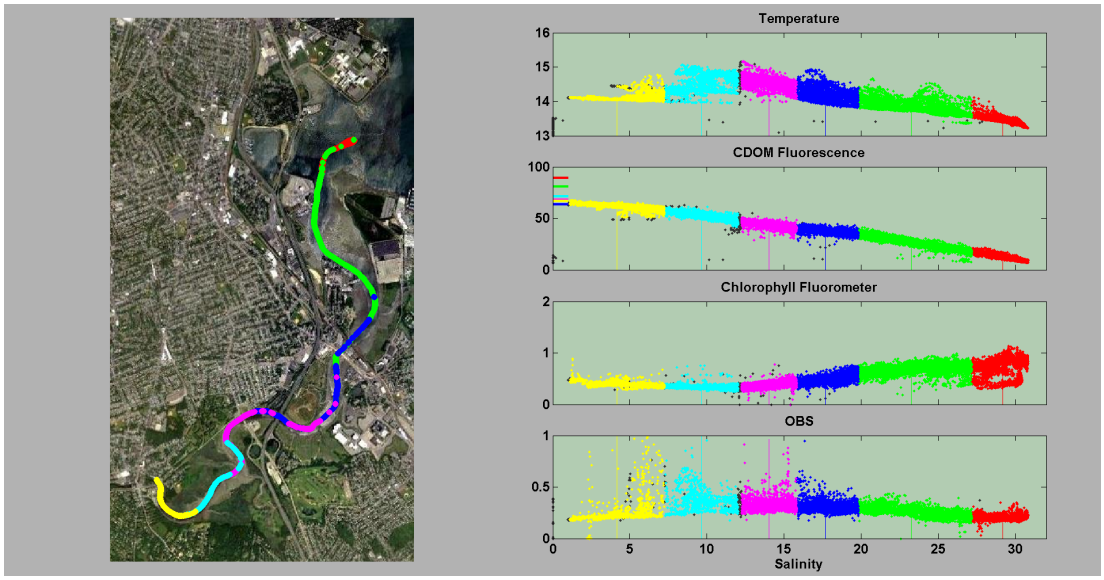
Appendix A15. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from September 11, 2012.



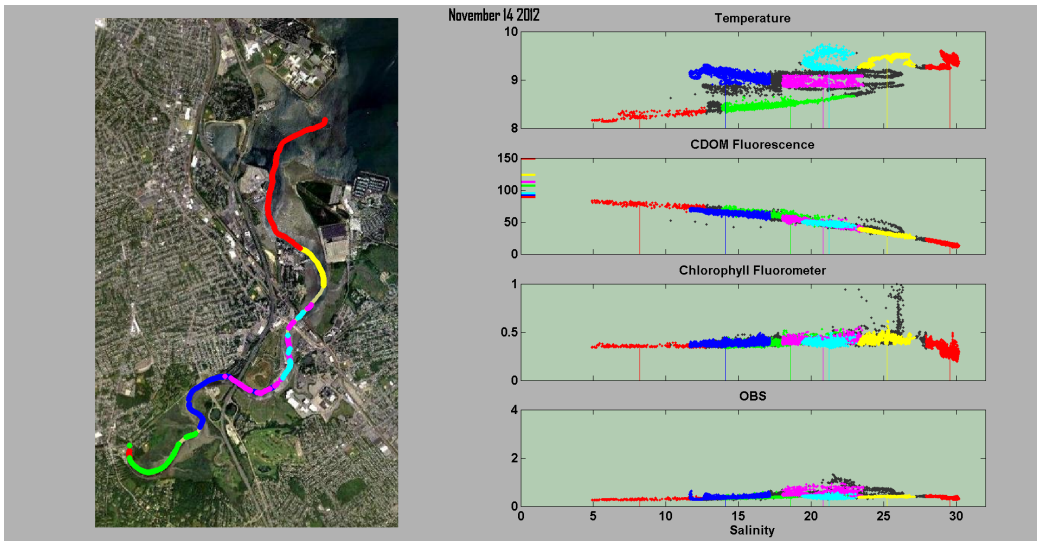
Appendix A16. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from October 16, 2012.



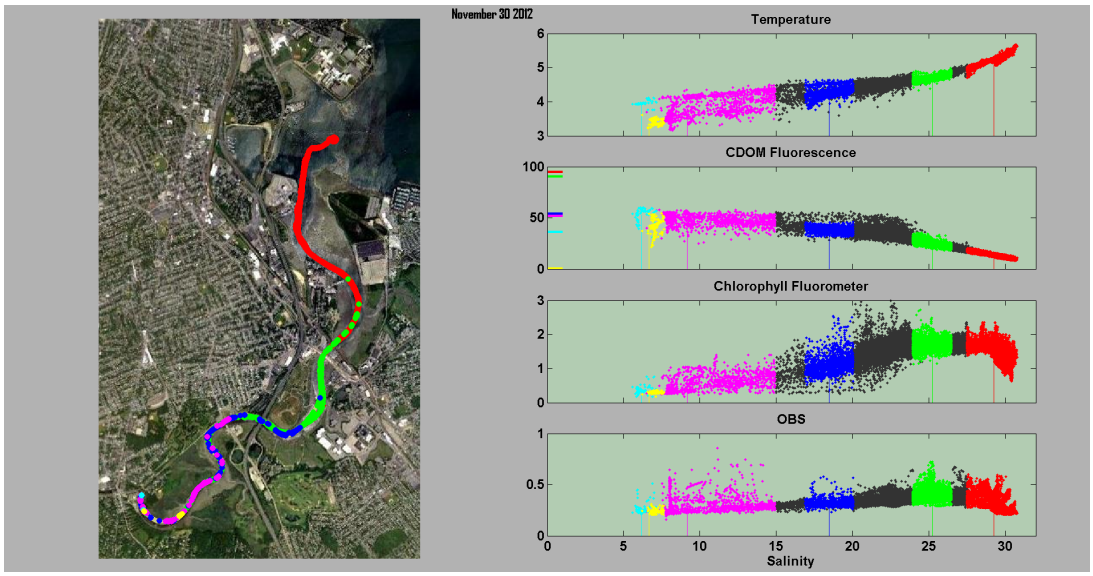
Appendix A17. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from October 23, 2012.



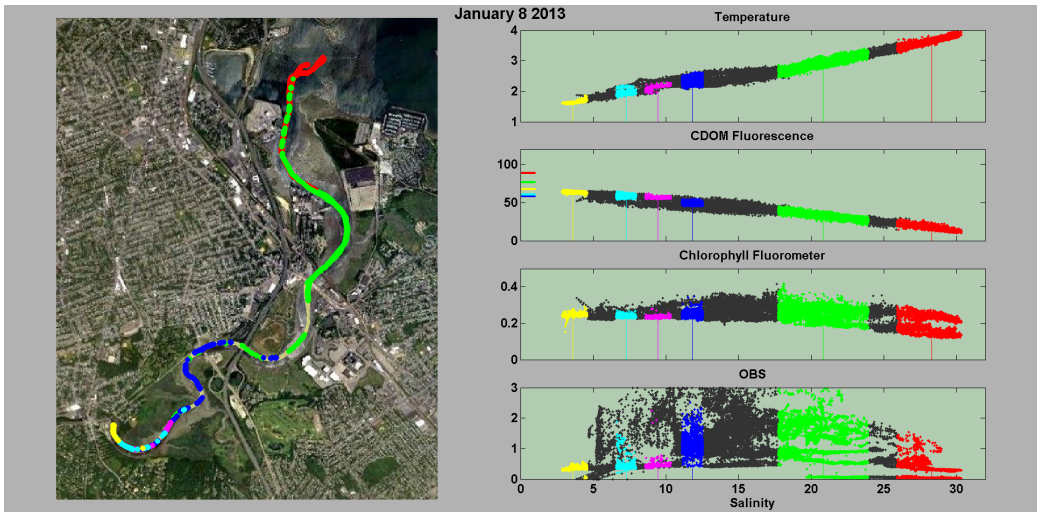
Appendix A18. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from November 12, 2012.



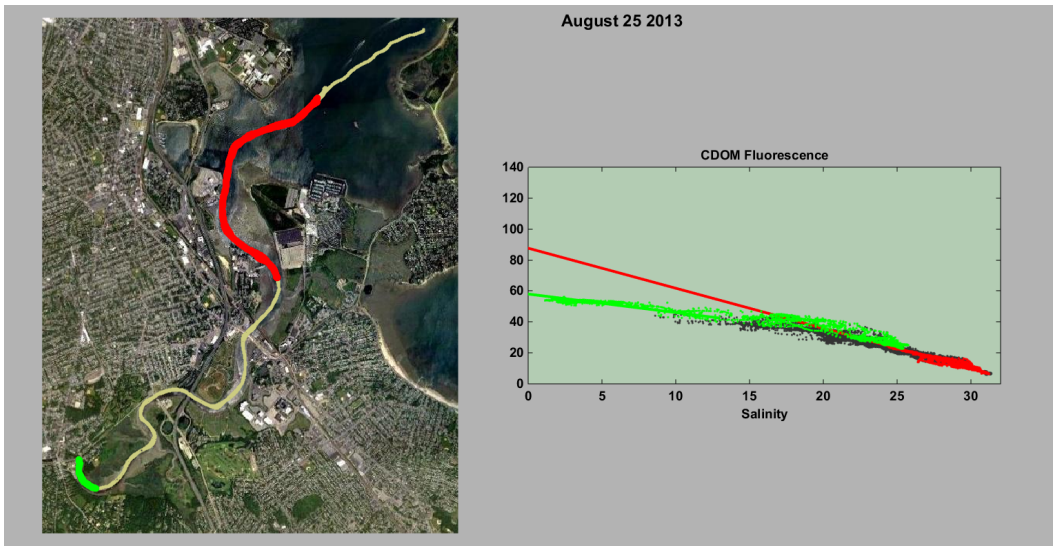
Appendix A19. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from November 30, 2012.



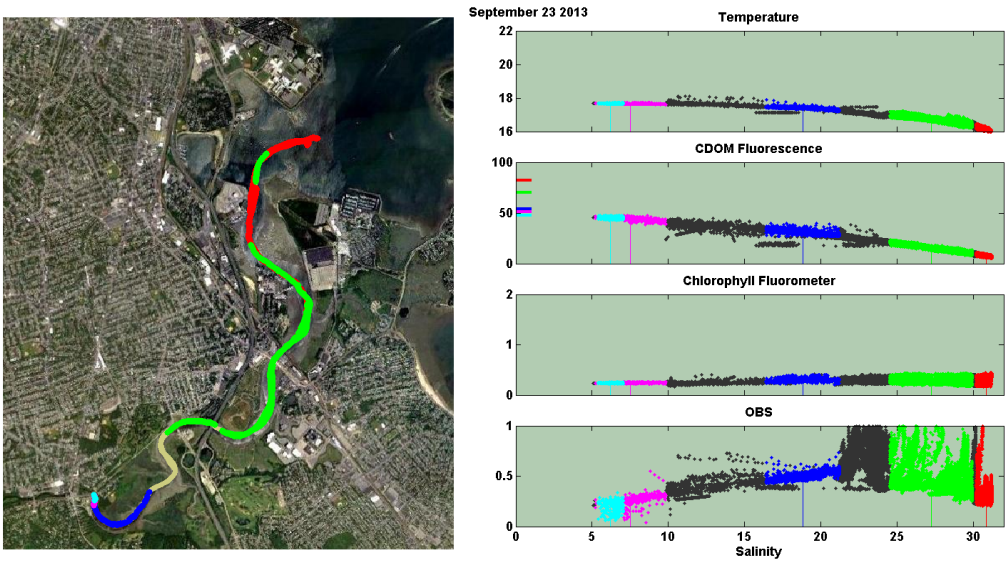
Appendix A20. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from January 30, 2013.



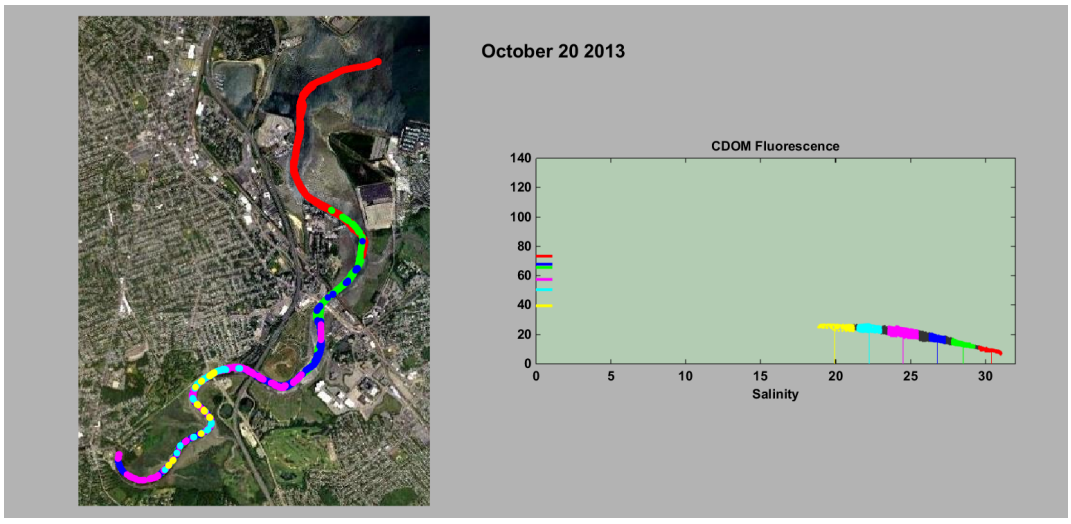
Appendix A21. CDOM-salinity relationship in the Neponset River from August 25, 2013.



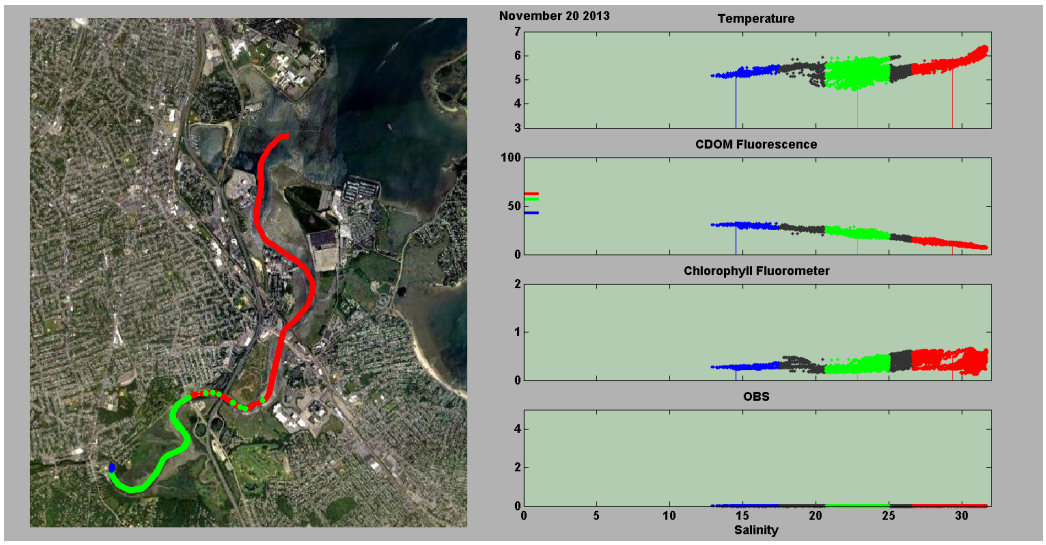
Appendix A22. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from September 23, 2013.



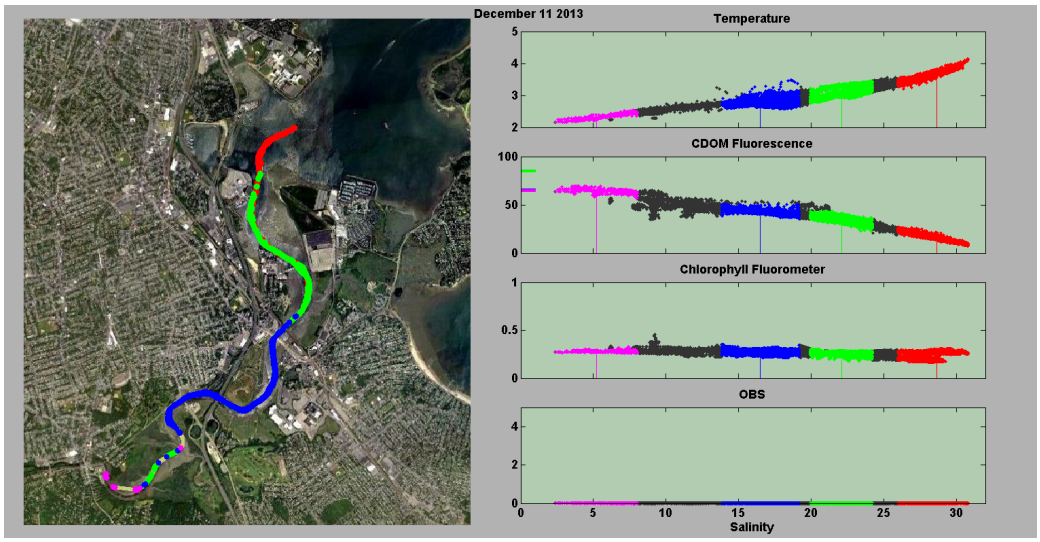
Appendix A23. CDOM-salinity relationship in the Neponset River from October 20, 2013.



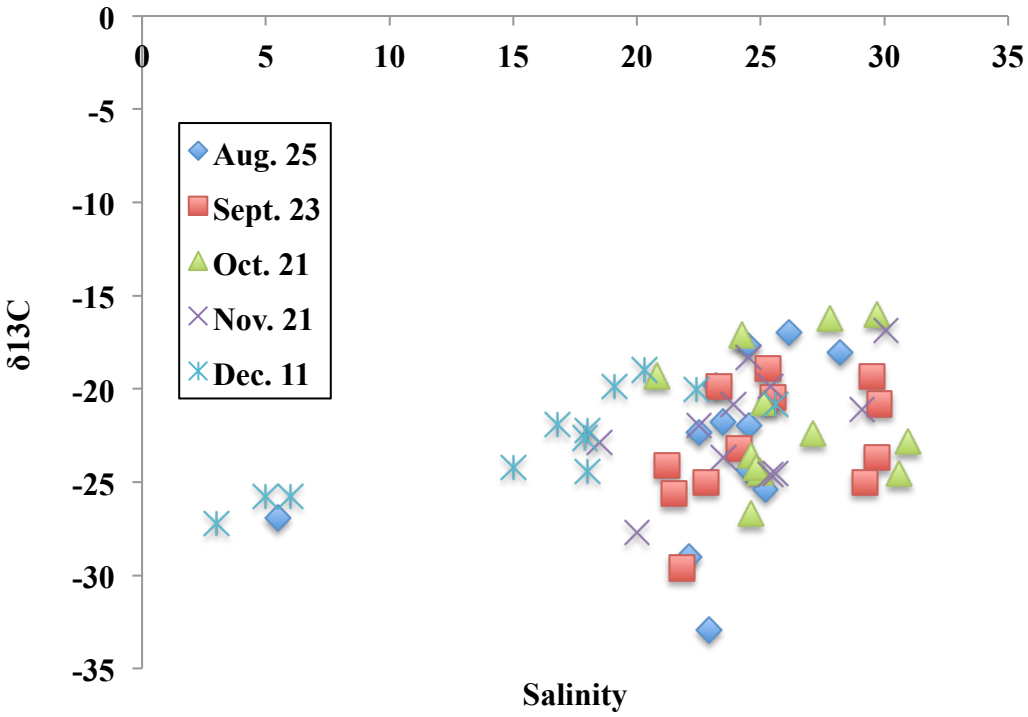
Appendix A24. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from November 20, 2013.



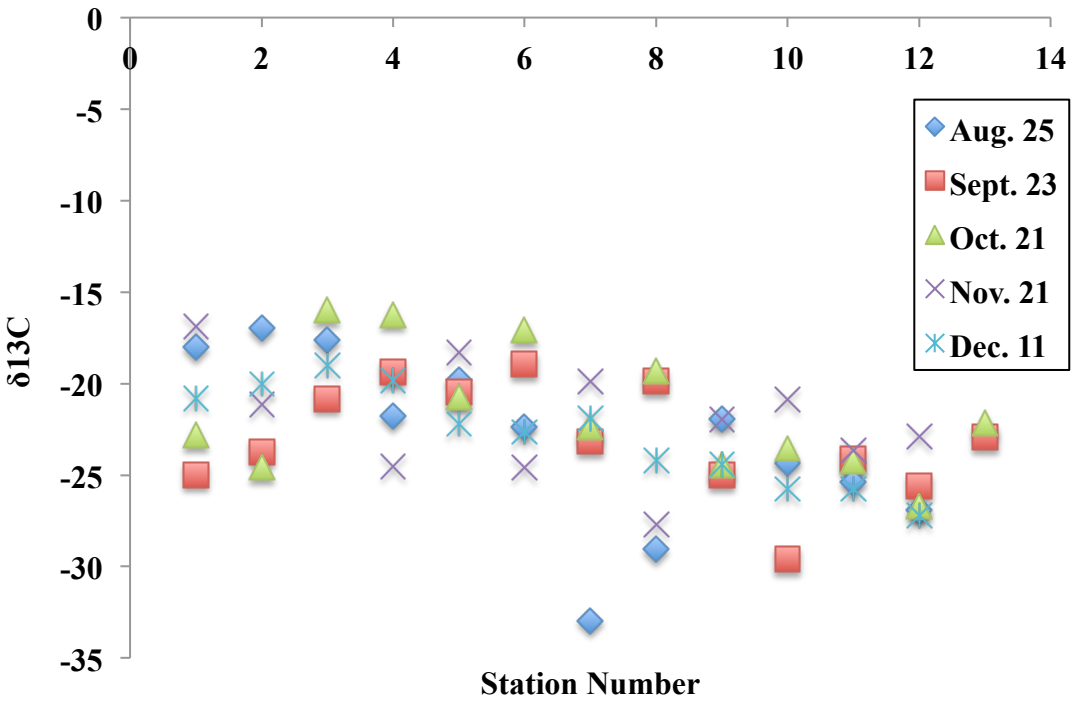
Appendix A25. Temperature, CDOM, chlorophyll and optical backscatter (OBS) plotted against salinity in the Neponset River from December 11, 2013.



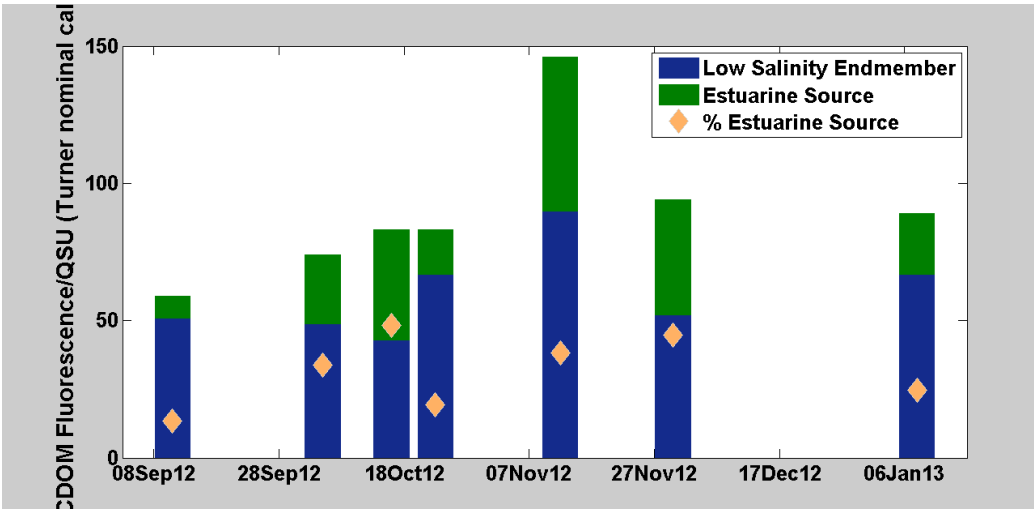
Appendix A26. Dissolved isotope data ($\delta^{13}C$) plotted against salinity for all 2013 cruises.



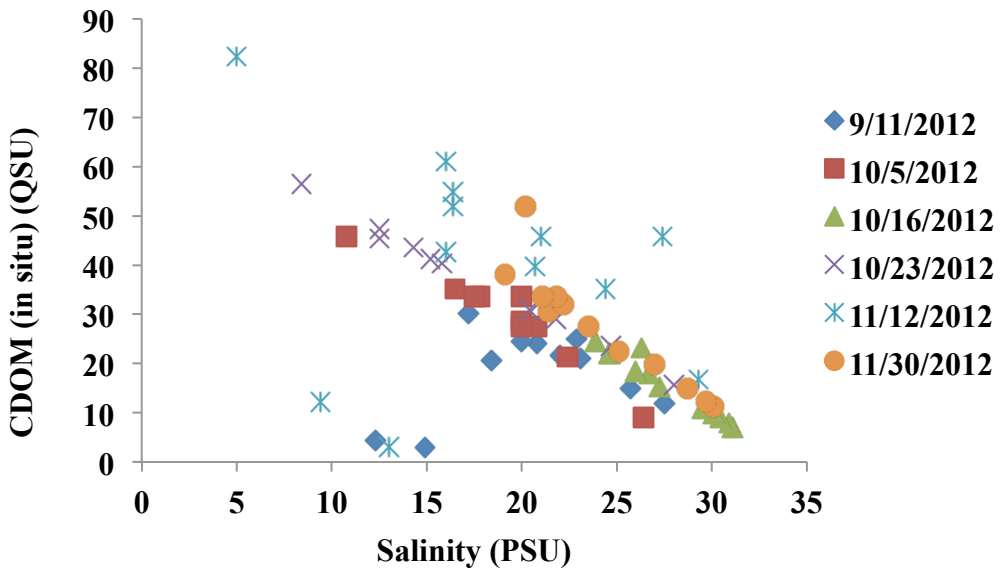
Appendix A27. Dissolved isotope data (δ ^{13}C) plotted against station number for all 2013 cruises.



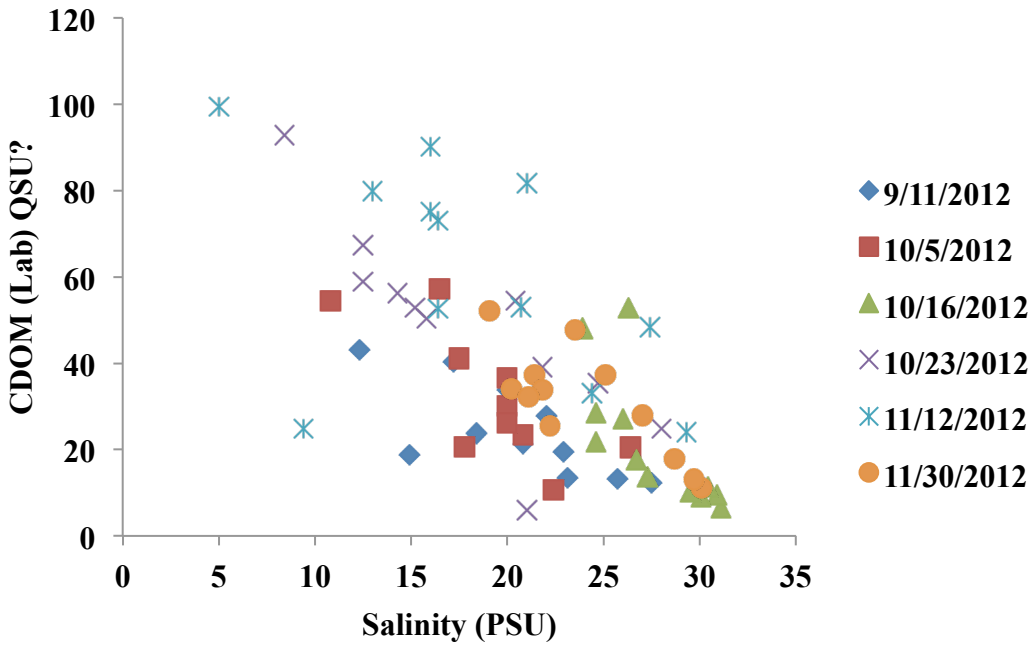
Appendix A28. Actual and apparent endmembers from 2012 cruises.



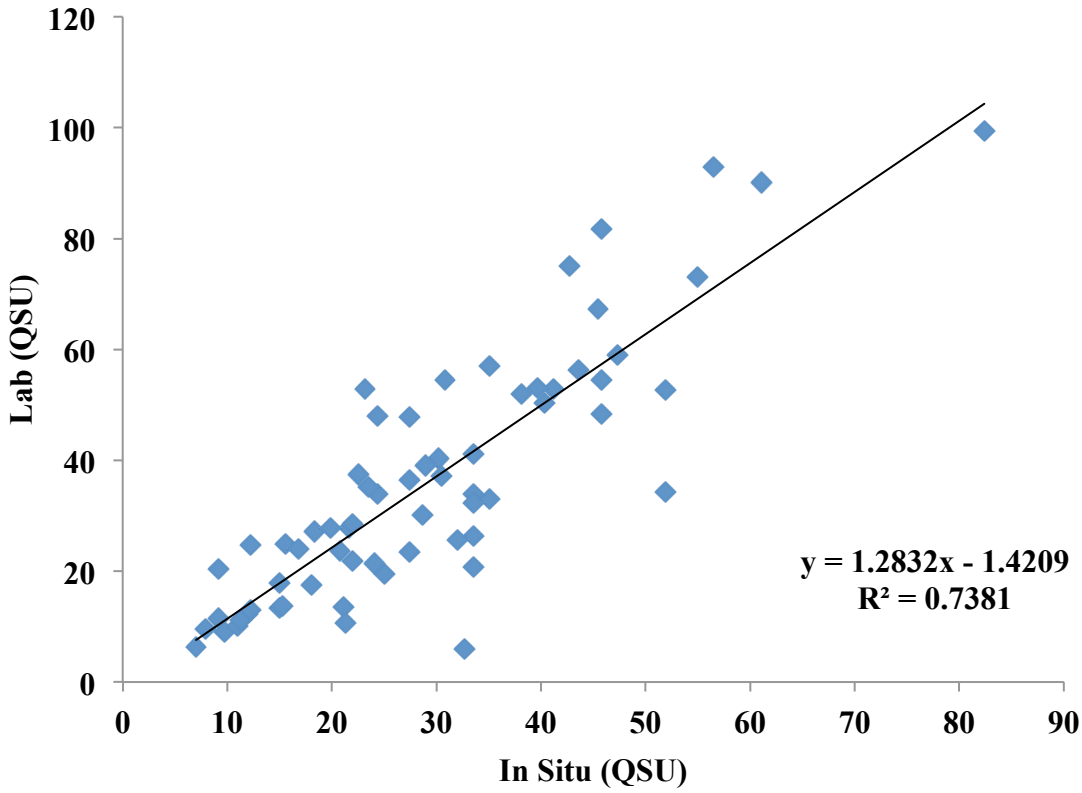
Appendix A29. *In situ* CDOM concentrations versus salinity for all 2012 crusies.



Appendix A30. Lab CDOM concentrations versus salinity for all 2012 cruises.

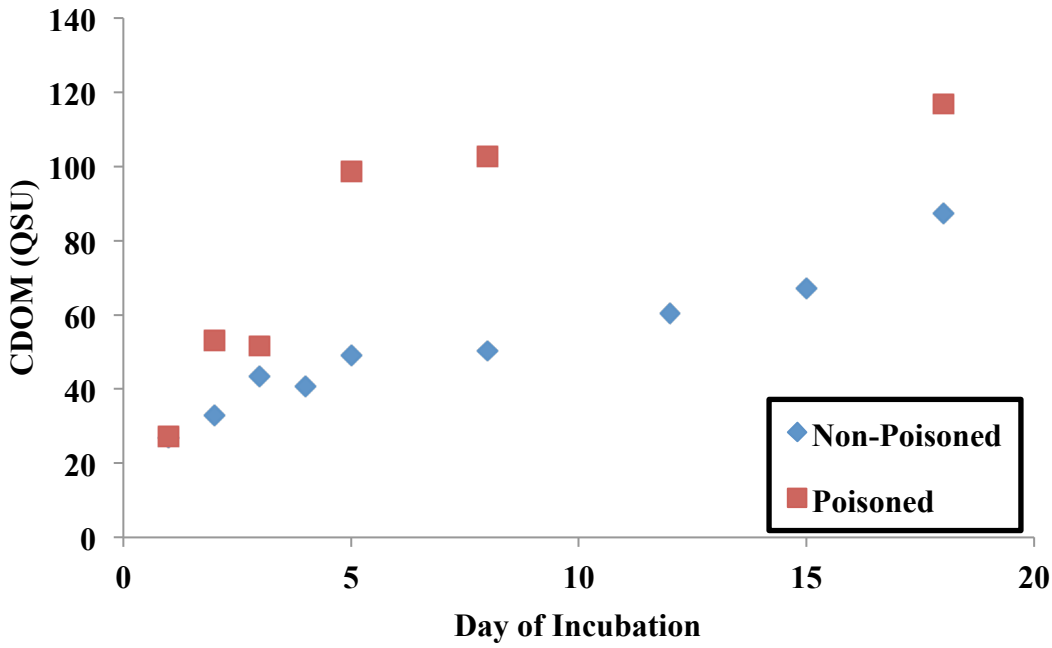


Appendix A31. *In situ* CDOM versus lab CDOM concentrations for all 2012 cruises.

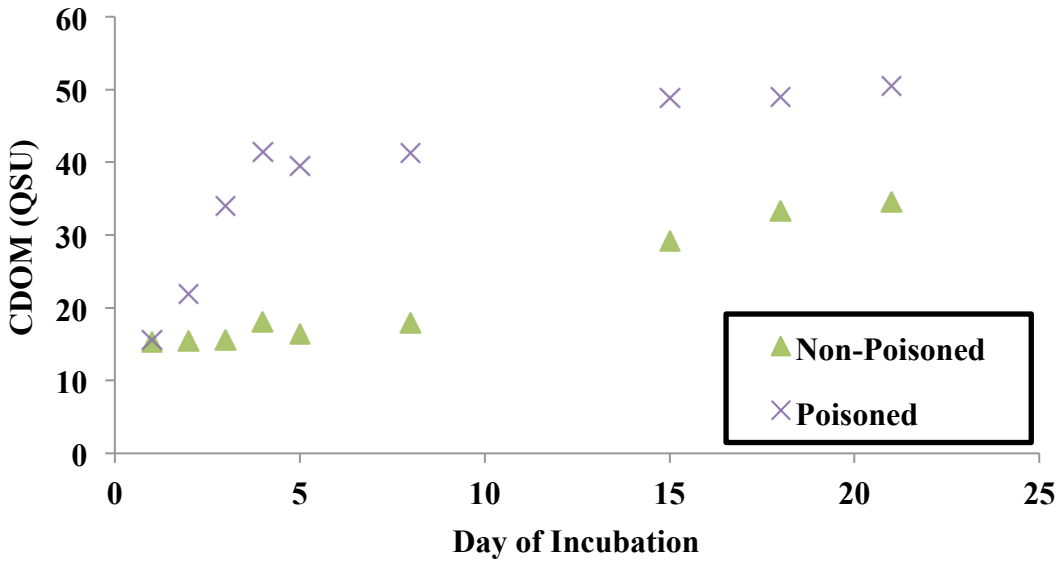


APPENDIX B

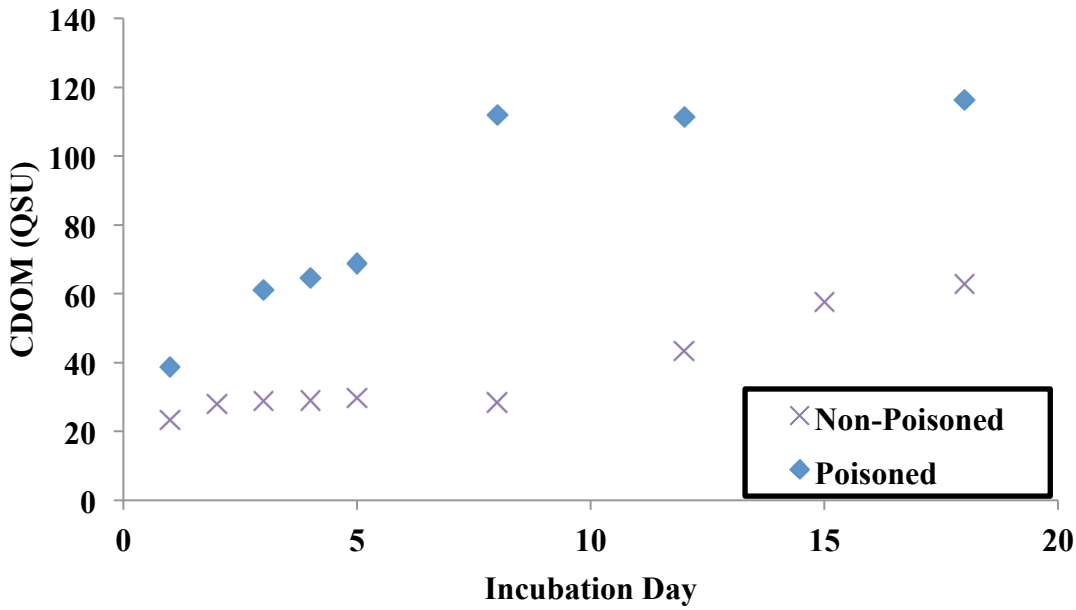
Appendix B1. Poisoned *S. alterniflora* AGB not exposed to sunlight in August 2013.



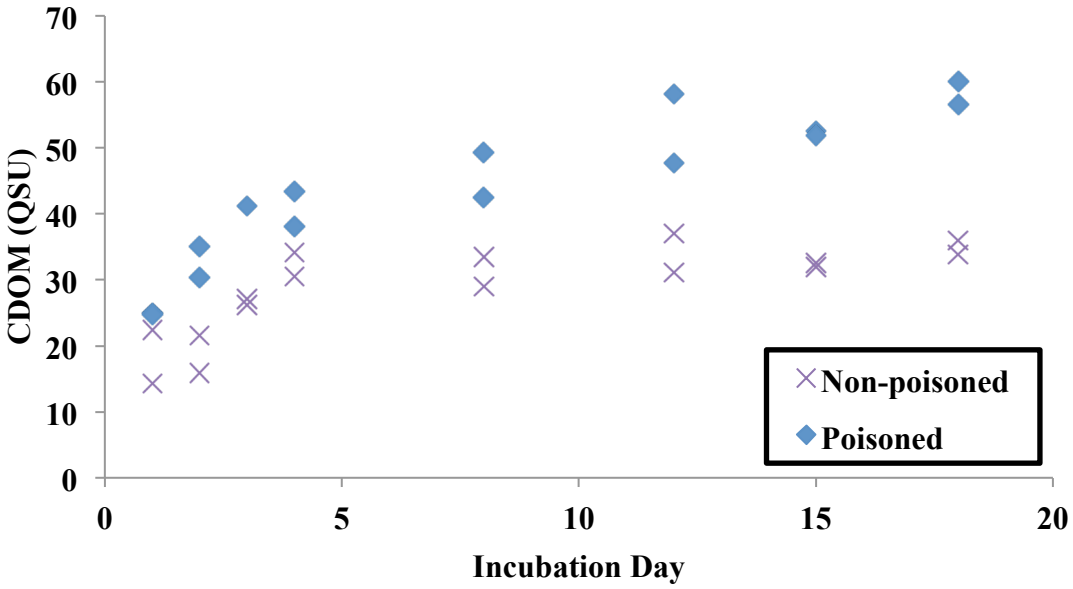
Appendix B2. Non-poisoned *S. alterniflora* BGB not exposed to sunlight in December 2012.



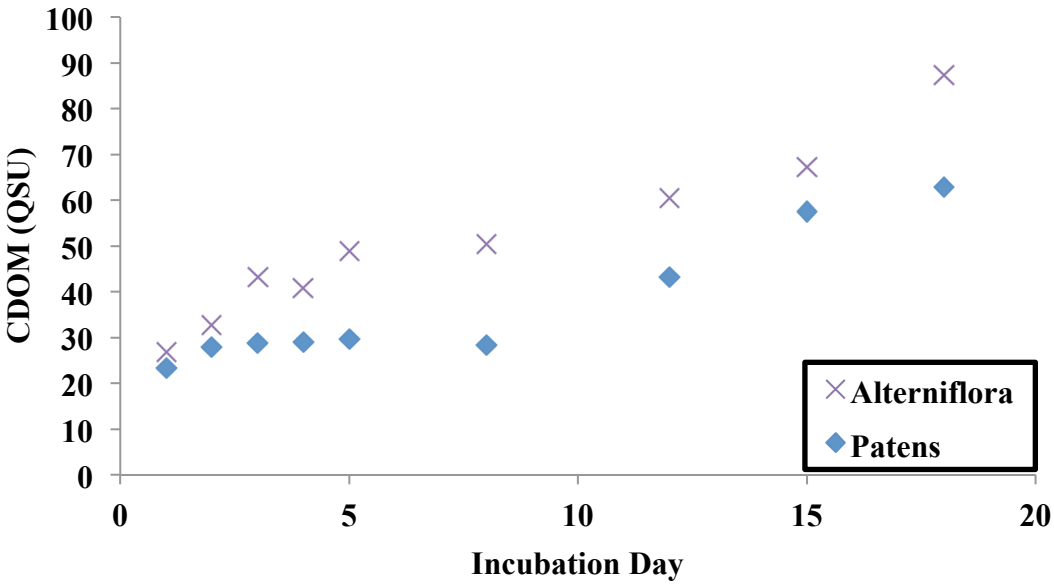
Appendix B3. Poisoned *S. patens* AGB not exposed to sunlight in August 2013.



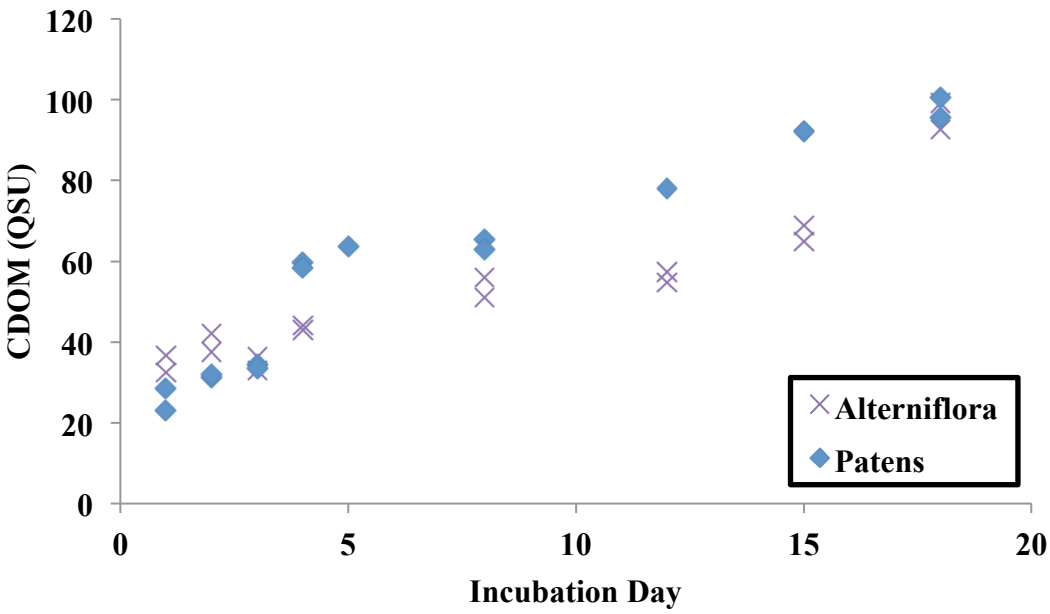
Appendix B4. Non-poisoned *S. patens* BGB not exposed to sunlight in October 2012.



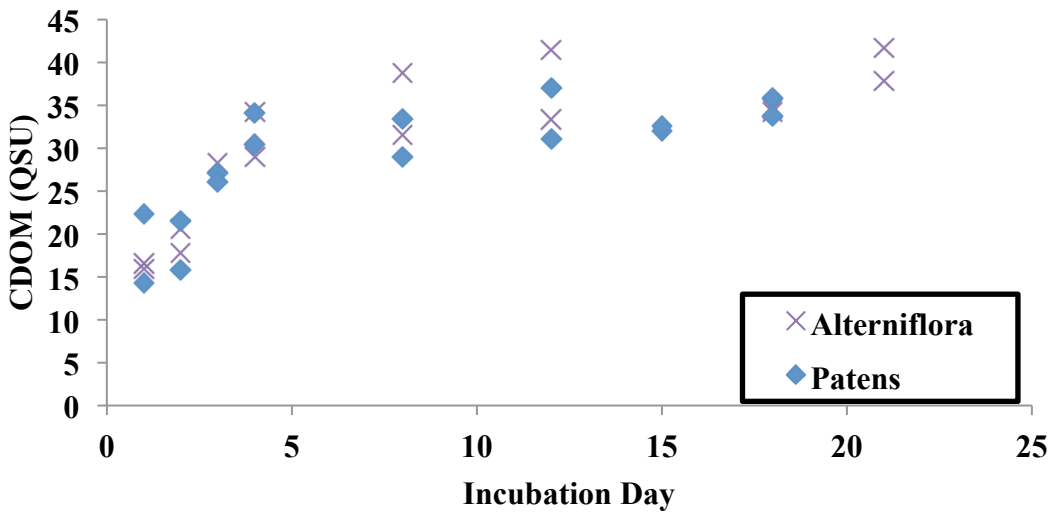
Appendix B5. Non-poisoned AGB not exposed to sunlight in August 2013.



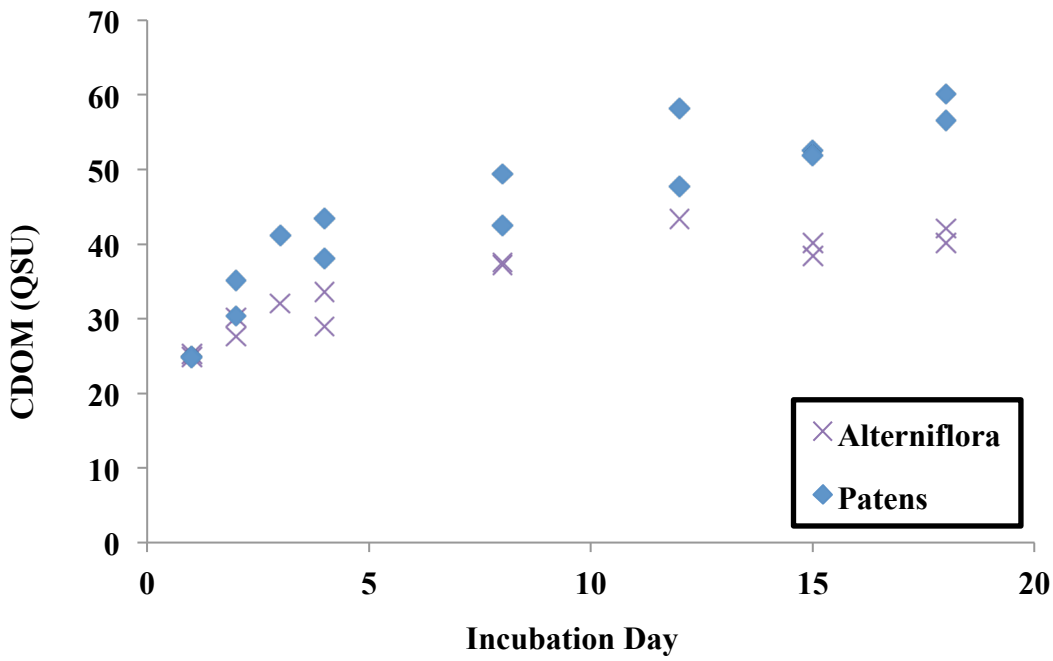
Appendix B6. Poisoned AGB not exposed to sunlight in December 2012.



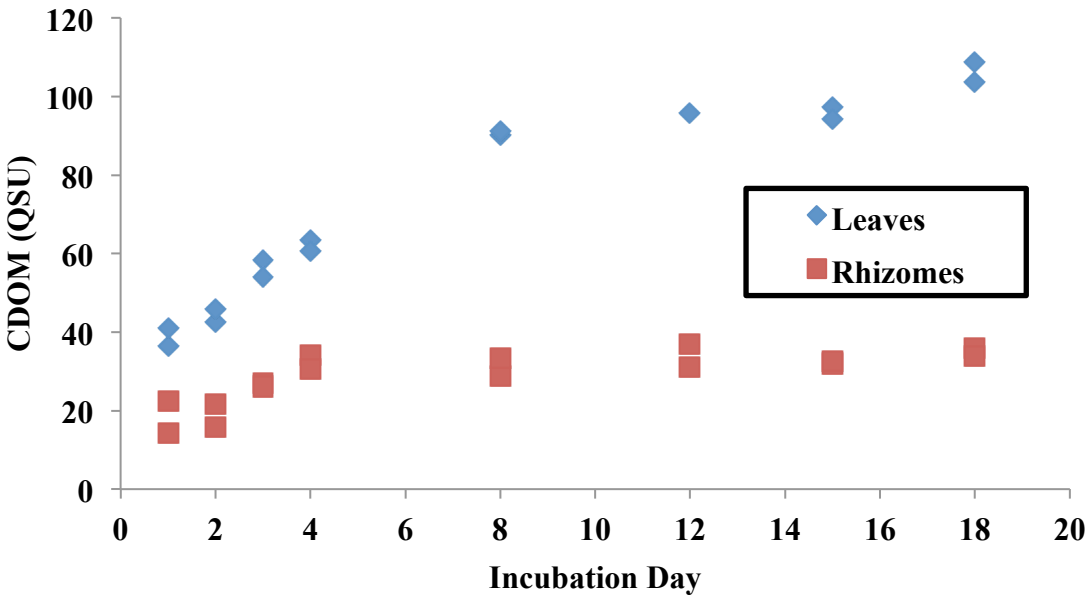
Appendix B7. Non-poisoned BGB not exposed to sunlight in October 2012.



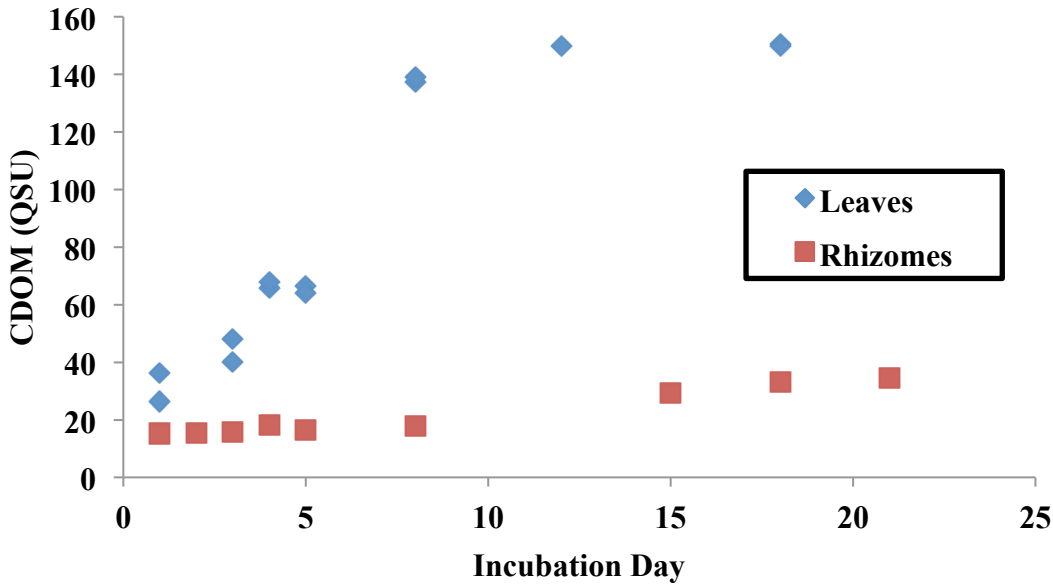
Appendix B8. Poisoned BGB not exposed to sunlight in October 2012.



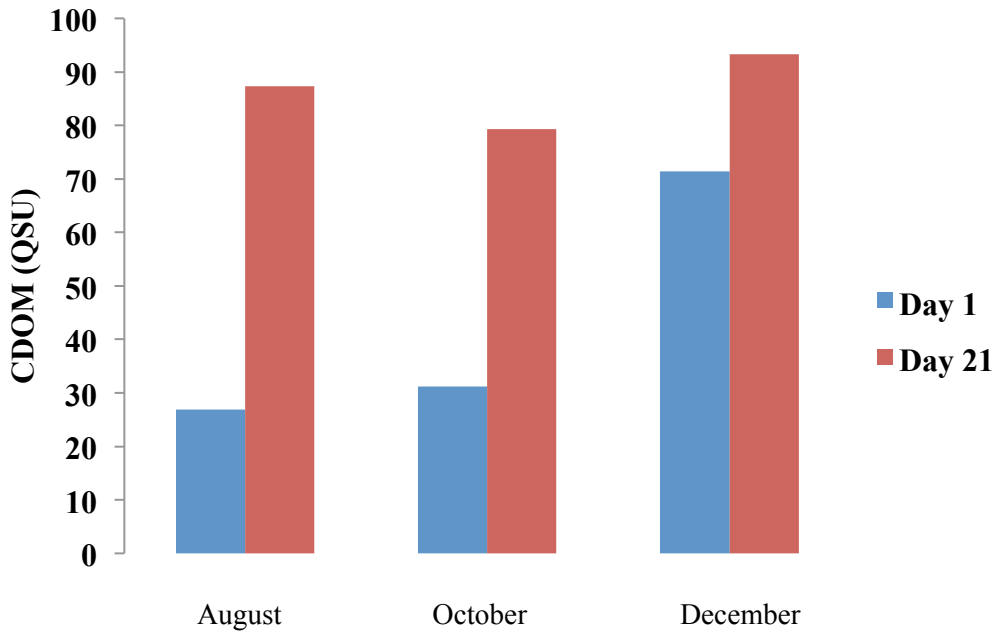
Appendix B9. Non-poisoned *S. patens* AGB and BGB not exposed to sunlight in October 2012.



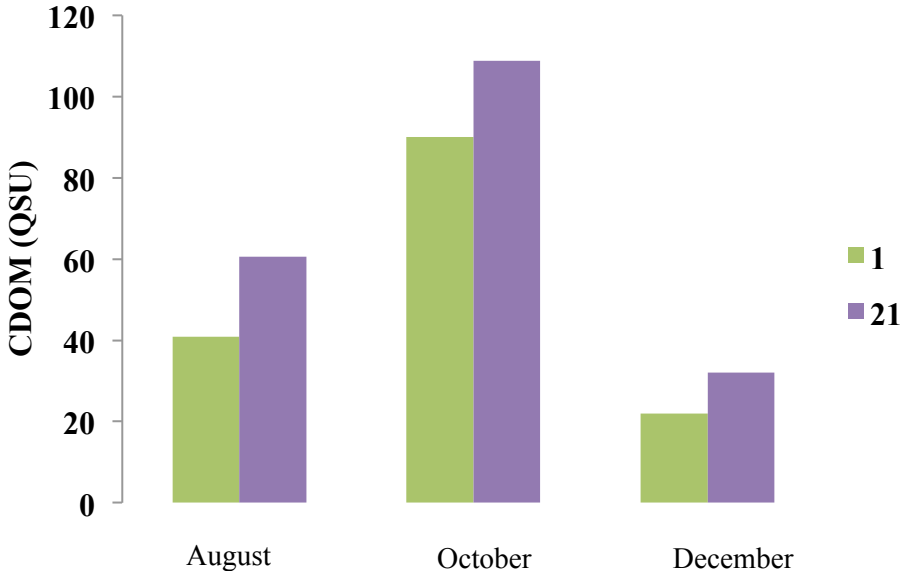
Appendix B10. Non-poisoned *S. alterniflora* AGB and BGB not exposed to sunlight in December 2012.



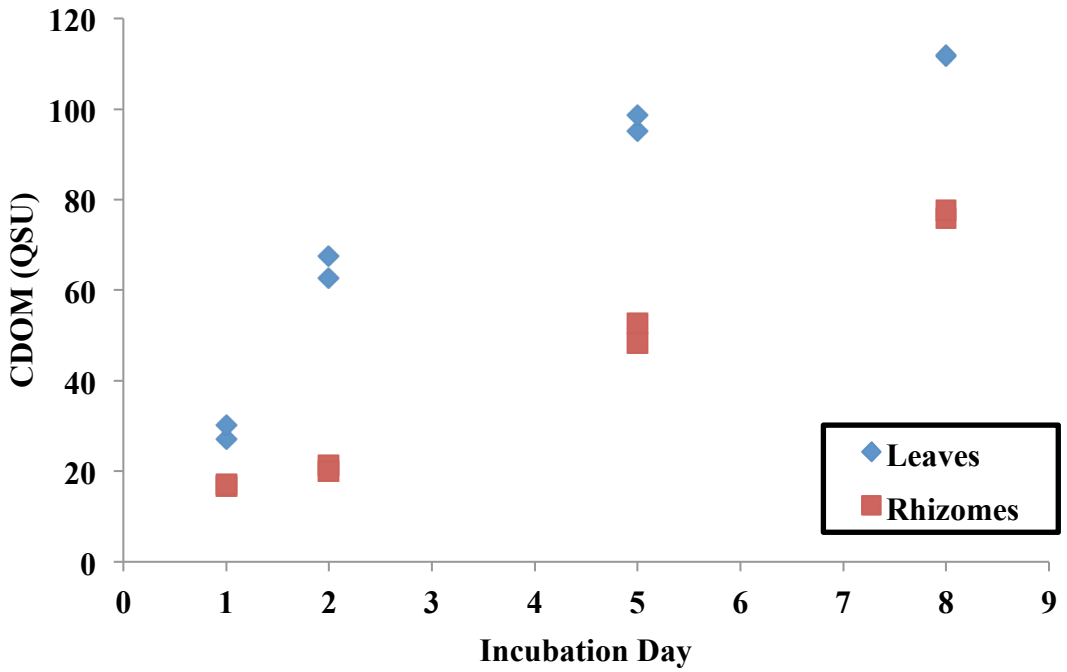
Appendix B11. Initial and final CDOM concentrations at the end of the indoor anoxia experiments for non-poisoned *S. alterniflora* AGB.



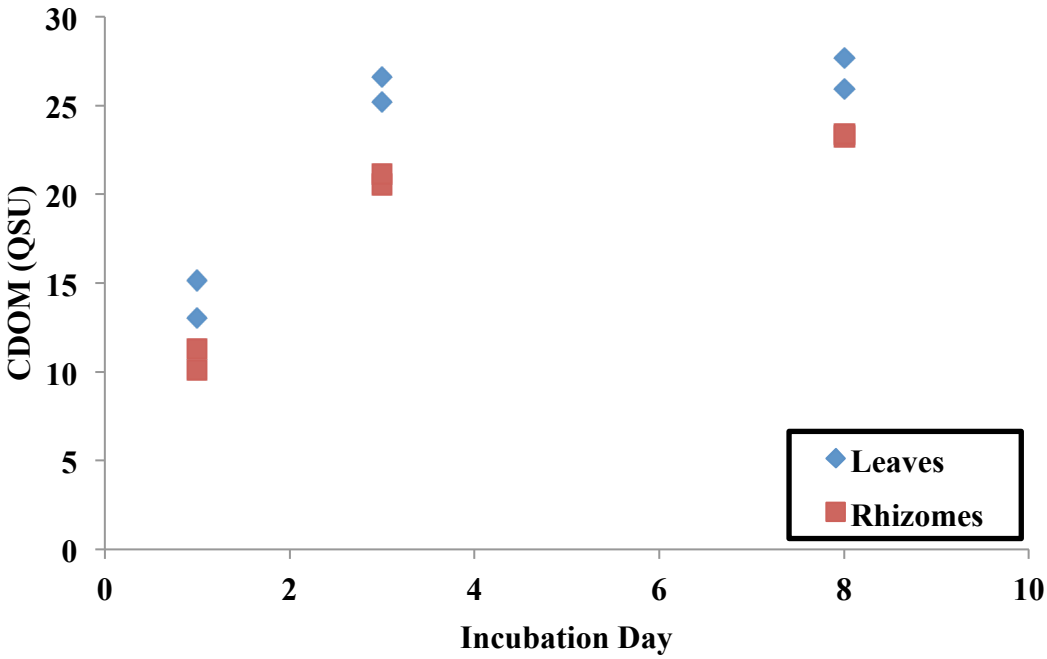
Appendix B12. Poisoned initial and final CDOM concentrations for *S. patens* BGB at the end of the indoor anoxia experiments.



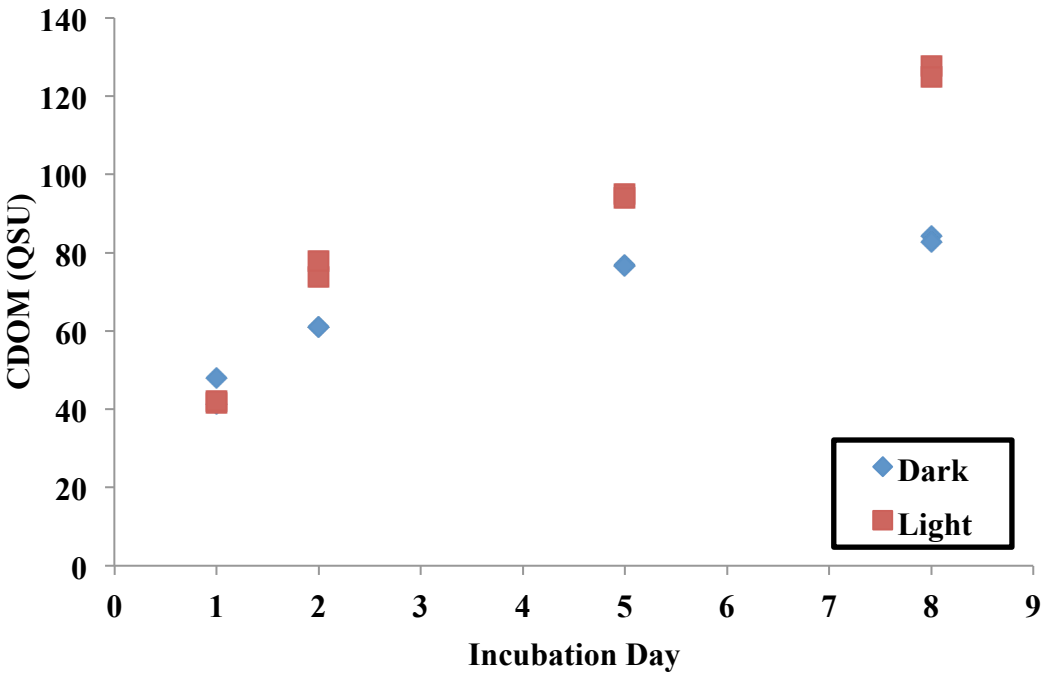
Appendix B13. Non-poisoned *S. patens* AGB and BGB not exposed to sunlight in November 2012.



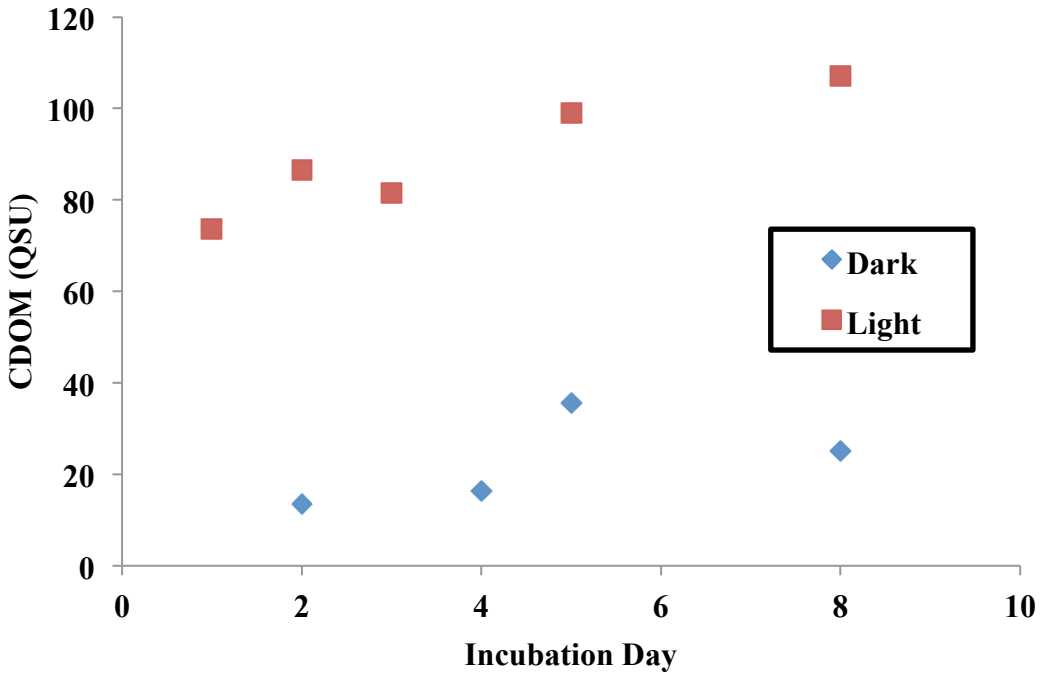
Appendix B14. Poisoned *S. alterniflora* AGB and BGB not exposed to sunlight in January 2013.



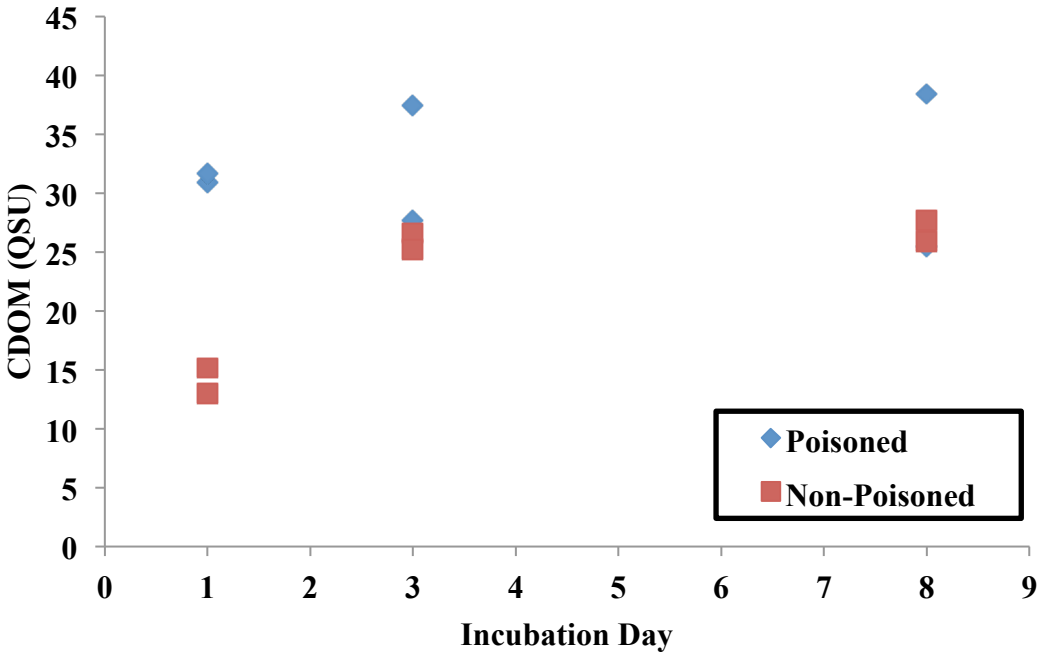
Appendix B15. Non-poisoned *S. alterniflora* BGB sunlight treatment results in November 2012.



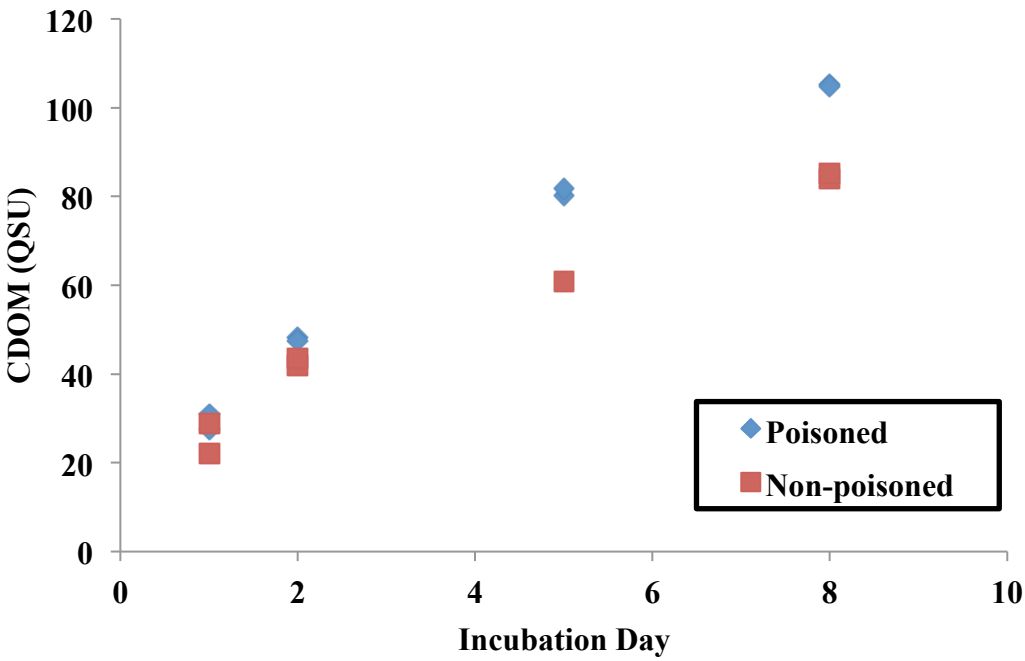
Appendix B16. Non-poisoned *S. patens* AGB sunlight treatment results from August 2013.



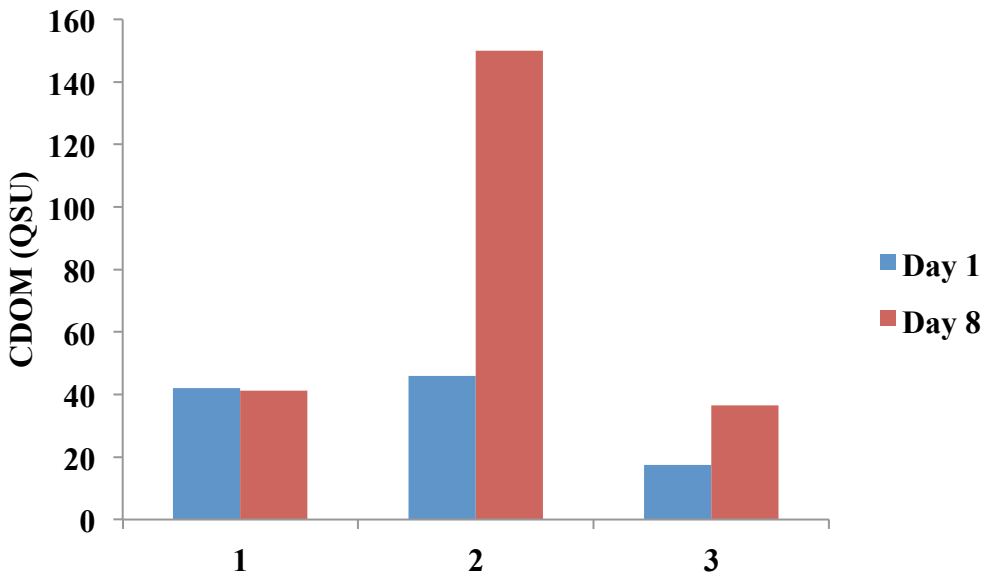
Appendix B17. *S. alterniflora* AGB microbial treatment results from January 2013.



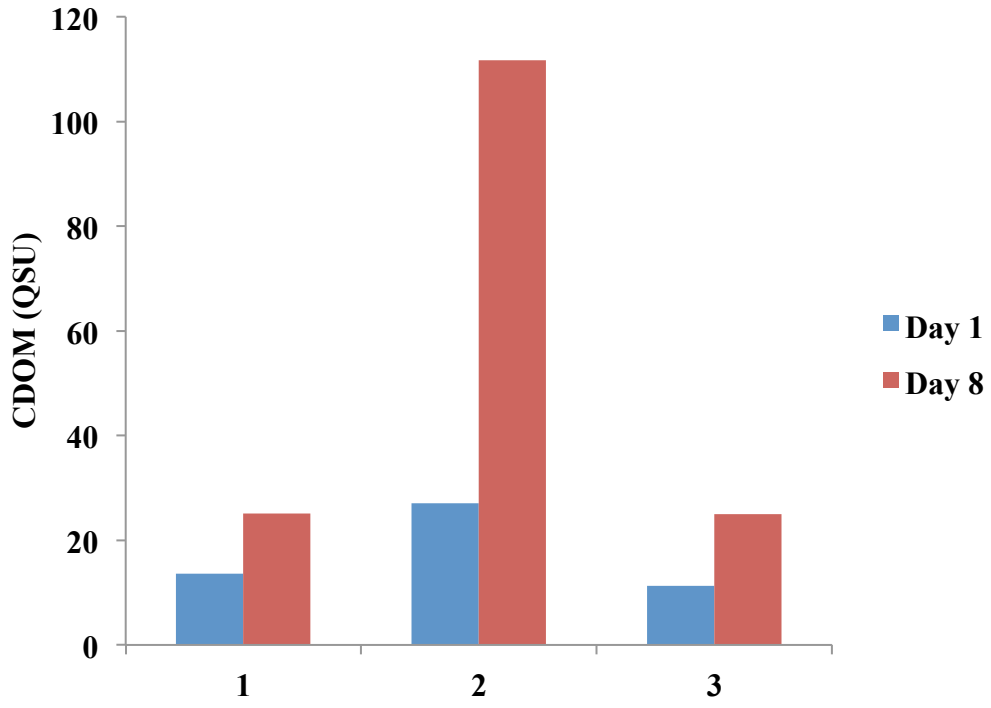
Appendix B18. *S. patens* BGB microbial treatment results from November 2012.



Appendix B19. Initial and final concentrations from three sunlight irradiation experiments for poisoned *S. alterniflora* BGB exposed to sunlight.



Appendix B20. Initial and final concentrations from three sunlight irradiation experiments for poisoned *S. patens* AGB not exposed to sunlight.



Appendix B21. Leaching concentrations at the end of the August 2013 anoxia incubation (normalized by biomass) for non-poisoned and poisoned AGB and BGB (mean ± SE). P-values are reported from t-tests with two-tailed distributions.

Treatment		*S. alterniflora* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. alterniflora* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value
Non-Poisoned	Oxic	356 ± 8	0.015	287 ± 30	0.025	250 ± 2	0.49	289 ± 5	0.022
	Anoxic	407 ± 2		383 ± 2		233 ± 33		126 ± 48	
Poisoned	Oxic	333 ± 7	0.0050	498 ± 5	0.0017	358 ± 5	0.77	375 ± 11	0.039
	Anoxic	288 ± 8		361 ± 10		359 ± 4		344 ± 6	

Appendix B22. Leaching concentrations by species at the end of the sunlight irradiation incubations (normalized by biomass) comparing plant species export across all seasons for poisoned and non-poisoned AGB and BGB for samples not exposed to sunlight (mean ± SE). P-values are reported from t-tests using two-tailed distributions.

Season	Species	Poisoned BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	Poisoned AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	Non-Poisoned BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	Non-Poisoned AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value
Summer 2012	*S. alterniflora*	91.8 ± 0.06	0.016	91.1 ± 3.7	0.026	66.1 ± 2.3	0.0083	67.6 ± 1.1	0.0050
	S. patens	73.5 ± 4.5		103 ± 0		53.1 ± 0.1		83.6 ± 1.9	
Fall 2012	*S. alterniflora*	228 ± 7	0.17	359 ± 18	0.0098	187 ± 1	0.0078	276 ± 8	0.016
	S. patens	243 ± 13		264 ± 4		152 ± 6		227 ± 9	
Winter 2013	*S. alterniflora*	39.9 ± 2.1	0.48	47.4 ± 3.5	0.13	88.9 ± 7.3	0.0037	13.9 ± 2.4	0.0054
	S. patens	38.9 ± 0.02		52.4 ± 1.4		27.2 ± 1.1		34.2 ± 1.8	
Spring 2013	*S. alterniflora*	75.2 ± 7.5	0.016	61 ± 2.2	0.42	17.0 ± 0.04	0.0004	33.6 ± 8.0	0.17
	S. patens	44.7 ± 1.8		62.7 ± 2.5		27.9 ± 0.02		42.2 ± 0.02	
Summer 2014	*P. australis*	47.4 ± 0.08	0.42	69.4 ± 8.6	0.81	88.1 ± 3.3	0.32	20.6 ± 2.8	0.87
	S. patens	44.6 ± 5.5		68.1 ± 2.1		82.8 ± 7.3		20.2 ± 3.5	

Appendix B23. Leaching concentration for samples at the end of the sunlight irradiation incubations (normalized by dry weight) comparing samples exposed to sunlight with those kept in the dark across all seasons for poisoned AGB and BGB (mean ± SE). P-values are reported from t-tests using one-tailed distributions.

Season	Treatment	*S. alternifl ora* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. alternifl ora* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value
Summer 2012	Light	118 ± 9	0.015	123 ± 4	0.0040	93.8 ± 2.9	0.0088	132 ± 9	0.012
	Dark	91.8 ± 0.1		91.1 ± 3.7		73.5 ± 4.5		103 ± 0	
Fall 2012	Light	279 ± 8	0.0052	436 ± 27	0.021	293 ± 6	0.0097	280 ± 5	0.021
	Dark	228 ± 7		359 ± 18		243 ± 13		264 ± 4	
Winter 2013	Light	48.3 ± 0.1	0.0087	60.1 ± 4.2	0.023	53.1 ± 0.1	0.0003	88.9 ± 3.6	0.0015
	Dark	39.9 ± 2.1		47.4 ± 3.5		38.9 ± 0.0		52.4 ± 1.4	
Spring 2013	Light	90.7 ± 5.3	0.040	66.9 ± 4.9	0.082	90.4 ± 1.2	0.0003	69.3 ± 2.9	0.039
	Dark	75.2 ± 7.5		61 ± 2.2		44.7 ± 1.8		62.7 ± 2.5	

Appendix B24. Leaching concentrations at the end of the sunlight irradiation incubations (normalized by biomass) comparing AGB and BGB by species across all seasons for samples not exposed to sunlight (mean ± SE). P-values are reported from t-tests using one-tailed distributions.

Season	Biomass Type	Poisoned *S. alterniflora* (x 10^{-4} mol C g^{-1} dry weight)	P-value	Poisoned *S. patens* (x 10^{-4} mol C g^{-1} dry weight)	P-value	Non-Poisoned *S. alterniflora* (x 10^{-4} mol C g^{-1} dry weight)	P-value	Non-Poisoned *S. patens* (x 10^{-4} mol C g^{-1} dry weight)	P-value
Summer 2012	BGB	91.8 ± 0.06	0.38	73.5 ± 4.5	0.0031	66.1 ± 2.3	0.18	53.1 ± 0.06	0.0006
	AGB	91.1 ± 3.7		103 ± 0		67.6 ± 1.1		83.6 ± 1.9	
Fall 2012	BGB	228 ± 7	0.0028	243 ± 13	0.047	187 ± 1	0.0010	152 ± 6	0.0028
	AGB	359 ± 18		264 ± 4		276 ± 8		227 ± 9	
Winter 2013	BGB	39.9 ± 2.1	0.034	38.9 ± 0.02	0.0015	88.9 ± 7.3	0.0014	27.2 ± 1.1	0.011
	AGB	47.4 ± 3.5		52.4 ± 1.4		13.9 ± 2.4		34.2 ± 1.8	
Spring 2013	BGB	75.2 ± 7.5	0.035	44.7 ± 1.8	0.0038	17.0 ± 0.04	0.028	27.9 ± 0.02	0.0001
	AGB	61 ± 2.2		62.7 ± 2.5		33.6 ± 8.0		42.2 ± 0.02	

Appendix B25. Leaching concentrations at the end of the sunlight irradiation incubations (normalized by biomass) for the microbial treatment for AGB and BGB by species across all seasons for samples not exposed to sunlight (mean ± SE). P-values are reported from t-tests using one-tailed distributions.

Season	Species	*S. alterniflora* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* BGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. alterniflora* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value	*S. patens* AGB (x 10^{-4} mol C g^{-1} dry weight)	P-value
Summer 2012	Poisoned	91.8 ± 0.06	0.0011	73.5 ± 4.5	0.0062	91.1 ± 3.7	0.0034	103 ± 0	0.0014
	Non-Poisoned	66.1 ± 2.3		53.1 ± 0.06		67.6 ± 1.1		83.6 ± 1.9	
Fall 2012	Poisoned	228 ± 7	0.0036	243 ± 13	0.003	359 ± 19	0.0072	264 ± 4	0.0094
	Non-Poisoned	187 ± 1		152 ± 6		276 ± 8		227 ± 9	
Winter 2013	Poisoned	39.9 ± 2.1	0.0031	38.9 ± 0.02	0.0011	47.4 ± 3.5	0.0020	52.4 ± 1.4	0.0021
	Non-Poisoned	88.9 ± 7.3		27.2 ± 1.1		13.9 ± 2.4		34.2 ± 1.8	
Spring 2013	Poisoned	75.2 ± 7.5	0.0021	44.7 ± 1.8	0.0016	61 ± 2.2	0.0012	62.7 ± 2.5	0.0019
	Non-Poisoned	17.0 ± 0.04		27.9 ± 0.02		33.6 ± 8.04		42.2 ± 0.02	

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