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Doc Dynamics In Eddies of the Sargasso Sea

Eric Matthew Lachenmyer
University of South Carolina - Columbia

DOC DYNAMICS IN EDDIES OF THE SARGASSO SEA

by

Eric M. Lachenmyer

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Accepted by:

Tammi L. Richardson, Director of Thesis

Erik M. Smith, Reader

Seth G. John, Reader

Lacy Ford, Vice Provost and Dean of Graduate Studies

ABSTRACT

Bacterial productivity and size-fractioned rates of dissolved organic carbon (DOC) excretion from primary and secondary producers were measured in two eddy types, one anti-cyclonic (February 2012) and one cyclonic eddy (July 2012), in the Sargasso Sea. Bacterial productivity (BP) rates in the cyclonic eddy were highest in the center (9.2 mgC m^{-2} d^{-1}) and edge (10.4 mgC$m^{-2}d^{-1}$) of the eddy compared to the anti-cyclone center (2.2 mgC m^{-2} d^{-1}) and edge (5.1 mgC m^{-2} d^{-1}). Rates of DOC excretion from ^{14}C-tracer experiments were not significantly higher than background; lack of accumulation of labeled material indicated very fast uptake of DOC by the bacterial community. Since rates were not measureable in the field, an inverse modeling approach was used to estimate flows to and from the DOC pool for three stations (center, edge, and outside) in the cyclonic eddy sampled in 2012. DOC excretion rates by phytoplankton were between 10.1 and 14.5 mg C m^{-2} d^{-1}. These values on average were 11.7 % of the total primary production. Generally, DOC excretion was higher inside the eddy compared to the edge and outside the eddy. Modeling results indicated that one of the largest potential fates of DOC in this ecosystem was advection out of the euphotic zone. The highest rates of DOC advection were seen inside the eddy center, decreasing moving to the edge and then outside of the hydrodynamic influences of the cyclonic eddy.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

Introduction

Dissolved organic carbon (DOC) fuels bacterial growth (Carlson et al., 1996) and represents the largest pool of reduced organic carbon in the ocean (Carlson, 2004) with a reservoir of about 662 ± 32 Pg C (Hansell & Carlson, 2013). The DOC pool is comprised of amino acids, lipids and carbohydrates (Kawasaki & Benner, 2006). There are three main categories of DOC: labile, which has a lifetime of less than a day, semi-labile with a lifetime of days to weeks, and refractory DOC which may exist for months to years (Carlson, 2002). Labile DOC is the only form that can be rapidly overturned by bacterial populations, while semi-labile DOC is resistant to rapid microbial degradation in the surface waters but is available for microbial remineralization once it reaches the mesopelagic zone (Carlson, 2004). The fate of DOC, especially the labile form, is recycled by heterotrophic bacteria within the microbial loop (Nelson and Carlson, 2012). This remineralization of DOC may result in the production of refractory carbon or DIC in the form of CO_2 (Reithaler, 2008). In the Sargasso Sea, rates of bacterial remineralization of DOC can be as high as 0.1 μM C/h (Carlson, 1996).

The production of DOC in ocean ecosystems is ultimately constrained by rates of primary productivity. Phytoplankton are thought to be responsible for production of a

high percentage of DOC in the ocean through excretion, phytoplankton cell lysis and via sloppy feeding by grazers (Goldman et al., 1992; Lancelot, 1979; Strom et al., 1997). Other sources of labile DOC include zooplankton excretion and egestion (Kirchman, 1992; Moller, 2007; Lampert, 1978) and cell lysis from viral infection (Proctor & Fuhrman, 1991; Fuhrman, 1992).

Rates of DOC excretion are also constrained by the abundance and taxonomic composition of the primary producers in the ecosystem. Smaller phytoplankton have been shown to excrete a higher percentage of their assimilated carbon as DOC than their larger counterparts (Malinsky-Rushansky and Legrand, 1996). This larger excretion of DOC can have potentially large impacts on food webs and may change the dynamics of the microbial loop. The release of DOC through sloppy feeding can also be affected by the size of the phytoplankton being consumed relative to the size of the grazer: as phytoplankton size increases zooplankton ingestion efficiency decreases, causing more POM and DOM to be created from grazing of larger organisms (Steinberg, 2004; Nelson, 2012).

Removal of DOC via bacterial uptake is the primary biological consumption process in the ocean (Pomeroy, 1974; Azam & Hodson, 1977; Azam et al., 1983) and bacterial production and primary production are closely linked (Brock et al., 1984). In many aquatic ecosystems, bacterial production varies between 10-20% of primary production, but in oligotrophic systems 40-60% of primary production may be cycled through the bacteria (Cole et al., 1988; Ducklow, 2000; Hoch & Kirchman, 1993;

Kawasaki & Benner, 2006). Although a significant portion of primary production can be released as DOC, only a small fraction, about 2% of the dissolved organic matter produced, is labile and thus can be quickly taken up and rapidly turned over (Polimene, 2006). Studies of DOC accumulation and fluctuation performed at the Bermuda Atlantic Time-series station (BATS, 31° 50'N, 64°10'W) show that during the winter/spring bloom period, DOC may comprise up to 86% of the total DOC pool while particulate organic carbon as suspended particles made up 14% (Carlson, et al., 2002; Lomas, et al., 2004). This illustrates that DOC is an important part of the Sargasso Sea ecosystem and that the quantification of the rates of DOC production and consumption is vital to characterizing carbon flows in this region.

Productivity in the Sargasso Sea is driven by its eddy system, which consists of three types: anti-cyclonic, cyclonic and mode-water eddies (McGillicuddy, 2007). Anti-cyclonic eddies are warm-core eddies identified by satellite sea surface altimetry as exhibiting a positive sea surface height (SSH) anomaly (McGillicuddy et al., 1999). Warm-core eddies spin clockwise and depress density layers, thus exhibiting downwelling at their centers, and elevate the sea surface due to the higher density of the water circulating within the eddy (Siegel et al., 1999; Sweeney et al., 2003). Conditions in this eddy type resemble the mean conditions at the BATS site which favor picoplanktonic organisms that have high surface to volume ratios and therefore have a greater capacity for nutrient uptake (Chisholm, 1992). Cyclonic eddies, in contrast, spin counter-clockwise, and elevate isopycnal surfaces, resulting in the upwelling of subsurface nutrient-rich water (McGillicuddy et al., 1999). These conditions should favor larger phytoplankton species

including highly productive diatom species with high half-saturation coefficients that put them at a disadvantage in the low nutrient conditions of a cyclonic eddy or open ocean waters (Chisholm, 1992). Mode water eddies have the same rotational direction as anti-cyclonic eddies but upwell in their interior because of the displacement of the seasonal pycnocline (Sweeney et al., 2003). The upwelling of nutrient-rich water can lead to long duration phytoplankton blooms, often of diatoms (Bibby and Moore, 2011).

Physical and biological conditions may vary during the formation ("spin-up"), intensification and decay phases of the eddy life cycle (McGillicuddy et al., 1997). During eddy formation, there are only minor effects on the surrounding waters including small amounts of isopycnal displacement. During eddy intensification, isopycnal displacement increases, followed by a significant increase in nutrient fluxes to the surface ocean; stimulating primary production. After a lag time, secondary production and export from the euphotic zone will increase. The weakening or decay of the eddy causes nutrient fluxes to diminish even though export production can still remain elevated compared to background conditions until nutrients are exhausted in the surface ocean (Sweeney et al, 2003)

Differences in phytoplankton community composition between eddy types imply that pathways of carbon flow through food webs may also differ between anti-cyclonic, cyclonic and mode-water eddies. Respiration rates, for example, differ between anti-cyclonic eddies, which have enhanced respiration rates as compared to cyclonic eddies (Gonzalez, 2001; Aristegui & Montero, 2005; Maixandeau, 2005). Even within eddy

types, sub-mesoscale variability in planktonic community composition has been observed. Nelson et al. (2013), for example, have shown that bacterial community composition near the center of a mode-water eddy differed from other uplifted isopycnals.

Our current knowledge of the influence of mesoscale eddy dynamics on bacterial communities is limited, and to date, effects of eddies on bacterial productivity have not been examined. In this study, DOC excretion and bacterial productivity were characterized along transects across two mesoscale eddy types (cyclonic and anti-cyclonic) in the Sargasso Sea. I specifically examined how plankton size, community composition and trophic interactions modify DOC dynamics and bacterial productivity in the euphotic zone. My specific research questions were:

1) How do rates of DOC excretion vary among different plankton size classes and differing eddy types in the Sargasso Sea?
2) How do rates of bacterial productivity differ among different eddy types in the Sargasso Sea?

This thesis is comprised of four sections including a general introduction (Section 1) and overall conclusions (Section 4). Section 2 describes field experiments on size-fractionated phytoplankton and zooplankton DOC excretion rates and measurements of bacterial productivity. Because some field measurements were difficult to make and for the large part unsuccessful, I have used a numerical technique known as “inverse modeling” to reconstruct flows of carbon that were difficult to measure (Vézina and Platt, 1988). Section 3 includes a brief introduction to inverse food web modeling and

the corresponding results and discussion. Section 4 summarizes the major findings of my research, including the potential influence of eddy circulation on bacterial productivity and food webs in the Sargasso Sea.

CHAPTER 2

DOC Excretion and Bacterial Productivity in Mesoscale Eddies of the Sargasso Sea

Physical, chemical and biological processes in the Sargasso Sea have been studied from bi-monthly sampling at the Bermuda Atlantic Time Series, BATS station since 1988 (Steinberg, 2001). The Sargasso Sea is an oligotrophic region that has strong seasonal pattern of primary production, regularly exhibiting spring blooms resulting from nutrient inputs from winter mixing. (Michaels et al., 1994). It has a shallow and well stratified mixed layer in the summer and fall, while in the winter increased mixing occurs (Sweeney et al, 2003). The Sargasso Sea is an important area in which to study carbon fluxes because of its capacity to drawdown atmospheric CO_2 (Bates, 1996; Takahashi et al, 2002). The system has been thoroughly studied by several long-term time series programs which have provided information on its chemistry and food webs and their effects and controls on the global carbon cycle (Lomas, 2013). Mesoscale eddies are common and play an important role in regions such as the Sargasso Sea by altering the seasonal fluctuations in the biogeochemistry of the system. These eddies can modify nutrient inputs to the system altering biological productivity during their lifetime. (McGillicuddy, 2007; Nelson et al., 2013).

2.1 ObjectiveThe specific objectives of this section of my thesis were to:

1) Quantify DOC excretion by varying size fractions of phytoplankton
2) Quantify DOC uptake by bacteria using ^{14}C-labeled DOC
3) Quantify DOC excretion rates of zooplankton
4) Determine rates of DOC production in different eddy types

I hypothesized that:

H_1: Euphotic zone integrated DOC excretion by picoplankton (.7-2 μm) will exceed that of the larger phytoplankton (>2 μm).

Rationale: Picophytoplankton are numerically dominant and are the main contributors to primary productivity in this region.

H_2: Rates of DOC production (phytoplankton excretion + zooplankton-mediated) will vary over a 24hr period, being highest during daytime.

Rationale: DOC production is closely linked to rates of primary productivity which should increase as light availability increases and thus excretion of excess carbon will occur at higher rates.

H_3: Total DOC production will be higher in cyclonic eddies as compared to anti-cyclonic eddies.

Rationale: Higher (upwelling-stimulated) rates of primary productivity in cyclonic eddies as compared to anti-cyclonic eddies will result in higher rates of DOC release.

H_4: Total DOC production will increase with increasing abundance of zooplankton and phytoplankton.

2.2 Methods

This research was conducted as part of a larger National Science Foundation (NSF)-funded project aimed at determining how plankton size, community composition, and trophic interactions modify carbon export from the euphotic zone in eddies of the Sargasso Sea. Water for measurements of DOC excretion rates and bacterial productivity were collected on three cruises on the R/V Atlantic Explorer in the Sargasso Sea in August 2011, March 2012 and August 2012 (Figure 2.1). Water was collected from multiple depths (usually near the surface, at the fluorescence max and two other intermediate depths) in the euphotic zone from Niskin bottles deployed on pre-dawn CTD casts (Sea-Bird, 24 position SBE-09 *plus*). Triplicate (independent) samples were collected from each depth. Samples were taken from the Niskin bottles using opaque tubing and were pre-screened with a 200 μm Nitex mesh to exclude large zooplankton. Table 2.1 shows the locations and depths sampled for experiments described below.

2.2.1 DOC excretion by phytoplankton

Rates of DOC excretion by phytoplankton were measured using ^{14}C-bicarbonate labeling according to Teira (2001). Water samples from multiple depths were distributed into 1-liter polycarbonate bottles. Samples were spiked with ^{14}C-bicarbonate (PerkinElmer Health Sciences Inc.) to a final activity of 0.08 μCi ml^{-1} and were incubated on an *in situ* array at the depth of collection for a 24 hr (dawn to dawn) period. After incubation,

samples were size-fractionated as follows: DOC excretion by organisms 0.7-200 µm in size was measured directly by filtering replicate (n=3) 1-liter aliquots of incubated sample through GF/F filters (= "total"). Duplicate 1-liter aliquots were filtered through a 20µm Nitex mesh, then through a 2 µm Nuclepore filter to yield excretion rates for the 2-20 µm size class. Finally, 1 liter aliquots were filtered through a 20 µm Nitex mesh then through a GF/F filter to yield rates for the 0.7 – 20 µm size class. Excretion by the 20-200 µm organisms was calculated as the difference between the "total" and the 0.7 to 20 µm size class. All particulate material was analyzed for ^{14}C incorporation (yielding rates of primary productivity) by a separate investigator (B. Bachman, PhD in prep). This same procedure was done for dark bottles which served as a control.

After size fractionation, 1 ml of filtrate from each bottle was acidified to a pH of 2 using 0.5 ml of 50% HCl and was de-gassed for 24 hours to release remaining inorganic ^{14}C. Scintillation cocktail (Ecolume) was then added to the samples; bottles were capped and counted using a Packard Tri-Carb 2000CA liquid scintillation counter on board the R/V Atlantic Explorer. Counts per minute were converted to disintegrations per minute using equation 1: $DPM = CPM_{sample} - CPM_{background} \div Detector\ Efficiency$ (1)

where DPM is the activity of the samples in units of disintegrations per minute; CPM_{sample} is the counts per minute produced by the sample; and $CPM_{background}$ is the back ground counts produced by the scintillation counter.

Rates of DOC excretion were calculated in units of mg C m^{-3} d^{-1} using equation 2:

$$DOC = (DPM_{24} - DPM_0 - DPM_D) \div (1.05) \times 25200\text{mg C}/m^2)(DPM_{TOT} \times time)^{-1} \quad (2)$$

where DPM_{24} = activity in the filtrate after 24 hour incubation; DPM_0 = activity of (depth-specific) T_0 particulate blank; DPM_D = average of (depth-specific) dark bottles; DPM_{TOT} = total activity DPM of isotope added multiplied by volume of water filtered (DPM/ml); 1.05 = constant that accounts for preferential uptake of the lighter isotope ^{12}C over ^{14}C; 25,200 = inorganic carbon concentration in seawater (mg m^{-3}).

2.2.2 DOC excretion by phytoplankton over a diel cycle

Water was collected from the fluorescence maximum before sunrise and was prescreened through a 200 µm mesh to remove large grazers. The water was then distributed into 24- 250 ml polycarbonate bottles and spiked with ^{14}C bicarbonate to a final activity of 0.08 µCi ml^{-1}. On deck simulated *in-situ* Incubations were conducted over a 24-hour period. Triplicate bottles were removed from the incubator at 0.08, 0.25, 0.5, 1, 3, 6, 12, and 24 hr time intervals. DOC excretion and rates of primary productivity at each time point were determined by filtering each bottle through a 0.2 µm SUPOR filter. Particulate material and filtrate (1 ml) was acidified to remove unincorporated ^{14}C, Ecolume was added and radioactivity of samples was quantified as described above.

2.2.3 Inhibitor addition experiments

Additional experiments using erythromycin additions were conducted to inhibit uptake of excreted DOC by bacteria (and to improve signal to noise) during on-board incubations. Water was collected from two depths (surface & fluorescence max) from a CTD cast before sunrise and was pre-screened through a 200 µm Nitex mesh to remove large grazers. Water was distributed into 8-250 ml bottles per depth, which included triplicates of control (no erythromycin) and treatment (addition of 10 µg/ml erythromycin) bottles plus two dark bottles for each depth. All bottles were spiked with ^{14}C bicarbonate to a final activity of 0.08 µCi ml^{-1} (as described in section 2.2.1) and incubated for 24 hours on-deck in flow-through incubators. Incubators were screened to simulate the light intensity at the depth of collection. After incubation, DOC excretion and rates of primary productivity were determined by filtering each bottle through a 0.2 µm SUPOR filter. Particulate material and filtrate (1 ml) were acidified to remove unincorporated ^{14}C; Ecolume was added and radioactivity of samples was quantified as described above.

2.2.4 Zooplankton Excretion Rates

To determine DOC excretion rates by zooplankton feeding on phytoplankton, water was collected from two depths in the euphotic zone (surface and fluorescence maximum). Two phytoplankton size classes were incubated separately (0.7-200 µm and 0.7-100 µm). To distinguish between the two size classes, half of the water from each depth was filtered through a 100 µm and or 200 µm Nitex mesh. Large zooplankton were collected from a 61 m trawl (mesh size 200µm), that filtered 293 m^3 during a tow conducted at

23:15 the night before the experiment. Copepods (*Pleuromamma* species) were collected and put into a 2-liter jar with filtered sea water (0.7 µm) for at least 4 hours to allow the copepods to clear their guts. Two different densities of copepods (2 or 5 individuals/liter) were added to 1 liter of water collected at each depth, with three replicates per copepod density. All bottles were spiked with ^{14}C bicarbonate to a final activity of 0.08 µCi ml^{-1} per bottle. Incubations were done on-deck for 24 hours, then collected and filtered through a 0.2µm SUPOR filter in red light conditions to limit production after experiment termination. Methods for sample processing are the same as described above in section (2.2.1).

2.2.5 Uptake of labile DOC by bacteria

Phytoplankton-derived ^{14}C-labeled DOC was prepared by collecting natural phytoplankton communities from the fluorescence maximum, adding ^{14}C bicarbonate to each bottle (to a final activity of 0.16 µCi/ml) and incubating on-deck (as in 2.2.3) for 4 hours. After incubation, samples were filtered through 0.2 µm cellulose membrane SUPOR filters under low light. Filters in sets of two were transferred to a snap cap vial and 2ml of boiling Milli-Q water was added to quickly lyse the cells. After vigorous vortexing, the solution was transferred to a 25ml Falcon tube. The combined filtrate was vortexed to create a homogenous sample. The extract was then acidified to a pH of 2 and left on a shaker table for 12 hours to eliminate unincorporated ^{14}C-bicarbonate. A small portion of this extract was taken and read on a liquid scintillation counter to determine ^{14}C activity. The produced ^{14}DOC was then stored in the refrigerator under

dark conditions until the next pre-dawn CTD cast. Water was then collected before dawn from the fluorescence max and apportioned into 0.25 L polycarbonate bottles. Triplicate samples (7 sets) were then spiked with 1ml of the previously created ^{14}DOC and incubated in the on-deck incubator (as in 2.2.3). Three vials were collected at each of the seven time points (T= 0, 0.25, 0.5, 1, 2, 3, and 6 hours) and were processed as described above.

2.2.6 Bacterial Productivity using ^{3}H-thymidine

On each cruise, bacterial productivity was estimated using the incorporation of ^{3}H-thymidine following standard BATS methods (Knap et al., 1997) according to:

$$Bacterial\ Production\ (cells/l/hr) = F \times ([3Hthymidine]pmol/l/hr) \quad (3)$$

where

F = Production of bacterial cells per mole ^{3}H-thymidine

The bacterial production (cells/l/hr) is then converted to carbon units using a conversion factor B,

$$Bacterial\ Production \times Bacterial\ Abundance \times B = ([Bacterial\ Production]pgC/l\ /hr)$$

where

$B = 0.00645\ pgC/cell$ (Kawasaki et al., 2006)

Bacterial abundance was calculated by DAPI stained cell counts on an inverted epifluorescence microscope by Dr. Michael Lomas' lab.

Samples were collected from Niskin bottles triggered at the same depths as those sampled for primary productivity. Polycarbonate centrifuge tubes were filled

directly from each Niskin after being rinsed three times with sample water. Triplicate tubes plus one blank were taken for each depth. Blanks were prepared by adding 100 μl of 100% tricarboxylic acid (TCA) to water samples designated as blanks, vortexed then set aside until samples were ready to be run. Samples were incubated in the dark at *in situ* temperatures. After 2-3 hours the incubation was ended by adding 100 μl of 100% TCA, and vortexing. All samples were stored in the dark in a refrigerator until extracted.

To extract, all samples were vortexed then centrifuged for 7 minutes at 2^{o}C and 14,000 rpm in an Eppendorf 5417R centrifuge. After centrifuging, samples were aspirated then an addition of 1.5 ml of 5% TCA consecutive centrifuging. The same procedure was followed as prior but instead with an addition of 1.5 ml of 80% ethanol. Samples were aspirated one last time then 1.5ml of scintillation cocktail (Ultima Gold) was added to all samples. All samples were then vortexed and left for 12hrs, vortexed again, and then counted in a liquid scintillation counter using ^{3}H setting for 2 minutes. The rate of incorporation was reported as ρmole ^{3}H-thymidine taken up per unit time after subtracting T_0 values

2.2.7 Statistical Analyses

A one sample T-test was run to determine if collected DOC samples were significantly lower than background values. A K-S test for normality was run and from this we concluded the data were not normally distributed ($p<0.01$; K-S= 0.077). The results from the T-test indicate that the mean DPM value of all of the samples was significantly lower than the background value (Value=35, N=436, p<001).

2.3 Results

Rates of DOC excretion as measured by ^{14}C-additions and subsequent size-fractionation were extremely low and were not significantly different from controls for any station on any cruise (Figure 2.2a, b). Time series simulated *in-situ* experiments showed results similar to the DOC samples collected from primary production experiments. Dark bottles in this experiment act as a background value, or control, because spiked ^{14}C bicarbonate should not be incorporated for use in photosynthesis by the incubated phytoplankton in the absence of light. Since no incorporation of labeled bicarbonate occurs, there should be no production of labeled DOC. Any rates of excretion seen in these bottles will act as the background rates for all other bottles. Rates of DOC production were significantly lower than the background rates at all time-points (0, 4, 8, 12, 16, 20, 24 hours) (Figure 2.3). There was incorporation of labeled bicarbonate seen after 12 hrs by increasing rates of POC production. The rates of incorporation follow the daily light cycle with a decline primary productivity after 20 hours of incubation (Figure 3).

The addition of erythromycin to incubation bottles resulted in little difference in DOC excretion rates compared to the control and dark bottles and were below background detection values (Figure 2.4a). Erythromycin addition did significantly, however, suppress primary production rates, $F= 14.637$; $p< 0.01$ thus there is a significant difference between the erythromycin addition and the non-antibiotic treatment (Figure 2.4b).

Rates of DOC production from sloppy feeding by copepods were low and were not significantly higher than background levels (Figure 2.5a). Integrated DOC production (100 m) from copepod treatments were not significantly different from one another, F= 0.423; p=0.689.

Rates of bacterial production (BP) increased from inside to the outside eddy stations on all cruises (Figure 2.6). Integrated bacterial production (to 100 m) did not scale with bacterial abundance collected from the same water samples (Figure 2.6). Rates of BP were similar at the BATS station between spring and summer seasons, but the cyclonic eddy showed higher rates of BP in the center(9.2 $mgCm^{-2}d^{-1}$) and edge(10.4 $mgCm^{-2}d^{-1}$) of the eddy compared to the anti-cyclone center(2.2 $mgCm^{-2}d^{-1}$) and edge (5.1 $mgCm^{-2}d^{-1}$). Bacterial productivity at the BATS station outside of the eddy influence was similar during cruises AE1101 (14.5 $mgCm^{-2}d^{-1}$), and AE1118 (13.7 $mgCm^{-2}d^{-1}$) (Figure 2.6).

2.4 Discussion

Dissolved organic compounds are almost exclusively consumed by bacteria and are either incorporated into the microbial food web and made refractory and or respired as CO_2 (Eichinger, 2006). I predicted that excretion rates of the picophytoplankton, namely cyanobacteria eg. *Synechococcus*, would exceed that of the larger phytoplankton, because the smaller cells are more abundant in oligotrophic ecosystems and are responsible for the majority of the primary productivity. Observations in other ecosystems have shown that, generally, rates of DOC excretion scale with rates of primary productivity (Ducklow, 1999). This means that in theory rates

of DOC production will vary over a 24 hr period, being largest during times of high light conditions. DOC should fluctuate on hourly to daily timescales in relation to phytoplankton responses to light. It can also vary unpredictably due to local release from phytoplankton enhanced by spikes in nutrients from mesoscale eddy interactions (Mouriño-Carballido & Neuer 2008). Past experiments using natural whole seawater incubations spiked with ^{14}C bicarbonate showed that dissolved primary production rates, or DOC excretion rates, were less variable than primary production and ranged from 1.3% to 81% of gross primary production (Lagaria et al, 2013); however these experiments were done in the Aegean Sea, which is a more productive region than the Sargasso Sea.

Results of experiments detailed in Section 2 clearly show that fluctuations in DOC production were not observed and that excretion of DOC by phytoplankton and by zooplankton is a difficult (if not impossible) rate to measure in the open ocean. The turnover rates of DOC (production by phytoplankton followed by consumption by bacteria) could be so rapid that pools of DOC do not accumulate over short timescales (Baxter & Sieberth, 1984; del Giorgio & Cole, 2000; Carlson et al, 2002). Another possible reason for low DOC detection is that GF/F filters have been shown to adsorb 100 times more DOC than polycarbonate filters, even after only a brief period of contact with ^{14}DOC extract, which could also result in a severe over-estimation of POC production (Maske & Garcia-Mendoza, 1994; Maranon, et al, 2004).

During my time series incubation I was unable to see any DOC production rates above background values. This could be because my shortest time scale for measuring DOC incorporation was 15 minutes; in 2007 Stoker's research showed that bacteria can take up DOC produced from phytoplankton exudate in the matter of minutes to seconds. Stoker found that a nutrient patch could become a bacterial hotspot within tens of seconds and have nutrient depletion to as much as 40% of the original nutrients remaining after only 3 minutes in situations with mobile bacteria (Stoker, 2007). Rapidly utilized DOC can be turned into either CO_2 through bacterial respiration, used for growth, or re-excreted into chemically resistant refractory DOM which usually has a residence time of over a year (Eichinger, 2009).

Even though antibiotics such as erythromycin have been seen to significantly inhibit protein synthesis in bacteria (Yokokawa et al, 2012), during my conducted experiments it limited cyanobacterial production during incubations. The primary species contributing to primary production in this system is the cyanobacteria *Synechococcus*; the erythromycin instead of only affecting heterotrophic bacteria inhibited the internal mechanisms of *Synechococcus* causing a decrease in PP compared to the control. It has been shown previously that erythromycin can reduce leucine incorporation up to 75 ± 11% (Yokokawa, 2012), which could have helped distinguish a rate of DOC excretion by phytoplankton without the influence of bacteria. Results could not be used since there was a significant reduction in rates of labeled rates of growth.

The role of grazers and "sloppy feeding" significantly contributing to the DOC pool has been seen in multiple circumstances (Moller, 2005; Moller, 2007; Steinberg et al, 2000). Copepods are linked to the microbial loop by contributing to the pool of dissolved organic material (DOM) through excretion, leakage from fecal pellets and "sloppy feeding" (Azam, 1983; Moller, 2001). Since only about half the carbon requirement of the bacteria can be directly met by release of organic carbon from phytoplankton, DOM production through zooplankton feeding may fill the gap (Baines &Pace, 1991). Moller (2005) found that copepods were capable of grazing on organisms >85 times smaller than they are. Even though copepods are capable of feeding on organisms much smaller than they are, larger cells would be preferentially grazed upon. Larger consumed cells would have a higher likelihood of producing excess DOC by sloppy feeding. However, in this system small cyanobacteria are the dominant producers, which if consumed by larger zooplankton would produce little to no excess DOC from consumption. Since we did not see any creation of labile DOC, in our experiment we have to assume that bacterial incorporation was equivalent to or surpassed the DOC production/excretion by our experimental sources, which includes larger phytoplankton. This caused rates of DOC production to be undetectable in our experimental treatments.

My inability to determine rates of DOC production above background value was seen in all experiments. This could have resulted from the ^{14}C bicarbonate having too low of a specific activity to be able to detect the rates of DOC production after it has passed through an additional trophic level. A secondary reason that detection may not

have occurred is that rates of bacterial incorporation of DOC were faster than we could detect, even during time series experiments. This explanation has been seen in a previous study conducted by Roman Stocker in 2007. He found that in nutrient poor water, bacteria gain significant growth advantages by "exploiting ephemeral nutrient patches" (Stocker, 2007). This means that bacteria were able to quickly take up nutrient pulses from sources such as phytoplankton leakage, cell lysis or fecal degradation within tens of seconds. The ephemeral patches can contain biologically labile organic compounds at concentrations two to three orders of magnitude above ambient seawater (Stocker, 2007). The consumption of these patchy nutrient pulses can have a strong influence on the total carbon turnover in the system by not allowing DOM to diffuse throughout the nearby water. In 2000, Goldberg found that that seasonally accumulated DOC could not be metabolized by the surface bacterioplankton over short time scales (Goldberg et al, 2000). However, he did find that the carbon being removed during incubation was glucose, a labile compound. Labile DOM production, such as carbohydrates and amino acids, by phytoplankton and utilization by bacteria appears to be to be tightly coupled, thus preventing accumulation of labile DOM during stratified conditions (Carlson et al, 2002). The lack of accumulation of labile organic compounds and steady DOC standing stocks in the upper 40m in the northwestern Sargasso Sea summer (Hansell & Carlson 2001) along with extremely low bioavailable carbohydrates (Pakulski & Benner, 1994) shows that bacteria could be rapidly utilizing recently produced labile DOC and causing rates of DOC production to be unobtainable by the methods used. The fact that we do not see any accumulation even though there is a

steady standing stock of DOC indicates the quantities in the water column have not been produced instantaneously and have been present for a long time.

A significant source of loss of ^{14}C during experiments is plausibly from high rates of bacterial respiration; this loss could account for the lack of DOC excretion signal. Rate measurements of bacterial respiration of not only ^{14}C but also ^{3}H have been seen to be up to 60% of the carbon or leucine that was taken up (Suttle et al, 1991). These respiration rates coupled with high bacterial activity and uptake rates would limit the ability to detect DOC excretion in low biomass regions like the Sargasso Sea. An additional discrepancy seen with the bacterial results was the lack of a trend between bacterial productivity and abundance. The bacterial abundance counts were conducted using DAPI stain; this stain binds the DNA of bacteria as it is taken up (Porter, 1980). Using this to determine cell abundance makes the assumption that all bacteria are uniformly active so that every cell is labeled exactly the same (Smith & del Giorgio, 2003). Often the dominant fraction of bacteria in an assemblage is unresponsive to activity probes like DAPI (Sherr et al. 1999, del Giorgo & Bouvier, 2002). It has been seen that the ranges for bacterial activity from cell hybridization in the open ocean generally lay between 39-96% (Glockner et al. 1999, Eilers et al. 2000). This range of bacterial activity leaves the claim that all bacteria are active and uniformly growing to be not well supported. The lack of agreement from bacterial production and abundance results is most likely subject to the lack of activity of all the bacteria and labeling occurring at the similar rates.

Since excreted DOC is largely actively available for uptake by bacteria, there is a direct link between primary and secondary production and bacterial production that is essential for the cycling of matter through the food web (Ducklow & Carlson 1992, Legendre & Rassoulzadegan 1996). Picophytoplankton namely *Synechococcus* are typically the most abundant primary producers within the Atlantic oceanic gyres (Partensky et al., 1999), and it is likely that bacteria in the euphotic zone of this oligotrophic habitat are specifically adapted to incorporating exudates produced by these cyanobacteria. Marine bacteria can form bacterial hotspots around exuded patchy nutrient inputs such as excreted DOC (Stocker, 2007). There is growing evidence that these picophytoplankton release DOC even under nutrient limited conditions (Bertilsson et al., 2005) like that of the Sargasso Sea. Uptake and cycling of DOC in low nutrient conditions has the potential to happen on short timescales, which is a possible explanation on why measuring DOC production and incorporation was not possible.

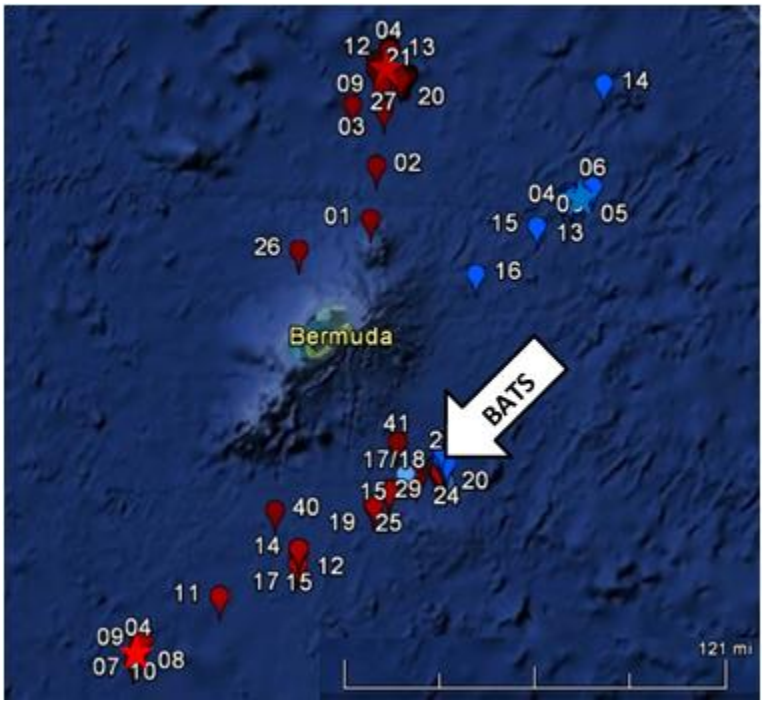

Figure 2.1. Cruise tracks and sampling locations. Red = AE1118 (cyclonic eddy); dark blue = AE1206 (cyclonic eddy); dark red = AE1219 (anti-cyclonic eddy). Stars indicate the eddy center, and numbers indicate the cast number from which water was collected.

Table 2.1 Experiments conducted in the Sargasso Sea in 2011 and 2012.

Cruise	Date	Location	Cast	Experiments Conducted	Depths (m)
AE 1118	7/23/2011	Center	2	DOC from PP & On deck simulated *in-situ*	(20,50,80,100) & (5,80)
	7/25/2011	Center	7	DOC from PP & On deck simulated *in-situ*	(20,50,80,100) & (5,80)
	7/28/2011	Edge	14	On deck simulated in-situ	(5,80)
	7/31/2011	BATS	21	DOC from PP & On deck simulated *in-situ*	(20,50,80,100) & (5,80)
	8/2/2011	BATS	27	DOC from PP & On deck grazer experiment	(20,50,80,100) & (5,80)
AE 1206	3/15/2012	Center	2	DOC from PP	(20,50,60,80)
	3/16/2012	Center	6	On deck grazer experiment	(45,85)
	3/17/2012	Center	14	Time Series : On deck simulated in-situ	(80)
	3/19/2012	BATS	18	On deck grazer experiment	(20,80)
	3/21/2012	BATS	28	Time Series : On deck simulated in-situ	(80)
AE 1219	7/20/2012	Center	6	DOC from PP	(20,50,85,100)
	7/20/2012	Center	7	Time Series : On deck simulated in-situ	90
	7/22/2012	Center	11	Antibiotic Experiment	90
	7/22/2012	Edge	14	Time Series : On deck simulated in-situ	93
	7/24/2012	Edge	24	Time Series : On deck simulated in-situ	90
	7/26/2012	BATS	30	^{14}DOC Time Series : On deck simulated in-situ	80
	7/30/2012	BATS	38	^{14}DOC Time Series : On deck simulated in-situ	80
Bacterial Production experiments were conducted at all sampling locations on every cruise.					

On all cruises, the Bermuda Atlantic Time Series (BATS; 31° 40’ N, 64° 10’ W) site was used as the “outside” eddy control station. “Center” refers to the geographical center of each eddy as measured by Sea Surface Height (SSH) anomalies. “Edge” refers to the outermost edge of each eddy determined by visual inspection of the SSH data.

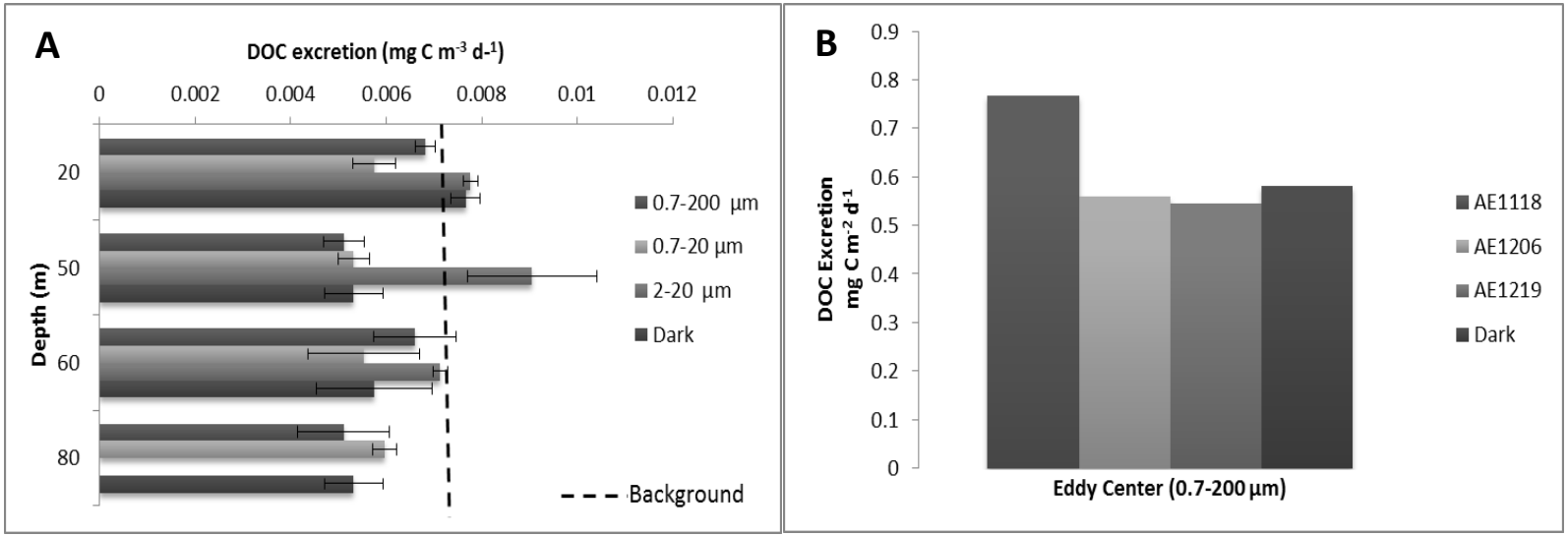

Figure 2.2. Representative data from phytoplankton DOC excretion experiments: (A) size-fractionated DOC excretion during the AE1206 cruise at the eddy center station. Triplicate samples were taken for each size fraction, including the dark bottle. (B) Integrated DOC excretion from the eddy center station conducted on all 3 cruises.

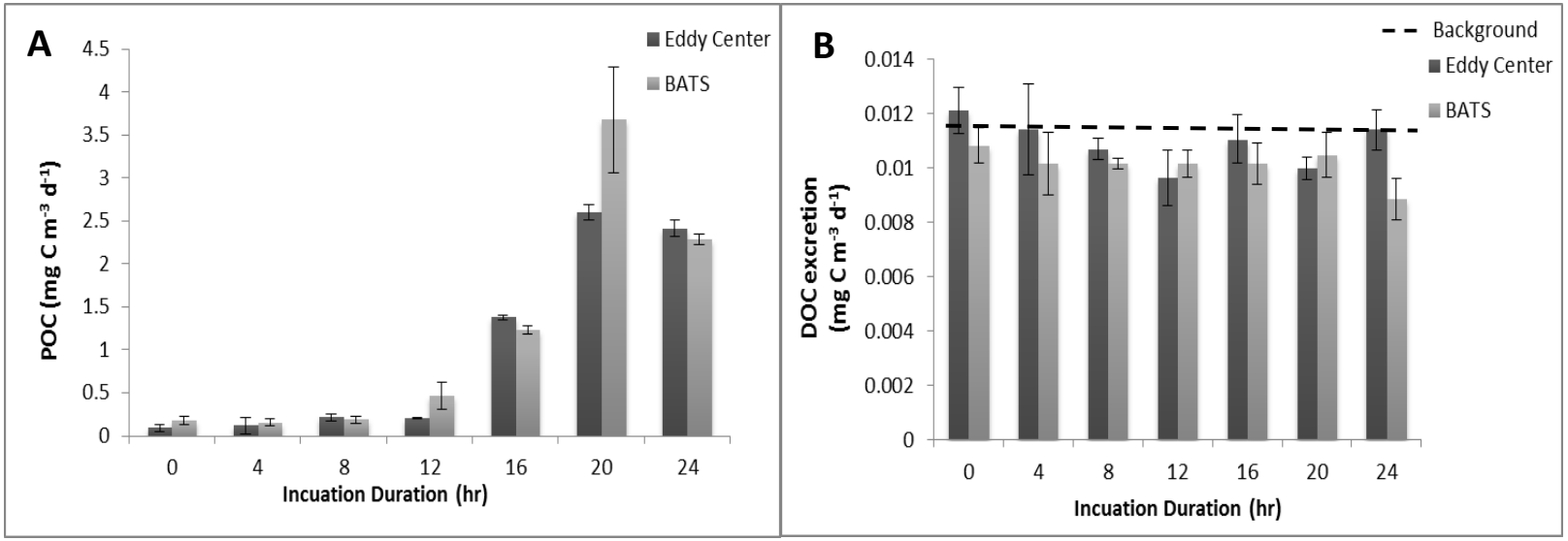

Figure 2.3. Time series DOC incorporation and excretion rate measurements from the AE1206 cruise at stations in the eddy center and at BATS. Triplicate samples were taken for each time point and DOC measurements were taken from the filtrate of the POC measurements.

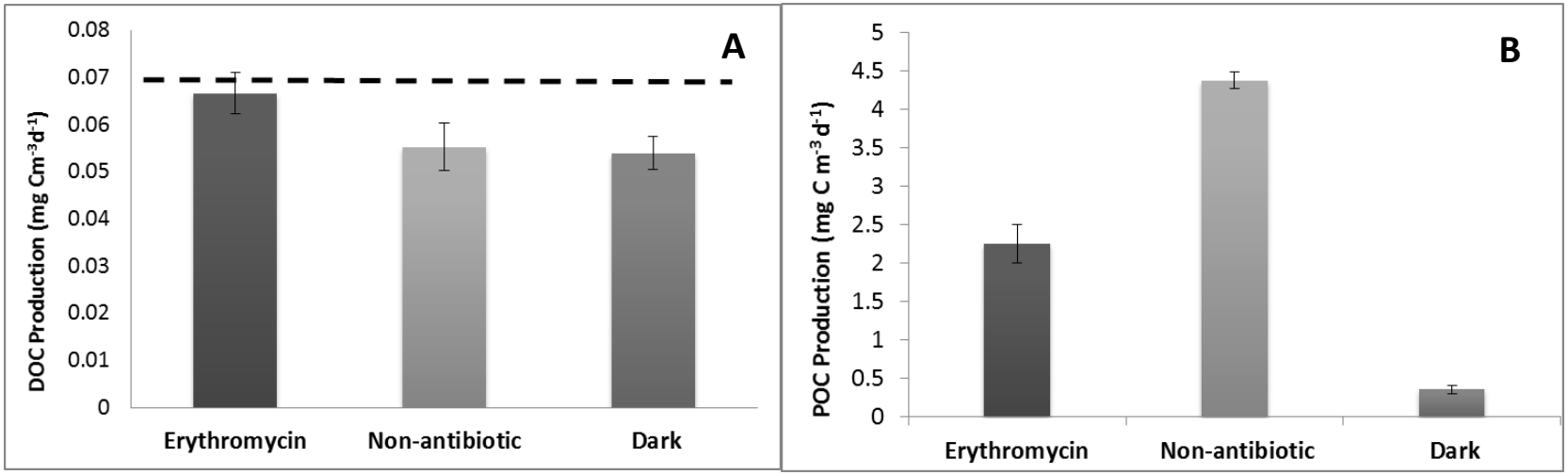

Figure 2.4 Representative data for antibiotic addition experiments on samples collected inside the eddy at the fluorescence maximum on cruise AE 1219. A) Measured rates of DOC excretion were not above background detection limits. B) Rates of primary productivity were suppressed from the erythromycin additions.

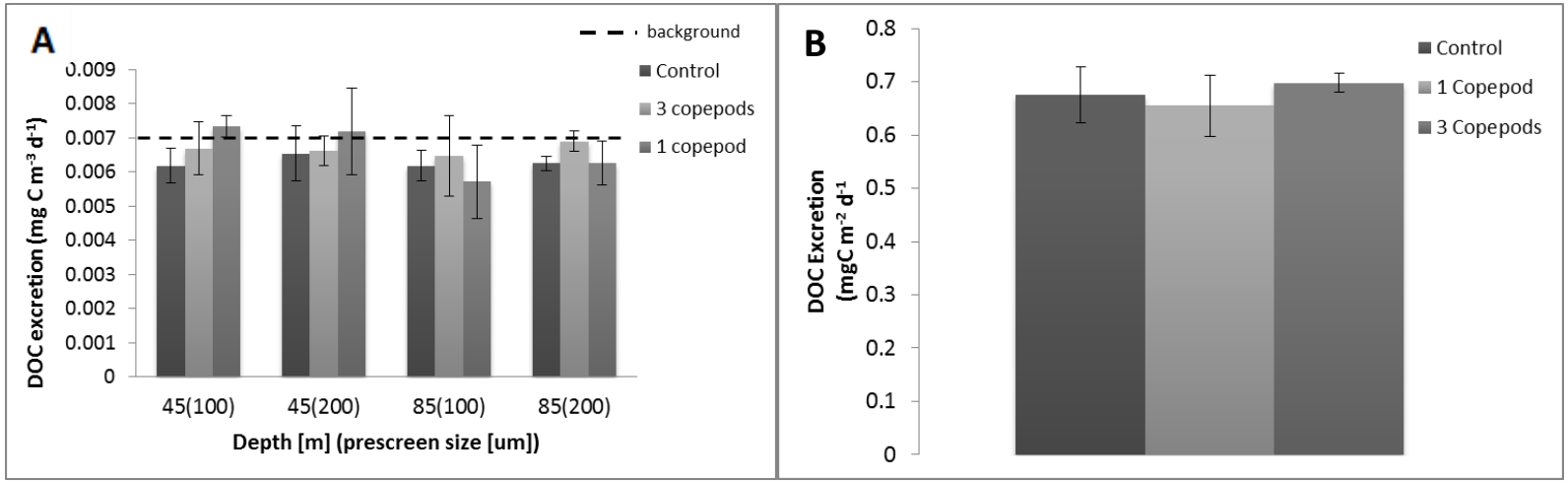

Figure 2.5. Simulated *in-situ* grazer-addition experiments conducted during the AE1206 cruise using water collected from a high Chl *a* depth (45m) & the Chl *a* maximum (85m). A) Measured rates of DOC excretion from size fractionated pre-screened incubations; measured rates were not above the background detection limits. B) Integrated rates (100 m) of DOC exertion and integrated to 100m.

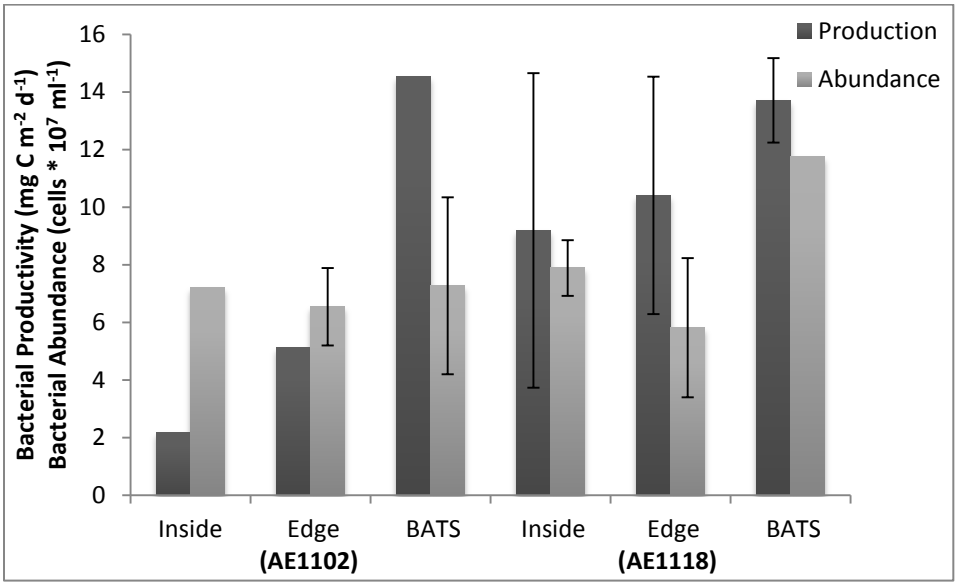

Figure 2.6. Rates of bacterial productivity and bacterial abundance, on cruise AE1102 on the left (in an anti-cyclonic eddy) and AE1118 on the right (in a cyclonic eddy). Values are integrated to 100 m. Error bars are standard deviations created from multiple profiles (N≥2) at the same location in the eddy.

CHAPTER 3

Inverse Modeling of DOC Flows in Mesoscale Eddy Food Webs of the Sargasso Sea

3.1 Introduction

As discussed in the prior section, it is sometimes difficult or impossible to measure carbon flows in food webs directly. When measurements are possible, it is often the case that only some interactions can be characterized and these only at limited locations and times. To fill in the gaps, numerical modeling can be used as a way to characterize the missing interactions and thus produce a complete picture of flows within an ecosystem (Vezina & Platt, 1988; Niquil et al., 2012; Bisset, 1999). In this section I describe my use of an inverse modeling approach to characterize DOC dynamics in eddies of the Sargasso Sea.

Models are said to be inverse when they are used to estimate unknown quantities from a set of known (measured) quantities in a system (Donali, 1999). Linear inverse modeling (LIM) relies on the principle of conservation of mass at steady state, this means that the sum of fluxes in and out of the system equals the rate of change in their standing stocks (Niquil et al, 2012). Past modeling procedures has been to select a single solution out of many probable ones; the most often applied of these is the least-squares criterion, which minimizes the sum of the squares of the residuals calculated

from the model (Vézina and Platt, 1988). The Ecopath framework is the most used in this type of procedure. Ecopath is mostly used to investigate higher trophic levels with the lower trophic levels simplified to largely undifferentiated compartments. Most recently, new methods have been developed to describe the solution by calculating a representative sample of all the possible solutions using a Monte Carlo approach (Kones et al., 2006; Van den Meersche et al., 2009; Van Oevelen, 2010; NIquil et al., 2012).

Four steps are used to create and setup the modeling criteria, the first is to define your knowns and unknowns. This involves determining how many compartments your model will have, then defining what flows are coupled with another, "who eats whom" or what enters or leaves the system. Once this is decided you can then throw out flows that are highly unlikely or impossible, for example, microzooplankton to phytoplankton (Niquil, et al, 2012). The second step is to set up your linear equalities, or mass balances. In most cases the simplest model is one where the sum of the flows entering the compartments equals the sum of the flows leaving. You will then be able to add the data collected from *in situ* experiments. The third step is constraining your model, so that flows like respiration does not exceed ingestion (Niquil et al, 2012). The last step is to represent the results and to select one solution, in our case the mean, or to define each unknown by the range of its possible solutions (Niquil et al, 2012).

Here, I constructed models for a cyclonic eddy (AE1118). Recognizing that eddies are heterogeneous with respect to sub-mesoscale physical, chemical, and biological characteristics, I constructed a model for each of three stations that were located in

different regions of the eddy: at the center, on the edge and outside the eddy. I used the same general model structure for all stations on the cruise.

3.2 Methods:

Each food web contained 40 flows and all webs were structured identically. The currency of each model is carbon (dissolved or particulate). The structure of the webs was based on the hypothesis that the size of the producers and consumers was a major determinant of the trophic dynamics of this system. Each of the 40 carbon flows used in the model are between two compartments or from a compartment to outside the system. Here, "outside" the system is defined as a flow to below the euphotic zone. The living components of the food webs included two phytoplankton compartments, three grazer compartments and one compartment for heterotrophic bacteria. We divided the phytoplankton into two size categories, small (0.2 to 2 μm) and larger phytoplankton (2–200 μm). All living compartments contributed to a DOC pool through excretion and could contribute to the detrital pool (Det) through mortality or defecation. Sloppy feeding by grazers would contribute to both Det and DOC pools. Detritus was transformed to DOC from dissolution processes mediated by microbial activity (Jumars et al., 1989). Flows leaving the system included respiration by all living compartments. All non-respiratory losses from the system were represented by flows to and from the external compartment by advection. POC could be exported through the detritus pathway or by consumption of mesozooplankton by higher trophic levels. Grazer compartments included microzooplankton (Mic; ciliates, flagellates, and/or small

copepods 20 – 200 μm) and mesozooplankton (Mes; mainly copepods, 200 – 2000 μm) and macrozooplankton (e.g. salps, jellies > 2000 μm).

Values for known flows were taken from biomass and process rate data generated by Richardson, Neuer, and colleagues on cruise AE 1118 (July 2011) (Bachman et al., in prep; Lomas et al., in prep.). All data can be accessed from the Biological and Chemical Oceanography Data Management Office at the Woods Hole Oceanographic Institution (http://bcodmo.org/). Data used for known flows includes measurements of size-fractionated primary productivity (Bachman et al., in prep). Microzooplankton grazing rates were taken from dilution experiments (Landry and Hassett, 1982) done by Neuer, de Martini et al. (manuscript in prep). Mesozooplankton grazing rates were measured by the R. Condon et al. on each cruise. Rates of bacterial production were from experiments by M. Lomas or by me as described in Section 2 of this thesis.

The inverse method of Vezina & Platt (1988) was used to reconstruct values for all flows in the system using code written in MATLAB 5.3. Detailed descriptions of the method can be found in Vezina & Platt (1988), Jackson & Eldridge (1992) and Donali et al. (1999). Table 3.1 summarizes the symbols that will be used to represent carbon pools in the food web, while Table 3.2 gives the mass balance equations.

As described in the section above, data were used directly or were combined to formulate six input equations or knowns: (1) small phytoplankton NPP, (2) large plankton NPP, (3) grazing rates of the microzooplankton community, (4) mesozooplankton grazing rates, (5) net bacterial production, and (6) detrital (POC) export. The approach assumes that biomass in any compartment is in steady state, i.e.,

the total flows entering any compartment are equal to the flows leaving a compartment, with the exception of the external compartment (Richardson et al., 2004). Combined with the 8 mass balance equations (Table 3.2), the total number of equations available to describe the system was 14. In this model there are 7 potential contributors to the DOC pool including small and large phytoplankton, micro-, meso- and macrozooplankton, bacteria, and detrital dissolution. The known biomass and carbon production values collected from experiments conducted during research cruises are shown in Table 3.3. Because there were 34 unknowns, the problem was a mathematically under-determined system with an infinite number of solutions. Biological constraints on the calculated flows are presented in Table 3.5. The Monte-Carlo based minimization scheme of van Oevelen et al. (2010) was used to find the best solution for each food web construction.

3.3 Results:

Flows calculated for all three models are presented in Table 3.6 and graphically in Figure 3.1 (A,B,C). The focus of these results will be on the estimated fluxes to and from the DOC pool. Average rates of DOC excretion by the small phytoplankton were higher than those of the large phytoplankton. (Figure 3.2). The location in respect to the eddy affected the DOC production of both phytoplankton size classes; we see that the cyclonic eddy displayed increased DOC production from the small phytoplankton inside the eddy compared to the edge, and at the BATS station (12.23, 7.86, 9.60 mmol C m^{-2} d^{-1}) respectively. The larger size class however showed little difference depending eddy sampling location, having little to no variation in DOC production between sampling

locations (Figure 3.2). Eddy influence on DOC production by grazers varied between size classes. Microzooplankton displayed increased DOC excretion at the inside and edge stations, while outside of eddy influence at the BATS station DOC excretion was reduced. Mesozooplankton showed an opposing trend having low DOC excretion values inside the eddy and increasing moving outward from the center to the BATS station. Macrozooplankton showed high DOC excretion values inside the eddy center, while at the edge and BATS station was reduced (Figure 3.3). Detrital input to the DOC pool increased from the Eddy center to outside the eddy; the same trend was seen from Bacterial DOC excretion (Figure 3.4).

There were two destinations that the produced DOC could go through the system, into the bacterial compartment as bacterial production, or out of the system as DOC advection, which in our models is the system exit (Ext) compartment. Bacterial incorporation of DOC increased moving from the eddy center to outside the eddy. The calculated values for DOC to Ext were highest in the center of the eddy and were lower at the edge and outside eddy stations (Figure 3.5).

3.4 Discussion

The size specific estimated phytoplankton DOC production rates ranged between 10.1-19.5% of integrated primary production; this falls into the 10-20% range that is typically seen in open ocean oligotrophic environments (Cole et al. 1988; Ducklow 2000; Kawasaki & Benner, 2006). DOC excretion was dominated by the small phytoplankton in all sampled locations excreting over three times the amount of the larger plankton. However, when you look at the percent excreted compared to primary production from

the large plankton excreted a greater percentage (10.5-19.5%) compared to that of the smaller plankton (10.1- 12.9%).

Consumption of primary producers can lead to varying rates of DOC production through “sloppy feeding” depending on the size of the zooplankton and the size of its prey (Moller, 2005). Each zooplankton size class had varying contributions to total DOC production in the three sampling locations. The macrozooplankton were the dominant DOC producers inside the eddy center, contributing values over double that of the smaller grazers. At the eddy edge and BATS station, the zooplankton excretion rates were more similar. For the inside station the macrozooplankton DOC production could have been higher from an increase in biomass inside the eddy influence. McGillicuddy found that zooplankton biomass inside an eddy in the Sargasso Sea became elevated compared to mean summertime conditions in 2004-2005 (McGillicuddy, 2007) Mesozooplankton showed increasing DOC production moving along that same transect having its highest DOC production rates at the BATS station.

There were a few inherent problems with the models; one of the largest was the lack of constraints available including grazing rates and respiration rates to put on the macrozooplankton. This was a problem because there were no collected values for rates into or leaving the macrozooplankton compartment. This allowed excess carbon distributed by the model to go into the macrozooplankton compartment. Another problem was the microzooplankton grazing rates that were used as a known value to help constrain the potential flow of carbon to that compartment. Grazing rates by

microzooplankton historically have had a large range when compared to primary production; Lessard & Murrell 1998 found the percent of primary production grazed by microzooplankton ranged from 0 – 245%. Another study by Calbet and Landry in 2004, found grazing rates globally ranged between 59 and 74% of primary production. Values collected from experiments conducted during our research had a slightly larger range (34.5 - 74.7%). Microzooplankton grazing rates have been found to be over-estimated and unlikely to show low grazing rates from dilution experiments (Dolan & McKeon, 2005). Problems with detecting low grazing rates are that they can be difficult to detect with regression analysis because of small n values, and detecting low grazing rates requires distinguishing slight differences in the start and end of chlorophyll concentrations, which could be difficult in the higher dilution treatments (Dolan & McKeon, 2005). Another problem could be that combined effects of grazer mortality in high dilution treatments and growth in undiluted treatments could result in over-estimation of grazing rates which is especially common in low chlorophyll waters (Dolan et al., 2000). Through an analysis of 185 dilution experiments Dolan found that the average rate of microzooplankton grazing does not exceed 50% of primary production. In some calculated values we have wide standard deviations for potential values, which are caused by the limited constraints on those compartments. Next to the macro and microzooplankton previously mentioned, the detritus to DOC rate has the largest error bars. This is because those values only have one constraint, having to be at least 10% of the sum of primary production, respiration and excretion, which causes the value to be widely variable. Another problem with the model was the inability to run a sensitivity

analysis for the calculated values. This occurred because the carbon inputs from primary production were completely used by other compartments, the most significant being the microzooplankton.

Many studies have shown that anti-cyclonic eddies exhibit increased bacterial production and biomass in the euphotic zone compared to outside locations (Baltar, 2010; Baltar, 2009), but others have also seen up to three times the amount of bacterial production during cyclonic eddies at the BATS site (Tarran, 2001; Ewart, 2008). In our study, however, we found the opposite trend, with bacterial production values suppressed within the influence of the eddy and increasing outside of it. With these varying results in bacterial production found to occur in eddy systems, their importance in carbon transfer in these systems is immensely important to quantify correctly. Bacteria play a major role in determining the fate of new production (Ewart, 2008). With increased bacterial biomass and production, high rates of organic carbon remineralization can lead to a significant fraction of the newly produced organic matter being regenerated in the euphotic zone minimizing the potential carbon flux of eddies (Legendre and Le Févre, 1995). Contrary to the findings produced from my model which showed the highest rates of DOC production outside of the eddy, a study by Lasternas in 2013 found that the production of DOC was significantly higher in anti-cyclonic eddies compared to cyclonic eddies and an outside station despite all locations having similar rates of primary production (Lasternas, 2013).

One of the largest flows of DOC in our model was the advection of DOC out of our system, which can be attributed from diffusion through the nutricline, from eddy-induced motion and turbulent mixing. Modeled DOC advection values ranged from 19.8 – 38.68 mg C m^{-2} d^{-1}. This value, however large, falls into the range of DOC advection found by Carlson et al in 1994; he found that DOC out of the upper ocean of the Sargasso Sea near Bermuda ranged from 0.99-1.21 mol C m^{-2} yr^{-1} and when translating this value to an average daily rate excluding seasonal influences, the range of DOC advection is 32.58 - 39.81 mg C m^{-2} d^{-1} (Carlson et al, 1994). In continuation the importance of the diffusive flux in removal of DOC from the surface ocean should not be overlooked. A study by Guo et al in 1995 calculated a diffusive flux out of the upper 250 m of 1.8 – 3.6 x 10^{-4} mol C m^{-2} d^{-1}, which converts to 2.2- 4.3 mg C m^{-2} d^{-1} from the Gulf of Mexico and the Mid Atlantic Bight (Guo et al, 1995). However, these stations are continental slope regions and not open ocean oligotrophic regions; the similar potential for the same magnitude of DOC diffusion is still probable. Downward fluxes of DOC from the upper 100 m can represent a significant fraction of the TOC flux and may play an important role in the carbon cycle of the ocean. Lateral advective DOC fluxes, however, could be orders of magnitude higher than POC fluxes, depending on physical influences conditions like eddies (Guo et el, 1995).

Globally, the pool of DOM is about the same in magnitude as atmospheric CO_2 (Moller 2007), and DOC is an important aspect and can make up a significant portion of the DOM pool. As oceans become more stratified and oligotrophic, smaller phytoplankton like *Synechococcus* can significantly increase in number and importance.

These cyanobacteria have vastly different cell structures and kinetics compared to large diatoms, which have shown to be very productive in drawing CO_2 out of the atmosphere. Thus, small changes in the phytoplankton community could have strong effects on atmospheric CO_2 (Gruber & Sarmiento, 1996). With increasing CO_2 in the earth's atmosphere coupled with lowering pH values and increased freshwater inputs, the global oceans could become more stratified having a similar ecosystem dynamic and composition to the Sargasso Sea (Riebesell et al., 2007). In addition to these physical changes at the sea surface coupled with ocean circulation processes, the fixation of CO_2 by phytoplankton transports carbon rich detritus to the ocean's interior "biological carbon pump"; this can play an important role in regulating global CO_2 on longer time-scales (Neuer et al., 2002). With large amount of eddy influence causing vertical mixing events, DOC could be sequestered out of the surface waters creating a significant carbon export out of the system (Carlson, 2002). With new insights on the potential for picoplankton to attribute significantly to export flux, (Richardson et al, 2007) the importance for understanding carbon flow in this oligotrophic region is vital. Understanding the pathway and the rates of carbon flows through this systems biological pump could shed light on how the carbon could move through the food web in the future with increasing CO_2 conditions.

3.5 Conclusion.

I quantified DOC excretion by plankton in the Sargasso Sea through a cyclonic eddy using inverse modeling. DOC excretion rates by phytoplankton were between 10.07 and 14.52 mg C m^{-2} d^{-1} from both size classes combined. These values on average

were 11.7 % of total primary production. Generally, DOC excretion was higher inside the eddy compared to the Edge and BATS station. Modeling results indicated that one of the largest potential destinations for DOC in our system was advection out of the euphotic zone. The highest rates of DOC advection were seen inside the eddy center, decreasing moving to the edge and then outside of the hydrodynamic influences of the cyclonic eddy. Direct measurement of DOC excretion by phytoplankton and zooplankton was unobtainable from our experimental procedures most likely from instantaneous DOC uptake as it was produced from excretion or other methods.

Table 3.1 Symbols used in the Sargasso Sea food web.

Symbol	Description
Ph1	Picophytoplankton
Ph2	nano → microphytoplankton
mic	microzooplankton
mes	mesozooplankton
mac	macrozooplankton
res	respiration
bac	bacteria
doc	dissolved organic carbon
det	detritus
ext	system exit

Table 3.2 Mass balance relationships used in inverse model analysis.

Mass Balance	Equation
Ph1 (.7-2µm)	gPh1_Ph1 - Ph1_res - Ph1_mic - Ph1_det - Ph1_mes - Ph1_mac - Ph1_doc
Ph2 (2-200µm)	gPh2_Ph2 – Ph2_res – Ph2_det – Ph2_mes – Ph2_mac – Ph2_doc
det	Ph1_det + Ph2_det + mic_det + mes_det + mac_det + bac_det – det_doc– det_Mic – det_mes – det_mac – det_ext
doc	Ph1_doc + Ph2_doc + mic_doc + mes_doc + mac_doc +bac_doc + det_doc – doc_bac –doc_ext
bac	doc_bac – bac_res – bac_mic –bac_mes – bac_det – bac_doc
mic	Ph1_mic + Ph2_mic + bac_mic + det_mic – mic_res – mic_mes – mic_mac – mic_det – mic_doc
mes	Ph1_mes + Ph2_mes + bac_mes + det_mes + mic_mes – mes_res – mes_det – mes_doc – mes_mac – mes_ext
mac	Ph2_mac + mic_mac + mes _mac + det_mac – mac_res – mac_doc – mac_det – mac_ext

gPh1 = gross primary production of phytoplankton (.7-2 µm), Ph1 = phytoplankton (.7-2 µm), gPh2 = gross primary production of phytoplankton (2-200 µm), Ph2 = phytoplankton (2-200 µm), det = detritus, doc = dissolved organic carbon, bac = bacteria, mic = microzooplankton, mes = mesozooplankton, mac = macrozooplankton, ext = external compartment, res = respiration. Flows are described by underscore _ = To; e.g. doc_bac indicates fluxes of carbon from the doc pool to bacteria.

Table 3.3 Biomass and carbon production values.

	AE1118		
Biomass (mg C m^{-2})	Inside	Edge	BATS
ph1	370.6	508.1	670.1
ph2	82.2	121.1	108.7
mic	15.2	15.2	12.4
mes	123.9	156.2	220.2
bac	637.1	261.7	518.5
mac	19.7	19.3	32.0
	AE1118		
Carbon Production (mg C m^{-2} d^{-1})	Inside	Edge	BATS
Cph1	117.3	77.6	74.1
Cph2	18.2	21.1	15.3
Cdet	24.1	31.2	20.5
Cbac	9.2	10.4	13.7
Cmic	50.0	58.0*	30.9
Cmes	3.8	5.0	6.7

Known sources of data as biological constraints for the flow of carbon through the modeled food web.

* (Highest values that would allow the model to run, actual value is 73.7. Replacement value is a realistic estimate of microzooplankton grazing.)

Table 3.4 Inverse analysis flow constraints for food web construction.

Process	Bound	Description	Equation	Reference
Respiration-Picoplankton	lower	At least 5% off Gross Primary Production (GPP)	5% GPP	Vezina andPlatt (1988)
Respiration-Picoplankton	upper	No more than 30% GPP	30% GPP	Vezina andPlatt (1988)
Respiration- large Phytoplankton(2-200µm)	lower	At least 5% off Gross Primary Production (GPP)	5% GPP	Vezina andPlatt (1988)
Respiration- large Phytoplankton(2-200µm)	upper	No more than 30% GPP	30% GPP	Vezina andPlatt (1988)
Respiration-microzooplankton	lower	At least 20% of total ingestion	0.2* (total ingestion by microzooplankton)	Vezina et al. (2000), Vezina and Pace (1994)
Respiration-microzooplankton	upper	No more than the maximum specific respiration (d^{-1}; a function of body size (W;pgC/cell) and temperature (T; 25°C))* microzooplankton biomass (mgC/m^3)	$1.7W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	Moloney and Field (1989)
Respiration-mesozooplankton	lower	At least 20% of total ingestion	0.2* (total ingestion by mesozooplankton)	Vezina et al. (2000), Vezina and Pace (1994)
Respiration-mesozooplankton	upper	No more than the maximum specific respiration (d^{-1}; a function of body size (W;pgC/cell) and temperature (T; 25°C))* mesozooplankton biomass (mgC/m^3)	$14W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	Moloney and Field (1989)
Respiration-Bacteria	lower	At least 20% of total DOC uptake	0.2* (Total bacterial ingestion)	Vezina et al. (2000), Vezina andPace (1994)
Respiration-Bacteria	upper	No more than the maximum specific respiration (d^{-1}; a function of body size (W;pgC/cell) and temperature (T; 25°C))* bacterial biomass (mgC/m^3)	$14W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	Moloney andField(1989)
Excretion- Picoplankton	lower	No less than 10% of Net Primary Production NPP	0.1(NPP)	Baines and Pace (1991)
Excretion- Picoplankton	upper	No more than 55% of NPP	0.55(NPP)	Baines and Pace (1991)
Excretion- large Phytoplankton(2-200µm)	lower	No less than 10% of NPP	0.1(NPP)	Baines and Pace (1991)
Excretion- large Phytoplankton(2-200µm)	upper	No more than 55% of NPP	0.55(NPP)	Baines and Pace (1991)
Excretion- microzooplankton	lower	10% of total ingestion	0.1 (total ingestion by microzooplankton)	Vezina and Pace (1994)
Excretion- microzooplankton	upper	100% of respiration	1*microzooplankton respiration	Vezina and Platt (1988)
Excretion- mesozooplankton	lower	10% of total ingestion	0.1 (total ingestion by microzooplankton)	Vezina and Pace (1994)
Excretion- mesozooplankton	upper	100% of respiration	1*microzooplankton respiration	Vezina and Platt (1988)
Assimilation efficiency-	lower	50% of total ingestion	0.5 (total ingestion by microzooplankton)	

microzooplankton				
Assimilation efficiency-microzooplankton	upper	90% of total ingestion	0.9 (total ingestion by microzooplankton)	
Assimilation efficiency-mesozooplankton	lower	50% of total ingestion	0.5 (total ingestion by mesozooplankton)	
Assimilation efficiency-mesozooplankton	upper	80% of total ingestion	0.8 (total ingestion by mesozooplankton)	
Bacterial Production efficiency	lower	Respiration + excretion is 50% of total ingestion	0.5 (Respiration + excretion)	
Bacterial Production efficiency	upper	Respiration + excretion is 90% of total ingestion	0.9 (Respiration + excretion)	
Gross Production efficiency-microzooplankton	lower	Respiration + excretion + DOC excretion is 50% of total ingestion	0.5 (respiration + exretion + DOC)	
Gross Production efficiency-microzooplankton	upper	Respiration + excretion + DOC excretion is 75% of total ingestion	0.75 (respiration + exretion + DOC)	
Gross Production efficiency-mesozooplankton	lower	Respiration + excretion + DOC is 50% of total ingestion	0.5 (respiration + exretion + DOC)	
Gross Production efficiency-mesozooplankton	upper	Respiration + excretion + DOC is 75% of total ingestion	0.75 (respiration + exretion + DOC)	
Detritus- system export	?	?	?	
Detritus-DOC	lower	Primary Production + respiration +excretion is 10% of detritus to DOC	.01(PP + respiration + excretion)	
Ingestion- mesozooplankton	upper	No more than the maximum specific ingestion (d^{-1}; a function of cell size (W;pgC/cell) and temperature (T;25°C))*mesozooplankton biomass (mgC/m^3)	$63W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	Moloney and Field (1989)
Ingestion- microzooplankton	upper	No more than the maximum specific ingestion (d^{-1}; a function of cell size (W;pgC/cell) and temperature (T;25°C))*microzooplankton biomass (mgC/m^3)	$63W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	
ingestion- bacteria	upper	No more than the maximum specific ingestion (d^{-1}; a function of cell size (W;pgC/cell) and temperature (T;25°C))*bacterial biomass (mgC/m^3)	$3.6W^{-0.25}*e^{(0.0693*(T-20))}$*biomass	Moloney and Field(1989)

GPP = gross primary production, DOC = dissolved organic carbon. Carbon content values (pg C $cell^{-1}$) were 0.00645 for bacteria (Kawasaki, 2011) , 1.7 for microzooplankton, 2214.1 for mesozooplankton. Temperatures were taken from individual CTD casts.

Table 3.5 Descriptions and values of carbon flows

Flow #	Flow symbol	Description	July- August 2012 (Inside)	July- August 2012 (Edge)	July- August 2012 (BATS)
1	gPh1_Ph1	GPP of picoplankton (0.7-2µm)	143.55	95.47	90.43
2	gPh2_Ph2	GPP of phytoplankton (2-200µm)	22.61	26.16	19.00
3	Ph1_res	respiration by picoplankton	26.26	17.85	16.31
4	Ph1_mic	grazing of picoplankton by microzooplankton	70.17	66.96	41.95
5	Ph1_det	detritus production by picoplankton	12.67	0.11	8.87
6	Ph1_mes	grazing of picoplankton by mesozooplankton	2.08	2.58	4.08
7	Ph1_mac	grazing of picoplankton by macrozooplankton	20.13	0.11	9.61
8	Ph1_doc	DOC production by picoplankton	12.23	7.86	9.60
9	Ph2_res	respiration of large phytoplankton	4.39	5.01	3.69
10	Ph2_mic	grazing of large phytoplankton by microzooplankton	5.29	16.18	3.61
11	Ph2_mac	grazing of large phytoplankton by macrozooplankton	4.54	0.11	3.13
12	Ph2_mes	grazing of large phytoplankton by mesozooplankton	1.74	2.47	2.66
13	Ph2_det	detritus production by large phytoplankton	4.36	0.11	2.92
14	Ph2_doc	DOC production by large phytoplankton	2.29	2.20	2.99
15	mic_res	respiration by microzooplankton	17.45	16.74	12.59
16	mic_mac	grazing of microzooplankton by macrozooplankton	20.70	19.07	8.68
17	mic_mes	grazing of microzooplankton by mesozooplankton	8.40	12.58	9.28
18	mic_det	detritus production by microzooplankton	21.19	26.54	14.06
19	mic_doc	DOC production by microzooplankton	8.00	8.41	2.07
20	mes_res	respiration by mesozooplankton	6.36	9.12	13.68
21	mes_det	detritus production by mesozooplankton	6.50	10.30	15.42
22	mes_doc	DOC production by mesozooplankton	2.75	4.56	7.00
23	mes_mac	grazing of mesozooplankton by macrozooplankton	4.22	8.56	13.72
24	mes_ext	Consumption of mesozooplankton by higher trophic levels	3.73	3.53	4.60
25	mac_res	respiration by macrozooplankton	17.14	5.24	5.85
26	mac_doc	DOC production by macrozooplankton	21.96	5.38	5.74
27	mac_det	detritus production by macrozooplankton	39.73	50.13	80.27
28	mac_ext	Consumption of macrozooplankton by higher trophic levels	20.17	5.09	6.82
29	doc_exit	export of DOC from the system	38.68	19.80	16.89
30	doc_bac	bacterial production (gross)	9.19	10.41	13.71
31	bac_res	Bacterial respiration	7.92	7.95	8.49
32	bac_mic	grazing of bacteria by microzooplankton	0.28	0.19	1.12
33	bac_mes	grazing of bacteria by mesozooplankton	0.29	0.62	1.09
34	bac_mac	grazing of bacteria by macrozooplankton	0.29	0.63	1.11
35	bac_det	detritus production by bacteria	0.29	0.63	1.10
36	bac_doc	DOC excretion by bacteria	0.12	0.40	0.79
37	det_doc	Dissolution of detritus to DOC	0.51	1.41	2.41
38	det_mac	grazing of detritus by macrozooplankton	49.11	37.38	62.42
39	det_mes	grazing of detritus by mesozooplankton	11.07	17.8	37.30
40	det_ext	export of detritus from the system	24.06	31.19	20.5

Descriptions and values of carbon flows within eddy systems of the Sargasso Sea during February-March and July- August 2011. Units are mmol C m^{-2} d^{-1}. Flows are described by underscore _ = To; e.g. doc_bac indicates fluxes of carbon from the doc pool to bacteria.

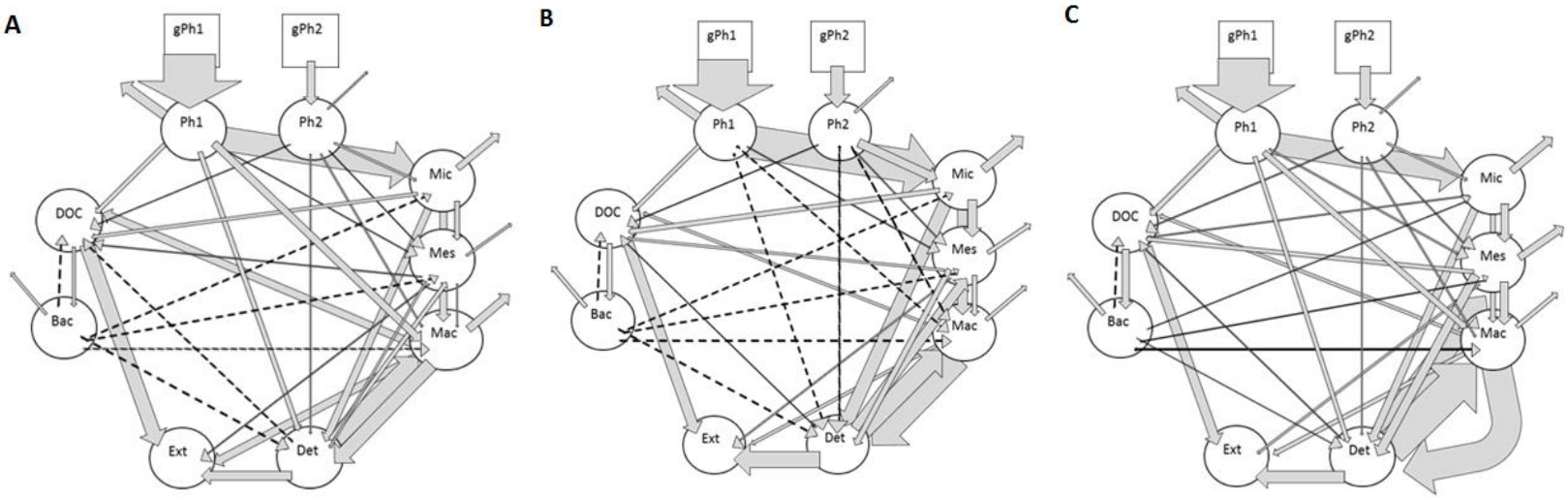

Figure 3.1. Food web constructed for station Inside (A), Edge (B) and BATS (C) for cruise AE1118 showing the food web structure. Arrow widths are proportional to the largest flow. Estimates for all flows are detailed in Table #. Abbreviations: gPh1, gPh2 = gross primary productivity of the picophytoplankton and larger plankton, respectivelyPh1= picophytoplankton, Ph2 = large phytoplankton.2µm, Mic = microzooplankton, Mes = mesozooplankton, Mac = macrozooplankton, Bac = bacteria, DOC = dissolved organic carbon, Det = detritus, Ext = external compartment. Dashed lines represent flows that are <1% of the largest flow. Arrows that are leaving the system correspond to modeled respiration values.

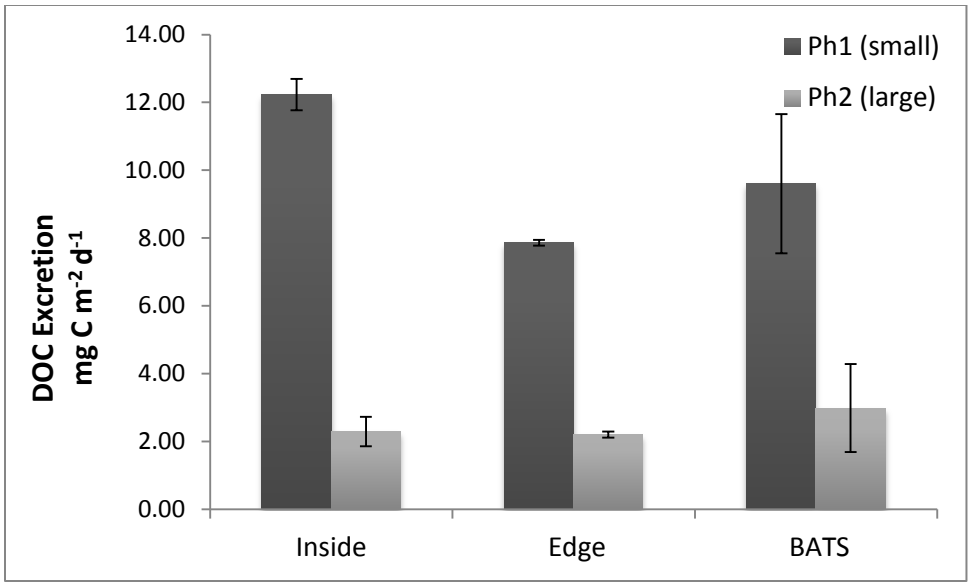

Figure 3.2.Modeled DOC excretion from size fractionated phytoplankton during the AE1118 cruise. Error bars are created from the standard deviation of the 10,000 iterated solutions produced by the model; values are the average of the all of the possible solutions created.

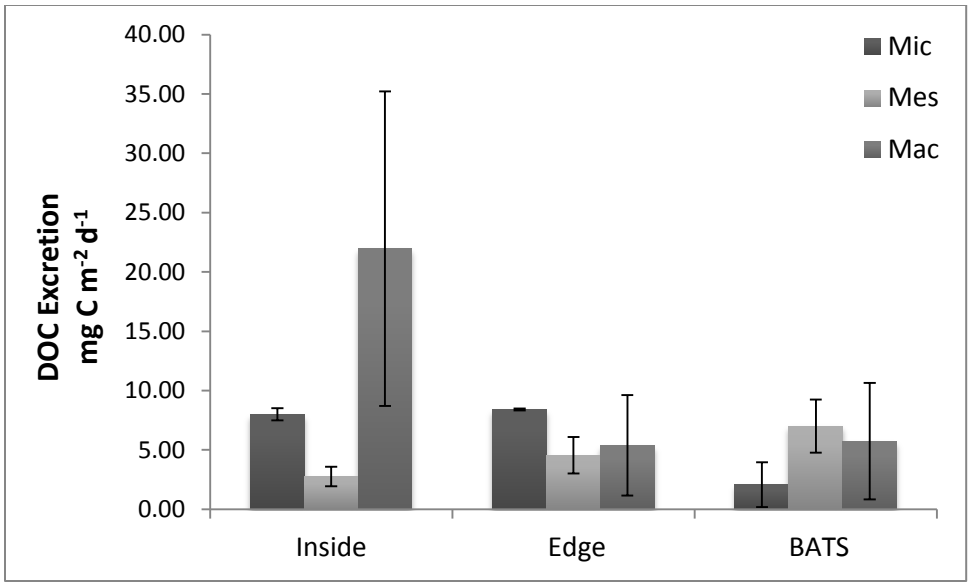

Figure 3.3. Modeled DOC excretion from size fractionated zooplankton during the AE1118 cruise. Error bars are created from the standard deviation of the 10,000 iterated solutions produced by the model; values are the average of the all of the possible solutions created.

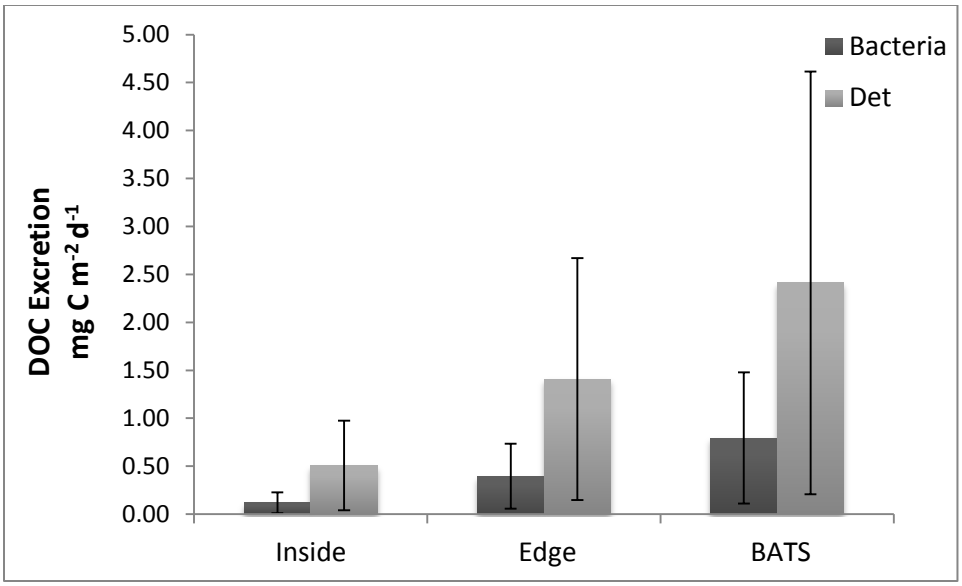

Figure 3.4. Modeled DOC excretion by bacteria and from detrital degradation during the AE1118 cruise. Error bars are created from the standard deviation of the 10,000 iterated solutions produced by the model; values are the average of the all of the possible solutions created.

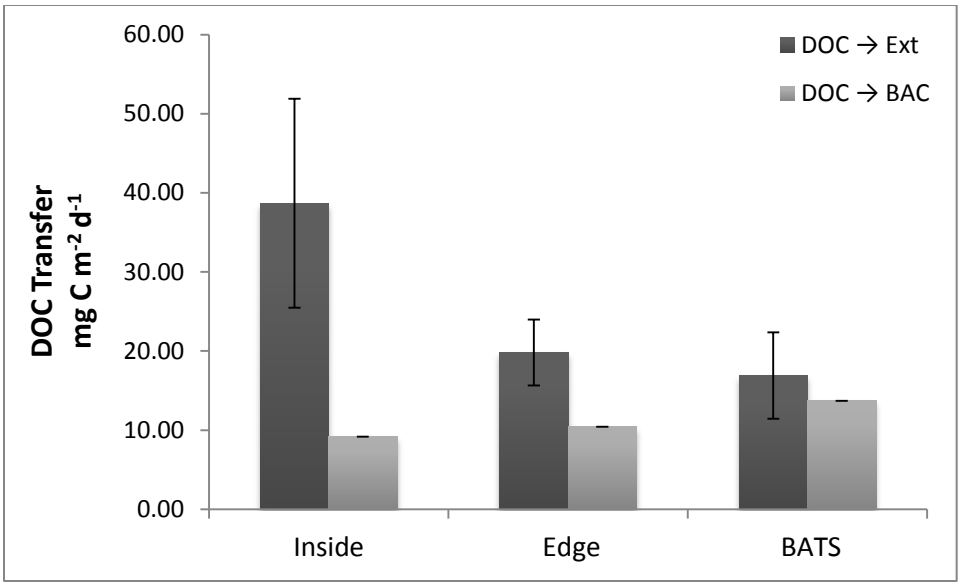

Figure 3.5. Modeled DOC loss from exiting the system (advection), and from incorporation by bacteria (bacterial production) during the cruise AE1118. Error bars are created from the standard deviation of the 10,000 iterated solutions produced by the model; values are the average of the all of the possible solutions created.

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