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**Papers from
the
SUMMER UNDERGRADUATE RESEARCH FELLOWSHIP
PROGRAM IN OCEANOGRAPHY
at
THE UNIVERSITY OF RHODE ISLAND
Graduate School of Oceanography
NARRAGANSETT, RHODE ISLAND
June – August 2014**

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GSO Technical Report No. 14-01

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PREFACE

This report presents the papers written by the fourteen participants in the 2014 Summer Undergraduate Research Fellowships in Oceanography (SURFO) program at the Graduate School of Oceanography (GSO), University of Rhode Island (URI). This past summer represented the 30th year in which the program has been coordinated and extended through the several disciplines in oceanography and ocean engineering at URI's Narragansett Bay Campus. The 2014 program will continue excellence beyond the official duration of the program with at least three projects presented at the AGU Fall 2014 and two projects at the ASLO 2015 meetings.

The participants in the 2014 SURFO program are grateful to the Department of Defense ASSURE Program and the National Science Foundation REU program for their support of the program through grant OCE-1156520. Additional funding to support Sierra Davis came from National Science Foundation grant PLR-1341585.

The SURFO program would like to thank all of those individuals at URI who contributed to the program's success including those who advised the students and who gave SURFO seminar presentations. In addition, our thanks to Kim Carey for her assistance in the preparation of this report as well as for administrative, financial and recruitment tasks. Finally, we would like to thank Kellen Rosburg who served as a graduate coordinator for the program.

Kathleen A. Donohue
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SURFO Site Directors

Observations on Ocean Mixing in the Argentine Basin

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Abstract. Cross-frontal eddy exchange between the Brazil and Malvinas Currents drives ocean mixing in the Argentine Basin and alters the temperature and salinity water mass properties tracked within these currents. This study aims to quantify the degree of modification undergone by select water masses in the Argentine Basin as well as locate mixing hotspots that contribute largely to the transformation of those water masses. A lever rule analysis was performed on mean temperature-salinity profiles to identify and quantify changes to the water mass properties of Brazil-Malvinas Confluence source waters and their resulting mixed product. Streamline-projection analysis was also performed to map out the progression of mixing across the Argentine Basin. It was found that the alteration of water masses within the Antarctic Circumpolar Current occurs within the first trough of the Brazil-Malvinas Confluence and that the proportion of Malvinas Current waters increases systematically in the poleward direction across the analyzed streamlines. Water mass modification in the Brazil-Malvinas Confluence was found to initiate within 0.5° - 1° of longitude due to intense cross-frontal eddy exchange that produce filaments. The water mass alterations then smooth and homogenize as the emergent Malvinas and Brazil Currents flow eastward across the Argentine Basin. Future studies focused on cross-frontal eddy exchange in the Brazil-Malvinas Confluence are being proposed to NSF, guided in part by this study.

1. Introduction

The Brazil-Malvinas Confluence region in the Argentine Basin is a segment of the Antarctic Circumpolar Current (ACC) with major contribution to poleward heat flux (Sun and Watts, 2002). The net poleward heat flux observed by Sun and Watts in the Argentine Basin is believed to stem from mixing between ACC and Subtropical Gyre waters in the Brazil-Malvinas Confluence (Sun and Watts, 2002) where ocean mixing is thought to be driven by cross-frontal eddy exchange (de Szoeke and Levine, 1981). In this study the extent and progression of mixing in the Argentine Basin was investigated using both lever rule and streamline-projection analysis.

The Brazil-Malvinas Confluence is the convergence zone of the Brazil and Malvinas Currents located off of the Argentinian Coast (see figure 1, Gordon, 1989). The Malvinas current is the northern portion of the ACC that flows northward along the coast of South America after emerging from Drake Passage and the Brazil Current is the southward flowing western boundary current of the subtropical gyre (Jullion, *et al*, 2010). At the Brazil-Malvinas Confluence the cold, fresh waters of the Malvinas Current meet and mix with the warm, salty waters of the Brazil Current. The two currents then proceed eastward, meandering across the Argentine Basin, carrying their respective post-confluence water mass properties.

Water mass properties such as salinity and temperature are indicators that construct oceanographic fingerprints for water masses, or water types. Differences in the temperature, salinity properties of different water masses enable us to track the movement of those water masses and the currents that carry them. When water masses with different water mass properties come together in the water column they will mix and form a mixed product. Mixing can cause alteration of water mass properties, a process called water mass modification.

One way to organize water flow in the ocean is through the use of streamlines, or paths of mean flow. Differences from the paths of mean flow or instabilities in the current

are called eddies. Eddies can separate into rotating bodies of water that detach from the mean flow and lead to cross-frontal eddy exchange. Cross-frontal eddy exchange occurs when parcels of water move across a front, a sharp gradient in water mass properties, and are subsequently broken up by and mixed with their surrounding waters. Sufficient cross-frontal eddy exchange can lead to observable water mass modification.

2. Research Methods

2.1. CTD data

The data used in this study consists of publicly available conductivity, temperature, and depth (CTD) transects of the Argentine Basin created from the Argo float data set. The Argo data set was created with a global array of free-drifting floats that collect salinity, temperature, and pressure measurements for every 10m of the upper 2000m of the ocean once every 10 days. A 20m surface mixed layer was assumed and any floats with gaps in data or not reaching 1800dbar were discarded.

The Argentine Basin was divided into 11 different sized sections (see figure 1) to study the progression of mixing from the Brazil-Malvinas Confluence to the Mid-Atlantic Ridge. The westernmost section contained Argo floats from both Drake Passage and the subtropical gyre, representing source waters of the Brazil and Malvinas Currents. The easternmost section of the Argentine basin consisted of Argo floats near the Mid-Atlantic Ridge and represented the resulting mixed product. Latitudinal boundaries for Argo floats were chosen to focus on streamlines of interest while avoiding complicated topographies that would obscure the results of the study. Only a subset of floats from the subtropical gyre, Drake Passage, and Mid-Atlantic Ridge sections was used in the lever rule analysis.

2.2. Lever Rule

The lever rule can be derived from the conservation of mass, heat, and salinity in the ocean. It states that the water mass properties of a mixed product will lie somewhere on a

line between the water mass properties of its sources. The lever rule also states that the mixed product can be thought of as a fulcrum, allowing the percent contribution from each source water to the mixed product to be calculated.

Mixing can only take place between neighboring waters. As a result mixing occurs between waters that share a vertical location in the water column, which is determined by density. Water mass properties of Brazil-Malvinas Confluence source waters were identified with temperature-salinity profiles of surface waters from Drake Passage and the subtropical gyre. The water mass properties of the Brazil-Malvinas Confluence's mixed product were identified with temperature-salinity profiles of the Mid-Atlantic Ridge. The mean water mass properties of the Argentine Basin mixed product fell between the mean water mass properties of the source waters. The percent

2.3. Gravest Empirical Mode

Mean cross-stream hydrographic structures for the 11 different sections of the Argentine Basin were developed using the gravest empirical mode (GEM, Watts, *et al.*, 2001) projection method. GEM fields are lookup tables for mean temperature, salinity properties as a two-dimensional function of depth and geopotential anomaly (g_{pan} , m^2/s^2) relative to 1800 dbar. At each pressure level contoured mean water mass properties are created from cubic splines fitted to CTD data as a function of g_{pan} .

2.4. Streamline-projection

A streamline-projection is created by concatenating multiple GEM fields along stream from the region into a three-dimensional matrix. From this matrix a desired geopotential streamline can be chosen and an along-stream hydrographic section of the region can be produced.

3. Results

3.1. Streamline and Density Dependent Ocean Mixing

Table 1 displays Malvinas Current contributions to Mid-Atlantic Ridge waters at different density layers and geopotential streamlines; it demonstrates mixing dependence in the Argentine Basin on density and streamline. With increasing density the proportion of Malvinas current waters present in the Mid-Atlantic Ridge mixed product increases. The proportion of Malvinas current waters present in the mixed product also increases across streamlines in a poleward direction. These results indicate that Malvinas current waters are more prevalent at greater depths in the water column and in more southern streamlines. The Brazil Current contribution behaves conversely across the analyzed streamlines and densities.

3.2. Water Mass Modification

The water masses transported by the Brazil and Malvinas Currents emerge from the Brazil-Malvinas Confluence with modified water mass properties due to intense cross-frontal exchange. Figure 2 demonstrates an influx of heat and salt from Brazil Current waters to Malvinas Current waters at shallower depths that correlates to the warming and salinification of ACC waters. Both temperature and salinity are seen to have increased after mixing in the Brazil-Malvinas Confluence at geopotential streamlines between 13-16 (m^2/s^2). Figure 3 highlights the location of mixing and water mass modification through deepening of both the thermocline and halocline between the two most westward sections of the Argentine Basin. Mixing continues to occur across the eastern sections of the Argentine Basin, however, further deepening in the thermocline and halocline is lesser in magnitude. At lower geopotential streamlines it is observed that the thermocline deepens to the lesser degree than at higher geopotential streamlines and that further water mass modification occurs, as demonstrated by a drop

Figure 1. A map of the Argentine Basin with depth contour intervals of 1000m. Argo floats used in this study are represented by circular markers with colors corresponding to the 11 sections of the Argentine Basin; dark green representing Brazil and Malvinas Current source waters from the subtropical gyre and Drake Passage and dark magenta representing the resulting Mid-Atlantic Ridge mixed product. The path of the Malvinas current (northern portion of the ACC) is roughly demonstrated by geopotential streamlines (units of m^2/s^2) 13 and 16, contoured in black, which are observed to flow north out of Drake Passage along the South American coast before turning back south and then flowing to the east. Geopotential streamlines 16 and 19 roughly represent the flow of the Brazil Current after it has followed the coastline south to the Brazil-Malvinas Confluence. The Brazil-Malvinas Confluence is represented here at the beginning of the path of geopotential streamline 16.

contributions from each source water were calculated along potential density surfaces.

Figure 2. Potential temperature (top) and salinity (bottom) GEM fields of Brazil and Malvinas Current source waters (left) and Mid-Atlantic Ridge (MAR) mixed product waters (right) with contour intervals $0.5\text{ }^{\circ}\text{C}$ and 0.1 psu . The warm, salty Brazil waters have mixed with cold, fresh Malvinas Current waters and modified the water mass properties of more southern geopotential streamlines, as demonstrated by the extension of higher temperature and salinity values into more southern (lower valued) geopotentials in Mid-Atlantic Ridge mixed product waters.

Figure 3. Along-stream projection of potential temperature (top) and salinity (bottom) in a northern ACC streamline ($gpan = 16$, left) and mid-ACC streamline ($gpan = 13$, right) with contour intervals $0.5 \text{ }^{\circ}\text{C}$ and 0.1 psu . Observable modification of water mass properties has initiated between the first and second (two most western) Argentine Basin GEM fields, as demonstrated by a deepening of the thermocline and halocline. The first and second Argentine Basin GEM fields are representative of the first trough of the BMC and span $.5\text{-}1^{\circ}$ longitude or $40\text{-}80 \text{ km}$.

Table 1. Results from the lever rule analysis showing percent contribution from Malvinas Current waters to the Mid-Atlantic Ridge mixed product. Malvinas Current contributions to the mixed product increase with density (depth in the water column) and across streamlines in the poleward direction. Brazil current contributions act conversely across analyzed densities and streamlines.

% Malvinas Current in MAR $\pm$ uncertainty				
	Geopotential Anomaly (m^2/s^2)	16	14	12
Density Surface (kg/m^3)	27.0	$57 \pm 7\%$	$66 \pm 7\%$	
	27.1	$72 \pm 17\%$	$81 \pm 16\%$	$84 \pm 15\%$
	27.1	$70 \pm 32\%$	$89 \pm 22\%$	$82 \pm 18\%$
	27.3	$100 \pm 12\%$	$100 \pm 5\%$	$100 \pm 10\%$
	27.4	$100 \pm 9\%$	$100 \pm 2\%$	$100 \pm 0\%$
	27.5			$100 \pm 10\%$

and Karen Tracey for guiding me through my first steps in scientific research.

in the thermocline between the 4th and 7th GEM field sections of the Argentine Basin.

5. Summary

The lever rule and streamline-projection methods have been applied in an in-depth analysis of the progression of ocean mixing in the Brazil-Malvinas Confluence and Argentine Basin. It has been found that the proportions of Malvinas Current waters are greater than the proportions of Brazil Current waters in the Mid-Atlantic Ridge mixed product both at greater depths and in more southern geopotential streamlines. It has also been found that water mass modification in the Argentine Basin occurs over a short distance, in the first trough of the Brazil-Malvinas Confluence, within $.5^\circ$ to 1° longitude or approximately 40 to 80 km. The results of this study demonstrate the need for future studies focused on cross-frontal exchange in the Brazil-Malvinas Confluence and seasonal variations contributing to surface changes in the Brazil-Malvinas Confluence.

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Method Development for Evaluating the Ammonium Nitrogen Isotopic Composition of Point Source Nutrient Inputs to Narragansett Bay

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Abstract. In much of the marine environment nitrogen is the limiting nutrient for primary production. However, when nitrogen inputs increase significantly, it can stimulate potentially harmful results including harmful algal blooms and decreased dissolved oxygen due to enhanced respiration. In the Narragansett Bay watershed, wastewater treatment facilities (WWTFs) are the largest source of anthropogenic nitrogen to the estuary system. WWTFs output nitrogen in the forms of ammonium (NH_4^+) and nitrate (NO_3^-), both of which are suitable for use by primary producers. In this study the aim was to refine a method for measuring the nitrogen isotopic composition of ammonium. The method needed to meet three main requirements. It must be able to separate ammonium from nitrate and dissolved organic nitrogen in the water samples. This separation must be done quantitatively in order to prevent fractionation of the isotopic composition in the samples. These first two requirements were met by ensuring that diffusion took place through a gas permeable membrane and by extending the diffusion period and therefore improving yield. Thirdly, the blank must be less than 10% of the sample size in order for it not to contribute significantly to the measured isotope value. I determined the origin of the blank contribution (magnesium oxide and vial caps) and made changes in the method to minimize it. Finally, the isotopic composition of WWTF samples was measured to see if they behaved like standards. A previous study completed the nitrate budget within the watershed. Quantification of the full isotope budget of DIN (ammonium and nitrate) allows study of the larger picture of nitrogen cycling within the Narragansett Bay watershed.

1. Introduction

Nitrogen is essential to the life of every organism on the planet, and as such plays a key role in marine environments. Coastal marine environments are naturally limited by the concentration of nitrogen present in the system; therefore if that concentration is increased by an anthropogenic source the growth of primary producers may be stimulated (Ryther et al. 1971). The increase in the supply of organic matter to an ecosystem is defined as eutrophication and is seen in the form of algal blooms (Nixon 1995). When these blooms die, they sink to the bottom and bacterial colonies begin the decomposition process. This process strips oxygen out of the water column and creates a low oxygen environment that is potentially harmful to other organisms in the area.

Nitrogen is part of several chemical species that are observed suspended in the water column, dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN). DIN in the form of nitrate and ammonium are key nutrients for primary producers and other organisms, however, ammonium uptake rate is much faster due to the fact that it is much easier to break down chemically, meaning it does not need to be reduced (Carpenter et al. 1983).

To gain a better understanding of the nitrogen cycle in areas where eutrophication is a problem, nitrogen isotopes (expressed as $\delta^{15}\text{N}$) can be used to study the characteristics of source water as well as of processing that happens in the estuary itself. The $\delta^{15}\text{N}$ is defined as

$$\delta^{15}\text{N} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000,$$

where R_{sample} is the ratio of the sample nitrogen and R_{standard} is the ratio of atmospheric nitrogen. The $\delta^{15}\text{N}$ value of any water parcel reflects small deviations from the ratio of ^{15}N to ^{14}N caused by biological reactions (Sigman et al 2009). These fractionations give information about the processes and

inputs that affect a water system's nitrogen isotopic composition most significantly. However, when studying nitrogen isotopes artificial fractionation in the lab causes by high blank percentages and incomplete recovery within the method want to be avoided because they give inaccurate and inconsistent information about the $\delta^{15}\text{N}$ of a sample.

When applying the original diffusion method described in the 1998 Holmes et. al. paper, it was observed that high blanks and incomplete recovery were causing artificial fractionation, which yielded inaccurate $\delta^{15}\text{N}$ values for samples. This method is designed to separate ammonium from other inorganic and organic nitrogen species in water samples so that the concentration and isotopic composition of the ammonium sample can be calculated. This is done by the use of acid base chemistry to manipulate the ammonium species. Sample water is exposed to a basic solution above a pH-9.7 so that ammonium will lose a proton and become the gaseous species ammonia. The ammonia gas is then to pass through a gas permeable membrane, which contains an acidified disk, which donates a proton to the ammonia effectively converting it back to aqueous ammonium and trapping it on the disk (shown in figure 1). The goal of this experiment was to modify this method in order to achieve the lowest blanks possible and to achieve complete recovery of the ammonium in the sample.

2. Materials and Procedures

2.1. Sample Collection

Riverine and wastewater treatment facility (WWTF) water samples were collected from March 2009 to January 2009 as well as February 2012 to January 2013 and will be referred to as the 2009 and 2012 data sets respectively (Schmidt et al.). Riverine samples were collected using a bucket lowered

from a bridge into the river from the last gauged point in the river. WWTF water samples were collected at the outflow pipe as final 24-hour effluent samples. After collection, the samples were filtered with glass fibers, and were acidified using hydrochloric acid (pH 2) or were frozen and stored at -20°C prior to analysis (Schmidt et al.).

Figure 1. Diffusion vial used in the diffusion of ammonium from samples.

Figure 2. Narragansett Bay riverine and wastewater treatment facility (WWTF) collection map. Rivers are marked by arrows, and WWTFs are marked by triangles.

2.2. Laboratory Analysis

The NH_4^+ $\delta^{15}\text{N}$ measurement is made by first isolating the NH_4^+ through manipulation of the acid-base chemistry of ammonia; ammonium is converted to ammonia when treated with base, and is then trapped on an acidified filter as ammonium in a gas permeable membrane. Teflon packets were made by placing 2 GF/F filter discs that had been soaked in 2M sulfuric acid into a packet made with 0.5-inch

Teflon tape. One packet and 15 mL of sample was added to each muffled 25 mL screw cap septa vial (muffling procedure was to put glassware wrapped in aluminum foil in a muffle oven at 460° for 4 hours). Then ~0.2g of sodium hydroxide was added to each vial (final concentration ~0.33M) and the caps were screwed on immediately. Sodium hydroxide was used in lieu of magnesium oxide due to the large blank (>60µM) observed with muffled MgO. Another concern about the use of magnesium oxide was that the MgO solution was only at a pH~8 and ammonium converts to ammonia gas at a pH~9.7. After a 10 day time period on an orbital shaker table, vials were removed and packets were allowed to dry in a desiccator for 24 hours. GF/F filter discs were removed from packet and placed in muffled 12 mL screw cap vials.

Then a persulfate method was followed in order to oxidize samples to nitrate in preparation for use in the denitrifier method (Robinson et al. 2004). Concentrations of samples were then measured using a chemiluminescence detector after reducing nitrate samples to NO_x gas with a hot vanadium (III) solution (Braman et al. 1989). After concentrations are known, the denitrifier method outlined by Sigman et al. (2001) was implemented. Each sample was then analyzed for N isotope composition by gas chromatography-isotope ratio mass spectrometry (GC-IR-MS). Nitrogen stable isotope ratios are given as the ratio of $^{15}\text{N}/^{14}\text{N}$ and are displayed as $\delta^{15}\text{N}$ ($\delta^{15}\text{N} = [(^{15}\text{N}/^{14}\text{N}_{\text{sample}} / ^{15}\text{N}/^{14}\text{N}_{\text{standard}}) - 1] \times 1000$). For each run on the GC-IR-MS working standards (IAEA N3, $\delta^{15}\text{N} = +4.7\text{‰}$; USGS 32, $\delta^{15}\text{N} = +18\text{‰}$; USGS 34, $\delta^{15}\text{N} = -1.8\text{‰}$) and samples were both analyzed in order to normalize delta values to the accepted standard (N_2 in air).

3. Assessment

We modified the Holmes et al., (1998) method to address two main requirements. The first is that the blank must be less than 10% of the sample size in order for it not to contribute significantly to the measured isotope value. The second is that the diffusion method must be able to quantitatively separate ammonium from nitrate and dissolved organic nitrogen in the water samples. Both of these are necessary in order to prevent fractionation of nitrogen isotopes so that the measured isotope values are accurate.

Samples ran with the original method were found to have a blank concentration of greater than 20 µM. This is not an acceptable blank size for quantitative work. With this in mind, a series of blank experiments were performed in which the nitrogen concentrations of each reagent used in the original method was calculated using a chemiluminescence analyzer for NO_x gas (Braman et al. 1989). This was done by adding each reagent to 1.5 mL of persulfate in vials and subjecting them to a boiling water bath for one hour and then analyzed.

Everything we tested, with the exception of the muffled magnesium oxide, contributed a relatively low blank. Interestingly, the neat magnesium oxide (not muffled) had a much lower blank than the muffled MgO, despite the fact that we muffled the reagent to volatilize any associated NH_4^+ . It was also noticed that the vial caps contributed significant

Component	Mean Blank (μM)	Standard Deviation
Sulfuric Acid	1.36	1.29
Milli Q	-0.41	0.21
Teflon Packet	1.74	0.19
Persulfate	0.73	0.04
Teflon Filter	2.63	0.77
GF/F	1.91	1.54
Muffled MgO	53.94	20.08
Neat MgO	1.25	0.10

**Persulfate representative of sodium hydroxide blank*

Figure 3. Original component, its mean blank contribution and the standard deviation between samples.

blanks occasionally. To avoid this, caps were changed to screw top septa caps with no glue. After these changes were made, blank concentration was found to be less than $10 \mu\text{M}$ and in most instances to be less than $5 \mu\text{M}$.

Samples ran with the original method were also found to not achieve complete diffusion into packets. Magnesium oxide was increasing the water sample pH~8, however ammonium does not completely convert to ammonia until a pH~9.7. This discrepancy may be because we were measuring fresh waters while the method was targeting seawater. Sodium hydroxide was substituted for MgO, increasing the sample pH to ~13, more than adequate for conversion of ammonium to ammonia. Sodium hydroxide from the persulfate blank in figure 4 was shown to have a small blank contribution.

It was also determined that the Teflon filters used in the original method plan were not solely gas permeable. This was determined by a 6-day diffusion method test in which both the Teflon filters and Teflon tape were tested for their ability to trap ammonium. It was observed that the Teflon tape trapped ammonium more sufficiently than the Teflon filters.

While both filter and tape packets show an increase in concentration with time, the Teflon tape trapped ammonium more effectively than the Teflon filters. We inferred that the filters, with pore sizes of $5 \mu\text{m}$, were allowing water to diffuse across their membrane. The non-linear relationship in figure 3 suggests that there was not complete recovery of ammonium in the Teflon tape packets after the six days on a shaker table that the original method suggests. A time series experiment was run in order to determine optimal diffusion time. The time series of $50 \mu\text{M}$ standards shows that 10 days doesn't quite achieve complete recovery.

A separate concentration series was prepared in which samples were taken off at 10 days and at 14 days to see if better recovery could be attained. The experiment showed that at 14 days recovery is complete and is the optimal wait time for samples to diffuse.

After all method changes were implemented (except changing caps), a set of 14 day standard samples and 14 day WWTF samples were prepared as two concentration series in order to see if method adjustments were successful.

Figure 4. Actual [N] compared to the observed [N] for packets made of teflon filters.

Figure 5. Actual [N] compared to the observed [N] for packets made of Teflon tape.

Figure 6. A 10-day time series with 50 μM standards.

Both sets of samples were relatively linear with acceptable R^2 values; both had a high blank possibly attributed to the blank that the caps were giving. Then these samples were measured using the denitrifier method to determine their $\delta^{15}\text{N}$ values on an isotope ratio mass spectrometer (figures 9 and 10). Both close in on a value as the blank percentage decreases, indicating that method adjustments made were successful (Accepted value for standard $\text{N}_2=20.4$). Mean for the N_2 Standard Series and the WWTF Sample Series were 17.07 ± 3.70 and 14.85 ± 2.05 respectively. However, with blank percentages so low, all variability cannot be blamed on the blank alone. Variability could also have been caused by human error while injecting samples into media for analysis. Another possible reason is that the blank could vary greatly between samples due to the fact that the blank from the caps is never consistent.

Another set of 14 day standard samples as well as a 14 day WWTF sample set were prepared using different containers

with septa caps (12 mL containers). Again an acceptably linear trend is shown in both series, which had a much smaller blank of $1.5 \mu\text{M}$ (figures 11 and 12). These samples were also analyzed by GCIRMS for their $\delta^{15}\text{N}$ values as shown in figures 13 and 14. (Accepted value for standard $\text{N}_1=0.4$). Mean for the N_1 Standard Series and the WWTF Sample Series were 1.04 ± 2.99 and 12.9 ± 2.86 respectively. Again the variability in the $\delta^{15}\text{N}$ for each series could be due to differences in blanks between samples or possible human error while injecting samples into media for analysis.

4. Discussion

Changes made in the method now ensure that complete recovery of ammonia and low blanks can both be achieved. With these key issues resolved, the modified method can be used to determine the isotopic composition of ammonium from anthropogenic nutrient inputs in Narragansett Bay, RI.

Figure 7. Shows [N] from a standard concentration series.

Figure 8. [N] from a WWTF sample concentration series.

Figure 9. $\delta^{15}\text{N}$ from a standard concentration series

Wastewater Treatment Facilities (WWTFs) are the largest anthropogenic source of nitrogen in Narragansett Bay watershed, and as such they have the potential to set the isotopic composition of the bay's nitrogen budget. Most of the WWTF in the watershed participate in biological nitrogen removal in two steps: nitrification, which converts

ammonium to nitrate and then denitrification, which converts nitrate to nitrogen gas that can be released to the atmosphere (EPA 2004). Because these processes are biological, there is a fractionation associated with them that changes the isotopic composition and we can compare it to the isotopic composition of the bay to see how much of an affect the

Figure 10. $\delta^{15}\text{N}$ from a WWTF sample concentration series.

Figure 11. [N] from a standard concentration series using septacaps.

Figure 12. [N] from a WWTF sample concentration series using septacaps.

discharge water has on setting the isotopic composition of the bay.

Previous studies show that the nitrate portion of WWTF discharge water has an isotopic composition of between 12‰ and 16‰ while Narragansett Bay estuary has a much broader

$\delta^{15}\text{N}$ vs % blank N1 Standard Series

Figure 13. $\delta^{15}\text{N}$ from a standard concentration series using septacaps.

$\delta^{15}\text{N}$ vs % blank WWTF Sample Series

Figure 14. $\delta^{15}\text{N}$ from a WWTF sample concentration series using septacaps.

range of 6‰ to 16‰ (Schmidt et al.). If the estuary's isotopic composition is completely controlled by the nitrate discharge from WWTFs, the range would be the same. There are two general possibilities for the lower $\delta^{15}\text{N}$ values that are observed in the estuary. One is that the anthropogenic ammonium input from WWTFs to NBW has a much lower $\delta^{15}\text{N}$ than the nitrate. The other possibility is that biological, chemical, and physical processes in the ecosystem itself are changing the isotopic composition of the bay due to fractionation. With an accurate modified method completed, finding the $\delta^{15}\text{N}$ of ammonium from WWTF discharge will be the next step in determining the sources of the bay's isotopic composition. After the $\delta^{15}\text{N}$ of ammonium from WWTFs is determined, the dissolved inorganic nitrogen budget input to Narragansett Bay from WWTFs will be completed. If there is still a discrepancy in the range of $\delta^{15}\text{N}$ in the bay as compared to the $\delta^{15}\text{N}$ input from WWTFs, biological activity in the bay can be examined in order to see how prevalent they are in changing the isotopic composition.

Eventually a more holistic understanding of the nitrogen cycle in Narragansett Bay watershed will be achieved.

5. Conclusion

Throughout this study the diffusion method of Holmes et al. was tested in order to find ways to diminish blanks and improve recovery. By eliminating magnesium oxide, increasing diffusion time to 14 days, and making Teflon packets out of Teflon tape, the data suggests that we have improved the method to avoid artificial fractionation. With this modified method, the $\delta^{15}\text{N}$ of ammonium output from WWTFs in Narragansett Bay watershed can be examined to infer how important ammonium is in setting the isotopic composition of the bay. This will allow for a complete knowledge of DIN input from wastewater treatment facilities and also allow the examination of in bay processes such as nitrogen fixation, nitrification, and denitrification for their contributions to the $\delta^{15}\text{N}$ observed in the bay. This method

can be adapted to examine other estuaries to gain a holistic understanding of the nitrogen cycle in each particular area.

Figure 15. All 28 WWTFs in NBW.

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Record of the Earliest West Antarctic Ice Sheet Beneath Ross Sea?

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Abstract. A West Antarctic Ice Sheet from earliest Oligocene time has been modeled with Global Climate Models that incorporated paleotopography restored for rift-related subsidence and glacial erosion. Although isotopic data support an Antarctic ice volume exceeding today's, stratigraphic evidence for the ice sheet advance has not been recognized beneath Ross Sea. We interpret a pre-~30 Ma 400 km-long by 50 km across erosional trough on seismic reflection profiles across Central Trough, located in western Ross Sea. Processes that can explain such a deep trough are then explored. In this preliminary study a tilted sub-aerially and wave-eroded basement unconformity is used to approximate post-~30 Ma vertical motions. One possible hypothesis is that the trough is evidence for advance of the earliest West Antarctic Ice Sheet onto the continental shelf at ~34 Ma.

1. Introduction

Oxygen and calcium isotopic data suggest the existence of ice with volume similar to today's Antarctic ice sheet at the onset of the Oligocene (~34 Ma). The positive shift of $\delta^{18}\text{O}$ directly after the Eocene indicates a large increase in ice volume and a decrease in ocean temperature as oxygen-16 is evaporated out of ocean water and trapped in glaciers (Pekar et al 2007). CO_2 levels were also decreasing during the mid-Cenozoic. Global Climate Models (GCMs) simulated the growth of an Antarctic ice sheet after removing the load of current ice and allowing isostatic rebound of crust (DeConto and Pollard, 2003). These rebounded elevations/depths produced a mostly marine archipelago for West Antarctica, and the GCMs were only able to produce an Eastern Antarctic Ice Sheet and not a West Antarctic Ice Sheet (WAIS). This work neglected crustal thinning due to hundreds of kilometers of extension across the Western Antarctic Rift System between 104 Ma and ~26 Ma (Wilson and Luyendyk, 2009). The resulting thin crust (Trey et al 1999) floats low on the mantle, and continues to subside due to thermal contraction and sediment loading. The subsidence and glacial erosion that had not been considered in the DeConto and Pollard (2003) study were restored to the continent (Wilson and Luyendyk, 2009; Wilson et al., 2012). The result of these added processes and conditions was that the paleotopography of Antarctica was much higher and the subaerial continent was much larger at the onset of the Oligocene than we see today. These increased land elevations allow for a larger than present-day WAIS to now develop on GCMs (Wilson et al 2012, 2013). Levels slightly lower than 750 ppm of CO_2 were used to simulate conditions at that time.

The sub-bottom of Ross Sea is comprised of sedimentary basins separated by basement ridges. From east to west these are Eastern Basin, Central High, Central Trough, Coulman High, and Victoria Land Basin (Figures 1, 2). Central Trough is located in Western Ross Sea and, north of the current Ross Ice Shelf edge, is about 400 km-long. This paper examines possible evidence that an ice stream from the WAIS eroded deep Central Trough at the onset of the Oligocene (Figure 2). With access to over 20,000 km of seismic reflection profiles collected by many countries and made available through the Seismic Data Library System, seismic stratigraphic horizons have been interpreted within and around the Central Trough area (Figure 2).

2. Methods and Data

Seismic reflection lines were obtained from the Antarctic Seismic Data Library System and loaded into capable industry software – both Opendtect and Kingdom Suite. The majority of these lines are multichannel seismic lines with lower resolution but deeper penetration beneath the seafloor (Figure 2). Using stratigraphy correlated across Central High to DSDP sites 270 and 272, and middle Miocene strata cored in the Central Trough at DSDP 273 (Hayes and Frakes 1975; ANTOSTRAT 1995), stratigraphic horizons were interpreted across and along Central Trough. Important horizons interpreted for this study include an unconformity at the top of high amplitude discontinuous reflections that we interpret as syn-rift, as well as a ~30 Ma horizon (RSU6), and a ~25 Ma horizon (Figure 3). Our top syn-rift horizon is similar to acoustic basement interpreted by ANTOSTRAT (1995), and our RSU6 is the same as ANTOSTRAT's. The RSU horizons of ANTOSTRAT

Figure 1. Location map of Ross Sea. Going from east to west: Eastern Basin (EB), Central High, Central Trough (CT), Coulman High, and Victoria Land Basin (VLB). Central Trough is the focus of this study. Figure from Decesari et al (2007).

(1995) are unconformities, as are our ~25 Ma horizon and top syn-rift. All interpreting was done in 3-dimensions on 2-dimensional data and “ties” of reflections from rock interfaces were made at intersections between profiles (“loop tying”) strategies. This strategy involves beginning an interpretation on one seismic line and carrying it over to another line where they intersect, allowing for interpretation to cover many directions and seismic stratigraphy to be consistent. Continuous loop tying allows for 3-dimensional horizons to be gridded as surfaces.

3. Results

We distinguished the acoustic basement of ANTOSTRAT (1995) as the top of rock basement lacking primary reflections, and the top of discontinuous, high amplitude reflections. We interpret the latter to be top of syn-rift sedimentary rocks, and the former is known to be metamorphic rock at DSDP Site 270 (Figure 2). The top rock basement on Central High is planar and very smooth, dipping away from an antiform crest into both Eastern Basin and Central Trough (Sorlien et al. 2012, 2014). Remnants of such a surface are also present on Coulman High (Figures 4-6). An erosional trough is deeply cut into the reflective syn-rift strata flanking the planar rock basement surface. This is deep Central Trough.

There is a ~3 kilometer relief of the unconformity along the axis of the trough. Two closed basins below 6 km are paired with ~3 km-deep sills downflow (north) (Figure 7). These basin-sill pairs represent important current reverse gradients. Not only are the basins very wide, they also have a distinct U-shape that continues northward throughout Central Trough. The trough transitions to a narrow, more V-shape north of the approximate location of the paleoshelf-break. Certain multichannel seismic reflection (MCS) profiles clearly image truncated reflections with vertical extent of

over one second two-way time. Additionally, possible numerous faults characteristic of extreme extension present below the unconformity do not significantly offset it. A few minor faults cut the unconformity and are present in the trough fill.

4. Discussion

We have documented a deep erosional trough that pre-dates ~30 Ma. The lack of major faulting of the erosional surface and the trough fill suggests that the final erosion post-dates rifting. Mid-Cenozoic rifting associated with Adare Trough may be limited to west of Central Trough (Davey et al. 2006, Granot et al. 2013). Rifting of Central Trough has been proposed to relate to 80-55 Ma extension (Cande and Stock, 2004; Wilson and Luyendyk, 2009). Therefore, erosion likely occurred sometime between 55 Ma and 30 Ma at depths that today, after differential subsidence, locally exceeds 6 km. We discuss the possible mechanisms for this erosion. Extensional grabens, river systems, submarine canyons, and ice stream erosion are possible hypotheses.

4.1. Differential Subsidence

At the Eocene-Oligocene boundary, Central High was a >200 km-wide island or subaerial ridge composed of rock “basement”, known to be metamorphic rock at DSDP site 270 (Sorlien et al. 2012, 2014). Subsidence below sea-level and subsequent shallow marine sediment aggradation is interpreted to have buried the metamorphic basement rock by 25 Ma (Figures 4, 5, 6). Seismic reflection profiles image smooth tilted basement resulting from differential subsidence related to rifting (post-rift thermal contraction) and sediment load. We have made assumptions on the

Figure 2. Left figure: Basemap of all seismic lines used in this study. Most of the lines are multichannel seismic reflection (MCS) while some of the lines are single channel seismic reflection (SCS). The blue dotted box is the area of the figure on the right, comprising of Central Trough and surrounding areas (Central High and Coulman High). Right figure: This is the gridded syn-rift horizon in two way time. The MCS profiles from figures 4-7 are located as A-A' through E-E'.

formation of the imaged smooth basement unconformity (top syn-rift). The first is that this basement unconformity formed through subaerial erosion and finally by wave erosion. The second assumption is that Oligocene-early Miocene sediment supply was sufficient enough to aggrade above the rock basement unconformity soon after it differentially subsided below low-stand sea-level (Sorlien et al. 2012, 2014). The present depth of the rock basement and the age of the immediately overlying sedimentary rock can be used to calculate subsidence rates for locations on Central High. These variable subsidence rates define tilt rates.

4.2. Sedimentation Rates

The sedimentation rate between the 30 Ma horizon (RSU6) and the 25 Ma horizon is known (Sorlien et al. 2012, Sorlien et al. 2014). The package of sediment between top syn-rift and RSU6 appears to be the same thickness on many seismic lines that cross cut the troughs. The arrows between top syn-rift, 30 Ma, and 25 Ma on Figure 5 are the same size. If a sedimentation rate between top syn-rift and RSU6 is similar to the rate for the interval above, it would make sense for the horizon to have been eroded at ~34 Ma and not 55 Ma.

4.3. Reverse Gradient

The gridded top syn-rift horizon shows closed basins in Central Trough as well as a current reverse gradient for northward flow (toward the deep ocean). The reverse gradients seen today include all differential subsidence afterwards. The tilting off of the Highs suggests that part of the reverse gradient was present at 34 Ma for at least the northern basin-sill pair. The differential subsidence pattern, but not magnitude, should be similar between 55 Ma and 34 Ma. This reverse gradient is an unlikely path for a river system or submarine canyon, as they tend to create steady gradients downward and toward the ocean. For these explanations of erosion to be tenable, restoration of differential subsidence along the trough axis as well as across it should produce a down-to-north slope. A more likely cause would be glacial or ice erosion, as discussed in the glacial/ice erosion paragraph below.

Differential subsidence, sedimentation rates, and the reverse gradient of the troughs within Central Trough allow for discussion between possibilities that may have caused the deep erosional surface into the reflective strata.

4.4. Extensional Grabens

Total extension to the north of Central Trough has been proposed to be ~50 km (Cande and Stock, 2004) between 80-55 Ma or between 130-200 km between 68-46 Ma (Wilson and Luyendyk, 2009). Evidence of rifting can be seen below the top syn-rift horizon. The trough fill is cut only by minor faults; extension across these faults in the lower trough fill may only represent a km or two of extension. Indeed, rift faults continued minor activity through late Oligocene time on Southern Coulman High (Decesari et al, 2007b; C. Sorlien unpublished revised interpretations in IODP data base). This lack of significant extension of the unconformity or trough fill is interpreted to

be due to the latest erosional surface occurring after major rifting ceased (55 Ma). The erosional surface occupies the deepest part of the basins. If the trough is an extensional graben rather than eroded through the synrift sediment of an extensional basin(s), there would be faulting of its base and tilting of the fill. Furthermore, when viewed with no vertical exaggeration at reasonable interval velocities for the trough fill, the trough flanks are gently sloping and are not similar to low-angle normal faults offshore California (e.g., Sorlien et al, 2013a, b). From this, an extensional graben explanation for the trough does not seem probable. It does, however, occupy an area of highly extended reflective strata, which could be non-marine.

4.5. U-Shaped Troughs, River Systems, Submarine Canyons

Because the trough fill is cut only by minor faults, and the erosional top syn-rift horizon cuts through the reflective strata, a river system through Central Trough would have had to form soon after the cessation of rifting. The troughs additionally are U-shaped. Typically, river systems and submarine canyons form V-shaped profiles in cross section. Both types of systems do not have reverse gradients downflow: water, landslides, and turbidites all flow downhill. The transition from a U-shaped trough at D-D' (Figure 6) to a V-shaped at and north of E-E' (Figure 7) may show that the distal limit of the proposed ice stream was at the paleo-shelf break. Our hypothesis for glacial erosion involves huge volumes of sediment, but there is a pathway to the slope and continental rise via the V-shaped narrow canyon.

Figure 3. Stratigraphy column of horizons mapped throughout the Ross Sea. The left side shows the top syn-rift as a violet horizon (wavy line, ~34 Ma). The 30 Ma year old horizon (RSU6) is in pink. And the 25 Ma horizon (mid-270) is in blue. Figure modified from Levy et al. (2012).

Figure 4. Here the top syn-rift horizon cuts deep into the reflective strata. We see sediment aggradation that buried metamorphic basement by ~25 Ma. A-A' is located on Figure 2.

Figure 5. Here planar and smooth basement of Central High is dipping away from an antiform crest farther east. Note the arrow between top syn-rift and RSU6 compared to the identical sized arrow between RSU6 and 25 Ma. If we assume a steady sedimentation rate between these two intervals, it would make sense for the syn-rift horizon to have been eroded at ~34 Ma and not 55 Ma. The wide (>50 km) trough is U-shaped, consistent with glacial erosion. The trough here is much shallower than A-A' on Figure 4. This represents the reverse gradient is observed downflow (northward). Image created using Kingdom Suite software.

4.6. Glacial and Ice Erosion

Ice streams behave differently depending on the surface below the stream. Hard rock creates a stiff surface for ice sheets and they tend not to move as freely. Sediment surfaces create permissive environments for ice streams to form (Tulaczyk, 1998). Bart and DeSantis (2012) recognized that ice streams form in topographic/bathymetric lows and erode troughs there, while erosion is nominal where ice streams are absent on topographic highs. This could be a reason for the erosional surfaces within Central Trough to be ice stream erosional surfaces. Wide U-shaped troughs are signs of glacially eroded surfaces. The top syn-rift erosional surface was compared to the seafloor surface

of the known glacially eroded Laurentian Channel between Nova Scotia and Newfoundland (Duchesne et al. 2010). A topographic profile across the Laurentian Channel was provided by Marie Helen Cormier, using GeoMapApp, and compared to a profile we drew across one of our closed top synrift basins. The width was almost the same, and the shape was also very similar if the Laurentian trough was displayed with ten times more vertical exaggeration. A better comparison would be to the eroded base of this or other troughs, rather than the partly-filled sea floor (Figure 8).

Figure 6. The planar rock basement platform that dips off of Central High is clearly. Space created from the horizontal axis rotation (tilting) off of the highs is seen in the trough here. This profile crosses the deep part of the northernmost basin within Central Trough, 60 km south of a much shallower sill. This is further evidence of the reverse gradient and isolated basins we see in Central Trough. Image created using Kingdom Suite software.

Figure 7. With a view to the northeast, the top syn-rift gridded horizon in this figure shows isolated basins and reverse gradient downflow (toward the ocean). Submarine canyons and river systems would not show a gradient like this one – it would be a steady downward gradient as they flow toward the ocean. All multichannel lines from Figure 2 were interpreted and used in this grid. If ice stream erosion did indeed form these basins, the southernmost basin in Central Trough (seen between A-A' and B-B') might have, in addition to flowing northward, also traveled northwest toward letter C (marking seismic line C-C'). Image created using Kingdom Suite software.

5. Conclusion

We interpret that the deep, U-shaped, and wide basins within Central Trough are erosional surfaces. Furthermore,

the erosional surfaces must have last eroded after rifting ended 55 Ma. Filling of the trough can be accomplished between 34 Ma and 30 Ma if sedimentation rates were similar to the known rates between 30 and 25 Ma. The

Figure 8. Here the top syn-rift erosional surface (D-D') was compared to the seafloor surface of glacially eroded Laurentian Channel (F-F'). The widths of both troughs are almost the same. Note that the Laurentian trough is displayed at 10x more vertical exaggeration than the top syn-rift horizon. Image provided by Milene Cormier using GeoMapApp, also refer to Duchesne et al. (2010)

main viable alternate hypothesis is that a river or submarine canyon system last eroded the trough soon after cessation of rifting, not likely to be older than 55 Ma. For that hypothesis to remain viable, combined tilt, modeling, backstripping, and thermal modeling would have to reproduce large differential subsidence along the trough axis sufficient to remove the reverse gradient. This reverse gradient is currently nearly 1 second two-way time (could be 1.5 km) across only 60 km from D-D' (Figure 6) to the next seismic profile seen to the north (Figure 7). If our earliest Oligocene ice stream erosion hypothesis stands up to scrutiny and modeling, then the extent and volume of the West Antarctic Ice Sheet at that time may have been even larger than recently modeled.

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Sea Surface Temperature Response to Tropical Cyclones

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Abstract. The primary goal of this project is to investigate the spatial structure and temporal evolution of the SST anomalies (SSTAs) associated with the passage of TCs, as well as their sensitivity to TC characteristics (including TC intensity and translation speed). Until now, the most thorough investigation of the amplitude of TC-induced SSTAs, the recovery of the SST after the TC passage, and their respective dependence on TC intensity and translation speed have been conducted using the satellite-derived Reynolds SST and TMI products. However, these products may not be very reliable in studying cold wakes after tropical cyclones because of the spatial and temporal averaging. The purpose of this study is to characterize the SST response to the TCs in a more comprehensive and systematic way based on analysis of more reliable SST data from several satellite data sources including AMSR and TMI. Our results show that the magnitude of the SSTA is dependent on both the translation speed and intensity of the tropical cyclones with slow moving category 1-2 storms producing the largest SSTA. The maximum SSTA tends to occur earlier in time for fast moving storms than slow moving storms. Consistent with previous studies, calculations show that the mean SSTA almost linearly correlates with the wind speed for TCs below category 3 intensity while for stronger TCs the SSTA levels off. Finally, the recovery time of TC generated SSTAs vary based on translation speed. For fast moving storms the recovery starts day two after storm passage and for slow moving storms recovery starts day three after storm passage.

1. Introduction

The strong winds associated with tropical cyclones (TCs) often generate a significant cooling of the sea surface during the TC passage. A resultant cold wake is left behind, which is captured by both satellite and in situ measurements of sea surface temperature. The study of cold wakes is important due to their impacts on weather and climate.

The TC induced Sea Surface Temperature Anomaly (SSTA) may hinder the development of the TC due to reduced energy supply, which is known as the negative feedback process (e.g., Bender et al. 1993). The degree to which TC development is inhibited depends on the magnitude of the SSTA and translation speed of the TC (Lin et al. 2009; Mei et al. 2012). This negative feedback process is important for TC intensity prediction (e.g., Bender and Ginis 2000). The TC induced cold wake may also affect the development of subsequent TCs depending on amplitude and persistence. Often the SST within a cold wake is reduced to a temperature of below 26°C, or the minimum temperature required for optimum TC development, therefore preventing subsequent tropical cyclones.

Previous studies on TC-induced SSTAs have primarily focused on the amplitude of cooling and spatial structure. Results show the amount of SST cooling varies significantly in different case studies. Composite techniques have recently been used to examine the average SST response to TCs. This technique enhances the signal to noise ratio and leads to more meaningful conclusions (Mei and Pasquero, 2012). Hart et al. (2007) were the first to use a composite technique to study the SST response averaged over a TC-centered 5° X 5° box and the subsequent SST recovery. They found the amplitude of cooling depends on TC intensity and cooling persists for 35-40 days. Shenkel and Hart (2010, 2011) consolidated these results. However, the Reynold's SST data used in these studies may not be the most accurate because it is unable to capture the signal

during and immediately after storm passage due to the masking effect of clouds and heavy rain on infrared satellites. Lloyd and Vecchi (2011) repeated this calculation using SST data from the Tropical Rain Measuring Mission Microwave Imager (TMI). They found a greater SSTA and shorter recovery period for TCs of same intensity compared to Hart et al. Until now the most thorough investigation of the spatial structure and temporal evolution was completed by Mei and Pasquero (2012). Mei and Pasquero show many interesting features, including the distribution of maximum cooling relative to the storm center and recovery time of the SSTA after storm passage. Mei and Pasquero use the National Hurricane Center Best Track Data set to find the location of the storm every 6 hours. Then for each 6 hour location they define a gridded domain with spatial resolution of 10 km by 10 km focused about the storm center with size 2500 km in the direction perpendicular to the track and 200 km in the direction parallel to the track. Daily TMI SST data are then interpolated onto these grids, producing a spatial map for each TC location. These maps are then composited based on date with respect to storm passage.

The purpose of this study is to characterize the SST response to TCs in a more comprehensive and systematic way based on composite analysis of more reliable satellite-derived SST data. After describing the data and methods used (section 2), we describe the spatial structure of TC-induced SSTAs, including the local maximum amplitude and the respective dependence on TC intensity, translation speed and mixed layer depth. Finally, we analyze the recovery of the SSTA in the days following the storm.

2. Methodology

This study focuses on the SST anomaly (SSTA) within the "cold wake" after the hurricane passage as well as the storm parameters that this SSTA depends on. The storm coordinates, maximum wind speed, translation speed, and radius of the maximum wind speed come from National

Figure 1. The gray shaded region in the above figure represents the gridded domain. The dotted line is the track of a tropical cyclone with each dot representing the location of the storm center at 6 hour intervals. A gridded domain is constructed for each dot along the TC track with size 600km in either direction perpendicular to the track and 100 km in either direction parallel to the track. (Adopted from Mei and Pasquero (2012)).

Hurricane Center's (NHC's) Best Track files which contain information every six hours. A gridded domain is then constructed to analyze the SST variability perpendicular to the storm track at each TC location. The domain extends 600 kilometers in either direction perpendicular to the storm track and 100 km in either direction parallel to the storm track (Fig. 1). A blend of TMI and AMSR-E satellite-derived SST data are interpolated on to these gridded domains, producing a spatial map of SST at each TC location. The SSTA is then calculated for each TC location with respect to the mean SST averaged over the 14 days prior to storm passage. Composite SSTAs are produced for each TC location and binned according to maximum wind speed and translation speed. This analysis is done for 133 storms in the Pacific Ocean (Fig. 2) and 92 storms in the Atlantic Ocean (Fig. 3) from 2004 to 2008.

2.1 Tropical cyclone data

The TC data are obtained from the National Hurricane Center (www.nhc.noaa.gov/data/#hurdat) and Joint Typhoon Warning Center archives. These archives contain TC track information based on a post-storm analysis of each tropical cyclone and make use of all available observations, including those that may not have been available in real time. The datasets known as Atlantic HurDat2 and NE/NC Pacific HurDat2 best tracks have text format with information every 6 hours on the location, maximum winds, radius of maximum winds, and translation speed of all known tropical cyclones and subtropical cyclones in the Atlantic and NE/NC Pacific basins (nhcwebmaster).

2.2 Satellite Data

In this study we use TMI and AMSR-E satellite SST observations. TMI stands for Tropical Rainfall Measuring Mission's (TRMM) Microwave Imager. It is a multi-channel, dual polarized, conical scanning passive microwave radiometer designed to measure rain rates, sea surface temperature, ocean surface wind speed, columnar

water vapor, and cloud liquid water over a wide swath under the TRMM satellite. The semi-equatorial (± 35 degree) orbit of TRMM allows for TMI to sample the surface at all times of day as opposed to the twice-per-day sampling of other microwave radiometers in near-polar orbits. All images produced by TMI cover a global region extending from 40S to 40N at a pixel resolution of 0.25 degree (~ 25 km). SST can be measured through clouds, which are nearly transparent at 10.7 GHz. This is a distinct advantage over the traditional infrared (IR) SST observations that require a cloud-free field of view. However, microwave retrievals are sensitive to sea-surface roughness, while the IR retrievals are not. Ocean areas with persistent cloud coverage are viewed on a daily basis with TMI. Gridded data are organized according to observation date. All dates and times are Coordinated Universal Time (UTC). TMI data has been available since December 1997 and has a daily temporal resolution including ascending and descending orbit segments. The daily average value is obtained by averaging the ascending and descending passes or assigning the available one if only one pass is available. Missing values are left unfilled (Remote Sensing Systems).

AMSR-E stands for Advanced Microwave Scanning Radiometer for EOS. It is a twelve-channel, six-frequency, passive-microwave radiometer system. Vertically and horizontally polarized measurements are taken at all channels. A key feature of these AMSR instruments is the ability to see through clouds, thereby providing an uninterrupted view of ocean SST measurements (Graham). TMI and AMSR-E Level 2 data provides about 14 full orbits (or swaths) worth of data every day. That doesn't guarantee it will be in the domain of the storm or even calm enough to read an accurate SST. The data has similar level 2 resolutions, so we shouldn't be biasing towards one satellite. The level 2 TMI and AMSR-E satellite data used in this project are archived on Peter Cornillon's disk storage, *satdat3*, at the University of Rhode Island Graduate School of Oceanography.

2.3 Creating a SST Map

TMI and AMSR-E level 2 data provide about 14 orbits or swaths worth of data every day. That does not guarantee the satellite swath will be in the domain of the storm track or the sea state conditions calm enough to read an accurate SST. The first step in creating a SST map is to determine the position of the SST domain. The domain is centered at the selected TC center location and extends 600 kilometers in either direction perpendicular to the storm track and 100 km in either direction parallel to the storm track. The grid points or bins are spaced at 10 km x 10 km resolution. The temporal range of SST data that is set for each domain is from 14 days prior to TC's arrival to the selected location until 14 days after. For each day within the temporal range defined above, the difference between that day and the date the storm passes each TC location is calculated. This difference can range from -14 to 14 because the temporal range is from 14 days prior to TC's arrival to a selected location until 14 days after. Each day is then categorized as background SST, immediate SST, or post storm SST depending upon whether the difference is negative, zero, or positive. The TC centered gridded domain for that day is also identified as background, immediate, or post storm.

Figure 2. Storm tracks in the Pacific Ocean analyzed in this study.

Figure 3. Storm tracks in the Atlantic Ocean analyzed in this study.

Next, both the TMI and AMSR-E data sets are searched day by day for swaths that occur within the temporal range and crossing the gridded domain. Whenever there is satellite data that occurs within the temporal range and crossing the gridded domain the SST is added to a grid point or bin, within the appropriate category relative to storm passage (background, immediate, or post storm). A counter is incremented to determine the number of swaths of satellite data in each bin because some bins contain multiple swaths. When all the satellite data for each day is processed the total SST in each bin is divided by the total number of swaths in that bin yielding an average SST spatial map (Fig. 4).

2.4 Calculating the SSTA

In order to calculate the sea-surface temperature anomaly the SST on the day following storm passage (post storm SST) is compared to the background SST which is obtained by averaging the SST over the 14 days prior to storm

passage. The difference between the two is the SSTA. An example of this calculation is shown in Fig. 5.

2.5 Producing Composite SSTAs

To better characterize the mean amplitude of the SSTAs and to directly compare with previous studies, we also calculate composite SSTAs by combining together SSTAs at individual storm locations in response to the TC passage. Composite SSTAs are produced by binning the SSTAs according to maximum wind speed and translation speed and then averaging the individual SSTAs to get the mean SSTA for each bin. Storms were binned into 3 categories of the maximum wind speed: weak (<33 m/s), Cat 1-2 (33 to 49 m/s), and Cat 3-5 (50 + m/s). Storms were also binned into 3 categories of the translation speeds: slow moving (<3.5 m/s), average speed (3.5 to 7 m/s), and fast moving (>7 m/s). The recovery of the SSTA in the days following the storm passage is also analyzed by comparing composite SSTAs. An example of the composite SSTAs for Cat 1-2 storms at days 1, 2 and 3 after the storm passage is shown in

Figure 4. Spatial map of SST at a single TC location produced by interpolating a daily blend of TMI and AMSR-E satellite-derived SST data onto a gridded domain.

Fig. 6.

To better identify the location of the local maximum cooling we also calculate the cross-track profiles of the SSTAs by averaging the SSTAs in each gridded domain in the along-track track direction. An example of such SSTA cross-track profile is shown in Fig. 7.

3. Results and Discussion

The spatial pattern of the composited SSTA generated by tropical cyclones shows probably the most well-known feature of the rightward-shifted cold wake in the Northern Hemisphere (Fig. 6). Next we examine in detail the local

Figure 5. Background SST (top panel), SST one day following the storm passage (middle panel) and SSTA (bottom panel) at a single TC location with represents the difference between the top and middle panels.

SSTA for Average Speed CAT 1-2 Storms: Day 1

Figure 6. Composite SSTAs for Cat 1-2 storms with the average translation speeds on day 1, 2, and 3 after the storm passage.

maximum amplitude of the SSTA, its location with respect to the track, the width of the anomaly, and their respective dependencies. The cross-track profiles of the SSTA in response to TCs of different intensities shown in Fig. 7 shows that stronger TCs generate more intense sea surface cooling in both hemispheres. For example, the average local maximum cooling produced by Cat 3–5 hurricanes is 2.4°C . This value is a little smaller than 2.68°C found by Mei and Pasquero (2013, Fig 8). Cat 1-2 storms produced maximum SSTA of 1.8°C , which is again smaller than 2.1°C shown in Fig 8.

Fig. 9 shows the dependence of SSTAs on the translation speed and maximum wind speed. The y-axis represents the SSTA in degrees Celsius and the x-axis represents the distance across the tropical cyclone track normalized by the radius of maximum winds. The reason for analyzing SSTA in terms of radius of maximum wind is to assess the location of the maximum SSTA regardless of the size of the storm. The largest SSTA occurs for slow moving Cat 1-2 storms in the Atlantic Ocean. In the wake of these storms the SST is on average almost 4°C colder than prior to the storm. It may be expected that Cat 3-5 storms would produce the largest SSTA due to them having stronger winds than Cat 1-2 storms thus producing more mixing, but these storms produce a SSTA of only slightly more than 2°C . It is fully unclear why Cat 1-2 storms produce larger SSTAs than these Cat 3-5 storms. However, one reason may be the negative feedback process that takes place in tropical

cyclones. The negative feedback process is when development of the TC is dampened by the TC-induced sea-surface temperature anomaly. Storms require a minimum SST of 26°C for development and the temperatures are often cooled to values below this during TC passage. Thus storms that produce more cooling could inhibit themselves from being able to strengthen (e.g., Bender et al. 1993; Schade and Emanuel 1999; Schade 2000; Cione and Uhlhorn 2003). This negative feedback process has been proven to be important in TC intensity prediction (e.g., Bender and Ginis 2000).

Another reason Cat 1-2 storms may produce a larger SSTA than cat 3-5 storms is due to errors in the satellite-derived SST data. Microwave retrievals of SST are sensitive to sea-surface roughness and high winds. Cat 3-5 storms produce higher winds and a rougher sea-surface than cat 1-2 storms, thus may affect the accuracy of the SST measurements. On the other hand, for slow moving storms the errors may occur because the storm is still close enough to produce rough seas and high winds.

Cat 3-5 storms with the average and fast translation speeds produce the largest SSTAs in the Pacific Ocean, which is expected because Cat 3-5 storms produce more wind driven mixing than Cat 1-2 or weak storms. The magnitude of the SST cooling for the average and fast moving storm is smaller than for the slower moving storms. Therefore the negative feedback process is reduced for these storms allowing them to reach higher intensities.

Figure 7. TC-induced SSTA as a function of the distance across the TC track on the day after the cyclone

In general, larger SSTAs occur in the Pacific Ocean than in the Atlantic Ocean. This difference in SSTA may be due to the differences in the mixed layer depths in the Atlantic Ocean than in the western Pacific Ocean (Fig. 10). The spatial variations in ocean mixed layer depth have a significant role in the SST response. Shallower mixed layer depths allow for greater SST cooling (Mao et al. 2000). Figure 10 shows that the mixed layer depth in the areas where the most storms occur is generally deeper in the Atlantic Ocean than in the western Pacific Ocean. It is more difficult for a TC to mix the warm water within the deep mixed layer with the cooler waters below. In contrast, it is easier for a TC to mix the warm waters within the shallow mixed layer with the cooler waters below.

After the storm passage the SSTA begins to gradually recover with each day after the storm. Figure 11 shows this gradual recovery well during the three days after storm passage. On day one after storm passage the SSTA is the strongest, it gets weaker on day 2 and even weaker on day 3. The pattern of this recovery is very similar in the Atlantic and Pacific Ocean basins. The results indicate that the occurrence of the maximum SSTA depends on translation speed. For fast moving storms (Fig. 12 left) the maximum SSTA occurs on day one after storm passage and begins to recover on day two. However, for slow moving storms (Fig. 12 right) the maximum SSTA does not occur until day two after storm passage and begins to recover on day three.

Figure 8. TC-induced SSTA as a function of the distance across the TC track on the day after the cyclone passage for tropical cyclones of different intensities in the Northern Hemisphere (adopted from Mei and Pasquero (2013)).

Figure 9. Shows dependence on translation speed and intensity for the Pacific Ocean slow moving storms (top left), the Atlantic Ocean slow moving storms (top right), the Pacific Ocean average speed storms (middle left), the Atlantic Ocean average speed storms (middle right), the Pacific Ocean fast moving storms (bottom left), and the Atlantic Ocean fast moving storms (bottom right).

Figure 10. Mixed layer depth in the month of September derived from the GDEM monthly climatology. The boxed areas represent the areas where most storms occur.

Figure 11. The recovery of SSTAs on day 1, 2, and 3 after storm passage in the Pacific Ocean (left) and the Atlantic Ocean (right) for the average translation speed.

Figure 12. The recovery of SSTAs on day 1, 2, and 3 after storm passage in the Pacific Ocean for fast (left) and slow (right) moving storms.

4. Summary

This study focused on the decrease in the SST within the “cold wake” after hurricane passage as well as the storm parameters that this SSTA depends on based on analysis of data from several satellite data sources including AMSR-E and TMI. Composite analysis was used to obtain the mean features of SST response to TC passage. Composite SSTAs are produced by binning the SSTA at each TC location according to storm parameters such as wind speed and translation speed at that location then averaging the individual SSTAs to get the SSTA for each bin. The recovery of the SSTA in the days following the storm passage was also analyzed by comparing composite SSTAs. This analysis was done for 133 storms in the Pacific Ocean and 92 storms in the Atlantic Ocean from 2004 to 2008.

Results show the magnitude of SSTAs depends on maximum wind speed, translation speed, and mixed layer depth. The maximum SSTA tends to occur earlier in time for fast moving storms than slow moving storms. Also, the recovery of SSTAs after storm passage depends upon translation speed. For fast moving storms the recovery starts day two after storm passage and for slow moving storms recovery starts day three after storm passage. It is speculated that for slow moving storms the resultant SSTA is less accurate due to the storm being close enough to cause rough sea-surfaces and high wind which lessens the ability of microwave imaging satellites such as TMI and AMSR-E to make accurate measurements of SST.

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Spectral Analysis of Submesoscale Energy Cascades Using Subtropical North Atlantic Sea Surface Temperature Fields

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Abstract. Mixing parameterizations of current climate models could be improved by a better understanding of energy cascades in the submesoscale ocean (1 – 10 km). This study uses spectral analysis to compare energy cascades in two different datasets that resolve processes of about 1 km in scale. The first dataset consists of 20 years of in situ measurements from an acoustic Doppler current profiler (ADCP, measures temperature and velocity) and about 10 years of in situ data from a thermosalinograph (TSG, measures temperature and salinity) both mounted on the *Oleander*, a container vessel that makes weekly round-trips between Port Elizabeth, New Jersey and Hamilton, Bermuda. The second dataset consists of sea surface skin temperature fields obtained from the Visible-Infrared Imager-Radiometer Suite (VIIRS) mounted on NASA’s Soumi-NPP spacecraft. The slopes of the ADCP and TSG potential energy spectra are between -2.4 and -2.6, the similarity suggesting they represent the same physical processes. Because the TSG produces higher resolution data than the ADCP, the TSG energy spectrum better resolves processes at scales < 10 km. When separated by region, the TSG energy spectra have different slopes in three distinct regions along the *Oleander* track: on the continental shelf and in the Gulf Stream the slopes are about -2.7, and in the Sargasso Sea the slope is about -2.5. All slopes determined from the temperature structure functions for the same regions are between 1.0 and 1.3, with the Sargasso Sea slope being the shallowest of the four (the three separated regions and the entire *Oleander* track). In theory, the energy spectrum slope (n) and the structure function slope (p) should be related by $n = p + 1$ if the temperature field is homogeneous. The deviations from theory may result from failure of this assumption and/or from the contribution of multiple processes to the spectra, which are combined differently for structure functions than for energy spectra. Of interest here is that our estimates show consistent differences in slopes in the different regions. Comparisons were made between TSG and VIIRS temperature structure functions in order to determine if surface properties are consistent with in situ data. From VIIRS temperature structure functions calculated along the *Oleander* track, we find that the VIIRS structure functions are very sensitive to noise and spikes in the data, and that there is still much to be learned from this dataset.

1. Introduction

From a human perspective, the scales that the Earth’s oceans span can be mind boggling; from the tiny to the vast, interactions between biology, chemistry, and physics occur at all scales in the seas. But how can we attempt to understand what is going on? And if there is a piece missing in our knowledge of the oceans, how can we have confidence in the predictions we make about the future of our planet? Recently, the physics of the submesoscale ocean (1 – 10 km in scale) (University of Oxford Department of Physics 2012) has been one focus of investigation for oceanographers. Because current global ocean and climate models are unable to resolve physical processes at these scales, they rely on parameterizations (Cornillon and Fox-Kemper 2014). These parameterizations could be improved by better knowledge of how energy cascades through the submesoscale ocean. Unfortunately, our access to such scales is typically limited by the resolution of the large-scale datasets available. Therefore we must find ways to take advantage of the data we do have access to in order to learn about submesoscale physics and ultimately improve our models.

This study uses two datasets, in situ and satellite data, that resolve submesoscale processes (explained in detail in Section 2.1). Our in situ dataset comes from the container ship *MV Oleander*. This dataset was chosen because it gives good statistics, and contains temperature, salinity, and velocity data. NASA satellite data was chosen because it has global coverage. To investigate submesoscale energy cascades, we use two analysis techniques: energy spectra,

determined from the Fourier transform of the data, and structure functions (defined below in Section 2.2). The goal of this analysis is to obtain power-law relationships and resulting slopes for the energy spectra and structure functions. We began with energy spectra because there are established theoretical values for energy spectra slopes that characterize submesoscale turbulence. As discussed by Callies and Ferrari (2013), for two-dimensional isotropic energy spectra, interior-quasigeostrophic turbulence will show a slope of -3 and surface-quasigeostrophic turbulence will show a slope of -5/3 (-1.67). For scales less than 10 km, the internal-wave continuum would appear in energy spectra as a slope of -2. Other processes such as internal oscillations do not have established characteristic energy spectra slopes.

Theory relates the slopes of the structure function in log-log space (p) with that of energy spectra (n), also in log-log space, for homogenous temperature fields by $n = p + 1$ (Deschamps *et al.* 1981). Therefore, if our assumption about the homogeneity of the temperature field holds, we can determine n from p , and establish the physical processes that the structure functions indicate. We have chosen to use structure functions in addition to energy spectra because, as stated by Deschamps *et al.* (1981), the structure function has a more regular shape, which could prove useful for analyzing data with a large amount of gaps (Deschamps *et al.* 1981). Ultimately, we will determine the potential of the two datasets for use in future investigations of submesoscale energy cascades. Establishing the usefulness of high-resolution, long-term datasets for determining the physics of the submesoscale ocean could ultimately improve the

parameterizations used in present-day models, and therefore the predictions about Earth's future oceans and climate.

2. Data and Methodology

2.1. In Situ and In Space

Two datasets were integral in this study. The first dataset comes from the container ship *MV Oleander*, which makes weekly trips from Port Elizabeth, New Jersey to Hamilton, Bermuda (Flagg *et al.* 1998). Near-surface in situ data were used from two instruments on the *Oleander*: an acoustic Doppler current profiler (ADCP), which measures two dimensional velocity and temperature, and a thermosalinograph (TSG), which measures temperature and salinity. The ADCP dataset spans the period 1994 to 2012. A narrow-band 150 kHz ADCP collected the 10-year span of data from 1994 to 2004. This dataset has a depth range of

350 m with a vertical resolution of ~ 8 m, and has a horizontal resolution of ~ 2.5 km (calculated based on ship speed and a data-averaging time of 5 minutes) (Wang *et al.* 2010). An Ocean Surveyor 75 kHz ADCP collected the data from 2005 through 2012. This dataset has a depth range of 750 m with a vertical resolution of ~ 8 m, and a horizontal resolution of ~ 1.5 km (from speed and averaging time of 3 minutes). For both ADCPs, the velocities used were measured at a depth of 35 m and the temperatures were measured at a depth of ~ 6 m below the surface. The TSG dataset spans the period 2001 to 2012. Its horizontal resolution of ~ 0.5 km is calculated from an averaging time of 1 minute. The TSG measured temperature 6 m below the surface.

The second dataset comes from the Visible-Infrared Imager-Radiometer Suite (VIIRS) on NASA's Soumi-NPP (National Polar-orbiting Partnership) spacecraft. This dataset consists of sea surface skin temperature measured in

Table 1. Latitudes used to separate the route into regions with possibly varying properties. These are approximate latitude ranges where the shelf, Gulf Stream, and Sargasso Sea are located. These latitudes are used for all results except where otherwise noted.

Region	Latitudes Used ($^{\circ}$)
Entire Section (New Jersey to Bermuda)	[32.45, 39.95]
Continental Shelf	[39.0, 39.95]
Gulf Stream	[36.0, 39.0]
Sargasso Sea	[32.45, 36.0]

Table 2. Energy spectra and structure function slopes determined from the entire TSG dataset spanning from January 2001 to January 2012. The energy spectra slopes were fit from -1.75 to -0.5 exclusive on the $\log_{10}(\text{Wavenumber})$ scale, corresponding to 3 to 56 km. The structure function slopes were fit from 0.2 to 2.0 exclusive on the distance scale (1.6 to 100 km), except for the Sargasso Sea curve that was fit from 0.5 to 1.7 exclusive (3 to 50 km). The fourth column shows the absolute values of the difference of the spectral slope and the function slope.

	Potential Energy Spectra Slope (n)	Temperature Structure Function Slope (p)	Difference ($n - p$)
Entire Route	-2.6 ± 0.01	1.2 ± 0.01	1.4
Continental Shelf	-2.6 ± 0.01	1.3 ± 0.003	1.3
Gulf Stream	-2.7 ± 0.01	1.2 ± 0.01	1.5
Sargasso Sea	-2.5 ± 0.01	1.0 ± 0.01	1.5

Table 3. Structure function slopes determined from the entire TSG dataset, January 2001 to January 2012, split by region and by meteorological season. The latitudes for the shelf are [39.0, 39.196), for the Gulf Stream are [36.0, 39.0), and for the Sargasso Sea are [32.95, 36.0). Note that these latitudes are slightly different than those from Table 1 and Figures 2 and 3. The slopes were all fit from 0 to 1 exclusive on the distance scale, which corresponds to 1 to 10 km.

	Spring	Summer	Fall	Winter
Continental Shelf [39.0, 39.196)	1.22 ± 0.03	1.31 ± 0.03	1.39 ± 0.04	1.38 ± 0.01
Gulf Stream [36.0, 39.0)	1.40 ± 0.02	1.28 ± 0.02	1.28 ± 0.02	1.38 ± 0.02
Sargasso Sea [32.95, 36.0)	1.34 ± 0.01	1.18 ± 0.01	1.25 ± 0.02	1.33 ± 0.02

the top 10 micrometers of the ocean surface. The temporal resolution is two times per day depending on clouds, and the horizontal resolution is 750 m, with additional satellite information allowing for a final resolution of 375 m.

All three of the instruments (ADCP, TSG, and VIIRS) have horizontal resolutions in the submesoscale range. This makes these datasets ideal for investigating the physics of the submesoscale ocean.

2.2. Processing and Analysis

The ADCP and TSG data were processed following the methods of Wang *et al.* (2010). We used transects that had at least 80% good data points, and linearly interpolated the data onto along-track grids for each section in order to eliminate sections that had gaps longer than 10 km. We used a grid spacing of 2 km for the 150 kHz ADCP data, and for the 75 kHz ADCP and the TSG data we used a grid spacing of 0.375 km. The spacing values were chosen based on the horizontal resolution of each dataset. After some additional quality control, removal of a linear temperature trend, and the application of a Hanning window, the power spectral densities (using the Fast Fourier Transform) of kinetic and potential energy were calculated for each section. As part of calculating the power spectral densities, the interpolated, detrended sections were zero-padded in order to make them all the same length when the Fourier analysis was performed (length, and therefore amount of padding, depended on the

grid spacing for each dataset). The final power spectral densities are ensemble averages of the corresponding (kinetic or potential) spectra from each section. The kinetic energy was calculated, ignoring the factor of 0.5, using two-dimensional velocities: $KE = (u^2 + v^2)$. The potential energy was calculated from temperature following the assumptions made and the equation used by Wang *et al.* (2010): $PE = \alpha (T^2)$, with $\alpha = 0.1 \text{ m}^2/\text{s}^2/^\circ\text{C}^2$. In order to ensure that our methods gave similar results to those of Wang *et al.* (2010), the kinetic and potential energy spectra of the 150 kHz ADCP data were calculated and overlaid on the results from Wang *et al.* (2010). We found that our results were very similar to theirs, indicating that our method of data processing was adequate for obtaining power-law slopes from energy spectra. We then calculated energy spectra using the 75 kHz ADCP data and the TSG data for the same time period (2005 to 2012) in order to compare the accuracy of the TSG with the ADCP. TSG potential energy spectra were also calculated using the entire TSG dataset (2001 to 2012) for the entire *Oleander* track, the continental shelf, the Gulf Stream, and the Sargasso Sea to investigate spatially varying physics. The latitude range for the entire route was $[32.45^\circ, 39.95^\circ]$, with latitudes for each region tabulated in Table 1.

Temperature structure functions were calculated using the entire TSG dataset (2001 to 2012), after applying the same quality control and interpolation methods as for the energy spectra. The structure function, $F(s)$, was calculated

Figure 1. Above are the 75 kHz (2005 to 2012) ADCP kinetic, in red, and potential, in blue, energy spectra, and the 2005 to 2012 TSG potential energy spectrum, in cyan. The black lines show the linear fits for each spectrum. The slopes are shown in the top right. The intervals for the curves fits are indicated in brackets and by the vertical lines in corresponding colors to the spectra. The similarity in the curves shows that the ADCP and TSG energy spectra represent the same processes.

by $F(s) = \langle (T(x) - T(x+s))^2 \rangle$, where T is temperature in $^{\circ}\text{C}$, x is the along-track distance in km, and s is the distance between the two temperature data points in km. The $\langle \rangle$ brackets denote averaging over the individual sections and over the spatial variable x . The structure function was calculated for each section, and then all the structure functions were ensemble averaged to obtain the final result. As with the TSG potential energy spectra, structure functions were calculated for the entire track, the continental shelf, the Gulf Stream, and the Sargasso Sea in order to investigate the physics occurring in each region. We then performed another structure function analysis by dividing the entire TSG dataset into meteorological season and region. The regions used were the same as before (shelf, Gulf Stream, and Sargasso Sea), except that the latitudes at the beginning and the end of the sections were different: the sections spanned $[32.95^{\circ}, 39.195^{\circ}]$ (see column one of Table 3). The seasonal-regional data was interpolated onto a two-dimensional 0.375 km grid to retain temporal information, and sections with at least 60% good points were used. Note that for the interpolated sections used for the seasonal-regional temperature structure functions discussed here, we interpolated the sections along a mean *Oleander* track, instead of along each track for each section as used previously.

For every slope value (energy spectra and structure

functions), the error in the slope was estimated using the bootstrap method. The errors are indicated in Tables 2 and 3 and on Figures 1 to 3. The ranges of x -values on which each linear regression was made are indicated on Figures 1 to 3. The approximate regions for the continental shelf, the Gulf Stream, and the Sargasso Sea are shown along the *Oleander* track in Figure 4.

To compare the VIIRS data with the TSG data, images of VIIRS sea surface temperature within one day of the start and end time of the *Oleander*'s voyage were interpolated onto the *Oleander* track using a Barnes filter (Barnes 1964). Before interpolation, great care was taken to eliminate all data points affected by clouds. Interpolated sections with at least 5% good data points were further processed in the same way as the original *Oleander* TSG sections. Here, we focus on VIIRS matches with one particular TSG section spanning from May 12, 2012 to May 13, 2012. Eight corresponding VIIRS passes were identified that fall within one day of the *Oleander* travel period. Of those eight, we chose two passes to compare to the entire *Oleander* section, and the same two to compare to the Sargasso Sea part of the section. These passes were run through the same structure function methods as before with the TSG data. Unfortunately, due to technical difficulty and time constraints, we were only able to test the 750 m VIIRS data, and not the 375 m data.

Figure 2. The above shows TSG potential energy spectra calculated using the entire TSG dataset (2001 to 2012). The blue is the entire *Oleander* track, green is the Sargasso Sea, magenta is the Gulf Stream, and red is the continental shelf (latitudes used are in Table 1). The black lines show the linear fits for each spectrum. The slopes are shown in the top right. The intervals for the curve fits are indicated in brackets and on the plot by the black vertical lines. This figure illustrates the differences in the slopes for the separated regions.

3. Results

3.1. ADCP vs. TSG Energy Spectra

The energy spectra and structure functions calculated reveal a number of significant results. The TSG data product is of higher-resolution than that of the ADCP. Therefore, processes smaller than 10 km are better resolved, which can be seen in Figure 1 where the cyan curve extends further into larger wavenumbers (smaller scales) than either of the ADCP's blue or red curves. This resolution allows us to do two things: (1) to better determine where the ADCP spectra become noise, and (2) to better resolve small-scale processes. Both are important for checking past studies and motivating future work. As seen in Figure 1, the -2.5 ± 0.02 slope of the ADCP potential energy spectrum (blue) and the -2.6 ± 0.01 slope of the TSG potential energy spectrum (cyan) are comparable. The shapes and magnitudes of these two curves are also very similar. This suggests that the two potential energy spectra represent the same physical processes. Moreover, we can conclude that the TSG dataset can be used to obtain accurate estimates of energy spectral slopes.

3.2. Dynamical Regimes

The *Oleander* route extends through at least three

dynamical regimes in the ocean: the continental shelf, the Gulf Stream, and the Sargasso Sea (refer to Table 1 and Figure 4). Figure 2 shows the potential energy spectra computed separately for each of these regions, and the resulting slopes are noted in column two of Table 2. Slopes of the energy spectra are estimated from -1.75 (3 km) to -0.5 (56 km) on the abscissa. Figure 2 indicates that all spectra have a small wavenumber (large scale) roll-off occurring at different length scales: at about 100 km for the shelf, about 250 km for the Gulf Stream, about 315 km for the Sargasso Sea, and at scales beyond our axes for the entire section. This is due to the zero padding during processing mentioned in Section 2.2. We find that none of the energy spectra slopes are particularly close to either -3 or -2 , but all are between these values, which suggest that multiple processes contribute to the observed variability. The slopes of the shelf and Gulf Stream regions (-2.6 ± 0.01 and -2.7 ± 0.01 , respectively) are somewhat steeper than the slope in the Sargasso Sea (-2.5 ± 0.01). We find that the slopes do differ for each region, but the differences between regions are small relative to the differences to any of the slopes predicted by the theoretical models (Section 1). The differences between regions, however, are significant based on our statistical test.

Figure 3. This figure shows TSG temperature structure functions for the entire TSG dataset (2001 to 2012, using the same interpolated sections as Figure 2). Blue shows the entire *Oleander* route, green shows the Sargasso Sea, magenta shows the Gulf Stream, and red shows the continental shelf. The black lines show the linear fits for each spectrum. The slopes are shown in the top left. The intervals for the curves fits are indicated in brackets and on the plot by the vertical lines in corresponding colors to the spectra. This figure illustrates the differences between the slopes for the separated regions, and demonstrates qualitative differences between energy spectra and structure functions when compared to Figure 2.

3.3. Structure Functions

Figure 3 shows TSG temperature structure functions for the entire *Oleander* track and for each of the regions separately, calculated using the same data sections used for the potential energy spectra in Figure 2. Note that in contrast to the energy spectra, the largest resolved length scales differ between the different regions, with the maximum length scale corresponding to the total length of the corresponding section. Slopes of the structure functions are estimated from 0.2 (1.6 km) to 2.0 (100 km) on the abscissa, with the exception of the Sargasso Sea curve, which was fit from 0.5 (3.2 km) to 1.7 (50 km), and are noted in column three of Table 2. We find that the slopes differ by region. Consistent with the slopes reported in Section 3.2, the shelf and the Gulf Stream have slopes (1.3 ± 0.003 and 1.2 ± 0.01 , respectively) that are steeper than the slope in the Sargasso Sea (1.0 ± 0.01). Assuming homogeneity, the structure function slopes (p) and energy spectra slopes (n) are related by $n = p + 1$ (Deschamps *et al.* 1981). As indicated in column four of Table 2, the differences of the slopes ($n - p$) are significantly different from a value of 1 for our results (i.e. 1.3 to 1.5). Our energy spectra show different spectral slopes at different length

scales, and the way these project on the structure functions may explain this discrepancy.

Spectral slopes computed separately for meteorological seasons in each of the three regions as before are given in Table 3 (note from Section 2.2 and in column one of Table 3 that slightly different latitudes were used for this analysis). In all regions, we find that slopes are steeper in winter than in summer and that there is an increase in slope values from summer through to winter. The phase of the seasonal cycle differs among the regions, however, with the minimum slope over the shelf occurring in spring, and in the Sargasso Sea and the Gulf Stream regions in the summer. Note that for this analysis we have interpolated all sections to the same mean track. As a result, we find that the slopes are steeper than the ones computed from sections interpolated on individual *Oleander* tracks. The reason for this discrepancy is not immediately clear, but possible explanations include the structure function is sensitive to noise, different sections passed the quality control for the different interpolation methods, and/or that the sections extended over different latitude intervals. Consistent with the previous results, we find, however, that the slope in the Sargasso Sea is generally shallower than that in the other regions.

Figure 4. The above is a characteristic VIIRS sea surface temperature (SST) image showing the entire *Oleander* track and the approximate regions for the continental shelf, the Gulf Stream, and the Sargasso Sea.

3.4. VIIRS

We ran into some different issues with the VIIRS data than we did with the *Oleander* ADCP and TSG data. First, we found that the VIIRS dataset, as expected, contained a lot of both small and large sections of data missing due to cloud cover. Anticipating this, we chose to use structure functions to analyze the VIIRS data, which tend to handle gaps more easily than does the calculation of the Fourier Transform from which the energy spectra are derived. It proved difficult to find good, full-length VIIRS passes that fell in the same time period covered by a TSG section (plus or minus one day). This resulted in only four nearly complete sections of VIIRS data in the six months previewed for a given matching TSG section. Therefore we compared single VIIRS structure functions, not an averaged function, with matching TSG sections. Figure 5 shows the structure function for a single TSG section (May 12, 2012 to May 13, 2012). It also shows the structure functions for two separate VIIRS passes, one on May 11, 2012 at about 0600 UTC and the other on May 12, 2012 at about 1720 UTC. From scales of 1 km (0 on the abscissa) to 100 km (2 on the abscissa) the three structure functions agree very well. Below about 1 km there is some flattening in the VIIRS structure functions. We found that the VIIRS temperature data had a lot more small-scale variability (possibly

instrument noise), which tends to amplify structure functions at small scales. Because we had to use single sections to produce adequate structure functions, we did not perform linear fits to the structure functions because we did not have enough data to get good statistics for these trials. These structure functions, then, serve to expand knowledge about how structure functions work and how they are affected by noise, gaps, etc.

The signal to noise ratio of the VIIRS data also seems to be very important in affecting the shape of the structure function, as illustrated in Figure 6, showing the structure function for the Sargasso Sea portion of the *Oleander* track (latitude range is the same as in Table 1) along a single TSG section and the corresponding structure functions for the two VIIRS passes. The TSG structure function slope and the VIIRS structure function slopes appear to diverge at about 1, or 10 km, on the abscissa. This could be because the signal to noise ratio is much lower in the Sargasso Sea. Because the Sargasso Sea alone (Figure 6) does not include the Gulf Stream (a large signal), the noise would have a larger effect. In Figure 5, the signal to noise ratio is much higher because the Gulf Stream is included and most likely has a larger effect than the noise. The flattening in the VIIRS slopes at small scales is again thought to result from noise. Also, because we used 750 m data for Figures 5 and 6, values for scales smaller than ~ 0.2 (1.5 km) are heavily

Figure 5. This figure shows the TSG temperature structure function (black) for the *Oleander* section from May 12, 2012 to May 13, 2012. Two 750 m resolution VIIRS passes are also shown: May 11, 2012 at about 0600 UTC (red) and May 12, 2012 at about 1720 UTC (blue). This figure illustrates the similarities between the TSG structure function and the VIIRS structure functions.

dependent on the interpolation scheme used to determine SST along the *Oleander* track from the VIIRS SST images.

4. Discussion

In our study, we have analyzed energy as a function of scale using three different data products: near-surface temperature measured by the ADCP and the TSG on board the *Oleander*, and sea surface skin temperature measured by VIIRS. Because the TSG data has a higher spatial resolution than the ADCP data, the TSG extended the range for which reliable estimates of spectral slopes could be computed – down to about 2.5 km. We only analyzed the TSG data measured on board the *Oleander*, however, data is available for a large number of ships. Our findings suggest that these data may provide an opportunity to study the submesoscale ocean on a larger scale.

All spectral potential energy slopes computed for the entire route, or regionally on the continental shelf, the Gulf Stream, or the Sargasso Sea, fall in the range predicted by different dynamical models, that is, between $-5/3$ and -3 . However, none of the spectra align particularly well with one specific model. This could indicate a few things. One, it could mean that there are multiple processes happening at

the same time. We averaged over time/season/year, so if there were differences between time periods, we would not see them in our spectra. Two, it could mean that there are different processes occurring at different locations. We attempted to look into this possibility by splitting up the route by sections, but we still average over distance within these regions to obtain spectra. That the Gulf Stream slope is 0.1 steeper and the Sargasso Sea slope 0.1 shallower than the slope of the entire route indicates that different physical processes are dominant in these regions. The regional slopes are still significantly different than any of the dynamical models, however, and we conclude that our energy spectra do not give a clear picture of the physics occurring along the *Oleander* route. We note that our results may underestimate the differences in the spectral slopes corresponding to dominant processes in the regions. Because the boundaries in between are highly dynamic, energy frequently “leaks” across the latitudes chosen as boundaries in our study. This non-homogeneity and non-locality may be another reason that our computed slopes do not agree well with any of the theoretical models; homogeneity is a key assumption underlying any of the predicted slopes.

Two statistical tools were used in our study to estimate spectral slopes: first, we directly computed energy spectra,

Figure 6. This figure shows the TSG temperature structure function (black) for the *Oleander* section from May 12, 2012 to May 13, 2012. Two 750 m resolution VIIRS passes are also shown: May 11, 2012 at about 0600 UTC (red) and May 12, 2012 at about 1720 UTC (blue). All structure functions are for the Sargasso Sea only (latitudes: [32.45, 36)). This figure illustrates the differences between the TSG structure function and the VIIRS structure functions, and the effect of signal to noise ratio in structure functions.

and second, we computed the second order structure function. From the structure functions we can see that again our results do not agree with theory. Instead of having issues with how the data were averaged, here we could be seeing a deviation from theory due to how the structure function combines multiple processes in one curve. We have confidence in our slope values because of the small calculated errors, but more than one process could be contributing to the linearity of the structure function, resulting in slope values that do not relate as predicted by theory. The seasonal/spatial structure functions from Table 3 show that there is much that could be done with the TSG data in terms of splitting it up in other ways in order to focus in on the submesoscale physics at a location at a certain time.

Due to major technical setbacks, we were unable to work with the VIIRS data as much as we would have liked. Therefore, we have not yet determined if the VIIRS data can be used to calculate accurate structure functions globally; this is an eventual goal to be reached for in future studies. However, we did learn much about the VIIRS data and structure functions. One, we have concluded that the techniques used to process the VIIRS data needs to be refined in order to handle the large amount of noise and gaps in the data. The processing of such satellite data needs to be carefully thought out and needs to be carried out consistently. Two, more TSG sections and matching VIIRS passes need to be identified and used in calculating average structure functions in order to obtain accurate results with good statistics. Without enough data, we cannot draw conclusions with confidence. Three, we found that structure functions are very sensitive to spikes in the data, and change shape with varying signal to noise ratios. Overall, we conclude that there is much more to be done with the VIIRS data (refining the processing methods, comparing night and day passes, working with the 375 m resolution data, looking at structure functions from around the world, etc.).

5. Final Thoughts

The submesoscale ocean has captured the attention of the oceanography community. It stands as one of the missing puzzle pieces in our knowledge of the ocean as a whole. So what can we use to investigate the physics of the submesoscales? Previous literature has shown the value of the *Oleander* ADCP data, and we have shown here the value of the higher-resolution *Oleander* TSG data. The TSG data can be used to create accurate potential energy spectra and temperature structure functions. The dataset can be split by region, by season, or both. TSG structure functions can also be compared to structure functions created with VIIRS data as a way to determine the usefulness of high-resolution

global satellite datasets. We can conclude that it is at least feasible to use satellite data to construct structure functions. And with more research, the possibilities of the global VIIRS dataset are endless.

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Adhesion strength of the green alga *Ulva cf. linza* and other ship-fouling organisms

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Abstract

Foul-release coatings have emerged as a potential environmentally friendly and effective antifouling alternative to traditional biocides. This study assessed the adhesion strength of soft ship-fouling organisms on either glass or foul-release surfaces using the turbulence generated by a water-jet apparatus as a proxy for vessel speed. The apparatus is expected to help evaluate the capacity of foul-release coatings to resist biofouling. We examined the adhesion strength of the zoospores of *Ulva cf. linza*, a cosmopolitan green alga that is commonly used in marine biofouling research, as a function of angle of impact and water turbulence generated by the water-jet apparatus. Slides were either untreated or treated with a HullKote™ coating. All slides were exposed to the apparatus at either a 63- or 90-degree angle and at pressures ranging from 0-74.6 kPa. Using a similar procedure, we tested the adhesion strength of a variety of fouling organisms grown together on untreated slides submerged in natural flow-through seawater. Within a given pressure, all slides exhibited highly variable average spore concentrations and average percent coverage, even with 20 fields of view. The high degree of variability in the adhesion strength of the involved fouling organisms may best be explained by the patchy nature of colonization. *Ulva* spores in particular often settle gregariously, forming large concentrated patches. Untreated and treated *U. cf. linza* slides had a significantly higher average concentration of settled spores at the control pressure than at higher pressures, and untreated slides prepared in flow-through seawater displayed a similar result using the average percent coverage. Only the average spore concentration for treated *U. cf. linza* slides exhibited a clear negative trend as pressure increased. This negative trend suggests the coating may be a viable antifouling approach.

1. Introduction

Biofouling is the unwanted colonization of a submerged surface. It is a process beginning with the adsorption of organic molecules, followed by the formation of a biofilm, a thin layer of microorganisms that later facilitates the growth of larger organisms (Dobretsov 2010, Thome et al. 2012). While the biofilm itself can indeed lead to the damage of parts of boats as well as increased drag, generally only the later phases (i.e. the growth of macroorganisms) cause serious problems for vessels. Antifouling coatings have long been used to effectively combat the establishment of a biofilm and the growth of larger organisms, but only relatively recently has there been an effort to develop effective, environmentally friendly coatings that do not employ biocides (Finnie and Williams 2010). Foul-release (FR) coatings seek to minimize the adhesive interaction between a fouling organism and a potential substrate, thereby either preventing colonization or increasing the likelihood of the release of that organism as the vessel increases speed (Finnie and Williams 2010). Many different types of FR coatings exist. For example, some rely on extremely hydrophobic compounds such as polytetrafluoroethylene (Webster and Chisholm 2010), others on hydrophilic-hydrophobic hybrids (Sundaram et al. 2014), and yet others that rely on disruptive surface microtopographies (Schumacher et al. 2007). All are designed to inhibit the formation of the biofilm and the growth of macroorganisms.

Ulva linza is a cosmopolitan green alga that contributes to the formation of the biofilm, and as such is often used in biofouling research. Although it reproduces both sexually and asexually, usually only the asexual zoospores are used in research as they adhere more quickly and more strongly than do the gametes or the zygotes (Callow et al. 1997). Studies have already assessed the adhesion strength of *U. linza* using a water jet apparatus on particular surfaces (e.g.

Granhag et al. 2004, Finlay et al. 2002, Krishnan et al. 2006), but relatively few have characterized the corresponding vessel speed needed to dislodge the organism. The study of *U. linza* is complicated by the need for a genetic identification of the species. Many species within the genus *Ulva* exhibit morphological overlap, making it impossible to identify them without an in-depth analysis of the genome (Guidone et al. 2014). In this paper, as a purely morphological evaluation of the species was used following Villalard-Bohnsack (1995), we will refer to the alga as *Ulva cf. linza*.

It is important to consider different types of fouling species when dealing with potential antifouling techniques, as adhesive capabilities and preferences for certain types of surface vary (Kavanagh et al. 2001). A certain FR coating that is effective at removing algal spores may not necessarily translate into successful removal of organisms such as diatoms and bacteria.

This study aims to assess the adhesion strength of *Ulva cf. linza* and other fouling organisms on plain glass surfaces as well as on hydrophobic FR-coated surfaces, and to relate this adhesive capacity to corresponding vessel speed. We used the pressure generated by a water-jet apparatus to simulate the pressure caused by a moving vessel, on a surface angled at either 63° or 90°. The results will help determine whether the particular FR coating is viable, and additionally whether the water-jet apparatus is an effective method for testing adhesion strength.

2. Materials & Methods

2.1 General overview

Slides were grouped by the type of colonizing organism (either *Ulva* or natural growth slides), and whether they were plain glass surfaces or if they had a FR coating. Slides were then exposed at either a 63- or 90-degree angle to the

Table 1. Schematic of the five experiments. The final column to the right indicates individual experiments, grouped first by the study organism and surface type.

Study organism	Surface type	Angle of exposure
<i>Ulva cf. linza</i>	HullKote™ -coated slides	90°
	Plain glass slides	90°
		63°
Natural growth	Plain glass slides	90°, first trial (June 23)
		90°, second trial (July 25)

water jet (Table 1). The algorithm designed to relate water pressure to boat speed is under development.

2.2 Slide Preparation

Glass slides (2.5 x 7.5 cm) were cleaned as described in Finlay et al. 2002. Slides were either settled by *U. cf. linza* spores or submerged vertically in unfiltered flow-through seawater (~12 turnovers per day) for 30 days to allow natural growth. For one experiment (*U. cf. linza*-settled slides run at 90° on July 11), slides were coated twice with HullKote™ FR (<http://www.mclubmarine.com/hullkote>), according to the manufacturer's instructions.

2.3 Sampling

U. cf. linza samples were collected from Fort Wetherill, Jamestown, RI (41° 28' 45.8'' N, 71° 21' 42.5'' W) and Beavertail Point, Jamestown, RI (41° 27' 10'' N, 71° 23' 52'' W) on June 13 and July 09 2014, respectively, just before spring tides. Mature, browning tips were collected and brought back to the laboratory on ice. Mature blades were sorted, rinsed in sterile filtered seawater, and stored on absorbent paper in the refrigerator overnight (~16 hours). Spore release was conducted following the method of Callow et al. (1997). Blades were sorted individually into tubes with 4 ml sterile filtered seawater (0.45-µm filter, autoclaved). Tubes were stored on ice to prevent spore settlement. Aliquots of spore suspension were taken from each tube in order to identify microscopically whether it contained quadriflagellate asexual zoospores or biflagellate gametes. Suspensions containing zoospores were filtered through a 10-µm plankton net and pooled. For samples

collected on June 13 the suspension was brought to 1.7×10^5 spores/ml. For samples collected on 09 July the suspension was brought to 5.0×10^5 spores/ml. The pooled suspension was stirred periodically and kept on ice to prevent spore settlement. Cell concentration was determined using a Fuchs-Rosenthal haemocytometer. Ten ml of the pooled spore suspension was pipetted into each compartment of a quadriPERM® culture vessel containing a glass slide (n=48 for June 13 samples, n=24 for July 09 samples). The slides were incubated overnight at 20° C (~17 hours).

Slides meant for natural growth testing were submerged on May 23 and once again on June 25 2014 (n=18 for each). These slides were removed approximately one month later, just prior to water-jet testing (June 23 and July 24, respectively).

2.4 Water Jet Testing

The water jet operated using a 7.5-mm brass nozzle with an actuator arm to move the nozzle across the slides at a constant speed of 4 cm/s (Figure 1). Slides were run under the water jet once either at 63° or 90°. Four experiments were conducted at 90° and only one conducted at 63° (*U. cf. linza*-settled plain glass slides). Aquarium line pressures ranged from 0-86 kPa. The resulting pressure at the nozzle was previously calculated after calibration using an Omegadyne Inc. transducer. Pressure at the nozzle ranged from 0.6 to 74.6 kPa. At the control pressure (0.6 or 0.7 kPa), the apparatus generated no water pressure, the aquarium line being turned off. Slides were mounted on a slide holder in sets of four for *U. cf. linza* spore experiments and in sets of three for natural growth experiments. Slides in each set were exposed to the same pressure. During each experiment one set of slides served as a control (aquarium line pressure off), and subsequent sets of slides exposed to increasing water pressures.

2.5 Cell counting

After exposure to water pressure, slides were brought back to the laboratory and immediately placed in a 4% glutaraldehyde-sterile filtered seawater solution for 30 minutes. The slides were subsequently transferred to a sterile filtered seawater bath, a 50:50 sterile filtered seawater and sterile deionized water bath, and two sterile deionized water baths for five minutes each. After letting them air-dry, the slides were analyzed by microscopy and NIS-Elements software. Counts were made for 20 fields of view (each 0.66 mm²) on all slides along the path of the

Figure 1. The water-jet apparatus used for testing adhesion strength. Nozzle at 63°.

water jet. For *U.cf. linza*-settled slides, the number of spores per mm² was determined using eye counts. For slides prepared in flow-through seawater, the percent coverage was determined using NIS Elements object count.

2.6 Statistics

Values for percent coverage were transformed by taking the arcsine of their square root. Spore concentrations in fields of view were analyzed using a nested PERMANOVA to determine whether there were significant differences between slides within given pressures. A one-way ANOVA was conducted to determine whether there were significant differences in either the average number of spores per mm² or percent coverage between pressures using JMP software v11. Tukey's Honestly Significant Difference (HSD) post-hoc tests were conducted.

3. Results

There was a high degree of variability in spore concentration and percent coverage between slides within a given pressure for all experiments (PERMANOVA, e.g. Table 2). Slides were treated as separate replicates for subsequent analyses.

As water pressure increased, the average number of spores per mm² for *U. cf. linza*-settled slides with HullKote™ FR coating exposed at 90° decreased significantly (ANOVA, $F=68.14$, $df=5$, $p<0.0001$) (Figure 2). Post-hoc tests revealed that there were significantly fewer spores per mm² for slides exposed at the highest pressure (69.9 kPa) than at several lower pressures such as 36.2, 24.3, or the control 0.7 kPa (Tukey's HSD, $p=0.008$, 0.001 , $p<0.0001$). Additionally, there were fewer spores per mm² for slides exposed at 59.8 kPa than at 24.3 or 0.7 kPa (Tukey's HSD, $p=0.016$, $p<0.0001$), and fewer spores per mm² for slides exposed at 48.0 kPa than at 24.3 or 0.7 kPa (Tukey's HSD, $p=0.049$, $p<0.0001$) (Figure 2).

There was a significant relationship between pressure and the average number of spores per mm² for *U. cf. linza*-settled glass slides exposed at 90° (ANOVA, $F=21.36$, $df=5$, $p<0.0001$). This was due to the significant difference between remaining settlement densities for the control (0.7 kPa) and all other pressures. There were no significant differences between any of the densities at other pressures (Tukey's HSD, $p>0.05$) (Figure 3).

Similarly there was a significant relationship between pressure and the average number of spores per mm² for *U. cf. linza*-settled glass slides exposed at 63° (ANOVA, $F=5.02$, $df=5$, $p=0.0047$). However, apart from significant differences between the control pressure and higher pressure, there was no clear pattern (Figure 4).

The first set of natural growth slides (tested on June 23) was potentially affected by grazing by *Littorina littorea*. The second set of natural growth slides (tested on July 25) was accidentally dried for a period of up to 12 hours. Natural growth on slides prepared in flow-through seawater consisted primarily of pennate diatoms and bacteria. Major diatom genera identified included *Cocconeis* spp., *Bacillaria* spp., *Entomoneis* spp., *Pleurosigma* spp., *Striatella* spp., *Achnanthes* spp., and *Licmophora* spp.

There was a significant relationship between pressure and the average transformed percent coverage for the first set of natural growth slides exposed at 90° (ANOVA, $F=3.46$, $df=5$, $p=0.03$). Again, this significant relationship was driven by the control group, as there were no significant differences between all other pressures (Tukey's HSD, $p>0.05$) (Figure 5).

There was a significant relationship between pressure and the average transformed percent coverage for the second set of natural growth slides exposed at 90° (ANOVA, $F=9.06$, $df=5$, $p=0.0009$). There were significant differences between several different pressures, but no clear pattern (Figure 6).

4. Discussion

The variability between slides within a given pressure for every experiment may be best explained by the patchy nature of colonization. For natural growth slides prepared in flow-through seawater, different diatom assemblages on different slides as well as the different taxa present on a single slide may lead to a patchy distribution, particularly after water-jet testing. Species such as those in the genus *Cocconeis*, for example, adhere much more strongly than other diatoms due to the strong adhesive that they secrete. Not only might they be able to colonize a surface at higher densities than other species, but also they could remain attached at greater pressures. *Cocconeis* spp. are able to position themselves very close to the surface of a substrate,

Table 2. Example of nested PERMANOVA results showing variability of between-slide comparisons within the control pressure (0.6 kPa) on glass slides exposed at 63°. Number of permutations = 9999. Asterisks indicate significant differences between the average number of spores per mm² on different slides.

Groups (slide #)	t	P_perm	#unique values
(1,2)	2.8090	0.0026*	9945
(1,3)	4.6397	0.0001*	9952
(1,4)	3.2348	0.0011*	9950
(2,3)	3.2214	0.0018*	9940
(2,4)	1.3559	0.1760	9936
(3,4)	1.9681	0.0544	9943

Figure 2. The relationship between water pressure at the nozzle (kPa) and the average number of spores per mm² on slides coated with FR HullKote™ and exposed at 90°. N=4 at each pressure. Values are means (+/- 1 SE). Different letters indicate significantly different values.

Figure 3. The relationship between water pressure at the nozzle (kPa) and the average number of spores per mm² on untreated glass slides exposed at 90°. N=4 at each pressure. Values are means (+/- 1 SE). Different letters indicate significantly different values.

Figure 4. The relationship between water pressure at the nozzle (kPa) and the average number of spores per mm² on untreated glass slides exposed at 63°. N=4 at each pressure. Values are means (+/- 1 SE). Different letters indicate significantly different values.

ideal for high-shear stress environments (Molino and Wetherbee 2014). *Ulva* spores are known to colonize surfaces gregariously (Callow et al. 1997), leading to a dense, patchy distribution. In addition, the adhesion strength of larger groups of spores is actually greater than that of individual spores (Finlay et al. 2002). This initial patchiness

may again be magnified by the use of a water jet, as individual spores are removed and larger groups remain. Gregarious settlement was particularly notable on the plain glass slides, yet almost completely absent on slides with FR coating.

HullKote™ FR coating slides were the only experimental treatment to exhibit a significant decrease in average spore concentration as pressure increased. This finding is consistent with literature in which *U. linza* spores adhere less strongly to hydrophobic surfaces (Krishnan et al. 2006). These results suggest that this particular FR coating functions well in regard to colonization by *U. cf. linza* spores: as pressure (and thus corresponding vessel speed) increases, the number of remaining spores per mm² decreases significantly. In contrast to the results on plain glass slides, *Ulva* spores had weaker adhesion strength while settled on HullKote™-coated slides.

No glass slides in the *U. cf. linza* experiments exhibited any clear pattern as pressure increased. Glass is a more hydrophilic surface than the HullKote™ coating, allowing more of the adhesive glycoprotein secreted by the spores to wet the surface and anchor them (Callow et al. 2005). This may explain the larger extent of gregarious settlement noted on glass slides. However, the hydrophilic nature of the glass

surface is not necessarily the only factor contributing to increased *U. cf. linza* adhesion strength. Glass slides may be significantly rougher than FR-coated slides, an important attribute in the colonization of a surface. *Ulva* spores will adhere more strongly to rough surfaces (Dillon et al. 1989), at least up to a point. Granhag et al. (2014) note that *U. linza* spores adhere most strongly to surfaces with an intermediate roughness (grain size = ~25 µm). In the face of water flow, the microenvironments generated by the roughness protect spores from shear forces, provided that the grain size is not so rough to form ridges (off of which they are removed at significantly lower pressures compared to smoother surfaces). Not only are the spores provided with refuge, but there is also an increase in overall surface area that allows for greater colonization. Glass slides prepared in this study were thoroughly cleaned, and preliminary profilometer tests revealed them to be smooth. Roughness therefore most likely did not play a great role in our experiments.

While it is likely that the spores used in this experiment were of *U. linza*, a genetic identification of the species would have been ideal. Species of the genus *Ulva* share similar life history patterns, but due to the widespread use of *U. linza* in antifouling research, it would have been best to

Figure 5. The relationship between water pressure at the nozzle (kPa) and the average transformed percent coverage on untreated glass slides exposed at 90°. First trial (June 23). N=3 at each pressure. Values are means (+/- 1 SE). Different letters indicate significantly different values.

Figure 6. The relationship between water pressure at the nozzle (kPa) and the average transformed percent coverage on untreated glass slides exposed at 90°. Second trial (July 25). N=3 at each pressure. Values are means (+/- 1 SE). Different letters indicate significantly different values.

identify it beyond any doubt. Given that the samples were collected from the same patches of mature *Ulva* blades, the zoospore suspensions were most likely all from the same species, but it cannot be said with complete certainty which one, given the morphological overlap with other species (Guidone et al. 2013).

The first natural growth experiment (conducted on June 23) exhibited no clear pattern as water pressure increased, indicating that the cells adhered strongly to the surface and were able to resist the forces generated in our range of pressure. The primarily diatom and bacteria assemblage adhered well to the glass surface. In stark contrast to the adhesive capabilities of *U. linza*, several genera of marine diatoms (e.g. *Navicula*, *Craspedostauros*, and *Amphora*) that contribute to biofouling actually adhere more strongly to hydrophobic surfaces (Holland et al. 2004, Krishnan et al. 2006, Sundaram et al. 2014), and so these species theoretically should adhere even more strongly to slides treated with the hydrophobic HullKote™ coating. This experiment is in progress, and will be important in characterizing whether or not the fouling diatoms observed in this study have adhesive capabilities to hydrophobic surfaces similar to those observed in the work of Holland et al. (2004).

The results from the second natural growth experiment varied from those of the first. Although there was no clear pattern as pressure increased, there were significant differences between the average transformed percent coverage at different pressures (Figure 6). These results may have been affected by the second natural growth experiment's exposure to air, since during the course of the growing process in the flow-through seawater the water levels dropped and exposed the slides for several hours. Any inference made from this particular experiment may therefore not necessarily reflect the adhesion strength and characteristics of the organisms that colonized these slides. These results may reflect the adhesion strength of fouling organisms on a substrate removed from water for an extended period of time, however.

The water-jet apparatus appears to be an effective method for measuring the adhesion strength of fouling organisms, despite the limited range of pressure allowed by the facility in which it was used. In the future, however, a greater range of pressures would be desirable, as would a greater diversity of surfaces, such as different types of FR coatings.

5. Conclusion

Colonization of a substrate, particularly in regard to biofouling, can be patchy by nature. In this experiment, *U. cf. linza* spores adhered less strongly to FR-coated slides, and more strongly to plain glass slides. This decreased adhesion strength on FR surfaces is likely due to hydrophobicity, but it may also be related to the texture and roughness of the surface. Growth in flow-through seawater adhered strongly enough to glass slides so as not to experience a significant decrease in percent coverage as water pressure increased. The different adhesive capabilities of *U. cf. linza* and organisms such as pennate diatoms further indicate that a single FR surface strategy such as hydrophobicity is not sufficient to prevent the formation of

a thick biofilm, and likely a combination of strategies is necessary.

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Survey of Tsunamis Formed by Atmospheric Forcing on the East Coast of the United States

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Abstract. High-frequency sea level oscillations along the United States East Coast have been linked to atmospheric pressure disturbances observed during large storm events. These oscillations have periods similar to tsunami events generated by earthquakes and submarine landslides, but are created by moving surface pressure anomalies within storm systems such as mesoscale convective systems or mid-latitude cyclones. Meteotsunamis form as in-situ waves, directly underneath a moving surface pressure anomaly. As the pressure disturbances move off the east coast of North America and over the continental shelf in the Atlantic Ocean, Proudman resonance, which is known to enhance the amplitude of the meteotsunami, may occur when the propagation speed of the pressure disturbance is equal to that of the shallow water wave speed. At the continental shelf break, some of the meteotsunami waves are reflected back towards the coast. The events we studied date from 2007 to 2014, most of which were identified using an atmospheric pressure anomaly detection method applied to atmospheric data from two National Data Buoy Center (NDBC) stations: Cape May, New Jersey and Newport, Rhode Island. The coastal tidal records used to observe the meteotsunami amplitudes include Montauk, New York; Atlantic City, New Jersey; and Duck, North Carolina. On average, meteotsunamis ranging from 0.1m to 1m in amplitude occurred roughly twice per month, with meteotsunamis larger than 0.4m occurring approximately 4 times per year, a rate much higher than previously reported. For each event, the amplitude of the recorded pressure disturbance was compared to the meteotsunami amplitude, while radar and bathymetry data were analyzed to observe the influence of Proudman resonance on the reflected meteotsunami waves. In-situ meteotsunami amplitudes showed a direct correlation with the amplitude of pressure disturbances. Meteotsunamis reflected off the continental shelf break were generally higher in amplitude when the average storm speed was closer to that of the shallow water wave speed, which suggests that Proudman resonance has a significant influence on meteotsunami amplitude over the continental shelf. Through the application of these findings the frequency and severity of future meteotsunamis can be better predicted along the east coast of the United States.

1. Introduction

Tsunami waves have long been associated with the occurrence of under water earthquakes, landslides or volcanic activity, but recently tsunami-like events have been documented on the East Coast of the United States in the absence of any of these traditional catalysts (Pasquet et al., 2013). These, previously mysterious, high frequency sea-level oscillations have been linked to moving atmospheric pressure disturbances seen during strong storm events in the region (Pasquet and Vilibic, 2013). Storm systems, particularly mesoscale convective systems (MCSs), create moving surface pressure disturbances as a result of processes associated with strong convection and precipitation observed as squall lines within these systems (Houze, 2004). With the addition of Proudman resonance, which describes an atmosphere-ocean resonant effect, a tsunami-like wave of significant amplitude, classified as a meteotsunami, can develop underneath these storm systems in response to the moving surface atmospheric pressure disturbance (Monserrat et al., 2006). Meteotsunamis on this coast have been recorded as in-situ waves directly underneath an atmospheric pressure disturbance associated with a storm system, or as reflected waves that travel independently from the storm system after being reflected off the continental shelf break in the Atlantic Ocean. Focusing on the region of coastline from Newport, Rhode Island (41.504 degrees north) to Duck, North Carolina (36.184 degrees north), this study aims to detect all atmospherically induced high frequency sea-level oscillations, or meteotsunamis, having amplitudes of 0.1m

or greater. Once identifying the desired meteotsunami events, correlations between meteotsunami amplitude and storm characteristics, like pressure disturbance strength and translational velocity, are examined in an attempt to better predict the severity and frequency of future meteotsunami events.

2. Data and Methods

2.1 Identifying and recording Meteotsunami Events

Within storm systems, like MCS's or mid-latitude cyclones, moving surface pressure disturbances often come in the form of squall lines. Squall lines are sections of increased convection within these storms, which create atmospheric pressure disturbances needed to form meteotsunamis (Houze, 2004). They are usually associated with a rapid increase in wind velocity as well as a sharp decrease in air temperature (Houze 2004). Standard 6-min meteorological data from National Data Buoy Center (NDBC) stations Cape May, New Jersey and Newport, Rhode Island was used to identify these atmospheric pressure disturbances by analyzing atmospheric pressure, maximum wind gust velocity and air temperature.

In order to analyze the amplitude of the pressure disturbances, the data was first high pass filtered over 6 hours to remove the low frequency oscillations seen in the atmospheric pressure at Cape May (Figure 1). To find atmospheric events we use a ratio of the atmospheric pressure standard deviation of a given 4-hour period over the atmospheric pressure standard deviation of the corresponding month. When this ratio was found to be

greater than 2.5, tidal data was examined to determine if a meteotsunami event had occurred. Newport's atmospheric pressure data was not included in this analysis because of time constraints, so this current analysis reflects the detection of storm system at the geographic mid-point of the coastline being studied. When determining whether or not a storm had occurred we also looked to confirm the presence of a large spike in the maximum wind gust velocity accompanied by a temperature drop within a few hours of a pressure disturbance at either Cape May, New Jersey or Newport, Rhode Island.

Once a list of pressure anomaly events was acquired, we used tidal data from NOAA Currents and Tides in order to observe each meteotsunami event. 6-min sea-level data from Duck, North Carolina; Atlantic City, New Jersey; and Montauk, New York were also high passed filtered over 6 hours to remove tidal and other low frequency oscillations seen in the data. If a sea-level oscillation greater than 0.1m in amplitude was observed at any station within a few hours of these meteorological characteristics a meteotsunami event was recorded (Figure 1).

Not all of the events show detectible atmospheric pressure disturbances at Cape May, New Jersey, but from the analysis of tidal data, more high frequency sea-level oscillations were identified as meteotsunamis. Atmospheric pressure data from Newport, Rhode Island, as well as radar images were used to link sea-level oscillations to storm events in the area that were not recorded at Cape May. For

each of the meteotsunami events identified in this study the maximum wind gust and the amplitude of the maximum pressure disturbance were recorded from both meteorological stations as well as the amplitudes of the meteotsunamis observed at the 3 tidal stations. Only events that occurred from 2007 until June of 2014 were used in this study due to limited availability of data.

2.2 Froude Number Analysis

To analyze the extent at which Proudman resonance affects the formation of meteotsunami waves, the Froude number can be used (Monserrat et al., 2006). The Froude number is defined as $Fr = U/c$, where U is the translational speed of the moving pressure disturbance and c is the shallow water wave speed defined as the square root of gh where g is the acceleration due to gravity and h is the depth of the water column. Proudman resonance occurs when the atmospheric pressure disturbance propagates at the same speed as the shallow water wave speed for the given water depth (Proudman, 1929). For this reason it is expected that the greatest meteotsunami amplitudes should be observed when $U \sim c$, or when $Fr \sim 1$ (Monserrat et al., 2006).

Using radar data from the NOAA National Climate Data Center and Bathymetry data from the NOAA National Geophysical Data Center the relationship between the Froude number and meteotsunami amplitude was analyzed for reflected meteotsunamis generated by storm systems

Figure 1. High pass filtered atmospheric pressure data from Cape May, New Jersey (Top) and Sea level data from Atlantic City, New Jersey (Bottom) during the Meteotsunami event on January 29th 2009. The time delay between the pressure disturbance seen at Cape May and the arrival of the meteotsunami at Atlantic City is highlighted in rectangles.

Figure 2. Bathymetry map of the continental shelf off the coast of New Jersey and Long Island, New York. The black dotted line shows the transect from the coast of New Jersey to the continental shelf break that was used to calculate the average shallow water wave speed used in the Froude number analysis. The transect is taken along a constant line of latitude at 39.4 degrees north because most storms that produce reflected meteotsunamis travel in a predominately west to east direction. Color indicates topography in meters.

Figure 3. A stem plot of 14 meteotsunami amplitudes recorded at Atlantic City, New Jersey after each meteotsunami reflected off the continental shelf is compared to the Froude number for each storm. The Froude number is calculated using the average storm velocity (U) found from radar images and the average shallow water wave speed (C) found from bathymetry data shown in Figure 2.

moving off the coast of New Jersey and over the continental shelf break. Only sea-level data from the NOAA tidal station at Atlantic City, New Jersey was used for this analysis. When distinguishing between in-situ events and events where meteotsunamis developed over the continental shelf and reflected off of the continental shelf break, radar images were used to observe probable location of

atmospheric pressure disturbances within storm systems traveling from west to east away from the east coast. In order for a meteotsunami to be categorized as reflected, a sea-level oscillation must have been observed at the Atlantic City tidal station after the suspected pressure disturbance moved off the coast and over the continental shelf break. In addition, radar data and atmospheric pressure data from NDBC station Cape May, New Jersey were analyzed to show that there was no pressure disturbance present over the tidal station at the arrival time of the reflected meteotsunami. Often a delay of 3–4 hours was observed between the occurrence of a pressure disturbance over Cape May and the reflected wave arriving at Atlantic City, an example of which can be seen in Figure 1, which displays the event of January 29th 2009.

To calculate the Froude number for each event, the average velocity of each storm (U) was compared to the average shallow water wave speed (c) that was calculated using a transect of bathymetry data that spanned the width of the continental shelf from the coast of New Jersey to the continental shelf break at a latitude of 39.4 degrees north. This transect, shown in Figure 2, was chosen not only because it represents a suitable path taken by the storm systems, but because it also avoids a canyon on the continental shelf that would create bias in our average shallow water wave speed. To calculate the velocity of the storm system and more importantly the higher levels of convection and precipitation where the pressure disturbance would exist, radar images were first analyzed in order to identify a window of time where the system was traveling off the coast and over the continental shelf. The radar data is recorded in units of reflectivity, which means thicker clouds and higher levels of precipitation will have larger values. For this reason to isolate the squall line we only used reflective data above 30 dBZ to calculate the average velocity of the pressure disturbances within the storm. By tracking the position of the high reflectivity radar data and dividing by the time between radar images an average velocity of the pressure disturbance for each event was found. The amplitude of each reflected meteotsunami recorded at Atlantic City is shown as a function of the Froude number of each event (Figure 3).

3. Results

Every meteotsunami event, in-situ and reflected, recorded during this study is represented in Figure 4. In general the larger meteotsunamis occurred when stronger atmospheric pressure disturbances were recorded. This trend does however show a strong geographic dependency, meaning that the strongest relationships exist between tidal stations and meteorological stations that are located closer together geographically. When Cape May observed larger pressure disturbances, Atlantic City detected meteotsunamis that were larger in amplitude. This same trend can be seen for Newport, Rhode Island and Montauk, New York. Although the amplitudes of the meteotsunamis seen at Duck, North Carolina show a better correlation with the size of the pressure disturbances seen at Cape May than at Newport, the relationship is not as strong as Atlantic City and Cape May. A correlation between maximum wind gust and meteotsunami amplitude is more difficult to observe on

Figure 4. Stem plots of maximum wind gust (Top), atmospheric pressure disturbance amplitude (Middle) and meteotsunami amplitude (Bottom) of every meteotsunami event detected from 2007 to 2014. The same colors were used between the three stem plots to represent atmospheric and tidal stations that were within close proximity of each other. Montauk and Newport, Rhode Island are shown in blue, Atlantic City, New Jersey and Cape May, New Jersey are shown in black, and Duck, North Carolina in red.

this figure, however it does show that there usually exists stronger winds during the winter months (Figure 4).

On average meteotsunamis occurred 2-3 times per month from 2007 to 2014. There was little seasonal variability in the frequency of events, however December and March seemed to be the most active months for meteotsunamis recorded in this study (Figure 5). Figure 6, as well as Figure 7, shows that the amplitudes of meteotsunamis vary greatly depending on the geographic location at which the meteotsunami was observed. From Figure 6 it can be stated that when compared to the other tidal stations, Atlantic City receives the largest meteotsunamis in the winter months, having average amplitudes of about 0.3m. Duck experiences larger meteotsunamis in the summer, when the average meteotsunami amplitude is just under 0.3m. On average, Montauk experiences smaller meteotsunamis, approximately 0.15m in amplitude, throughout the year, but does show increased amplitudes in the winter months. Figure 7 illustrates that the occurrence of meteotsunamis approaching 0.5m or larger, although rare, are experienced occasionally at the tidal station in Montauk. This figure also shows that even though Atlantic City experienced some of the largest meteotsunamis in this study, the majority of the meteotsunamis recorded were below 0.4m in amplitude. Duck, although not observing the highest meteotsunami amplitudes, did show the most consistent occurrence of meteotsunamis in the range of 0.4m to 0.5m.

Figure 3 confirmed that the largest reflected meteotsunami amplitudes were experienced when the Froude number was equal to 1. Although this figure does not show a perfect relationship between each event's Froude number and meteotsunami amplitude, it provides enough evidence to illustrate that generally larger reflected meteotsunamis are formed by storm systems traveling over the continental shelf close to the shallow water wave speed. Since our value for the average shallow water wave speed is not changing, this figure shows that the amplitude of the meteotsunami drops relatively sharply if the storm system is traveling faster or slower than the shallow water wave speed. The meteotsunami amplitudes do however decrease less rapidly with increasing values of Fr over 1 as compared to decreasing values of Fr less than 1 (Figure 3).

4. Discussion

From Figure 4 the strongest relationship between the amplitude of air pressure disturbances and amplitude of meteotsunamis are seen at stations within close proximity of one another. This is an expected result, because storm systems effecting Rhode Island and New York will not always affect the New Jersey and North Carolina coasts. As for Duck, North Carolina there was no nearby NOAA meteorological station utilized for this study so a correlation between air pressure disturbance strengths and

Figure 5. Bar graph showing the average number of meteotsunami events per month from 2007 to 2014. This average is representative of a meteotsunami being recorded at any three of the NOAA tidal stations used during this study.

meteotsunami amplitudes is more difficult to deduce. This reasoning works well for in-situ meteotsunamis because when a strong pressure disturbance is above a meteorological station, the tidal stations nearby will also be affected. As for the reflected waves we found that sometimes there is an absence of a pressure anomaly recorded at the coastal stations. From radar images, it can be shown that storms can intensify and develop squall lines after they travel passed the NDBC meteorological stations, which prohibits any detection of a pressure disturbance. Despite the obstacles of reflected waves and a range of distances between meteorological and tidal stations, this figure shows that stronger pressure disturbances produce larger meteotsunami amplitudes.

Figure 4 also shows that maximum wind speeds within the storms seem to fluctuate seasonally. Winter months show increased max wind gust, which is an indication of increased storm strength. Figure 5 also shows December and March to have the largest frequency of events, while Figure 6 depicts larger amplitudes at Montauk and Atlantic City during these winter months. This would imply that, particularly for the more northern states, the increased occurrence and amplitude of meteotsunamis could be explained by increased storm strength seen during the winter months.

The overall frequency of events in this study was larger than previously reported. When comparing this study to the recent study done by Pasquet et al, 2013 in the same region

of coastline, our study analyzed the occurrence of meteotsunamis of a much wider range of amplitudes having only a minimum amplitude requirement of 0.1m. Even with this large range, meteotsunamis between 0.3m and 0.5m in amplitude were large contributors to the total number of events. The size of the average meteotsunami amplitudes did vary from station to station with Montauk having much smaller amplitudes than the other 2 stations (Figure 6, Figure 7). This could be due to varying geographical features, like bathymetry or shape the inlets or bays where these stations are located. These factors could lead to different amounts of topographic resonant effects that could either enhance or weaken each meteotsunami (Monserrat et al, 2006).

The Froude number analysis showed that, as expected, the largest reflected meteotsunami amplitudes occurred when the propagation speed of the pressure disturbance was closest to the shallow water wave speed (Figure 3). As storm velocity increases, past a Froude value of 1, we do not see a smooth decrease in the meteotsunami amplitude. This provides evidence that the amplitude of these meteotsunamis were not only dependent on storm speed, but most likely the strength of the pressure disturbance as well. The storms chosen for this analysis followed similar paths across the continental shelf, but did not all possess similar pressure disturbance amplitudes. This is the suspected cause of the irregular trend in meteotsunami amplitude as the Froude number increases.

Figure 6. Bar graph showing the average amplitude of meteotsunamis observed during each month from 2007 to 2014. Montauk is shown in black, Atlantic City, NJ in grey, and Duck, NC in white.

Figure 7. Histogram of the distribution of amplitudes from all meteotsunami events from 2007 to 2014. When any tidal station recorded a meteotsunami of 0.1m or greater, amplitudes of sea-level oscillations were recorded at all three stations. Because Montauk (black) predominately saw the smallest meteotsunami amplitude it sometimes recorded meteotsunami amplitudes of less than 0.1m. No meteotsunami amplitudes less than 0.1m were recorded as events at Atlantic City, New Jersey (grey) or Duck, North Carolina (white). For this reason all meteotsunamis less than 0.2m in size are represented in the 0.2m bin.

5. Conclusion

Meteotsunamis on the east coast of the United States are potentially dangerous when the right factors come together. The amplitude and propagation speed of moving surface pressure disturbances are two very important factors that contribute to the strength of meteotsunamis events. Storms with increasing pressure disturbance amplitudes caused a definite increase in the amplitudes of in-situ meteotsunamis when traveling over the stations used in this study. This trend is most likely seen over the continental shelf as well, but there is no data available to identify pressure disturbances on the continental shelf. From the utilization of the Froude number it can also be stated that the speed of the pressure disturbance and the path over the continental shelf it propagates along directly affects the amplitude of the meteotsunami that develops. This study proves that some coastal areas are more prone to large meteotsunamis than others, making topographic resonance another aspect to take into consideration when predicting the occurrence of hazardous meteotsunamis. When trying to predict meteotsunamis events, this study has shown that the combination of large pressure disturbances, traveling at the shallow water wave speed, as well as topographic resonant

factors along the coast can be a suitable indicator of the occurrence of a large meteotsunami.

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“Dirty” Deployments in Narragansett Bay: Polyethylene Uptake Rates of Persistent Organic Pollutants (POPs)

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Abstract. Persistent organic pollutants (POPs) released into the environment have been found harmful to human health and, under the stipulations of the 2001 Stockholm Convention Treaty, must be both regulated and researched. Methods used to measure concentrations of POPs in the water include passive polyethylene (PE) samplers, which are considered among the least expensive and most versatile sampling options currently available. However, when deploying PE samplers in the ocean, the use of perforated metal deployment cages may be necessary to protect the samplers from biofouling and physical harm. This study evaluates the effect of deployment cages on POP uptake rates (R_s) in passive polyethylene samplers located in Narragansett Bay, RI. The study focused on polycyclic aromatic hydrocarbons (PAHs), categorized as legacy POPs. It was determined that while dissolved PAH concentrations could be calculated without performance reference compounds (PRCs), there was no consistent relationship of uptake rates between thin samplers inside and outside the deployment cage and between thick and thin samplers inside the cage. These results indicated that site-specific conditions played a greater role in PAH uptake rates than previously assumed and that PRCs should continue being used in passive PE sampler analysis. Future directions for this research include comparison of the PAH uptake rate data to other types of POPs, such as polybrominated diphenyl ethers, organochlorine pesticides, and polychlorinated biphenyls.

1. Introduction

Persistent organic pollutants (POPs) are a diverse collection of carbon-based compounds that are known to be toxic and bioaccumulate.¹ They range from legacy contaminants, including organochlorine pesticides (OCPs), to emerging contaminants, such as polybrominated diphenyl ethers (PBDEs).^{1,2} While the 2004 Stockholm Convention Treaty on POPs has eliminated major global production of industrial POPs, chemical transport of POPs throughout Earth's atmosphere and oceans continues to cause concerns of exposure and accumulation, particularly in the Arctic.^{2,3} Developing a global distribution map of POP concentration would be expedient towards the advancement of international POPs policies and of regulatory communities.¹⁻³

Traditional methods for measuring dissolved concentrations of POPs, which are generally hydrophobic organic compounds (HOCs) frequently require difficult phase separation procedures, leading to the development of passive sampling.⁴ The earliest passive samplers were modeled after mussels, with Huckins's semipermeable membrane devices (SPMDs) containing triolein.^{4,6} Although the recovery of HOCs in these samplers has proven effective and the methods extensively studied, SPMDs are fragile and require additional cleanup steps in the laboratory, costing time, money, and equipment.^{4,7} One of the least expensive and most versatile options currently for passive sampling emerged in the early 2000s; low-density polyethylene (PE) sampling sheets sample HOCs in both the water and the atmosphere by diffusion into the plastic:

$$C_{w/a} = \frac{C_{PE}}{K_{PEw/a}} \quad (1)$$

where $C_{w/a}$ is the concentration of HOCs in the water or in the atmosphere, C_{PE} is the HOCs concentration in the polyethylene, and $K_{PEw/a}$ is the PE-water or the PE-air

partitioning coefficient at equilibrium.^{4,7-9} PEs obtain equilibrium (14-30 days) in the field faster than SPMDs, and the cleanup process is eliminated because PEs are not reused.

However, a disadvantage of PE samplers is that the plastic sheets have very little mass, which can cause difficulties during the extraction process. Thick polyethylene samplers with greater mass can be used for field sampling, but that may aggravate the issue of seasonal biofouling at some deployment sites. Biofouling, or the accumulation of organisms on objects in the water, can severely reduce the uptake rate of POPs into the PE samplers, making it take longer to reach equilibrium.^{10,11} The effects of biofouling are generally accounted for by using performance reference compounds (PRCs), which are assumed to dissipate at the same rate as the target compounds' uptake rate into the polyethylene; however, the process of spiking PEs with PRCs is a timely procedure and the use of PRCs released deuterated compounds into the environment. An alternative to PRCs is to reduce the overall level of biofouling using perforated metal deployment cages, which also protect the PE samplers from physical harm during deployment and retrieval. This study examines the effect of the deployment cage on the POPs sampling rates in both thick and thin polyethylene sheets and evaluates whether samplers can be deployed without performance reference compounds.

2. Polycyclic Aromatic Hydrocarbons (PAHs)

This study focused on polycyclic aromatic hydrocarbons (PAHs), a legacy POP mainly derived from petroleum and a common organic output of forest fires and engine emissions. PAHs can range from 2- to 6-ring families (Figure 1) and, although low molecular weight species are generally more abundant than high molecular weight species, all PAHs have carcinogenic and mutagenic properties. The increasing number of automobiles in use has increased the concentration of PAHs in the

atmosphere, which places humans at a high risk of exposure.¹²⁻¹⁵

Figure 1. Selected polycyclic aromatic hydrocarbons (PAHs): naphthalene, acenaphthylene, phenanthrene, pyrene, fluoranthene, benzo(a)pyrene, and benzo(g,h,i)perylene.¹³⁻¹⁴

3. Polyethylene Sampler Preparation

Thin polyethylene sheets (Figure 2A) were cut from commercial sheeting (Carlisle Plastics, Inc., Minneapolis, MN) with a thickness of 51 μm (10*30 cm strip of ~1-2 g each). PEs were precleaned twice overnight in dichloromethane (DCM). After precleaning, PEs were immersed in an 80:20 (v/v) MeOH/H₂O solution spiked with PRCs at a nominal concentration of 5 μg per sampler in MeOH for four days.¹⁷ Three deuterated PAHs were selected to act as PRCs: naphthalene-d₈, pyrene-d₁₀, and benzo[a]pyrene-d₁₂. Once spiked, PEs were strung on stainless steel wires, placed in precleaned aluminum foil packets, numbered, and frozen until the time of deployment in water. Several PEs were saved as laboratory blanks to determine initial PRC concentrations.⁸

Thick PE sheets (800 μm thickness, 10*30 cm strip of ~30-32 g each) were also purchased from commercial sheeting (Carlisle Plastics, Inc., Minneapolis, MN). PEs

(Figure 2B) were cleaned twice in DCM overnight, but no PRCs were used. Prior to deployment, the thick PEs were cut into two pieces (10*15 cm strip of ~15-16 g each) and analyzed separately. Previous studies have shown that LDPE thickness does not contribute to significant differences on partitioning coefficients,^{4,7,17} extraction procedures for both thick and thin PEs were the same for this study.

Each deployment cage (Figure 2C) had one whole thin PE sampler (10*30 cm) and one half thick PE sampler (10*15 cm) inserted inside and one thin sampler attached to the outside of the cage. At each sampling site, the deployment cages were positioned such that the cage was ~1 m below the water surface.

3. Sampling Site Descriptions

Two sets of samplers, inside and outside of the deployment cages, were placed out in Narragansett Bay in June 2014 (Figure 3). The first set of deployment cages was set up in Narragansett Bay (41° 49.2365 N, 71° 41.8943 W), off the dock at the University of Rhode Island (URI) Graduate School of Oceanography (GSO) for two weeks in June 2014. Narragansett Bay (NB), considered fairly shallow at a mean depth of 8.3 m, covers an area of ~300 km² and has a hydraulic residence time of 26 days. The bay is considered fairly saline (~25-31 psu), although the bay's two major passages receive freshwater input from urban rivers. The estuary is partially mixed, with stratification occurring during the summer months.^{8,18} The second set was deployed in Greenwich Bay (41° 40.304 N, 71° 36.563 W) for two weeks in June 2014. Greenwich Bay (GB) is a semi-enclosed estuary within NB that covers an area of 9.8 km² with an 8.8 day residence time, and the Warwick Neck peninsula blocks large amounts of NB main flow water from entering the bay.¹⁹

Figure 2. (Top left) Thin polyethylene sampling sheet, (bottom left) thick polyethylene sampling sheet, and (right) 2 ft. perforated metal deployment cages.

Figure 3. Sampling sites in Narragansett Bay, off of the GSO dock at the University of Rhode Island (bottom star) and at Greenwich Bay (top star).

4. Methods

4.1 PAH Analysis

All glassware used was combusted for 4 h at 450°C and all utensils were triple-rinsed with methanol (MeOH), acetone (Acet), and *n*-hexanes (Hex) before and between uses. Solvents were purchased from Fischer Scientific.

Deuterated surrogate recovery standards (20.0 ng OCPs, 20.0 ng PCBs, 20.0 ng PBDEs, 25.0 ng PAHs) were added to the samplers prior to the PE sampler extraction in Hex (100 mL) for at least 18 h. The extracts were then concentrated under nitrogen gas in a TurboVap II concentrator before being purified on sodium sulfate and silica gel columns (1:1 DCM:Hex). The extracts were concentrated down to less than 200 µL and placed in GC vials with inserts in preparation for GC analysis.²⁰ P-terphenyl-d₁₄ (200.0 ng) was used as the internal standard.

PAH analysis was conducted on an Agilent 6890 gas chromatograph (GC) with an Agilent 5973N mass spectrometer (MS) operated in the negative electron ionization mode in selected ion monitoring (SIM) mode (60 min). Chromatograms were integrated by hand and calibration curves were made for each PAH analyzed in GCMS-SIM mode using concentrated standards (0.01 ng/µL, 0.05 ng/µL, 0.1 ng/µL, 0.5 ng/µL, 1.0 ng/µL, 5.0 ng/µL, 10.0 ng/µL).⁸

4.2 Calculating Dissolved PAH Concentrations

The dissolved POPs concentrations in the water (C_{diss}) can be an important calculation for assessing biological exposure. For the thin polyethylene samplers with performance reference compounds (PRCs), the dissolved POP concentrations can be calculated using the overall *in situ* site-specific loss constant with Equation 2:⁷

$$k_e = \ln\left(\frac{C_{PRC,t=0}}{C_{PRC,t}}\right) * t^{-1} \quad (2)$$

where k_e is the site-specific loss (1/day), $C_{PRC,t=0}$ is the initial PRC concentration in the polyethylene (ng/µL), $C_{PRC,t}$ is the post-deployment PRC concentration (ng/µL), and t is the overall deployment time (days). k_e is then applied to Equation 3:⁷

$$C_{diss} = \frac{C_{PE}}{K_{PEW} * (1 - e^{-k_e * t})} \quad (3)$$

where C_{diss} is the dissolved POP concentration at the sampling site (pg/L), C_{PE} is the normalized POP concentration in the polyethylene (pg/kg), and K_{PEW} is the polyethylene-water partitioning coefficient. A second aspect of the PRC concentrations is the ability to calculate how equilibrated the PE samplers have become during the deployment period, with Equation 4:⁹

$$\% \text{ equilibrium} = \left(\frac{C_{PRC,t=0} - C_{PRC,t}}{C_{PRC,t=0}} \right) * 100 \quad (4)$$

This information is necessary because it is easier to calculate the dissolved POPs concentrations at equilibrium than during the equilibration period, as shown by Equation 3. However, not every PE sampler used in this experiment was spiked with PRCs prior to deployment. Lohmann et. al (2013) proposed an alternate method of calculating C_{diss} with Equation 5:²⁰

$$C_{diss} = \frac{C_{PE}}{K_{PEW} * (1 - e^{-\frac{R_s * t}{K_{PEW} * v}})} \quad (5)$$

where R_s is the POP uptake rate (L/day) and v is the sampler volume (L). An equation for calculating R_s was proposed from Khairy and Lohmann (2014):⁹

$$R_s = \frac{C_{PE}}{t * K_{PEW}} \quad (6)$$

although Equation 6 is modified from the original in that K_{PEa} is substituted for K_{PEW} . While the original R_s equation was effective for atmospheric samples, it was unknown whether the same concept could be applied to water samples. The equilibrium values for each individual POP can also be calculated without using PRCs:⁹

$$\% \text{ equilibrium} = \left(1 - \exp\left(\frac{-R_s * t}{K_{OW} * V_{PE}}\right) \right) * 100 \quad (7)$$

where K_{OW} is the octanol-water partitioning coefficient.

5. Results and Discussion

5.1 Sampler PAH Concentrations

Table 1. Equilibrium states for individual PAHs in samplers deployed at Narragansett Bay and Greenwich Bay calculated using Equation 7. Asterisk (*) denotes samplers that collected PAHs from sediment porewater. 51OUT=thin PE, outside cage; 51IN=thin PE, inside cage; 800IN=thick PE, inside cage; ND=not detected.

PAH	Narragansett Bay			Greenwich Bay		
	51OUT	51IN	800IN	51OUT	51IN*	800IN
Naphthalene	100%	100%	100%	100%	100%	100%
Biphenyl	100%	100%	100%	100%	ND	100%
Acenaphthene	100%	100%	100%	100%	100%	100%
Acenaphthylene	100%	100%	100%	100%	100%	100%
Fluorene	100%	100%	100%	100%	100%	100%
Dibenzothiophene	100%	100%	100%	100%	100%	100%
Phenanthrene	100%	100%	100%	100%	100%	100%
Pyrene	100%	100%	100%	100%	100%	100%
Fluoranthene	100%	100%	99.4%	100%	100%	100%
Retene	100%	96.8%	ND	ND	10.1%	ND
Benz(a)anthracene	92.7%	16.6%	2.1%	97.1%	67.2%	17.6%
Chrysene	75.0%	19.7%	2.9%	49.1%	30.2%	3.8%
Perylene	96.9%	26.3%	3.0%	99.9%	97.3%	39.8%
Benzo(a)pyrene	54.0%	5.2%	30.2%	66.6%	72.6%	16.1%
Benzo(g,h,i)perylene	6.5%	1.5%	0.1%	4.1%	2.1%	0.1%
Indeno(1,2,3-c,d)pyrene	8.6%	5.2%	0.7%	6.3%	2.4%	0.7%

Table 2. Optimized site rate (L/day), calculated using Equation 7 and PRC concentrations in field samplers and procedural blanks. Asterisk (*) denotes samplers that collected PAHs from sediment porewater. 51OUT=thin PE, outside cage; 51IN=thin PE, inside cage; NB=Narragansett Bay; GB=Greenwich Bay.

Sampler	Percent Loss	Predicted Loss	Site Rate (L/day)
NB 51OUT: naphthalene-d8	93.7%	100%	133.0
NB 51OUT: pyrene-d10	76.6%	99.9%	
NB 51OUT: benzo(a)pyrene-d12	62.0%	62.0%	
NB 51IN: naphthalene-d8	97.4%	100%	137.9
NB 51IN: pyrene-d10	76.8%	99.9%	
NB 51IN: benzo(a)pyrene-d12	63.3%	63.3%	
GB 51OUT: naphthalene-d8	96.5%	100%	227.2
GB 51OUT: pyrene-d10	95.9%	99.9%	
GB 51OUT: benzo(a)pyrene-d12	80.8%	80.8%	
GB 51IN: naphthalene-d8*	91.3%	100%	175.2*
GB 51IN: pyrene-d10*	92.1%	100%	
GB 51IN: benzo(a)pyrene-d12*	63.6%	63.6%	

Table 3. Dissolved concentrations for select PAHs inside and outside the deployment cage using Equation 5 and the optimized uptake rate values from Table 2. The optimized rate inside the cage for the thin PE samplers has been applied to the thick samplers. Asterisk (*) denotes samplers that collected PAHs from sediment porewater. 51OUT=thin PE, outside cage; 51IN=thin PE, inside cage.

PAH	Narragansett Bay: C _{diss} (pg/L)			Greenwich Bay: C _{diss} (pg/L)		
	51OUT	51IN	800IN	51OUT	51IN*	800IN
Acenaphthene	696.4	355.8	145.8	497.0	545.2*	164.0
Pyrene	611.7	504.1	212.8	547.6	452.7*	507.5
Benzo(a)pyrene	596.0	408.2	2158.3	841.2	9909.0*	1055.2

Four distinct sampler categories were defined: thin PE outside the deployment cage (51OUT), thin PE inside the cage (51IN), thick PE inside the cage (800IN), and the procedural blank (PB). Narragansett Bay (NB) samplers and

Greenwich Bay (GB) samplers are distinguished from one another.

After calculating the concentration of each individual PAH (ng/ μ L) in the GC vial with the calibration curves, the total PAH distribution (ng) was derived for each sampler

category (Figure 4), of which the 800IN samplers collected the greatest total mass of PAHs of the four sampler categories. The normalized PAH concentrations (ng/g) by sampler mass provided a clearer comparison of the Narragansett and Greenwich Bay data per sampler category (Figure 5). For 51OUT, 800IN, and PB categories, the comparable normalized concentrations indicated that similar amounts of PAHs were sampled between the two sites, which matched with literature values.⁸ The poor correlation between the NB-51IN and GB-51IN samplers likely occurred because it was discovered that the bottom section of the GB-51IN samplers had been submerged in the sediment during the deployment period, such that the PAHs collected were from both sediment porewater and water and therefore not compatible to the passive water polyethylene samplers.

5.2 PRC-Calculated vs. Uptake Rate-Calculated C_{diss}

There is very little deviation of data from the linear 1:1 curve between the PRC-calculated C_{diss} and the rate-calculated C_{diss} (Figure 6), suggesting that Equation 6 can indeed be applied. This indicates that Equation 5 provides effective C_{diss} values when using R_s values calculated from Equation 6, such that Equation 6 R_s outputs are also reliable for PE samplers deployed both inside and outside the deployment cages. Use of Equation 7 to calculate individual PAH equilibrium states (Table 1) further suggests that PRCs

may not be required for polyethylene analysis.

5.3 Thin Polyethylene: Outside vs. Inside

For direct comparison of the thin polyethylene sheets inside versus outside the deployment cage, Equation 7 was used to calculate the optimized uptake rate, specific to each PE sampler, with equilibrium values derived from PRC concentrations (Table 2). The normalized concentrations (ng/g) were calculated using procedural blanks, rather than field blanks. For the samplers deployed off of the GSO dock (NB), the optimized uptake matched very closely, with NB-51OUT equal to 133.0 L/day and NB51IN slightly higher at 137.9 L/day. However, when the optimized uptake rates were applied to Equation 5, it was found that there was low agreement between dissolved PAH concentrations for select PAHs (acenaphthene, pyrene, and benzo(a)pyrene) between the 51OUT and 51IN samplers (Table 3). This information, in addition to the disparity of the optimized Greenwich Bay uptake rates (GB-51OUT = 227.2 L/day, GB-51IN = 175.2 L/day), indicated that site-specific conditions play a stronger role in POP sampling rates than previously thought and that PRCs should continue being used for polyethylene analysis, in contrast to the results of Figure 6 and Table 1.

This conclusion was supported by the log transform of the 51OUT R_s values plotted against 51IN R_s values (Figure 7) because the slopes between Narragansett and Greenwich Bay samplers differ significantly. Had the slopes been

Figure 4. Total PAH mass accumulated by sampler category and deployment location. NB=Narragansett Bay; GB=Greenwich Bay.

Figure 5. Normalized PAH concentrations to polyethylene sampler mass. The thin PE samplers inside the deployment cage at Greenwich Bay were not used for further analysis.

Figure 6. PRC-calculated dissolved PAH concentrations (pg/L) plotted against rate-calculated dissolved PAH concentrations (pg/L). The linear 1:1 curve is present to show that the two methods for C_{diss} calculations match well.

Figure 7. Log transform plot comparing the uptake rates (L/day) of the thin PE inside the deployment cage and of the thin PE outside of the deployment cage. Narragansett Bay: $y=1.04(\pm 0.07)x - 0.13(\pm 0.09)$, $r^2=0.94$, $SE=0.33$. Greenwich Bay: $y=0.79(\pm 0.08)x + 0.32(\pm 0.10)$, $r^2=0.87$, $SE=0.38$.

Figure 8. Log transform plot comparing the uptake rates (L/day) of the thick PE inside the deployment cage and of the thin PE inside of the deployment cage. Narragansett Bay: $y=1.13(\pm 0.12)x - 0.19(\pm 0.15)$, $r^2=0.87$, $SE=0.59$. Greenwich Bay: $y=1.46(\pm 0.14)x - 0.54(\pm 0.14)$, $r^2=0.89$, $SE=0.54$.

similar, that would have indicated that a generic POPs sampling rate could be derived from thin PE samplers inside the deployment cages. Instead, site-specific variations have a large enough impact that performance reference compounds should continue being used in passive PE sampling.

5.3 Thin and Thick Polyethylene Comparison

The next portion of the study was to compare the POPs uptake rates of the thin and thick PE samplers inside the

deployment cages. A log transform of the 51IN R_s values plotted against 800IN R_s values (Figure 8) showed similar results as Figure 7 in that the Narragansett and Greenwich Bay sampler slopes differ significantly. The contrasting sampling rates and C_{diss} values (Table 3) between 51IN and 800IN again demonstrate that site-specific conditions play the greatest role in determining POP uptake rates into the polyethylene samplers.

6. Conclusion

The results of this study show that while thick polyethylene passive samplers can be used in field deployment cages without performance reference compounds and can be accurately analyzed to calculate the concentrations of freely dissolved POPs, it is advisable to continue using PRCs in PE analysis due to the influence of site-specific conditions on POP uptake rates. Future directions include analyzing the PEs for other types of POPs, including polybrominated diphenyl ethers, organochlorine pesticides, and polychlorinated biphenyls, and then comparing the PAH uptake rate data.

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Multi-decadal Variability in *Mnemiopsis leidyi* (Ctenophora) Abundance in Narragansett Bay: Climate Change or Prey Mediated?

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Abstract. The mean temperature of Narragansett Bay has increased roughly 2°C since the early 1980's. Although small, this increase in water temperature may affect the population dynamics of indigenous animals in the Bay. Due to the warming of Narragansett Bay, the ctenophore, *Mnemiopsis leidyi*, has been reportedly blooming earlier in the year and increasing in abundance. To investigate these changes, three data sets were analyzed: two transect series from 1982 and 1985-1987, and a 40-year time series with data from 1972-2010 at Station 2 located in the lower West Passage of the Bay. There was no apparent long-term increase in abundance or shift in phenology over the 40-years of sampling, nor was there a strong correlation between temperature and *M. leidyi* abundance. *Mnemiopsis leidyi* typically bloomed in the summer months but also bloomed in the winter months. The transect data showed an inverse relationship between *M. leidyi* and zooplankton abundance, and this relationship was found to occur throughout the bay. *Mnemiopsis leidyi* abundance was exceptionally variable both temporally and spatially. Since there was no discernable relationship between *M. leidyi* variance and the increase in water temperature, the inverse relationship between *M. leidyi* and zooplankton better explains the variability in *M. leidyi* abundance. Therefore, it is suggested that prey mediation instead of climate change (i.e. warming) is affecting the multi-decadal and annual variability of *M. leidyi* abundance in Narragansett Bay.

1. Introduction

The lobate ctenophore, *Mnemiopsis leidyi*, has received much attention for its ability to alter planktonic ecosystems through predation whilst also tolerating a wide range of physical factors such as temperature and salinity (Salihoglu et al. 2011; Costello et al. 2012). The majority of the studies focusing on *M. leidyi* have been conducted in the Mediterranean, Black, and Caspian Seas, where *M. leidyi* has proliferated as an invasive species and devastated planktonic ecosystems and local fisheries (Costello et al. 2012). Although *Mnemiopsis leidyi* is indigenous to Narragansett Bay, RI (Kremer & Nixon 1976), it is still important to understand the population dynamics of the ctenophore in its home range. *Mnemiopsis leidyi* is known as a boom-and-bust species because its abundance increases in the summer months (May – October) and plummets in the winter months (November – April) (Kremer & Nixon 1976; Deason 1982; Sullivan et al. 2001; Costello et al. 2006a; Costello et al. 2006b; Costello et al. 2012; Beaulieu et al. 2013). One of the reasons for the bloom is that warm water temperature can increase the growth rate of *M. leidyi* (Robinson & Graham 2014). During the time of the ctenophore bloom, the Bay dynamics can change because the ctenophore blooms are a large sink for carbon, nitrogen and phosphorus (Pitt et al. 2009) and can release grazing pressure on phytoplankton, causing algal blooms (Deason & Smayda 1982a). The inter- and intra-annual variability of *M. leidyi* abundance is controlled by a combination of factors such as prey availability, temperature and mortality (Kremer 1994). Since many of the common predators of *M. leidyi* (e.g. the ctenophore *Beroë ovata*) are not indigenous to Narragansett Bay, the two main factors that could control the variability of *M. leidyi* abundance are prey availability and temperature.

The inverse relationship between *Mnemiopsis leidyi* and zooplankton is well documented in Narragansett Bay (Kremer 1979; Deason 1982; Deason & Smayda 1982a; Deason & Smayda 1982b; Sullivan et al. 2007). During the beginning of late spring/early summer, the summer

copepod, *Acartia tonsa*, abundance increases as its resting cystic eggs hatch from the bottom of the Bay (Sullivan et al. 2007). *Mnemiopsis leidyi* abundance starts to increase in the summer months and *A. tonsa* abundance subsequently decreases due to predation by *M. leidyi* (Deason 1982). Although *M. leidyi* blooms result in a substantial decline of *A. tonsa* population size, *M. leidyi* bloom size is dependent on copepod abundance prior to the ctenophore bloom (Deason & Smayda 1982a; Kremer 1994). While prey availability is an important determinant of *M. leidyi* abundance, its abundance is also affected by the annual oscillation of temperature (Kremer 1994; Costello et al. 2006a; Costello et al. 2006b; Costello et al. 2012). During the cold winter months, *M. leidyi* overwinters in shallow embayments situated in the upper portion of the Bay (Costello et al. 2006a; Beaulieu et al. 2013), and starts to reproduce once surface water temperature is warm enough (~10°C) (Costello et al. 2006b; Salihoglu et al. 2011; Costello et al. 2012). Since the shallow embayments warm earlier in the year, *M. leidyi* found in the upper bay reproduce earlier in the year and reach a higher maximum abundance (Kremer & Nixon 1976; Deason 1982; Costello et al. 2006b). These upper bay sites are said to be the source population for *M. leidyi* since the ctenophores can be transported downstream through advection (Costello et al. 2006b).

The surface water temperature in Narragansett Bay has risen roughly 2°C since the early 1980's (Nixon et al. 2004; Costello et al. 2006b), which affects the population dynamics of the animals in the bay whose annual cycles are controlled by temperature (Sullivan et al. 2007). The current hypothesis of *M. leidyi* response to bay warming is that ctenophore abundance is increasing yearly (Sullivan et al. 2001; Link & Ford 2006) and blooms are occurring earlier (Sullivan et al. 2001; Costello et al. 2006a). The combination of both increased abundance and shifted phenology can result in a drastic decline of *A. tonsa* abundance (Costello et al. 2006b). However, there is conflicting evidence towards this hypothesis. For example,

the global increase of jellyfish and ctenophores has been widely accepted (Brotz et al. 2012; Purcell 2012) but when further analyzed Condon et al. (2012) found no concrete evidence to confirm a global increase of jellyfish and ctenophores. Lucas et al. (2014) found a positive linear regression between temperature and both Thaliacea and Cnidaria abundances, but no correlation between temperature and Ctenophora abundance. Additionally, many of the studies conducted in Narragansett Bay were short-term studies, which could miss long-term ctenophore abundance fluctuations (Condon et al. 2012). Because of this conflicting evidence, I used three data sets to investigate whether the variability in *M. leidyi* abundance is an effect of temperature or prey availability.

2. Materials and Methods

2.1. Time series data set

From 1972 to 2010, surface temperature was measured and ctenophore abundance sampled at Station 2, located in the lower West Passage of Narragansett Bay ($41^{\circ} 34' 07''$ N, $71^{\circ} 23' 31''$ W) (Figure 1). Station 2 is an open bay station that has a depth of 8m. Ctenophore abundance and temperature data were collected weekly from 1972 to 1997, and then after a 7-year gap from 2005 to 2010. During the 1972 to 1997 collections, the first 12 years (1972-1983) were only sampled during the summer to late fall months and after 1983, the samples were collected weekly. For the samples collected in the 1972 to 1997 period, the ctenophores were collected using a 1mm mesh net with a 1m x 1m square frame towed vertically off the stern of the boat. Once the net was pulled on-board, the ctenophores

Figure 1. Station 2 is located in the lower West Passage of Narragansett Bay. This was the location where the long-term data set (1972-2010) samples were taken.

were counted (number m^{-2}) and biovolume recorded ($mL m^{-2}$). Temperature data was measured to the nearest $25^{\circ}C$ using a Fisher Scientific thermometer. The 2005 to 2010 ctenophore and temperature data was obtained from the public GSO URI plankton website (www.gso.uri.edu/phytoplankton).

Figure 2. In Narragansett Bay, the locations of the 7 stations used in both transect data sets, 1982 and 1985-1987, are located on the west Passage of the Bay.

2.2. Transect data sets

This study used two transect data sets, one from June to October 1982, and the other from July 1985 to June 1987. Both data sets included samples collected at 7 stations in the west Passage of the Bay (Figure 2). Station 1 was located in Greenwich Bay Cove, a sheltered embayment. Both Stations 2 and 3 were located in the mouth of the Providence River and are shallow embayments, with freshwater input from the river. Station 4 was located south of Nayatt Point and was the deepest station with a depth of 14m. Station 5 was the most dynamic station because it was located in the juncture of where the Providence River flowing southward and the East Passage flowing northwestward meet. Stations 6 and 7 were located in the lower West Passage and are open-bay stations. For the 1982 data set, ctenophores were sampled every three days from June to October. Ctenophores were sampled using vertical hauls of a 1mm mesh net with a 1m x 1m square frame. The ctenophores were measured using displacement volume ($mL m^{-3}$). Zooplankton were collected using

replicate double oblique tows pulled behind the boat at 1-2 knots. The net had a 0.30 m opening and 153 μm mesh size, and was equipped with a calibrated General Oceanics flow meter. The zooplankton were preserved in 5% buffered formalin and split with a plankton splitter. One half was counted to the highest possible taxonomic category and the other half was processed for dry weight estimation. For the 1985-1987 transect data, ctenophores and zooplankton were sampled using the same protocol as in 1982.

2.3. Data analysis

The time series data set from Station 2 was used to analyze the variability in ctenophore abundance over time and the long-term relationship between ctenophore abundance and temperature. To analyze the annual variability of ctenophore abundance, the yearly maximum ctenophore abundance was regressed against time. Maximum ctenophore abundance was used due to it being the only metric uniform throughout the data. The week *M. leidyi* reached its maximum abundance for each year was

Figure 3. Maximum ctenophore abundance is regressed against time, from 1972-2010. The black line is the regression line. Note the gap between 1997 and 2005 was a period with no data from the long-term data set. There was no significant linear relationship between year and maximum ctenophore abundance (number m⁻²) ($R^2 = 0.02$, $df = 27$, $P\text{-value} > 0.05$).

Figure 4. The week at which *M. leidyi* reached maximum abundance is regressed against time, from 1972-2010. The black is the regression line. There is a gap from 1997 to 2005 because there was no data present in the data set. There was no significant linear relationship between peak week and time ($R^2 = 0.01$, $df = 27$, $P\text{-value} > 0.05$).

regressed against time. A one-way ANOVA was run to look at yearly mean ctenophore abundance by month, and a Tukey HSD was used to analyze which pair-wise comparison had significant variance. The maximum abundance in the time series recorded for each month was examined to determine whether there was a particular month when *M. leidyi* was absent.

To analyze the relationship between ctenophore abundance and temperature, a couple of approaches were used. The first approach was a regression of ctenophore abundance against temperature for each year in the data set, and then by month, with the data compiled from all years. That effort analyzed the linear relationship of ctenophore abundance over time. Next, years were divided as either hot or cold using three parameters: average temperature, maximum temperature and minimum temperature of each year. A hot year was defined as one in which the temperature was above the average temperature for each of the three parameters (i.e., average, maximum or minimum) and a cold year was defined as having a temperature below the average temperature for the same temperature categories. For all years, the maximum abundance and the week at which the maximum abundance occurred were recorded. Six one-way ANOVAs were run with average temperature, maximum temperature and minimum temperature as the three independent variables, and

maximum abundance and peak week as the dependent variables. For each ANOVA, a Tukey HSD was run to analyze the pair-wise comparison within the ANOVA. Since the data was not normally distributed, a non-parametric Wilcoxon test was run to analyze the data with assumptions of non-normality.

The two transect data sets were used to analyze the relationship between ctenophore abundance and zooplankton abundance. For each data set, the zooplankton abundance was regressed against ctenophore abundance. To visually analyze the data, ctenophore and zooplankton abundance over time were plotted on seven graphs for all seven stations. For the 1982 data set, ctenophore and zooplankton abundance vs. time were graphed using the entire data set. Since the 1985-1987 data set was longer, three sets of graphs were made for each station. The first graphed zooplankton and ctenophore abundance for the entire time of sampling, the second only included data from 1986, and the third included the data from the same months that the 1982 sampled. All statistics were run using the statistical program JMP 10.0 and graphs were made in Excel Version 14.4.2.

3. Results

3.1. Time series data set

Figure 5. This is the plot of the maximum abundance of ctenophores recorded for each month out of the entire set. Note that the y-axis is in a log scale. The graph shows that *M. leidyi* can be present at any time of the year.

The variability in ctenophore abundance over time regressed against the yearly maximum in *Mnemiopsis leidyi* abundance showed no statistically significant linear relationship between maximum abundance and time during 1972-2010 ($R^2 = 0.02$, $df = 27$, $P\text{-value} > 0.05$) (Figure 3). There was no linear relationship between the week at which maximum ctenophore abundance occurred and time ($R^2 = 0.01$, $df = 27$, $P\text{-value} > 0.05$) (Figure 4). The one-way ANOVA revealed that there was a statistically significant difference in ctenophore yearly mean abundance for the months of January (f ratio = 2.561, $df = 67$, $P\text{-value} < 0.01$), April (f ratio = 1.875, $df = 64$, $P\text{-value} < 0.05$), August (f ratio = 1.625, $df = 106$, $P\text{-value} < 0.05$), September (f ratio = 1.800, $df = 96$, $P\text{-value} < 0.05$) and October (f ratio =

Figure 6. Ctenophore and zooplankton abundance plotted against time for 1982. Top to bottom, Station 1 through 4.

5.576, $df = 90$, $P\text{-value} < 0.0001$). The Tukey HSD showed that in January, April, September and October, the year that was most variant statistically was 1993, 1997, 2006, and 2005, respectively (all $P\text{-values} < 0.05$). For many of the years, *M. leidyi* abundance increased in the summer months and declined in the winter months such as 1988. However, some years did not follow this pattern and ctenophore abundance was high during the winter months (e.g. 1995). The maximum abundance ever recorded for each month revealed that *M. leidyi* can be present at any month of the year (Figure 5).

Collectively, the data showed that the relationship between ctenophore abundance and temperature was not strong. In the regression analysis of ctenophore abundance vs. temperature for each year, only 8 out of 30 years had a statistically significant linear relationship between

ctenophore abundance and temperature. The 8 years with a significant correlation between *M. leidyi* abundance and temperature were 1975 ($R^2 = 0.28$, $df = 15$, $P\text{-value} < 0.05$), 1981 ($R^2 = 0.39$, $df = 10$, $P\text{-value} < 0.05$), 1988 ($R^2 = 0.19$, $df = 30$, $P\text{-value} < 0.05$), 1989 ($R^2 = 0.15$, $df = 46$, $P\text{-value} < 0.01$), 1990 ($R^2 = 0.37$, $df = 25$, $P\text{-value} < 0.001$), 2006 ($R^2 = 0.45$, $df = 42$, $P\text{-value} < 0.0001$), 2008 ($R^2 = 0.10$, $df = 49$, $P\text{-value} < 0.05$) and 2009 ($R^2 = 0.10$, $df = 26$, $P\text{-value} < 0.05$). All six of the ANOVAs showed no statistical significance for both the maximum abundance and peak week for each of the temperature categories (average, maximum and minimum) (all $P\text{-values} > 0.05$) and the Tukey HSD showed that none of the pair-wise comparisons were significantly different ($P\text{-value} > 0.05$). The non-parametric Wilcoxon test showed that there was a statistically significant difference in maximum ctenophore abundance when

Figure 7. Ctenophore and zooplankton abundance plotted against time for 1982. Top to bottom, Station 5 through 7.

grouped by minimum temperature ($P < 0.01$).

3.2. Transect data sets

Both transect data sets showed an inverse relationship between ctenophore and zooplankton abundance. In the 1982 data set, there was a statistically significant negative linear relationship between ctenophore and zooplankton abundance ($R^2 = 0.05$, $df = 163$, $P < 0.01$). The graphs constructed from the 1982 data set also revealed an inverse relationship for ctenophore and zooplankton abundance at all 7 stations (Figures 6-7). In the 1985-1987 data set, there was also a statistically significant negative linear relationship between ctenophore and zooplankton abundance ($R^2 = 0.02$, $df = 402$, $P < 0.01$). There was an indication of a winter bloom for both the winters of 1985-1986 and 1986-1987, where *M. leidy* abundance declined around December, increased in January and then decreased again in March. During the decline in March, the winter copepod *A. hudsonica* was abundant, but *M. leidy* abundance did not increase again until *A. tonsa* was abundant (Figure 8).

4. Discussion

Throughout the 40 years of data, there was no discernable relationship between *M. leidy* abundance and temperature. Although Narragansett Bay has warmed over the past 30 years, the expected response of *M. leidy* to climate change as put forth in Sullivan et al. (2001) and Costello et al. (2006a), did not occur. *Mnemiopsis leidy* did not bloom earlier in the year, nor was there a significant increase in abundance. This lack of a response was not surprising because the time series data showed that

temperature did not entirely control the variability in *M. leidy* abundance. The years when *M. leidy* maximum abundance was the highest did not correlate with the warmest years, and *M. leidy* was present and bloomed during winter months. The size of the winter blooms were smaller than the size of the summer blooms, but in some years the maximum abundance did occur in the winter (e.g. 1995). Interestingly, despite the winter bloom size, *M. leidy* abundance always decreased during March, which was the month bay temperature began to increase.

Since temperature did not appear to control the variability in *M. leidy* abundance, prey abundance was the most suitable factor. The two transect data sets confirmed the previously reported inverse relationship between ctenophore and zooplankton abundance (Kremer 1979; Deason 1982; Deason & Smayda 1982a; Deason & Smayda 1982b; Sullivan et al. 2007) and showed that the inverse relationship occurs bay-wide. Costello et al. (2006b) also found the inverse relationship between ctenophore and zooplankton abundance and argued that due to top-down control of *M. leidy* on *A. tonsa*, the population of the summer copepod has been decimated in the past years. However, Smayda & Borkman (unpublished data) have recently shown that *A. tonsa* abundance has increased over the past 20 years (Figure 9), irrespective to the grazing pressure of *M. leidy*. Therefore, the abundance of *M. leidy* could be controlled by the abundance of zooplankton. Both Deason & Smayda (1982a) and Kremer (1994) found that the size of the zooplankton population prior to ctenophore bloom could be indicative of the ctenophore bloom size. In a model study, Salihoglu et al. (2011) showed that without sufficient food, the rate of increase for each *M. leidy* life stage was stalled. Furthermore, Kremer & Reeve (1989)

Figure 8. Data from Station 1 in the transect data. This Station was exemplary of the general pattern seen throughout all 7 stations. Ctenophore abundance is on the first y-axis and copepod abundance is on the second y-axis. Time is plotted on the x-axis and the dates are from the year 1986.

discovered that reproductive sized ctenophore population was sustained with a minimum prey concentration of 8 prey L^{-1} . Since prey availability is important for *M. leidy* survival and reproduction, it is a selective predator (Sullivan 2014) and strong competitor (Reeve et al. 1978). *Mnemiopsis leidy* can feed at night to take advantage of nocturnal prey (Sullivan 2014) and vertically migrate to lower depths where it encounters higher prey concentration (Haraldsson et al. 2014). Turbulent water can reduce the efficiency of prey capture, so *M. leidy* can also vertically adjust its position in the water column to escape conditions that hinder prey capture (Sutherland et al. 2014).

In many papers focusing on ctenophore abundance and climate change, prey availability is a factor that is usually overlooked or explained as a casualty from the increase in *M. leidy* abundance. However, it is important to view prey availability as a factor that can affect ctenophore abundance, as it is an important component in every life stage of *M. leidy*. While adult *M. leidy* are strict carnivores that consume mesozooplankton (Deason & Smayda 1982b), larval *M. leidy* graze upon the microplankton (Sullivan & Gifford 2004). The taxonomic composition and abundance of the microplankton assemblage can affect the survival of larval *M. leidy*, which in turn can determine the success and timing of adult *M. leidy* blooms (Sullivan & Gifford 2004). The grazing pressure on the mesozooplankton by adult *M. leidy* can also initiate a positive feedback loop: reduced mesozooplankton decreases the grazing pressure on the microplankton, which increases the prey abundance for larval *M. leidy* (McNamara et al. 2013). Although this study did not look at the microplankton assemblage, it is important to note that microplankton abundance could also have affected the variance in ctenophore abundance.

The results of this study are conflicting with prior studies in Narragansett Bay (Sullivan et al. 2001; Costello et al. 2006a; Costello et al. 2006b), which highlight the importance of using different sampling methods. Most of the studies on *M. leidy* abundance used double-oblique tows with a circular net but this study and a few others (e.g., Deason & Smayda 1982a) used the 1m x 1m square net for a vertical tow. The time series data used the abundance measurement of numbers m^{-2} and the transect data used the abundance measurement of biovolume, $mL m^{-2}$. Kremer & Nixon found that biovolume could be a misleading measurement because water makes up the majority of ctenophore mass (Kremer & Nixon 1976). Also, the amount of ctenophores sampled could vary between a vertical tow with a square net and an oblique tow with a circular net. The discrepancy between different sampling methods is one that should be solved as it could lead to different results. Nonetheless, my results were consistent throughout the three data sets, which included both sampling methods and abundance measurements.

5. Conclusion

Prey availability rather than sea surface temperature affects the variability in *Mnemiopsis leidy* abundance. My data showed a clear inverse relationship between zooplankton abundance and ctenophore abundance, but no discernable relationship between temperature and ctenophore abundance. Despite the increase in sea surface temperature in Narragansett Bay, contrary to popular belief, *M. leidy* abundance has not increased, nor has it started to bloom earlier in the year. All three data sets showed a clear winter presence of *M. leidy* as well as the possibility of

Figure 9. The abundance of both *Acartia hudsonica* and *A. tonsa* are regressed against time. There was no significant increasing trend in *A. hudsonica* abundance (P -value > 0.05) but there was a significant increasing trend in *A. tonsa* abundance (P -value < 0.05) [Smayda and Borkman, unpublished].

winter blooms. The ability of *M. leidyi* population to bloom is dependent on the amount of zooplankton present, and this is likely to be the causative factor in the variability in *M. leidyi* abundance. Temperature increase in Narragansett Bay could increase zooplankton abundance and, thus, indirectly increase ctenophore abundance.

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Revisiting Antarctic Circumpolar Current Estimates

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Abstract. The Antarctic Circumpolar Current (ACC) is the world's strongest current, and acts as a conduit that transports water between Atlantic, Pacific, and Indian Oceans. ACC transport is a key metric used to evaluate the accuracy of ocean and climate models. The canonical transport of 134 Sv through Drake Passage, the narrowest choke point of the ACC, derives from a year-long experiment conducted in 1979 (DRAKE79). Recent studies suggest that this historical value may be biased low by as much as 20%. DRAKE79 transport estimates resulted from a complicated synthesis of historical data and *in-situ* measurements, and relied heavily on the outcome of referencing three hydrographic sections with directly measured currents. This study focuses on evaluating DRAKE79's geostrophic referencing technique. We hypothesized that the horizontal spacing and temporal averaging of current meters led to a bias in the historical estimate. Southern Ocean State Estimate (SOSE) was used as a test bed to evaluate DRAKE79 methods. A mean AAC transport of 181.5 ± 17.6 Sv was obtained by applying DRAKE79 methods to 2005 SOSE output. This value is greater than SOSE's "true" geostrophic transport (153.0 ± 5.7) by 29 Sv. This difference resulted primarily from linear interpolation between two lost moorings; however the horizontal spacing of the current meters did not resolve the narrow jets of the ACC regardless of mooring loss. Within SOSE, geostrophic transports referenced with velocities at all mooring locations resulted in a mean transport of 161.0 ± 10.2 Sv. Temporal smoothing of the reference velocities, using up to a 20-day running mean, had minimal impact on the mean transport estimate. A next step would evaluate whether the mooring positions should be modified within SOSE to capture the same circulation features as DRAKE79.

1. Introduction

The Antarctic Circumpolar Current (ACC) is a strong wind-driven eastward current. The ACC acts as a conduit transporting water between the Atlantic, Pacific, and Indian Oceans. Due to its size and connection to the world's ocean ACC transport is a key metric used to evaluate the accuracy of ocean and climate models. ACC transport is concentrated in three fronts, the Subantarctic Front, the Polar Front and the Southern Antarctic Circumpolar Front (Orsi et al. 1995). Transport is not evenly distributed across Drake Passage, the majority of the ACC transport is due to the northernmost fronts; the Subantarctic Front and the Polar Front (Whitworth et al. 1982).

Drake Passage is the ACC's narrowest channel as it travels around Antarctica. Measuring ACC transport in Drake Passage is challenging; measurements have only been made here on two occasions. Transport can be measured with a variety of techniques. One approach is to use current meters to directly measure the current speeds. This approach places a heavy demand on resources because the point-wise current meter measurements must resolve the horizontal and vertical structure of the velocity field. Another approach is to measure the vertical and horizontal density distribution to determine the geostrophic shears using the dynamic method. This methodology requires a known 'reference velocity' to render the geostrophic velocities 'absolute'. A yearlong experiment that took place in Drake Passage in 1979 (DRAKE79) used the later approach and obtained a canonical transport of 134 Sv ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$). Recent studies suggest that the DRAKE79 ACC transport may be biased low by 20% (Donohue et al. A Four-year Time Series of ACC Transport through Drake Passage from Moored Observations, unpublished manuscript). We hypothesize that the 1979 estimate is biased low by the DRAKE79 methodologies.

The DRAKE79 total transport estimate resulted from a complicated synthesis of historical data and *in-situ* current, pressure, and temperature measurements, and utilized three hydrographic sections. The geostrophic referencing of the three hydrographic sections was critical in their methods. The DRAKE79 approach relied heavily on the outcome from referencing three hydrographic sections with directly measured currents.

A hypothesis is put forward that the horizontal spacing as well as the temporal averaging of the current meters led to a bias in the historical measurement. The horizontal spacing of measurements (~45 km) may have not resolved the narrow jets of the ACC. In addition, two critical moorings were lost in a particularly energetic region of Drake Passage within mooring line. DRAKE79 chose averaging periods for the reference current meters that minimized the difference between measured and geostrophic shears.

The study uses the Southern Ocean State Estimate (SOSE), as a test bed to evaluate the DRAKE79 methods. SOSE is a general circulation model with $1/6^\circ$ horizontal resolution that is informed by real observations (Mazloff, 2010). ACC circulation through Drake Passage is well modeled in SOSE with accurate spatial representations of all three fronts compared with ADCP data. SOSE's Polar Front is weaker than ADCP observations. The opposite is true for SOSE's Subantarctic Front. SOSE surface eddy kinetic energy agrees well with observations, but is weak at near bottom depths (T. Chereskin, personal communication 2013).

Here we examine the methods of DRAKE79. Using the literal DRAKE79 mooring locations we mimic the geostrophic transport calculation using SOSE 'point' current meter mooring velocities to reference geostrophic shears. We examine the sensitivity to the loss of the critical moorings and examine the sensitivity optimal averaging to overall transport.

2. Methods

2.1. Historical Methods

The 1979 ACC transport estimate (Whitworth et al. 1982) derived from a complex synthesis of historical data, hydrographic sections, and current meter measurements. A

mooring line spanning Drake Passage from 68°W 54°S to 60°W 63°S consisted of 17 current meter moorings (Fig. 1). Moorings in northern and central Drake Passage were spaced at approximately 45 km. Southern moorings were spaced at 65 km intervals. These moorings utilized current meters at 500 and 2500 meters. Hydrocasts between moorings at three discrete times during the one-year study provided a meridional density gradient. Data were not recovered from two of the 17 moorings (ML3 and ML4).

Figure 1. Bathymetric map (1000 m contour interval) indicating the location of DRAKE79 moorings (triangles) with unrecovered moorings denoted by a red X. Locations of SOSE (solid lines) and observed (dashed lines; Orsi 1995). Sub-Antarctic and Polar Fronts are shown by red and blue lines, respectively.

Figure 2. Time series of SOSE baseline (gray; 153 Sv) and geostrophic (black; 161 Sv) transport. SOSE geostrophic transport is higher by 8 Sv, so mooring spacing has a small, but noticeable effect on total transport.

Linear interpolation between moorings ML2 and ML5 provided velocity data at moorings ML3 and ML4.

Results of the 1979 study relied heavily on geostrophic referencing techniques. The dynamic method yielded vertical geostrophic shear profiles, $u_g(z)$, referenced to zero at 2500 m for each hydrocast pair. For pairs with deepest common level shallower than 2500 m, geostrophic shear was referenced to zero at the deepest common level. Optimal averaging was applied in attempt to form an accurate representation of transport between hydrocasts. Whitworth et al. (1982) assumed remaining long-period current fluctuations to be geostrophic. Applying a moving average should remove ageostrophic motion from the record. Whitworth et al. (1982) rationalized that optimal averaging period would not be critical away from fronts where flow is assumed to be steady. Near the fronts, the averaging period would be dependent on the motion of the front relative to the mooring and might need to be longer for an adequate representation of the flow. This value differed from mooring to mooring.

To reduce influence from ageostrophic flow, an optimal averaging technique was applied. Current meter measured velocities were rotated to form cross-track velocities, and then smoothed using seven different moving-average periods (6 hr to 20 day) to create seven additional time-series. For each day the optimal averaging period was determined by selecting the moving-average period that reduced the absolute difference between offsets at 500 and 2500 m, C_{500} and C_{2500} , respectively, where offsets are defined by

$$C_{500}(t) = u_{ref}(z = 500m, t) - u_g(z = 500m, t)$$

$$C_{2500}(t) = u_{ref}(z = 2500m, t) - u_g(z = 2500m, t)$$

and $u_{ref}(z, t)$ is the current meter measured velocity. The final optimally-averaged geostrophic referenced velocity, $u_{tot}(z, t)$, is then given by

$$u_{tot}(z, t) = u_g(z, t) + \frac{C_{500}(t) + C_{2500}(t)}{2}$$

Here, the final term is the optimal offset added to daily geostrophic shear.

2.2. SOSE method

Here, the Southern Ocean State Estimate (SOSE) was taken as the real ocean to evaluate the historical methods described above. A mooring line in SOSE was created using the 1979 mooring latitude and longitude (Fig. 1). Modeled

Figure 3. Scatter plot comparison of SOSE geostrophic transport using all moorings (y-axis) with SOSE baseline transport (x-axis). Transports are significantly, but weakly correlated.

Figure 4. Time series transport comparison of SOSE geostrophic transport using linearly interpolated values at ML3 and ML4 to SOSE baseline transport. Linear interpolation of ML3 and ML4 biases the transport estimate above baseline transport by almost 28 Sv.

CTD casts were created at SOSE grid points chosen to retain a constant slope of the modeled mooring line, while minimizing the distance from midpoints between adjacent mooring sites. Between each modeled CTD pair, a velocity profile was determined. The profile represents the average cross-track velocity between the CTD stations. Model velocity at 500 m and 2500 m was linearly interpolated to mooring locations and rotated to cross-track, produced reference velocities at each mooring location. These reference velocities were used to geostrophically reference SOSE velocity profiles in a method mirroring Whitworth et al. (1982).

To evaluate the linear interpolation across lost moorings, a second modeled mooring line was created. Velocity across M2 and M5 was linearly interpolated and modeled velocity records at ML3 and ML4 were replaced with interpolated values. This resulted in a second dataset: a duplicate of the modeled line with interpolated values replacing ML3 and ML4.

The sensitivity of transport estimates to optimal averaging period was also tested. The optimal averaging technique described above was adapted and applied to the modeled mooring line (with interpolated M3 and M4) to create a third dataset. Here, smoothing periods of 1, 3, 5, 7, 11, 15, and 21 days were used to reduce computational complexity.

Finally, a 4th time-series was created using the actual SOSE grid points across Drake Passage. This is the “true”, or baseline, SOSE transport, and yielded a time-averaged transport of 153.0 ± 5.7 Sv. This value acted as a comparison metric for evaluation of the three point-referenced time series.

To summarize, datasets used in this study were: i) velocity profiles between each CTD pair, referenced to zero at 2500 m depth, ii) a modeled mooring line taken at 1979 mooring locations, iii) a duplicate of the modeled line with linearly interpolated values replacing velocity records at ML3 and ML4, iv) a duplicate of the interpolated dataset with optimal averaging periods applied (optimal transport),

and v) a baseline transport calculated using SOSE grid points across Drake Passage.

3. Results and Discussion

The horizontal spacing of the DRAKE79 moorings were expected to resolve the estimated 30-40 km widths of the two northern fronts in Drake Passage (Subantarctic Front and Polar Front; Fig. 1). To test this, SOSE geostrophic transport using all moorings was compared to SOSE baseline transport (Fig. 2 & 3). Average SOSE geostrophic transport was 161.0 ± 10.2 Sv. This estimate fell within one standard deviation of the SOSE baseline transport and was biased higher by 8 Sv. A time series transport comparison showed some temporal agreement (Fig. 2) with a low, but statistically significant correlation coefficient ($R^2=0.25$; Fig. 3). Hence, we conclude that the horizontal spacing of the

Figure 5. Scatter plot comparison of interpolated mooring transport (y-axis) with SOSE baseline transport (x-axis). SOSE true transport and interpolated M3 and M4 are not correlated.

1970 moorings did not resolve the narrow jets of the ACC.

The transport estimate was more sensitive to linear interpolation of ML3 and ML4 than to horizontal spacing of moorings. Replacing SOSE geostrophic velocity at ML3 and ML4 with linearly interpolated values increased the total transport estimate to 180.8 ± 21.1 Sv, an upward bias of 27.8 Sv from the SOSE baseline, and 19.8 Sv above SOSE mooring referenced geostrophic transport. This difference is evident in both time series comparison and scatter plot representations (Fig. 4 & 5), with essentially no correlation to baseline transport ($R^2 = 0.03$) and weak correlation to the case of no interpolation ($R^2 = 0.24$). The source of this difference is evident in observed time series of velocity at moorings ML2 through ML5, which show little agreement between ML2 and ML5 ($R = -0.19$), and a positive shift of ML3 and ML4 velocity when interpolation is applied (Fig. 6). Hence, the total transport was overestimated due to linear interpolation of velocities at the

missing mooring sites.

Whitworth et al. (1982) suggested that transport estimates should not be dependent upon optimal averaging periods away from ACC fronts. In close proximity to the fronts, however, averaging periods may need to be quite long to reduce the influence of geostrophic motion on geostrophic transport estimates. Hence, some level of sensitivity was expected to be seen in modeled transport. The optimal transport estimate was 181.5 ± 17.6 Sv. A time-series transport comparison showed close agreement between interpolated and optimal transport, with optimal transport having consistently, but subtly, lower amplitude (Fig. 7). Optimal transport showed little correlation with SOSE baseline transport ($R=0.09$), but high correlation with interpolated transport ($R=0.91$). Hence, little sensitivity is attributed to the choice of optimal averaging period, and linear interpolation created the largest bias in transport estimates.

Figure 6. Time series of cross track SOSE geostrophic velocity for SOSE 2005 data for ML2, ML3, ML4, and ML5 (blue; bottom-to-top) and interpolated ML3 and ML4 velocity (red). Interpolation biases ML3 and ML4 velocity high.

Figure 7. Time series transport comparison of SOSE baseline (black), optimal (red), and SOSE geostrophic (ML3/4 interpolated; blue) transport. Application of optimal averaging to interpolated transport causes little to no bias.

4. Conclusions and Future Work

Fronts in Drake Passage account for approximately 60% of the total ACC transport (Whitworth et al. 1982), so adequate meridional instrument spacing is necessary for an accurate transport estimate. Contrary to the assumptions of Whitworth et al. (1982), DRAKE79 moorings were not spaced closely enough to adequately resolve the narrow ACC jets. The Subantarctic and Polar Fronts have an average width of 44 km and meander over lateral distances of about 75 to 100 km (Gille, 1994). The fronts have a slightly smaller average width than the spacing of the DRAKE79 moorings. So there is a possibility that the jets were not adequately resolved.

The loss of moorings ML3 and ML4 in an energetic region of the ACC impacted the 1979 transport estimate. Our analysis of SOSE indicated that linear interpolation of velocity at ML3 and ML4 overestimated velocity, and hence biased transport high by almost 28 Sv. It is possible, however, that modeled fronts in the SOSE data analyzed here differ from those observed in 1979, due to the high meander and eddy activity of the ACC through Drake Passage. Further analysis is necessary to determine the level of agreement between observations in 1979 and SOSE. One future step would be to examine more appropriate mooring locations in SOSE other than the literal DRAKE79 locations. The moorings from 1979 may have captured other different circulation features than SOSE in 2005.

Despite the fact that averaging periods may be important in the vicinity of ACC fronts, we found little sensitivity of transport estimates to application of optimal averaging.

Hence, the largest impact on ACC transport estimates came from interpolation, not from optimal averaging techniques, with the possibility of additional bias introduced by low horizontal resolution of instrument arrays.

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Measuring the Diffusion Coefficients of Emerging Contaminants in Low-Density Polyethylene

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Abstract. Hydrophobic organic contaminants (HOCs) are anthropogenic pollutants that persist in the environment, bioaccumulate in biota, and cause adverse health effects. Polyethylene passive sampling is a novel technique to measure trace legacy HOCs in a variety of media. However, the semi-polar nature of some emerging contaminants is raising concern whether the apolar low-density polyethylene (LDPE) passive sampler is an appropriate sampling approach. The diffusion coefficients (D) polybrominated diphenyl ethers and antimicrobial compounds were determined in LDPE using a modified film-stacking technique at 20°C and 10°C. Log D (m^2/s) ranged between -10.80 to -13.00 and -11.20 to -13.39 for temperatures 20°C and 10°C respectively. This range is consistent with values reported in literature for polychlorinated biphenyls and polycyclic aromatic hydrocarbons. A strong linear correlation between log D and molecular weight was obtained both at 20°C and 10°C. The product of PBDE diffusion coefficients and partitioning coefficients were found to be 1-4 log units greater than the product of legacy HOC coefficients. This evidence implies that LDPE is an adequate sampler for emerging contaminants and that the uptake of PBDEs is boundary-controlled in most cases.

1. Introduction

Hydrophobic organic contaminants (HOCs) cause adverse health effects in humans and other organisms.^{1-7,9-20,25}

Thousands of chemicals are produced in industry for a wide range of uses; of these, over 600 have potential to persist in the environment and bioaccumulate in biota.¹ The concentrations of many of these potentially harmful chemicals have never been measured in the environment because traditional sampling methods such as active sampling are cost intensive and do not have the ability to adequately characterize large spatial distributions without strenuous effort.^{1,2,3} Polyethylene passive samplers (PEs) have been validated as a economical and accurate sampling approach for groups of HOCs such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs).³⁻⁶ In the early 1990's, PEs were developed to uptake HOCs in the environment with the idea the samplers would mimic the uptake of HOCs by fish.⁶⁻⁸ These PEs were initially developed to be biphasic semi-permeable membrane devices, which contained a polymeric shell with a triolein filling.^{6,7} However, after application of the semi-permeable membrane devices, it was found that the polymeric material would be suitable to use as a passive sampler by itself.⁸ In fact, a variety of single phased polymers have become widely used as PEs to measure HOCs in the environment.^{3-7,9-11}

Polyethylene passive sampling, as opposed to active sampling, is a favourable technique to measure HOCs in the environment. Foremost, passive sampling does not require a power source and is significantly less expensive than active sampling. Low detection limits are not sacrificed when using the less expensive PEs. Passive sampling gives the investigator the ability to deploy a larger number of samplers throughout the area of interest. In turn, more data from the area can be collected to establish spatial and temporal trends to assess the fate and transport of HOCs in the environment. Legacy HOCs such as PCBs and PAHs,

have been extensively studied, and their diffusion coefficients in LDPE have been reported in literature. Knowing the diffusion coefficient strengthens the validation that LDPE is an adequate passive sampler for HOCs.³

Groups of semi-polar emerging contaminants such as polybrominated diphenyl ethers (PBDEs) and antimicrobial compounds have not been thoroughly studied with respect to passive sampling and diffusion. Since PBDEs and some antimicrobial compounds have only been used in production for a few decades evidence of persistence is relatively recent.¹²⁻¹⁴ PBDEs are a group of semi-polar HOCs that are added to a variety of commercial household products such as plastics, furniture, foams, and textiles to hinder combustion in emergency situations. Although these flame retardants were introduced for fire safety precautions, PBDEs are found to be reproductive toxicants, carcinogens, endocrine disruptors, and effect neurological processes.^{5,9,13,15} Antimicrobial compounds such as triclosan are semi-polar antimicrobial agents that indiscriminately kill microorganisms. For that reason, they are used in soaps and detergents.^{4,12,16-20} However, triclosan has also been introduced in toothpastes, clothing, carpets, plastics, toys, and even pacifiers.¹² The toxicity and endocrine disrupting effects triclosan has on organisms is cause for concern because humans are exposed to the chemical frequently. The widespread advertising of antimicrobial products has led to increasing fear of bacteria even though the use of triclosan out of a healthcare setting is deemed unnecessary by experts. The overuse of triclosan led to Minnesota banning the inclusion of triclosan in cleaning products in May 2014.¹⁶ The penta and octa PBDE congeners have been banned around the United States as well.¹³ Since both PBDEs and antimicrobial compounds show persistent characteristics, it is important to measure the concentrations of these HOCs in the environment. Although dissolved concentrations of these semi-polar HOCs have been reported in literature with confidence, it is important to understand how PEs uptake these HOCs, which can be described by diffusion.⁹

The uptake of HOCs into polyethylene is primarily controlled by two steps, diffusion across the aqueous boundary layer and diffusion through the membrane itself. Most passive sampler deployments are aqueous boundary layer controlled since the resistance of the membrane is minute compared to the resistance from the aqueous boundary layer.^{6,7} The continual difference in chemical potential between polyethylene and the sampling medium allows for spontaneous diffusion of analyte into the polyethylene until equilibrium is reached.^{8,22} The relatively low crystallinity of polyethylene, about 40%, gives polyethylene a significant amount of free volume to sequester HOCs over time.^{6,23} In this study, the diffusion coefficients in polyethylene of PBDEs and methyl triclosan (a degradation product of triclosan) have been measured to understand how these HOCs behave during the polyethylene passive sampling process.

The diffusion coefficient is a measure of the rate at which a compound moves throughout the polymer membrane and is directly proportional to the mass transfer coefficient.⁸ A greater diffusion coefficient gives a compound the ability to diffuse faster into the polymer, and results in a larger sampling rate; preferably, the sampling rate is not limited by resistance from chemicals diffusing throughout the membrane. This scenario is an example of an aqueous boundary layer controlled uptake rate. On the other hand, if a compound has a low diffusion coefficient, the sampling rate will be significantly lower, and the uptake rate is most likely membrane controlled. Previous studies have shown that as the molecular weight increases, the diffusion coefficient decreases.^{8,21-23} The combination of compounds having high molecular weights, high partitioning coefficients, and low diffusion coefficient may result in the passive sampling process being membrane controlled. PBDEs have relatively high molecular weights compared to legacy HOCs and antimicrobial compounds are more polar

than legacy HOCs. Thus, it is important to estimate the diffusion coefficients of PBDEs and antimicrobial compounds in polyethylene to predict how the uptake of these HOCs is controlled and ultimately whether polyethylene is an adequate device to measure these HOCs.

2. Materials and Methods

2.1. Chemicals and Preparation

0.7 mm thick polyethylene was purchased from American Plastics and was cut into 5.0 x 7.0 cm² pieces. Prior to the film-stacking experiments, the polyethylene sheets were pre-extracted in hexanes for two days followed by a solvent change to acetone for one day to remove non-polymerized oligomers and other impurities.⁸ Triclosan, methyl triclosan, n-nonylphenol, n-octylphenol, t-octylphenol, nonylphenol-technical mix, PBDEs 28, 49, 47, 100, 99, 154, 153, and 183 standards (Accustandard) were used for diffusion coefficient analysis. ¹³C Triclosan and ¹³C methyl triclosan (Cambridge Isotope Laboratories) and PBDE 35, 71, and 128 (Accustandard) were used as internal standards for quantitative analysis. PBDE 71 (Accustandard) and p-terphenyl-*d*14 (Ultra Scientific) were used as injection standards for the quantification of PCDEs and antimicrobials respectively. Chemicals used for diffusion coefficient analysis were spiked into 11 pre-extracted polyethylene sheets using a 80:20 methanol water solution, similar to the method developed by Booij et al.²⁴ The polyethylene and solution were mixed together on a shaker table for over a week, which was determined to be enough time for the chemicals to penetrate the polyethylene and reach equilibrium.²⁴

2.2. Film-Stacking Experiments

A single spiked polyethylene sheet was laid on top of 5 unspiked pre-extracted polyethylene sheets. The stack was placed into an aluminum foil casing to prevent analytes from evaporating out of the polyethylene. The aluminum foil casing was put between two wooden shims. A clamp was used to apply uniform pressure across the polyethylene surfaces and to make sure the spaces between the polyethylene sheets were minimized. The film-stacking experiment was executed at varying times and temperatures.⁸ Experiments executed at 20°C were allowed to diffuse between one day and four days. Experiments executed at 10°C were allowed to run between 4 days and 6 days. The contact times were chosen based on a trial experiment where after one day of diffusion the polyethylene sheets were extracted and analyzed to determine how far each compound diffused through the stack. Times for the subsequent experiments were estimated based on the observed concentration gradient. After the allotted amount of time was reached, the polyethylene sheets were separated into individual aluminum foil casings. Shortly after retrieving the polyethylene, each sheet was cut into three equally sized sheets, paying attention to the orientation of the polyethylene. A diffusion coefficient will be estimated for the left, middle, and right side of each polyethylene sheet in order to determine discrepancy in the estimated coefficient. However, this report includes data from the middle part of the polyethylene sheets only.

Figure 1. To demonstrate the ability of smaller molecules to diffuse faster throughout the polyethylene, the concentration at time t is plotted relative to the starting concentration of the system. BDE 47 was able to diffuse significantly farther throughout the polyethylene stack than BDE 154 after 144 hours at 10°C. The plotted points represent the experimental data and the fitted line is the theoretical concentration profile fitted to estimate the diffusion coefficient of each compound in LDPE.

Table 1. A full list of compounds, their molecular weight (g/mol), the similar weighted congener's relative symmetry, and corresponding log D (m²/s) at 20°C and 10°C are displayed.

Compound	Symmetry	Molecular Weight (g/mol)	Log D (m ² /s at 20°C)	Log D (m ² /s at 10°C)
BDE 28	N/A	406.9	-10.99	-11.33
BDE 49	Unsymmetrical	485.8	-11.54	-11.50
BDE 47	Symmetrical	485.8	-11.45	-11.67
BDE 100	Symmetrical	564.7	-11.82	-12.13
BDE 99	Unsymmetrical	564.7	-11.91	-12.21
BDE 154	Symmetrical	643.6	-12.60	-12.64
BDE 153	Unsymmetrical	643.6	-12.66	-12.63
BDE 183	N/A	722.5	-13.07	-13.46
Methyl Triclosan	N/A	303.6	-10.80	-11.00
Average PBDE D			-12.00	-12.20

2.3 Sample Preparation and Analysis

Each polyethylene sheet was extracted separately for 24 hours in about 10 mL of hexanes. After extraction, the solution was concentrated to about 1 mL in a water bath set to 30°C under a steady stream of nitrogen gas. The samples were concentrated further under a steady stream of nitrogen gas to about 200 µL. The samples were injected with injection standards PBDE 71 and p-terphenyl-*d*14. Multiple injection standards were needed because two separate curves were used for analysis. Analyses were conducted with an Agilent 6890 gas chromatograph coupled with a 5973 mass spectrometer with splitless injection (275°C), electron impact ionization (EI, 70eV, transfer line 300°C) in selected-ion monitoring mode. The temperature program for AM analysis was as follows, 80°C held for 1 min, 12°C min⁻¹ to 220°C, 10°C min⁻¹ to 280°C, and held for 12 minutes. For PBDE analysis the temperature program was as follows, 90°C held for 2 min, 7.5°C to 310°C, and held for 4 minutes. Blanks were prepared for each separate experiment executed, but samples were not blank corrected because blank concentrations were less than 10% of sample concentrations.²⁶

2.4 Estimation of Diffusion Coefficient

In order to derive the diffusion coefficient, Fick's second law of diffusion was solved using appropriate boundary conditions that fit the experimental setup. Fick's second law of diffusion is defined as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where D is the diffusion coefficient (m²/s), C is the concentration of analyte in the system (ng/g PE), x is the distance away from the initial position (m), and t is how long the diffusion experiment was allowed to diffuse (seconds). The boundary conditions used to solve the partial differential equation were at each impermeable wall, the flux in concentration (dC/dx) was equal to zero.²⁷ Fick's second law was solved by nonlinear least squares regression. If enough time was allotted that the diffusion

within the stack was close to equilibrium, this experiment was determined insufficient to estimate the diffusion coefficient. Similarly, if not enough time was allotted to result in sufficient diffusion through the stacks, the diffusion coefficient obtained was not included in the final data.⁸ An example of comparing the calculated experimental concentration gradient against the diffusion model is shown in Figure 1.

3. Results and Discussion

3.1 Temperature's Effect on Diffusion Coefficients

Data for triclosan and the alkylphenols were not obtained because of separation and volatilization issues during the gas chromatography separation. The estimated diffusion coefficients for each PBDE congener and methyl triclosan as well as the average of the PBDE congener diffusion coefficients at 20°C and 10°C for both temperatures are presented in Table 1. Since diffusion is dependent on the chemical potential gradient between polyethylene and the sampling medium, it was hypothesized that as the temperature, and consequentially energy of the

Figure 2. The plot of Log D at 20°C and 10°C versus molecular weight of PBDEs in LDPE demonstrates a high correlation. The circle points represent the 20°C data and the triangle points represent the 10°C data. Both lines of best fit would allow accurate estimation of diffusion coefficients of PBDEs not measured in this study.

system decreases, the rate of diffusion within the polyethylene would decrease as well.²² After analysis of the left and right stacks of polyethylene sheets, the diffusion coefficients should be a better representation of their true values. However, for most of the analyzed compounds, the diffusion coefficient decreases with decreasing temperature. If the diffusion coefficient does not decrease from 20°C to 10°C, the 20°C diffusion coefficient is within ± 0.1 log units of the 10°C diffusion coefficient. Knowing how much the diffusion coefficient changes as a function of temperature is important because many passive sampling applications are not at standard conditions. To be able to predict whether the uptake of HOCs is boundary layer controlled or membrane controlled at temperatures close to freezing, the diffusion coefficients must be estimated.

3.2 Relation of Molecular Weights with Diffusion Coefficients

As the molecular weight of the PBDEs increase, the diffusion coefficients decrease, as displayed in Table 1. This has been observed in previous studies.^{8,21-23} As the size of the molecule increases, the path of motion the compound has through the polyethylene is restricted. With fewer paths to take, the molecule diffuses slower throughout the polyethylene. After plotting the diffusion coefficients as a function of molecular weight, strong correlations were found for both 20°C and 10°C with r^2 values ≥ 0.95 . This relationship yields the ability to extrapolate the diffusion coefficients of PBDEs not measured in this study. Although there is good agreement in linearity within the PBDE group, when including methyl triclosan in the plot, the r^2 value significantly decreases. This confirms that groups of compounds with different chemical properties will have

significantly different diffusion coefficients with respect to molecular weight.^{8,21-23} Thus, a linear relationship between diffusion coefficients of differing compound groups has yet to be established.

3.3 Effect of Bromine Atoms Positions on D

Even though strong correlations between log D and molecular weight have been reported, structural differences in compounds within the same group may have an influence on the diffusion coefficient. The symmetry, flexibility, and structure of molecules have a strong influence on how compounds diffuse throughout polymers.^{8,23} PBDEs all have the same general structure; two phenyl rings are connected by an ether and the phenyl rings are substituted with bromine atoms. The only difference in chemical structure is the number and position of bromine atoms. PBDEs 47 and 49 contain four bromines, PBDEs 99 and 100 contain 5, and PBDEs 153 and 154 contain 6. With respect to the pairs, Table I presents which congener has a higher degree of symmetry than the other. An interesting observation is that congeners with less symmetry also have greater diffusion coefficients. The change in symmetry of the molecule might increase the diameter and the overall volume of the molecule making it more difficult to diffuse throughout the polyethylene than its corresponding congener.

3.4 Polychlorinated Biphenyls vs. Polybrominated Diphenyl Ethers

It has previously been reported in literature that a good indication of passive sampler efficacy for a particular compound is an evaluation of both its partitioning

Table 2. The log D and K_{PEW} values for PCBs, PAHs, and PBDEs are displayed. The product of the diffusion coefficient and partitioning coefficient in LDPE for PCBs, PAHs, and PBDEs are calculated. Log D values for PCBs and PAHs were obtained from Rusina et al., (2010). Log K_{PEW} values for all compounds were obtained from Lohmann, (2012).

Compound	Log D (m ² /s) at 20°C	Log K_{PEW}	Log[D* K_{PEW}]
PCB 153	-13.28	6.8	-6.48
PCB 156	-13.34	7.2	-6.14
PCB 170	-13.56	7.3	-6.26
PCB 180	-13.57	7.1	-6.47
PCB 187	-13.5	7.1	-6.40
Acenaphthylene	-12.26	3.5	-8.76
Acenaphthene	-12.36	3.6	-8.76
Anthracene	-12.36	4.2	-8.16
Chrysene	-13.28	5.6	-7.68
Benzo[a]pyrene	-13.72	6.2	-7.52
BDE 28	-10.99	5.7	-5.29
BDE 49	-11.54	6.26	-5.28
BDE 47	-11.45	6.3	-5.15
BDE100	-11.82	6.9	-4.92
BDE 99	-11.90	6.9	-5.00
BDE 154	-12.60	7.4	-5.20
BDE 153	-12.65	7.4	-5.25
BDE 183	-13.07	7.98	-4.09

coefficient and diffusion coefficient. Specifically, the magnitude of the product of these values yields an idea of a sampler's ability to sequester that compound efficiently. Even though a compound may have a high partitioning coefficient, the compound may be limited to membrane controlled uptake due to a low diffusion coefficient. Ideally, a compound will have a high affinity for the polyethylene while the uptake during deployment is not limited by the membrane. It is generally accepted that in most applicable passive sampling situations, the uptake of PCBs and PAHs are boundary layer controlled. Since PBDEs are on the factor of 2 to 3 times larger molecules than PCBs, there was concern at the beginning of this study that the diffusion coefficient of PBDEs would be significantly high, resulting in membrane controlled uptake rates. However, the diffusion coefficients of PBDEs were found to be larger than diffusion coefficients reported in literature for PCBs and PAHs. Even though the partitioning coefficients of PCBs are generally greater than PBDEs, the product of the partitioning coefficient and diffusion coefficient of PBDEs was 1-2 log units larger than PCBs, which is shown in Table II. Similarly, the product of the coefficients was 2-4 log units greater

for PBDEs than PAHs. This relationship indicates that polyethylene is an efficient sampler to measure PBDEs, and in most applicable situations, the uptake of PBDEs would be boundary layer controlled. Finding larger diffusion coefficients for PBDEs than PCBs and PAHs despite the large difference in molecular weight should not be a surprise. It was previously shown that lower molecular weight PAHs were found to have a greater diffusion coefficient than higher molecular weight PCBs because the fused aromatic rings of PAHs, make their structure extremely rigid.⁸ Similarly, the structure of PCBs are more rigid than the larger PBDE molecules because of the single carbon-carbon bond between the two aromatic rings in PCBs. Although the phenyl rings in PBDEs are connected by an ether, which was hypothesized to slow the diffusion of PBDEs in apolar polyethylene, this extra bond might also give PBDEs more flexibility when diffusing through polyethylene polymer chains. In result, the ether functional group in PBDEs had significantly less effect on diffusion than hypothesized. The flexibility of the molecule dominated any effect the semi-polar functional group had on the diffusion coefficient. Since the product of the diffusion and partitioning coefficient for PBDEs is larger than for PCBs and PAHs, we conclude that LDPE is an efficient passive sampler for PBDEs and for most applicable situations the uptake rate of PBDEs during deployment will be boundary layer controlled.

4. Conclusion

Diffusion coefficients for PBDE congeners and methyl triclosan were estimated at two different temperatures. The diffusion coefficient was found to decrease as temperature decreases. For both temperatures, log D versus molecular weight showed strong correlations for PBDEs but did not correlate with methyl triclosan indicating this relationship is class specific. Estimated diffusion coefficient values were compared to the compound properties and structure of PBDEs. PBDE congeners that are more symmetrical tended

to have larger diffusion coefficients. The product of partitioning and diffusion coefficients was used to measure polyethylene's ability to sequester PBDEs in sampling situations. Despite the size and semi-polar nature of PBDEs, polyethylene is an adequate sampler for the PBDEs because the product of the coefficients was significantly greater for PBDEs than PCBs and PAHs. Ultimately, polyethylene passive sampling has been proven to be able to sequester PBDEs efficiently and for most applicable situations the uptake rate is predicted to be boundary layer controlled rather than membrane controlled.

5. Future Work

In future research, the samples will be re-run on a clean column in hopes to receive data for triclosan and alkylphenols. A derivatization method of the hydroxyl group of triclosan has been developed and can be used if necessary. In addition, the film-stacking method will be executed for larger and more polar organophosphate esters and dechlorane plus. The goal of the study is to derive diffusion coefficient for PBDEs, antimicrobial compounds, alkylphenols, organophosphates, and dechlorane plus for temperatures 20°C, 10°C, 0°C and possibly -20°C. A linear relationship between diffusion coefficients and molar volume will be established because molar volume is a better indication of molecular size than molecular weight. A linear relationship between diffusion coefficients and other chemical properties will be investigated in an attempt to establish a linear relationship between multiple compound classes. Finally, the product of diffusion coefficient and partitioning coefficient will be evaluated for each compound at varying temperatures to determine how temperature affects passive sampling uptake rates.

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CF₃SF₅ Diffusivity

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Abstract. Trifluoromethyl sulfur pentafluoride (CF₃SF₅) is an inert, non-toxic, fluorinated compound; it does not occur naturally and consequently, its concentration in the environment is very low. These properties make it a potential tracer for ocean processes such as air-sea gas exchange. However, the data from these studies cannot be analyzed until the diffusion coefficient for CF₃SF₅ is determined. The purpose of this experiment is to determine the diffusion coefficient for CF₃SF₅ in pure water over a temperature range of 3 to 30°C and in sea water over a temperature range of 15 to 30°C. A standard gas containing known concentrations of CF₃SF₅ and sulfur hexafluoride (SF₆) was prepared. The standard gas was allowed to diffuse across a water barrier, stabilized with agar gel, and the diffused gas was swept into an electron-capture gas chromatograph to measure the resulting gas concentration. The diffusion rates for both CF₃SF₅ and SF₆ were measured to determine the diffusion coefficients for each species. The experimentally determined diffusion coefficient for SF₆ was compared to its value from the literature to validate the experimentally determined diffusion coefficient for CF₃SF₅. The diffusion coefficients for CF₃SF₅ in pure water ranged from 5.8×10^{-6} to 1.5×10^{-5} , increasing with temperature. The values were 5-7% less in sea water; however it is unclear whether the decrease in diffusivity was due to the variability in the experimental method. The diffusion coefficients for SF₆ matched the literature data reasonably well, validating the experiment.

1. Introduction

Trifluoromethyl sulfur pentafluoride (CF₃SF₅) is an inert halocarbon in the class of gasses collectively referred to as ignoble gases for the non-reactive properties they share with the noble gases, but also for their potentially deleterious environmental impacts. For example, the chlorofluorocarbons, also ignoble gases, are responsible for stratospheric ozone depletion, as determined by the Centre for Atmospheric Science (Science 2007). CF₃SF₅ is similar in many respects to sulfur hexafluoride (SF₆) a gas used extensively in industry to electrically isolate high voltage equipment. Both CF₃SF₅ and SF₆ absorb radiation strongly in the infrared spectrum, making them greenhouse gases: CF₃SF₅ and SF₆ have 18,000 and 23,900 Times the global warming potential (GWP) of CO₂ (Sturges et al. 2000; Direct 2013). CF₃SF₅ has no known industrial use and its anthropogenic source remains unknown. Its existence was previously thought to be the result of electrolytic degradation of SF₆; however *Pepi et al.* (2005) determined that this is not the case. Globally, both gases exist at the part per trillion level in the atmosphere and their concentrations are increasing at a rate of about 6% per year (Suen 2008).

The electronegative (or insulating property) of these two gases, makes them detectable at extremely low concentrations by using gas chromatography with electron capture detection. This, in combination with the fact that they are inert and nearly non-existent in the natural environment makes them potentially valuable tracers for physical processes. SF₆ has been used extensively in tracer release experiments, providing a better understanding to many aspects of oceanography and environmental fluid mechanics (see e.g. Ho, 2002; Ledwell et al., 2000). Recently, *Law and Watson* (2001), *Tanhua et al.* (2004), and *Bullister et al.* (2006) have determined that SF₆ can be potentially used as a transient tracer in the ocean, given its rate of monotonic increase in the atmosphere (Geller et al. 1997; Maiss and Brenninkmeijer 1998). There is currently a high demand for a new transient tracer because the previously used chlorofluorocarbons have lost their

effectiveness as a result of their declining atmospheric mixing ratios. It can become problematic if SF₆ is used in both tracer release experiments and as a transient tracer due to interference between the two uses. Therefore, it is necessary to find a new tracer for tracer release experiments so that SF₆ can become a dedicated transient tracer. Because of its potential value as a transient tracer, the scientific community has declared a moratorium on deep ocean tracer releases of SF₆ to avoid further contaminating the oceanic background.

Ho and Smethie Jr. (2008) determined CF₃SF₅ has the potential to replace SF₆ in tracer release experiments. CF₃SF₅ has several properties that make it a potential tracer. As stated above, it shares many of the ideal tracer properties with SF₆, and current experimental methods can be readily adapted to include measurement of both CF₃SF₅ and SF₆, which utilize the same techniques for injection, sampling, and analysis.

In order to fully interpret the results of tracer release experiments with CF₃SF₅, it is necessary to determine its physical properties, including its solubility in water and its diffusion coefficient. The purpose of this experiment is to determine the diffusion coefficient of CF₃SF₅ in pure water over a temperature range of 3°C to 30°C and in sea water over a temperature range of 15°C to 30°C.

2. Experimental Method

A standard gas containing CF₃SF₅, SF₆, and nitrous oxide (N₂O) was prepared by serial dilutions using pressurized nitrogen as the primary diluent. The targeted concentrations for CF₃SF₅, SF₆, and N₂O were 119 ppmv, 476 ppmv, and 4% respectively. These mixing ratios were chosen to allow a measureable gas concentration before and after the diffusion process. SF₆ and N₂O were included in the gas standard, as their diffusion coefficients could potentially be determined to validate the experiment. The diffusion coefficient for SF₆ was determined and compared to the values obtained by *King and Saltzman* (1994).

The experimental method was based on the ideas developed by *Barrer* (1941). The standard gas was allowed to diffuse across a water barrier while the concentration of the diffused gas was closely monitored. At steady state, the flux across the water barrier took the form of Fick's First Law:

$$\Phi = \frac{D\Delta C}{l}$$

where Φ is the flux, D is the diffusion coefficient, ΔC is the difference in concentration across the water barrier, and l is the height of the water barrier. Since the solubility of CF_3SF_5 in water is estimated by *Ho and Smethie Jr.* (2008), the flux can be rewritten in terms of the gas solubility on each side of the water barrier. The diffusion coefficient for CF_3SF_5 in water can then be expressed as:

$$D = \frac{C_2 f_2 l}{C_1 \alpha A}$$

where C_1 is the gas phase concentration before diffusing through the water barrier, C_2 is the gas phase concentration after diffusing through the water barrier, f_2 is the volumetric flow rate of the diffused gas, α is the Ostwald solubility, and A is the cross-sectional area of the water barrier.

The gas concentration before diffusion (C_1) was determined by diluting the standard gas, measuring the diluted gas concentration, and accounting for the dilution step. Two Kimax® 1000 ml flasks were massed, filled with DI water at room temperature, and then remassed to accurately determine their volumes. The flasks were then purged with nitrogen at 5 psi for 5 minutes before being covered with septum stoppers. A Hamilton MICROLITER™ syringe was used to inject the flasks with 150-300 μl of the standard gas. The diluted gas solution was then injected into a VICI® 8-port valve where it loaded a 25 μl sample loop. Ultra high purity nitrogen purged the

gas in the sample loop into a SRI 8610C gas chromatograph (GC) and electron capture detector (ECD). The concentration of the diluted gas was determined by linearly interpolating between data points on a calibration curve for CF_3SF_5 and another calibration curve for SF_6 . The calibration curves were prepared by injecting a 7.7 ppbv CF_3SF_5 standard and a 155.9 ppbv SF_6 standard into 10 μl , 25 μl , 100 μl , 0.25 ml, and 1.0 ml, and 1.012 ml sample loops.

The gas concentration on the outlet of the diffusion cell (C_2) was determined using the experimental method illustrated in Figure 1. The standard gas flowed from its gas cylinder, through 1/8 inch inner diameter steel tubing, and into a Cole-Parmer flowmeter to keep the flow of gas controlled at 0.003 standard liters per minute. The flow of gas then passed through 1/8 inch inner diameter vinyl tubing and into a diffusion cell housing the water barrier. The diffusion cell consisted of a lower chamber below the water barrier and an upper chamber above the water barrier. The undiffused gas passed through the lower chamber and was vented into the atmosphere. Some of the standard gas diffused from the lower chamber, through the water barrier, and into the upper chamber of the diffusion cell. Ultra high purity nitrogen with a controlled flow then swept the diffused gas from the upper chamber into a VICI 8-port valve equipped with a sample loop. Pure nitrogen purged the sample loop into the GC-ECD to measure the gas concentration. The concentration of the diffused gas was determined by linearly interpolating data points on the calibration curves. New calibration curves were prepared every few days to account for a drift in the ECD readings. The concentration of the diffused gas was measured every 14 minutes to monitor when the diffusion process reached steady state. The process took 4-14 hours to reach steady

Figure 1. A schematic of the experimental method used to diffuse the standard gas across a water barrier. The CF_3SF_5 and SF_6 concentrations were monitored using gas chromatography with an electron capture detector. The concentrations were monitored until the process reached steady state.

Figure 2. Diffusion coefficients of SF_6 in pure water and sea water compared to the equation made by *King and Saltzman* (1994). The results for this experiment are in agreement with previous studies. There was significant variability between data points, attributed in part to the nonlinearity of the SF_6 calibration curve. The diffusion coefficient in sea water tended to be lower than in pure water; however whether this result is attributed to the sea water or the variability in the experimental method is unclear.

state depending on the temperature and height of the water barrier.

The water barrier consisted of an agar solution approximately 0.8% by mass. A gas permeable Millipore 10 μm membrane filter was used to support the agar solution in the diffusion cell. The height of the water barrier (l) was determined by measuring the mass of the agar solution placed into the diffusion cell. The mass of the agar solution after the diffusion process was used to calculate the gel thickness. *Langdon and Thomas* (1971) determined that the use of agar solution rather than pure water decreased the calculated diffusion coefficients by approximately 1.9%. Therefore, all the diffusion coefficients were increased by 1.9% to account for the effect of the agar solution. The flow rate of the diffused gas (f_2) was determined by measuring the flow rates of the inlet gases with flow meters. The flow rate of the diffused gas was approximately equal to the flow rate of nitrogen running through the upper chamber of the diffusion cell. The Ostwald Solubility for SF_6 was calculated using the equation developed from *Bulliser et al.* (2002). The Ostwald solubility of CF_3SF_5 (α) was determined to be approximately half of that for SF_6 by *Ho and Smethie Jr.* (2008). The surface area of the water barrier (A) was determined by measuring the diameter of the diffusion cell.

The diffusion cell was submerged in a Blue M constant refrigerated bath to find the diffusion coefficient through a range of temperatures. The temperature of the diffusion cell was closely monitored with an Omega thermocouple. Diffusions were run at 3.0°C, 15.0°C and 30.0°C. A 35

parts per thousand solution of Instant Ocean® Sea Water was used to find the diffusion coefficient in sea water over the same range in temperatures. A Professional Plus sensor was used to measure the concentration of the sea water.

3. Results and Discussion

3.0. Diffusion Process

The concentrations of CF_3SF_5 and SF_6 in the standard gas were found to be 1817 and 816 ppbv respectively. The reason for the CF_3SF_5 concentration greatly exceeding the target concentration is unknown. The dilution step involved in determining the standard gas concentration introduces an uncertainty of 9-12% between trials for these measured concentrations. The flow rates, f_2 , for each trial ranged from 0.004-0.016 standard liters per minute. The flow rate was adjusted to position the diffused gas concentration in the same region of the calibration curve for each trial. The height of the agar gel varied from 0.43-0.57 cm for each trial. The area of the diffusion cell was determined to be 11.7 cm^2 .

3.1. Diffusivity of SF_6 in Pure Water

The diffusion coefficient for SF_6 in pure water was measured at 3.0 °C, 15 °C, and 30.0 °C with two trials completed for each temperature. As expected, the diffusion coefficients increased with temperature, as seen in Figure 2. The diffusion coefficients increased by 39% from 3.0 °C to

15 °C and then increased by 84% from 15 °C to 30.0 °C. It makes sense for diffusivity to increase with temperature due to the increase in kinetic energy.

The results for the diffusion coefficient at 3.0 °C and 15 °C matched the results obtained by *King and Saltzman* (1994) reasonably well, validating the diffusion coefficient for CF_3SF_5 . The SF_6 diffusion coefficient at 30°C that we determined appeared to be 14% larger than the value estimated by *King and Saltzman* (1994), however this is based upon a comparison with their empirical relationship. Those authors did not measure diffusivity above 25 °C, so a direct comparison was not possible.

In this experiment, there was a 5.2-27% discrepancy between trials at the same temperature, indicating uncertainty in the values. The uncertainty can be attributed in part to the instruments used. The hydrophobic Millipore membrane filters repelled the agar solution in the diffusion cell, creating a slightly variable agar gel thickness. Also, the Cole-Parmer flowmeters would often produce fluctuating flow rate readings despite having a quoted accuracy of 0.8%, potentially causing a variable flow rate of the diffused gas. Lastly, the thermocouple in the refrigerated bath read a temperature that constantly fluctuated by 0.1°C, potentially affecting the solubility of gas in the agar solution.

The calibration curve shown in Figure 3 shows the overall linearity between the peak areas produced by the ECD and the number of SF_6 moles injected into the GC. Overall, there was not a linear relationship between peak areas and number of injected SF_6 moles. This produced uncertainty in

finding the SF_6 concentration of the standard gas as well as the SF_6 concentration of the gas after diffusing across the water barrier. The nonlinearity of the SF_6 calibration curve was the largest source of error in determining the diffusion coefficients for SF_6 .

3.2. Diffusivity of CF_3SF_5 in Pure Water

The diffusivity of CF_3SF_5 in pure water was also measured at 3.0° C, 15° C, and 30.0° C with two trials completed for each temperature. The results are presented graphically in Figure 4. The diffusion coefficients increased by 33% from 3.0 °C to 15 °C and then increased by 28% from 15 °C to 30.0 °C. There was a 5.7-10.5% discrepancy between trials at the same temperature, indicating some uncertainty in the values. The uncertainty can be attributed to the same variability in the analytical procedure.

The diffusion coefficients for CF_3SF_5 were approximately 22% less than the diffusion coefficients for SF_6 in the temperature range of 3.0 °C to 15 °C. The diffusion coefficients for CF_3SF_5 were then 46% less than the diffusion coefficients for SF_6 at 30.0° C. It makes sense for CF_3SF_5 to have lower diffusion coefficients than SF_6 because it diffuses less easily through water as a result of its larger molecular mass. The relationship between diffusivity and molecular mass can be quantified using Graham's Law. Figure 5 compares the experimentally determined coefficients for CF_3SF_5 to its theoretical diffusion coefficients based on Graham's Law and the experimentally determined coefficients for SF_6 . Diffusivity for CF_3SF_5 was

Figure 3. An example of a calibration curve used for SF_6 . The nonlinearity of the calibration curve introduced potential error in determining the standard gas and diffused gas concentrations. The flow rate of nitrogen was adjusted to position the diffused gas concentration in the most linear area of the calibration curve (a peak area of 7000-12000). The dilution step positioned the diluted gas in the same area on the curve.

Figure 4. Diffusion coefficients of CF₃SF₅ in pure water and sea water. The CF₃SF₅ diffusion coefficients were lower than the SF₆ diffusion coefficients, as expected due to its increases molecular mass. More trials should be completed better determine the accuracy of the coefficients.

generally less than expected from Graham's Law, particularly at high temperatures, indicating that there must be factors other than molecular mass that affect diffusivity between the two species.

The calibration curve shown in Figure 6 shows the overall linearity between the peak areas produced by the ECD and the number of CF₃SF₅ moles injected into the GC. Overall, there was a linear relationship between the peak areas and

Figure 5. Diffusion coefficients of CF₃SF₅ compared to expected results from Graham's Law. The CF₃SF₅ diffusion coefficients did not match the results expected from Graham's Law, particularly at points obtained from higher temperatures. This indicates that there are factors other than molecular mass that cause the diffusion coefficient of CF₃SF₅ to be lower than the diffusion coefficient for SF₆.

Figure 6. An example of a calibration curve used for CF₃SF₅. The overall linearity of the calibration curve increased the confidence in the standard gas and diffused gas concentrations.

the number of injected CF₃SF₅ moles. This provided accuracy in the CF₃SF₅ concentration of the standard gas as well as the CF₃SF₅ concentration of the gas after diffusing across the water barrier. Therefore, there was a higher level of confidence in the determined diffusion coefficients for CF₃SF₅ than the determined diffusion coefficients for SF₆.

3.3. Diffusivity of SF₆ and CF₃SF₅ in Sea Water

The diffusion coefficient for SF₆ in sea water was measured at 15° C and 30° C with one trial completed for each temperature. The diffusion coefficients for SF₆ were 6-19% lower in sea water than pure water unlike the experiment performed by *King and Saltzman* (1994) where there was no noticeable difference in the diffusion coefficient between pure and sea water. Likewise, the diffusion coefficients for CF₃SF₅ were 5-7% lower in sea water than pure water. There is not enough data to determine whether the decreased diffusion coefficients are due to the sea water or the variability in the experimental method. It would make sense for the diffusion coefficients to decrease in sea water due to sea water's increased ionic strength and viscosity. Work done by the *International Towing Tank Conference* (2011) demonstrates that the viscosity of water increases by 6-7% in a 35 parts per thousand salt water solution. Therefore it would make sense for the diffusion coefficients to decrease by a similar magnitude.

4. Conclusion

The diffusion coefficient for CF₃SF₅ and SF₆ were measured over a temperature range of 3-30°C in pure water and over a temperature range of 15-30°C in sea water. The measured diffusion coefficient for SF₆ in pure water was in reasonable agreement with previous studies, validating the measured diffusion coefficient for CF₃SF₅. The diffusion coefficients for SF₆ in pure water varied by 5.2%-27% between trials. The large discrepancy between trials was attributed to the nonlinearity of the SF₆ calibration curve. The diffusion coefficients for CF₃SF₅ varied by 5.7-10.5% between trials and were deemed accurate due to the linearity of the CF₃SF₅ calibration curve. More trials should be conducted to ensure that the diffusion coefficients yield a low standard deviation. The diffusion coefficients for SF₆ were 6-19% lower in sea water than in pure water. Likewise, the diffusion coefficients for CF₃SF₅ were 5-7% lower in sea water. It is not clear whether diffusivity decreases due to the sea water or the variability in the experimental method. In previous studies, the diffusion coefficient for SF₆ did not change between pure water and sea water; however it would make sense physically for diffusivity to decrease in salt water. It is recommended to better determine the solubility of CF₃SF₅ in both pure and salt water to determine a more accurate diffusion coefficient.

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Transcriptome assembly and differential expression analysis for four strains of *Heterosigma akashiwo*

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Abstract. Harmful algal blooms (HABs), also called “red tides”, cause considerable economic damage to both commercial fisheries and the tourism industry, but mechanisms controlling formation are poorly understood. The HAB species *H. akashiwo* exhibits considerable genetic and physiological variability and is toxic to some predators; these characteristics enable this raphidophyte to reduce grazing pressure and form blooms. This study focuses on the process of assembling multiple transcriptomes from four strains of *H. akashiwo* and analyzing their expressed transcript levels. Particular attention is paid to low and high salinity differential gene expression in CCMP3107 and CCMP3374. An assembly was also generated from the four strains’ combined transcriptomes to determine if a more complete assembly would result. The *de novo* assembler ABySS was used for assembly. Assembly statistics were analyzed to determine which parameters assembled the transcripts best in terms of N50 values (the length of contig such that half of all bases in the assembly are made of sequences of equal or longer length) and, to a lesser degree, total number of contigs assembled. I found that parameter ‘k’ (size of k-mer) had the greatest impact on the quality of assembly. The combined assembly incorporating all of the transcriptomes was found to have a comparable N50 value to the separate strain assemblies and reported significantly more contigs than each of the strains assembled separately - a 156% increase over the highest contig retrieval from strain 3374. This may indicate an increased recovery of transcripts or novel transcripts generated. Strains CCMP3107 and CCMP3374 were cultured under similar experimental conditions, so their assembled transcriptomes were compared to determine genetic differences with respect to salinity. Significantly different (posterior probability>0.95) expressed genes and transcripts were identified by Analysis of Sequence Counts (ASC). CCMP3374 has significantly (p-value = 0.0007828, Wilcoxon test) more down-regulated genes than 3107. This work presents a case study of next-generation sequencing applied to understanding of HAB formation and plankton ecology.

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Transient Separation-Like Airflow over Wind Waves and Its Impact on Air-sea Momentum Flux

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Abstract. Accurate predictions of momentum exchanges between ocean and atmosphere are essential to understanding various air-sea coupled processes. It is usually assumed that when airflow separates at the wave crest, it enhances the form drag (pressure force on the wave) and increases the air-sea momentum flux and the drag coefficient. It is also assumed that airflow can separate only when waves below are breaking. However, recent laboratory observations suggest that separation like airflow patterns are ubiquitous and may occur over steep but non-breaking waves. In this study we investigate the airflow over a finite amplitude non-breaking wave train using a three-dimensional large eddy simulation. First, instantaneous velocity, vorticity, and pressure fields are examined. The airflow sometimes exhibits separation like flow patterns, identified with thin high vorticity layers detached from the surface and separation bubbles below. At other times the airflow remains attached to the surface. The pressure acting on the windward slope of the wave varies significantly depending on the flow pattern. Next, conditional phase averaging of the airflow is performed depending on the pressure force (pressure multiplied by the wave slope) acting on each wave. It is found that smaller pressure force is associated with separated airflow, while larger pressure force is associated with attached airflow. When incoming wind speed above the wave crest is faster, the flow remains attached, whereas slower incoming wind tends to enhance detachment of the airflow. These observations question some of the traditional assumptions of airflow separations and their impact on air-sea momentum flux.

1. Introduction

Accurate predictions of the air-sea momentum and heat fluxes are critically important for long term climate modeling and short term weather forecast including hurricane predictions. Over the past few decades, hurricane tracking forecasts have improved significantly, but the ability to predict the intensity of hurricane has made little progression (DeMaria et al 2013). This is partially due to the insufficient understanding of the air-sea momentum and heat fluxes under hurricane conditions. In particular, one of the most poorly understood processes that control the air-sea fluxes is the airflow separation above ocean surface wave. Airflow separation occurs when the near-surface air is no longer able to follow the undulating surface, and therefore takes off from the crest of the wave and generates a separation bubble on the leeside of the wave crest. When the separated air flow reattaches to the surface further downstream, it applies enhanced pressure force (form drag) on the windward side of the next wave crest. This effectively enhances the transfers of momentum between atmosphere and ocean. Airflow separations likely influence the air-sea heat fluxes as well, because they modify the near surface turbulence field and the dispersion of spray spume droplets generated at breaking wave crests.

There are two traditional assumptions of airflow separation over surface wave: (1) flow separation always enhances the form drag on the surface wave; (2) airflow separates only from breaking surface wave crests (Banner and Melville, 1976; Gent and Taylor, 1997). These two assumptions have been routinely made in previous modeling studies of air-sea momentum flux. However, recent experimental results by M. Buckley and F. Veron have challenged the second assumption: even when waves are not breaking, the near-surface air may become detached from the undulating surface and exhibit a “separation-like” behavior.

Motivated by the recent observational study, this project investigates separation-like flow patterns and their impact on air-sea momentum flux over non-breaking surface waves.

2. Modeling and Methods

2.1 Large Eddy Simulation (LES) Modeling

The project utilizes the time-series velocity and pressure data generated by Dr. Peter Sullivan of National Center for Atmospheric Research. The data were obtained using three-dimensional LES, which is carried out over a sinusoidal non-breaking wave containing five wave crests, and wind above the surface, both moving along the x-axis (with y-axis being cross-wind and z-axis the upward direction).

The water surface is defined as

$$z = \zeta(x) = a \cos(kx)$$

and the velocities at the water surface are obtained using the linear deep water wave solutions:

$$\begin{aligned} u &= a \omega \cos(kx) - c, \\ w &= -a \omega \sin(kx) \end{aligned}$$

where a is the amplitude of the wave, k is the wavenumber, $\omega = (gk)^{1/2}$ is the angular frequency, and $c = \omega/k$ is the phase speed of the wave. In this simulation the wave slope is set $ka = 0.226$. The wind forcing is set $u^*/c = 0.632$, where u^* is the wind friction velocity. The corresponding wind speed is approximately $U_{10} = 20$ c. For example, a 10 m wave corresponds to an 80 m/s wind, which is definitely in the hurricane regime. On the other hand, a 1 m wave corresponds to a 20 m/s wind, which is much lower than the typical wind speed of hurricane, but is often achievable in laboratory. For more details about the numerical simulation, see Hara and Sullivan (2014).

Figure 1. Top panel a) Instantaneous vorticity contour plot of a particular sample where strong flow separation pattern is observed. Bottom panel b) same as a) but for the case where strong flow attachment is observed.

2.2 Data Analysis

2.21 Quantities of Study

The project studies the quantities of y-vorticity

$$\omega_y = \frac{\partial u}{\partial z} - \frac{\partial \omega}{\partial x}$$

and the surface drag

$$D = \int p \frac{d\zeta}{dx} dx$$

where ζ is water surface height. The integration is made over an empirically determined range where pressure is large. (For more details on how to locate the appropriate range of pressure integration, see Appendix I).

2.22 Method of Analysis

Traditionally, airflows over non-breaking waves are analyzed by phase-averaging all quantities because it is assumed that the airflow separations do not occur and the turbulent fluctuations remain reasonably small. However, since the project is to investigate transient, flow separation-

like events, it is necessary to examine instantaneous snapshots of all variables sliced along the x-z plane at a particular y-value.

To determine the impact of separation-like events on the form drag, an individual snapshot of flow field on the x-z plane between adjacent crests is treated as an individual sample (Figure 4). For each sample, the surface drag on the windward side, defined as (4), is calculated. Then all of the drag values are bracketed into different ranges, and the y-vorticities and u-velocities of samples are averaged separately within each range of drag values (conditional phase averaging). In this manner, the relation between form drag and flow separation patterns can be quantitatively analyzed.

3. Results

In the figures presented below, all the variables are normalized by the velocity scale u^* and the surface wave length.

Samples of instantaneous y-vorticity are observed to be greatly varying in time and in space. Some samples (Figure 1 a) demonstrate unambiguous flow separation patterns, while others (Figure 1 b) show airflows remaining attached on the leeward side of the crest.

The histogram of drag values (Figure 2) shows that most samples have drags between 0.00 and 0.06 (normalized by the wind friction velocity and wavelength). However, a small number of samples have very low drags (-0.02 to 0.00), while another small group of samples have very high drags (0.06 to 0.08). Examination of the averaged y-

vorticities and u-velocities of the low-drag and high-drag ranges reveals that the low-drag is associated with more separation and a lower incoming wind velocity near the crest (Figure 3 a), while the high-drag is associated with less separation and a larger velocity near the crest (Figure 3 b).

Figure 2. Distribution of drag values. The histogram of drag values shows that most drag values are between 0 and 0.06, with small numbers of drag values between -0.02 to 0 (low forcing), and 0.06 to 0.08 (high forcing).

Figure 3. Top panel a) Low drag, conditionally averaged vorticity contour plot. Low velocity incoming wind results in strong separation but small drag. (The number in the bracket (731) indicates the number of samples averaged to produce this plot). Bottom panel b) High drag, conditionally averaged vorticity contour plot. High velocity incoming wind results in more attached flow but large drag.

Figure 4. Instantaneous contour plot of pressure. Each region from crest to crest, as demarcated between adjacent bold black lines, is treated as an individual sample. The high pressure signature on the windward side of each crest (dark red) is clearly observed.

Figure 5. Phase averaged pressure multiplied by wave slope as a function of x . The two solid vertical blue lines represent the region where the pressure force exceeds a set threshold (blue dashed line). The integration to calculate the drag in (4) is performed over this region

4. Discussion

The great variation in the patterns of flow separation is in agreement with M. Buckley and F. Veron's experimental finding that flow separation can take place even when waves are not breaking, contradicting the traditional assumption that airflow can only separate over breaking waves. This finding suggests that we need to reexamine the fundamental definition of airflow separation over wind waves.

The behaviors of wind velocity and drag in relation to flow separation is completely opposite to the standard

understanding of airflow separation over wind waves. In common examples of flow separation, such as wind hitting a cylinder, higher incoming wind speed results in more separation and larger drag, while lower incoming wind leads to less separation and smaller drag on the surface wave. However, the result over a non-breaking wave train shows that a slower incoming wind causes more separation but smaller drag (Figure 3 a), while a faster incoming wind yields less separation but large drag (Figure 3 b). The result contradicts the traditional assumption that the extent of flow separation is positively correlated to the form drag

experienced by the surface wave, and raises questions about the impact of airflow separation on air-sea momentum flux.

To expand this study, the LES modeling can be performed in a wide range of wind and wave conditions, including typical open ocean conditions. For instance, multiple waves in the same or different directions can be included in the simulation, or the wind and wave can be made misaligned. Also, most importantly, all computational findings should be validated against experimental results, since the LES methodology includes empirical parameterizations that need to be tested.

Conclusion

Airflow separation over wind waves is an important phenomenon that significantly modifies air-sea momentum flux. Traditionally it is assumed that airflow only separates if waves are breaking, and that flow separation always enhances the form drag on the surface wave. Motivated by the recent experimental findings that demonstrate airflow separation-like behaviors over non-breaking waves, this project examines the data generated by Large Eddy Simulation that simulates wind blowing over a sinusoidal, periodic, non-breaking waves. Qualitative analysis of flow field snapshots shows a wide range of behaviors, from strong separation-like flows to flows remaining attached on the leeward side of the wave crest. Conditional phase averaging of the vorticities based on the drag values demonstrates a negative correlation between the degree of flow separation and the form drag. These results contradict the traditional assumptions about airflow separation over wind waves and its effect on the wave form drag. Further investigation of airflow separation under different wave and wind conditions, coupled with experimental corroborations, must be performed to determine the impact of airflow separation on air-sea momentum fluxes.

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Appendix I: Surface Drag Calculation

This section details the procedures for selecting the appropriate range of integration to calculate the form drag (D) of each sample using (4).

Instantaneous snapshot of pressure (Figure 4), similar to that of vorticity, demonstrates a significant degree of variations. However, the location (not intensity) of the high pressure region on the windward side of the crest does not fluctuate significantly. Therefore, it is reasonable to empirically determine a fixed range of integration to calculate the form drag for all samples. In order to select the optimal integrating region we first calculate the surface pressure force

$$p \frac{d\zeta}{dx}$$

of each sample. Secondly, phase average the pressure force values of all samples and plot the result as a function of x (Figure 5). Thirdly, near the high-forcing peak, select a region where the pressure force exceeds a certain (empirically chosen) threshold as shown in Figure 5. This selected region is used for the calculation of the drag (D) for all samples.