Particulate Organic Carbon Flux in the Subpolar North Atlantic as Informed by Bio-Optical Data from the Ocean Observatories Initiative

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Abstract

The biological carbon pump in the North Atlantic Ocean is powered by the annual spring phytoplankton bloom. These primary producers use inorganic carbon in the surface oceans and convert it into organic carbon, a fraction of which is exported out of the surface mixed layer and sequestered at depth. Determining the rate of carbon flux below the maximum winter mixed layer depth, driving sequestration on annual or longer timescales, is critical to understanding the North Atlantic carbon cycle.

To constrain daily-to-annual scale changes in carbon export in the subpolar North Atlantic, I analyzed seven years of daily optical backscatter depth profiles (200-2600 m) collected from the subsurface profiler mooring at the Ocean Observatories Initiative (OOI)'s Global Irminger Sea Array from September 2014 to May 2021. This is the longest-running time series of daily, year-round optical backscatter profiles that has been collected in this region, providing novel opportunities to assess seasonal and interannual variations in particulate organic carbon (POC) flux to depth.

This analysis, focused on large particles and aggregates identified from optical backscatter spikes, shows annual pulses of sinking particles initiating in May to June during each year of our seven-year time series, consistent with these export pulses being driven by organic matter production during the spring

phytoplankton bloom. These pulses of particles sink through the water column at rates ranging from 10 and 30 meters per day, and though particle concentration attenuates through the water column due to remineralization, coherent large particle pulses generally extend deeper than 1500 m, the deepest maximum annual mixed layer depth over this period. Although deep winter mixing in this region requires sinking particles to penetrate much deeper than in other parts of the ocean to be sequestered long-term, pulses of large particles consistently penetrate to below even the deepest annual mixed layer depths in the region, highlighting the importance of these large particle pulses to carbon sequestration at depth in the subpolar North Atlantic.

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Dedication

For Filipino Sailors,
serving aboard ships of:

-commerce,
-pleasure,
-war,

and of course…

-discovery.

Epigraph

"I live in Boston so I'm used to small spaces."
– Lieutenant Commander Jonny Kim
United States Navy, Medical Corps
National Aeronautics and Space Administration, Astronaut Corps
University of San Diego, Class of 2012

Acknowledgements and Preface

> *"The mark of a great ship handler is never getting into situations that require great ship handling."*
> **– Fleet Admiral Ernest J. King, United States Navy**

The "Master" of a merchant vessel is her Captain. The historical naval rank of Sailing Master follows this tradition, and was a warrant officer grade immediately above that of Midshipman[1]. To this day, every vessel is required to have at least one Master aboard while underway. Sailors refer to the individuals holding a "master's ticket" by different titles: Captain, Skipper, Master Mariner. Regardless of the form of address, what is clear is that a Master is a thoroughly experienced sailor.

While the *Magisterii Scientiae*[2] that Boston College is conferring differs in some respects, as an oceanographer, I can only think of the similarities. Through the last few years, I have studied maps and worked with other scientists at sea and ashore to accomplish some mission, to dredge up some deeper truth about the ocean planet we inhabit. I have shown both a depth and breadth of seafaring knowledge, and plan to use it in service of others.

Once, I gave a talk about how a ship is a neighborhood[3] in and of itself. In graduate school I have found that to be especially true. I would like to individually thank the members of my community, my shipmates, for their unwavering love and support over the last few years.

My family name is Cuevas, which can translate to "*caves*" in English, a fitting name for a Master of Geology. My nuclear family has been the hearth in that cave, and I know I can always return home in order to find safety and warmth.
To my Mom, Imelda Dy Cuevas, thank you for encouraging me to pursue education and curiosity. From you, I learned how to be an Engineer Project Manager: how to solve the problem at hand, while also picking apart the same functional system.
To my Dad, J. Michael Cuevas, thank you for teaching me how to think like a Field Engineer[4]. It has helped me piece apart the systems I work in to find a deeper truth, grounded in reality.
To my sister, Janel Cuevas Son: I would advise you to do as I have, and take the Master's and run.
To my grandmother, Lola Adelaida Deling Dy, thank you for always encouraging me to do my best and pursue my wildest ambitions. I've done it!

[1] And for those of you keeping track at home, yes, my last held grade was that of a Midshipman.

[2] I'm not being pretentious here; the degree is literally awarded in Latin.

[3] In fact, in Tagalog, *barangay* means "neighborhood," and is descended from the word *balangay*, which is one of the oldest forms of watercraft endemic to Southeast Asia. I did a video about this once. But I digress.

[4] Yes, both of my parents are engineers. It's honestly a wonder I'm not a ship's chief engineer.

To my brother-in-law, Staff Sergeant Hwaseok Son, thank you for creating a home with my sister. I am honored that we are family.
And lastly, but certainly not least, to my nephew, Kai Son. You are a new arrival to this, ever-changing ocean planet and I hope we give you one you can be proud of.

My lab group has been my family here at Boston College. The Marine Biogeochemistry Research Group enabled me to do the work that I do through their support and kindness, and I hope that the findings described in this thesis help drive future discoveries from this amazing group of scientists.
My advisor, Professor Hilary Palevsky, thank you for being the advisor I needed for this point of my career and this point of my life. I am forever thankful for your care of our team as happy human beings before successful scientists, and I will treasure the memories we've made in this research group, be they about ducks, boats, or duck boats.
Jake Supino, we've been connected since even before you arrived at Boston College. Your wit and sense of humor are things I always look forward to seeing in the lab, and I appreciate your skills as a chef as well as your dedication to your work as a scientist. I sense this will not be the end of our friendship.
Meg Yoder, your drive and determination are admirable. Since entering grad school together, you have always pushed me to try my best to understand the systems we work in, and I am thankful for your work ethic and tenacity.
Stevie Walker, it has been my genuine pleasure to watch you become an increasingly independent scientist. I look forward to your next steps as you embark on doctoral work of your own, and develop new insights into our understanding of the biological pump! Go Huskies!
Dr. Kristen Fogaren, thank you for being the cool aunt of the research group. You've taught me to take my work seriously but to take care of my heart and my brain first when I get lost in the woods. Thank you for being a valuable mentor these last few years, and for reminding me to shake it off when things got rough.

Oftentimes in a sailor's career, they will be called before some committee and asked to showcase that they are "basically qualified[5]." I would like to thank the additional members of my qualifying examination committee, Professors Xingchen Tony Wang and Mark Behn, for truly pushing me to the limits of my knowledge, and showing there was still more for me to learn. It was no secret that when I chose to attend graduate school, I wanted to be able to learn from the world's greatest oceanographers. I truly believe I have had the chance to learn from a few of them.
Mark, thank you for acting as a lighted buoy both for my science and for my time as a graduate student. I treasure the guidance you have provided both to ensure a robust oceanographic study and to have a balanced and happy graduate student life. I will not be able to make the next meeting, as I will be at sea.

[5] Aboard a submarine, this ceremony would be accompanied by a reading from The Book, after the sailor receives their Fish. But the last time I was involved with a submarine, it caught fire. Underwater. Ask me later, it's a great story.

Tony, I appreciate the support you have offered throughout my time here at Boston College, as well as the intensive geochemical and paleoceanographic training you have offered to me. I am sure I will use it well in these coming years.

The graduate community at Boston College is currently growing, preparing to welcome new teachers of the earth sciences into the fold. I'm glad to have kept good company and would like to thank members of my cohort and other graduate students, the researchers who were in the trenches alongside me.
Emma Woodford, thanks for being there for me at every step of the process. I appreciate how naturally our friendship came, right from admitted students' day. We were able to grow and learn together, and now we're both ready for the professional world in the ocean sciences.
Sky Goliber, I'm so glad we were able to become close during our time in grad school. Casual nights playing Nintendo Switch at your apartment in the company of animals were always appreciated.
Char Lorthioir, we've been able to see each other across at least five states at this point! It's always a pleasure to hang out with you, and I'm glad we've been able to hang out and keep each other sane during the actual writing process of our theses.
Becca Richards, thank you for understanding who Lew Zealand is, a man who has appeared in every Muppet movie.
Yueqian Adam Wang, I consider myself fortunate that we've been able to connect in person the last couple of years. I always like sharing a meal with you or talking about skateboarding or programming.
Olivia Burek, I always look forward to seeing you at work or at parties! Whether we're talking about pierogies or seeing our families overseas, I can always count on you for a great conversation.
Mike Armstrong, thanks for being my defenseman. I appreciate that I can talk to you about both sports and the intricacies of nearshore sedimentary flow, and I'm excited for what's next for both of us.
Dylan Seal, thank you for always being around and for sharing stories about the amazing rocks you worked with.
Danielle LeBlanc, thank you for being a great "shipmate" during our virtual cruise, and for being a colleague, mentor, and friend in my first year of graduate school. You helped ease the shift into graduate life, and I'm excited to see what climate stories in deep time we can tell next!

Of course, every sailor must return to shore, and have the good company of friends to spend shore leave with. Thanks to each of these people for playing some part in keeping me happy when off-duty.
Dr. Tyler Burch, I'm glad we were able to continue our friendship in the Greater Boston Area. From research to baseball to music to statistics to Mexican food, I always enjoy our chats.
Dr. Kelsey McCoy, as covered by the hit ska act Suburban Legends, thank you for being a friend! I am taking your advice to heart, taking the master's, and running, for one big reason: I am ready for the next thing.

George Brody Marino IV, thanks for being the person to talk to about both Water/Ground-typed Pokémon as well as groundwater interactions. The National Oceanic and Atmospheric Administration is truly lucky to have you, and I consider myself lucky to have your friendship.
Naaim Siddiqi, it was a pleasure running a Speakeasy with you and continuing to collaborate and create #content together in spite of our ever busier and busier schedules.
Jenn Ngo, it's been wild being at school at the same time again! I await your success in the law, Deputy!
Greg Catangay, thanks for being a billet brother to me. It is always great to visit you when I'm on leave in San Diego, and I look forward for us to learn more about sharks in the very near future.
Dan Matthews, thank you for supporting me in every possible way throughout our friendship. I will never forget our times out on the Chesapeake or on San Diego Bay.
EMN2(SS)[6] Alex Payette, thank you for always being willing to swap sea stories. Your acerbic wit and love of literature has kept me well-read and scurvy-free these last couple of years.
Tori Cohen, I'm glad we could connect and enjoy pirate media, strange webcomics, and books together.
Kate Thompson, I am proud of the chemistry you have been able to do in the frigid north. Stand on guard, and keep producing *miracles*.
Anna Kendrick, thank you for the laughs and the memories, from singalongs to getting stuck in the woods.
To my godbrothers, Lieutenant John Berba and Captain[7] Miguel Ortiz. I'm glad we've been able to stay close as we've each embarked on our own paths.

To the Academic Research Fleet—I simply could not have done this work without you. You being the ships, the crew, and the scientists who have provided the platform that my work and the work that countless other scientists builds upon.
RV *Robert Gordon Sproul*, thank you for giving me a chance to go to sail before I was even a graduate student. You've trained me and several other San Diego Toreros well, and we are Ready for Sea.
RV *JOIDES Resolution*, thank you for allowing me to fulfill a dream job. It was my dream as an undergraduate student to sail with you, and I'm glad to have been your Education and Outreach Officer, even as part of a Shore Party. I hope your impending retirement treats you well, old girl.
RV *Sally Ride*, thank you for giving me an opportunity to physically return to the ocean before finishing my degree. Leading a cruise aboard you was a genuine pleasure, and I hope we were able to ignite the sparks of passion and creativity in our students.

[6] Electrician's Mate (Nuclear), Second Class, Qualified in Submarines. Yes, enlisted Navy ratings just look Like That.

[7] Army Captain. Let's not get a big head, here.

RV *Kilo Moana*[8], you empowered me to live every young oceanographer's dream of sailing in the Kingdom of Hawai'i. Thank you for giving me a chance to share that dream with yet more students.

I would also like to thank Rick Riordan and the other faculty of Harding-Pencroft Academy. As yet another distinguished alumnus, I hope I have made House Dolphin proud in my efforts to explore and communicate the wonders of the deep.

I'd also like to congratulate Boston College Men's Ice Hockey for becoming the 2024 Men's Hockey East Champions. Hoisting the Lamoriello Trophy is no small feat, and I'm proud to have been a Boston College Eagle during this championship run.

This thesis represents my past three years spent "before the mast." Graduate school is not an easy undertaking. I have shed many tears, both of happiness and sorrow, in order to reach this point. From here, I have my next set of orders. I'll see you all ashore in the West End, in hallowed halls of a Museum of Science once frequented by Captain Spock, and more recently by Commodore Geordi LaForge[9].

Jose M. Cuevas
Port of Boston
May 2024

[8] Because you're going to ask, *Kilo Moana* may be translated as "one who is looking for understanding of the deep sea" or more simply as "oceanographer."

[9] I met LeVar Burton. That's not related to anything, it's just cool and fits the nautical theme here.

1. Introduction

1.1. The Subpolar North Atlantic Ocean's Biological Carbon Pump

Ocean absorption of carbon dioxide from the atmosphere is an important mechanism in the global carbon cycle (DeVries, 2022). The annual net atmosphere-ocean flux of 2.6±0.4 Pg C yr^{-1} offsets a significant fraction of the annual release of 10 Pg C yr^{-1} into the atmosphere from the burning of fossil fuels, indicating that the ocean acts as a strong carbon sink (DeVries, 2022; Friedlingstein, *et al.*, 2023; Watson, *et al.*, 2020). While the majority of the ocean's absorption of anthropogenic carbon has been driven by chemical and physical mechanisms, biological processes also play an important role in the ocean's ability to sequester carbon into its depths and in regulating global climate (Boyd, *et al.*, 2019).

The biological carbon pump is the biologically driven flux of organic carbon through various pathways, by which carbon is fixed by phytoplankton in the surface ocean, and sinks or is transported out of the surface and is stored in the deep ocean (Boyd, *et al.*, 2019). For example, the biological gravitational pump is driven by the gravitational settling of particles downwards through the water column, and accounts for nearly 90% of the vertical dissolved carbon gradient. Sinking rates within this mechanism are governed by Stokes' Law, meaning particles with larger radii (and consequently, larger particles) will generally sink faster (Boyd, *et al.*, 2019). Deeper in the water column, there is a characteristic decline in particulate organic carbon (POC) flux as a fraction of the sinking POC is lost to respiration (termed as remineralization), defined by a power law relationship known as the Martin Curve (Martin, *et al.*, 1987). In order for carbon to be sequestered in the deep ocean on time scales of at least one year, it must sink below the maximum annual mixed layer depth (the deepest depth in contact with the atmosphere over the course of a year) which occurs during the winter in most parts of the ocean. Some carbon will be remineralized within the seasonal thermocline (the portion of the water column between the shallowest and deepest seasonal mixed layer depths) and be reintroduced into the mixed layer (and subsequently, the atmosphere) when the mixed layer depth deepens again during the winter (Palevsky & Nicholson, 2018). Only the carbon which avoids remineralization within the seasonal thermocline *and* sinks below the maximum annual mixed layer depth is stored on climate-relevant timescales.

The subpolar North Atlantic Ocean has received significant attention in the scientific community's efforts to study the role of the biological carbon pump in marine carbon cycle (Sanders, *et al.*, 2014). The North Atlantic experiences a large annual spring phytoplankton bloom, which drives a significant flux of POC from the surface oceans (Briggs, *et al.*, 2011). The bloom's biological community is dominated by relatively large phytoplankton such a diatoms and coccolithophores, which both possess biomineralized tests that promote sinking (Sanders, *et al.*, 2014; Rembauville, *et al.*, 2017; Lacour, *et al.*, 2019). However, in addition to these biological processes driving strong flux of carbon to the deep ocean, the subpolar North Atlantic also exhibits some of the deepest winter mixed layers on the planet, with regions such as the Irminger Sea[1] developing

[1] Named for Danish Vice Admiral Carl Irminger.

mixed layers in excess of 800 m and the Labrador Sea[2] up to 1800 m (Holte, *et al.*, 2017). Sinking organic particles must sink past the maximum winter mixed layer depth in order to be sequestered on annual or longer timescales (Palevsky & Nicholson, 2018). Assessment of the role of the subpolar North Atlantic biological pump in sequestering carbon from the atmosphere on climate-relevant time scales therefore requires continuous year-round biogeochemical observations of the water column, especially organic particles sinking below the winter mixed layer depth. However, wintertime research cruises are not possible at these latitudes due to harsh weather conditions, which has restricted the temporal range of prior studies using shipboard methods.

1.2. The Ocean Observatories Initiative

The Ocean Observatories Initiative (OOI) is a National Science Foundation (NSF)-funded project dedicated to long-term multidisciplinary observations of ocean basins (Smith, *et al.*, 2018; Trowbridge, *et al.*, 2019). OOI employs common sensors throughout its multiple arrays, enabling open science practices while providing publicly available time series data sets capturing important oceanographic variables at a variety of sites (Palevsky, *et al.*, 2024). Global Arrays, such as those located at Station Papa[3], in the subarctic northeast Pacific, or in the Irminger Sea of the subpolar North Atlantic, are composed of both

[2] Named for Portuguese explorer João Fernandes Lavrador, and let's be honest, that's more than a little weird.

[3] Ocean Station Papa has a fascinating history. During World War II, weather data played an important role in the Battle of the Coral Sea, and in 1942 the United States Navy established Ocean Weather Station Peter in the Gulf of Alaska (50ºN, 140ºW). USCGC *Haida* (WPG-45) was assigned to weather ship duty at this post, and since then various weather and ocean observing efforts have occurred at this site (Freeland 2007).

moored and mobile assets appropriate for measuring air-sea interactions and quantifying chemical, physical, and biological properties through the entire water column.

The OOI Global Irminger Sea Array (60.4582ºN, 38.4407ºW) consists of four moorings arranged in a triangular configuration (Figure 1). This site was prioritized by OOI in its early planning stages as it is a location associated with strong atmospheric forcing and ocean-atmosphere coupling, enabling strong carbon sequestration driven by physically- and chemically-driven uptake, in addition to organic carbon from the annual spring phytoplankton bloom that sinks through the water column and is sequestered at depth (Smith, *et al.*, 2018; Trowbridge, *et al.*, 2019). The OOI has maintained this array since September 2014 and returns to this site annually to maintain and re-deploy gliders and moorings. The OOI intends to observe this site for at least two decades, which will elucidate questions about the interplay between the atmosphere and the surface and deep ocean (Smith, *et al.*, 2018; Trowbridge, *et al.*, 2019).

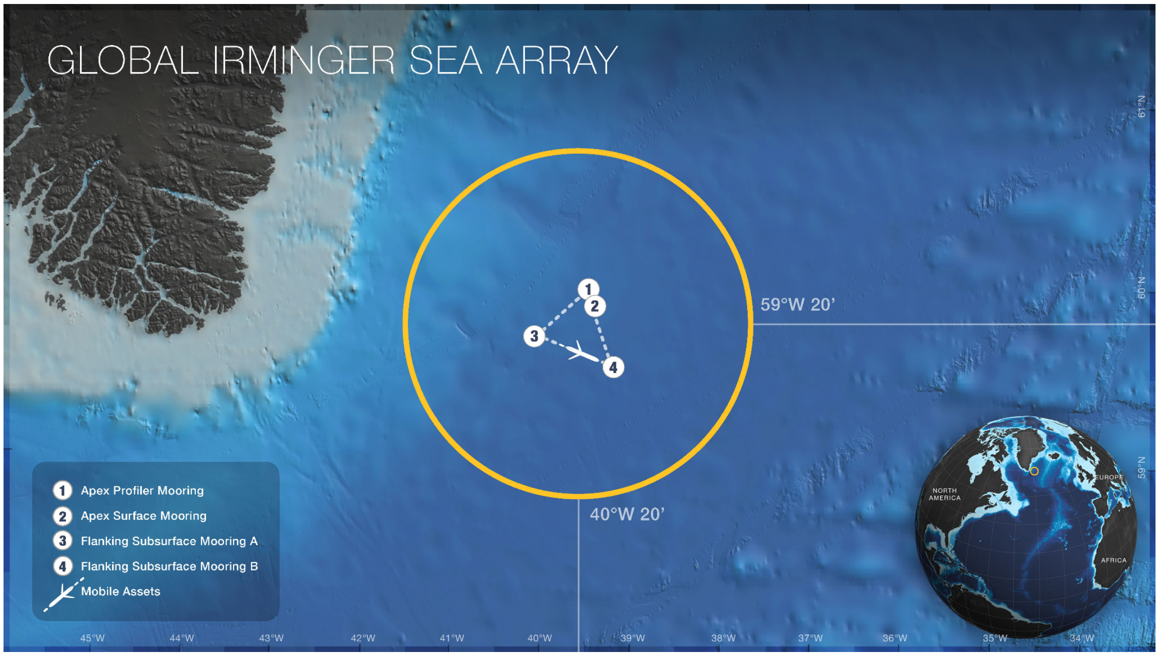

Figure 1. Map of the Ocean Observatories Initative's Global Irminger Sea Array (NSF Ocean Observatories Initiative). This thesis focuses on bio-optical measurements, namely chlorophyll-*a* (μg/L) and optical backscatter (m^{-1}), drawn from Sea-Bird/WET Labs ECO fluorometers on the Apex Profiler Mooring (1). For a summary of all biogeochemical sensors deployed across the entire array, see Figure A.2 in Palevsky et al. (2023).

1.3. Thesis Overview

In this thesis, I use bio-optical backscatter data drawn from the OOI Global Irminger Sea Array to investigate the seasonal and annual patterns of POC export via the biological carbon pump in the Irminger Sea. The OOI Global Irminger Sea Array is the longest time series available (nine years and counting) of biogeochemical and bio-optical water column profile measurements at daily-scale resolution in the subpolar North Atlantic. I use the bio-optical data available at this site in order to elucidate the timing and magnitude of the annual spring phytoplankton bloom, and subsequent POC export. This investigation is driven by the following questions:

1. What is the annual rate of POC flux driven by large sinking particles in the Irminger Sea?

2. How much POC sinks below the maximum annual mixed layer depth, such that it is sequestered from the atmosphere on annual or longer time scales, and how much is instead remineralized within the seasonal thermocline, and ventilated back into the atmosphere when the mixed layer deepens in winter?
3. How does POC flux driven by large sinking particles attenuate deeper within the water column due to remineralization?
4. How do interannual variability in the timing and the magnitude of the annual spring phytoplankton bloom and winter mixed layer deepening influence interannual variability in the amount of carbon sequestered by POC flux?

2. Methods

The data analyzed in this thesis are derived from the OOI Irminger Sea subsurface profiler mooring, located at the northernmost apex of the array (Figure 1).

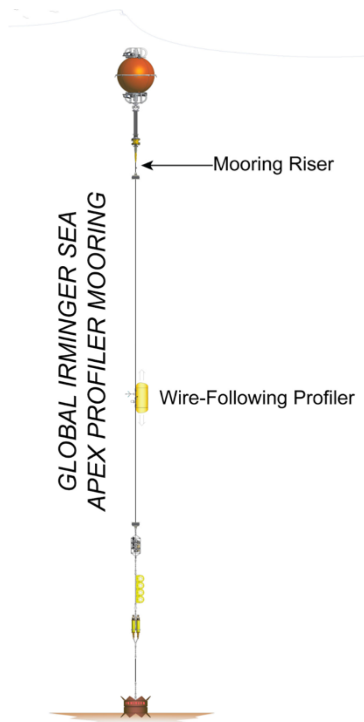

Figure 2. A schematic of the Apex Profiler Mooring at the Global Irminger Sea Array (NSF Ocean Observatories Initiative). The Wire-Following Profiler (WFP) generates profiles between 240 and 2592 m depth roughly every 20 hours. This WFP carries a Sea-Bird Scientific/WET Labs ECO Puck™ 2-wavelength fluorometer, a Falmouth Scientific ACM-Plus single point velocity meter, an Aanderaa 4330 oxygen optode, and a Sea-Bird SBE 52MP CTD, which measures salinity (from conductivity), temperature, and depth (from pressure).

The subsurface Wire-Following Profiler (WFP), a design modified for OOI based on the McLane Moored Profiler, collects both upwards and downward-moving vertical profiles from nominal depths of 240 - 2592 m, with profiles occurring roughly every 20 hours (Figure 2). Bio-optical data are collected by a Sea-Bird Scientific/WET Labs ECO Puck™ 2-wavelength fluorometer (NSF Ocean Observatories Initiative), which measures optical backscatter (at a red wavelength of between 640 and 730 nm, roughly 700 nm) and fluorometric chlorophyll-*a* concentration. The WFP also carries a 3-D single point velocity meter (Falmouth Scientific ACM-Plus), an oxygen optode (Aanderaa 4330), and a Sea-Bird SBE 52MP CTD, which measures salinity (determined from conductivity), temperature, and depth (determined from pressure).

The OOI program conducts annual turn-around cruises to the Irminger Sea Array[4], during which the prior year's WFP mooring is recovered and a new WFP mooring with an identical configuration and set of sensors is deployed. These cruises are imperative for several reasons. First, sensors such as the WET Labs ECO Puck™ will "drift" as the light source ages and require regular *in situ* calibration. Additionally, biofouling communities impact the measurements collected by the WFP's sensors (Palevsky, *et al.*, 2023) and must be removed as part of regular sensor maintenance and refurbishment.

OOI standard practices for bio-optical sensor deployment and calibration, and for raw data processing completed internally by the OOI program are provided in Chapter 5 of the OOI Biogeochemical Sensor Data Best Practices and User Guide (Palevsky, *et al.*, 2023). Bio-optical data from the WFP made publicly available by the OOI were downloaded for use in this study from the OOINet Data Portal (NSF Ocean Observatories Initiative). Data used in this study are the Level 2 total optical backscatter (m^{-1}), Level 1 fluorometric chlorophyll-*a* concentration (μg/L), Level 1 temperature (°C), Level 2 practical salinity, and seawater pressure (dbar). Temperature, salinity, and pressure are converted from

[4] These cruises typically use Woods Hole Oceanographic Institution's RV *Neil Armstrong* (AGOR-27).

the OOI-provided units to conservative temperature, absolute salinity, and depth using the Thermodynamic Equation of Seawater - 2010 (TEOS-10) equations as implemented in the Gibbs Seawater Oceanographic Toolbox (McDougall & Barker, 2011). Mixed layer depths are calculated from WFP data using a combination of chlorophyll-*a*, temperature, and salinity data (Yoder, *et al.*, 2024).

Prior to interpretation, total optical backscatter data were filtered to identify and remove outliers (comparable to a Gross Range or Climatology Test; see Palevsky, *et al.*, 2023). For the analysis in this thesis, the threshold selected for total optical backscatter outlier removal was 0.005 m^{-1}, chosen based on a histogram of all total optical backscatter data measured by the WFP across all 8 deployment years (2014-2021) analyzed here (Figure 3a). These anomalously large optical backscatter measurements could reflect sensor malfunction or, more likely, represent conditions such as a particle being stuck on the fluorometer's optical window.

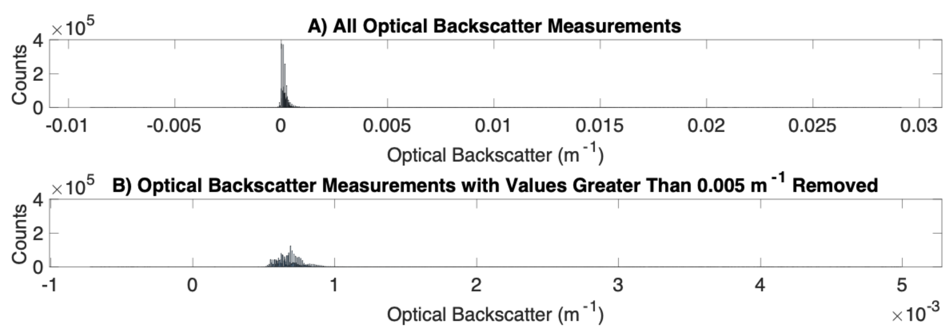

Figure 3. a) Histogram of all total optical backscatter measurements from the OOI Irminger Sea WFP over the full time series record analyzed in this thesis. Values greater than 0.005 m^{-1} were defined as outliers and removed prior to further analysis. These outlier values most likely reflect particles stuck onto the sensor's optical window, which can produce anomalously large optical backscatter signals that do not reflect the particles within the surrounding water column. b) Total optical backscatter measurements remaining after removing the full profiles from all points identified as outliers (6.34% of the data shown in panel a).

. For all points identified as outliers, the full profile containing the outlier was removed from the dataset prior to subsequent analysis. Ultimately, 172,646 points (reflecting every point within 208 profiles containing at least one outlier) out of the total 2,722,109 observations are removed, representing 6.34% of the data. Particulate backscattering (b_{bp}) was calculated from the remaining total optical backscatter data (Figure 3b) following Equation 1 from Briggs, *et al.* (2011):

$$b_{bp} = 2\pi\chi(\beta_{total} - \beta_{sw}) \quad \text{Eqn. 1}$$

where β_{total} is total optical backscatter, β_{sw} is the volume scattering function of seawater, calculated following Zhang *et al*. (2009), and the χ factor for ECO pucks is 1.077 (Sullivan, *et al.*, 2013).

This analysis focuses on the largest, fastest-sinking particles, which are mostly likely to penetrate deep within the water column prior to being remineralized. Optical backscattering due to large particles was determined from b_{bp} by applying a filter to identify spikes due to large individual particles, separating these spikes from the portion of the signal due to small labile and refractory particles (Figure 4; Briggs, *et al.*, 2011; 2020).

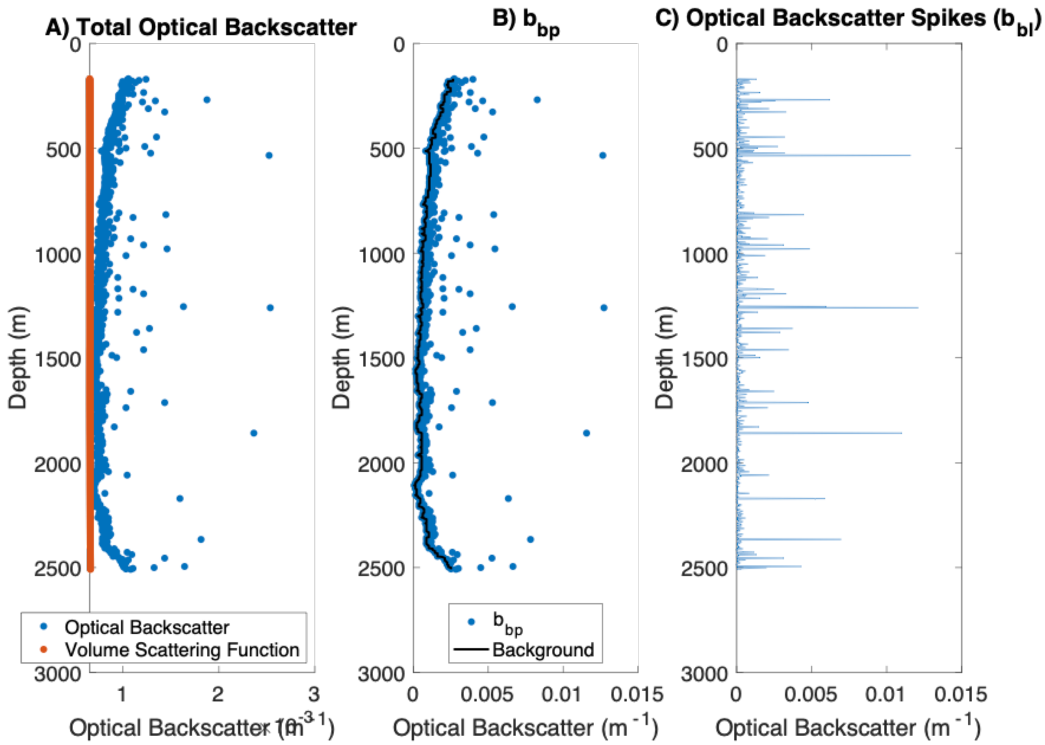

Figure 4. Example of the processing approach applied to all profiles in the time series, shown for a profile from July 7, 2015. a) Measured total optical backscattering (β_{total}) and the seawater volume scattering function (β_{sw}), which are used to calculate b) particulate backscatter (b_{bp}), following equation 1. For each profile, the small labile and refractory particle portion of the b_{bp} signal is calculated by taking a 20-point moving maximum of the 20-point moving minimum (shown as the background line in black panel b). c) Optical backscatter spikes , representing large particles, are the b_{bp} data from panel b minus the background signal.

For each profile, the small labile and refractory particle portion of the b_{bp} signal is calculated by taking a 20-point moving maximum of the 20-point moving minimum, which is roughly at 50-meter resolution through the entire water column, similar to prior analysis with Argo float data (Briggs, *et al.*, 2011; 2020). The background is then subtracted from the b_{bp} signal to determine the particulate backscattering from large particles (b_{bl}).

The timing and magnitude of annual pulses of large sinking particles were calculated within 50-meter depth bins between 200 and 2000 meters (e.g., 200 to 250 meters, 250 to 300 meters, …, 1950 to 2000 meters), for a total of 36 depth bins. Profiles within the WFP time series record contain a median of 20 b_{bl} measurements per depth bin, and profiles are only used for further analysis if all depth horizons within the profile contain at least 14 b_{bl} measurements per depth bin. The maximum of each large sinking particle pulse within each depth bin is identified by calculating the 6-profile (~120 hour) moving mean of the 95th percentile of all b_{bl} data within a given depth bin from each profile (example for three depth bins shown in Figure 5).The 95th percentile was selected to identify the largest particles observed while reducing sensitivity to potential outlier values when using the maximum b_{bl} within each depth bin (Figure A1). The time and magnitude of the annual maximum of the 6-profile moving mean within each 50-m depth bin was identified and used for further analysis of the sinking pulses described below. In 2016, two sinking pulses were evident, and two maxima are calculated for this year: one prior to and one after August 1.

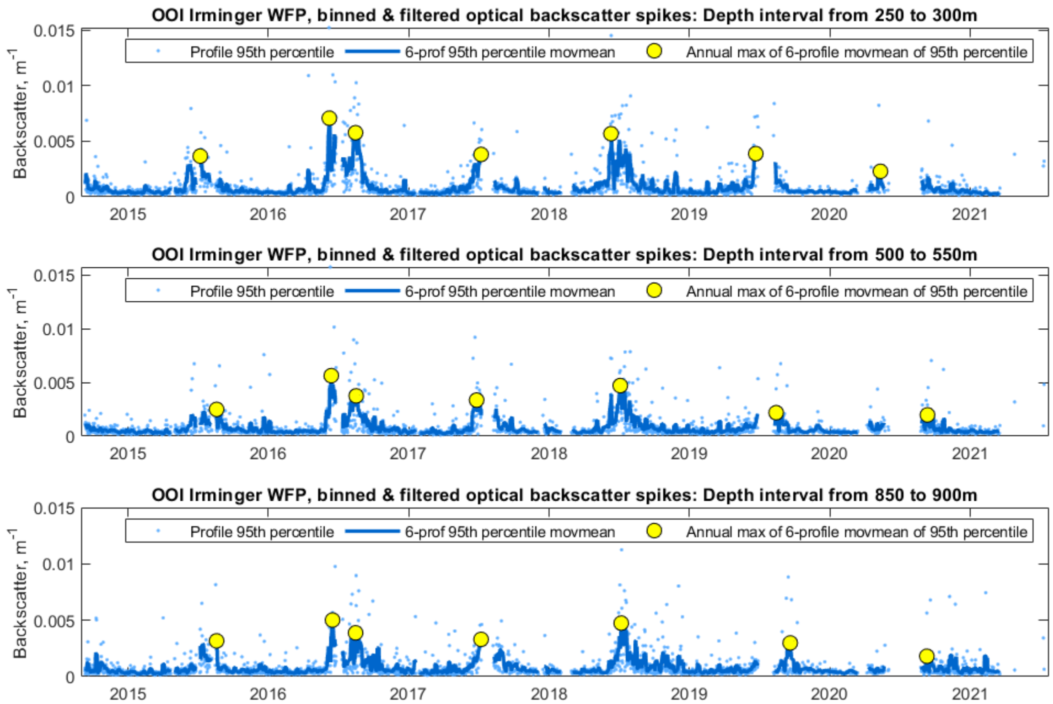

Figure 5. Time series of optical backscatter spikes (processed as illustrated in Figure 4) at three selected depth horizons (250 to 300 m, 500 to 550 m, and 850 to 900 m). Dots are the 95th percentile of all spikes within the 50-m depth bin for each profile and lines are the 6-profile moving mean of the profile-specific data points shown with the dots. The yellow dots show the annual maximum value of the 6-profile (~120 hour) moving mean, which identifies the timing and magnitude of the annual spring-summertime pulse of large sinking particles at each depth. In 2016, two sinking pulses were evident in the record, and so two maxima were identified, one from each pulse.

3. Results and Discussion

Figure 6 shows the entire 7-year time series of large particles identified from the WFP data throughout the water column below 200 m. As expected based on prior work (e.g. Briggs, *et al.*, 2011), we observe a strong export pulse of large particles occurring in the summer months, after the development of the annual spring phytoplankton bloom. Our observations throughout the full water column and full annual cycle show that these particles penetrate deep into the water column, in multiple years clearly evident to below 1500 m (Figure 6).

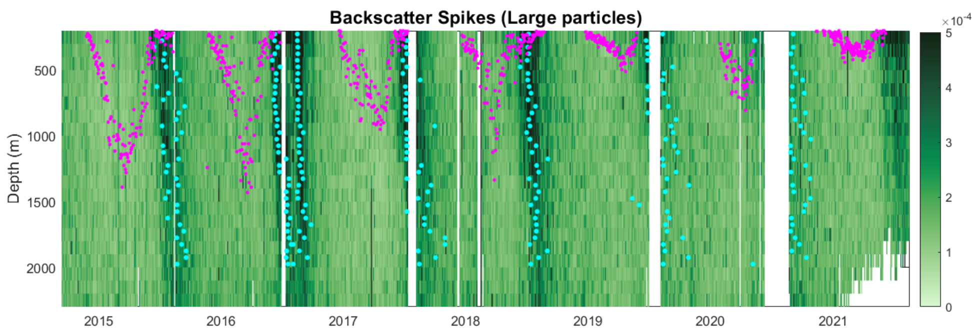

Figure 6. The 7-year time series of large particles, determined from optical backscatter spikes. The cyan dots show the identified annual maximum of each large sinking particle pulse within each 50-m depth bin (see Figure 4 for details and illustration of how maxima are identified). The magenta dots show the depth of the mixed layer during periods where the mixed layer reaches to at least 200 m.

The deep depths reached by these sinking particles are important to the ability of this export flux to contribute to long-term carbon sequestration, since winter mixing also extends to nearly 1500 m in many years within this time series record. The full time series also record also shows strong interannual variability, both in the concentrations of large particles within each annual pulse of sinking particles and the depth of winter mixing, with larger pulses of sinking large particles as well as deeper winter mixing in the earlier part of the OOI record (2014-2018) as compared to the subsequent years (2019-2021).

To quantitatively assess the fate of the sinking particles from each export pulse, POC flux attenuation may be described using a power law relationship, commonly referred to as the "Martin Curve" expressed here as Equation 2 (Martin, *et al.*, 1987; Buesseler, *et al.*, 2020):

$$F_z = F_{100}\left(\frac{z}{100}\right)^{-b} \qquad \text{Eqn. 2}$$

Under this parameterization, F_z is the sinking flux of POC (mol C m^{-2} d^{-1}), at depth z. The other side of the equation expresses the POC flux at a reference depth of 100 meters as F_{100}, with the fraction $z/100$ expressing the relationship between depth z and reference depth 100 meters. The exponent b describes the attenuation of POC flux between these depths. The unitless b value of 0.86, determined based on the original dataset compiled by Martin, *et al.*, 1987 represents a roughly 90% decline in POC flux between 100 meters and 1000 meters (Buesseler, *et al.*, 2020). The b scaling parameter may be found using known sets of depths and optical backscatter values for the water column within an annual export pulse.

Remineralization of sinking particles through the water column leads to attenuation with depth of both the POC flux, and of the concentration of POC itself. Here, we use a modified version of this power law expression to describe the attenuation of POC with depth (Cael & Bisson, 2018):

$$y = cx^{-b} \qquad \text{Eqn. 3}$$

The y parameter is the depth (m) of a bin containing optical backscatter spikes, while the x parameter is the maximum size of an optical backscatter spike in the same bin (m^{-1}; a proxy for large POC concentration), while c acts as a scaling coefficient. The *b* scaling parameter is found using known sets of depths and optical backscatter values for a water column within a given annual export pulse and describes attenuation in the same way that *b* does in Martin's original expression. We constructed this parameterization on an annual basis for this study, using depth of the local maxima at each depth horizon (m) as the independent variable and the magnitude of the local maxima (m^{-1}) as the dependent variable (Figure 7).

Figure 7 shows the sinking rates and flux attenuation for large particle pulses from three years within this time series, selected because they each include a complete gap-free record of the sinking particle pulse. To determine the sinking rate, we use a linear regression fit with date/time as the independent variable and depth (m) as the dependent variable. We find that in 2015, 2016, and 2018, the export pulse occurs in the boreal summer into the early autumn, and that the sinking rate is between 10 and 30 meters per day, which is consistent with values found in the literature (Briggs, Dall'Olmo, & Claustre, 2020).

We use the same particle pulses to calculate flux attenuation. By fitting optical backscatter spike size (m^{-1}) and depth (m) to Equation 3, we find *b* scaling parameters ranging from 0.877 (similar to the original *b* value from Martin, *et al.*, 1987) to 1.34, with greater values of *b* indicating slower flux attenuation with depth.

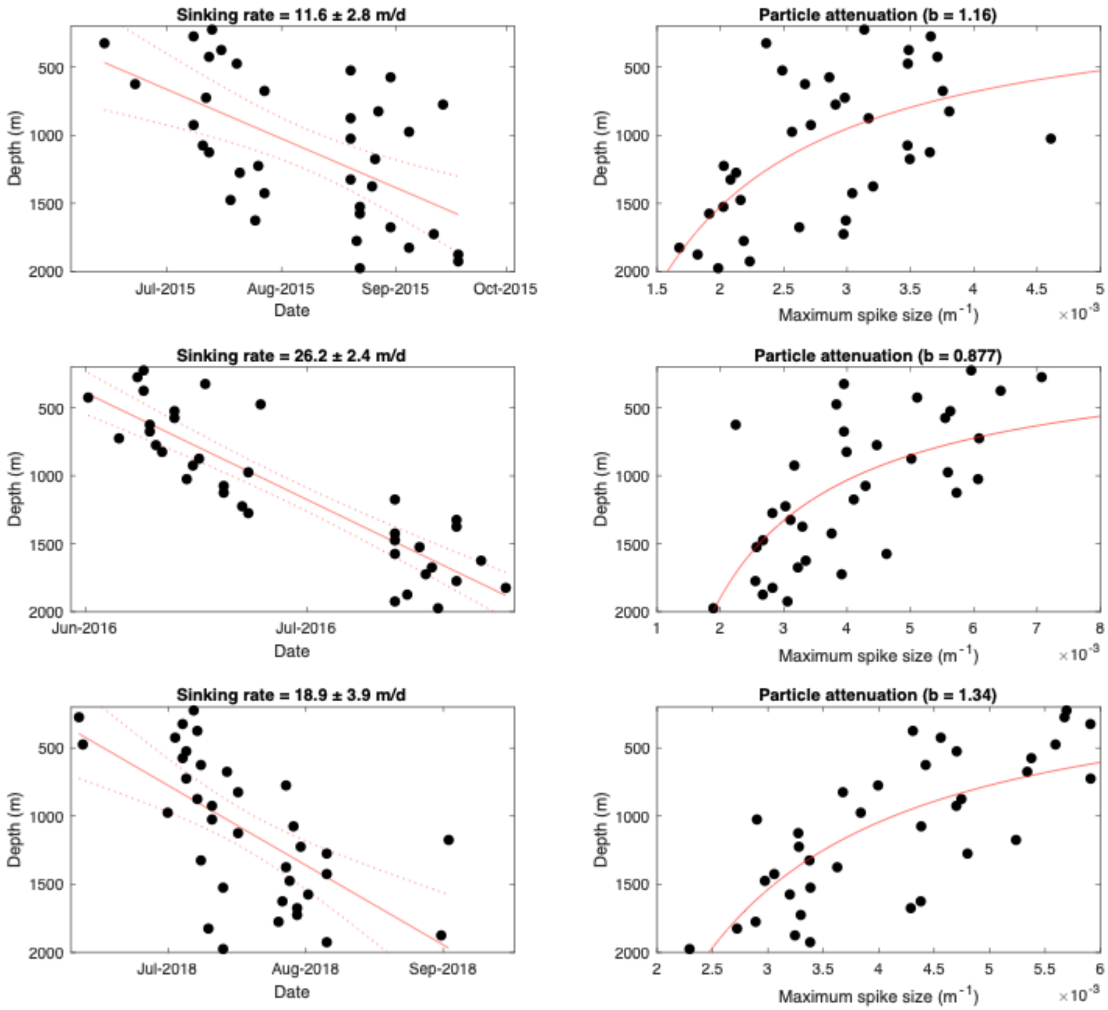

Figure 7. Calculation of sinking rates and attenuation of POC within large particle pulses from 2015 (top), the first pulse from 2016 (middle), and 2018 (bottom). The left-hand plots show the date of the maximum of the large particle pulse identified for each 50-m depth bin (see example shown in Figure 5 and cyan dots in Figure 6). Sinking rate is determined by linear regression (red line, with the dashed lines showing the regression uncertainty). The sinking rates shown at the top of each plot are the slope of the linear regression. The right-hand plots show the magnitude of the maximum spike within each 50-m depth bin. The red lines are a fit to the data following the form $y = cx^{-b}$ (Eqn 3).

These results highlight the importance of both seasonal and interannual variability in the seasonal timing and annual magnitude of carbon export and long-term sequestration via the biological carbon pump in this region. We observed both strong interannual variability in both the maximum annual mixed layer depth (ranging from 400 to 1300 m over this time series) and the timing and magnitude of the sinking particle pulse driven by the annual spring phytoplankton bloom, which together influence the magnitude of carbon sequestered by sinking particles over annual and longer time scales. These findings are consistent with results of a mixed layer DIC budget analysis, which found high interannual variability in the magnitude of organic carbon flux from the seasonal mixed layer (Yoder, *et al.*, 2024). The ultimate amount of carbon sequestered long-term will depend on the interplay between the magnitude of flux from the surface ocean, the rate of attenuation within the water column, and the depth below which sinking flux must penetrate to reach deeper than the subsequent winter's deepest mixed layer depth. This thesis shows that, amidst these competing influences, pulses of large particles consistently penetrate to below even the deepest annual mixed layer depths in the region (Figure 6), highlighting the need for further work to evaluate the role of large sinking particles in driving long-term biological carbon sequestration in this region.

4. Conclusions and Future Work

This work shows the power of the combined time-series of physical and biogeochemical sensor data provided by the OOI. The continuous time series at the Irminger Sea Array clearly captures the seasonal and interannual variability of the phytoplankton bloom at this site through the entire water column and can be used to evaluate the timing and magnitude of carbon export, as well as how carbon export attenuates with depth. While the maximum annual mixed layer depth varies year to year, optical backscatter spikes indicating POC are evident deeper within the water column, showing that carbon sequestration occurs at some magnitude every year within the Irminger Sea.

A seasonal export pulse was observed continuously from start to finish in three of the seven years of observations used in this analysis. In all of these years, the sinking rate is between 10 and 30 meters per day, all within the same order of magnitude and consistent with values seen in the literature (Briggs, Dall'Olmo, & Claustre, 2020). In 2016, the *b* scaling parameter was found to be 0.877, which is comparable to that expressed in Martin's expression of the Martin Curve (1987), indicative of a similar decline in POC flux of roughly 90% between 100 and 1000 meters. These results are in line with our present understanding of the marine carbon cycle and show that OOI's public data can be used to conduct biogeochemical analyses over long time intervals in inhospitable ocean basins.

In the late stages of preparing this thesis, the NSF announced a $220 million award to continue operating and funding the OOI for an additional five years. This award ensures that this time series can be extended into the next decade, providing further context on the role of interannual and seasonal variability in North Atlantic carbon export. Similarly, one could apply the analyses described here to other profiler-equipped OOI arrays, which would elucidate the mechanisms of the carbon cycle in other ocean basins.

OOI arrays are not the only autonomous oceanographic platforms equipped with biogeochemical sensors. These methods draw on prior work that has previously been and will likely continue to be applied to Slocum Gliders[5] and Argo floats[6], especially to capture near-surface POC export. The combination of moored profilers, such as the WFP data analyzed here, and mobile profiling gliders and floats, all increasingly equipped with biogeochemical sensors, offer synergistic capabilities. As the deployment of such bio-optical sensors continues to grow worldwide, this will potentially expand the geographic footprint of similar analyses of POC flux to a global scale, further improving our understanding of the biological carbon pump in the marine carbon cycle.

[5] The Slocum glider is named after Captain Joshua Slocum, who was the first person to circumnavigate the planet alone, aboard the *Spray*. He disappeared in November 1909 aboard the *Spray*, headed for the Amazon. Tangentially, there are also gliders known as Spray gliders, after Slocum's vessel of choice.

[6] Yes, like the *Argo* of Greek myth. The logo for this collaboration appropriately features a Greek trireme, though it may also reference the RV *Argo* (ARS-27) formerly operated by the Scripps Institution of Oceanography, whose bell adorns Sumner Auditorium to this day. As a fun curiosity, the author has had the pleasure of deploying two BGC-Argo floats while underway aboard the RV *Sally Ride* (AGOR-28), also operated by Scripps.

Appendix

"I am Lord Nelson. See, here's my fin."
- Vice Admiral Horatio Nelson

The code for this analysis may be found on GitHub, at the following address: https://github.com/joemcuevas/Irminger_Jose_Backscatter.
The master script is called `EngineRoomStartUp.m`, and it will call other functions to do calculations as elaborated in the pseudocode. This pseudocode can serve as an introduction for a researcher who would like to replicate this analysis, or apply it to similarly-formatted bio-optical data.

MATLAB Guide

Functions
backscatterpresentationfig.m - Produces a green gridded plot based on the optical backscatter measurements at each depth at each temporal point, as well as the maximum optical backscatter measurement every fifty meters within each annual sinking pulse.
BGCPlot.m - Plots the chlorophyll concentration at the surface and at depth over the entire time series, using all fixed-depth sensors as well as the wire-following profiler data.
Briggs2011PlotFun.m - This function plots an individual optical backscattering profile before and after the removal of the background noise.
ChlaBksctrPlotFun.m - Plots chlorophyll and potential density as a function of depth, and relative to the mixed layer depth.
ChoiceJustificationPlotting.m - Produces figures for the Methods section

Variables

Pseudocode and Calculations

- All calculations are run through the EngineRoomStartUp.m script
    - Add paths containing downloaded OOI data and all essential functions
    - Download OOI Global Irminger Sea profiler fluorometer data for all seven years using the load_HYPM_flord_fun.m function.
        - Each annual deployment is saved into its own data structure (Yr1wfp, Yr2wfp, … Yr7wfp)

    - Data are downloaded from the OOI Data Explorer
    - NetCDF (.nc) files for all seven deployments are unpacked
      - Unpacks variables of time, longitude, latitude, temperature (°C), practical salinity, pressure, optical backscatter (m-1), total scattering coefficient (m-1), and chlorophyll concentration (**μ**g/L)
      - Calculates absolute salinity, conservative temperature, and potential density using the Gibbs Seawater Toolbox
      - Converts fluorometer time to MATLAB time using convertTime.m
      - Calculates depth (m based on pressure and latitude using the Gibbs Seawater Toolbox)
      - Assigns profile indices
  - Remove outliers using OutlierFilterFun.m
    - Run over each annual deployment's data structure
    - Outliers defined as all optical backscatter readings greater than or equal to 0.005 m-1
    - Replaces all data in all profiles containing any outliers with NaN values
    - Calculate the number of outliers removed this way
  - All deployments are placed into a single data structure using wfpmergescript.m
    - New wfpmerge structure contains time, depth, density, backscatter without outliers (m-1), backscatter with outliers, total scattering coefficient, chlorophyll concentration, profile index, up/down index, depth grid, and a second profile index data field
  - Remove the background from the optical backscatter
    - Uses the wfpmergeindexfilter.m script
    - Applies a 50 m moving maximum of a 50 m moving minimum over each optical backscattering profile in order to calculate the background signal
    - Subtracts the background from each profile
  - Load mixed layer depth data

- Calculate Sinking Rates with SinkingPulseVertHP.m
  - Define depth intervals and bins
    - Minimum Depth 200 m, Maximum Depth 2000 m, Intervals 50 m
    - Express as a vector ([mindepth:depthint:maxdepth]) for use in further calculations
  - Initialize profile by depth bin-sized structure to hold variables
    - Using an optical backscatter profile to approximate daily-scale changes
  - Loop over each profile and extract all optical backscatter spikes within a given depth bin
    - Calculate mean, standard deviation, maximum, median, and 95th percentile for each depth bin
  - Quality check by removing all profiles with an insufficient number of data points
    - Tolerance set at 14 points (based on histogram of number of points per bin)
  - Create a filtered data set using only usable depth profiles
    - Keeps summary statistics and profiles of profiles containing sufficient data
  - Address hiatuses in data set
    - Identify large temporal gaps
    - Insert NaNs into data set where large gaps exist
  - Calculate moving mean over binned data
    - Moving mean calculated over every six profiles (representing 120 hours)
  - Calculate maximum of sinking pulse in each year for each depth bin
    - Date window set between 1 May and 31 October for every year between 2015 and 2020 inclusive
    - Saves maximum backscatter value, index of that value, and time of that value for each year and depth.
- SinkingPulseAndMartinCurveCalculationsBinned
  - Calculate Sinking Rate
    - Run linear regression for a given year using time as the independent variable and depth as the dependent variable

- Define a custom fit for the Martin Curve using the equation ‘c*x.^-b’ and the fittype function
  - Calculate the c and b parameters using depth as the independent variable and optical backscatter spike magnitude as the dependent variable

- Visually grid optical backscatter spikes
  - Create time and depth grids
    - 3 day depth bins running from start of first deployment to end of final deployment
    - 100 m depth bins running from 0 to 2573 meters (entirety of water column)
  - Grids saved as fields within the wfpmerge structure
- Plot all data using SinkingPulseAndMartinCurveCalculationsBinned.m and backscatterpresentationfig.m

Appendix Figures

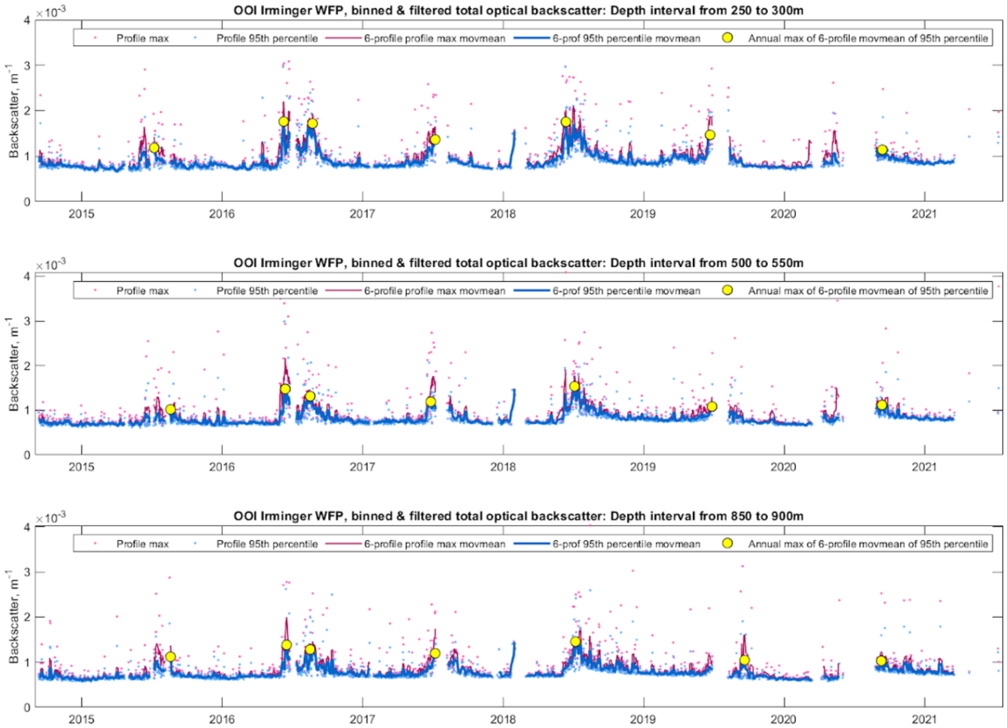

Figure A1. Time series of optical backscatter spikes (processed as illustrated in Figure 4) at three selected depth horizons (250 to 300 m, 500 to 550 m, and 850 to 900 m). Dots are the 95th percentile of all spikes within the 50-m depth bin for each profile and lines are the 6-profile moving mean of the profile-specific data points shown with the dots. The yellow dots show the annual maximum value of the 6-profile (~120 hour) moving mean, which identifies the timing and magnitude of the annual spring-summertime pulse of large sinking particles at each depth. In 2016, two sinking pulses were evident in the record, and so two maxima were identified, one from each pulse.

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