Seawater radioisotope (234Th) and carbon from sampling conducted at the Compass Station in Bedford Basin, Nova Scotia, Canada from April to August 2019

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Data Type: Cruise Results
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Project
» Ocean Frontier Institute Seed Fund Grant: Bedford Basin 2019 (Bedford Basin 2019)

Contributors	Affiliation	Role
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Abstract
These data include seawater radioisotope (234Th) and carbon data collected at the Compass Station in Bedford Basin, Nova Scotia, Canada at three time periods from April to August 2019. Niskins (2L to 10L) were used to obtain the water samples. Four liters of water were used for total 234Th and ~42 L were used to filter size-fractionated particulate 234Th and carbon. Two in-line filters were used: >51 µm and ~ 1 µm. Filters were analyzed via non-destructive beta counting (234Th) and then for carbon content. These data were collected in conjunction with sediment coring samples that were measured for 234Th and carbon content to assess carbon export and the carbon budget of Bedford Basin.

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Coverage

Spatial Extent: **Lat**:44.692 **Lon**:-63.642
Temporal Extent: 2019-04-11 - 2019-08-08

Methods & Sampling

Methods & Sampling:
Data were collected on three cruises conducted as day trips in 2019 (from April to August) aboard the SigmaT, as indicated by the sampling dates. The SigmaT is a local vessel with an appropriate winch for the deployment of coring equipment and Niskins. This vessel is privately owned and operated. All samples were taken at the Compass Station. Drs. Erin Black and Stephanie Kienast can be contacted about all cruises and equipment deployments.

Water column samples were collected with 2- to 10-liter (L) Niskin bottles on a Seabird SBE 19plus CTD (with oxygen and fluorescence sensors) deployed using a winch wire. The bottle volume used was governed by equipment availability. On a given date, the same Niskin volume was used for all samples (i.e., all 2L bottles for one event and all 10L bottles for another).

Total 234Th
When using 10L Niskins, the 4L total Thorium-234 (234Th) samples were immediately taken upon recovery to avoid any settling effects. When 2L bottles were used, the water contained in two 2L Niskins was combined for the same depth. For the total 234Th collection and analysis, 4L of seawater was emptied from the Niskins into volume-mass calibrated bottles for each discrete depth. Total 234Th sample processing (i.e. acidification and precipitation) followed Black et al. 2018. Amendments to these methods are noted here. In summary, the bottles were acidified on the day of sampling in the lab with nitric acid and then spiked with 1 milliliter (mL) of 2.8 decays per minute per gram (dpm/g) 230Th yield monitor using an autopipette. After ~8 hours of equilibration, solutions of KMnO4 and MnCl2 were added to the 4L bottles. The pH was raised above 8 to allow for precipitation. After ~8 hours the custom filter heads were added to the bottles and the total 234Th was collected (as a precipitate) on 25 millimeter (mm) QMAs. All beta counting of the filters was performed at Woods Hole Oceanographic Institution (WHOI). No blank corrections were made to the total 234Th activities because initial process blank counts (0.29 counts per minute (cpm)) were indistinguishable from the average value (± s.d.) for the beta detectors running for 24 hours with no sample (0.28 ± 0.04 cpm). Consistency in beta counter efficiency was monitored using technetium-99 and uranium (via supported 234Th) standards. The total 234Th samples were beta counted first (before the particulate samples) within 4 to 10 days of filtration and then again at least 5 months after filtration. After all beta counting was complete, a Thorium-229 (229Th) recovery yield monitor of 7.7 × 10^3 dpm per gram was added for the filter digestion and ICP-MS analysis. The average recovery was 83% with an s.d. of 13.5% and a median of 85%. The uncertainties on total 234Th are derived from counting statistics and the extrapolation of errors associated with sample processing (i.e. mass and volume measurements, ICPMS recovery analysis).

Particulate, size fractionated 234Th and carbon
~42 liters were collected at each depth with the Niskins and the water was temporarily stored in cleaned plastic barrels prior to filtration. For the particulate 234Th collection, a custom-built 142 mm apparatus was used to vacuum pump sample water from the barrel through a 51 micrometer (µm) pore size nitex filter and a pre-combusted 1 µm pore size quartz microfiber filter (QMA) in sequence. Filters were visually examined for swimmers and a 400 µm pre-filter test found none (August sampling). Photos were taken of all filters in the lab for general assessment of particle loading and color differences, which included the 400 µm screen pre-filter test material. The particulate material from the nitex screens was rinsed onto pre-combusted 25 mm QMA using filtered seawater (<1 µm) and dried overnight. The 142 mm QMA were dried similarly and then a 25 mm punch was collected for successive 234Th and carbon measurements. The particulate samples were beta counted within 6 to 12 days of filtration and then again at least 5 months after filtration. Uncertainties on particulate 234Th activities are derived from counting statistics and error propagation from sampling processing.

Particulate dipped blanks were collected aboard the ship using the 40-meter (m) samples on all dates. A plastic housing (for the dipped blank), containing a 51 µm filter and a 1 µm filter, was submerged in the 40 m barrel until vacuum filtration ended. The plastic housing allowed for the free exchange of sample water. The average beta count for the 51 µm dipped blanks was 0.27 ± 0.2 cpm and for the 1 µm dipped blanks was 0.30 ± 0.4 cpm. As these averages were statistically indistinguishable from empty detector cpm, no blank corrections were required for 234Th analyses.

Particulate carbon content was analyzed in the CERC.OCEAN facility at Dalhousie University. Water column particle filters were analyzed for carbon content using a Costech Instruments Elemental Combustion System 4010. Half of the 25 mm water column QMA filters were analyzed at a time (and both halves were analyzed separately as replicates as indicated). The carbon analysis for the six dipped blanks indicated a small correction was needed for the large and small particle filters. Average dipped blank values were 4% and 9% of the total sample value, respectively. It is important to note that due to the low volume sampled for particulates (~42L) and the subsequent subsampling of half of a 25 mm punch from the small particle QMA filters, there were three samples with blank averages totaling 14-21% of the sample carbon values. With additional instrument uncertainties for the carbon measurements, it is recommended that the full 25 mm filter be used or that a greater volume is collected. The latter may be difficult with high-volume pumps (i.e., McLanes or Challenger pumps), as they have been observed to clog and stop before pumping 40L in coastal waters.

The rinsing of the 142 mm nitex screens to transfer the large particle material onto a 25 mm filter can create a variable distribution on the filter. Thus, the entire 25 mm filter is beta counted for 234Th, but only ½ of the filter is typically used for CHN analysis (due to the size of the filters). The cutting of the 25 mm filter can introduce uncertainty because of inequal halving of the filter and due to the choice of where to place the cut (if there is variable distribution of the particle material). For six of the nitex screens (April and May samples), both halves were analyzed for particulate carbon. The average relative standard deviation (RSD) of the two halves was 17%. For the April and May samples, we could add the two filter values together for the total particulate organic carbon (POC). To be conservative, when we did not have POC concentrations for both halves of the filter in August, we automatically assumed a minimum 20% uncertainty on the single half concentration. This was assumed for the small particle QMA filters as well, although they are much easier to cut. Eliminating the need for cutting the filters or using a partitioned-circle template to cut is recommended in future studies.

Total Particulate RAp234
RAp234 is the residual β activity of particulate 234Th and behaves in a similar manner to lithophile elements (Lin et al. 2016). The residual β activity is found by beta counting the large and small particle filters well after all the shorter-lived and unsupported isotopes have decayed away (e.g. unsupported 234Th). This would be after ~120 days or five half-lives of 234Th. Data from this study has a method limit for RAp234 equivalent to 2 times the s.d. of the dipped blank mean value of RAp234 or 1.54 becquerels per cubic meter (Bq m^-3). The small particle data dominates the RAp234 activity signal (small particle RAp234 makes up 86%-99% of the total RAp234). Any assumed issues with the large particle 234Th data (i.e. completing first counts quickly) do not impact the RAp234 values because the activities of the longer-lived isotopes contributing to the 'background' counts will not change significantly over the counting period. To provide a conservative estimate of uncertainty, a set value of 20% was applied to all total RAp234 values. Propagated counting and measurement uncertainties ranged from 8% to 20%.

Data Processing Description

Known Issues/Problems:
Data quality flags
The data quality flags used are as suggested by the GEOTRACES program (see www.geotraces.org/geotraces-quality-flag-policy/). Most values were flagged as 'probably good' (2), per the suggestion on this website. The (1) flag was not used at all. Standard data quality flags are used as follows:
2 = probably good,
3 = probably bad,
4 = bad,
6 = below detection,
9 = missing data.

Missing data is only used once where the sample was analyzed and there was a subsequent issue with the instrument. Otherwise, NaN is used for depths where no result exists for a given parameter.

Potential large particle 234Th issues
All large particle 234Th data (and derived large particle C:234Th ratios) have been flagged with '3', indicating that we have substantial doubts about the data quality. Large particle POC:234Th ratios >100 µmol:dpm, as seen in this study, have been measured elsewhere when swimmers are trapped on the filters. However, in this study, no swimmers were found. Thus, the large particle 234Th activities seem to be abnormally high and we believe the most likely cause is the low 234Th large particle activities. This could have resulted from a limited sample volume and the delay in beta counting the filters (which needed to be shipped outside of Canada for counting at Woods Hole Oceanographic Institution, MA, USA). The large particle blank filter average was ~0.27 cpm, indistinguishable from the 'empty' detector counts. The large particle 234Th sample gross counts average for all dates was 0.42 cpm with a s.d. of 0.11 cpm. While 0.42 cpm is above the background (0.27 cpm) with the detector uncertainty (0.05 cpm), counts in the 0.35 cpm to 0.45 cpm range are significantly closer to the detection limit than is typical. There is no definite proof that invalidates the large particle count data for this study, but we urge caution in using both the large particle activities and the large particle POC:234Th ratios until additional sampling is performed in the basin and/or in other shallow coastal regimes. Additional discussion of these large particle 234Th activities can be found in the associated publication (submitted).

Variable particle loading and filtration speed
During the initial April sampling campaign, there were issues with pump speed stability, which resulted in poor particle distribution for some of the 142 mm QMAs. Particle loading on the 65 m sample was close to normal and replicate 234Th punches had similar activities of 30.5 dpm and 33.6 dpm (uncertainties are 3.3 dpm). For comparison, the range in small particle 234Th activities for all filters (all dates) was 14 to 53 dpm. Since the activities were within the uncertainties of the measurements and the particle distribution was 'systematically' patchy, the two 234Th activities were averaged and a single POC half from the first punch were used to extrapolate to the full 142 mm filter values. A slightly worse distribution of particles was found on the 40 m sample. Our rough image analysis of high, medium, and low loading regions indicated that our first punch was more representative of the average particle loading of the filter than the second punch. Thus, we used the

234Th and POC from the first punch to determine the full filter values. The last filter from 20 m had the worst distribution of particles over the total filter area by far and the 234Th activities for the two punches at 14 dpm and 47 dpm clearly reflected the differences in the outer and inner filter regions. The rough image analysis of 'lighter' and 'darker' parts of the filter suggested a 34% vs. 66% loading split. The 34% corresponded to punch 1 with the 14 dpm 234Th activity. We weighted the 234Th activities by the estimated percent of the filter to get a total 234Th activity for the 142 mm filter. Unfortunately, we were unable to process both POC samples for these replicate punches and only have the POC concentration for the 14 dpm punch (i.e., likely less POC than the other 66% of the filter). We used the POC from the single replicate to extrapolate the full filter POC value and note this is likely the lower limit of how much POC would be present at 20 m in April.

BCO-DMO Processing:
- renamed fields to comply with BCO-DMO naming conventions (replaced spaces with underscores);
- converted dates to format YYYY-MM-DD;
- added column for ISO8601 date format.

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Data Files

File
seawater.csv (Octet Stream, 4.58 KB) MD5:13346326c23eb6b11e3271a7534a007e Primary data file for dataset ID 889642

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Related Publications

Black, E. E., Algar, C. K., Armstrong, M., & Kienast, S. S. (2023) Insights into constraining coastal carbon export from radioisotopes. Frontiers in Marine Science, volume 10. doi: 10.3389/fmars.2023.1254316
Results

Black, E. E., Buesseler, K. O., Pike, S. M., & Lam, P. J. (2018). 234Th as a tracer of particulate export and remineralization in the southeastern tropical Pacific. Marine Chemistry, 201, 35–50. doi:10.1016/j.marchem.2017.06.009
Methods

Lin, W., Chen, L., Zeng, S., Li, T., Wang, Y., & Yu, K. (2016). Residual β activity of particulate 234Th as a novel proxy for tracking sediment resuspension in the ocean. Scientific Reports, 6(1). https://doi.org/10.1038/srep27069
Methods

Owens, S. A., Buesseler, K. O., & Sims, K. W. W. (2011). Re-evaluating the 238U-salinity relationship in seawater: Implications for the 238U–234Th disequilibrium method. Marine Chemistry, 127(1-4), 31–39. doi:10.1016/j.marchem.2011.07.005
Methods

Pike, S. M., Buesseler, K. O., Andrews, J., & Savoye, N. (2005). Quantification of 234Th recovery in small volume sea water samples by inductively coupled plasma-mass spectrometry. Journal of Radioanalytical and Nuclear Chemistry, 263(2), 355–360. doi:10.1007/s10967-005-0062-9 https://doi.org/10.1007/s10967-005-0594-z
Methods

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Parameters

Parameter	Description	Units

Station_ID	Station number (always 1 which is the Compass Station in Bedford Basin)	unitless
Latitude	Latitude of sampling location reported to 3 decimal places. Samples were all taken at the Compass Station in Bedford Basin.	degrees [+N, -S]
Longitude	Longitude of sampling location reported to 3 decimal places. Samples were all taken at the Compass Station in Bedford Basin	degrees [+E, -W]
Sampling_Date	Date (UTC) that seawater samples were collected from Niskins immediately after recovery	unitless
Sampling_Time	Approximate time (UTC) that seawater samples were collected from Niskins immediately after recovery	unitless
ISO_DateTime_UTC	Date and time (UTC) that the sewater samples were collected in ISO8601 format.	unitless
Event_ID	There are three sampling events (1, 2, 3) corresponding to sampling date groupings for seawater and sediment sampling. Event 1 for seawater sampling will correspond to Event 1 for sediment sampling, and so on.	unitless
Depth	Depth within the water column (0 m is the surface of bedford basin). The bottom depth is estimated to be around 70 m at the Compass Station (+/- 5 m).	meters (m)
Th_234_T_CONC	Activity of total thorium-234 from ODF rosette Niskins or above-McLane pump Niskins	decays per minute per liter (dpm/L)
Unc_Th_234_T_CONC	Uncertainty for Th_234_T_CONC. Derived from counting statistics and error propagation for mass/volume measurements and ICP-MS recovery analysis. See report for additional details.	decays per minute per liter (dpm/L)
Flag_Th_234_T_CONC	Data qualtiy flag for Th_234_T_CONC: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
Th_234_LPT_CONC	Activity of large particle (>51 µm) thorium-234 from Niskin sampling and shipboard vacuum filtration.	decays per minute per liter (dpm/L)
Unc_Th_234_LPT_CONC	Uncertainty for Th_234_LPT_CONC. Derived from counting statistics and error propagation for sample processing.	decays per minute per liter (dpm/L)
Flag_Th_234_LPT_CONC	Data quality flag for Th_234_LPT_CONC: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
Th_234_SPT_CONC	Activity of small particle (1-51 µm) thorium-234 from Niskin sampling and shipboard vacuum filtration.	decays per minute per liter (dpm/L)
Unc_Th_234_SPT_CONC	Uncertainty for Th_234_SPT_CONC. Derived from counting statistics and error propagation for sample processing.	decays per minute per liter (dpm/L)
Flag_Th_234_SPT_CONC	Data quality flag for Th_234_SPT_CONC: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
C_LPT_CONC	Concentration of particulate organic carbon on large particles (>51 µm) from Niskin sampling and shipboard vacuum filtration.	micromoles carbon per liter (umol/L)

Unc_C_LPT_CONC	Uncertainty for C_LPT_CONC.	micromoles carbon per liter (umol/L)
Flag_C_LPT_CONC	Data quality flag for C_LPT_CONC: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
C_SPT_CONC	Concentration of particulate organic carbon on small particles (1-51 µm) from Niskin sampling and shipboard vacuum filtration.	micromoles carbon per liter (umol/L)
Unc_C_SPT_CONC	Uncertainty for C_SPT_CONC.	micromoles carbon per liter (umol/L)
Flag_C_SPT_CONC	Data quality flag for C_SPT_CONC: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
DerRatio_LPT_CTh	Derived ratio of large particle organic carbon to thorium-234 activity. Note: Values have been calculated from the raw carbon and thorium data values, not the rounded reported values in this published dataset. Raw ratio values and uncertainties are reported here. Ratios that account for significant figures and extrapolation can be calculated directly from the carbon and thorium data published here.	micromoles carbon per decays per minute (umol/dpm)
Unc_DerRatio_LPT_CTh	Uncertainty for DerRatio_LPT_CTh. Uncertainties are extrapolated from the particulate organic carbon uncertainty and the thorium-234 uncertainty.	micromoles carbon per decays per minute (umol/dpm)
Flag_DerRatio_LPT_CTh	Data quality flag for DerRatio_LPT_CTh: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
DerRatio_SPT_CTh	Derived ratio of small particle organic carbon to thorium-234 activity. Note: Values have been calculated from the raw carbon and thorium data values, not the rounded reported values in this published dataset. Raw ratio values and uncertainties are reported here. Ratios that account for significant figures and extrapolation can be calculated directly from the carbon and thorium data published here.	micromoles carbon per decays per minute (umol/dpm)
Unc_DerRatio_SPT_CTh	Uncertainty for DerRatio_SPT_CTh. Uncertainties are extrapolated from the particulate organic carbon uncertainty and the thorium-234 uncertainty.	micromoles carbon per decays per minute (umol/dpm)
Flag_DerRatio_SPT_CTh	Data quality flag for DerRatio_SPT_CTh: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
Der_U_238_CONC	Uranium concentration derived from salinity using Owen et. al. 2011 uranium-salinity relationship.	decays per minute per liter (dpm/L)
Unc_Der_U_238_CONC	Uncertainty for Der_U_238_CONC. Calculated from the uncertainty estimates published in Owen et. al. 2011.	decays per minute per liter (dpm/L)
Flag_Der_U_238_CONC	Data quality flag for Der_U_238_CONC: (2) probably good. Note: Data flags are used here but these are salinity derived uranium activities only (uranium activities were not directly measured).	unitless

Sal_CTD	Salinity from the CTD package sensor.	Practical Salinity Units
Unc_Sal_1SD__CTD	Uncertainty for Sal_CTD. Uncertainty on salinity senor measurements which are binned to 1 m intervals with corresponding standard deviations.	Practical Salinity Units
Flag_Sal_CTD	Data quality flag for Sal_CTD: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	unitless
RAp234_TPT_CONC	RAP234 activities or the residual ? activity derived from beta counting after all unsupported 234Th has decayed away. RAP234 was first described in Lin et al. (2016). The residual background counts are reported for total particulates (large and small particle background counts were summed).	Becquerels per cubic meter (Bq/m^3)
Unc_RAp234_TPT_CONC	Uncertainty for RAp234_TPT_CONC. Propagated counting and measurement uncertainties ranged from 8% to 20%. To provide a conservative uncertainty estimate, a 20% uncertainty was applied to all values.	Becquerels per cubic meter (Bq/m^3)
Flag_RAp234_TPT_CONC	Data quality flag for RAp234_TPT_CONC: (2) probably good.	unitless

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Instruments

Dataset-specific Instrument Name	Costech Instruments Elemental Combustion System 4010
Generic Instrument Name	Costech International Elemental Combustion System (ECS) 4010
Dataset-specific Description	Water column particle filters were analyzed for carbon content using a Costech Instruments Elemental Combustion System 4010 owned and operated by Dalhousie University.
Generic Instrument Description	The ECS 4010 Nitrogen / Protein Analyzer is an elemental combustion analyser for CHNSO elemental analysis and Nitrogen / Protein determination. The GC oven and separation column have a temperature range of 30-110 degC, with control of +/- 0.1 degC.

Dataset-specific Instrument Name	Niskin bottle
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Niskins (2L to 10L) were used to obtain the water samples.
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	Riso Laboratory Anti-coincidence Beta Counters
Generic Instrument Name	Riso Laboratory Anti-coincidence Beta Counters
Dataset-specific Description	234Th samples were analyzed using a Riso Anti-coincidence Beta Counter.
Generic Instrument Description	Low-level beta detectors manufactured by Riso (now Nutech) in Denmark. These instruments accept samples that can be mounted on a 25mm filter holder. These detectors have very low backgrounds, 0.17 counts per minute, and can have counting efficiencies as high as 55%.

Dataset-specific Instrument Name	Seabird SBE 19plus with oxygen and fluorescence sensors
Generic Instrument Name	Sea-Bird SBE 19plus V2 SEACAT CTD
Dataset-specific Description	See https://www.seabird.com/sbe-19plus-v2-seacat-profiler-ctd/product?id=607...
Generic Instrument Description	Self-contained self-powered CTD profiler. Measures conductivity, temperature and pressure (Digiquartz sensor) in both profiling (samples at 4 scans/sec) and moored (sample rates of once every 5 seconds to once every 9 hours) mode. Available in plastic or titanium housing with depth ranges of 600m and 7000m respectively. Miniature submersible pump provides water to the conductivity cell. Compared to the previous 19plus, the V2 incorporates an electronics upgrade and additional features, with six differentially amplified A/D input channels, one RS-232 data input channel, and 64 MB FLASH memory.

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Project Information

Ocean Frontier Institute Seed Fund Grant: Bedford Basin 2019 (Bedford Basin 2019)

Coverage: Compass Station in Bedford Basin, Nova Scotia, Canada

In coastal regions, the transport of carbon from surface waters to the seafloor is a key mechanism of carbon burial and it has been suggested that one-fifth of the carbon entering coastal areas off of eastern North America (from the atmosphere and through rivers) is subsequently buried in these coastal areas (Najjar et al., 2018). However, direct measurements coupling carbon fluxes in coastal waters to accumulation in sediment remains a challenge.

Bedford Basin is a well-studied coastal system in Nova Scotia, Canada (Bedford Basin Monitoring Program) that can provide unique insight into carbon cycling in these shallow marine regions. To quantify sinking particulate carbon and benthic-pelagic carbon cycling, and to examine the potential factors influencing coastal carbon budgets, carbon content and radioisotope (i.e., Thorium-234) measurements were collected at the Compass Station in Bedford Basin at four time periods (February to August 2019). Sediment cores and seawater samples were analyzed. Size fractionated filtration was performed to examine differences in 'sinking' (>51 micrometers) and 'suspended' (1-51 micrometers) particulate organic carbon and Thorium-234.

References Cited:
Najjar, R. G., et al. (2018). Carbon Budget of Tidal Wetlands, Estuaries, and Shelf Waters of Eastern North

America. In Global Biogeochemical Cycles (Vol. 32, Issue 3, pp. 389–416). American Geophysical Union (AGU). https://doi.org/10.1002/2017gb005790

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Funding

Funding Source	Award
Ocean Frontier Institute (OFI)	OFI Seed Fund Phase II

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