Water geochemistry from surface samples collected along the Neuse River, Neuse River Estuary, and Pamlico Sound in North Carolina between October and December 2016, following the passage of Hurricane Matthew

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Project
» RAPID: Collaborative Research: Carbon and nutrient responses in an estuarine-coastal complex impacted by floodwaters from Hurricane Matthew (HMATT)

Contributors	Affiliation	Role
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Abstract
Water geochemistry from surface samples collected along the Neuse River, Neuse River Estuary, and Pamlico Sound in North Carolina between October and December 2016, following the passage of Hurricane Matthew.

Table of Contents

Coverage

Spatial Extent: **N**:35.675008 **E**:-76.2006 **S**:34.94888 **W**:-78.43603
Temporal Extent: 2016-10-12 - 2017-10-17

Methods & Sampling

Raw water surface samples were collected at sites along the Neuse River (NR), Neuse River Estuary (NRE), and Pamlico Sound (PS) in North Carolina over a period of three months, between October and December 2016, following the passage of Hurricane Matthew on October 9, 2016. Sampling was conducted approximately weekly across the NR, NRE, and PS sites. Riverine samples were collected, in 1 L brown HDPE bottles, from bridge overpasses along the main-stem of the NR at USGS gaged locations. Estuarine and sound samples were collected, in 1 L opaque HDPE bottles and frozen for shipment to NCSU, by the Neuse River Estuary Modeling and Monitoring Project ("ModMon") located at the University of North Carolina at Chapel Hill's Institute of Marine Science (UNC-IMS) in Morehead City, NC. Collection bottles were cleansed in a detergent bath, rinsed profusely with Milli-Q ultrapure water, and left to air dry before sampling. We conducted additional sampling in an area of

freshwater riparian wetlands between the last riverine site on the NR near Fort Barnwell, NC and first estuarine site on the NRE at the Street's Ferry Bridge crossing near Vanceboro, NC in March and October 2017.

Raw water samples were thawed at room temperature, and a known volume of water was filtered through pre-combusted (at 45C for 5 hours) 0.7 m Whatman glass fiber filters (GF/F) via vacuum. Prior to sample filtration, 150 mL of Milli-Q water was used to rinse each filter. The filtrate was collected into 60 mL polycarbonate bottles (detergent-washed and rinsed thoroughly with Milli-Q water) for optical analyses and 40 mL amber-tinted borosilicate glass vials (detergent-washed, rinsed thoroughly with Milli-Q water, and combusted at 45C for 5 hours) for dissolved organic carbon (DOC) concentration and stable carbon isotope (13C-DOC) analyses. Filtrate was stored at 4C until optical measurements were made, generally within 48 hours. Filtrate for DOC analysis was acidified to a pH of 2 with 85% phosphoric acid (H3PO4), then stored at 4C until measurements were completed. GF/F filters were stored at -20C until particulate organic carbon (POC) concentration and stable carbon isotopes (13C-POC) could be measured.

Absorbance measurements were made with a Varian Cary 300UV spectrophotometer in 1 cm quartz cuvettes, over a range of wavelengths (200-800 nm), and then blank corrected using Milli-Q ultrapure water. (Osburn and Morris, 2003)

Fluorescence was measured on a Varian Eclipse spectrofluorometer under the following conditions: excitation (Ex) wavelengths from 240 to 450 nm at 5 nm intervals, emission (Em) wavelengths from 300 to 600 nm at 2 nm intervals. The fluorescence data was concatenated into excitation-emission matrices (EEMs), which display qualitative information about OM within a system, such as the sources of organic matter (Coble, 2007).

Samples for DOC were immediately filtered through 0.2 um polyethersulfone filters into glass vials, capped with Teflon-lined septa and stored without headspace at 4C until analysis. DIC concentration ([DIC]) and delta-13C-DIC value was measured on a OI Analytical TOC analyzer (Doctor et al., 2008)

To quantify DOC concentration, [DOC], samples were first sparged with ultrapure Argon gas for 20 minutes to remove dissolved inorganic carbon (DIC). Sparged samples were analyzed on an OI Analytical 1030D Aurora total organic carbon analyzer, using wet chemical oxidation, coupled to a Thermo Delta V Plus isotope ratio mass spectrometer (IRMS) to determine stable isotope values, expressed as the standard delta notation, 13C-DOC (Osburn and St. Jean, 2007). [DOC] were blank-corrected for ultra-pure Milli-Q water, then calculated using a linear regression curve of known caffeine standards with concentrations from 1 to 20 mg C per L. 13C-DOC values were blank corrected and referenced to the Vienna Pee Dee Belemnite (VPDB) scale via a linear regression of six caffeine (IAEA-600, -27.7 +/- 0.04‰) and two sucrose (IAEA-C6, -10.8 +/- 0.03‰) International Atomic Energy Agency (IAEA) standards. Precision for [DOC] and 13C-DOC values were +/- 0.4‰ based on reproducibility and calibration to sucrose standard. Milli-Q blanks were ran every 10 samples for quality control and confidence of instrument.

Frozen GF/F filters were thawed, then dried at 60C for at least 24 hours in an oven to prepare for measurement of particulate carbon and nitrogen concentrations ([POC] and [PN] respectively) and the stable isotope of [POC], 13C-POC. Analysis was conducted on a Thermo Finnigan Flash Series 1112 Elemental Analyzer (EA), coupled to a Delta V IRMS via a Conflo III interface. Calibration curves were made using acetanilide, L-glutamic acid (USGS-40), caffeine (IAEA-600), oxalic acid (NIST-4990C), and sucrose (IAEA-C6) standards. Weighed standards (0.200-0.600 mg) were placed in low blank tin capsules (4 x 6mm), while dried GF/F filters were folded then placed in larger low blank tin capsules (10 x 12mm). Carbon and nitrogen peak locations on the EA, [POC], and [PN] were determined using acetanilide standards with percent content values of 71.09% and 10.36% for carbon and nitrogen, respectively. 13C-POC for each sample was determined by converting the measured value to the VPDB scale using a linear fit regression of the L-glutamic acid (-26.39‰), caffeine (-27.77‰), oxalic acid (-17.8‰), and sucrose (-10.8‰) standards. Similar to the precision for [DOC] and 13C-DOC, 13C-POC values were +/- 0.4‰ based on reproducibility and calibration to known standards.

Synoptic measurements were collected using a handheld YSI probe and include salinity, pH, temperature, dissolved oxygen concentration (DO), DO saturation (%DO), Total Dissolved Solids (TDS), and Specific Conductivity (Spec. Cond.).

Data Processing Description

Data Processing: Excel used for spreadsheets; Matlab (v 2016 to 2018) is used to process absorbance and fluorescence results and data and to conduct statistical testing. SigmaPlot is used for data visualization.

Problem Report: Some gaps in data occur when sample sites were inaccessible or when samples were lost

during shipment or during analysis.

BCO-DMO Processing: modified parameter names (removed special characters; replaced spaces and hyphens with underscores; added "peak" to peak ratios for clarity).

[table of contents | back to top]

Data Files

File
geochemical_data.csv (Comma Separated Values (.csv), 109.89 KB) MD5:043b35716a060890e6cd8ea7157c8fa3 Primary data file for dataset ID 755923

[table of contents | back to top]

Related Publications

Coble, P. (2007). Marine Optical Biogeochemistry: The Chemistry of Ocean Color. Chem. Rev., 2007, 107 (2), pp 402–418. doi:10.1021/cr050350
Methods

Doctor, D. H., Kendall, C., Sebestyen, S. D., Shanley, J. B., Ohte, N., & Boyer, E. W. (2008). Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. Hydrological Processes, 22(14), 2410–2423. doi:10.1002/hyp.6833
Methods

Osburn, C. L., & Morris, D. P. (n.d.). Photochemistry of chromophoric dissolved organic matter in natural waters. UV Effects in Aquatic Organisms and Ecosystems, 185–218. doi:10.1039/9781847552266-00185
Methods

Osburn, C. L., & St-Jean, G. (2007). The use of wet chemical oxidation with high-amplification isotope ratio mass spectrometry (WCO-IRMS) to measure stable isotope values of dissolved organic carbon in seawater. Limnology and Oceanography: Methods, 5(10), 296–308. doi:10.4319/lom.2007.5.296
Methods

Paerl, H. W., Crosswell, J. R., Van Dam, B., Hall, N. S., Rossignol, K. L., Osburn, C. L., … Harding, L. W. (2018). Two decades of tropical cyclone impacts on North Carolina's estuarine carbon, nutrient and phytoplankton dynamics: implications for biogeochemical cycling and water quality in a stormier world. Biogeochemistry, 141(3), 307–332. doi:10.1007/s10533-018-0438-x
Results

[table of contents | back to top]

Parameters

Parameter	Description	Units
Sample_ID	Osburn Lab Sample Identifier	unitless
Site_Location	Project Site Identifier	unitless
Year	4-digit year of Sample	unitless
Month	2-digit month of Sample	unitless
Day	2-digit day of Sample	unitless
Time	Local Time of Sample (EST); fomrat: HH:MM:SS	unitless
Timezone	Time zone (UTC miunus 5 hours)	unitless
Lat	Latitude of Sample Location; positive values = North	Decimal degrees

Lon	Longitude of Sample Location; positive values = East	Decimal degrees
Temp	Water Temperature	Degrees Celsius
Salinity	Salinity of Water	PSU
GFF_IW	Initial Weight of Glass Fiber Filter	Milligrams (mg)
GFF_FW	Final Weight of Glass Fiber Filter	Milligrams (mg)
GFF_Diff	The difference in Weight of the Glass Fiber Filters	Milligrams (mg)
River_Dis	River Discharge taken from USGS gaging sites along the Neuse River	Cubic meters per second (m^3/s)
Spec_Con	Specific Conductance of Water	Microsiemens per Centimeter (uS/cm)
DO	Dissolved Oxygen	Milligrams per Liter (mg/L)
DO_Sat	Dissolved Oxygen Saturation	Percentage
pH	pH of the Sample	unitless
TDS	Total Dissolved Solids	Milligrams per Liter (mg/L)
VF	Volume of water Filtered through GF/F	Milliliters (mL)
TSS	Total Suspended Solids (Difference of Weighed Filter/Volume Filtered)	Milligrams per Liter (mg/L)
POC	Particulate Organic Carbon	Micrograms per Liter (ug/L)
PN	Particulate Nitrogen	Micrograms per Liter (ug/L)
CDOM	Absorbance coefficent of sample at 254 nanometers	1/meters
DIC	Dissolved Inorganic Carbon	Milligrams per Liter (mg/L)
DOC	Dissolved Organic Carbon	Milligrams per Liter (mg/L)
d13C_DOC	Carbon Stable Isotope Ratio of Dissolved Organic Carbon	Permille (‰)
d13C_POC	Carbon Stable Isotope Ratio of Particulate Organic Carbon	Permille (‰)
d15N_PN	Nitrogen Stable Isotope Ratio of Particulate Nitrogen	Permille (‰)
C_to_N	Atomic Carbon to Nitrogen Ratio	unitless
SUVA254	Specific Ultraviolet Absorbance at 254 nanometers	Liters per Milligram Carbon per Meter (L/(mgC m))
S275_295	Spectral Slope from 275 to 295 nanometers	1/nm
S350_400	Spectral Slope from 350 to 400 nanometers	1/nm
SR	Slope Ratio (S275-295:S350-400)	unitless
Max_Fl_Em	Fluorescence Emission Maximum	Nanometers (nm)
Max_Fl	Maximum Fluorescence Value	QSE
B	Tyrosine-like, Protein-like Fluorescence peak	QSE
T	Tryptophan-like, Protein-like Fluorescence peak	QSE
A	Humic-like Fluorescence peak	QSE
C	Humic-like Fluorescence peak	QSE
M	Marine Humic-like Fluorescence peak	QSE
N	Unknown fluorescence peak	QSE
FI	Fluorescence Index	unitless
BIX	Biological Index	unitless
HIX	Humic Index	unitless

T_to_B_peak	Ratio of T peak to B peak	unitless
T_to_M_peak	Ratio of T peak to M peak	unitless
T_to_N_peak	Ratio of T peak to N peak	unitless
T_to_C_peak	Ratio of T peak to C peak	unitless
A_to_T_peak	Ratio of A peak to T peak	unitless
A_to_C_peak	Ratio of A peak to C peak	unitless
A_to_M_peak	Ratio of A peak to M peak	unitless
M_to_C_peak	Ratio of M peak to C peak	unitless
C_to_N_peak	Ratio of C peak to N peak	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Thermo Scientific FlashEA 1112 Nitrogen and Carbon analyzer
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	POC & PN. Calibrated with acetanilide.
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset-specific Instrument Name	Cary Eclipse Spectrofluorometer
Generic Instrument Name	Fluorometer
Dataset-specific Description	DOM Fluorescence. Calibrated with quinine sulfate solution after normalization to instrument's water Raman peak.
Generic Instrument Description	A fluorometer or fluorimeter is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light. The instrument is designed to measure the amount of stimulated electromagnetic radiation produced by pulses of electromagnetic radiation emitted into a water sample or in situ.

Dataset-specific Instrument Name	Thermo Scientific Delta V Isotope Ratio Mass Spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	13C-DOC, 13C-POC and 15N-PN. The isotope-ratio mass spectrometer (IRMS) allows the precise measurement of mixtures of naturally occurring isotopes. Reference CO2 and N2 gases are calibrated to NIST- or IAEA-traceable standards of known isotopic composition. Seawater DOC is calibrated with the Hansell Deep Sea Reference.
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset-specific Instrument Name	Cary UV 300 Spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	DOM absorbance. Instrument checks performed regularly.
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Dataset-specific Instrument Name	OI Analytical Aurora 1030 W Total Organic Carbon (TOC) Analyzer
Generic Instrument Name	Total Organic Carbon Analyzer
Dataset-specific Description	DOC & DIC. Calibrated with stock solutions of sodium bicarbonate (DIC) and caffeine (DOC). A certified reference material (CRM) for DIC is analyzed regularly as a check standard.
Generic Instrument Description	A unit that accurately determines the carbon concentrations of organic compounds typically by detecting and measuring its combustion product (CO2). See description document at: http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf

Dataset-specific Instrument Name	YSI Pro Plus multiparameter meter
Generic Instrument Name	YSI Professional Plus Multi-Parameter Probe
Dataset-specific Description	Temp, Salinity, pH, DO, DO%, TDS, Spec. Cond. Sensors calibrated with reference solutions prior to each use. DO and pH sensors are replaced and new sensors calibrated approximately every year.
Generic Instrument Description	The YSI Professional Plus handheld multiparameter meter provides for the measurement of a variety of combinations for dissolved oxygen, conductivity, specific conductance, salinity, resistivity, total dissolved solids (TDS), pH, ORP, pH/ORP combination, ammonium (ammonia), nitrate, chloride and temperature. More information from the manufacturer.

[table of contents | back to top]

Project Information

RAPID: Collaborative Research: Carbon and nutrient responses in an estuarine-coastal complex impacted by floodwaters from Hurricane Matthew (HMATT)

Coverage: Coastal waters of eastern North Carolina (Pamlico Sound) 35.09 N 76.52 W

NSF abstract:

This project constitutes a rapid-response effort to investigate the effects of the extreme flooding event of Hurricane Matthew on coastal cycling of carbon and nutrient elements. The investigators aim to improve our understanding of how estuaries and coastal systems respond to extreme events by measuring carbon, nitrogen, and phosphorus loading into the Neuse River Estuary-Pamlico Sound (NRE-PS) coastal ecosystem. The NRE-PS is the urgent study site to examine resulting effects of Hurricane Matthew on coastal environments because it is downstream of the most intense flooding that occurred, and it is located on the North Atlantic "hurricane track", likely to be impacted by future extreme events. Furthermore, it is the focus of a long-term monitoring program in that system, the Neuse River Estuary Modeling and Monitoring Program (ModMon), which was initiated in 1993. That date is significant because it preceded a recent rise in Atlantic tropical cyclone activity and has been able to capture the biogeochemical and ecological effects of major storms that have impacted the NC coast, including Hurricanes Fran (1996), Floyd (1999), Isabel (2003), and Irene (2011). Incorporating intensive sampling of the Hurricane Matthew flooding in the context of these ongoing observations will enable a comparison of the material fluxes into this coastal environment resulting from a major tropical storm and provide a comparison with other coastal environments. Outcomes of this work will be communicated widely via existing outreach efforts of each investigator's research programs to local and regional resource managers, regulators, and other stakeholders. Nutrient loading will be critical information for stakeholders because the Neuse Estuary is an EPA 303(d) listed waterway impaired for nitrogen. Project results can aid in understanding the effects of extreme weather events on ecosystem disturbances and inform coastal carbon flux estimates.

Specific questions to be addressed in the context of this project include: 1) How do coastal carbon and nitrogen budgets respond to floodwaters from tropical storms and hurricanes? 2) What is the biological and photochemical reactivity of this material? The first question can be answered via a relatively short, yet intense, period of observations, such as is proposed here. The second question, which has potential teleconnections to climate in terms of carbon fluxes, food web responses, and other ecosystems processes, requires a longer duration study. However, Question 2 could be answered by further study of samples collected during a short and intense period of sampling proposed to answer Question 1. Work proposed in this project will result in estimates of fluxes and reservoirs of key constituents such as dissolved inorganic carbon (DIC), dissolved and particulate organic carbon and nitrogen (DOC, POC, DON, PON), and N and P nutrients, as well as chlorophyll biomass and pigment analyses.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1706009
NSF Division of Ocean Sciences (NSF OCE)	OCE-1705972

[table of contents | back to top]