## Dissolved inorganic nitrogen, chlorophyll-a, and primary production from bioassay experiments during the R/V Hugh R. Sharp cruise HRS1414 in the Mid and South-Atlantic Bight in August of 2014 (DANCE project)

Website: https://www.bco-dmo.org/dataset/734364 Data Type: Cruise Results, experimental Version: 1 Version Date: 2018-04-25

#### Project

» <u>Collaborative Research: Impacts of atmospheric nitrogen deposition on the biogeochemistry of oligotrophic</u> <u>coastal waters</u> (DANCE)

Contributors	Affiliation	Role
Sedwick, Peter N.	Old Dominion University (ODU)	Principal Investigator, Contact
<u>Mulholland,</u> <u>Margaret</u>	Old Dominion University (ODU)	Co-Principal Investigator
<u>Najjar, Raymond</u>	Pennsylvania State University (PSU)	Co-Principal Investigator
York, Amber D.	Woods Hole Oceanographic Institution (WHOI BCO- DMO)	BCO-DMO Data Manager

#### Abstract

Three bioassay experiments were conducted in August of 2014 during the R/V Hugh R. Sharp cruise HRS1414 which generated measurements of dissolved inorganic nitrogen, chlorophyll-a and primary productivity. Treatments included various nutrient (N,Fe,P) additions and rainwater. This dataset was utilized in the following publication: Sedwick. P. N., et al. "Assessing phytoplankton nutritional status and potential impact of wet deposition in seasonally oligotrophic waters of the Mid-Atlantic Bight." Geophysical Research Letters (2018): doi: 10.1002/2017GL075361

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## Coverage

**Spatial Extent**: N:38.6053 **E**:-72.2534 **S**:38.38 **W**:-72.4761 **Temporal Extent**: 2014-08 - 2014-08

#### Methods & Sampling

Experimental seawater collection: For shipboard bioassay experiments, whole seawater and resident biota were collected from  $\sim$ 4 m depth whilst underway at  $\sim$ 5 knots, using a trace-metal clean towfish system

(Sedwick et al., 2011). This seawater was used to fill two 60 L polyethylene carboys in parallel inside a shipboard trace-metal clean container laboratory, after passing through pre-cleaned 180 µm nylon screen to exclude larger organisms, then subsequently used to fill the experimental incubation bottles (see below). Three bioassay experiments were performed (Sedwick et al., 2018), for which seawater was collected during three separate deployments of the towfish system.

For bioassay experiment 1, seawater was collected on 1 August, 2014, between 16:55 and 17:35 local time, between 38.6053°N, 72.2534°W (start) and 38.5692°N, 72.2354°W (end). Single determinations of iron and macronutrient concentrations in seawater from the towfish that was filtered in-line through a 0.8/0.2  $\mu$ m AcroPak Supor filter capsule (Pall) yielded the following results:

Dissolved iron (DFe): 0.55 nM (start), 0.43 nM (end)

Dissolved nitrate+nitrite (NO3+NO2): 0.07 µM (start) 0.08 µM (end)

Dissolved phosphate (PO4): 0.19 µM (start), 0.20 µM (end)

Dissolved ammonium (NH4): not determined

For bioassay experiment 2, seawater was collected on 4 August, 2014, between 11:10 and 12:10 local time, between 38.3800°N, 72.4743°W (start) and 38.3847°N, 72.4761°W (end). Single determinations of iron and macronutrient concentrations in seawater from the towfish that was filtered in-line through a 0.8/0.2 μm AcroPak Supor filter capsule (Pall) yielded the following results:

Dissolved iron (DFe): 0.33 nM (start), 0.32 nM (end)

Dissolved nitrate+nitrite (NO3+NO2): 0.07 µM (start) 0.07 µM (end)

Dissolved phosphate (PO4): 0.19  $\mu$ M (start), 0.20  $\mu$ M (end)

Dissolved ammonium (NH4): 0.01  $\mu$ M (start), 0.01  $\mu$ M (end)

For bioassay experiment 3, seawater was collected on 9 August, 2014, between 15:19 and 15:54 local time, between 35.5305°N, 72.2760°W (start) and 35.5165°N, 72.2703°W (end). Single determinations of iron and macronutrient concentrations in seawater from the towfish that was filtered in-line through a 0.8/0.2 μm AcroPak Supor filter capsule (Pall) yielded the following results:

Dissolved iron (DFe): 0.89 nM (start), 0.90 nM (end)

Dissolved nitrate+nitrite (NO3+NO2): 0.05 µM (start) 0.07 µM (end)

Dissolved phosphate (PO4): not determined

Dissolved ammonium (NH4): 0.03 µM (start), 0.01 µM (end)

Bioassay experiment protocols: The shipboard bioassay experimental protocols are described by Sedwick et al. (2018). For each experiment there were 6 different incubation treatments (control, iron, nitrate, nitrate+iron, nitrate+iron+phosphate, rainwater), with triplicate bottles for each treatment sampled at each of three timepoints. Each bottle was completely subsampled for measurements of nutrients (NO3+NO2, NH4), chlorophyll-a and primary productivity. For the initial (time = 0) measurements, the seawater that remained in the 60 L polyethylene carboys after filling the incubation bottles was transfered into a 20 L polyethylene carboy from which subsamples were taken for measurements of NO3+NO2 after filtration through 0.8  $\mu$ m pore size AcroDisc Supor syringe filters (Pall), for chlorophyll-a after filtration on to combusted 0.7  $\mu$ m pore size GF/F filters (Whatman), and for incubation with carbon-13 labeled bicarbonate for estimation of primary production. For initial (t = 0) NH4 concentrations, we use mean values measured in seawater sampled from the towfish outlet after in-line filtration (see above).

Analytical procedures:

DFe: Filtered seawater samples were acidified at-sea to pH ~1.8 with Fisher Optima grade ultrapure hydrochloric acid, and then stored at room temperature until post-cruise analysis at Old Dominion University. Dissolved iron was determined by flow injection analysis with colorimetric detection after in-line preconcentration on resin-immobilized 8-hydroxyquinoline (Sedwick et al., 2015), using a method modified from Measures et al. (1995). Analyses were performed on a volumetric basis, so concentrations are reported in units of nanomole liter-1 (nM). Analytical precision is estimated from multiple (separate-day) determinations of the SAFe seawater reference materials, which yield uncertainties (expressed as one relative standard

deviation on the mean, or one sigma) of ~15% at the concentration level of SAFe S seawater (0.090 nM), and ~10% at the concentration level of SAFe D2 seawater (0.90 nM). The analytical limit of detection is estimated as the DFe concentration equivalent to a peak area that is three times the standard deviation on the zero-loading blank (manifold blank), which yields an estimated detection limit below 0.04 nM (Bowie et al., 2004). Blank contributions from the ammonium acetate sample buffer solution (added on-line during analysis) and hydrochloric acid (added after collection) are negligible.

NO3+NO2: Dissolved nitrate and nitrite was determined at sea using an Astoria Pacific nutrient autoanalyzer using standard colorimetric methods with an estimated detection limit of 0.14  $\mu$ M (Parsons et al., 1984; Price and Harrison, 1987). In surface waters, nitrate and nitrite were determined using the same autoanalyzer equipped with a liquid waveguide capillary cell (World Precision Instruments) (Zhang, 2000) to achieve an estimated detection limit of 0.02  $\mu$ M.

PO4: Dissolved phosphate was determined at sea using an Astoria Pacific nutrient autoanalyzer using standard colorimetric methods with an estimated detection limit of 0.03  $\mu$ M (Parsons et al., 1984; Price and Harrison, 1987).

NH4: Dissolved ammonium was determined at sea using the manual orthophthaldialdehyde method (Holmes et al., 1999), with an estimated detection limit of 10 nM.

Chl-a: Chlorophyll-a was determined at sea using the non-acidification method with a Turner 10-AU fluorometer (Welschmeyer, 1994).

PP: Primary production was measured using carbon stable istopes (Mulholland et al., 2006).

Missing data identifiers: ND = not determined (single measurement) NR = not reported (contamination likely, only used for NH4 data)

#### **Data Processing Description**

Please note that this dataset containing statistical averages (mean and sd) will be updated in future to provide the unaggregated individual measurements.

BCO-DMO Data Manager Processing Notes:

\* added a conventional header with dataset name, PI name, version date

\* modified parameter names to conform with BCO-DMO naming conventions

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#### **Data Files**

File
bioassays.csv(Comma Separated Values (.csv), 3.08 KB) MD5:f58a2cd16dd8c5535b36d021e3334c38
Primary data file for dataset ID 734364

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## **Related Publications**

Bowie, A. R., Sedwick, P. N., & Worsfold, P. J. (2004). Analytical intercomparison between flow injectionchemiluminescence and flow injection-spectrophotometry for the determination of picomolar concentrations of iron in seawater. Limnology and Oceanography: Methods, 2(2), 42–54. doi:<u>10.4319/lom.2004.2.42</u> *Methods* 

Holmes, R. M., Aminot, A., Kérouel, R., Hooker, B. A., & Peterson, B. J. (1999). A simple and precise method for measuring ammonium in marine and freshwater ecosystems. Canadian Journal of Fisheries and Aquatic

Sciences, 56(10), 1801–1808. doi:<u>10.1139/f99-128</u> *Methods* 

Measures, C. I., Yuan, J., & Resing, J. A. (1995). Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. Marine Chemistry, 50(1-4), 3–12. doi:<u>10.1016/0304-4203(95)00022-j</u> *Methods* 

Mulholland, M. R., Bernhardt, P. W., Heil, C. A., Bronk, D. A., & O'Neil, J. M. (2006). Nitrogen fixation and release of fixed nitrogen by Trichodesmium spp. in the Gulf of Mexico. Limnology and Oceanography, 51(4), 1762–1776. doi:<u>10.4319/lo.2006.51.4.1762</u> *Methods* 

Parsons, T. R., Y. Maita, and C. M. Lalli. "A Manual of Chemical and Biological Methods of Seawater Analysis", Pergamon Press (1984). ISBN: <u>9780080302874</u> *Methods* 

Price, N. M., & Harrison, P. J. (1987). Comparison of methods for the analysis of dissolved urea in seawater. Marine Biology, 94(2), 307–317. doi:10.1007/bf00392945 <u>https://doi.org/10.1007/BF00392945</u> *Methods* 

Sedwick, P. ., Sohst, B. M., Ussher, S. J., & Bowie, A. R. (2015). A zonal picture of the water column distribution of dissolved iron(II) during the U.S. GEOTRACES North Atlantic transect cruise (GEOTRACES GA03). Deep Sea Research Part II: Topical Studies in Oceanography, 116, 166–175. doi:<u>10.1016/j.dsr2.2014.11.004</u> *Methods* 

Sedwick, P. N., Bernhardt, P. W., Mulholland, M. R., Najjar, R. G., Blumen, L. M., Sohst, B. M., Sookhdeo, C., & Widner, B. (2018). Assessing Phytoplankton Nutritional Status and Potential Impact of Wet Deposition in Seasonally Oligotrophic Waters of the Mid-Atlantic Bight. In Geophysical Research Letters (Vol. 45, Issue 7, pp. 3203–3211). American Geophysical Union (AGU). https://doi.org/10.1002/2017gl075361 https://doi.org/10.1002/2017GL075361

Results

Sedwick, P. N., Marsay, C. M., Sohst, B. M., Aguilar-Islas, A. M., Lohan, M. C., Long, M. C., ... DiTullio, G. R. (2011). Early season depletion of dissolved iron in the Ross Sea polynya: Implications for iron dynamics on the Antarctic continental shelf. Journal of Geophysical Research, 116(C12). doi:<u>10.1029/2010jc006553</u> *Methods* 

Welschmeyer, N. A. (1994). Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. Limnology and Oceanography, 39(8), 1985–1992. doi:<u>10.4319/lo.1994.39.8.1985</u> *Methods* 

Zhang, J.-Z. (2000). Shipboard automated determination of trace concentrations of nitrite and nitrate in oligotrophic water by gas-segmented continuous flow analysis with a liquid waveguide capillary flow cell. Deep Sea Research Part I: Oceanographic Research Papers, 47(6), 1157–1171. doi:10.1016/s0967-0637(99)00085-0 <a href="https://doi.org/10.1016/S0967-0637(99)00085-0">https://doi.org/10.1016/S0967-0637(99)00085-0</a> Methods

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## Parameters

Parameter	Description	Units
experiment	bioassay experiment identifier (1, 2 or 3)	unitless
treatment	Experimental amendment: start = unamended starting seawater; C = control (unamended); N = +nitrate; Fe = +iron; N+Fe = +nitrate+iron; N+Fe+P = +nitrate+iron+phosphate; rain = +rainwater	unitless
time	incubation time (elapsed time)	hours
mean_NO3_NO2	Mean nitrate plus nitrite concentration	micromoles per liter (umol/L)
SD_NO3_NO2	Standard deviation of mean nitrate plus nitrite concentration	micromoles per liter (umol/L)
mean_NH4	Mean ammonium concentration	micromoles per liter (umol/L)
SD_NH4	Standard deviation of the mean ammonium concentration	micromoles per liter (umol/L)
mean_Chl_a	Mean chlorophyll-a concentration	micrograms per liter (mg/L)
SD_Chl_a	Standard deviation of the mean Chl-a	micrograms per liter (mg/L)
mean_PP	mean primary productivity	micromoles C per liter per day (umol C/L/d)
SD_PP	Standard deviation of mean primary productivity	micromoles C per liter per day (umol C/L/d)

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## Instruments

Dataset- specific Instrument Name	Turner Designs 10-AU fluorometer
Generic Instrument Name	Fluorometer
Dataset- specific Description	Fluorometer: Chl-a
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	Shimadzu RF1501
Generic Instrument Name	Fluorometer
Dataset- specific Description	Spectrofluorophotometer: NH4
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	Europa 20/20 isotope ratio mass spectrometer
Generic Instrument Name	Mass Spectrometer
Dataset- specific Description	Mass Spectrometer (PP): Europa 20/20 isotope ratio mass spectrometer equipped with an automated nitrogen and carbon analysis for gas, solids, and liquids (ANCA-GSL) preparation module.
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

Dataset- specific Instrument Name	Astoria Pacific nutrient autoanalyzer
Generic Instrument Name	Nutrient Autoanalyzer
Dataset- specific Description	Macronutrient analysis: NO3+NO2, PO4
Generic Instrument Description	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

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# Deployments

## HRS1414

Website	https://www.bco-dmo.org/deployment/731505	
Platform	R/V Hugh R. Sharp	
Start Date	2014-07-29	
End Date	2014-08-16	

## **Project Information**

# Collaborative Research: Impacts of atmospheric nitrogen deposition on the biogeochemistry of oligotrophic coastal waters (DANCE)

**Coverage**: Offshore Mid-Atlantic Bight and northern South-Atlantic Bight between latitudes 31.60°N and 38.89°N, and longitudes 71.09°W and 75.16°W

#### NSF abstract:

Deposition of atmospheric nitrogen provides reactive nitrogen species that influence primary production in nitrogen-limited regions. Although it is generally assumed that these species in precipitation contributes substantially to anthropogenic nitrogen loadings in many coastal marine systems, its biological impact remains poorly understood. Scientists from Pennsylvania State University, William & Mary College, and Old Dominion University will carry out a process-oriented field and modeling effort to test the hypothesis that deposits of wet atmospheric nitrogen (i.e., precipitation) stimulate primary productivity and accumulation of algal biomass in coastal waters following summer storms and this effect exceeds the associated biogeochemical responses to wind-induced mixing and increased stratification caused by surface freshening in oligotrophic coastal waters of the eastern United States. To attain their goal, the researchers would perform a Lagrangian field experiment during the summer months in coastal waters located between Delaware Bay and the coastal Carolinas to determine the response of surface-layer biogeochemistry and biology to precipitation events, which will be identified and intercepted using radar and satellite data. As regards the modeling effort, a 1-D upper ocean mixing model and a 1-D biogeochemical upper-ocean will be calibrated by assimilating the field data obtained a part of the study using the adjoint method. The hypothesis will be tested using sensitivity studies with the calibrated model combined with in-situ data and results from the incubation experiments. Lastly, to provide regional and historical context for the field measurements and the associated 1-D modeling, linked regional atmospheric-oceanic biogeochemical modeling will be conducted.

Broader Impacts. Results from the study would be incorporated into class lectures for graduate courses on marine policy and marine biogeochemistry. One graduate student from Pennsylvania State University, one graduate student from the College of William and Mary, and one graduate and one undergraduate student from Old Dominion University would be supported and trained as part of this project.

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## Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1260574</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1260454</u>

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