# Nutrients and iron in shipboard aerosol and rain samples collected during R/V Hugh R. Sharp cruise HRS1414 in the Mid-Atlantic Bight and northern South-Atlantic Bight from July to August of 2014 (DANCE project)

Website: https://www.bco-dmo.org/dataset/738744 Data Type: Cruise Results Version: 1 Version Date: 2018-06-18

#### Project

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

Contributors	Affiliation	Role
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#### Abstract

Shipboard aerosol and rain samples were collected during R/V Hugh R. Sharp cruise HRS1414 offshore in the Mid-Atlantic Bight and northern South-Atlantic Bight from July to August of 2014. Samples were analyzed for nutrients and iron.

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# Coverage

**Spatial Extent**: N:38.5334 **E**:-70.0543 **S**:33.4254 **W**:-74.3724 **Temporal Extent**: 2014-08-02 - 2014-08-14

#### Methods & Sampling

Aerosol sample collection: Aerosols were collected on cellulose filters using a Tisch Series 235 high-volume (~1 m3 air min-1) aerosol sampler equipped with a cascade impactor designed for the separation of coarse (>1  $\mu$ m) and fine (<1  $\mu$ m) aerosol fractions. The sampler was mounted on a platform atop the ship's wheelhouse as far forward as possible. Relative wind speed and direction were monitored during aerosol sample collection, and the sampler was operated only when the ship was steaming into the prevailing wind, in an effort to avoid

contamination from the ship's exhaust and superstructure. The cascade impactor was loaded with Whatman 41 cellulose filters that had been pre-cleaned at Old Dominion University using 0.1 N and 0.5 N hydrochloric acid, following a procedure modified from Baker et al. [2006]. Six filters (five 25 cm x 25 cm slotted sheets and one 20.3 cm x 25.4 cm backing sheet) were used for the collection of each aerosol sample. Air flow rates were calculated using manufacturer-provided flow conversion tables and the pressure decrease across the filters, which was measured at the start and end of sample collection using a handheld digital manometer (Dwyer Series). The total air volume sampled was estimated from the period of sample collection and the average value of the initial and final flow rates.

Aerosol sample processing: Immediately following collection, the aerosol-laden filters were unloaded and subsampled within a Class-100 clean air bench. Fixed portions of the aerosol-laden cellulose filters corresponding to each aerosol size fraction (<1  $\mu$ m and >1  $\mu$ m) were transferred into 47 mm diameter perfluoroalkoxy alkane filter funnel assemblies (Savillex) loaded with acid-cleaned 0.4  $\mu$ m polycarbonate filter membranes, and leached with 750 ml of 18.2 M $\Omega$ -cm resistivity deionized water (Barnstead Nanopure), in a flow-through protocol modfied after Buck et al. [2006]. Aliquots of the leachate solutions were immediately transferred into (i) acid-cleaned 125 ml low-density polyethylene bottles (Nalgene), then acidified with 500  $\mu$ l 6N ultrapure hydrochloric acid (Fisher Chemical, Optima), for post-cruise analysis of soluble aerosol iron, and (ii) 60 mL polypropylene tubes (Falcon) for shipboard analysis of soluble aerosol nitrate+nitrite, phosphate and ammonium. In addition, separate portions of the aerosol-laden cellulose filters corresponding to each aerosol size fraction (<1  $\mu$ m and >1  $\mu$ m) were stored in pre-cleaned ziploc polyethylene bags for microwave acid digestion at Old Dominion University. The microwave acid digestion procedure was adapted from Morton et al. [2013], with the resulting digest solutions evaporated to near dryness and then diluted with 20 mL of 1% ultrapure nitric acid (Fisher Chemical, Optima).

Rainwater sample collection: Two methods were used to collect the rain samples at sea. Samples Rain-01 and Rain-02 were collected in two acid-cleaned 2 L wide-mouth fluorinated high-density polyethylene bottles (Nalgene) mounted inside a polyethylene bucket, using an N-Con Systems automated rain sampler. Samples Rain-03, Rain-04 and Rain-05 were manually collected using an acid-cleaned high-density polyethylene funnel (Nalgene) connected by a Teflon collar to an acid-cleaned 2 L low-density polyethylene bottle (Nalgene). Both sample collected whilst the ship was steaming into the prevailing wind, in an effort to avoid contamination from the ship's exhaust and superstructure. The ODU Rain Composite combines samples collected on the Old Dominion University campus during summer 2014 using the manual funnel sampling method.

Rainwater sample processing: Immediately following collection, rainwater sample containers were capped and transferred to a shipboard Class-100 clean air bench for processing. From each sample, aliquots were transferred into (i) 60 mL polypropylene tubes (Falcon), which were frozen for post cruise analysis of nitrate+nitrite, phosphate and ammonium, and, when there was sufficient sample volume (ii) acid-cleaned 125 ml low-density polyethylene bottles (Nalgene) and acidified to pH 1.8 with 6N ultrapure hydrochloric acid (Fisher Chemical, Optima) for post-cruise analysis of total iron (more strictly, total acid-labile iron). In addition, if the volume of sample was sufficient, the rainwater was filtered through an acid-cleaned 0.4 µm polycarbonate membrane using a 47 mm diameter perfluoroalkoxy alkane filter funnel assembly (Savillex), and the filtrate transferred into an acid-cleaned 125 ml low-density polyethylene bottles (Nalgene) and acidified to pH 1.8 with 6N ultrapure hydrochloric acid (Fisher Chemical, Optima) for post-cruise analysis of total iron (more strictly, total acid-labile iron). In addition, if the volume of sample was sufficient, the rainwater was filtered through an acid-cleaned 0.4 µm polycarbonate membrane using a 47 mm diameter perfluoroalkoxy alkane filter funnel assembly (Savillex), and the filtrate transferred into an acid-cleaned 125 ml low-density polyethylene bottles (Nalgene) and acidified to pH 1.8 with 6N ultrapure hydrochloric acid (Fisher Chemical, Optima) for post-cruise analysis of dissolved iron.

DFe and TFe: Dissolved iron and total iron was determined in aerosol leachate solutions (DFe), aerosol digest solutions (TFe), filtered rainwater (DFe) and unfiltered rainwater (TFe, or more strictly, total acid-labile iron) were determined at Old Dominion University using a ThermoFisher Element2 high-resolution inductively-coupled plasma mass spectrometer (HR-ICP-MS). Sample solutions were introduced into the ICP-MS without preconcentration, and quantified using matrix-matched external standard solutions prepared with SPEX CertiPrep Claritas PPT grade standards. An indium internal standard was used to correct for instrumental drift. Analytical limits of detection are estimated as 0.57 nM for DFe and for TFe in ulfiltered rainwater, and 53 nM for TFe in the aerosol digest solutions. The values presented for DFe and TFe in samples represent concentrations after subtracting the concentrations of the corresponding field blanks (Rain-Sampler-Blank, Rain-Funnel-Blank, or Aer-Blank). Atmospheric loadings of soluble aerosol iron (Sol Aer Fe) and total aerosol iron (Tot Aer Fe) were calculated from DFe in aerosol leachates and TFe in aerosol digest solutions, respectively, and the total air volume sampled in each case, after correcting for the fraction of the active filter area that was leached (for DFe) or digested (for TFe).

NO3+NO2: Dissolved nitrate plus nitrite was determined in aerosol leachate solutions and rainwater with 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). Atmospheric loadings of soluble aerosol nitrate plus nitrite (Sol Aer NO3+NO2) were calculated from NO3+NO2 in aerosol leachates and the total air volume

sampled, after correcting for the fraction of the active filter area that was leached.

PO4: Dissolved phosphate was determined in aerosol leachate solutions and rainwater with 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). Atmospheric loadings of soluble aerosol phosphate (Sol Aer PO4) were calculated from PO4 in aerosol leachates and the total air volume sampled, after correcting for the fraction of the active filter area that was leached.

NH4: Dissolved ammonium was determined in aerosol leachate solutions and rainwater using the manual orthophthaldialdehyde method (Holmes et al., 1999), with an estimated detection limit of 10 nM. Atmospheric loadings of soluble aerosol ammonium (Sol Aer NH4) were calculated from NH4 in aerosol leachates and the total air volume sampled, after correcting for the fraction of the active filter area that was leached.

#### **Data Processing Description**

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
- \* mu symbol changed to micron in sample id.
- \* comment column added and "pre-cruise" moved to comment from date column.

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### **Data Files**

```
File

rain.csv(Comma Separated Values (.csv), 3.23 KB)

MD5:a81eda47334610fc58b99ba17ae62e57

Primary data file for dataset ID 738744
```

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# **Related Publications**

Baker, A. R., Jickells, T. D., Witt, M., & Linge, K. L. (2006). Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean. Marine Chemistry, 98(1), 43–58. doi:10.1016/j.marchem.2005.06.004

Methods

Buck, C. S., Landing, W. M., Resing, J. A., & Lebon, G. T. (2006). Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise. Geochemistry, Geophysics, Geosystems, 7(4), n/a-n/a. doi:<u>10.1029/2005gc000977</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* 

Morton, P. L., Landing, W. M., Hsu, S.-C., Milne, A., Aguilar-Islas, A. M., Baker, A. R., ... Zamora, L. M. (2013). Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment. Limnology and Oceanography: Methods, 11(2), 62–78. doi:<u>10.4319/lom.2013.11.62</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. 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 Methods

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## Parameters

Parameter	Description	Units
Sample_ID	unique identifier for each sample	unitless
Comment	sample comment	unitless
Date	local date (month/day/year) of collection	unitless
Duration	duration of sample collection (aerosols) (NA: not applicable)	minutes
Start_Lat	latitude at start of sample collection (NA: not applicable)	decimal degrees
End_Lat	latitude at end of sample collection (NA: not applicable)	decimal degrees
Start_Long	longitude at start of sample collection (NA: not applicable)	decimal degrees
End_Long	longitude at end of sample collection (NA: not applicable)	decimal degrees
Air_Volume	volume of air filtered (aerosols) (NA: not applicable)	meters cubed (m3)
DFe	dissolved iron concentration; (rainwater or aerosol leachate) (NA: not applicable; BDL: below detection limit)	nanomoles per liter (nmol/L)
Sol_Aer_Fe	soluble aerosol iron (atmospheric loading) (ND: not determined; BDL: below detection limit)	nanomoles per meter cubed (nmol/m3)
TFe	total iron concentration; (rainwater or aerosol) (ND: not determined; BDL: below detection limit)	nanomoles per liter (nmol/L)
Tot_Aer_Fe	total aerosol iron; (atmospheric loading) (NA: not applicable; BDL: below detection limit)	nanomoles per meter cubed (nmol/m3)

NO3_NO2	dissolved nitrate plus nitrite concentration (rainwater or aerosol leachate) (BDL: below detection limit)	micromoles per liter (umol/L)
Sol_Aer_NO3_NO2	soluble aerosol nitrate plus nitrite (atmospheric loading) (NA: not applicable)	nanomoles per meter cubed (nmol/m3)
PO4	dissolved phosphate (rainwater or aerosol leachate) (BDL: below detection limit)	micromoles per liter (umol/L)
Sol_Aer_PO4	soluble aerosol phosphate (NA: not applicable; BDL: below detection limit)	nanomoles per meter cubed (nmol/m3)
NH4	dissolved ammonium (rainwater or aerosol leachate)	micromoles per liter (umol/L)
Sol_Aer_NH4	soluble aerosol ammonium (NA: not applicable)	nanomoles per meter cubed (nmol/m3)

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# Instruments

Dataset-specific Instrument Name	Tisch Series 235
Generic Instrument Name	Aerosol Sampler
Dataset-specific Description	Tisch Series 235 high-volume aerosol sampler equipped with a cascade impactor.
Generic Instrument Description	A device that collects a sample of aerosol (dry particles or liquid droplets) from the atmosphere.

Dataset- specific Instrument Name	ThermoFisher Element2
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset- specific Description	Iron analysis (DFe and TFe): ThermoFisher Element2 high-resolution inductively-coupled plasma mass spectrometer.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset- specific Instrument Name	Astoria Pacific nutrient autoanalyzer
Generic Instrument Name	Nutrient Autoanalyzer
Dataset- specific Description	Macronutrient analysis (NO3+NO2, PO4): Astoria Pacific nutrient autoanalyzer.
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.

Dataset-specific Instrument Name	ADS 00-120
Generic Instrument Name	Precipitation Sampler
Dataset-specific Description	Rain Sampler: N-CON Systems ADS 00-120 sampler
Generic Instrument Description	A device that collects a sample of precipitation (rain, hail or snow) as it falls.

Dataset-specific Instrument Name	Shimadzu RF1501
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Spectrofluorophotometer (NH4): Shimadzu RF1501.
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.

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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	

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# **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

#### 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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