# Chemical composition of 'model' Primary Marine Aerosol (mPMA) and seawater measured on R/V Endeavor EN589 during Sept. - Oct. 2016

Website: <u>https://www.bco-dmo.org/dataset/750917</u> Data Type: Cruise Results

Version: 1 Version Date: 2018-12-05

### Project

» <u>Collaborative Research: Coupled Ocean-Atmosphere Recycling of Refractory Dissolved Organic Carbon in</u> <u>Seawater</u> (Refractory DOC Recycling)

### Program

» United States Surface Ocean Lower Atmosphere Study (U.S. SOLAS)

| Contributors         | Affiliation   | Role                   |
|----------------------|---|------------------------|
| Keene, William C.    | University of Virginia (UVA)                        | Principal Investigator |
| <u>Copley, Nancy</u> | Woods Hole Oceanographic Institution (WHOI BCO-DMO) | BCO-DMO Data Manager   |

#### Abstract

This dataset describes the ionic composition of western North Atlantic seawater and the corresponding chemical composition of mPMA produced from that seawater in a high-capacity generator over ranges of operating conditions. Measurements were taken during cruise EN589 on RV/Endeavor during September and October 2016.

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## Coverage

**Spatial Extent**: N:42 **E**:-67 **S**:35 **W**:-70 **Temporal Extent**: 2016-09-21 - 2016-10-14

## **Dataset Description**

This dataset describes the ionic composition of western North Atlantic seawater and the corresponding chemical composition of mPMA produced from that seawater in a high-capacity generator over ranges of operating conditions. Measurements were taken during cruise EN589 on RV/Endeavor during September and October 2016.

The ionic data reported in this file were generated by William Keene (<u>wck@virginia.edu</u>) and John Maben and the OCwe data were generated by David Kieber (<u>djkieber@esf.edu</u>). Please direct any related questions accordingly.

Sampling and Analytical Methods: Samples were collected on RV/Endeavor cruise 589. Locations, times, and conditions at the four hydrographic stations are available under Supplemental Documentation. During some periods, size-resolved mPMA was sampled from the generator's headspace at 30 L min-1 with two non-rotating Multi-Orifice Uniform Deposit Impactors (MOUDIs, [Marple et al., 1991]) operated in parallel. Substrates and back filters from one impactor were analyzed for major ions and those from the other impactor were analyzed for water extractable organic carbon (OCwe). The aerodynamic cut diameters for the impactor's size fractions were 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, and 0.18 µm. Impactors were configured with precombusted 47-mm diameter aluminum substrates and 37-mm diameter quartz backup filters.

During some periods, bulk mPMA was sampled in parallel at 30 L min-1 on two precombusted 47-mm quartz filters, one of which was analyzed for major ions, OCwe, and surfactants and the other for total OC and radiocarbon age.

During two periods, bulk mPMA was sampled in parallel at 30 L min-1 on two 90-mm Teflon filters. One sample was analyzed for major ions and OCwe and the other was stored for photochemical manipulation experiments.

After recovery, samples of size-resolved and bulk mPMA for analysis of major ions were transferred to precleaned 10-mL HDPE tubes, stored frozen, subsequently extracted in 5 mL deionized water (DIW), and analyzed at the University of Virginia (UVA) using a Dionex duel channel model ICS 3000 high-performance ion chromatograph (IC). The anion channel was configured with Thermo Scientific Dionex guard (IonPac AG 18: 4 x 50 mm) and analytical separator (IonPac AS 18: 4 x 250mm) columns and electrolytically regenerated suppressor (AERS 500: 4mm). The cation channel was configured Dionex Guard (IonPac CG16: 5 x 50mm) and analytical separator (IonPac CG16: 5 x 250mm) columns and a Thermo Scientific Dionex electrolytically regenerated suppressor (CERS 500: 4mm).

Size-segregated mPMA sampled with cascade impactors and in bulk on quartz filters for analysis of OCwe were transferred to precombusted 10-mL Pyrex tubes, extracted immediately after recovery in 5 mL DIW, stored frozen, and analyzed in triplicate with a Shimadzu Model TOC-V CSH carbon analyzer at the State University of New York (SUNY).

Bulk mPMA sampled on Teflon filters were extracted immediately after recovery in five sequential aliquots of DIW (total of 25 mL). Subsamples of extracts were stored frozen on site and analyzed for major ions at UVA and for OCwe at SUNY using methods described above.

Data for mPMA samples were corrected based on median concentrations of analytes measured in dynamic handling blanks (N = 5 for impactor and 8 for bulk samples) that were loaded and unloaded during the campaign and subsequently processed and analyzed using procedures identical to those used for samples.

Unfiltered seawater for analysis of major ions was sampled in precleaned 10-mL HDPE tubes, stored frozen, and analyzed by IC at UVA.

Average detection limits (DLs) for mPMA analytes were estimated following Keene et al. [1989, JGR] and are summarized (see Supplemental Documents)

Average precisions for inorganic mPMA analytes are estimated to be  $\pm 4\%$  of the measured concentrations or  $\pm 0.5$ \*DLs, whichever are the greater absolute values. Precisions for OCwe correspond to the standard deviations for triplicate measurements.

Measured concentrations of all ionic constituents in seawater were substantially higher than estimated DLs. Average precisions are approximately  $\pm 2\%$  of the measured concentrations.

Refer to the following papers for additional details regarding the design and operation of the marine aerosol generator, analytical methods, and data quality.

#### **Data Processing Description**

BCO-DMO Processing:

- added conventional header with dataset name, PI name, version date

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

- replaced blank cells with nd (no data)
- re-formatted date and time from m/d/yy HH:MM to ISO format yyyy-mm-ddTHH:MM:SS
- added station latitude and longitude

## **Data Files**

#### File

aerosol\_seawater\_chem\_comp.csv(Comma Separated Values (.csv), 17.29 KB) MD5:8975dd9014ae74aec9406d0c115ed416

Primary data file for dataset ID 750917

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## Supplemental Files

File

#### Chemical composition table

filename: chemical\_composition\_table.png

(Portable Network Graphics (.png), 10.21 KB) MD5:6b8aa48ea86017c7417a8b9cedb2aee7

Average detection limits (DLs) for mPMA analytes were estimated following Keene et al. [1989, JGR]: Cl, Br, SO4, Na, K, Mg, Ca, OC(we)

# EN589 station locations and conditions

filename: EN589\_stations.pdf

(Portable Document Format (.pdf), 84.01 KB) MD5:1708f79a5f07195d73cf6f1c2cc42993

Locations, times, and conditions at the four hydrographic stations during the Endeavor cruise EN589.

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## **Related Publications**

Keene, W. C., Long, M. S., Reid, J. S., Frossard, A. A., Kieber, D. J., Maben, J. R., ... Bates, T. S. (2017). Factors That Modulate Properties of Primary Marine Aerosol Generated From Ambient Seawater on Ships at Sea. Journal of Geophysical Research: Atmospheres, 122(21), 11,961–11,990. doi:10.1002/2017jd026872 https://doi.org/10.1002/2017JD026872

Methods

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., ... Sander, R. (2007). Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface. Journal of Geophysical Research, 112(D21). doi:10.1029/2007jd008464 <u>https://doi.org/10.1029/2007JD008464</u> *Methods* 

Keene, W. C., Talbot, R. W., Andreae, M. O., Beecher, K., Berresheim, H., Castro, M., … Winiwarter, W. (1989). An intercomparison of measurement systems for vapor and particulate phase concentrations of formic and acetic acids. Journal of Geophysical Research, 94(D5), 6457. doi:10.1029/jd094id05p06457 <u>https://doi.org/10.1029/JD094iD05p06457</u> *Methods* 

Kieber, D. J., Keene, W. C., Frossard, A. A., Long, M. S., Maben, J. R., Russell, L. M., ... Bates, T. S. (2016). Coupled ocean-atmosphere loss of marine refractory dissolved organic carbon. Geophysical Research Letters, 43(6), 2765–2772. doi:10.1002/2016gl068273 <u>https://doi.org/10.1002/2016GL068273</u> *Methods* 

Long, M. S., Keene, W. C., Kieber, D. J., Frossard, A. A., Russell, L. M., Maben, J. R., ... Bates, T. S. (2014). Light-enhanced primary marine aerosol production from biologically productive seawater. Geophysical Research Letters, 41(7), 2661–2670. doi:10.1002/2014gl059436 <u>https://doi.org/10.1002/2014GL059436</u> *Methods* 

## **Parameters**

| Parameter                  | Description  | Units   |
|----------------------------|--|---|
| Campaign_Sequence_Number   | Campaign sequence number corresponding to a given set<br>of generator operating conditions as detailed in the<br>companion file (EN589 Marine Aerosol Generator Operating<br>Conditions).                                      | unitless  |
| Sample_Type                | Sample type: Size-resolved mPMA sampled with a cascade<br>impactor (CI); bulk mPMA sampled on a quartz filter (B);<br>bulk mPMA sampled on a Teflon filter for photochemical<br>manipulation experiments (P); or seawater (S). | unitless  |
| Sample_ID                  | Sample ID number   | unitless  |
| CI_50_Aerodynamic_Cut_Diam | Aerodynamic cut diameter for CI samples (µm at ambient relative humidity).   | micrometers   |
| S_Sample_Location          | Location at which seawater was sampled (I denotes inlet to<br>generator; O denotes outlet from generator). Duplicate<br>measurements at the same time and location are denoted<br>by 'Dup'.                                    | unitless  |
| ISO_DateTime_local_start   | Size-resolved and bulk mPMA sample start date and time or seawater sampling date and time; ISO 8601:2004E format.  | unitless  |
| ISO_DateTime_local_end     | Size-resolved and bulk mPMA sample stop date and time;<br>ISO 8601:2004E format.   | unitless  |
| CI                         | Cl- concentration: For mPMA in nmol m-3 air; for seawater in $\mu$ M.  | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| Br                         | Br- concentration: For mPMA in nmol m-3 air; for seawater<br>in μM.  | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| SO4                        | SO42- concentration: For mPMA in nmol m-3 air; for seawater in $\mu$ M.  | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (μΜ)<br>for S |

| Na       | Na+ concentration: For mPMA in nmol m-3 air; for seawater in $\mu$ M.                       | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
|----------|---|---|
| К        | K+ concentration: For mPMA in nmol m-3 air; for seawater<br>in μM.                          | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| Mg       | Mg2+ concentration: For mPMA in nmol m-3 air; for seawater in $\mu$ M.                      | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (μΜ)<br>for S |
| Ca       | Ca2+ concentration: For mPMA in nmol m-3 air; for seawater in $\mu$ M.                      | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| OCwe     | Water-extractable organic carbon (OCwe) concentration for mPMA in nmol C m-3 air.           | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| OCwe_STD | OCwe precision for mPMA in nmol C m-3 air   | nanomol/cubic<br>meter (nmol m-<br>3) for mPMA;<br>micromol (µM)<br>for S |
| Comments | Comments  | unitless  |
| lat      | general latitude of sampling; north is positive [added by<br>BCO-DMO from supplemental doc] | decimal degrees   |
| lon      | general longitude of sampling; east is positive [added by<br>BCO-DMO from supplemental doc] | decimal degrees   |

## Instruments

| Dataset-<br>specific<br>Instrument<br>Name | Shimadzu Model TOC-V CSH carbon analyzer   |
|--|--|
| Generic<br>Instrument<br>Name              | Total Organic Carbon Analyzer  |
| Dataset-<br>specific<br>Description        | Used to measure total organic carbon concentration   |
| Generic<br>Instrument<br>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: <a href="http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf">http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf</a> |

## Deployments

#### EN589

| Website     | https://www.bco-dmo.org/deployment/710271   |  |
|-------------|---|--|
| Platform    | R/V Endeavor  |  |
| Report      | http://dmoserv3.bco-<br>dmo.org/data_docs/Refractory_DOC_Recycling/EN589_Post_Cruise_Report_10.20.16.pdf  |  |
| Start Date  | 2016-09-16  |  |
| End Date    | 2016-10-15  |  |
| Description | The main purpose of this cruise was to study the organic matter put into the atmosphere as particles (also called aerosols) that are generated from bursting bubbles at the sea surface. To do this, the investigators deployed an aerosol generator to reproduce a model surface ocean using the ship's clean flow-through seawater system. The ship occupied four hydrographic stations: two biologically productive stations and two stations in the Sargasso Sea. To support the aerosol generator work, over fifty CTD casts were conducted to collect seawater and to characterize the physical, chemical, and biological properties of the water column. Cruise description excerpted from EN589 post-cruise report: EN589_Post_Cruise_Report_10.20.16.pdf. Related documents: EN589_Cruise_Plan.pdf |  |

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## **Project Information**

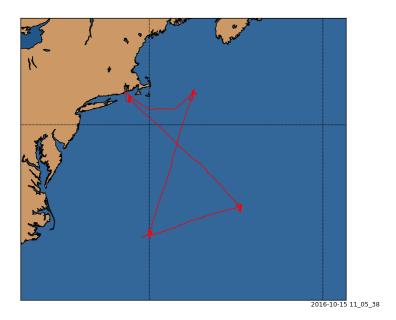
#### Collaborative Research: Coupled Ocean-Atmosphere Recycling of Refractory Dissolved Organic Carbon in Seawater (Refractory DOC Recycling)

**Coverage**: Northwest Atlantic Ocean

The oceans hold a massive quantity of organic carbon that is greater than all terrestrial organic carbon biomass combined. Nearly all marine organic carbon is dissolved and more than 95% is refractory, and cycled through the oceans several times before complete removal. Refractory dissolved organic carbon (RDOC) concentrations are uniform with depth in the water column and represent the "background" carbon present throughout the oceans. However, very little is known regarding RDOC production and removal processes. One potential removal pathway is through adsorption of RDOC onto surfaces of rising bubbles produced by breaking waves and ejection via bubble bursting into the atmosphere. Building on prior research, the investigators will evaluate the importance of ocean- atmosphere processing in recycling marine RDOC during a research cruise in the northwestern Atlantic Ocean. Results of the research will provide important insights regarding the coupled ocean-atmosphere loss of RDOC, thereby improving understanding of and ability to predict the role of RDOC in oceanic and atmospheric biogeochemistry, the global carbon cycle, and Earth's climate. The research will involve three early career faculty, and will provide training for undergraduate and graduate researchers.

Recent results based on a limited set of observations indicate that the organic matter (OM) associated with primary marine aerosol (PMA) produced by bursting bubbles from breaking waves at the sea surface is comprised partly to wholly of RDOC rather than OM of recent biological origin as has been widely assumed. The injection of RDOC into the atmosphere in association with PMA and its subsequent photochemical oxidation is a potentially important and hitherto unrecognized sink for RDOC in the oceans of sufficient magnitude to close the marine carbon budget and help resolve a long-standing conundrum regarding removal mechanisms for marine RDOC. This project will involve a shipboard investigation and modeling study to (1) quantify the relative contributions of marine refractory dissolved organic carbon (RDOC) to primary marine aerosol organic matter (PMA OM) produced from near-surface seawater in biologically productive and oligotrophic regions and from North Atlantic Deep Water, and to (2) determine the importance of atmospheric photochemical processing as a recycling pathway for RDOC. To test these hypotheses, a high-capacity aerosol generator will be deployed at four hydrographic stations in the NW Atlantic Ocean to characterize (1) the natural abundance of 14C in PMA and in surface and deep seawater; (2) the surface tension and physical properties of bubble plumes; (3) sizeresolved production fluxes, chemical composition, organic carbon enrichments, spectral absorbance, and photochemical evolution of PMA; and (4) the carbon content, optical properties, and physical properties of seawater. The importance of RDOC recycling via PMA production and photochemical evolution will be interpreted with model calculations.

#### EN589 Cruise Track



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#### **Program Information**

#### United States Surface Ocean Lower Atmosphere Study (U.S. SOLAS)

Website: http://www.us-solas.org/

Coverage: Global

The Surface Ocean Lower Atmosphere Study (SOLAS) program is designed to enable researchers from different disciplines to interact and investigate the multitude of processes and interactions between the

coupled ocean and atmosphere.

Oceanographers and atmospheric scientists are working together to improve understanding of the fate, transport, and feedbacks of climate relevant compounds, and also weather and hazards that are affected by processes at the surface ocean.

Oceanographers and atmospheric scientists are working together to improve understanding of the fate, transport, and feedbacks of climate relevant compounds.

Physical, chemical, and biological research near the ocean-atmosphere interface must be performed in synergy to extend our current knowledge to adequately understand and forecast changes on short and long time frames and over local and global spatial scales.

The findings obtained from SOLAS are used to improve knowledge at process scale that will lead to better quantification of fluxes of climate relevant compounds such as CO2, sulfur and nitrogen compounds, hydrocarbons and halocarbons, as well as dust, energy and momentum. This activity facilitates a fundamental understanding to assist the societal needs for climate change, environmental health, weather prediction, and national security.

The US SOLAS program is a component of the International SOLAS program where collaborations are forged with investigators around the world to examine SOLAS issues ubiquitous to the world's oceans and atmosphere.

<u>» International SOLAS Web site</u>

#### Science Implementation Strategy Reports

<u>US-SOLAS</u> (4 MB PDF file) <u>Other SOLAS reports</u> are available for download from the US SOLAS Web site

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## Funding

| Funding Source                           | Award              |
|--|--------------------|
| NSF Division of Ocean Sciences (NSF OCE) | <u>OCE-1536608</u> |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1536605        |
| NSF Division of Ocean Sciences (NSF OCE) | <u>OCE-1536674</u> |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1536597        |

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