

Total nitrogen, nitrate, ammonium and oxygen isotope composition of atmospheric particulates collected on Changdao Island, China from September 22, 2019 to September 5, 2020

Website: <https://www.bco-dmo.org/dataset/948530>

Data Type: Other Field Results

Version: 1

Version Date: 2025-01-15

Project

» [Collaborative Research: Characterization of Reactive Nitrogen in The North Pacific Atmosphere](#) (North Pacific Atmos)

| Contributors | Affiliation | Role |
|---------------------------------------|-----------------------------------------------------|---------------------------|
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Abstract

These data include the content of total nitrogen, nitrate isotope (^{15}N), ammonium isotope (^{15}N), and oxygen isotope (^{17}O and ^{18}O) composition of atmospheric particulates collected on Changdao Island, China. Aerosol sampling was conducted from September 22, 2019 to September 5, 2020. A high-volume aerosol sampler (model 2031, Qingdao Laoying Environmental Technology Co) operating at $1.0 \text{ m}^3 \text{ min}^{-1}$ with $25 \times 20 \text{ cm}$ filters was used. Recognizing the deposition of atmospheric particulates has the potential to understanding the important role of atmospheric deposition to the nitrogen cycle and biogeochemistry in the ocean. These data assess the contribution of atmospheric deposition to inorganic nitrogen and were collected by Dr. Ren Pen (pren@qnlm.ac) at the Ocean University of China.

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Coverage

Location: North Pacific Ocean

Spatial Extent: **Lat:**38.17306 **Lon:**120.75556

Temporal Extent: 2019-09-22 - 2020-09-05

Methods & Sampling

Aerosol sampling was conducted from September 22, 2019 to September 5, 2020. A high-volume aerosol sampler (model 2031, Qingdao Laoying Environmental Technology Co) operating at $1.0 \text{ m}^3 \text{ min}^{-1}$ with $25 \times 20 \text{ cm}$ filters was used. Aerosol samples were for 24-72 h for each filter, with a total of 108 samples collected.

Data Processing Description

We measured the concentrations of total nitrogen (TN), nitrate isotopes (^{15}N), ammonium isotopes (^{15}N), oxygen isotope (^{17}O and ^{18}O), and a suite of ion concentrations (calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+), Chloride (Cl^-) and sulfate (SO_4^{2-}). TN measurements were conducted at the Center for Isotope Geochemistry and Geochronology (CIGG) at the Qingdao National Laboratory for Marine Science and Technology (QNLN) in Qingdao, China. All other measurements were conducted at the Department of Earth, Environmental, and Planetary Sciences at Brown University in Providence, RI (USA).

TN was measured using an elemental analyzer (Elementar vario Isotope select) with an analytical standard deviation of $\pm 0.04\%$ for TN ($n = 6$). After the frozen samples were received at Brown University, a 5×5 cm square was cut from the center of the filter at room temperature and extracted in a pre-cleaned bottle with ~ 100 mL of MQ water (exact amounts were recorded via weight) and then sonicated for 1 h. After sonication, the filters were removed, and the samples were frozen at 20°C until further analyses.

The concentration of ammonium, nitrate, and nitrite were determined colorimetrically (indophenol blue) using a discrete UV-Vis analyzer (Westco Smartchem 200). U.S. EPA Compliant Methods 350.1 (O'Dell, 1993), 353.2 (Revision 2.0), and 354.1 were followed for ammonium, nitrate, and nitrite, respectively. Standard lab protocols were followed, including calibration to standards as well as blanks and in-house quality control measurements. The pooled standard deviation (1σ) for ammonium was $0.6 \mu\text{mol L}^{-1}$, and $0.3 \mu\text{mol L}^{-1}$ for nitrate and nitrite.

The denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) was used to complete nitrate ($^{15}\text{N}/^{14}\text{N}$) and oxygen ($^{18}\text{O}/^{16}\text{O}$) isotope analyses on a continuous flow isotope ratio mass spectrometer. Values were reported in ‰ relative to standards. The azide method (Zhang et al., 2007) was used to complete ammonium ($^{15}\text{N}/^{14}\text{N}$) isotope analyses on a continuous flow isotope ratio mass spectrometer. Values were reported in ‰ relative to standards (IAEA- N_2 and USGS-25) and the pooled standard deviation for duplicates ($n = 13$ pairs) and replicates ($n = 20$) was 0.3‰ and 0.5‰ , respectively.

Concentrations of calcium, magnesium, sodium, and potassium were measured on an Inductively Coupled Plasma (ICP) atomic emission spectrometer. Samples were filtered with $0.45\text{-}\mu\text{m}$ filters and an aliquot of each sample solution was made 2% acidic with nitric acid. A commercial standard (IV-4) for each specific element was run roughly every 10 samples. The relative standard deviation for the standards was $\leq 3.3\%$ for all four elements. Chloride and sulfate concentrations were measured on an Ion Chromatography (IC) instrument (Dionex Integrion HPIC) using suppressed conductivity detection. Anions were determined using a Dionex AS19- $4 \mu\text{m}$ guard (4×50 mm) and analytical column (4×250 mm) with 20 mM KOH as eluent with a flow rate of 1 mL min^{-1} . All samples were filtered with $0.45\text{-}\mu\text{m}$ filters before being analyzed. In-house quality control standards were run approximately every six samples. The pooled standard deviation for duplicates was $2.0 \mu\text{mol}$ for both chloride and sulfate ($n = 13$ pairs and 12 pairs, respectively). The relative standard deviation for the low and high concentration QCs were $\leq 6.4\%$ and $< 3.4\%$, respectively.

Instruments:

High-volume aerosol sampler (model 2031, Qingdao Laoying Environmental Technology Co) operating at $1.0 \text{ m}^3 \text{ min}^{-1}$ with 25×20 cm filters.

Elemental analyzer: the concentrations of TN were measured using an elemental analyzer (Elementar vario Isotope select).

Discrete UV-Vis analyzer (Westco Smartchem 200): for ammonium, nitrate, and nitrite concentrations.

Continuous Flow Isotope Ratio Mass Spectrometer: for ammonium, nitrate, and oxygen isotope values.

Inductively Coupled Plasma (ICP) atomic emission spectrometer: to measure concentrations of calcium, magnesium, sodium, and potassium.

Ion Chromatography (IC) (Dionex Integrion HPIC): to measure chloride and sulfate concentrations.

BCO-DMO Processing Description

* Adjusted parameter names to comply with database requirements

* Converted sampling latitude and longitude notation from decimal, minute, seconds to decimal degrees.
Rounded these fields to 5 decimals
* Converted date to ISO notation (Y-m-d)

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Related Publications

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. K., & Hilkert, A. (2002). Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method. *Analytical Chemistry*, 74(19), 4905–4912. doi:[10.1021/ac020113w](https://doi.org/10.1021/ac020113w)

Methods

MacFarland, A. B., Walters, W. W., & Hastings, M. G. (2024). Solid Phase Extraction Methodology for Robust Isotope Analysis of Atmospheric Ammonium. *ACS Earth and Space Chemistry*, 8(5), 1039–1047.

<https://doi.org/10.1021/acsearthspacechem.3c00375>

Results

O'Dell, J.W., 1993a. In: Method 350.1, Revision 2.0: Determination of Ammonia Nitrogen by Semi-automated Colorimetry. US EPA. https://www.epa.gov/sites/default/files/2015-08/documents/method_350-1_1993.pdf

Methods

O'Dell, J.W., 1993b. In: Method 353.2, Revision 2.0: Determination of Nitrate-Nitrite By Automated Colorimetry. US EPA. https://www.epa.gov/sites/default/files/2015-08/documents/method_353-2_1993.pdf

Methods

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. *Analytical Chemistry*, 73(17), 4145–4153. doi:[10.1021/ac010088e](https://doi.org/10.1021/ac010088e)

Methods

Zhang, L., Altabet, M. A., Wu, T., & Hadas, O. (2007). Sensitive Measurement of $\text{NH}_4+^{15}\text{N}/^{14}\text{N}$ ($\delta^{15}\text{NH}_4+$) at Natural Abundance Levels in Fresh and Saltwaters. *Analytical Chemistry*, 79(14), 5297–5303.

doi:[10.1021/ac070106d](https://doi.org/10.1021/ac070106d)

Methods

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Parameters

| Parameter | Description | Units |
|-------------------------------|-------------------------------------------------------------------------------------------------------|---------------------------------------------------------|
| CollectionTime | The sampling date in ISO format yyyy-mm-dd | unitless |
| latitude | Sampling latitude, south is negative | decimal degrees |
| longitude | Sampling longitude, west is negative | decimal degrees |
| CollectionPeriod_Hrs | Time during sampling in format hh (Time Zone: UTC) | hours |
| TotalAirVolume_m3 | Total air volume during the sampling | liter (L) |
| ParticleWeight_g | Atmospheric particulates weight of each samples | mg |
| AmmoniumConcentration_ugPerm3 | Concentrations of total particulates matter | micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) |
| NitrateConcentration_ugPerm3 | Concentrations of total particulates matter | micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) |
| NitriteConcentration_ugPerm3 | Concentrations of total particulates matter | micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) |
| Delta15N_Nitrate | Nitrogen isotope ratio ($^{15}\text{N}/^{14}\text{N}$) of atmospheric nitrate (NO_3^-). | parts per thousand (permil) (‰) |
| Delta15N_Ammonium | Nitrogen isotope ratio ($^{15}\text{N}/^{14}\text{N}$) of atmospheric ammonium (NH_4^+). | parts per thousand (permil) (‰) |
| Delta18Oxygen_Nitrate | Oxygen isotopic ratio ($^{18}\text{O}/^{16}\text{O}$) of atmospheric nitrate (NO_3^-) | parts per thousand (permil) (‰) |
| Delta17N_Nitrate | Measured isotope value of atmospheric nitrate (NO_3^-) | parts per thousand (permil) (‰) |

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Instruments

| | |
|-----------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dataset-specific Instrument Name | model 2031, Qingdao Laoying Environmental Technology Co |
| Generic Instrument Name | Aerosol Sampler |
| Dataset-specific Description | High-volume aerosol sampler (model 2031, Qingdao Laoying Environmental Technology Co) operating at 1.0 m ³ min ⁻¹ with 25 × 20 cm filters. |
| Generic Instrument Description | A device that collects a sample of aerosol (dry particles or liquid droplets) from the atmosphere. |

| | |
|-----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dataset-specific Instrument Name | Elementar vario Isotope select |
| Generic Instrument Name | Elemental Analyzer |
| Dataset-specific Description | Elemental analyzer: the concentrations of TN were measured using an elemental analyzer (Elementar vario Isotope select). |
| 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 | |
| Generic Instrument Name | Inductively Coupled Plasma Mass Spectrometer |
| Dataset-specific Description | Inductively Coupled Plasma (ICP) atomic emission spectrometer: to measure concentrations of calcium, magnesium, sodium, and potassium. |
| 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 | Dionex Integrion HPIC |
| Generic Instrument Name | Ion Chromatograph |
| Dataset-specific Description | Ion Chromatography (IC) (Dionex Integrion HPIC): to measure chloride and sulfate concentrations. |
| Generic Instrument Description | Ion chromatography is a form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. (from http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic....) |

| | |
|-----------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dataset-specific Instrument Name | |
| Generic Instrument Name | Isotope-ratio Mass Spectrometer |
| Dataset-specific Description | Continuous Flow Isotope Ratio Mass Spectrometer: for ammonium, nitrate, and oxygen isotope values. |
| 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 | Westco Smartchem 200 |
| Generic Instrument Name | Spectrophotometer |
| Dataset-specific Description | Discrete UV-Vis analyzer (Westco Smartchem 200): for ammonium, nitrate, and nitrite concentrations. |
| 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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Project Information

Collaborative Research: Characterization of Reactive Nitrogen in The North Pacific Atmosphere (North Pacific Atmos)

Coverage: coastal China atmosphere, Northwestern Pacific waters and atmos, Hawaii atmosphere

NSF Award Abstract:

Nitrogen is an essential element for life, and its availability can limit the growth of phytoplankton in the surface waters of the oceans. One source of nitrogen to surface waters is deposition from the atmosphere, which is the result of reactive nitrogen emissions from both human (anthropogenic) activities and natural processes. Anthropogenic nitrogen emissions to the atmosphere and nitrogen deposition to the oceans have increased exponentially since preindustrial times. In fact, global modeling studies have suggested that as much as 80% of total nitrogen deposition to the oceans is anthropogenic in origin, and that the magnitude of input to the global oceans rivals estimates of biological nitrogen fixation. The impacts associated with this increased nitrogen deposition are clear in both terrestrial and coastal systems, but the implications for open ocean biogeochemistry are less well studied. Recent work in the North Pacific Ocean (NPO) has suggested that increased nitrogen due to anthropogenic atmospheric deposition is detectable even in the open ocean, while other work can explain nutrient dynamics based upon natural biological and physical processes. The investigators propose to study the influence of both anthropogenic and natural sources on the deposition of nitrogen (as nitrate, ammonium, and organic nitrogen) in the NPO. This will be based on collection of aerosol and rainwater samples year-round at two sites: (1) Chang-Dao Island, China where they expect high anthropogenic nitrogen inputs; and (2) Oahu, Hawaii where they expect marine sources to dominate. They will also collect ship-based samples in the marine boundary layer via already planned short-term research cruises in each season. In addition to the scientific outcomes, this project will provide for human resources and professional development of the team members (faculty members, a graduate student, undergraduate student, and technicians), advance international collaborations, and contribute to education and public outreach. Identifying the sources of nitrogen deposition to the open ocean is crucial for understanding

anthropogenic impacts on biogeochemical cycles. A primary question is, is nitrogen deposition the result of external, anthropogenic processes or does it represent recycled nitrogen from the ocean's point of view? The specific objectives of this project are to: characterize the atmospheric composition and sources of inorganic (ammonium and nitrate) and organic nitrogen with an emphasis on seasonality; diagnose the influence of air-sea exchange versus anthropogenic sources of nitrogen on atmospheric deposition; and determine the isotopic composition of gaseous and particulate inorganic nitrogen in the marine boundary layer via ship-based sample collections in the NPO. Using concentration and isotopic measurements of reactive nitrogen species, in addition to transport and chemical box modeling, the study aims to characterize nitrogen deposition in two locations with very different source influences. This study will provide the first comprehensive, seasonal analysis of the isotopic values of reactive nitrogen species in the NPO atmosphere where nitrogen deposition is considered intense. Ultimately this project will lead to a better understanding of how anthropogenic changes in the atmospheric nitrogen cycle may influence the biogeochemistry of the surface ocean as well as the composition of the marine atmosphere. This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

| Funding Source | Award |
|----------------------------------------------------------|-----------------------------|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1851318 |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1851343 |

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