Results from experiment examining 15N-labeled contaminants in commercial 15N2 gas: Detected 15N-labeled ammonium (NH4) in commercial 15N2 gas (15N2 Contamination project)

Website: https://www.bco-dmo.org/dataset/542884
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Project
» The Ocean Nitrogen Imbalance Paradox: Environmental Controls on the Denitrification Isotope Effect (15N2 Contamination)

Contributors	Affiliation	Role
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Dataset Description

delta 15N NH4 measurments from experiments on 15N-labeled contaminants in commercial 15N2 gas; data used in Dabundo et al. 2014.

Refer to the following publication for more information:
Dabundo, R., Lehmann, M.F., Treibergs, L., Tobias, C.R., Altabet, M.A., Moisander, P.H., and Granger, J. 2014. The Contamination of Commercial 15N2 Gas Stocks with 15N–Labeled Nitrate and Ammonium and Consequences for Nitrogen Fixation Measurements. PLoS ONE, 9(10): e110335. doi:10.1371/journal.pone.0110335

See related datasets:
delta 15N NO3
direct N2O
N2
particulate N

Methods & Sampling

Data was acquired from an isotope ratio mass spectrometer using Isodat 3.0 software.

Ammonium Calculations: The delta 15N NH4 calculation is analagous to the delta 15N NO3 calculation outlined in the "Nitrate isotope corrections" supplementary file (PDF), but with a different blank adjustment, and IAEA N1 replacing IAEA N3 in the transformation from delta 15N IAEA N-3 vs. tank to delta 15N tank vs. IAEA N-3. The blank correction is as follows:

delta15N_blank = [delta15N(2) * area_of_sample - delta15N(2)_blank_average *

area_of_blank_average)]/(area_of_sample - area_of_blank_average)

delta 15N NH4 is then calculated from delta15N_blank by reference to IAEA N1 and IAEA N2 standards.

Refer to the following publication for more information:
Dabundo, R., Lehmann, M.F., Treibergs, L., Tobias, C.R., Altabet, M.A., Moisander, P.H., and Granger, J. 2014. The Contamination of Commercial 15N2 Gas Stocks with 15N–Labeled Nitrate and Ammonium and Consequences for Nitrogen Fixation Measurements. PLoS ONE, 9(10): e110335. doi:10.1371/journal.pone.0110335

Summary of methods from Dabundo et al. 2014:
Reagents:
Four lecture bottles of 98+ at% 15N-labeled N2 gas were purchased from Sigma-Aldrich, three from lot # SZ1670V, and one from lot # MBBB0968V. Two 1L lecture bottles of 98+ at% 15N2 were purchased from Cambridge Isotopes from lot #'s I1-11785A and I-16727. One 1L lecture bottle of 98+ at% 15N2 was purchased from Campro Scientific from lot # EB1169V. Ammonium and nitrate solutions were prepared with salts or with solutions obtained from different distributors: sodium nitrate (NaNO3), potassium nitrate (KNO3), and ammonium chloride (NH4Cl) from Fisher Scientific; analytical-grade potassium nitrate from Fluka Analytical and a gravimetric solution of ammonium chloride from SPEX CertiPrep.

Preparation of nitrate & ammonium solutions:
Aqueous solutions of natural abundance (unlabeled) ammonium and nitrate salts were equilibrated overnight with an air headspace supplemented with an injection of 15N2 gas (to determine whether the 15N2 gas stocks contained 15N-labeled ammonia (NH3) or nitrate and/or nitrite (NOx) contaminants). After equilibration, the 15N/14N ratio of ammonium and the 15N/14N and 18O/16O ratios of nitrate/nitrite in solution were measured, as well as the 15N/14N ratio of N2 gas in the headspace. The isotope ratios of nitrate and ammonium were compared to those in control solutions, which were not supplemented with 15N2 gas. Experiments with the Campro Scientific 15N2 stock were verified for 15N-nitrate/nitrite contaminants only (and not for 15N-ammonium).

Initial experiments consisted of 40 mL or 100 mL solutions of 10, 50, 100, 200, or 300 umol/L nitrate and 5 umol/L ammonium chloride in 60 mL or 120 mL serum vials that were sealed with stoppers. The 20 mL of air headspace in each of the treatment vials was supplemented with 0.1 mL of 15N2 gas from respective bottles from each of the three suppliers. The solutions were equilibrated overnight on a shaker, after which the 15N/14N and 18O/16O isotope ratios of nitrate were analyzed. The 15N/14N isotope ratio of ammonium was also analyzed in experimental solutions treated with the Sigma-Aldrich and Cambridge Isotopes stocks.

Additional experiments were carried out in which 2 mL 15N2 gas was equilibrated overnight in 20 mL serum vials containing 10 mL solutions of 10 umol/L sodium nitrate, after which the 15N/14N and 18O/16O ratios of nitrate were measured. Similarly, 10 mL solutions of 5 umol/L ammonium chloride were dispensed in 20 mL serum vials and equilibrated overnight with 2 mL 15N2 gas, after which the 15N/14N isotope ratios of ammonium were analyzed.

Nitrate and ammonium concentrations:
Nitrate concentrations in the experimental solutions were verified via reduction to nitric oxide in hot vanadium (III) solution followed by detection with a chemiluminescence NOx analyzer (model T200 Teledyne Advanced Pollution Instrumentation). Ammonium concentrations were measured by derivatization with orthophthaldialdehyde (OPA) and fluorometric detection on an AJN Scientific f-2500 Fluorescence Spectrophotometer.

Ammonium N isotope ratio analyses:
The ammonium d15N NH4 was measured using the hypobromite-azide method. Ammonium in basic solution was converted to N2O via oxidation to nitrite (NO2-) with hypobromite, followed by reduction of nitrite to N2O with sodium azide in acetic acid. The d15N of the N2O analyte was measured on the GC-IRMS. Measurements were calibrated using solutions made from the international standard ammonium salts, IAEA-N1 and IAEA-N2.

Data Processing Description

Samples with the same ID are replicated measurements.

BCO-DMO Edits:
- Modified parameter names to conform with BCO-DMO naming conventions;

- Denoted 'Control' and 'Standard' in the lot_number column;
- Replaced spaces with underscores.

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Data Files

File
NH4.csv (Comma Separated Values (.csv), 6.51 KB) MD5:699a3ff316911ad6d00a0a53b329d24f Primary data file for dataset ID 542884

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Parameters

Parameter	Description	Units
lecture_bottle	Identifier of the lecture bottle of 15N-labeled N2 gas.	dimensionless
solution	Solution volume.	milliliters (mL)
headspace	Headspace volume.	milliliters (mL)
N2_injection	Quantity of 15N-labeled N2 gas supplemented in the headspace.	milliliters (mL)
lot_number	Lot number of the 15N-labeled N2 gas; or 'Control' or 'Standard' for controls and standards respectively.	dimensionless
sample_ID	Sample identification number.	dimensionless
area	Area	?
uncorr_d45_44	Uncorrected d45/44 ratio.	dimensionless
uncorr_d46_44	Uncorrected d46/44 ratio.	dimensionless
delta_15N_NH4	delta 15N NH4.	per mille (o/oo)

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Instruments

Dataset-specific Instrument Name	T200 Teledyne Advanced Pollution Instrumentation
Generic Instrument Name	Chemiluminescence NOx Analyzer
Dataset-specific Description	Nitrate concentrations in the experimental solutions were verified via reduction to nitric oxide in hot vanadium (III) solution followed by detection with a chemiluminescence NOx analyzer (model T200 Teledyne Advanced Pollution Instrumentation).
Generic Instrument Description	The chemiluminescence method for gas analysis of oxides of nitrogen relies on the measurement of light produced by the gas-phase titration of nitric oxide and ozone. A chemiluminescence analyzer can measure the concentration of NO/NO2/NOX. One example is the Teledyne Model T200: https://www.teledyne-api.com/products/nitrogen-compound-instruments/t200

Dataset-specific Instrument Name	IR Mass Spec
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Data was acquired from an isotope ratio mass spectrometer using Isodat 3.0 software.
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	AJN Scientific f-2500 Fluorescence Spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Ammonium concentrations were measured by derivatization with orthophthaldialdehyde (OPA) and fluorometric detection on an AJN Scientific f-2500 Fluorescence Spectrophotometer.
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

The Ocean Nitrogen Imbalance Paradox: Environmental Controls on the Denitrification Isotope Effect (15N2 Contamination)

Description from NSF award abstract:
This study will test the sensitivity of the amplitude of the denitrification isotope effect to culture conditions pertinent to the ocean environment. The isotope effect amplitude will be explored with respect to electron donor, trace oxygenation, and temperature, in both batch and continuous culture experiments of denitrifiers.

The proposed work will also involve measurements of the enzymatic isotope effect of the respiratory nitrate reductase of denitrifiers, measurements of its enzymatic activity among cultures, and examination of cellular nitrate transport kinetics of denitrifying strains. The experiments are designed to reveal the physiological basis of the modulation of the isotope effect amplitude, which will further resolve this manifestation in the environment.

In regards to the broader significance and importance of this study, these new experimental data will provide a basis for integration of nitrogen isotope dynamics in ocean models to test how key environmental parameters can affect the global ocean distribution of nitrogen isotopes.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1233897
NSF Division of Ocean Sciences (NSF OCE)	OCE-1130495
Swiss National Science Foundation (SNSF)	R Equip 121258

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