

Flow through sediment core incubations for nitrogen concentration and isotopic fluxes collected in 2013 on the Island of Sylt, Germany in the North Sea.

Website: <https://www.bco-dmo.org/dataset/827378>

Data Type: experimental

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Project

» [Collaborative Research: Nitrous Oxide Production and Fluxes in Coastal Sediments: Response to Environmental Change](#) (Coastal_Nitrous_Oxide)

Contributors	Affiliation	Role
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Abstract

Flow through sediment core incubations for nitrogen concentration and isotopic fluxes collected in 2013 on the Island of Sylt, Germany in the North Sea.

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Coverage

Temporal Extent: 2013-08-14 - 2013-08-22

Acquisition Description

Sediments were collected from three intertidal sites near Königshafen on the island of Sylt in the North Sea, Germany. The 'Schlickwatt (CL)' and 'Mischwatt (SLT)' sites were located inside a small lagoon, while the 'Sandwatt (SD)' site was more openly exposed to wind and waves. Thirty intact push cores (30cm length, 10cm OD) were taken using polycarbonate core liners having vertical lines of silicone sealed holes (\varnothing 3mm) at 1-cm intervals to allow porewater collection. Cores were retrieved leaving ~10 cm of overlying water and sealed with double o-ring caps to minimize gas exchange during transport, and brought immediately back to the laboratory. The gas-tight sealed sediment cores were incubated in the dark at *in situ* temperatures (19°C) while being continuously supplied with filtered seawater at a flow rate of 1.8 0.06 ml/min for ~8 days. For experimental manipulations, four different inflow seawater compositions were used: "Low nitrate" (air sparged; ~20uM; LN), "Low oxygen, low nitrate" (sparged with N₂ to 30-35% O₂ saturation; ~20uM; LOLN), "High nitrate" (amended with NaNO₃ to ~120uM (above background nitrate); HN) and "low oxygen, high nitrate" (combined treatments; LOHN). Samples of each sediment core effluent were taken twice per day.

Concentrations of NO₃⁻ + NO₂⁻ were measured by chemiluminescence after reduction in a hot acidic vanadyl sulfate solution on a NO_x analyzer (Braman and Hendrix, 1989). Concentrations of NO₂⁻ were quantified by using the Griess-Ilosvay method followed by measuring absorption 540nm, and NO₃⁻ was quantified by difference (Grasshoff et al., 1999). Concentrations of NH₄⁺ were measured by fluorescence using the OPA

method (Holmes et al., 1999). Concentrations of N₂O were made using the integrated peak area of the m/z 44 beam on the IRMS, standardizing to analyses of known amounts of N₂O (injected into N₂ sparged seawater in 160ml serum bottles) and normalizing to sample volume (158ml).

All N and O isotopic composition measurements (d₁₅N and d₁₈O (or d₁₇O)); where d₁₅N = [(15R_{sample}/15R_{Air})-1]*1000 in units of ‰, and 15R = 15N/14N and where d₁₈O = [(18R_{sample}/18R_{VSMOW})-1]*1000 in units of ‰, and 18R = 18O/16O (or 17O/16O) were made after conversion of analytes to nitrous oxide, followed by purification with a customized purge and trap system similar to that previously described (McIlvin and Casciotti, 2010) and analysis on a continuous flow IsoPrime 100 isotope ratio mass spectrometer (IRMS). D₁₇O refers to the excess 17O beyond that defined by the terrestrial fractionation line for the oxygen isotope system and is defined as D₁₇O = d₁₇O*0.52 - d₁₈O. Nitrate was converted to N₂O using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) after removal of nitrite by addition of sulfamic acid (Granger and Sigman, 2009). Corrections for drift, size and fractionation of O isotopes during bacterial conversion were carried out as previously described using NO₃- standards USGS 32, USGS 34 and USGS 35 (Casciotti et al., 2002; McIlvin and Casciotti, 2011), with a typical reproducibility of 0.2‰ and 0.4‰ for d₁₅N and d₁₈O, respectively. Nitrate D₁₇O measurements were made on separate aliquots by routing denitrifier-produced N₂O through a gold tube (1/16" OD) held at 780°C, thermally decomposing the N₂O into N₂ and O₂, which were chromatographically separated using a 2m column (1/16" OD) packed with molecular sieve (5Å) before being sent into the IRMS (Kaiser et al., 2007; Komatsu et al., 2008). Nitrate standards USGS 35 and USGS 34 were used to normalize any scale contraction during conversion, with typical reproducibility of D₁₇O measurements of 0.8‰. All samples for nitrite N and O isotope measurements were converted to N₂O within 2 hours of collection using the azide method (McIlvin and Altabet, 2005). Internal nitrite isotope standards (WILIS 10, 11 and 20) were run in parallel at 3 different sizes to correct for any variations in sample size and instrumental drift, with a typical reproducibility for both d₁₅N and d₁₈O is 0.2‰. Based on calibrations against isotope standards USGS 32, 34 and 35 for d₁₅N (Böhlke et al., 2003) and N₂₃, N7373, and N10129 for d₁₈O (Casciotti et al., 2007), the values of internal standards WILIS 10, 11, and 20 are reported here as -1.7, +57.1, and -7.8‰ for d₁₅N and +13.2, +8.6 and +47.6‰ for d₁₈O, respectively. Nitrite D₁₇O measurements were made after conversion to N₂O using the azide method and normalized using a combination of NO₂- and NO₃- isotopic standards. D₁₇O values of NO₂- isotope standards WILIS 10 and WILIS 11 were calibrated previously against USGS 34 and USGS 35 using the denitrifier method followed by thermal decomposition of N₂O to N₂ and O₂ as described above - yielding D₁₇O values of 0‰ for both. For sample NO₂-, raw d₁₇O and d₁₈O values were first normalized for oxygen isotopic exchange with water during the azide reaction (McIlvin and Altabet, 2005) using the calibrated d₁₇O and d₁₈O values of WILIS 10 and WILIS 11. During the same IRMS run, N₂O produced from USGS 34 and USGS 35 via the denitrifier method was also thermally converted and analyzed as N₂ and O₂. Because any isotope fractionation occurring during these reactions is mass dependent (e.g., D₁₇O is unaffected), the D₁₇O of NO₂- can be calculated by normalizing to D₁₇O values of these NO₃- standards. We disregard the small amount of oxygen isotope exchange occurring during the denitrifier method, as this would have only a small impact on the calculated D₁₇O values. Total reduced nitrogen (TRN, e.g., DON + NH₄⁺) was measured in a subset of incubation cores by oxidation of the total dissolved nitrogen (TDN) pool via persulfate digest - followed by d₁₅N analysis using the denitrifier method, similar to that previously described (Knapp et al., 2005). The d₁₅N of the TRN pool was then calculated by mass balance by subtracting the molar contribution of the measured d₁₅N of NO₃- and NO₂- pools to the TDN pool. Based on the measurement of NH₄⁺ concentrations, the DON flux was generally of the same magnitude as the NH₄⁺ flux (not shown). For dissolved N₂O, samples were extracted from the 160ml serum bottles using a purge and trap approach similar to that previously described (McIlvin and Casciotti, 2010). Liquid samples were quantitatively transferred from the sample bottle into a purging flask using a 20psi He stream, followed by He-sparging (~45 min) and cryogenic trapping using the same system described above for nitrate and nitrite derived N₂O. Isotopic composition of the dissolved N₂O was measured by direct comparison against the N₂O reference tank. The composition of this tank (d₁₅N bulk = -0.7‰; d₁₈O = +39.1‰; site preference (SP) = -5.3‰, where SP = d₁₅N alpha - d₁₅N beta, and alpha and beta refer to the central and outer N atoms in the linear N₂O molecule, respectively) was calibrated directly against aliquots of two previously calibrated N₂O tanks from the Ostrom Lab at Michigan State University, having been calibrated by Tokyo Tech. Several sample analyses of tropospheric N₂O from the study site using this system yielded isotope values of +6.8 - 0.7‰ for d₁₅N bulk, +44.1 - 1.7‰ for d₁₈O and +17.4 - 2.2‰ for SP. Reported values have been corrected for any size linearity of isotopic ratios (31/30, 45/44 and 46/44) by using a series of reference tank subsamples injected into 20ml headspace vials using a gastight syringe. Precision for replicate analyses of our reference gas analyzed as samples for d₁₅N is 0.3‰, for d₁₈O is 0.4‰ and for SP is 0.8‰. The D₁₇O of N₂O was calculated similar to that described above for NO₂-. After extraction and cryotrapping, the N₂O sample is thermally decomposed to N₂ and O₂ and chromatographically separated before measurement on the IRMS. Regular analyses of N₂O converted from NO₃- isotope standards (USGS 35 and USGS 34) via the denitrifier method were made to normalize D₁₇O values.

Processing Description

Mass fluxes were calculated as a function of the steady-state difference between influent and effluent concentrations ($[C]$), flow rate (r) and sediment surface area (A) using: $\text{Flux} = ([C]\text{change} * r)/A$. Error estimates of fluxes incorporate variations in both measured flow rates as well as steady state concentrations.

For dissolved ions, effluent was directed into HDPE bottles and allowed to fill for ~60 minutes before subsampling, filtering (0.2 μ m) and freezing (-20°C). Separate 20ml aliquots were taken for measurement of dissolved inorganic nitrogen concentrations (nitrate, nitrite and ammonium) and stable isotopic composition. Concentrations of nitrite and ammonium were made immediately, while nitrate concentrations were measured back in the Wankel lab at WHOI. Samples for dissolved N₂O were directed through gas impermeable PEEK tubing directly into pre-evacuated Tedlar gas sampling bags followed by gentle transfer into 160ml serum bottles using a ¼" OD silicone tubing, filling from the bottom to minimize turbulence and gas exchange. Sample water was allowed to overflow the bottle volume for at least two volumes before crimp-sealing and preserving with 100 μ l of a saturated HgCl₂ solution.

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
- * blank values in this dataset are displayed as "nd" for "no data." nd is the default missing data identifier in the BCO-DMO system.
- * removed all spaces in headers and replaced with underscores
- * removed all units from headers
- * converted dates to ISO Format yyyy-mm-dd
- * created Date_Local column to replace Date column
- * created ISO_DateTime_Local from Time_Stamp column
- * set Types for each data column

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Related Publications

Braman, R. S., & Hendrix, S. A. (1989). Nanogram nitrite and nitrate determination in environmental and biological materials by vanadium(III) reduction with chemiluminescence detection. *Analytical Chemistry*, 61(24), 2715–2718. doi:[10.1021/ac00199a007](https://doi.org/10.1021/ac00199a007)

Methods

Böhlke, J. K., Mroczkowski, S. J., & Coplen, T. B. (2003). Oxygen isotopes in nitrate: new reference materials for 18O:17O:16O measurements and observations on nitrate-water equilibration. *Rapid Communications in Mass Spectrometry*, 17(16), 1835–1846. doi:[10.1002/rcm.1123](https://doi.org/10.1002/rcm.1123)

Methods

Casciotti, K. L., Böhlke, J. K., McIlvin, M. R., Mroczkowski, S. J., & Hannon, J. E. (2007). Oxygen Isotopes in Nitrite: Analysis, Calibration, and Equilibration. *Analytical Chemistry*, 79(6), 2427–2436. doi:[10.1021/ac061598h](https://doi.org/10.1021/ac061598h)

Methods

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

Granger, J., & Sigman, D. M. (2009). Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method. *Rapid Communications in Mass Spectrometry*, 23(23), 3753–3762.

doi:[10.1002/rcm.4307](https://doi.org/10.1002/rcm.4307)

Methods

Grasshoff, K., Kremling, K., & Ehrhardt, M. (Eds.). (2009). *Methods of seawater analysis*. John Wiley & Sons. <https://isbnsearch.org/isbn/978-3-527-61399-1>

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:[10.1139/f99-128](https://doi.org/10.1139/f99-128)
Methods

Kaiser, J., Hastings, M. G., Houlton, B. Z., Röckmann, T., & Sigman, D. M. (2007). Triple Oxygen Isotope Analysis of Nitrate Using the Denitrifier Method and Thermal Decomposition of N₂O. *Analytical Chemistry*, 79(2), 599–607. doi:[10.1021/ac061022s](https://doi.org/10.1021/ac061022s)
Methods

Knapp, A. N., Sigman, D. M., & Lipschultz, F. (2005). N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site. *Global Biogeochemical Cycles*, 19(1). doi:10.1029/2004gb002320 <https://doi.org/10.1029/2004GB002320>
Methods

Komatsu, D. D., Ishimura, T., Nakagawa, F., & Tsunogai, U. (2008). Determination of the ¹⁵N/¹⁴N, ¹⁷O/¹⁶O, and ¹⁸O/¹⁶O ratios of nitrous oxide by using continuous-flow isotope-ratio mass spectrometry. *Rapid Communications in Mass Spectrometry*, 22(10), 1587–1596. doi:[10.1002/rcm.3493](https://doi.org/10.1002/rcm.3493)
Methods

McIlvin, M. R., & Altabet, M. A. (2005). Chemical Conversion of Nitrate and Nitrite to Nitrous Oxide for Nitrogen and Oxygen Isotopic Analysis in Freshwater and Seawater. *Analytical Chemistry*, 77(17), 5589–5595. doi:[10.1021/ac050528s](https://doi.org/10.1021/ac050528s)
Methods

McIlvin, M. R., & Casciotti, K. L. (2010). Fully automated system for stable isotopic analyses of dissolved nitrous oxide at natural abundance levels. *Limnology and Oceanography: Methods*, 8(2), 54–66. doi:[10.4319/lom.2010.8.54](https://doi.org/10.4319/lom.2010.8.54)
Methods

McIlvin, M. R., & Casciotti, K. L. (2011). Technical Updates to the Bacterial Method for Nitrate Isotopic Analyses. *Analytical Chemistry*, 83(5), 1850–1856. doi:[10.1021/ac1028984](https://doi.org/10.1021/ac1028984)
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

Wankel, S. D., Ziebis, W., Buchwald, C., Charoenpong, C., de Beer, D., Dentinger, J., ... Zengler, K. (2017). Evidence for fungal and chemodenitrification based N₂O flux from nitrogen impacted coastal sediments. *Nature Communications*, 8(1). doi:10.1038/ncomms15595 <https://doi.org/10.1038/NCOMMS15595>
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Parameters

Parameter	Description	Units
N_number	Internal Lab ID	dimensionless
Study_Name	Study Identifier	dimensionless
Date_Local	Date Sample Collected	%Y-%m-%d
Bottle_Fill_Start	Time Water Sample Collection began	%H:%M
Bottle_Fill_Stop	Time Water Sample Collection ended	%H:%M
Gas_Bag_Start	Time Gas Sample Collection began	%H:%M
Gas_Bag_Stop	Time Gas Sample Collection ended	%H:%M
Time_Stamp	Time Registered for Sample	mm/dd/yy hh:mm
Elapsed	Time Since Incubation Initiation	Hours
Unique_ID	Unique Sample Identifier	dimensionless
Comment	Comment, Sample ID	dimensionless

Site_Type	Predominant Sediment Type	dimensionless
Core_ID	Unique Sediment Core ID	dimensionless
Duplicate_ID	Core A or B	dimensionless
Treatment	Experimental Treatment	unitless
Timepoint	Sequential Sampling Time point	dimensionless
Flow_Rate	Seawater Flow Rate through core	mL/min
Inflow_NO2	Inflow nitrite concentration	uM
Inflow_NH4	Inflow ammonium concentration	uM
Inflow_NO3	Inflow nitrate concentration	uM
Inflow_N2O	Inflow Nitrous oxide concentration	uM
Effluent_NO2	Effluent nitrite concentration	uM
Effluent_NH4	Effluent ammonium concentration	uM
Effluent_NO3	Effluent nitrate concentration	uM
Effluent_DON	Effluent dissolved organic nitrogen	uM
Effluent_TDN	Effluent total dissolved nitrogen	uM
Effluent_N2O	Effluent nitrous oxide concentration	nM
O2_Flux	Calculated Dissolved Oxygen Flux	mmol m ⁻² d ⁻¹
NO2_Flux	Calculated Nitrite Flux	mmol m ⁻² d ⁻¹
NH4_Flux	Calculated Ammonium Flux	mmol m ⁻² d ⁻¹
NO3_Flux	Calculated Nitrate Flux	mmol m ⁻² d ⁻¹
DON_Flux	Calculated DON Flux	mmol m ⁻² d ⁻¹
N2O_Flux	Calculated N2O Flux	umol m ⁻² d ⁻¹
NO3_d15N	Nitrate nitrogen isotope ratio	per mil
NO3_d18O	Nitrate oxygen isotope ratio	per mil
NO3_D17O	17O isotope excess in nitrate	per mil
NO2_d15N	Nitrite nitrogen isotope ratio	per mil
NO2_d18O	Nitrite oxygen isotope ratio	per mil
NO2_D17O	17O isotope excess in nitrite	per mil
TDN_d15N	Total dissolved nitrogen isotope ratio	per mil
TRN_d15N	Total reduced nitrogen isotope ratio	per mil
N2O_d15N	Nitrous oxide nitrogen isotope ratio	per mil
N2O_d18O	Nitrous oxide oxygen isotope ratio	per mil
N2O_SP	Nitrogen Isotope Site Preference N2O	per mil
N2O_D17O	17O isotope excess in N2O	per mil
ISO_DateTime_Local	Date/Time (Local) ISO formatted	%Y-%m-%dT%H:%M

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Instruments

Dataset-specific Instrument Name	Turner Designs Aquafluor Fluorometer
Generic Instrument Name	Fluorometer
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	Isoprime 100 Isotope Ratio Mass Spectrometer
Generic Instrument Name	Mass Spectrometer
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	Shimadzu UV 2550 Spectrophotometer
Generic Instrument Name	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.

Dataset-specific Instrument Name	Teledyne 200e NOx Analyzer
Generic Instrument Name	Chemiluminescence NOx Analyzer
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/NO ₂ /NO _x . One example is the Teledyne Model T200: http://www.teledyne-api.com/products/T200.asp

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Project Information

Collaborative Research: Nitrous Oxide Production and Fluxes in Coastal Sediments: Response to Environmental Change (Coastal_Nitrous_Oxide)

Coverage: Wadden Sea Field Station, Sylt, Germany; Santa Catalina Island, California, USA

NSF Abstract:

Although marine sediments are known "hotspots" of nitrous oxide (N₂O) production and emission, current estimates and future projections of this potent greenhouse gas from coastal areas, especially in response to lower levels of dissolved oxygen and increased nitrogen inputs, are an approximation at best. Scientists from the University of Southern California and Woods Hole Oceanographic Institute plan to improve upon these values by determining N₂O dynamics at two coastal sites, Sylt, the German Wadden Sea, and Santa Catalina Island, a California Coastal lagoon. To attain their goal, they will carry out in-situ, high resolution microsensor measurements of N₂O, oxygen, nitrate, nitric oxide, hydrogen sulfide, pH, redox potential, and temperature in conjunction with sediment and pore water analyses. Some of the sediment cores to be collected will be subjected to changes in oxygen content and nitrate concentrations in the overlying water to determine changes in nitrogen cycling activity and N₂O flux as a function of low oxygen or nitrate addition. Using experimental incubations, the isotopic composition of N₂O, nitrate, and ammonia will be measured to provide a quantitative estimate of net isotopic flux and N₂O cycling processes. The combined use of microprofiling and multi-isotope approaches will provide not only detailed insight into N₂O production and flux at these sites, but also yield data for a recently developed metabolic model to simulate and predict N₂O dynamics under varying environmental conditions.

Broader Impacts: The research would strengthen the collaboration with German scientists. The proponents plan to create a webpage to discuss the technologies used in their project, as well as the activities taking place during their field trips. One postdoc and one undergraduate student from the University of Southern California 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)	OCE-1259971
NSF Division of Ocean Sciences (NSF OCE)	OCE-1260373

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