# Mean d15N of individual amino acids and bulk organic matter for five plankton size fractions

Website: https://www.bco-dmo.org/dataset/715977

Data Type: Cruise Results

Version: 1

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#### Project

» The Use of Nitrogen Isotopes of Amino Acids To Understand Marine Sedimentary 15N Records (Amino Acid Sediment 15N)

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#### **Abstract**

Mean d15N of individual amino acids and bulk organic matter for five plankton size fractions from R/V Sarmiento de Gamboa Malaspina\_2011 in the Subtropical North Atlantic Ocean from January to March 2011

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# Coverage

Spatial Extent: Lat:24 Lon:-24 Temporal Extent: 2011-01 - 2011-03

# **Dataset Description**

Mean d15N of individual amino acids and bulk organic matter for five plankton size fractions.

#### Methods & Sampling

# Sampling

Plankton samples were obtained during Leg 8 of the Malaspina-2010 expedition on R/V Sarmiento de Gamboa (January-March 2011), on a transect predominantly along  $24^{\circ}$ N, between the Canary Island and Florida. Briefly, plankton samples were collected by vertical tows of a microplankton net (40  $\mu$ m mesh size) and a mesoplankton net (200  $\mu$ m mesh size) through the upper 200 m of the water column. Sampling was between 10:00 and 16:00 h GMT. Plankton was separated into five size fractions (40–200, 200–500, 500–1000, 1000–2000 and 2000  $\mu$ m) by gentle filtration of the samples by a graded series of nylon sieves (2000, 1000, 500, 200 and 40  $\mu$ m). Large gelatinous organisms were removed before filtration. Aliquots for each size fraction were collected on pre-weighed glass-fiber filters, dried (60°C, 48 h) and stored in a desiccator before

determination of biomass (dry weight), carbon and nitrogen content and natural abundance of stable carbon and nitrogen isotopes ashore. Nominal values of the individual size of organisms in each size fraction were estimated as the geometric mean of the values defining each size interval and expressed as carbon content ( $\mu$ g C) in a logarithmic scale

## Bulk δ15N analysis

After determination of dry weight, finely ground aliquots of each size fraction were packed in tin capsules for elemental and stable isotope analysis by conversion into CO2 and N2 in an elemental analyzer (Carlo Erba CHNSO 1108) coupled to an isotope-ratio mass-spectrometer (Finnigan Mat Delta Plus).

# Compound-specific amino acid δ15N analysis

Samples for CSI-AA were selected to span gradients in 15Nbulk values. We chose plankton from four sampling stations in each of the three zones (eastern, central and western regions). Individual samples were then pooled (quantitatively, so that each subsample was represented equally in the final composite) to have enough material in each size fraction for CSI-AA. In total 15 samples in the transect were chosen for CSI-AA. Approximately 1 mg of total dry plankton material was then hydrolyzed for subsequent analysis.

The  $\delta15N$  values of individual AAs were measured via GC-IRMS, after 6 N HCl acid hydrolysis and the formation of TFA ester derivatives following previously published methods. Briefly, amino acids were liberated by hydrolysis (6 N HCl, 20 hr at 110uC) under nitrogen, and TFA derivatives subsequently prepared from free AA: isopropyl esters were made with a 1:5 mixture of Acetyl Chloride (AcCl):2-propanol (110uC, 60 minutes), and then acylated using a 1:3 mixture of Dichloromethane:Trifluroacetyl acetate (DCM:TFAA) (100uC, 15 minutes). Derivatized AAs were dissolved in DCM to a final ratio of approximately 2 mg of original dry sample to 250 ml DCM. After derivatization, samples were analyzed by a thermos Trace Ultra gas chromatograph coupled to a Finnegan Delta-Plus isotope ratio mass spectrometer (GC-IRMS). AAs were separated using a 50 m, 0.32 ID Hewlett Packard Ultra-1 column with 1 mm film thickness. AAs were measured based on n = 4 injections, and the average mean deviations for individual AA d15N measurements across all sample replicates was 0.5%.

Under these conditions, we determined  $\delta15N$  values for 12 AAs: glutamic acid + glutamine (Glx), aspartic acid + asparagine (Asp), alanine (Ala), Isoleucine (Ile), Leucine (Leu), Proline (Pro), valine (Val), glycine (Gly), serine (Ser), Lysine (Lys), phenylalanine (Phe), and Threonine (Thr). Each AA was run four times on the GC-IRMS.. AA values were categorized and presented in 3 groups, based on their relative 15N values changes with trophic transfer: the source AAs (Gly, Ser, Lys, Phe), the trophic AAs (Glx, Asp, Ala, Ile, Leu, Pro and Val), and one "metabolic" AA (Thr).

# Trophic position and $\Sigma V$

To calculate CSI-AA based TP of plankton we used the most widely used current equation and TEF value, based on the isotopic offset between Glx and Phe:

TP =  $(\delta 15 \text{NG/x} - \delta 15 \text{NPhe} - 3.4)/7.6 + 1$ 

where  $\delta$ 15NGIx and  $\delta$ 15NPhe are measured values, +3.4% is the assumed isotopic difference between the Glx and Phe in primary producers, and +7.6% is the assumed 15N enrichment in Glx relative to Phe with each trophic transfer from food source to consumer (TEF value). The standard errors in the estimation of TP, computed by propagation of analytical error in the individual AA determinations, did not exceed 0.1 TP.

The  $\delta15N$  value of total hydrolysable AAs ( $\delta15NTHAA$ ) is used as a proxy for total protein  $\delta15N$  value, and was estimated as the molar-weighted average of individual  $\delta15N$  values:

 $\delta 15NTHAA = \Sigma (\delta 15NAA * mol% AA)$ 

where  $\delta 15$ NAA is the  $\delta 15$ N value of each individual AA measured and mol%AA is the molar percentage contribution of each AA. In our study we used the  $\delta 15$ N value of each individual AA and mol%AA were obtained from Lehman (2009).

The degradation index  $\Sigma V$  is a measure of the relative resynthesis of the original autotrophic AA pool in detritus or different organisms (plankton size fractions, in our case) was for each size individual fraction sample as the mean deviation of  $\delta 15N$  of individual trophic amino acid, from their average:

 $\Sigma V = \Sigma (AAi - Avg trp) / n$ 

Where AAi were individual δ15N amino acid values, Avg trp is the average value and n the total number of

trophic amino acids.

# **Data Processing Description**

Thermo-Finnigan Isodat software and Microsoft Excel 2013.

#### **BCO-DMO Processing:**

- changed column names to comply with BCO-DMO standards
- added columns for significant differences to capture the superscript letters that accompanied some data point. All added columns are named after the amino acid with " significant difference".
- combined some headers to capture the metadata used to describe several columns (example trophic AA Glx)
- changed > to greater than
- changed Σ to sigma

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## **Data Files**

#### File

plankton.csv(Comma Separated Values (.csv), 3.89 KB) MD5:b8e026a04712989f68dcb424c02a058e

Primary data file for dataset ID 715977

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# **Related Publications**

Mompeán, C., Bode, A., Gier, E., & McCarthy, M. D. (2016). Bulk vs. amino acid stable N isotope estimations of metabolic status and contributions of nitrogen fixation to size-fractionated zooplankton biomass in the subtropical N Atlantic. Deep Sea Research Part I: Oceanographic Research Papers, 114, 137–148. https://doi.org/10.1016/j.dsr.2016.05.005

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#### **Parameters**

Parameter	Description	Units
Zone	Location where plankton size fractions were analyzed; The West Central or Eastern Zone.	unitless
plankton_size_fraction	Plankton size fraction range	microns
Bulk_15N	15N/14N isotopic ratio total sample	per mil

Bulk_15N_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Glx	Gln+Glu d15N value	per mil
trophicAA_Glx_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Asp	Aspartic Acid + Asparagine d15N value	per mil
trophicAA_Asp_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Ala	Alanine d15N value	per mil
trophicAA_Ala_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Ile	Isoleucine d15N value	per mil
trophicAA_Ile_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Leu	Leucine d15N value	per mil
trophicAA_Leu_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
trophicAA_Pro	Proline d15N value	per mil
trophicAA_Pro_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil

trophicAA_Val	Valine d15N value	per mil
trophicAA_Val_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
sourceAA_Gly	Glycine d15N value	per mi
sourceAA_Gly_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
sourceAA_Ser	Serine d15N value	per mil
sourceAA_Ser_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
sourceAA_Lys	Lysine d15N value	per mi
sourceAA_Lys_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
sourceAA_Phe	Phenylalanine d15N value	per mil
sourceAA_Phe_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
metabAA_Thr	Threonine d15N value	per mil
metabAA_Thr_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	per mil
CSI_AA_TP	Trophic Position	unitles

CSI_AA_TP_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	unitless
CSI_AA_sigmaV	CSIAA Degradation Parameter	unitless
CSI_AA_sigmaV_significant_difference	Significant difference; The significant differences between fractions for each zone are indicated with differenent letters (a b and c); Cases with no letters indicate no significant differences within the zones sampled.	unitless

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# Instruments

Dataset- specific Instrument Name	PDZ Europa ANCA-GSL elemental analyzer
Generic Instrument Name	Elemental Analyzer
Dataset- specific Description	Interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK)
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	Thermo Trace GOLD GC
Generic Instrument Name	Gas Chromatograph
Dataset- specific Description	Used with MAT 253 isotope ratio mass spectrometer (IRMS) via a GC-III combustion (C) interface (Thermo-Finnigan Corporation)
Generic Instrument Description	Instrument separating gases, volatile substances, or substances dissolved in a volatile solvent by transporting an inert gas through a column packed with a sorbent to a detector for assay. (from SeaDataNet, BODC)

Dataset- specific Instrument Name	PDZ Europa 20-20 isotope ratio mass spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset- specific Description	Used with PDZ Europa ANCA-GSL elemental analyzer
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	MAT 253 isotope ratio mass spectrometer (IRMS)
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset- specific Description	Used with Thermo Trace GOLD GC
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	Light meter
Generic Instrument Name	Light Meter
Dataset- specific Description	Used to measure irradiance
Generic Instrument Description	Light meters are instruments that measure light intensity. Common units of measure for light intensity are umol/m2/s or uE/m2/s (micromoles per meter squared per second or microEinsteins per meter squared per second). (example: LI-COR 250A)

Dataset- specific Instrument Name	pH sensor
Generic Instrument Name	pH Sensor
Dataset- specific Description	Used to measure pH
Generic Instrument Description	An instrument that measures the hydrogen ion activity in solutions. The overall concentration of hydrogen ions is inversely related to its pH. The pH scale ranges from 0 to 14 and indicates whether acidic (more $H+$ ) or basic (less $H+$ ).

Dataset-specific Instrument Name	Salinity sensor
Generic Instrument Name	Salinity Sensor
Dataset-specific Description	Used to measure salinity
Generic Instrument Description	Category of instrument that simultaneously measures electrical conductivity and temperature in the water column to provide temperature and salinity data.

Dataset-specific Instrument Name	Water Temperature Sensor	
Generic Instrument Name	Water Temperature Sensor	
Dataset-specific Description	Used to measure temperature	
Generic Instrument Description	General term for an instrument that measures the temperature of the water with which it is in contact (thermometer).	

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# **Deployments**

Malaspina 2011

Website	https://www.bco-dmo.org/deployment/680974	
Platform	R/V Sarmiento de Gamboa	
Start Date	2011-01-28	
End Date	2011-03-09	

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# **Project Information**

The Use of Nitrogen Isotopes of Amino Acids To Understand Marine Sedimentary 15N Records (Amino Acid Sediment 15N)

**Coverage**: California Margin , Santa Barbara Basin , CA current system, Eastern Tropical Pacific

The bioavailability of nutrients plays a crucial role in oceanic biological productivity, the carbon cycle, and climate change. The global ocean inventory of nitrogen (N) is determined by the balance of N-fixation (sources) and denitrification (sinks). In this three-year project, a researcher from the University of California, Santa Cruz, will focus on developing compound-specific N isotope (d15N) analysis of amino acids as a new tool for understanding N source and transformation of organic matter in paleo-reservoirs. The offsets in the isotopic ratios of individual amino acid groups may yield information about trophic transfer, heterotrophic microbial reworking, and autotrophic versus heterotrophic sources. By measuring and comparing the bulk and amino acid d15N in size-fractioned samples from plankton tows, sediments traps, and multi-cores in oxic and suboxic depositional environments, the researcher will: (1) Provide a proxy of the d15N of average exported photoautotrophic organic matter; and (2) Provide a new level of detail into sedimentary organic N degradation and preservation.

#### Broader impacts:

This project will improve understanding of the fundamental underpinnings and behaviors of d15N amino acid patterns and how they behave in contrasting sedimentary environments, while also developing a potential paleoceanographic proxy. Funding will support a graduate student and undergraduate research at the institution. The researcher will also conduct community outreach in the form of a workshop/tutorial on the proxy development.

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# **Funding**

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1131816

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