Triple Oxygen Isotopes for quantifying Gross Primary Production (GPP)

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Why measure GPP?

- GPP represents total energy available for the ecosystem (maximal production)
- interesting dynamics in combination with NCP

Example: Response to melting sea ice

From Ji et al., submitted
Why measure GPP?

- GPP represents total energy available for the ecosystem (maximal production)
- Particularly interesting dynamics in combination with NCP

**Example: Response to melting sea ice**

GOP = gross oxygen production

From Ji et al., submitted
How does the method work?

- Three isotopes of O: $^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$
- Ratio serves as a “made-in tag”
GOP from Triple Oxygen Isotopes

\[ 17\Delta = \text{measure of ratio of } ^{16}\text{O}, ^{17}\text{O}, \text{ and } ^{18}\text{O} \]

\[ = \ln(\delta^{17}\text{O}/1000+1) - 0.5179\ln(\delta^{18}\text{O}/1000+1) \times 10^6 \]

\[ GOP = \text{gross oxygen production} \]

Atmosphere

UV Radiation \rightarrow \text{Mass Independent Fractionation}

\[ \text{more } ^{17}\text{O than } ^{18}\text{O} \]

Photosynthetic O\(_2\) \rightarrow \text{Mass Dependent Fractionation}

\[ \text{more } ^{18}\text{O than } ^{17}\text{O} \]

Ocean

\[ ^{17}\Delta \text{ of } O_2 = 249 \text{ per meg} \]

\[ \text{Calculate} \]

\[ \text{GOP} = kO_{eq} \]

\[ = \frac{X_{dis}^{17} - X_{eq}^{17}}{X_{dis}^{17}} - \lambda \frac{X_{dis}^{18} - X_{eq}^{18}}{X_{dis}^{18}} \]

\[ = \frac{X_{P}^{17} - X_{dis}^{17}}{X_{dis}^{17}} - \lambda \frac{X_{P}^{18} - X_{dis}^{18}}{X_{dis}^{18}} \]
Measuring Triple Oxygen Isotopes of O₂

Measure $^{16}$O, $^{17}$O, and $^{18}$O

Separate O₂ and Ar from N₂

Isotope Ratio
Mass Spectrometer

Gas Chromatography Column

Cryogenic Trap (<12 K)

Condense O₂ and Ar

Remove water

Sample Manifold
Brief History

- Seminal papers by Luz et al. in 1999 and 2000 with simple equation
- Developed further by Michael Bender and Paul Quay in early 2000s...

\[ GP = KC_0(\Delta_{\text{diss}} - \Delta_{\text{eq}})/(\Delta_{\text{max}} - \Delta_{\text{diss}}) \]

from Luz and Barkan, 2000

from Hendricks et al. 2004
Brief History

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- 2011 to present: equations developed further, 1D and 3D modeling, new considerations appear
Advantages of TOI for GPP

• In situ technique: Doesn’t disturb the biology!
• Don’t need assumption that light = dark respiration
• Integrates over large spatial and temporal scales
• Relatively easy to collect (but hard to measure!) \(\rightarrow\) enables hundred(s) of GOP rates per cruise
• Provides the NCP/GOP ratio: a measure of carbon cycle efficiency

High Export = Leaky
Low Export = Efficient Recycling

Productivity on summer New England shelf as part of NES-LTER
Disadvantages

- Need specialized equipment to measure samples
- Biases caused by physical transport and steady state assumption
- Usually used only to give rate integrated over mixed layer
Special Considerations

- Best to calculate photosynthetic end member from $\delta^{18}O$ of seawater (and $\delta^{17}O$ if possible)
- Cryogenic trapping really necessary in analysis
- Gives $O_2$ production $\rightarrow$ Mehler reaction and photorespiration need to be taken into account if want carbon production

*from Manning et al., 2017*
Outstanding Questions

• How best to correct for lateral (and vertical) physical transport?
• What is best factor to use to estimate NPP from GPP?
• Are there processes that affect the $^{17}O$ signature? Bubbles? Non-standard metabolism?

Haskell et al 2017
Extra slides
Diel Cycles in $^{17}\Delta$

Sometimes diel cycles are observed despite expected time scale of $O_2$

From Howard et al., 2017
Energy flow diagrams

• Can be constructed if GPP, NPP and NCP are all measured

from Manning et al., 2017b
Why the isotopic composition of seawater matters

modified from Manning et al., 2017
Photosynthetic End Member

modified from Manning et al., 2017
Biases in GOP from $^{17}\Delta$ method from Nicholson et al., 2014.
Photosynthetic Electron Flow

From Hughes et al. 2018