Using different flavours of oxygen to measure biological production from ship-based and autonomous platforms

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Flavours of oxygen

- molecular dioxygen: \( \text{O}_2 \)
- oxygen triple isotopologues: \( ^{16}\text{O}_2, ^{16}\text{O}^{18}\text{O}, ^{16}\text{O}^{17}\text{O} \)
- abiotic gas exchange analogue: \( \text{O}_2 \) and \( \text{Ar} \)
- "abiotic" deep-water mixing analogue: \( \text{O}_2 \) and \( \text{N}_2\text{O} \)
Sampling and analysis

- continuous $\text{O}_2$ concentration measurements by optode
- continuous $\text{O}_2$/Ar ratio measurements by MIMS or EIMS
- $\text{O}_2$ isotopologues by isotope-ratio mass spectrometry (IRMS)
- $\text{N}_2\text{O}$ concentrations by laser cavity absorption spectroscopy
Platforms
Production ($P$), respiration ($R$) [$N = P - R$], gas exchange, mixing
In vitro vs. in situ net production

Net community production (mmol CO₂ m⁻² day⁻¹)

In vitro observations

In situ observations

Minimum value.

Maximum value.

Net community production (mmol CO₂ m⁻² day⁻¹)
Advantages & disadvantages

+ in principle, unambiguous measurement of $N$ and $P$
+ no sampling biases (bottle effects, temperature, light)
+ ease of sampling (non-research vessels, no incubations)
+ integrates over $O_2$ residence time in the mixed layer (days to weeks)
+ scalable / high spatial coverage possible

— uncertainty of gas exchange coefficient ($\pm 20\%$)
— currency is $O_2$, not $C$
  — photosynthetic coefficient?
  — $P$ includes other non-carbon fixing, $H_2O$-splitting reactions
— integrates vertically over mixed layer depth, but may include contributions from below
Using Ar to correct for the physical $O_2$ component
Net community production $N = P - R$

O$_2$ mass balance:

$$Z_{mix} \frac{\partial c(O_2)}{\partial t} = N - k(O_2)c_{sat}(O_2) \Delta(O_2) + F_{inj} \chi(O_2) + F_{exch} \frac{\alpha(O_2) \chi(O_2)}{Sc(O_2)} + K_z \frac{\partial c(O_2)}{\partial z} \bigg|_{z_{mix}}$$

Biological O$_2$ flux:

$$F_{bio}(O_2/Ar) = kc_{sat}(O_2) \Delta(O_2/Ar) = N + K_z \frac{\partial c_{sat}(O_2) \Delta(O_2/Ar)}{\partial z} \bigg|_{z_{mix}}$$

$$N \approx F_{bio}(O_2/Ar)$$
Production in the Bellingshausen Sea

Mixture of open ocean and coastal sampling locations

Effect of Ar correction:

Outgassing

Intriguing
Entrainment correction "removes" apparent net heterotrophic areas

\[ F_e = z_{mix} \frac{\Delta c}{\Delta t} = \frac{1}{2} \frac{(\Delta z_{mix})^2}{\Delta t} \frac{\partial c(O_2)}{\partial z} \bigg|_{oxy}. \]
Using N₂O to correct for vertical fluxes
Using N\textsubscript{2}O as "abiotic" analogue to correct for vertical O\textsubscript{2} fluxes

Upwelling brings up
- high N\textsubscript{2}O
- high CO\textsubscript{2}
- low O\textsubscript{2}
- high nutrient

Re-equilibration by gas-exchange and net production.

N\textsubscript{2}O has negligible surface sources and sinks:

\[
Z_{\text{mix}} \frac{dc(N_2O)}{dt} = -k(N_2O)\left[ c(N_2O) - c_{\text{equ}}(N_2O) \right]
\]

\[
Z_{\text{mix}} \frac{dc(O_2)}{dt} = N(O_2) - k(O_2)\left[ c(O_2) - c_{\text{equ}}(O_2) \right]
\]

\[
N(O_2) = k(N_2O)\left[ c(N_2O) - c_{\text{equ}}(N_2O) \right] \frac{dc(O_2)}{dc(N_2O)} + k(O_2)\left[ c(O_2) - c_{\text{equ}}(O_2) \right]
\]
Correction of $F_{bio}(O_2/Ar)$ for vertical mixing using $N_2O$ to give $N(O_2/Ar)$
Gross production using oxygen triple isotopologues
\((^{16}\text{O}_2, ^{16}\text{O}^{17}\text{O}, ^{16}\text{O}^{18}\text{O})\)
Oxygen isotope transfer from $O_2$ to $CO_2$ via $O_3$

$O_2 + h\nu \rightarrow O + O$

$O_2 + O(^3P) + M \rightarrow O_3 + M$

$tropopause$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$

$O(^1D) + CO_2 \rightarrow CO_2 + O(^3P)$
\[ \Delta^{(17}\text{O}) = \delta^{(17}\text{O}) - \lambda \delta^{(18}\text{O}) \]

Choose \( \lambda = \gamma_R = 0.5179 = \frac{^{17}\varepsilon_R}{^{18}\varepsilon_R} \), where \( \varepsilon_R \) is the respiratory kinetic isotope fractionation

Reference: tropospheric Air-\( \text{O}_2 \)

photosynthetic \( \text{O}_2 \): \( \Delta_{\text{max}}^{(17}\text{O}) = 249 \text{ ppm (???) (180 to 264 ppm} \)
Effect of photosynthesis, respiration and gas exchange on $O_2$ analogues
Calculating the ratio of gross O\textsubscript{2} gross production \( P \) to gross O\textsubscript{2} influx: \( g = \frac{P}{k c_{\text{sat}}} \)

Luz & Barkan (2000):

\[
g = \frac{P}{k c_{\text{sat}}} \approx \frac{\Delta(^{17}\text{O}) - \Delta_{\text{sat}}(^{17}\text{O})}{\Delta_{\text{max}}(^{17}\text{O}) - \Delta(^{17}\text{O})}
\]

Prokopenko et al. (2011):

\[
g = \frac{^{17}\delta - ^{17}\delta_{\text{sat}}}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta - ^{18}\delta_{\text{sat}}}{1 + ^{18}\delta} - \gamma_R \frac{^{17}\delta_{\text{p}} - ^{17}\delta}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta_{\text{p}} - ^{18}\delta}{1 + ^{18}\delta}
\]

Kaiser (2011):

\[
g = \frac{(1 + ^{17}\varepsilon_E)\frac{^{17}\delta - ^{17}\delta_{\text{sat}}}{1 + ^{17}\delta} - \gamma_R (1 + ^{18}\varepsilon_E)\frac{^{18}\delta - ^{18}\delta_{\text{sat}}}{1 + ^{18}\delta} + s (^{17}\varepsilon_E - \gamma_R^{18}\varepsilon_E)}{\frac{^{17}\delta - ^{17}\delta}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta_{\text{p}} - ^{18}\delta}{1 + ^{18}\delta}}
\]

Gross O₂ production in the Bellingshausen Sea

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Unrecognised systematic uncertainties due to phytoplankton composition

Relative deviation from base case, $\Delta_{\text{max}}^{(17}\text{O}) = 185$ ppm

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Global measurements and modelling of oxygen triple isotopologues

Juranek et al. 2010
Reuer et al. 2007
Hendricks et al. 2005
Juranek et al. 2012
Cassar, unpublished
Stanley, unpublished
Stanley et al. 2012
Yamaguchi, unpublished
Luz and Barkan 2009
Quay et al. 2010
Stanley, unpublished
Castro–Morales et al. 2013
Yeung et al. 2013
Munro et al. 2013
Sarma 2008
Huang et al. 20012
Prokopenko, unpublished
Prokopenko et al. 2011
Quay et al. 20012
Hamme et al. 2012
Net community production from underwater ocean gliders
RRS James Clark Ross cruise JR255A "GENTOO", Jan 2012

Ship track coloured by sea surface temperature

Iceberg

Antarctic Peninsula

Glider tracks

Sea ice edge
Glider O$_2$ measurements
Depth-integrated net community production

\[ \Delta t = 16 \text{ d} \]

\[ N(O_2) = (27 \pm 4) \text{ mmol m}^{-2} \text{ d}^{-1} \]
In-situ measurements can help avoid ship sampling biases

Intake design on research ships

Moon pool
To understand variability on small to large scales, collaboration of all scientific disciplines is required. Novel sensors and autonomous observation platforms will be key elements of future ocean biogeochemistry. Biogeochemical data can supplement and sometimes substitute physical measurements.

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