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

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Flavours of oxygen

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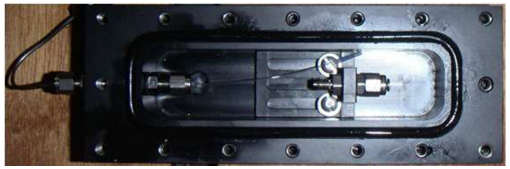
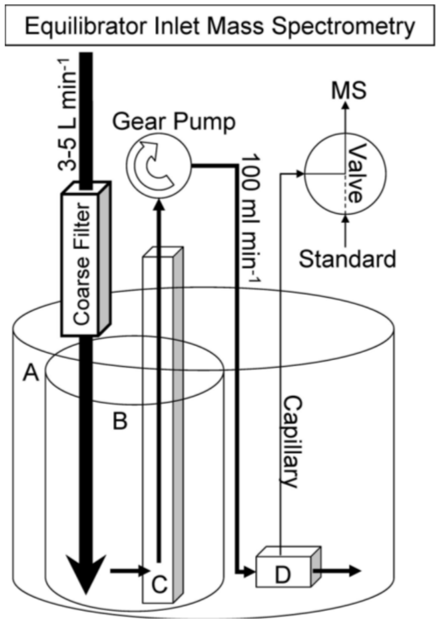
- molecular dioxygen: O_2
- oxygen triple isotopologues: $^{16}O_2$, $^{16}O^{18}O$, $^{16}O^{17}O$
- abiotic gas exchange analogue: O_2 and Ar
- "abiotic" deep-water mixing analogue: O_2 and N_2O

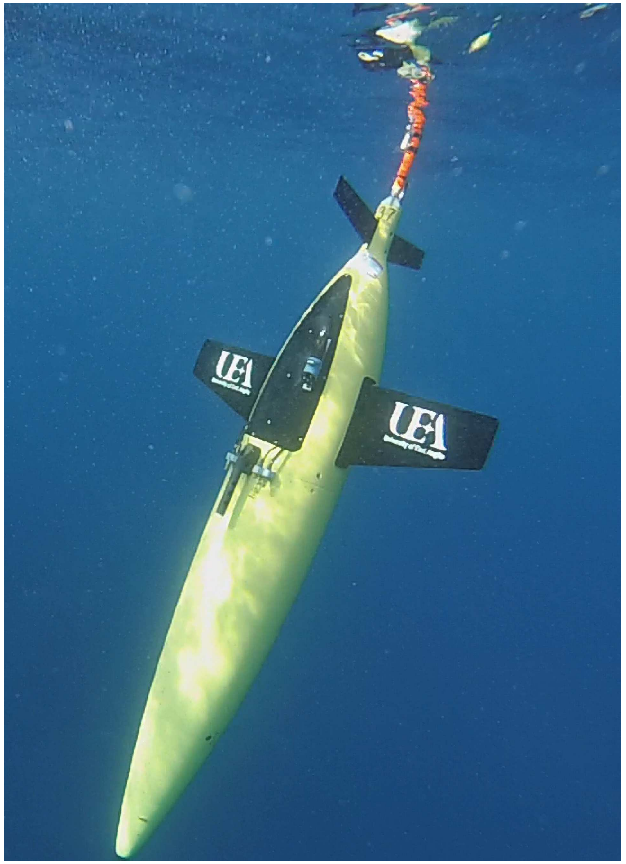
Sampling and analysis

- continuous O_2 concentration measurements by optode
- continuous O_2/Ar ratio measurements by MIMS or EIMS
- O_2 isotopologues by isotope-ratio mass spectrometry (IRMS)
- N_2O concentrations by laser cavity absorption spectroscopy

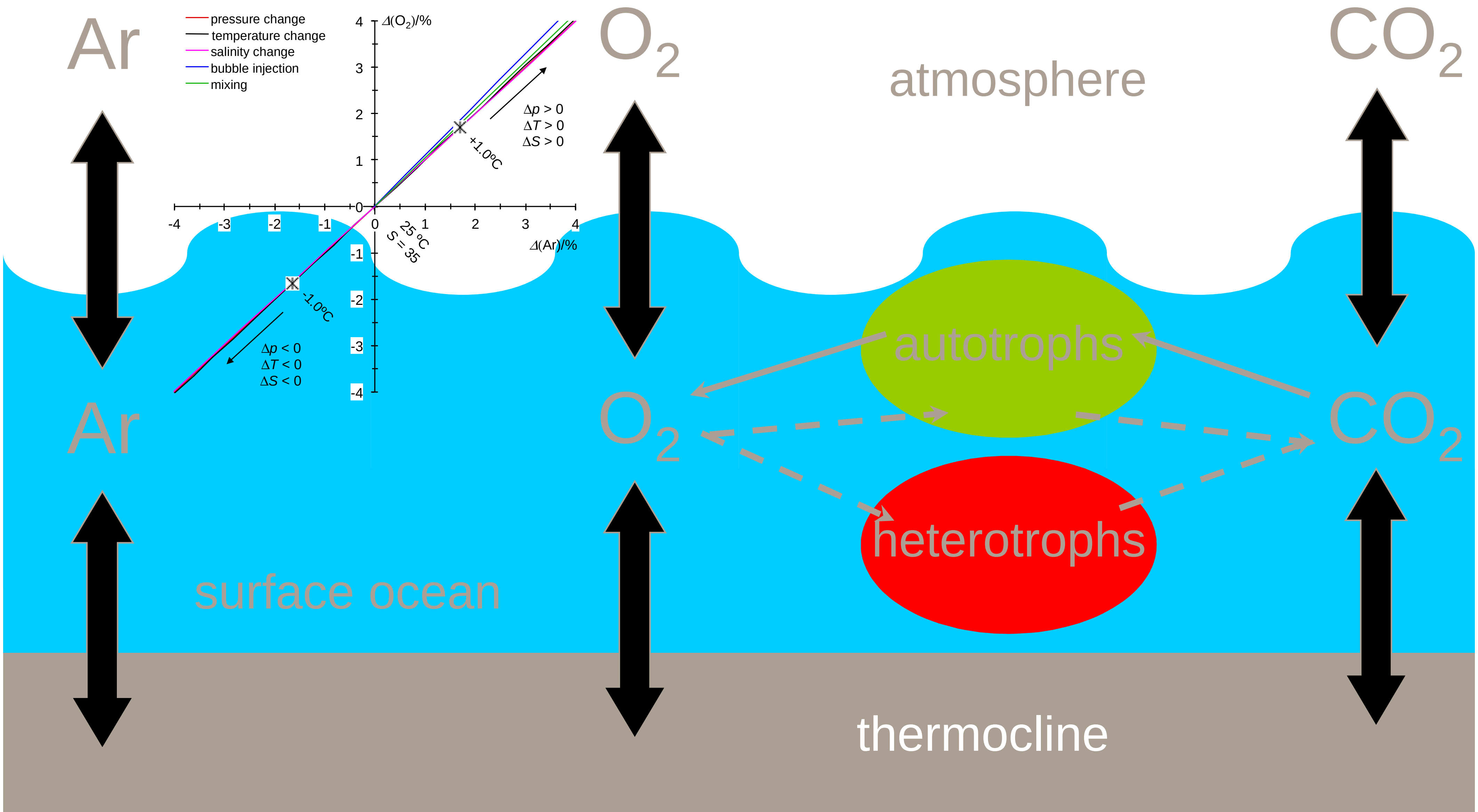




Platforms

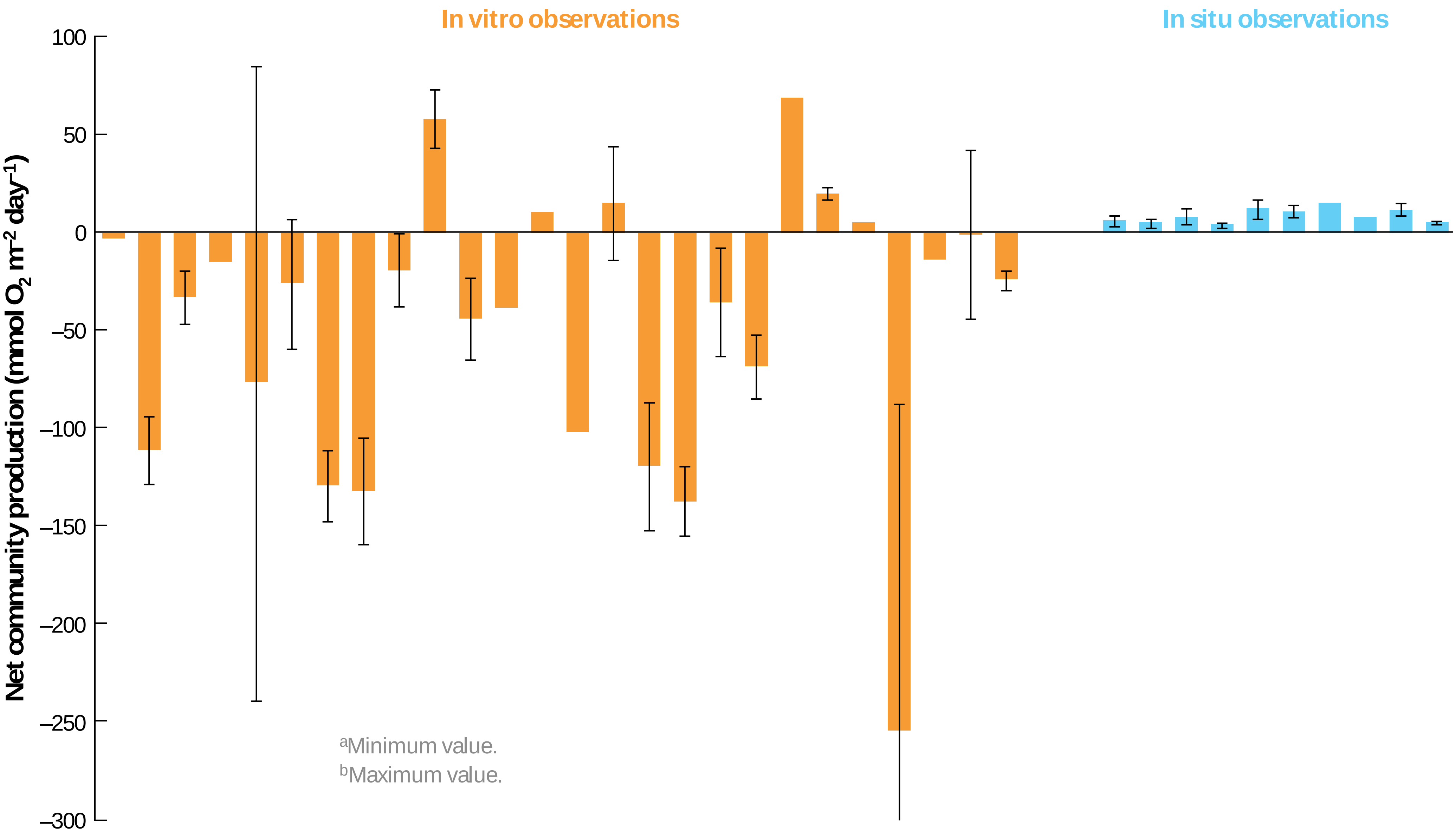


Production (*P*), respiration (*R*) [*N* = *P* – *R*], gas exchange, mixing



In vitro vs. in situ net production

Williams et al. Ann. Rev. Mar. Sci. 2013



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

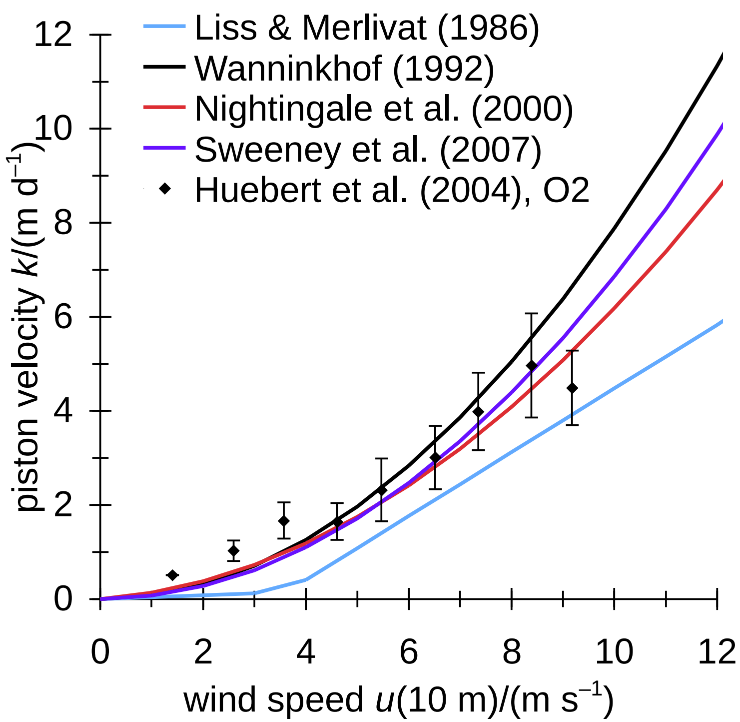
— uncertainty of gas exchange coefficient (±20 %)

— currency is O_2, not C

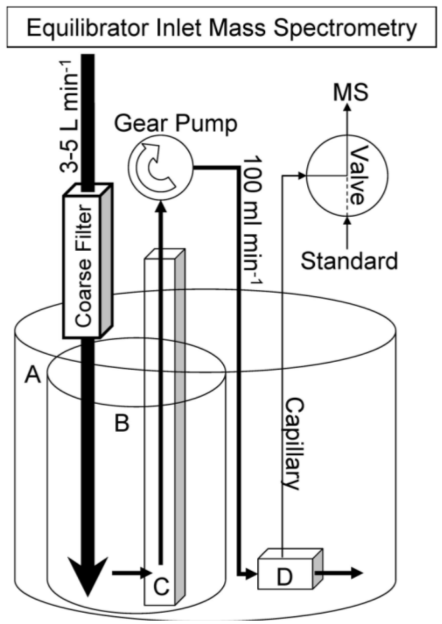
— photosynthetic coefficient?

— *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:

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

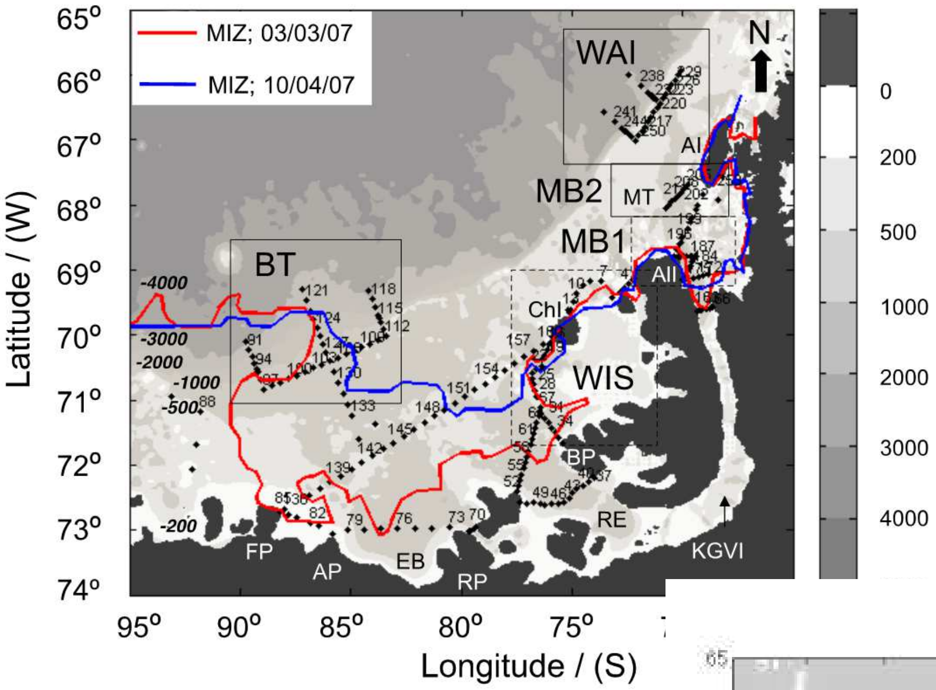
Biological O_2 flux:

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

$$N \approx F_{bio}(O_2/Ar)$$

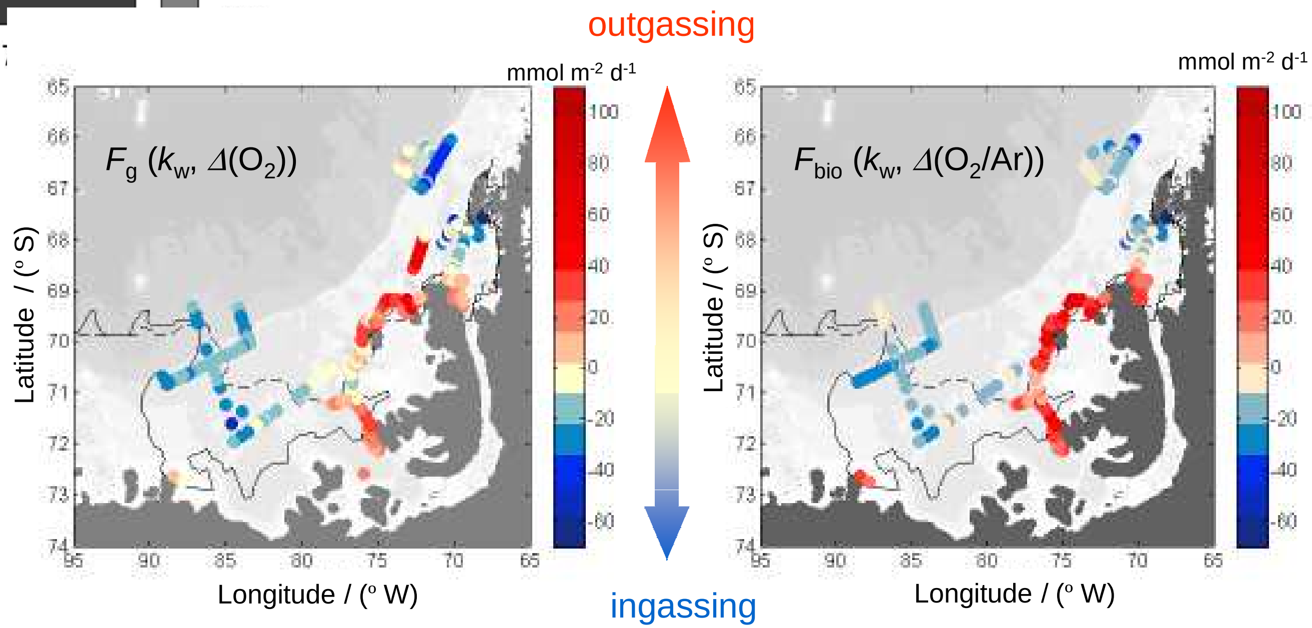
Kaiser et al. Geophys. Res. Lett. 2005

Production in the Bellingshausen Sea



Mixture of open ocean and coastal sampling locations

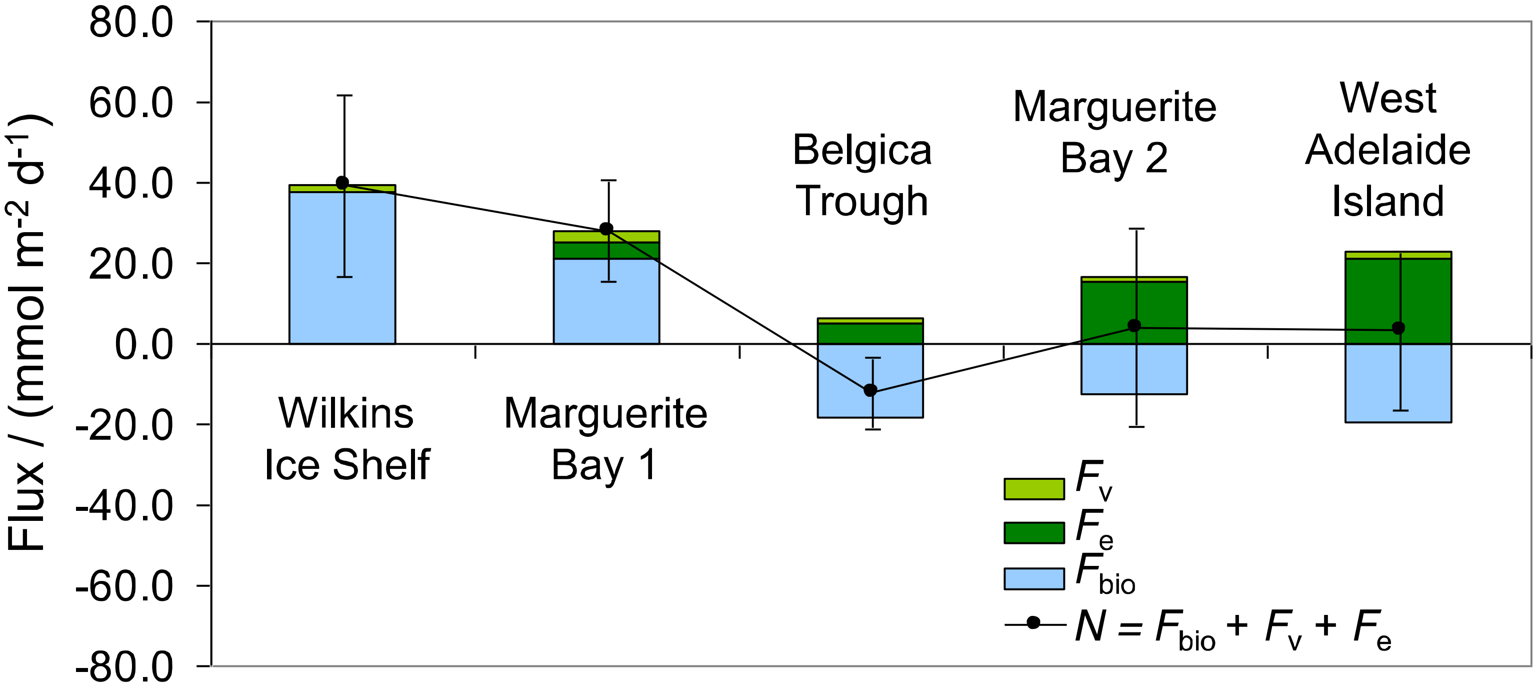
Effect of Ar correction:



Castro-Morales et al. Biogeosciences 2013

Entrainment correction "removes" apparent net heterotrophic areas

$$F_e = z_{miz} \frac{\Delta c}{\Delta t} = \frac{1}{2} \frac{(\Delta z_{mix})^2}{\Delta t} \frac{\partial c(O_2)}{\partial z}\bigg|_{oxy} .$$



Castro-Morales et al. Biogeosciences 2013

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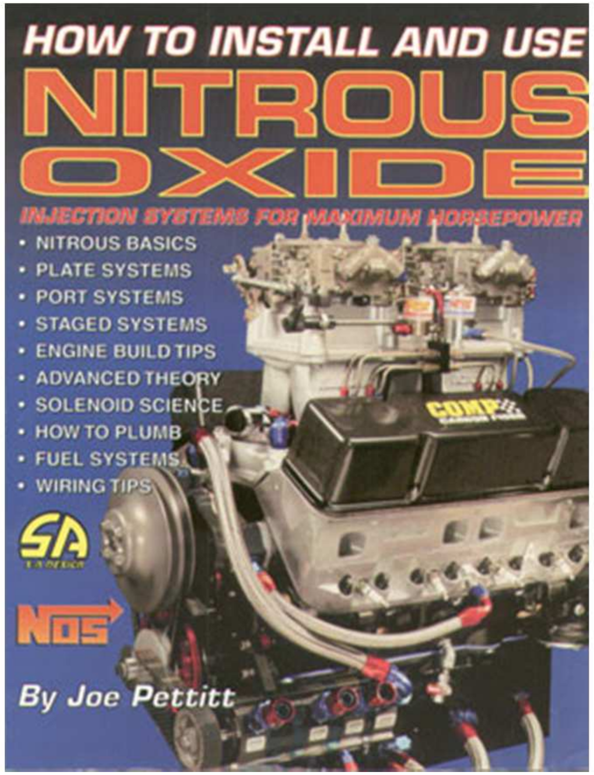
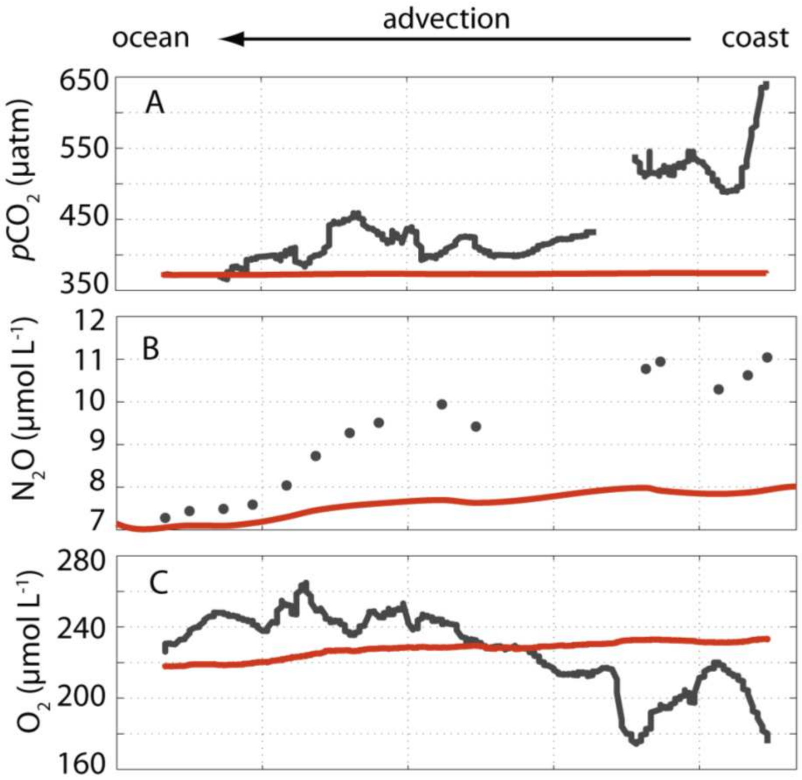
Using N_2O to correct for vertical fluxes



Using N_2O as "abiotic" analogue to correct for vertical O_2 fluxes



Upwelling brings up

- high N_2O
- high CO_2
- low O2
- high nutrient

Re-equilibration by gas-exchange and net production.

N_2O has negligible surface sources and sinks:

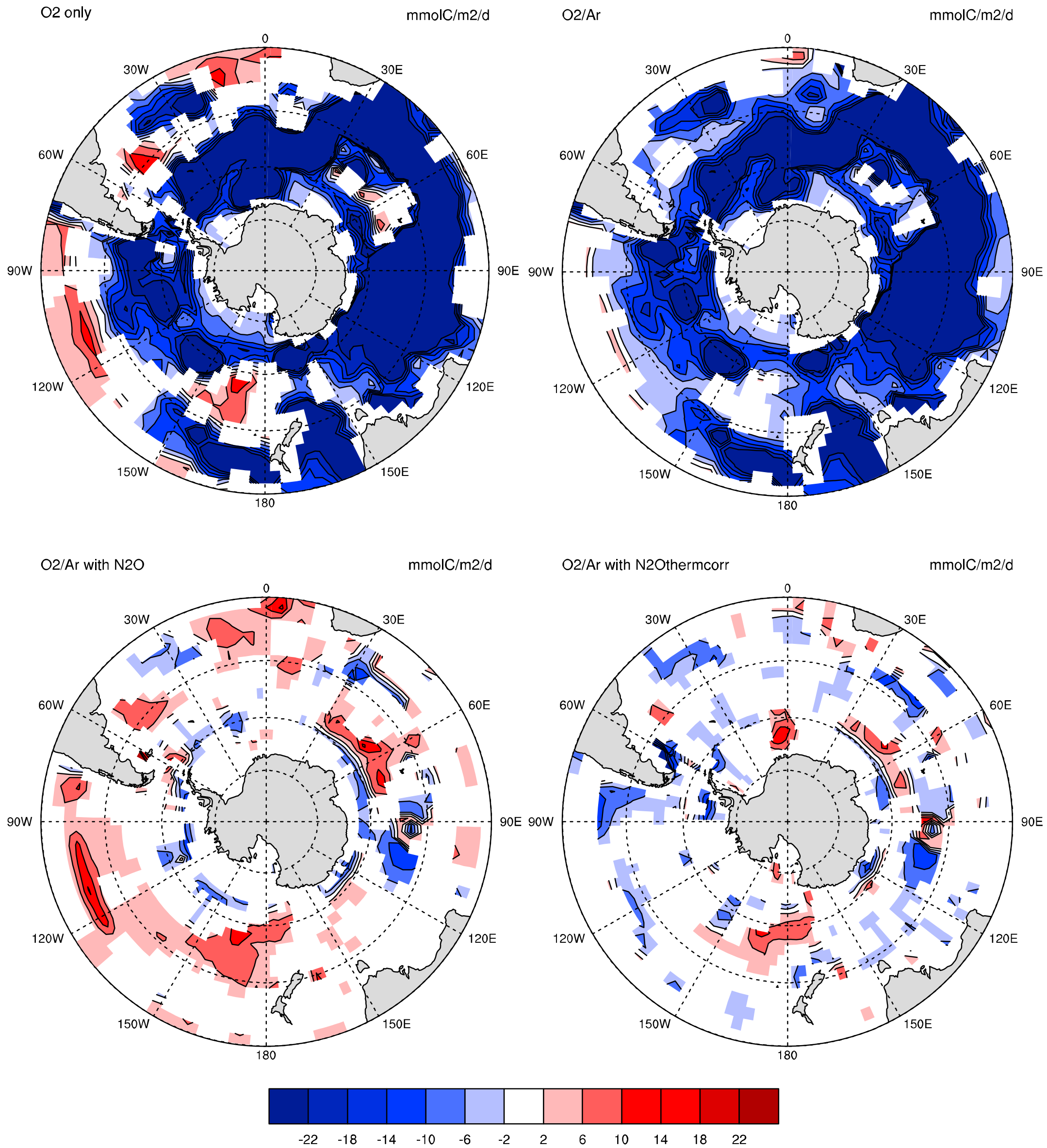
$$z_{\text{mix}} \frac{dc(\mathrm{N_2O})}{dt} = -k(\mathrm{N_2O})\left[c(\mathrm{N_2O}) - c_{\text{equ}}(\mathrm{N_2O})\right]$$

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

$$N(\mathrm{O_2}) = k(\mathrm{N_2O})\left[c(\mathrm{N_2O}) - c_{\text{equ}}(\mathrm{N_2O})\right]\frac{dc(\mathrm{O_2})}{dc(\mathrm{N_2O})} + k(\mathrm{O_2})\left[c(\mathrm{O_2}) - c_{\text{equ}}(\mathrm{O_2})\right]$$

Steinhoff et al. Biogeosci. 2012; Kaiser Biogeosci. 2012

Correction of $F_{bio}(O_2/Ar)$ for vertical mixing using N_2O to give $N(O_2/Ar)$



Cassar et al. Geophys. Res. Lett. 2014

Gross production using oxygen triple isotopologues ($^{16}O_2$, $^{16}O^{17}O$, $^{16}O^{18}O$)

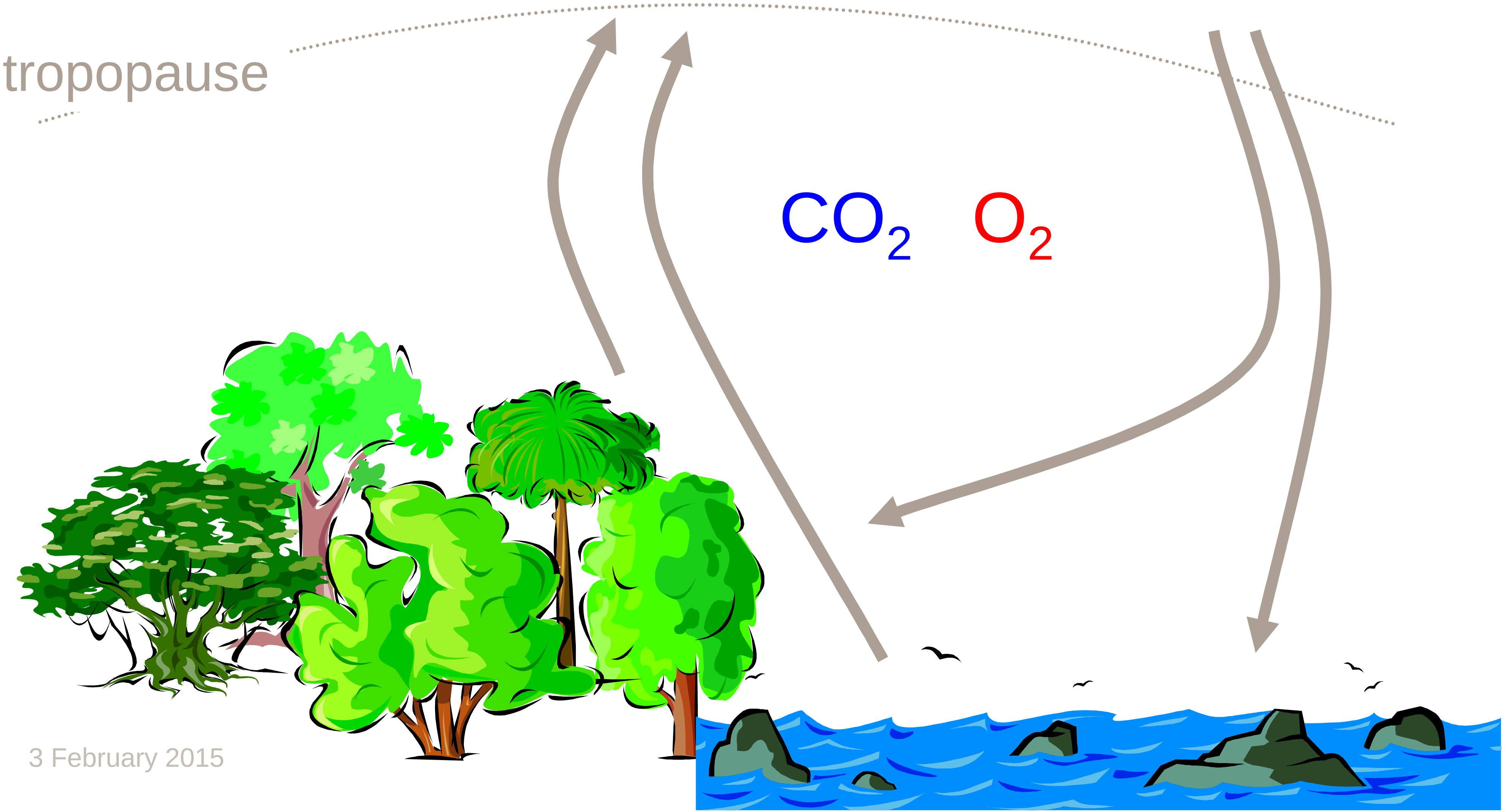
Oxygen isotope transfer from O_2 to CO_2 via O_3

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

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

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

$$O(^1D) + CO_2 \rightarrow CO_2 + O(^3P)$$



^{17}O excess, $\Delta(^{17}O)$, of photosynthetic O_2

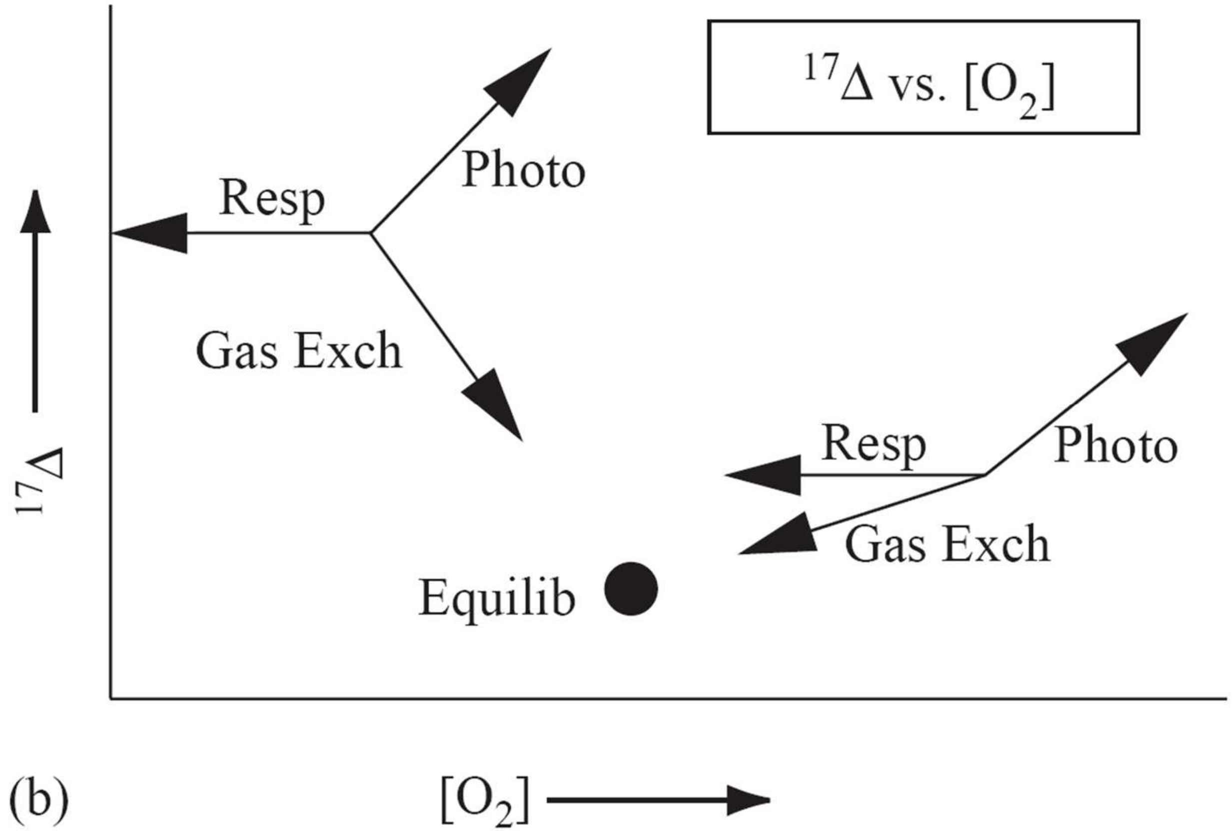
$$\Delta(^{17}\mathrm{O}) = \delta(^{17}\mathrm{O}) - \lambda\delta(^{18}\mathrm{O})$$

Choose $\lambda = \gamma_R = 0.5179 = {}^{17}\varepsilon_R \,/\, {}^{18}\varepsilon_R$,
where ε_R is the respiratory kinetic isotope fractionation

Reference: tropospheric Air-O_2

photosynthetic O_2: $\Delta_{max}(^{17}O)$ = 249 ppm (???)
(180 to 264 ppm)

Effect of photosynthesis, respiration and gas exchange on O_2 analogues



Hendricks et al. Deep-Sea Res. I 2004

Calculating the ratio of gross O_2 gross production P to gross O_2 influx: $g = P / (kc_{sat})$

Luz & Barkan (2000):

$$g = \frac{P}{kc_{sat}} \approx \frac{\Delta(^{17}O) - \Delta_{sat}(^{17}O)}{\Delta_{max}(^{17}O) - \Delta(^{17}O)}$$

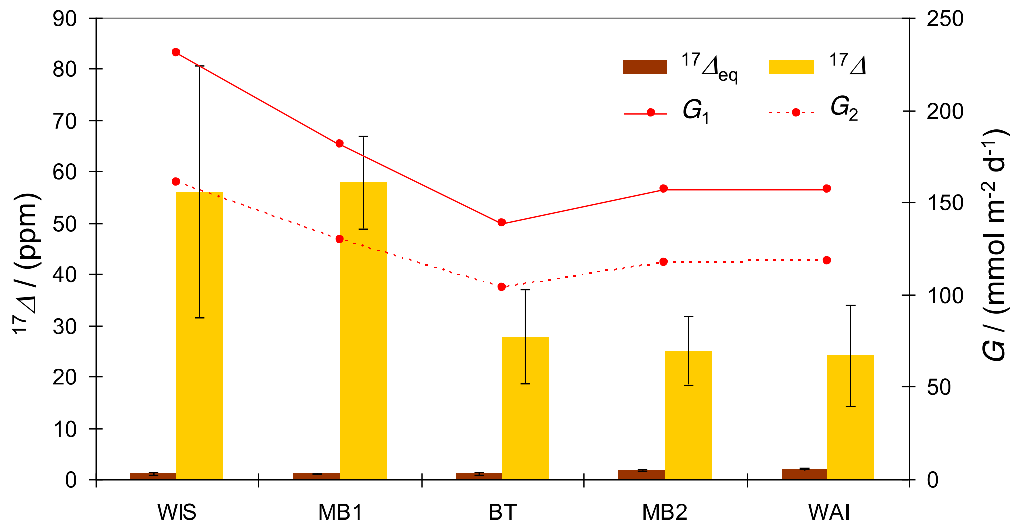
Prokopenko et al. (2011):

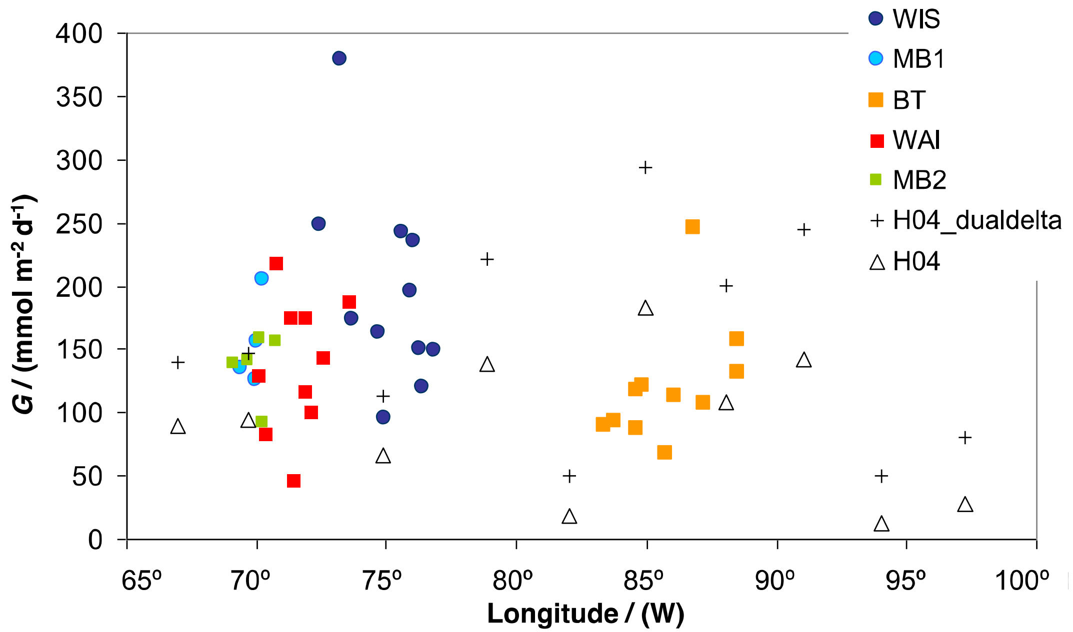
$$g = \frac{\frac{^{17}\delta - ^{17}\delta_{sat}}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta - ^{18}\delta_{sat}}{1 + ^{18}\delta}}{\frac{^{17}\delta_P - ^{17}\delta}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta_P - ^{18}\delta}{1 + ^{18}\delta}}$$

Kaiser (2011):

$$g = \frac{(1 + ^{17}\varepsilon_E)\frac{^{17}\delta - ^{17}\delta_{sat}}{1 + ^{17}\delta} - \gamma_R (1 + ^{18}\varepsilon_E)\frac{^{18}\delta - ^{18}\delta_{sat}}{1 + ^{18}\delta} + s(^{17}\varepsilon_E - \gamma_R {}^{18}\varepsilon_E)}{\frac{^{17}\delta - ^{17}\delta}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta_P - ^{18}\delta}{1 + ^{18}\delta}}$$

Gross O_2 production in the Bellingshausen Sea





Castro-Morales et al. Biogeosciences 2013;
Hendricks et al. DSR I 2004

Unrecognised systematic uncertainties due to phytoplankton composition

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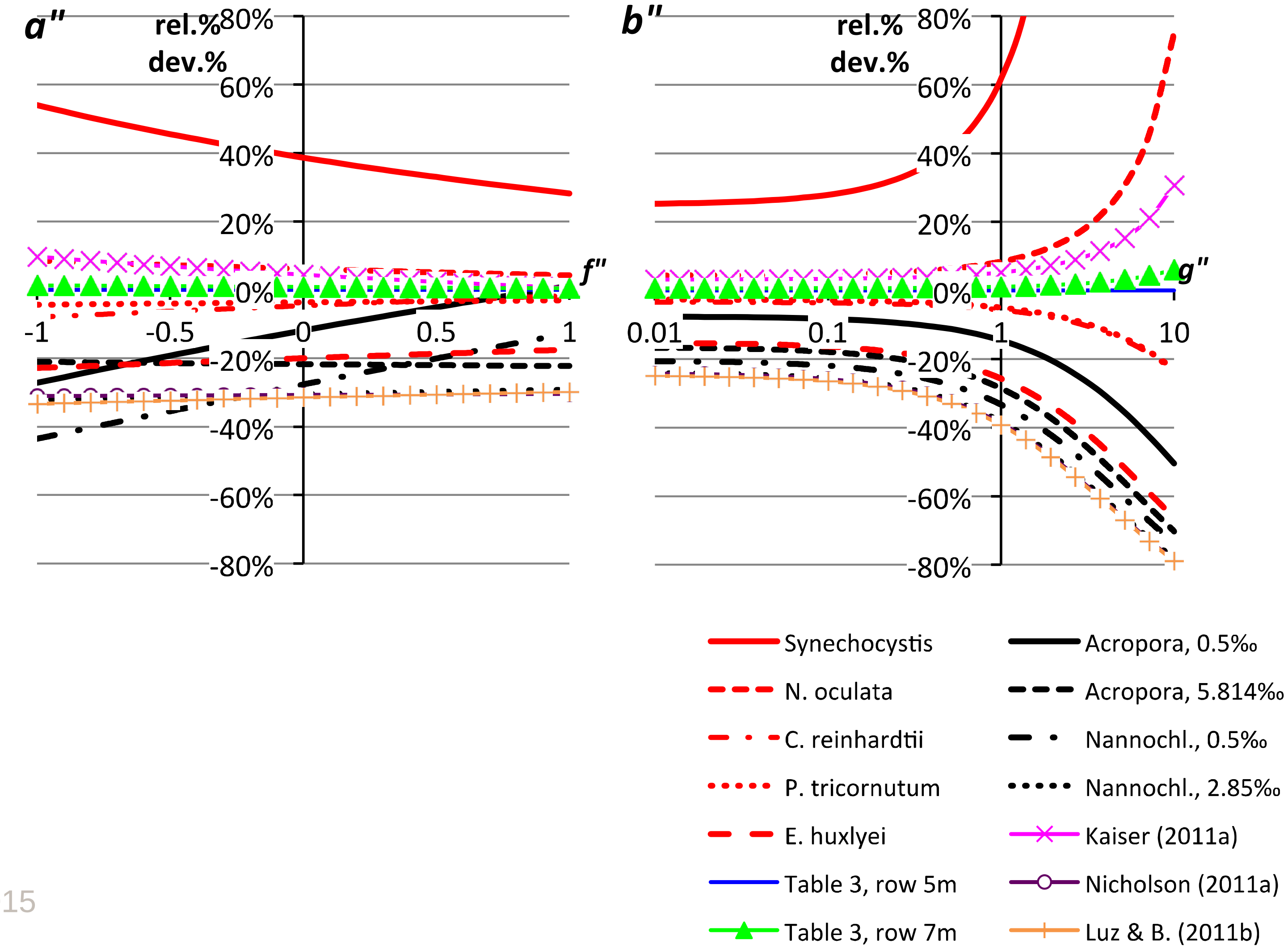
Relative deviation from base case, $\Delta_{max}(^{17}O)$ = 185 ppm



Kaiser & Abe Biogeosciences 2012

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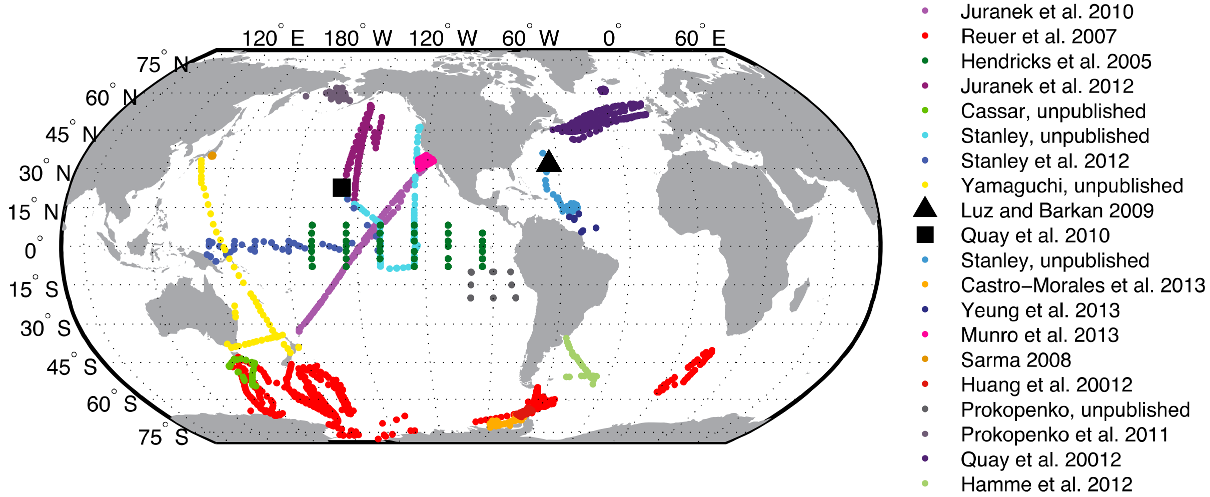
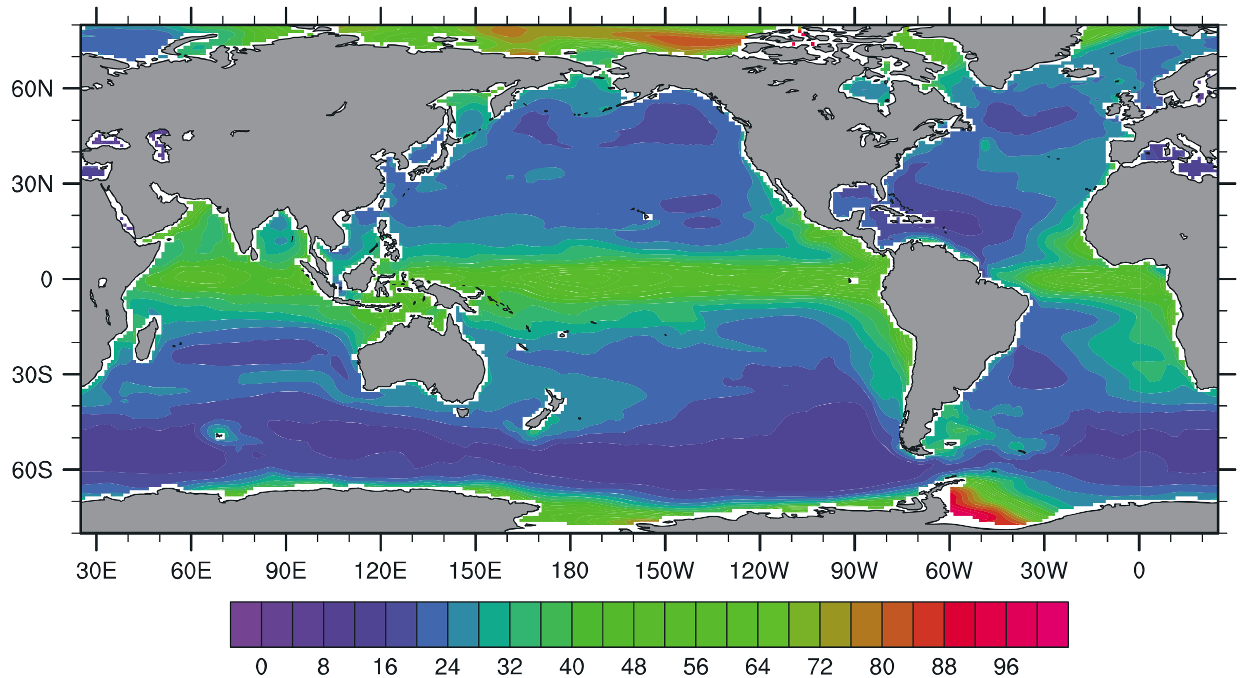
Global measurements and modelling of oxygen triple isotopologues





Nicholson et al. Global Biogeochem. Cycles 2014

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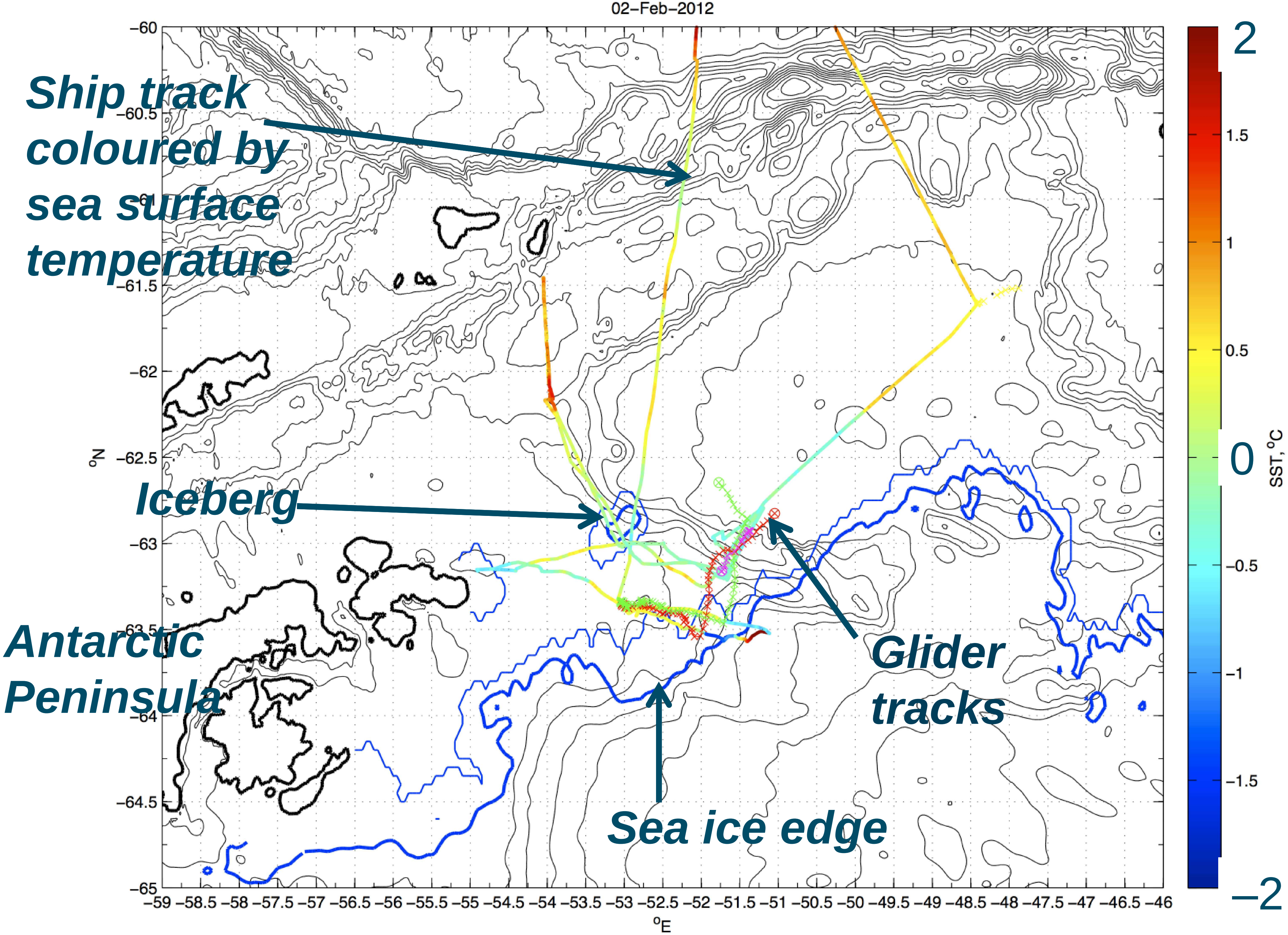
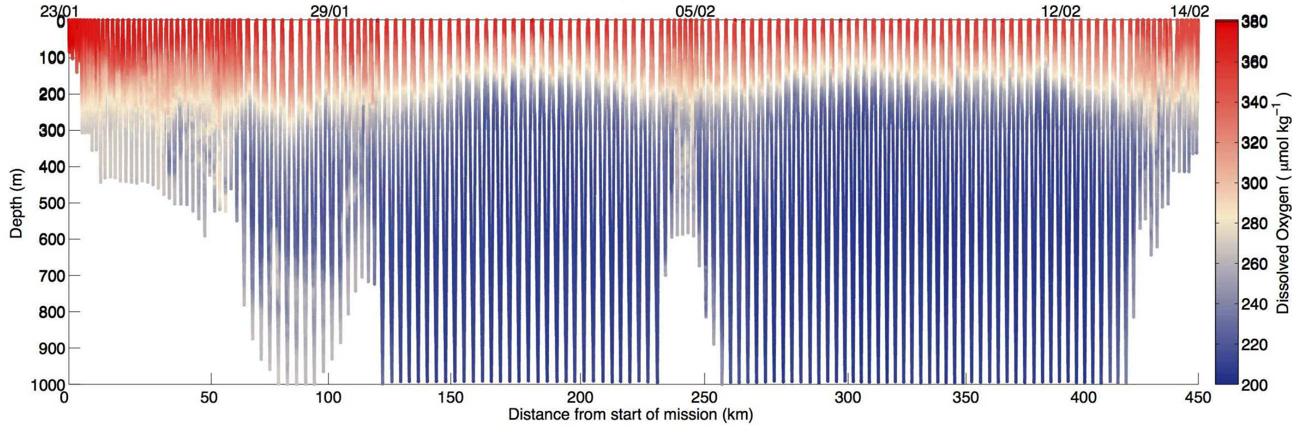
Net community production from underwater ocean gliders

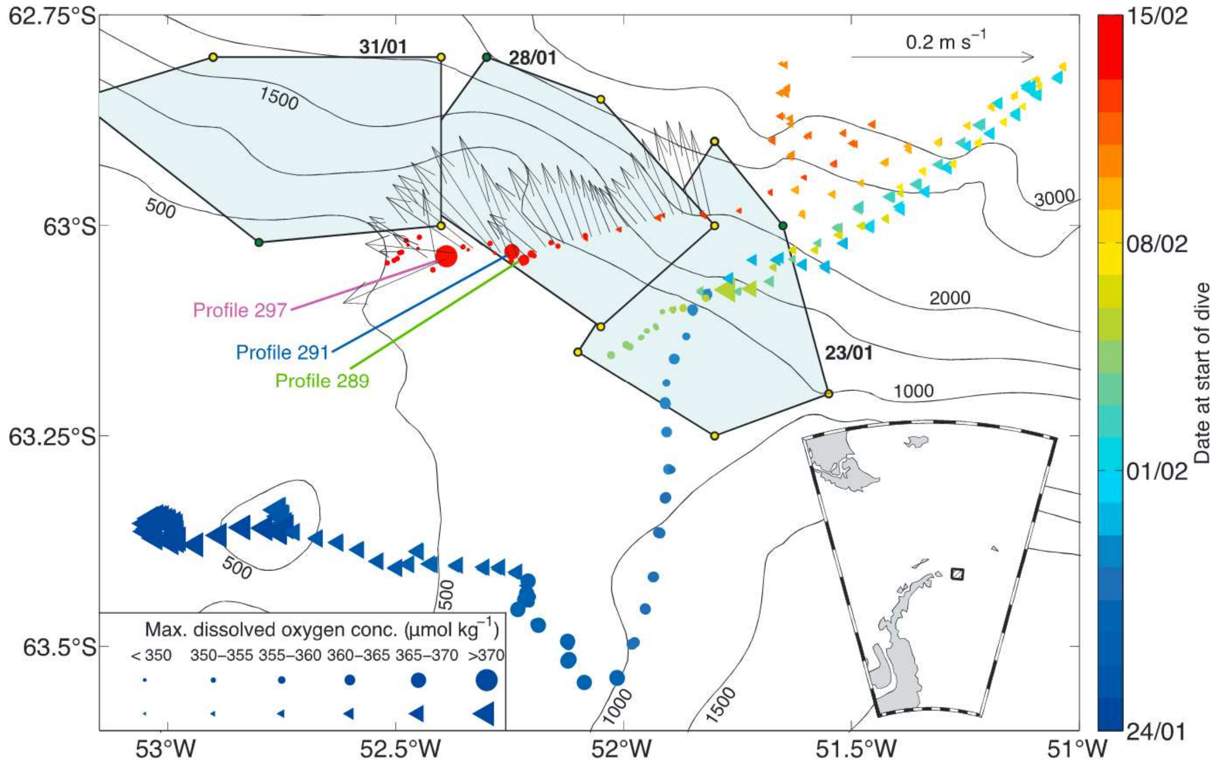
3 February 2015

RRS James Clark Ross cruise JR255A "GENTOO", Jan 2012



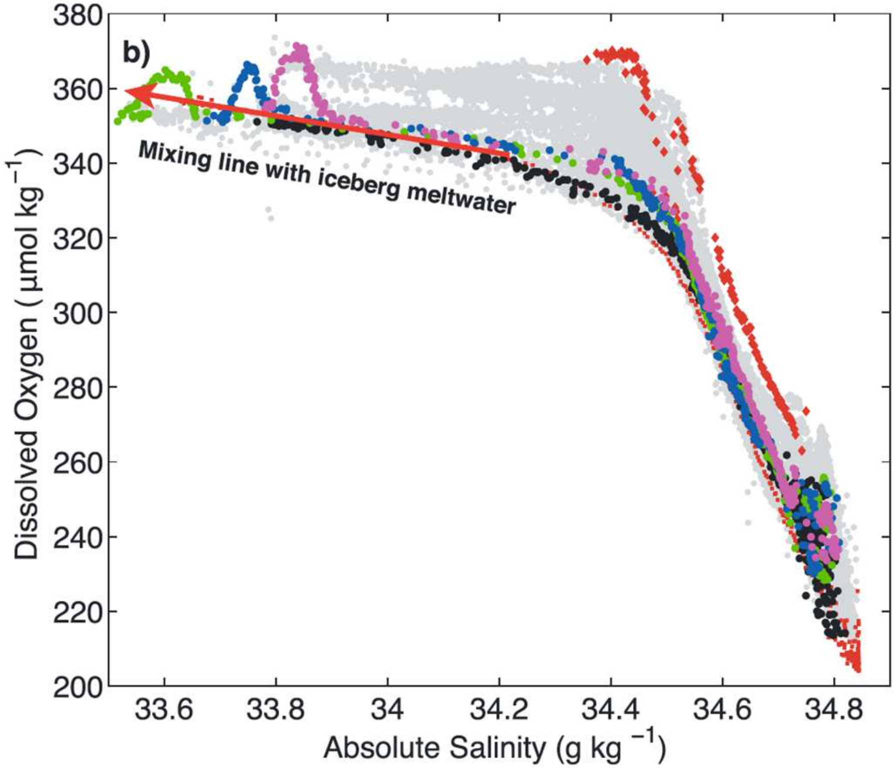
Glider O_2 measurements

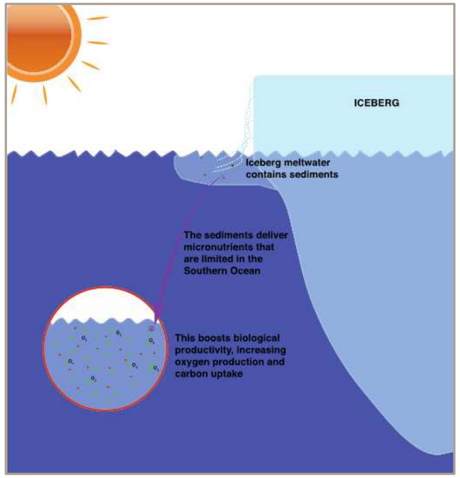


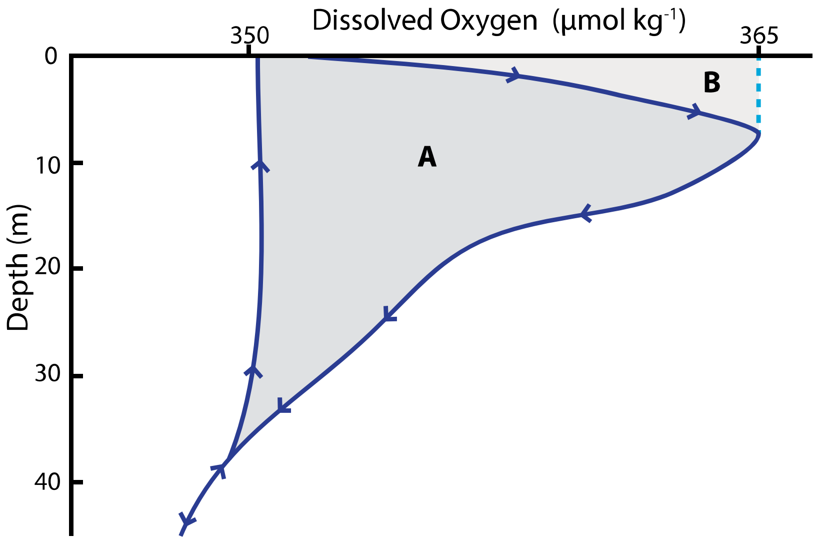


Biddle al. Geophys. Res. Lett. 2015

Depth-integrated net community production





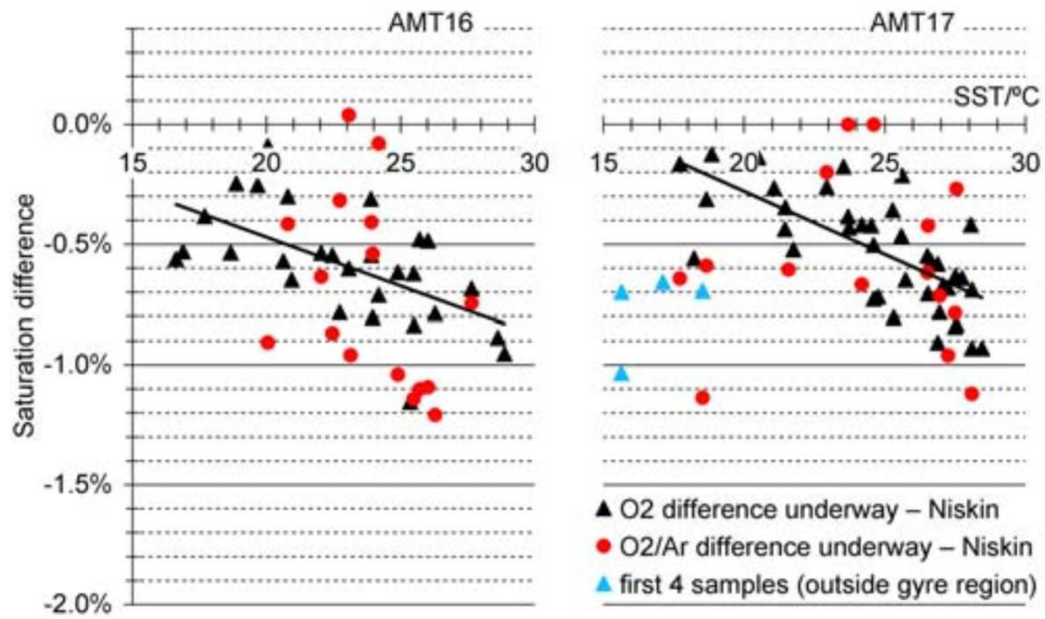


Δt = 16 d

$N(O_2) = (27 \pm 4)$ mmol m^{-2} d^{-1}

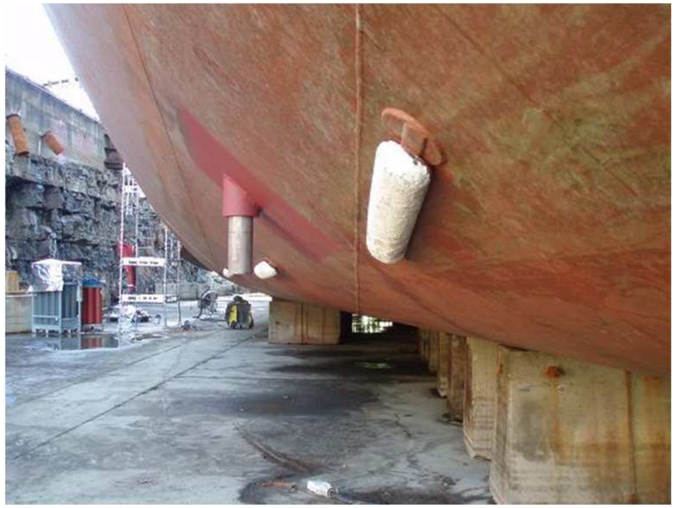
Biddle al. Geophys. Res. Lett. 2015

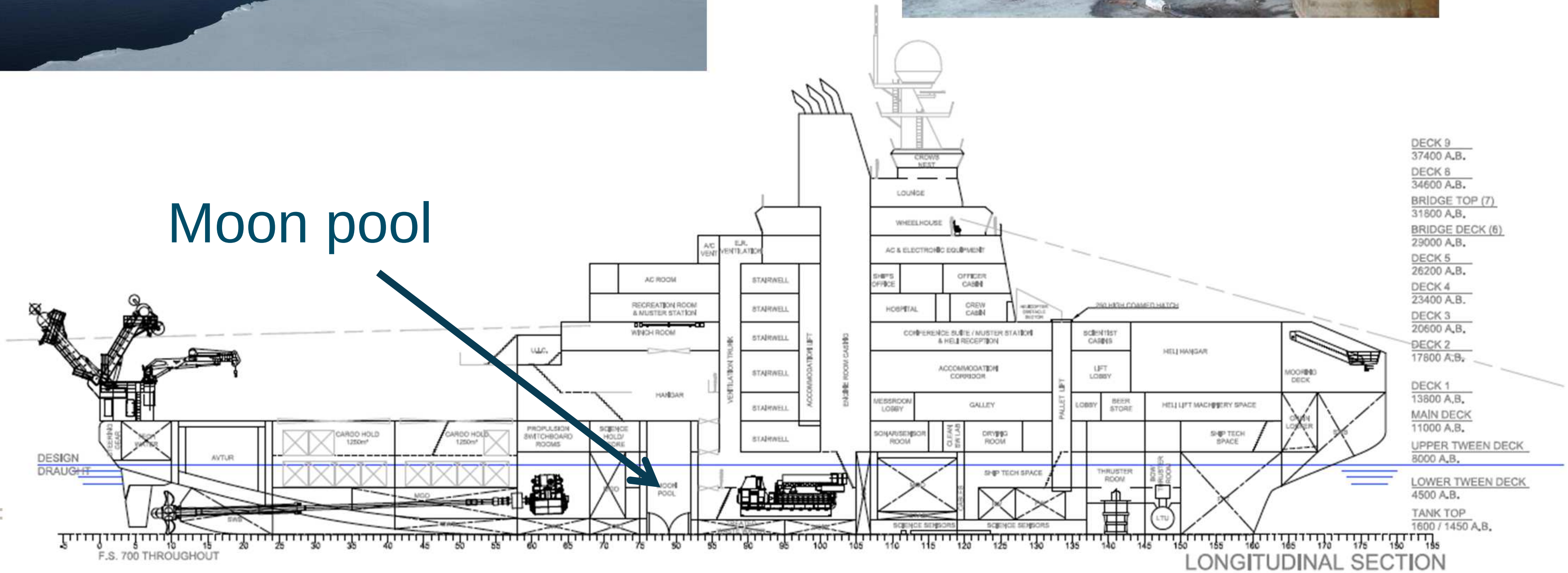
In-situ measurements can help avoid ship sampling biases



Juranek et al. Geophys. Res. Lett. 2010

Intake design on research ships





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Conclusions

- 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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