

# Observing metabolic rates in the ocean with autonomous sensors: drifting toward metabolic balance

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Lucile Packard  
FOUNDATION



The lecture focuses on applications of chemical sensors on autonomous platforms to measurement of rates of carbon, oxygen and nitrogen cycling.

- 1) Carbon, oxygen and nitrogen based production observed in coastal waters.
- 2) The balance of oxygen production and consumption in oligotrophic waters.
- 3) Carbon export on the scale (almost) of an ocean basin.
- 4) Coast again.

For a general chemical sensor review see: Johnson, K. S., J. A. Needoba, S. C. Riser, and W. J. Showers. 2007. Chemical sensor networks for the aquatic environment. Chemical Reviews, 107, 623-640, doi 10.1021/cr050354e.











# LOBO Land/Ocean Biogeochemical Observatory

HOME LOBOVIZ LOBOCAM WIRELESS GE ABOUT CONFIG CONTACT

## Latest

2007-03-16 13:00:00 UTC

Temperature	0.85	C
Current Out/In (+/-)	0.176	m/s
Salinity	30.79	
Conductivity	2.65	S/m
Nitrate	1.4	$\mu\text{M}$
Turbidity	0.83	NTU
Dissolved O2	8.91	ml/l
O2 Saturation	8.09	ml/l
Dissolved Organics	8.32	QSDE
Chlorophyll	2.53	$\mu\text{g/l}$
Battery Voltage	12.3	Volts

Google EARTH WAP Device

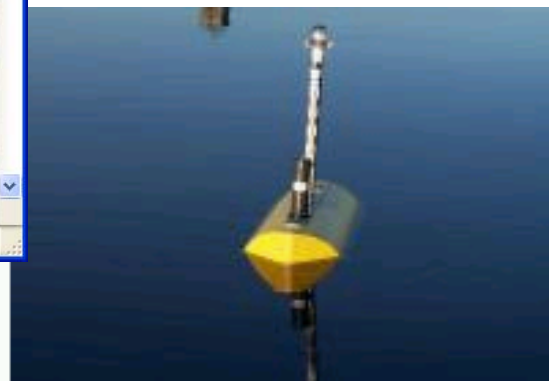
## LOBO Cam



## LOBO-0010 Northwest Arm, Halifax, Canada



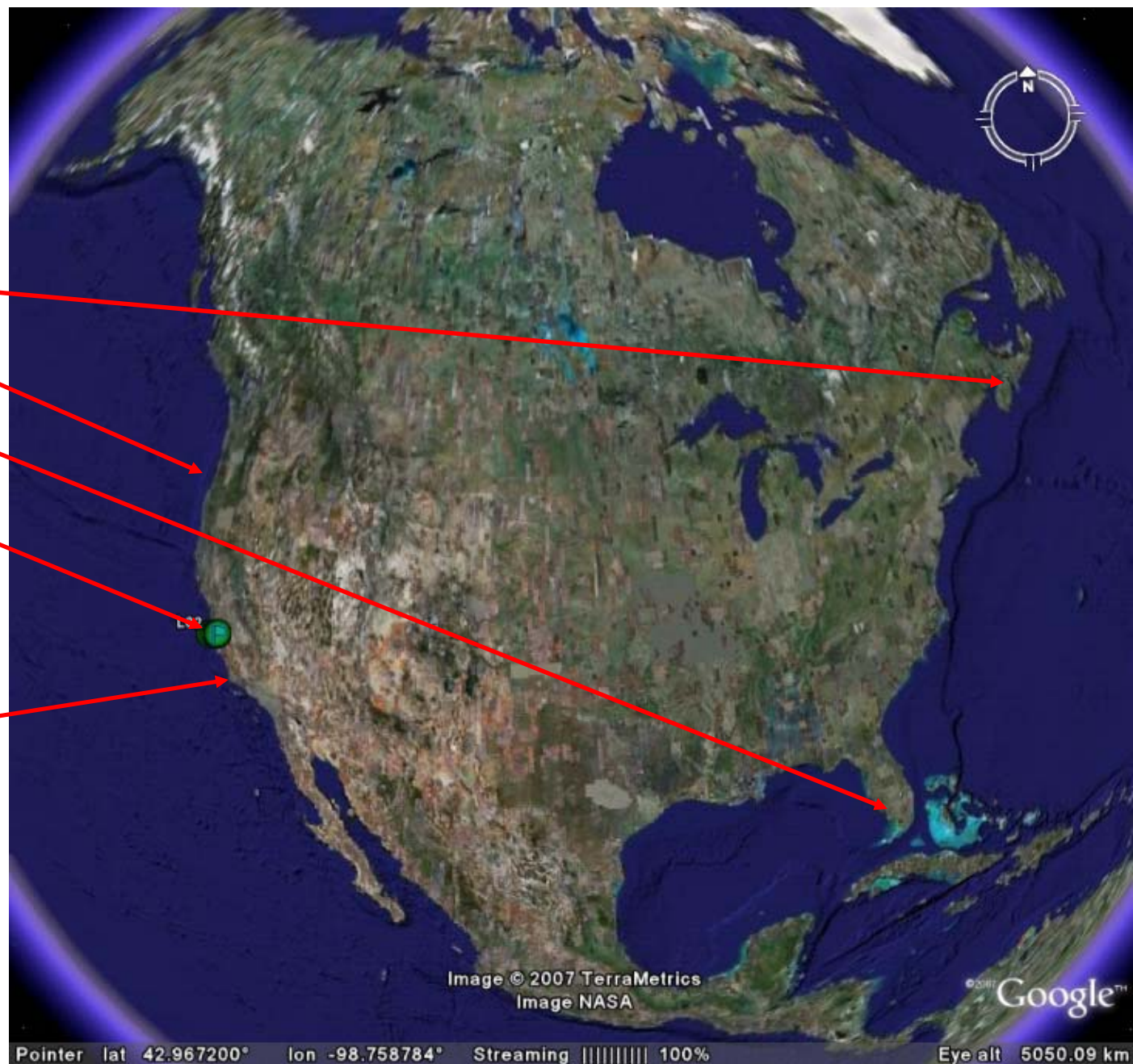
LOBO available now as commercial product from Satlantic. Easy to link LOBO data systems and observe coastal biogeochemistry on large scales.



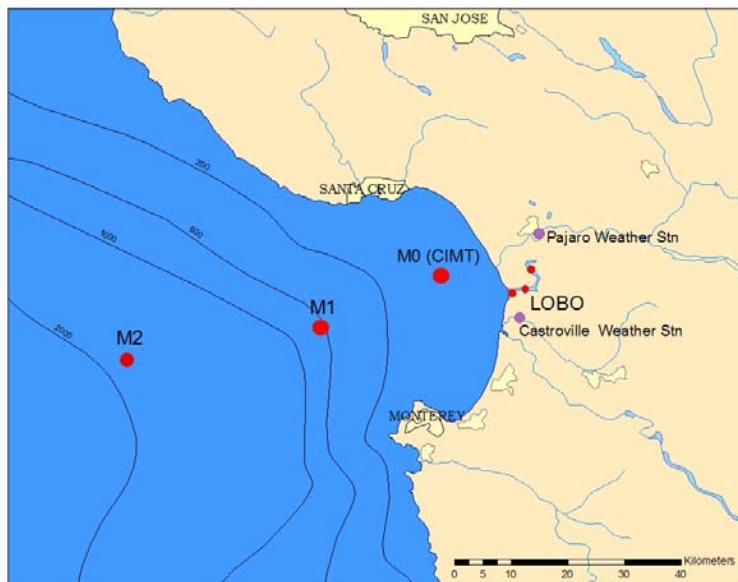
The LOBO comes complete with floating platform, power and wireless telemetry system, integrated sensor suite, automated processing software and web based data visualization and display software. Just deploy the platforms, install the software, configure the system using a simple GUI, and your data is live on the web. The system is designed for both rapid deployments and long term monitoring, making it easy for users to install and operate.



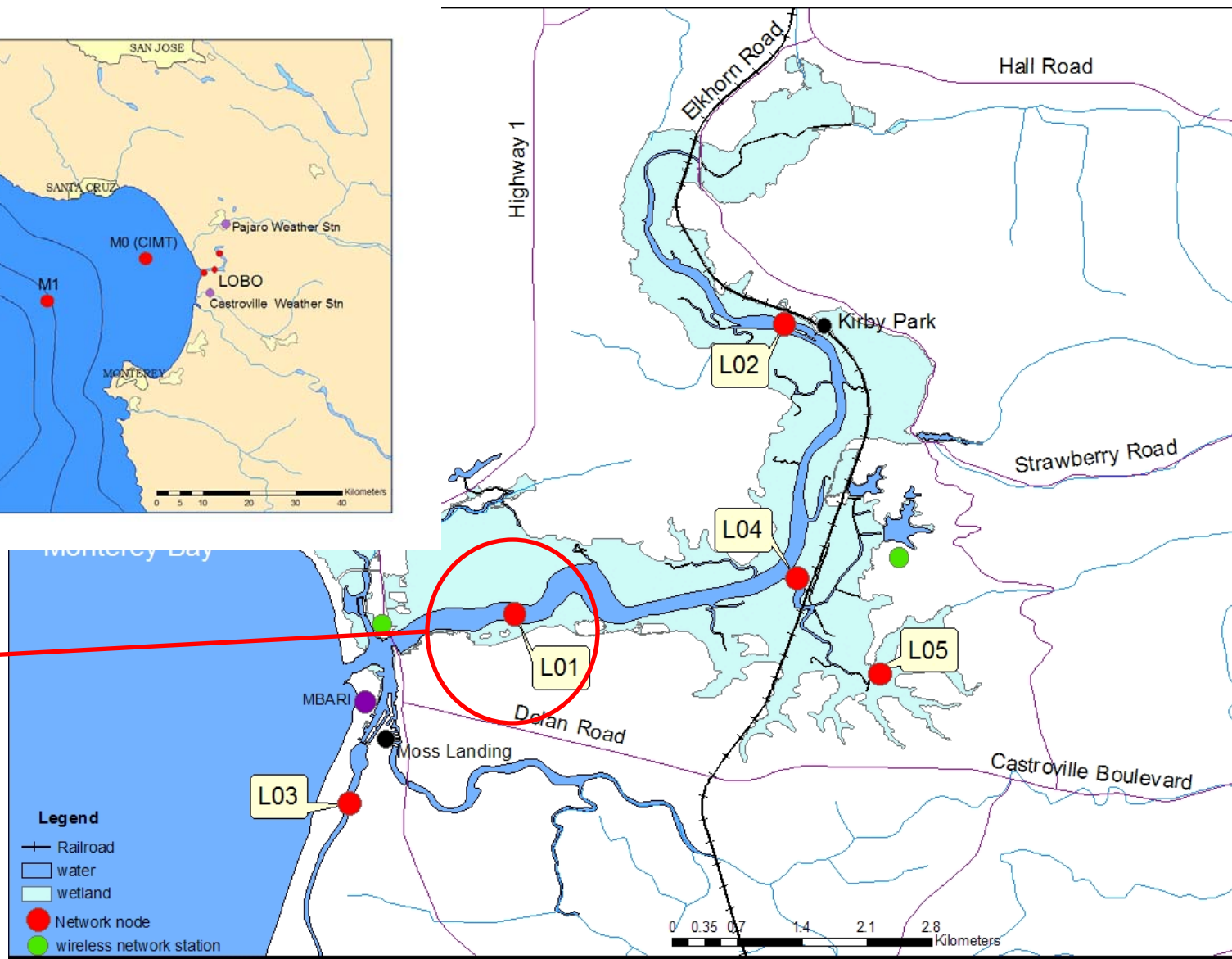
Systems in  
California, Nova  
Scotia, Florida 1  
and Oregon. 1  
Soon, a North 8  
American,  
INTEGRATED 5  
Coastal Ocean  
Observing  
System will  
exist. 4



# LOBO chemical sensor network: [www.mbari.org/lobo](http://www.mbari.org/lobo)



Next 2  
slides at  
L01





Data goes directly to Internet and is in the public domain. Real-time QC applied. <http://www.mbari.org/lobo>

LOBOViz Version 3.0 - Mozilla Firefox

File Edit View History Bookmarks Tools Help

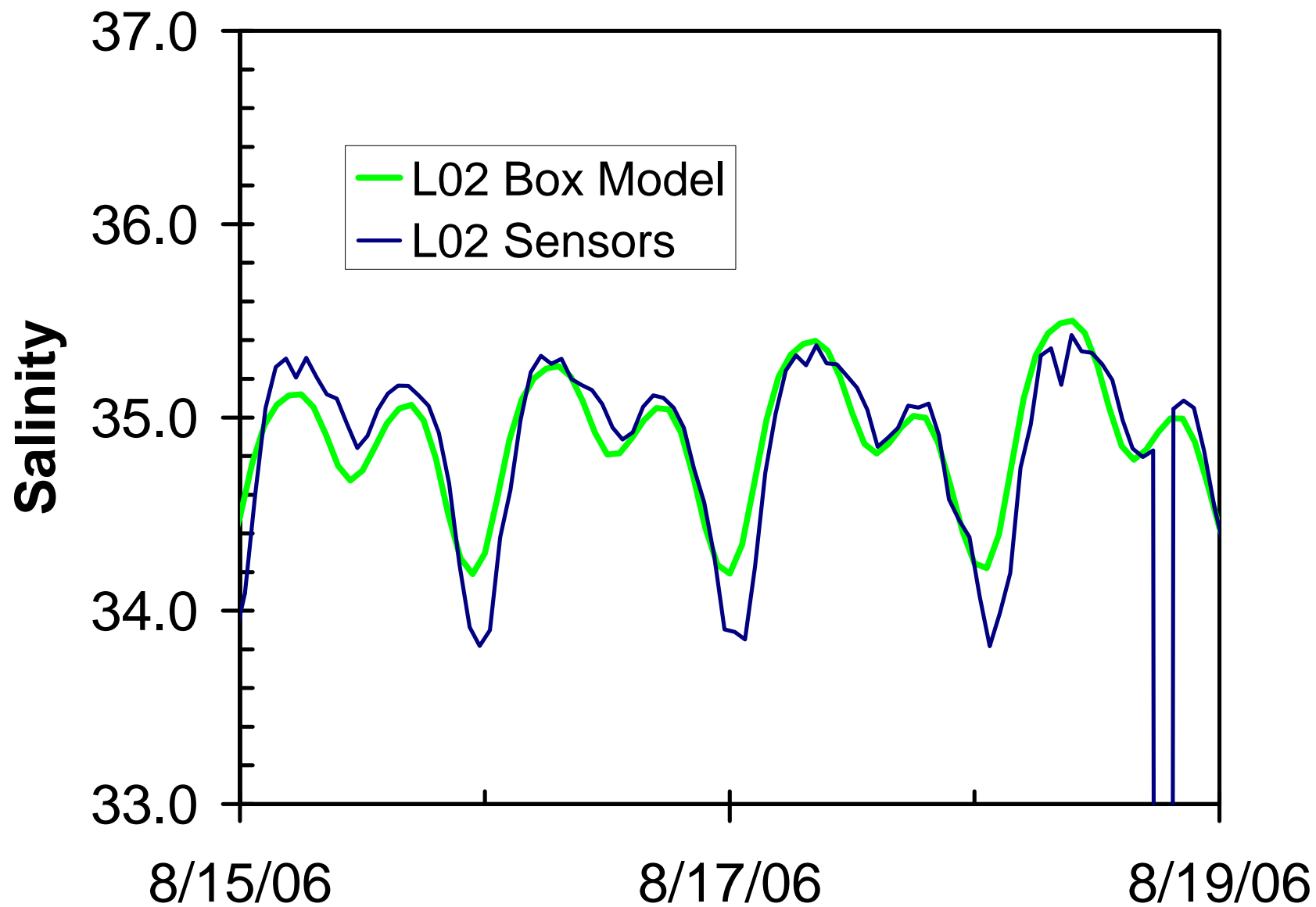
<http://www.mbari.org/lobo/loboviz.htm> Google

MBARI - LOBOVIZ Chem Sensors M1 ISU... LOBO Home LOBO Data JUL\_DAY Periodic Table of Elem... Microsoft Outlook Web...

## LOBOViz 3.0 - LOBO Network Data Visualization

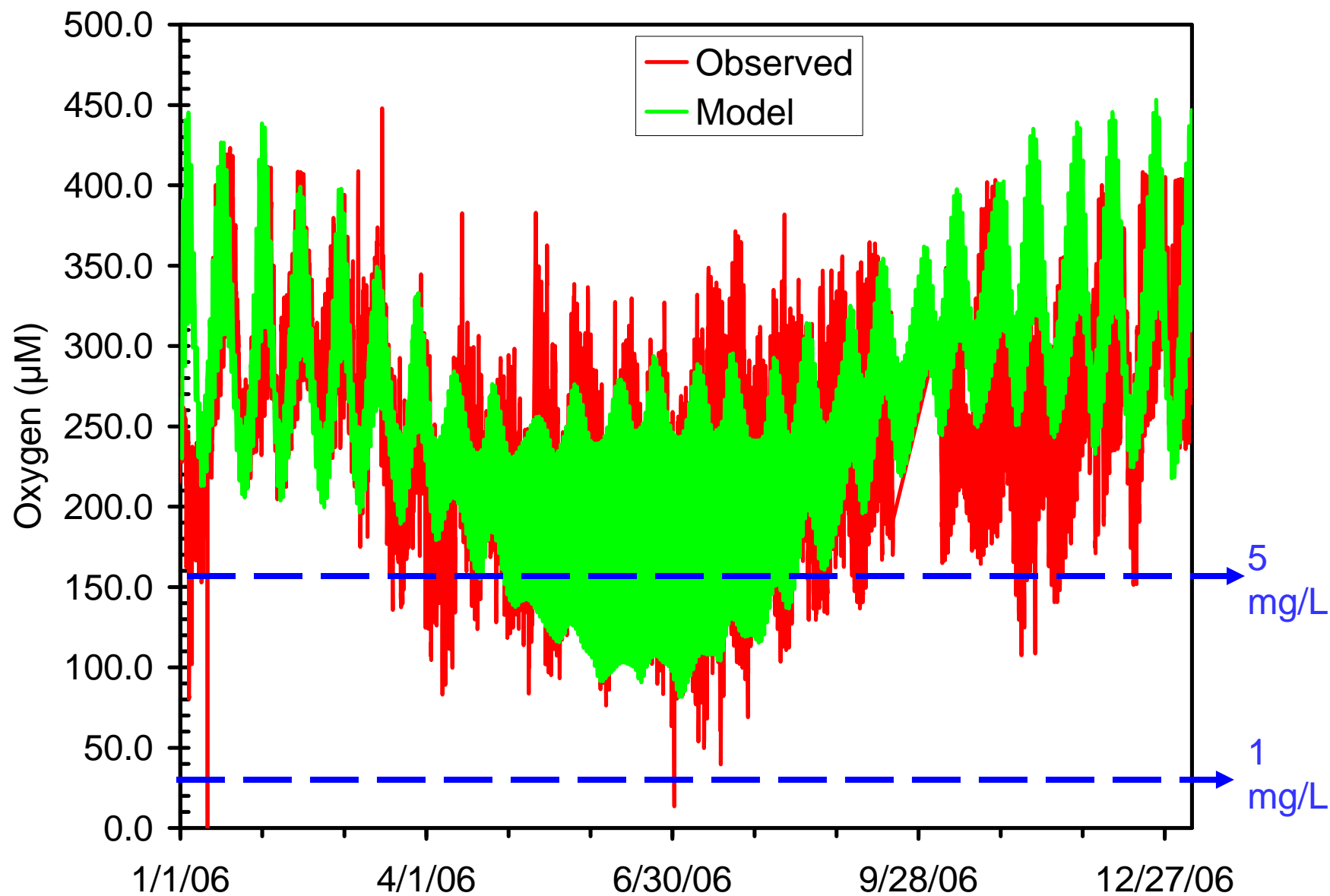
[Quick Instructions](#) [View a demonstration of LOBOViz](#) [Network description page](#)

	Select Location(s)	Select one X variable	Select Y variable(s)	
<b>How many graphs?</b> One Two Three	<b>Graph 1</b> L01SURF/Main Channel L02SURF/Kirby Park L03SURF/Old Salinas River L04SURF/Parsons Entrance L05SURF/Parsons Slough L10SURF/Halifax Canada	<b>Graph 1</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	<b>Graph 1</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	<b>Autoscale X &amp; Y axes</b> (non-date variables only) On Off Enter Ranges if Autoscale is Off (Min & max range default to 0 and 200. Use for Date Scale) X Min: <input type="text"/> X Max: <input type="text"/> Y Min: <input type="text"/> Y Max: <input type="text"/> Y Stack: (In a single graph multiple Y variables or multiple stations are stacked vertically if it is On)
<b>Data Quality:</b> All Data Good and Questionable Good Only	<b>Graph 2</b> L01SURF/Main Channel L02SURF/Kirby Park L03SURF/Old Salinas River L04SURF/Parsons Entrance L05SURF/Parsons Slough L10SURF/Halifax Canada	<b>Graph 2</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	<b>Graph 2</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	
<b>What dates?</b> All Dates available Week Ending on End Date Month Ending on End Date Specify Start/End Date	<b>Graph 3</b> L01SURF/Main Channel L02SURF/Kirby Park L03SURF/Old Salinas River L04SURF/Parsons Entrance L05SURF/Parsons Slough L10SURF/Halifax Canada	<b>Graph 3</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	<b>Graph 3</b> Date Nitrate[μM] WaterDepth[m] Salinity Temperature[°C] SensorDepth[m]	<b>Autoscale X &amp; Y axes</b> (non-date variables only) On Off Output Type: <input type="text"/>
<b>Change dates: (MM/DD/YYYY)</b> Start Date: 11/01/2003 End Date: 10/24/2007				

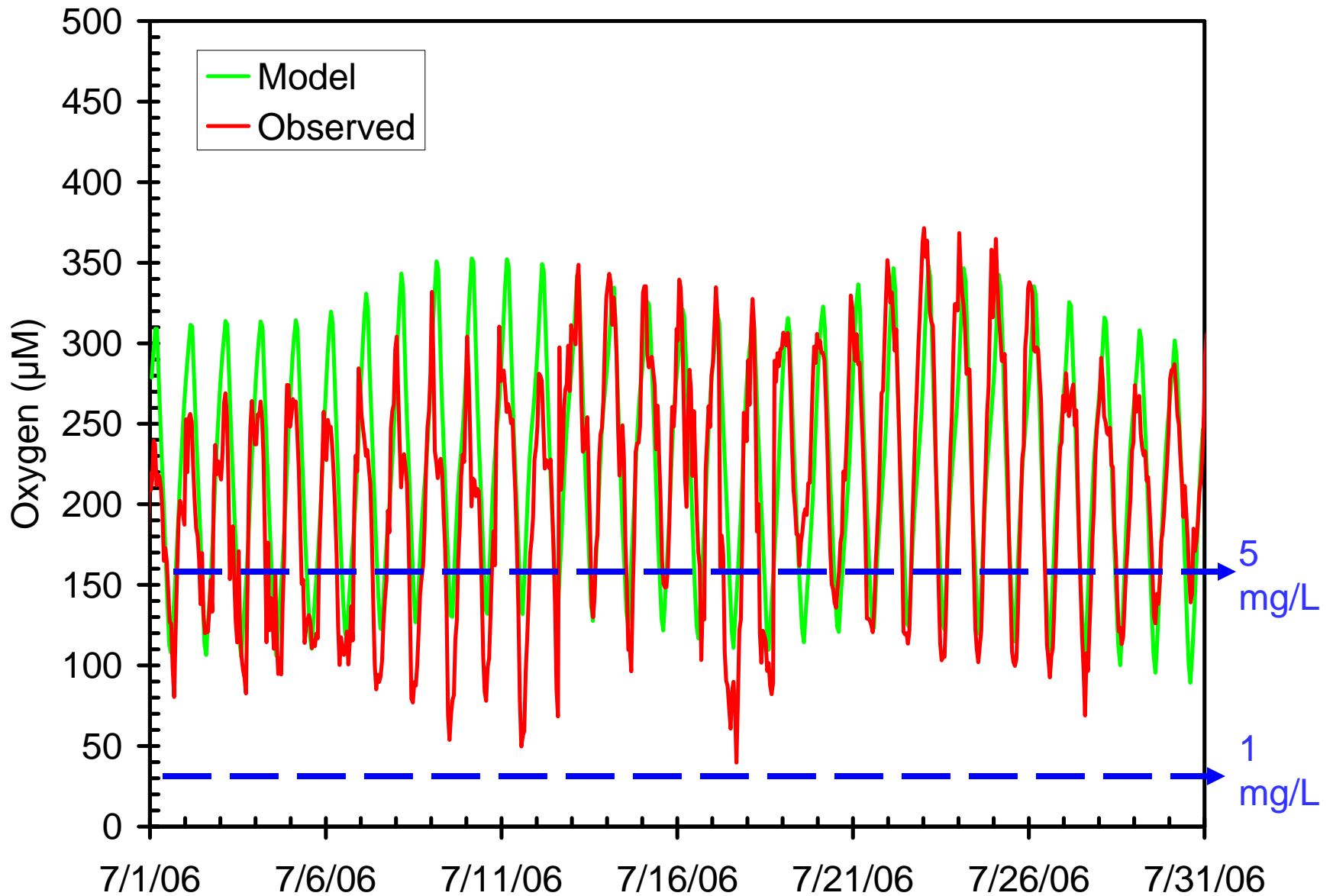




# Annual cycle of oxygen modeled near Kirby Park and observed on L02 mooring.

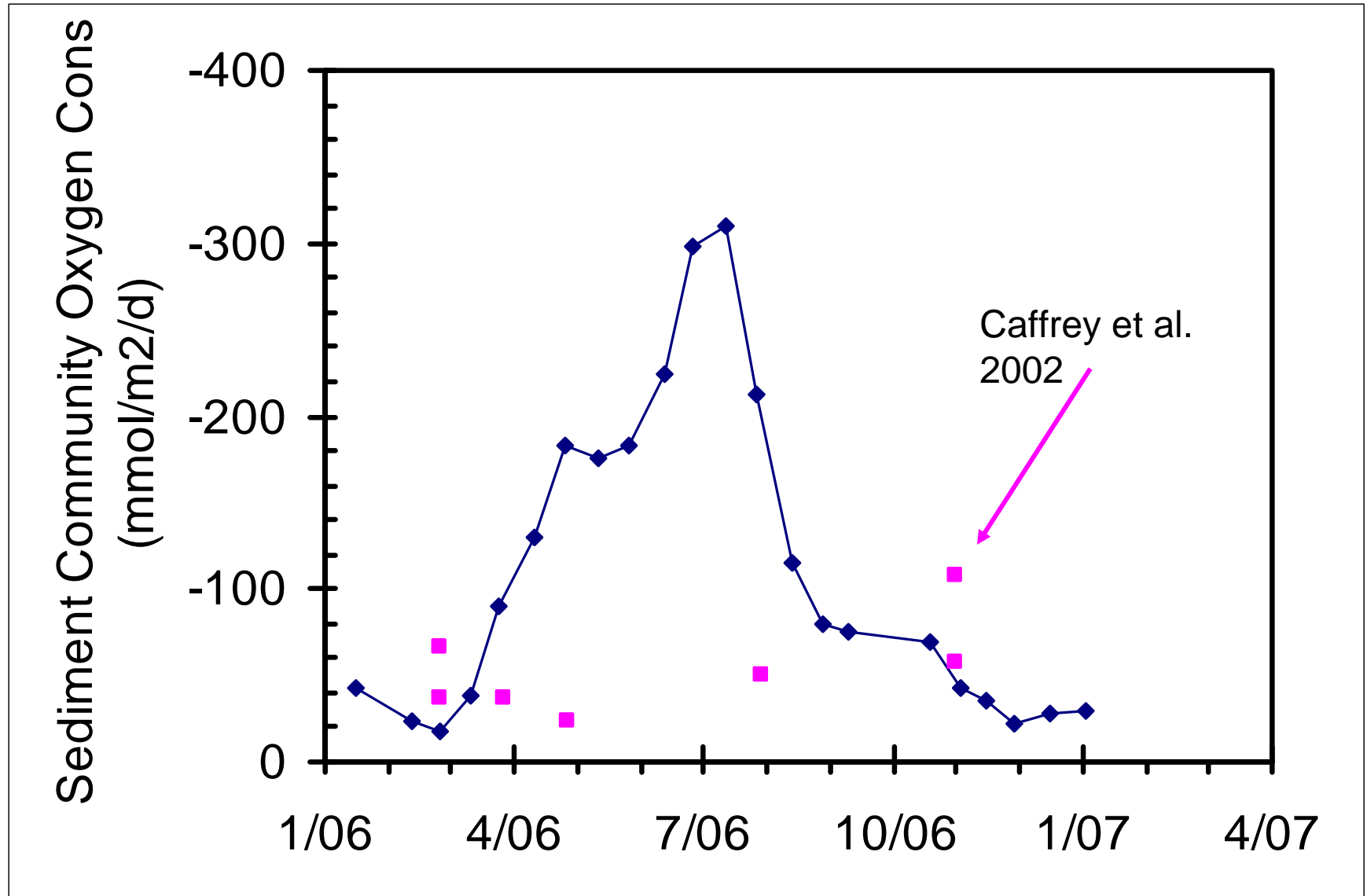


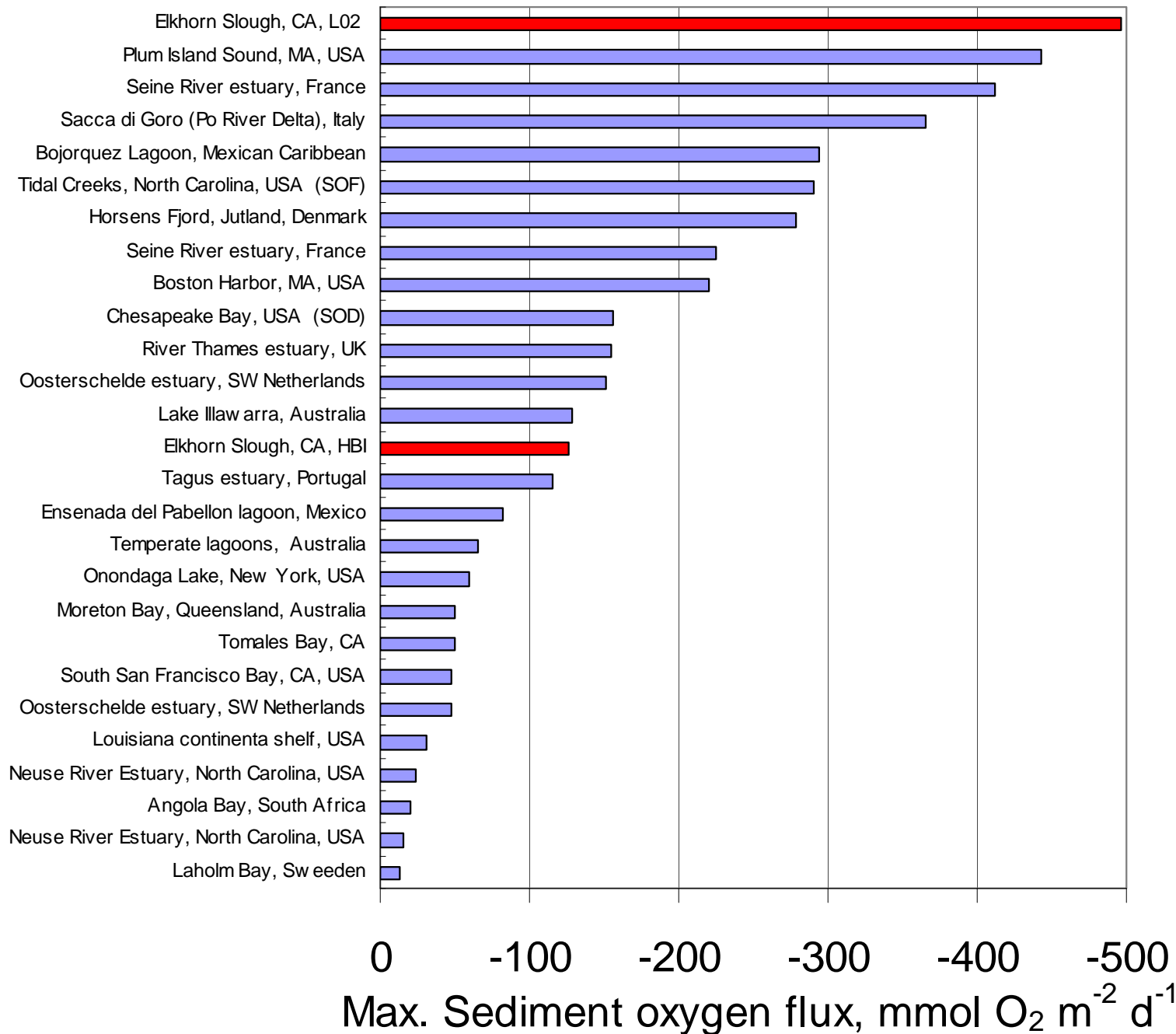
Full Mty. Bay tide range. 0/402 hrs < 100  $\mu\text{M}$   $\text{O}_2$





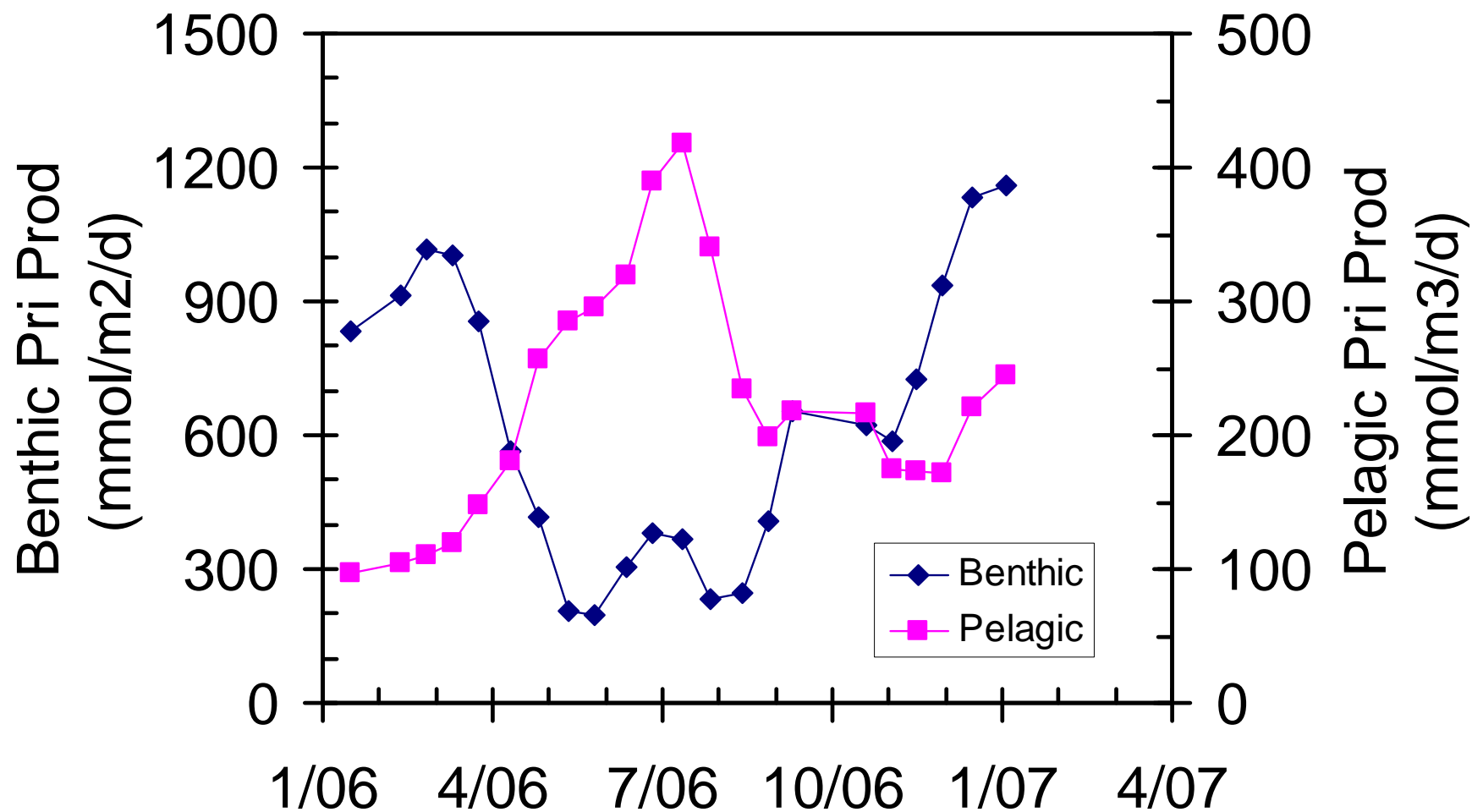
Annual cycle of respiration by sediment community (excludes plants) – clams, worms, meiofauna, bacteria..... Caffrey data roughly similar but does not capture wetland/intertidal processes.



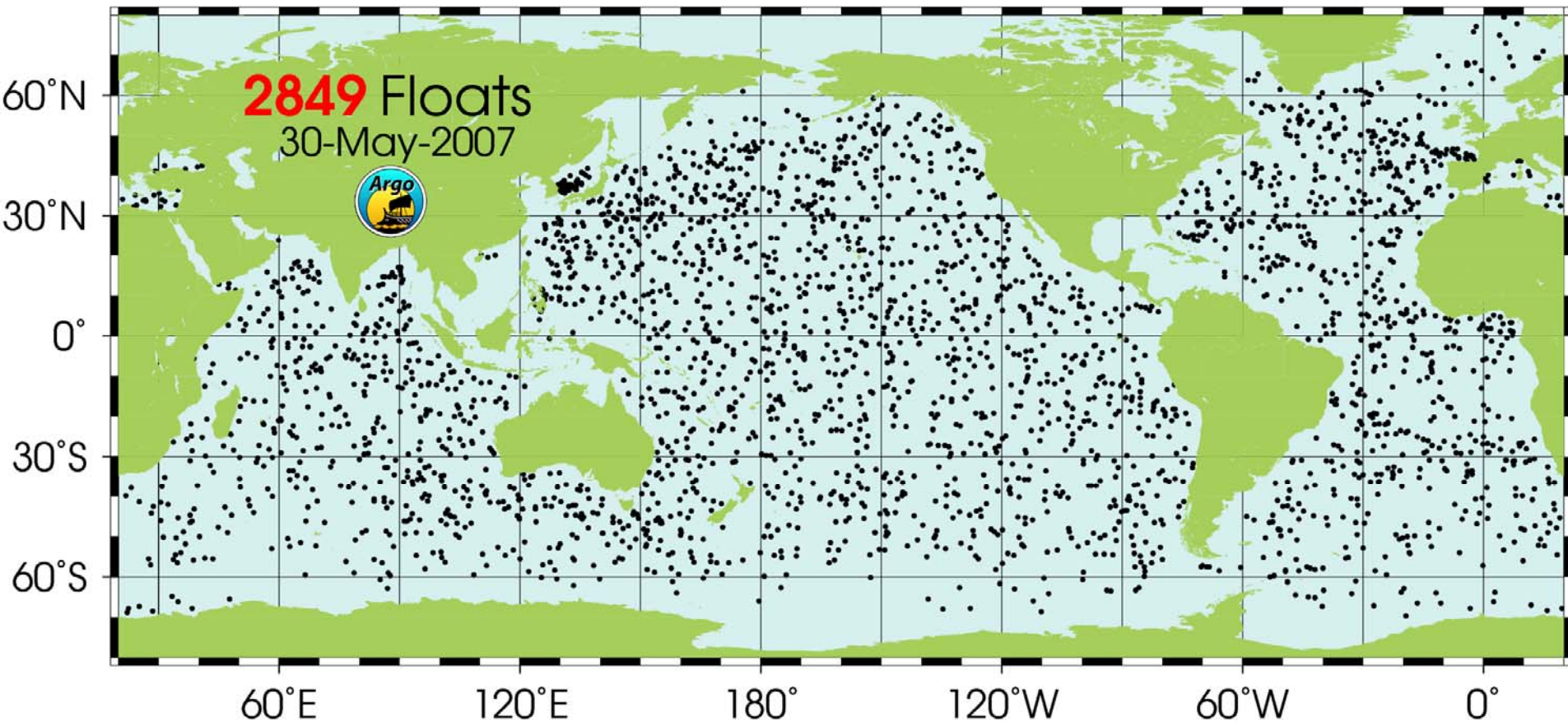




Annual cycles of pri. prod. on bottom and in water column.



The take home message: it's now possible to instrument the world ocean with a reasonably low-cost chemical sensor network that would give us the spatial and temporal variability of net community production, carbon export, nutrient flux...



## REPORTS

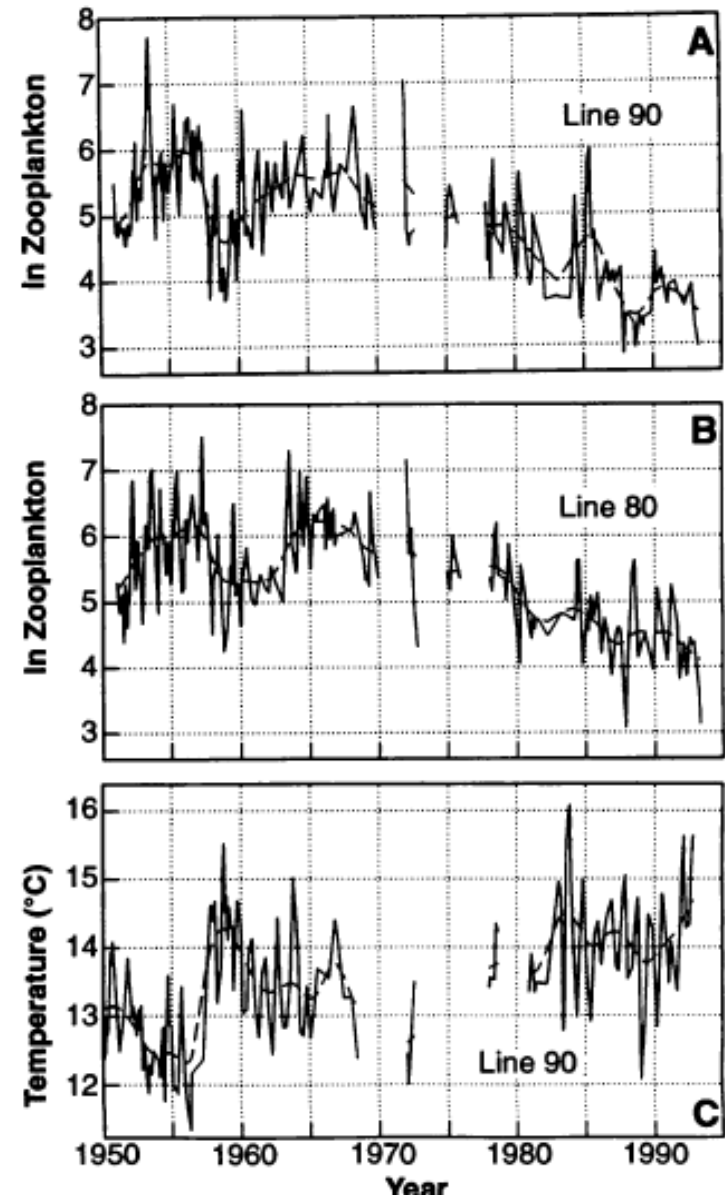
### Climatic Warming and the Decline of Zooplankton in the California Current

Dean Roemmich and John McGowan

Since 1951, the biomass of macrozooplankton in waters off southern California has decreased by 80 percent. During the same period, the surface layer warmed—by more than 1.5°C in some places—and the temperature difference across the thermocline increased. Increased stratification resulted in less lifting of the thermocline by wind-driven upwelling. A shallower source of upwelled waters provided less inorganic nutrient for new biological production and hence supported a smaller zooplankton population. Continued warming could lead to further decline of zooplankton.

The CalCOFI time series. Not very many ocean time series and most sparsely sampled in time.

Ken's rule of thumb – highest achievable sampling frequency is where cost of ship time = cost of science.



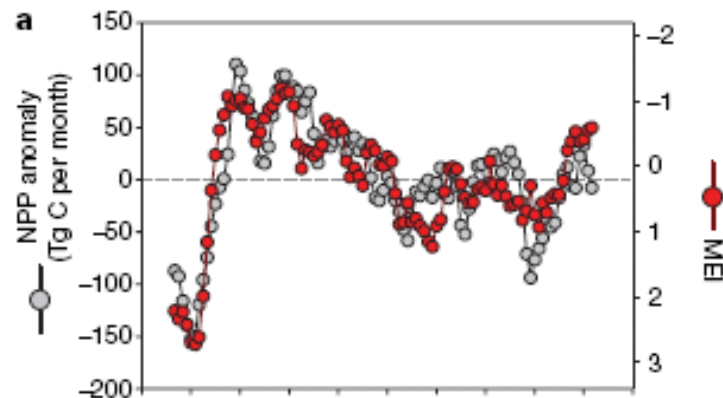


# LETTERS

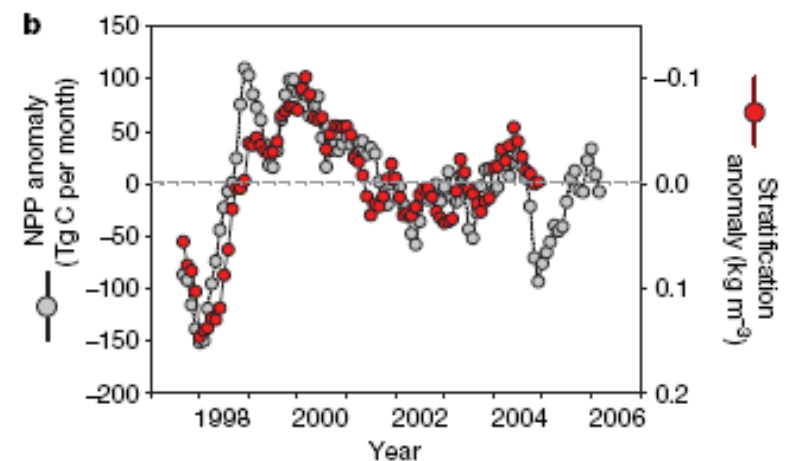
Global satellite time series, but only measure ocean color and infer productivity.

## Climate-driven trends in contemporary ocean productivity

Michael J. Behrenfeld<sup>1</sup>, Robert T. O'Malley<sup>1</sup>, David A. Siegel<sup>3</sup>, Charles R. McClain<sup>4</sup>, Jorge L. Sarmiento<sup>5</sup>, Gene C. Feldman<sup>4</sup>, Allen J. Milligan<sup>1</sup>, Paul G. Falkowski<sup>6</sup>, Ricardo M. Letelier<sup>2</sup> & Emmanuel S. Boss<sup>7</sup>



Variation in Pri. Prod and Multi-variate ENSO Index.



Variation in Pri. Prod and surface density gradient of ocean.

A fundamental question: what is the metabolic balance of the open ocean? Net autotrophic (produces oxygen and organic carbon) or net heterotrophic (consumes oxygen and organic carbon)?

## Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems

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\* Institute of Ecosystem Studies, Box AB, Millbrook, New York 12545-0129, USA

† Department of Biology, McGill University, 1205 Dr Penfield, Montreal, Quebec H3A 1B1, Canada

PLANKTONIC bacteria are a fundamental component of the organic carbon cycle in aquatic systems<sup>1</sup>. Organic carbon consumption by planktonic bacteria is the sum of bacterial production (BP) and bacterial respiration (BR). It is now estimated that 30–60% of phytoplankton production (the amount of inorganic carbon fixed by phytoplankton photosynthesis, corrected for phytoplankton respiration) in marine and freshwater systems is processed by bacteria<sup>1–3</sup>. These estimates of carbon flow through bacteria are conservative, however, because losses due to bacterial respiration are seldom directly measured<sup>4,5</sup>. We report here that bacterial respiration is generally high, and tends to exceed phytoplankton net production in unproductive systems (less than 70 to 120 µg carbon per litre per day). A large proportion of the world's aquatic systems have phytoplankton productivities below this value<sup>6</sup>. Bacterial growth efficiency (BGE) is the result of BP and BR [BGE = BP/(BR + BP)]. Comparisons of our models of bacterial respiration with published models of bacterial secondary production<sup>1,7</sup> show that bacterial growth efficiency must range from less than 10% to 25% in most freshwater and marine systems, well below the values commonly assumed in many current ecological models<sup>1,2,8,9</sup>. The imbalance between

## The CO<sub>2</sub> Balance of Unproductive Aquatic Ecosystems

Carlos M. Duarte\* and Susana Agusti

Community respiration ( $R$ ) rates are scaled as the two-thirds power of the gross primary production ( $P$ ) rates of aquatic ecosystems, indicating that the role of aquatic biota as carbon dioxide sources or sinks depends on its productivity. Unproductive aquatic ecosystems support a disproportionately higher respiration rate than that of productive aquatic ecosystems, tend to be heterotrophic ( $R > P$ ), and act as carbon dioxide sources. The average  $P$  required for aquatic ecosystems to become autotrophic ( $P > R$ ) is over an order of magnitude greater for marshes than for the open sea. Although four-fifths of the upper ocean is expected to be net heterotrophic, this carbon demand can be balanced by the excess production over the remaining one-fifth of the ocean.

Aquatic ecosystems cover 70% of Earth's surface (1) and contribute 45% of the global primary production (2). Yet, the role of their biota in the global CO<sub>2</sub> budget remains a subject of debate (3–5). Many freshwater ecosystems act as CO<sub>2</sub> sources (6); in contrast, oceanic ecosystems are assumed to act as CO<sub>2</sub> sinks (7, 8). This assumption has been challenged by calculations suggesting that the coastal ocean may be net heterotrophic (9) and by the finding that bacterial metabolism exceeds phytoplankton production in unproductive waters (10), which

make up >30% of the ocean. These conclusions are based on indirect calculations and controversial assumptions (3). Here, we compare the gross primary production ( $P$ ) and respiration ( $R$ ) rates of aquatic communities to elucidate whether the biota of aquatic ecosystems acts as net CO<sub>2</sub> sources ( $R > P$ ) or sinks ( $R < P$ ). We compiled data obtained over the past five decades from studies in which oxygen evolution was used as a surrogate for carbon fluxes (11).

Community metabolism varied by over four orders of magnitude across aquatic ecosystems (Table 1). Marshes tended to be more productive than other aquatic ecosystems, whereas open sea communities showed the lowest production and respiration rates (Table 1). The

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# The balance of plankton respiration and photosynthesis in the open oceans

P. J. le B. Williams

*School of Ocean Sciences, University of Wales, Bangor LL59 5EY, UK*

carbon balance. There is no evidence of the large regional imbalances observed previously<sup>2</sup>. I conclude that the form of data analysis is critical.

NATURE | VOL 394 | 2 JULY 1998

## TECHNICAL COMMENTS

### Regional Carbon Imbalances in the Oceans

Recent studies (1, 2) have suggested that respiration exceeds photosynthetic oxygen production in large areas of the oceans. If correct, the conclusion has profound implications for our understanding of the oceanic carbon cycle. C. M. Duarte and S. Agustí conclude that four fifths of the ocean are net

is the gross primary production rate. This equation is an unsatisfactory model when extrapolating across ecosystems of widely different productivities because the term "a" is not constant, but dependent on the scale of local photosynthesis [table 1 in the report (2)]. The  $P = aPb$  relationship attempts to fit a sin-

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*Spain*

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*David G. Bowers*

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# Respiration in the open ocean

Paul A. del Giorgio<sup>\*†</sup> & Carlos M. Duarte<sup>†‡</sup>

<sup>\*</sup> *Département des sciences biologiques, Université du Québec à Montréal, CP 8888, succ Centre Ville, Montréal, Québec H3C 3P8, Canada*

<sup>‡</sup> *IMEDEA (CSIC-UIB), Instituto Mediterráneo de Estudios Avanzados, C/Miquel Marqués 21, 07190 Esporles (Islas Baleares), Spain*

<sup>†</sup> *These authors contributed equally to this work*

A key question when trying to understand the global carbon cycle is whether the oceans are net sources or sinks of carbon. This will depend on the production of organic matter relative to the decomposition due to biological respiration. Estimates of respiration are available for the top layers, the mesopelagic layer, and the abyssal waters and sediments of various ocean regions. Although the total open ocean respiration is uncertain, it is probably substantially greater than most current estimates of particulate organic matter production. Nevertheless, whether the biota act as a net source or sink of carbon remains an open question.

## brief communications

NATURE | VOL 420 | 28 NOVEMBER 2002 | www.nature.com/nature

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### COMMUNICATIONS ARISING

#### Global carbon cycle

## Metabolic balance of the open sea

The rise of oxygenic photosynthesis nearly three billion years ago led to the accumulation of free oxygen and to the subsequent diversification of life on Earth; today, nearly half of all oxygen production derives from the photosynthetic activities of marine phytoplankton<sup>1</sup>. The conclusion that the open sea — and therefore much of our planet's surface — is in a net heterotrophic metabolic state<sup>2–4</sup> is enigmatic and is a first-order question in the global carbon cycle, as discussed by del Giorgio and Duarte<sup>5</sup>. Our

understanding of carbon sequestration processes. David M. Karl\*, Edward A. Laws\*, Paul Morris\*, Peter J. leB. Williams†, Steven Emerson‡

*\*Department of Oceanography, University of Hawaii, Honolulu, Hawaii 96822, USA  
e-mail: dkarl@hawaii.edu*

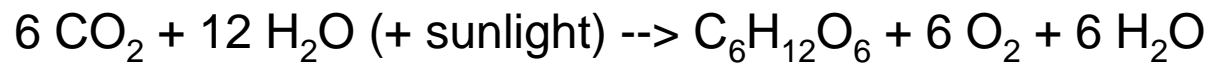
*†School of Ocean Sciences, University of Wales, Bangor LL59 5PP, UK*

*‡School of Oceanography, University of Washington, Seattle, Washington 98195, USA*

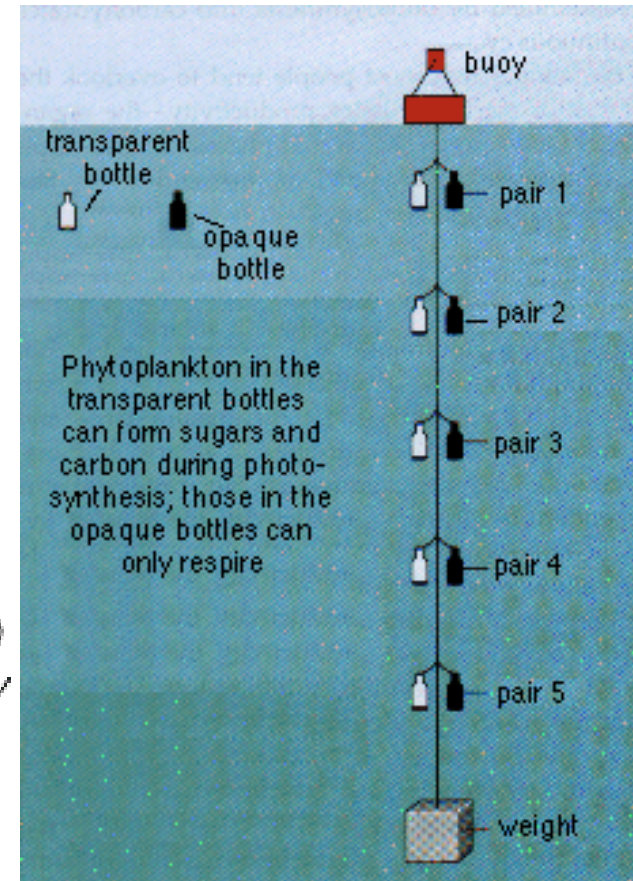
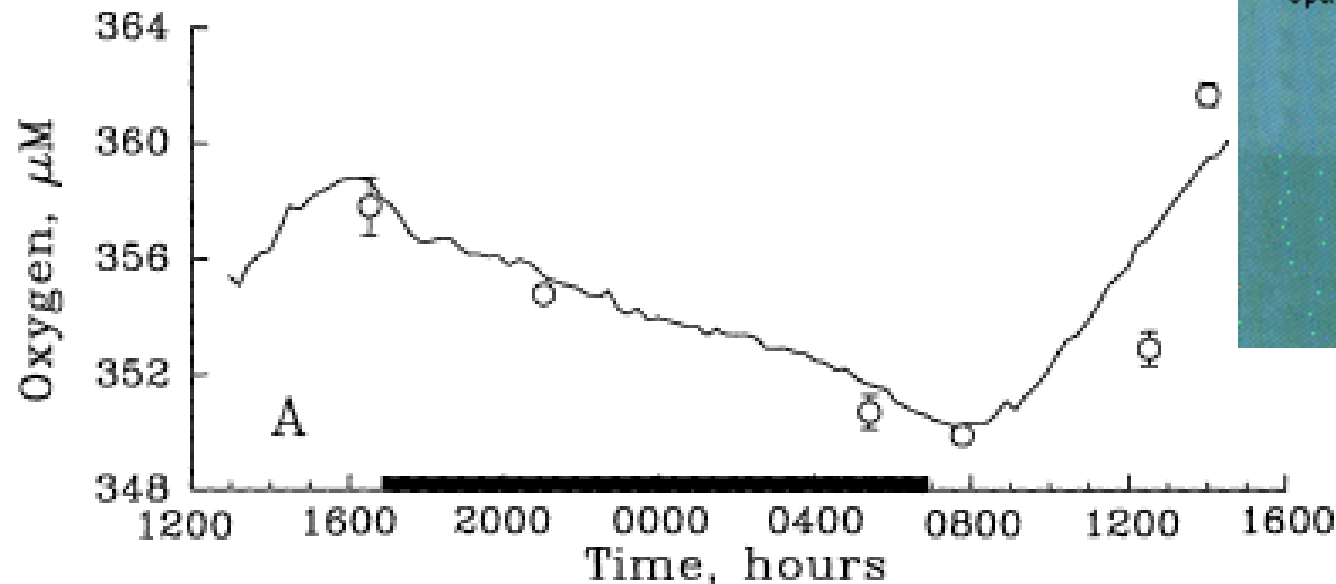
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The Light Bottle/Dark Bottle or Oxygen method of determining primary production:



About 1 mole of oxygen produced for each mole of carbon incorporated into organic compounds. Oxygen traces primary production and respiration.





## Net community production and metabolic balance at the oligotrophic ocean site, station ALOHA

Peter J. le B. Williams<sup>a,\*</sup>, Paul J. Morris<sup>b</sup>, David M. Karl<sup>b</sup>

<sup>a</sup>*Marine Science Laboratories, School of Ocean Sciences, University of Wales, Menai Bridge, Bangor, Gwynedd LL59 5EY, UK*

<sup>b</sup>*School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI, 96822, USA*

Received 18 August 2003; received in revised form 14 June 2004; accepted 14 June 2004

Available online 12 September 2004

To test the hypothesis that in oligotrophic areas of the ocean respiration exceeds production, a 12-month study was undertaken of in vitro-determined net oxygen production and consumption in the top 150 m of the water column at the extreme oligotrophic site, Station ALOHA, in the North Pacific subtropical gyre. Throughout the year the water column was observed to be in metabolic deficit, the calculated cumulative shortfall being  $9 \pm 1.7 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$  (approximately  $100 \text{ g C m}^{-2} \text{ a}^{-1}$ ), an amount equivalent to 40% of measured production (annual estimated rates of production and consumption were, respectively, 22 and  $31 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$ ).

In summary, we ..... observe a deficit in oxygen (and thus organic carbon) production equivalent to about .... about 40% of measured production. We are inclined to the view that this deficit in part results from a limitation of the in vitro approach in that it fails to take adequate account of **the intermittent nature of primary production.**

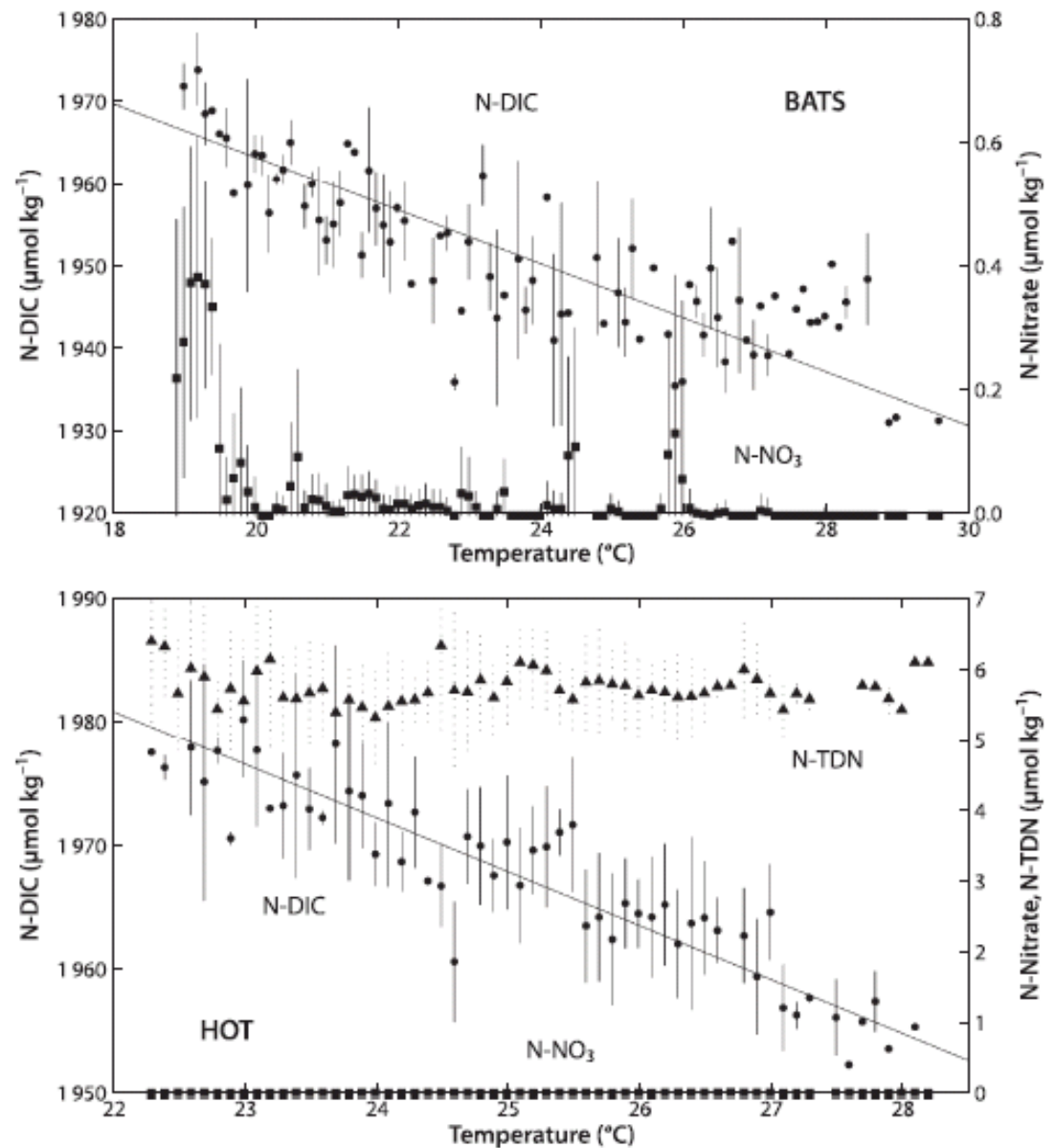


Two questions:

Is the oligotrophic ocean autotrophic?

What supplies the nutrients if it is autotrophic?

Fig. 10.11. Relationships between carbon removal and fixed nitrogen in the surface waters of the subtropical North Atlantic (*top*: BATS) and subtropical North Pacific (*bottom*: HOT) during the period of summertime warming of the sea surface. At the BATS site, DIC normalized to a salinity of 35 (N-DIC) shows a systematic decrease with increasing temperature even in the absence of nitrate. At the HOT site, a similar summertime N-DIC drawdown in the absence of nitrate (the surface water nitrate concentration at Sta. ALOHA during the summer period is always less than  $0.01 \mu\text{mol kg}^{-1}$ ). Analyses of salinity-normalized total dissolved N (N-TDN) also failed to document a simultaneous loss of fixed N from the much larger pool of dissolved organic N



## Chapter 10

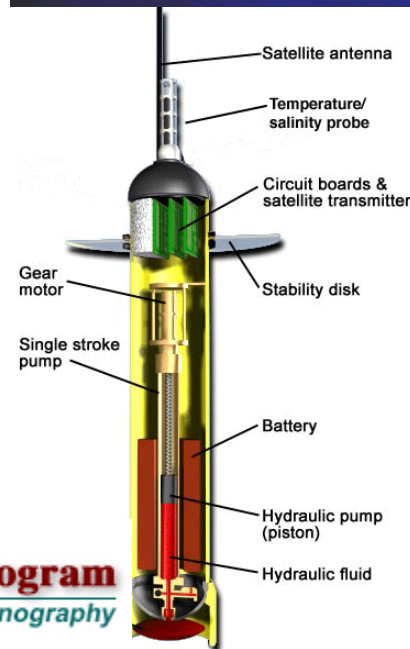
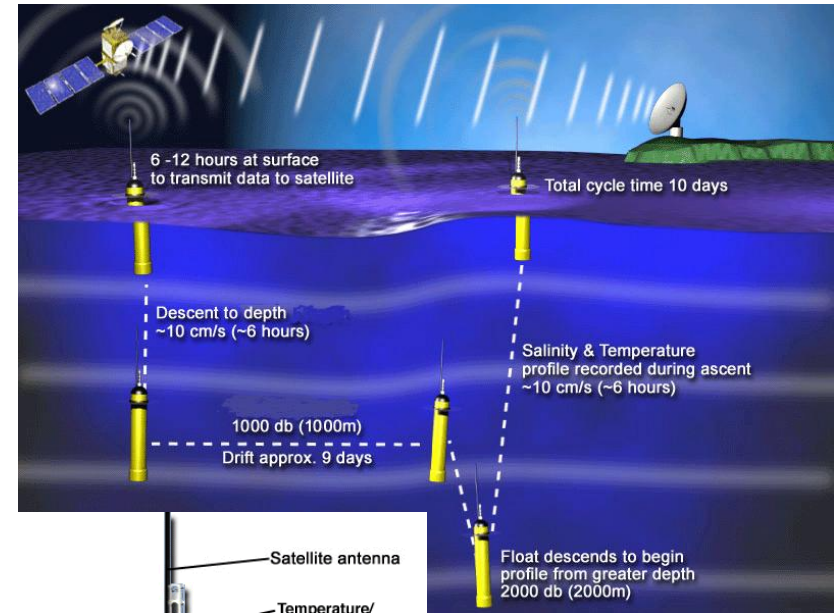
### Temporal Studies of Biogeochemical Processes Determined from Ocean Time-Series Observations During the JGOFS Era

David M. Karl · Nicholas R. Bates · Steven Emerson · Paul J. Harrison · Catherine Jeandel · Octavio Llinás  
Kon-Kee Liu · Jean-Claude Marty · Anthony F. Michaels · Jean C. Miquel · Susanne Neuer · Y. Nojiri · Chi Shing Wong

# Ocean metabolism observed with oxygen sensors on profiling floats in the Pacific

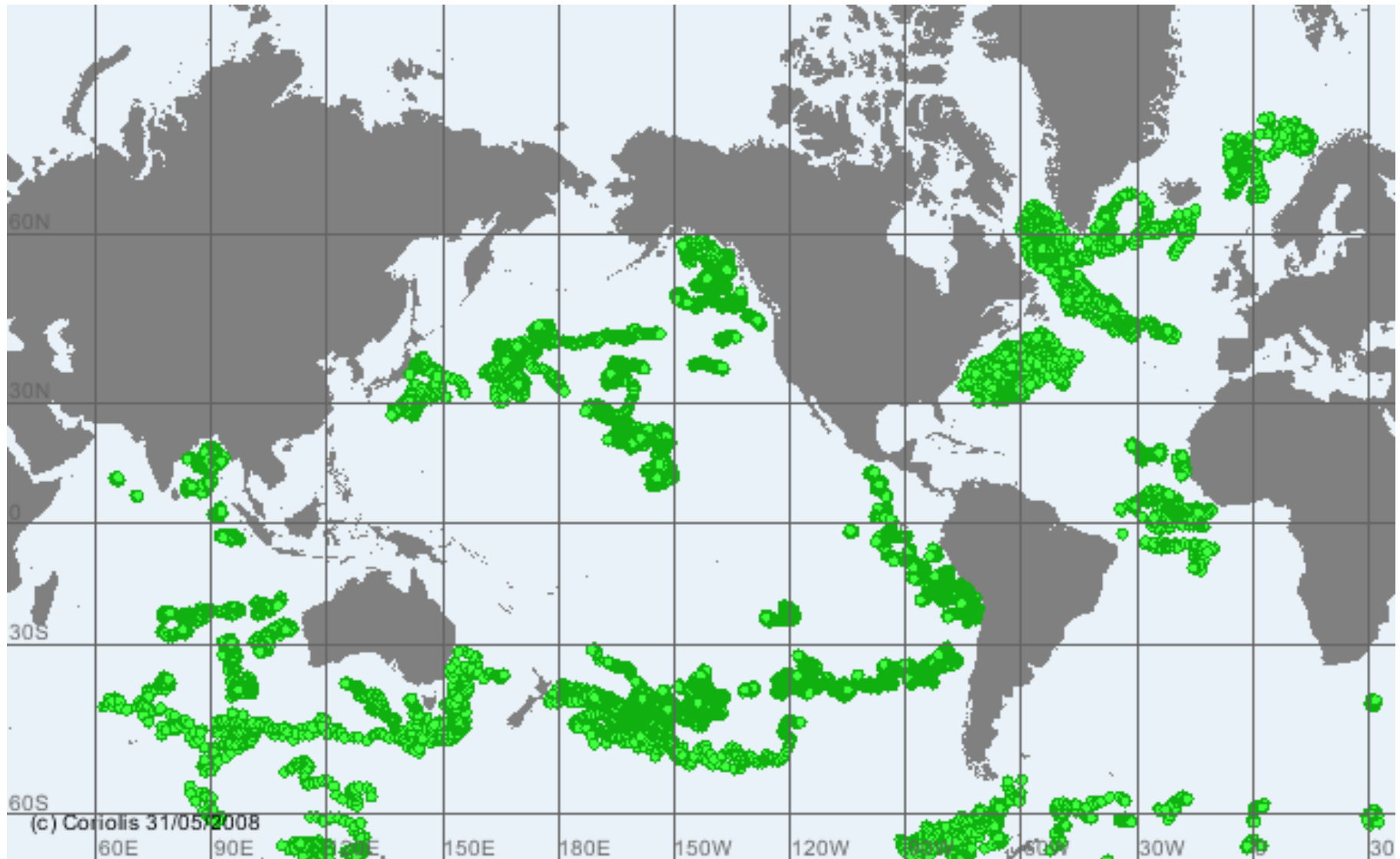
A collaboration with Steve Riser, UW

- >100 UW oxygen floats deployed in Pacific since 2002



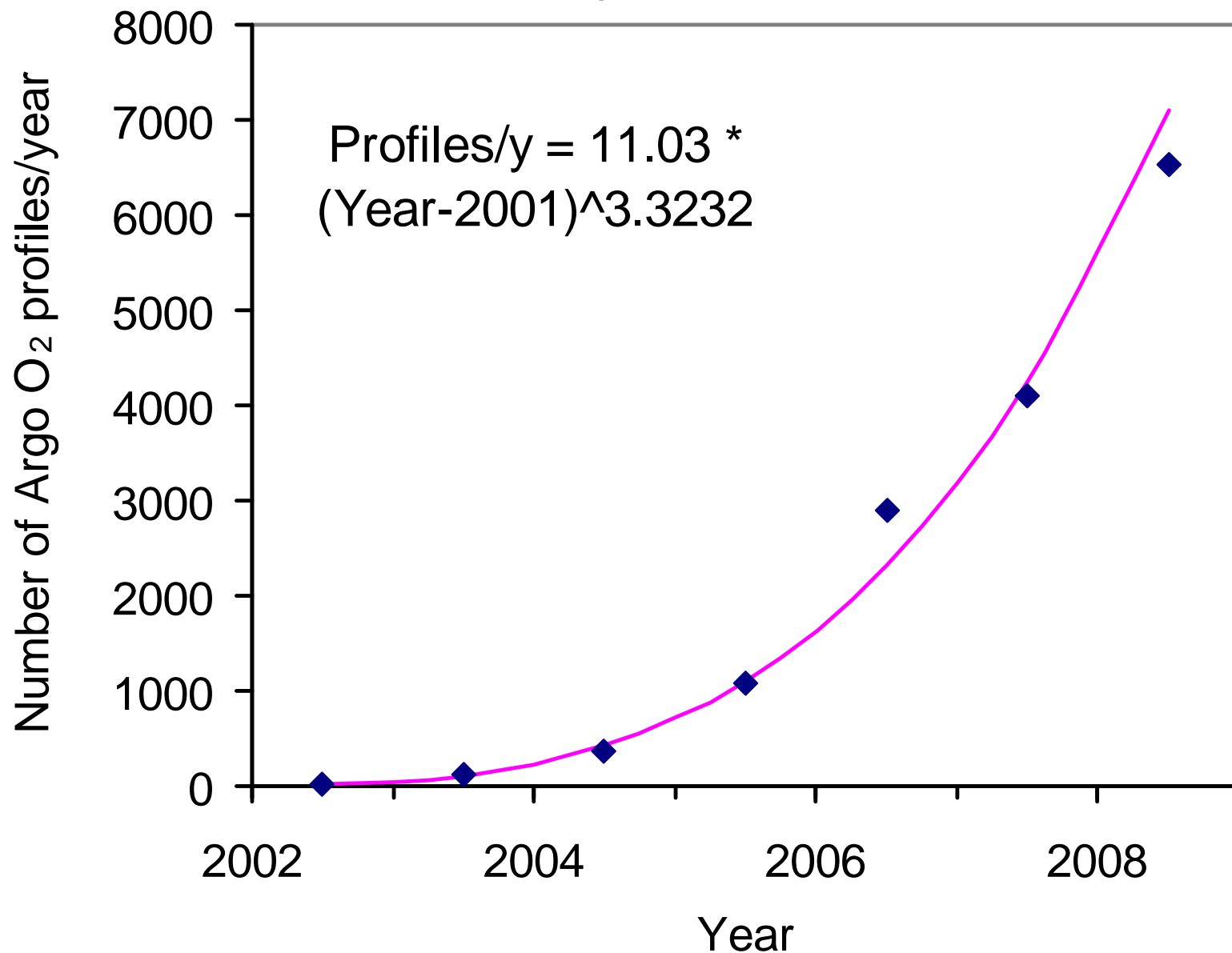
**National Oceanographic Partnership Program**  
*Promoting Partnerships for the Future of Oceanography*

5219 Argo profiles with O<sub>2</sub> in the past year.





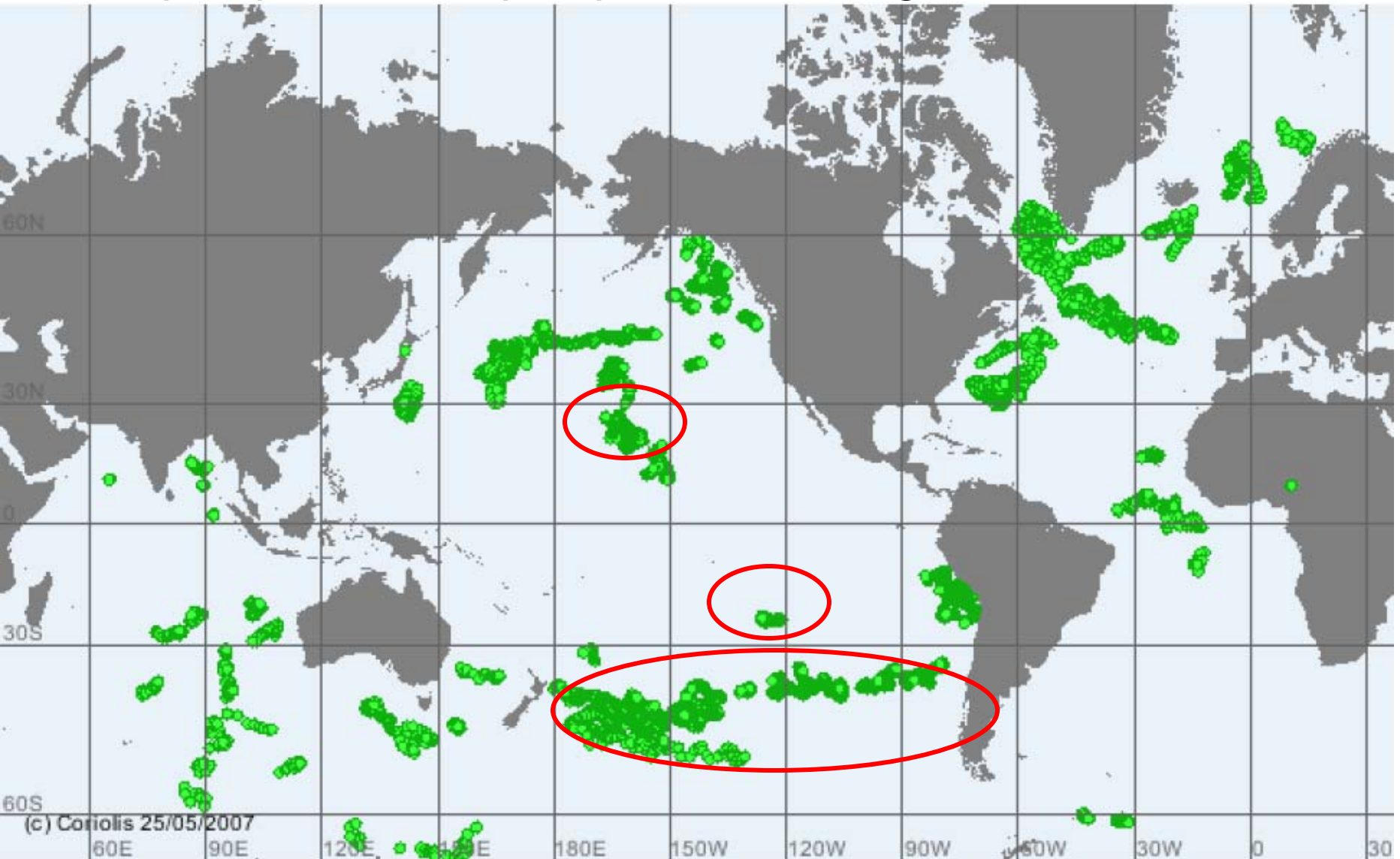
Number of O<sub>2</sub> profiles per year is  
doubling every 15 months



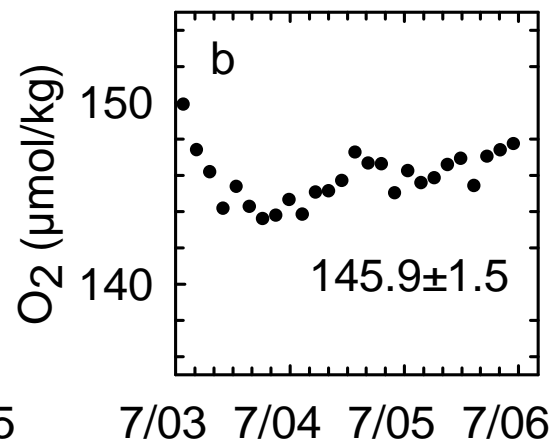
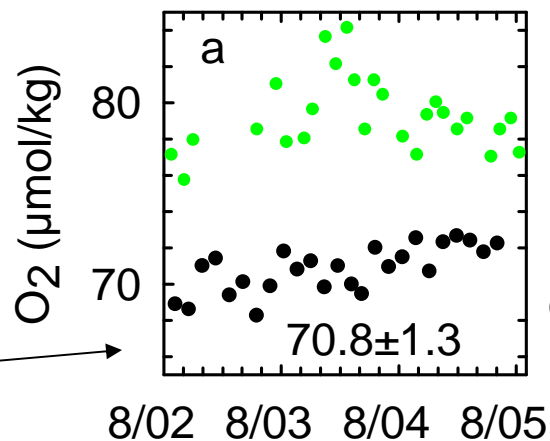
Data available for (almost) all O<sub>2</sub> floats at:

<http://usgodae1.fnmoc.navy.mil/ftp/outgoing/argo/>

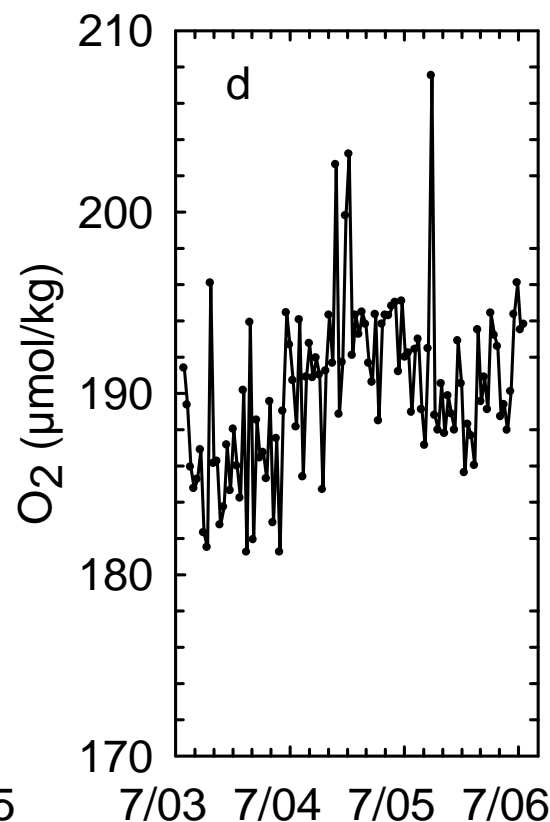
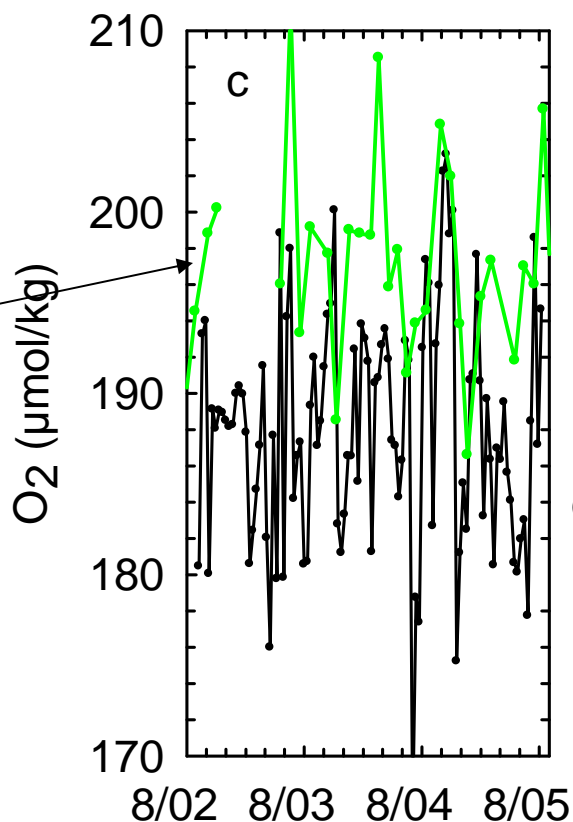
<ftp://ftp.ifremer.fr/pub/pub/ifremer/argo>



Oxygen sensors on profiling floats have proven to be exceptionally stable. The floats park at 1000 m and little fouling occurs.

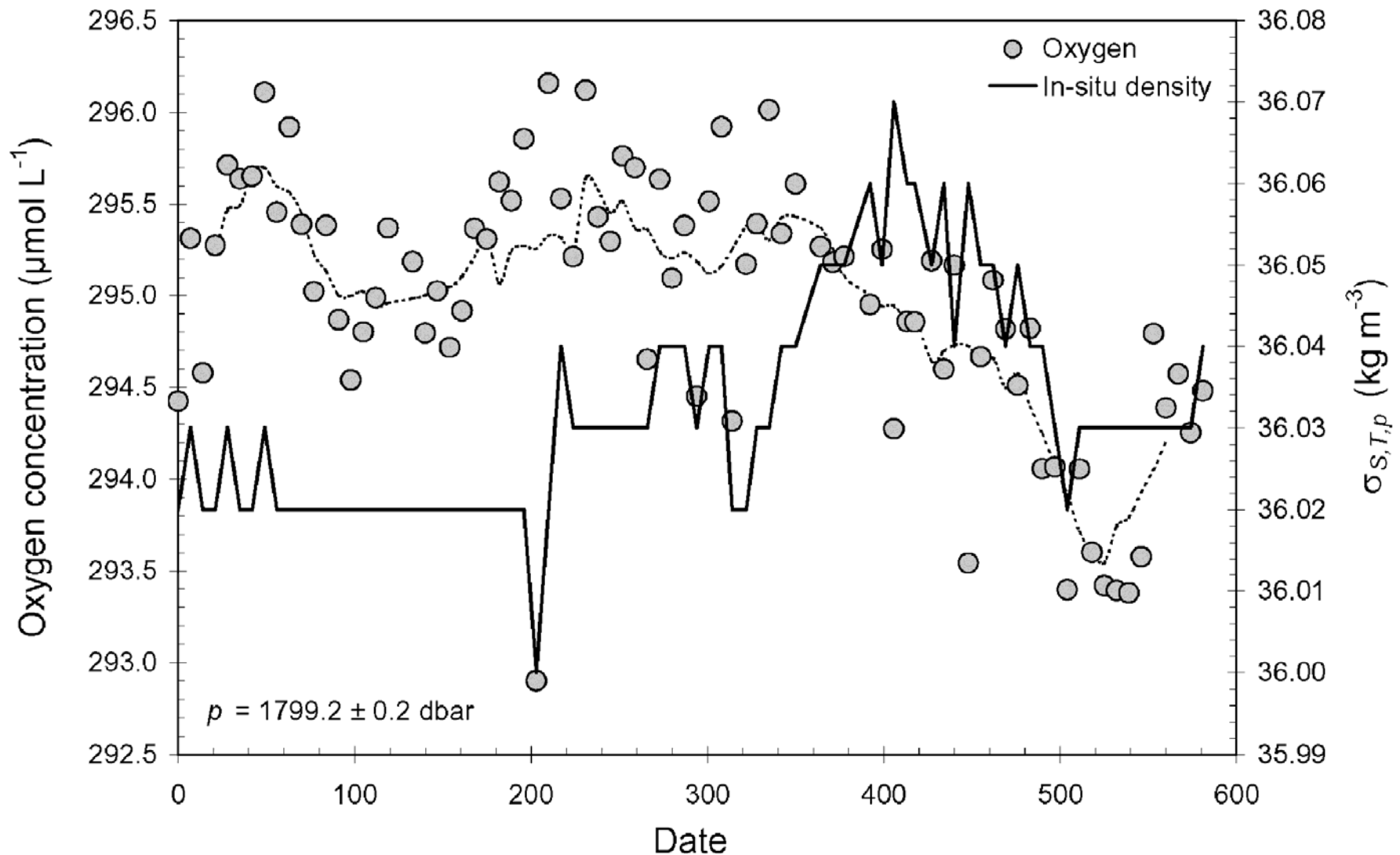


Noisier at 200 m, but noise (1 standard deviation) is the same as in the HOT Winkler titration data – green lines. That's real variability. Important point is there is NO DRIFT at 200 m, just below the euphotic zone.

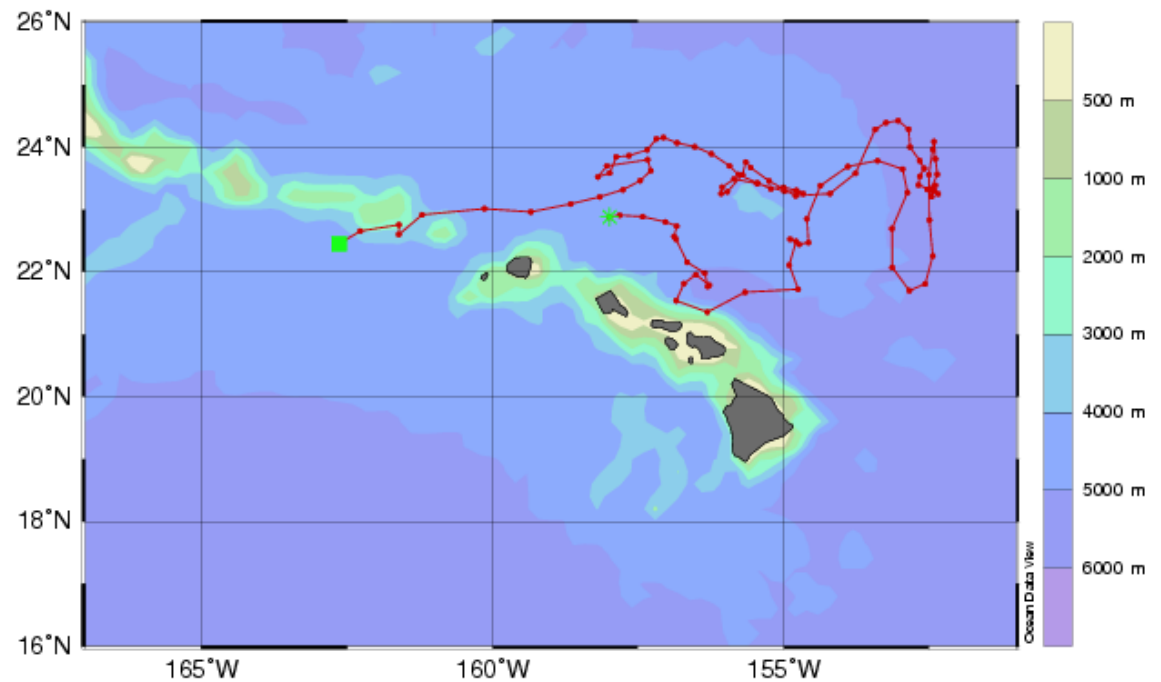




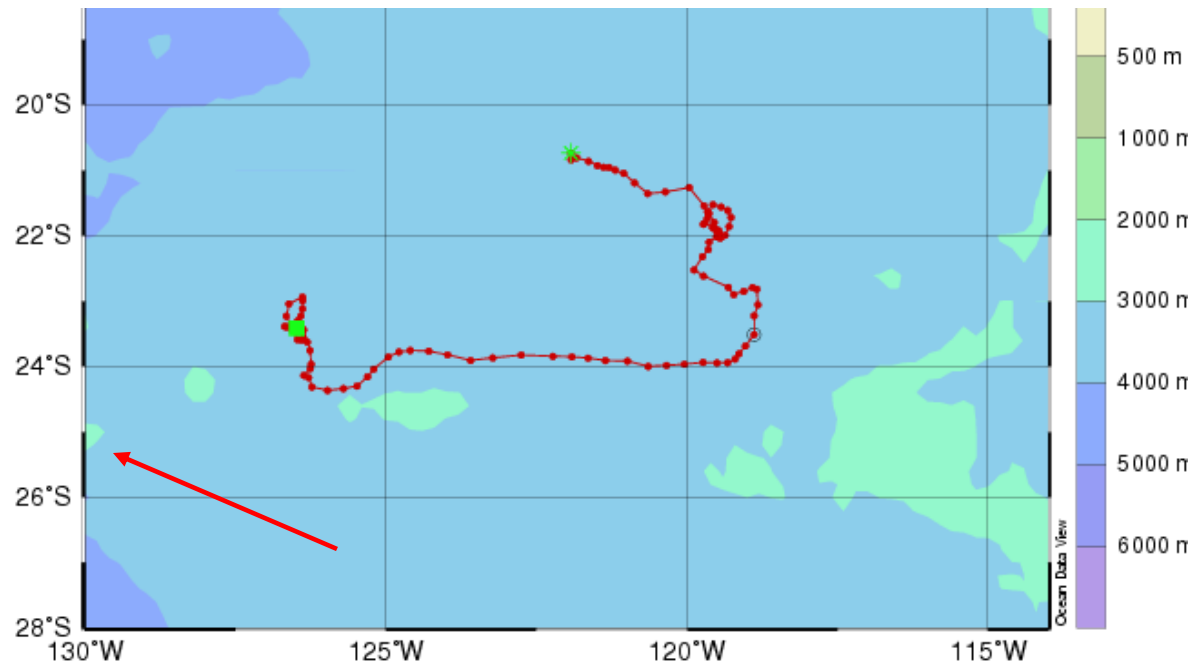
An Aanderaa oxygen optode on a vertical profiling float in the North Atlantic is stable to  $295.0 \pm 0.7 \mu\text{mol/L}$  over nearly two years at 1800 m depth (Kortzinger et al., 2006; Tengberg et al., 2006). Much of the oxygen variability may be real!!! These sensors could be precise to 0.1%. That's fantastic!!!!



Trajectory over  
3 years for  
float 0894  
(WMO  
#4900093)  
near HOT,



and float 1326  
(#5900420) in  
the South  
Pacific gyre  
near????



Pitcairn Island!

Population of 45.

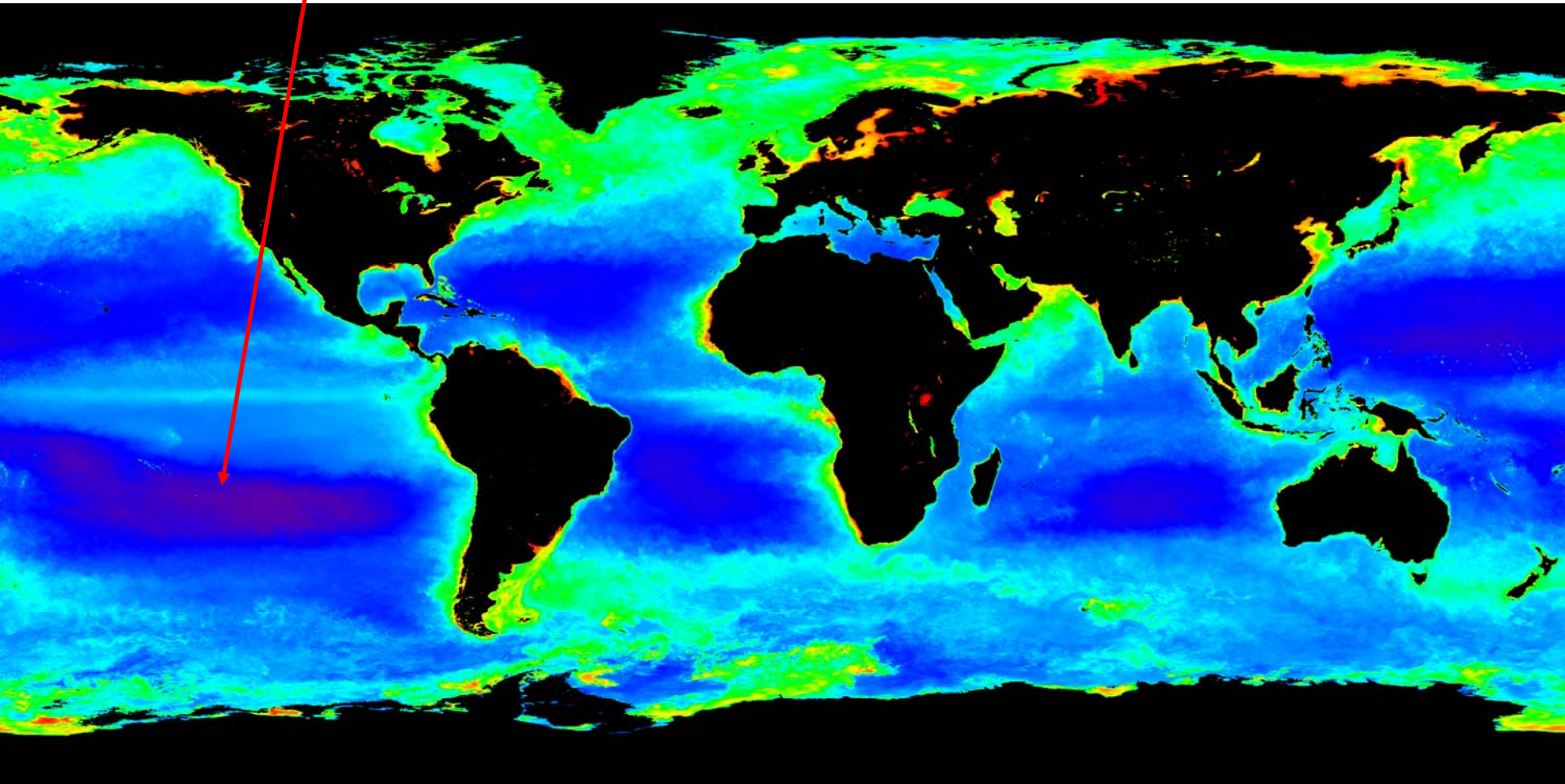
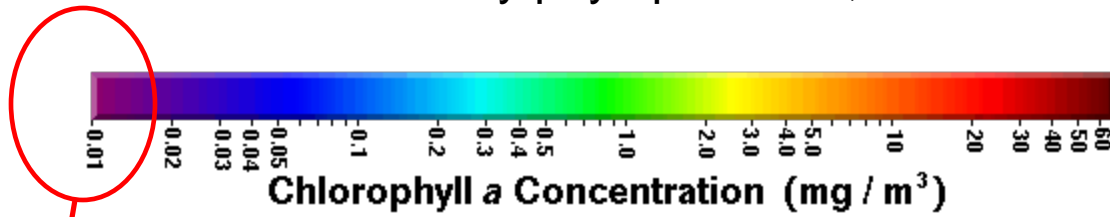
The islanders are descendants of the Bounty mutineers and the Tahitians who accompanied them in 1790.

HOT and POT – the Pitcairn Ocean Time-series.

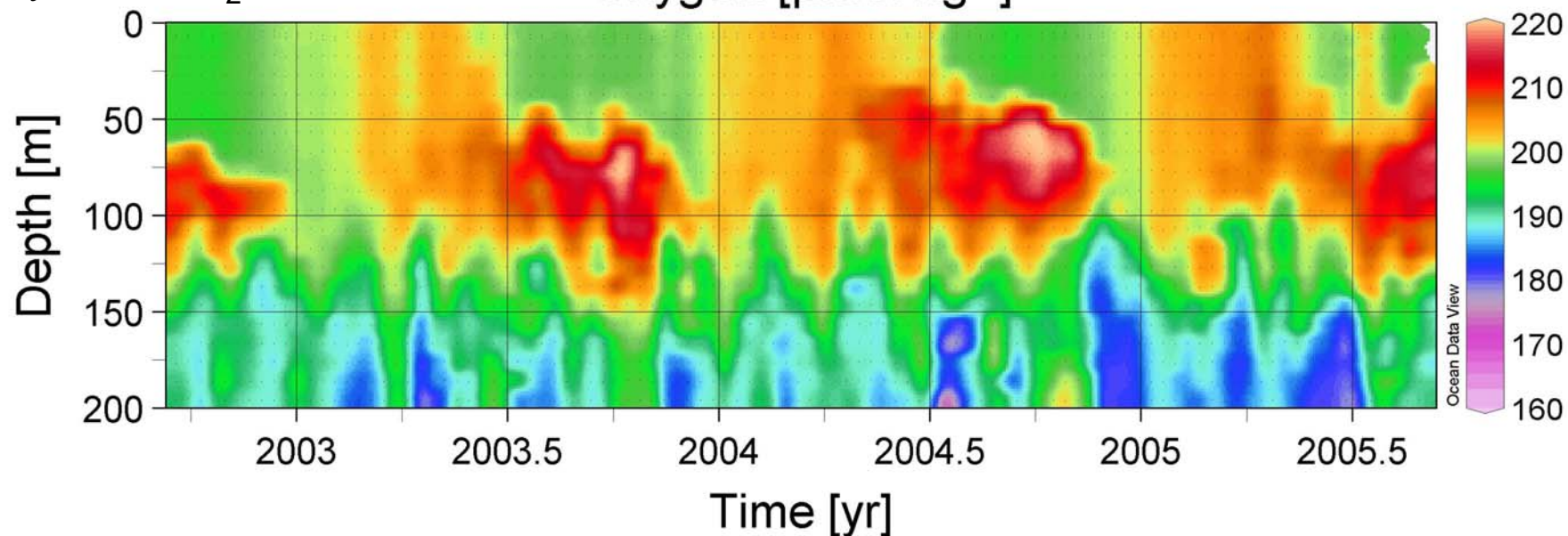




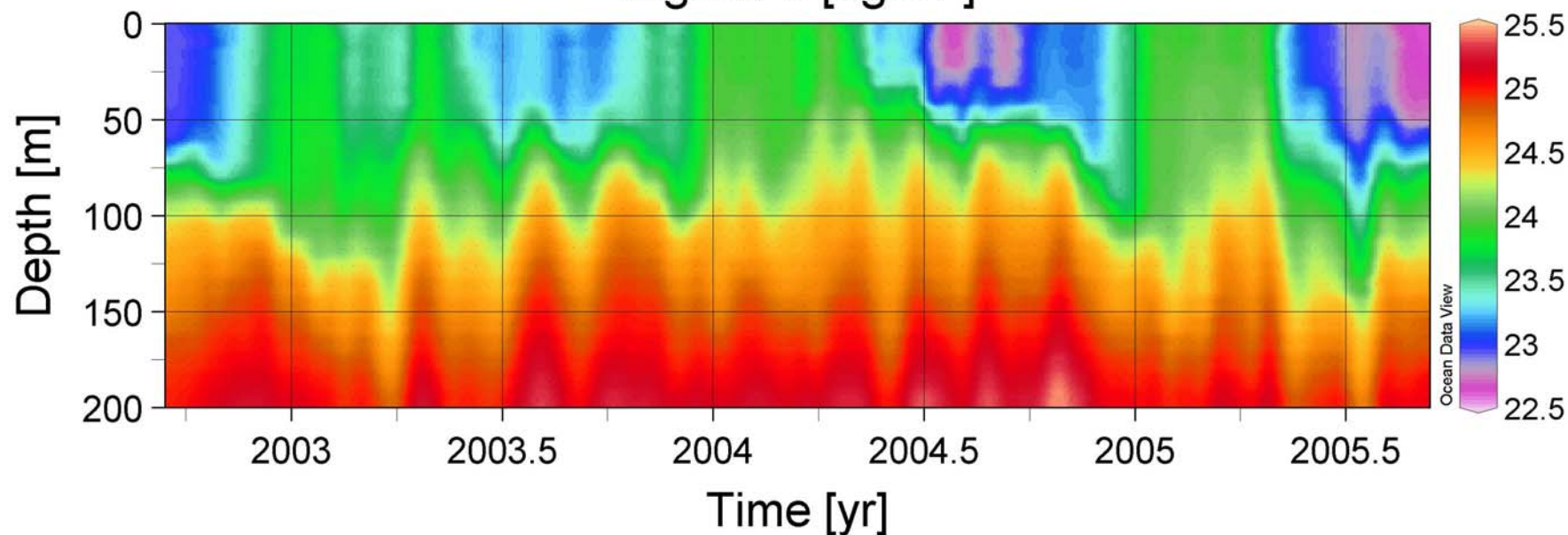
2006 Average Ocean Chlorophyll (MODIS). Not many people  
and not many phytoplankters, either.



3 years of O<sub>2</sub> data near HOT    Oxygen [ $\mu\text{mol kg}^{-1}$ ]



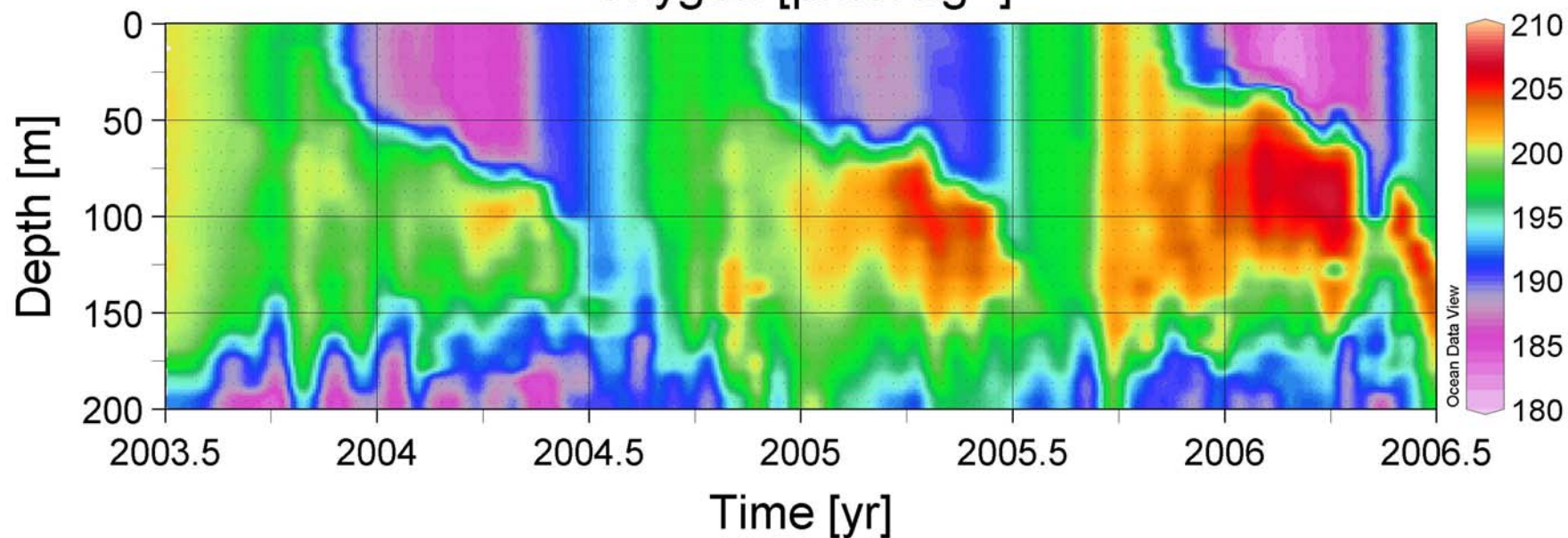
Sigma-0 [ $\text{kg/m}^3$ ]



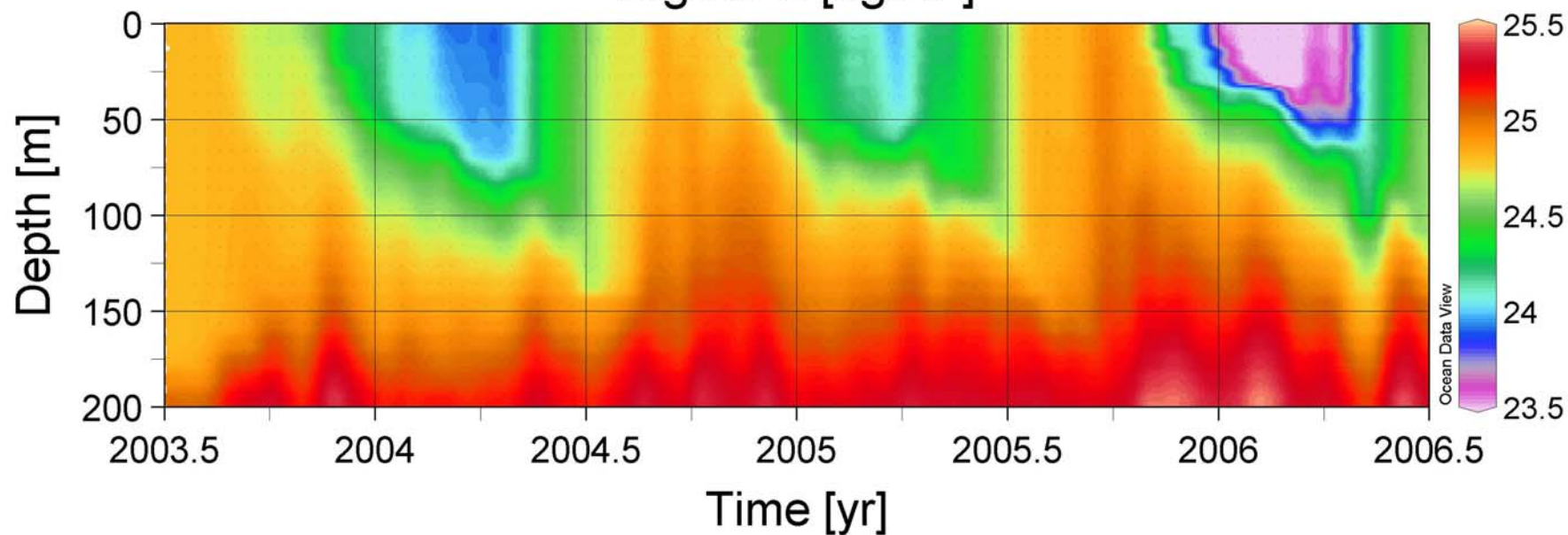


3 years of O<sub>2</sub> at POT

Oxygen [ $\mu\text{mol kg}^{-1}$ ]



Sigma-0 [ $\text{kg/m}^3$ ]





# Influential past work

Deep-Sea Research, Vol. 28A, No. 9, pp. 901 to 919, 1981.  
Printed in Great Britain.

0198-0149/81/090901-19 \$02.00/0  
© 1981 Pergamon Press Ltd.

## The Pacific shallow oxygen maximum, deep chlorophyll maximum, and primary productivity, reconsidered

ERIC SHULENBERGER\* and JOSEPH L. REID†

(Received 18 September 1980; in revised form 10 January 1981; accepted 1 February 1981)

← **SOM & NCP**

*Journal of Marine Research*, 55, 117–151, 1997

Different zones of  
annual oxygen cycle  
& Nodal depth

## Analysis of the mean annual cycle of the dissolved oxygen anomaly in the World Ocean

by Raymond G. Najjar<sup>1</sup> and Ralph F. Keeling<sup>2</sup>

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 93, NO. C12, PAGES 15,679–15,700, DECEMBER 15, 1988

## Application of a Model of Upper-Ocean Physics for Studying Seasonal Cycles of Oxygen

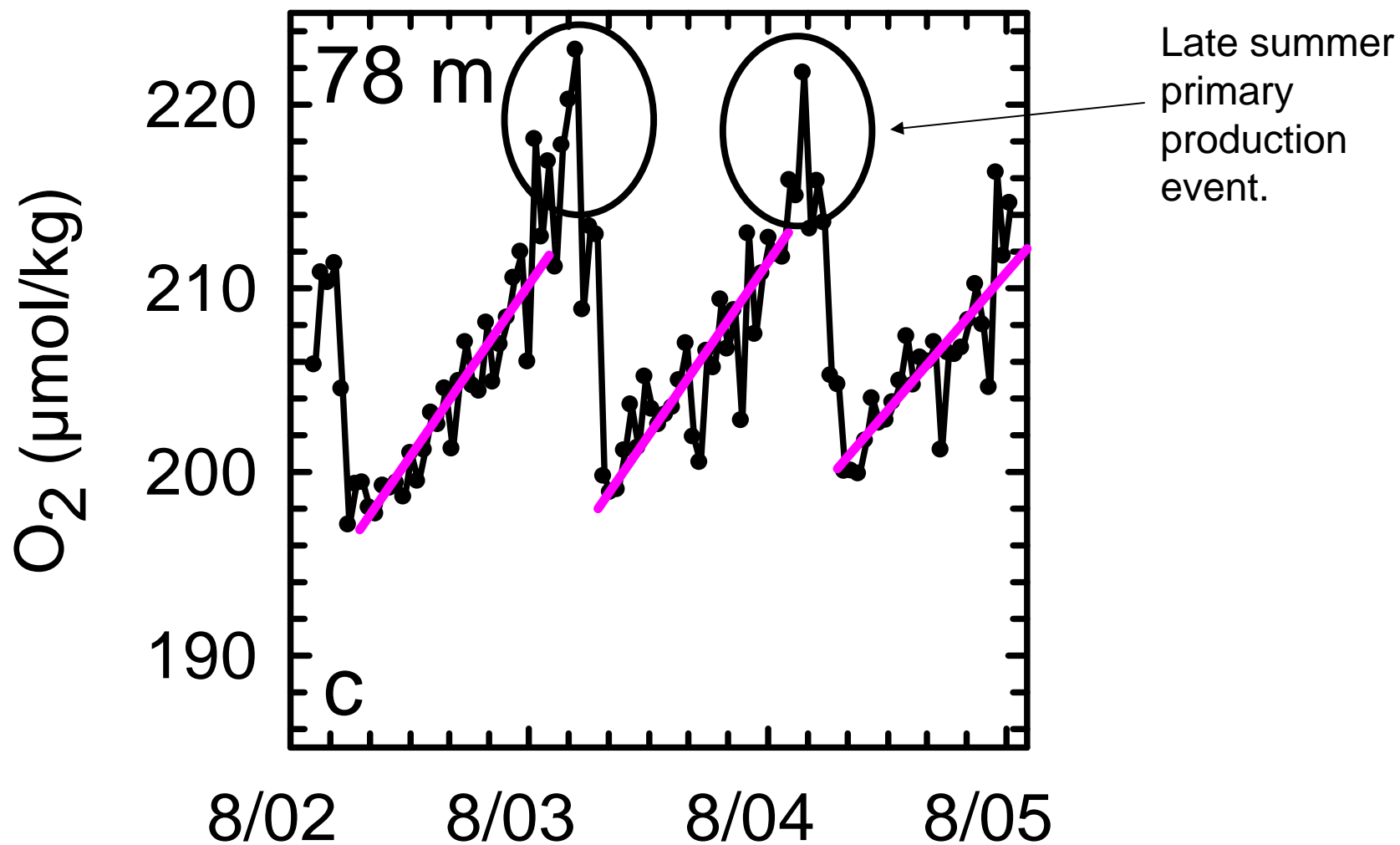
DAVID L. MUSGRAVE,<sup>1</sup> JAMES CHOU, AND WILLIAM J. JENKINS

*Woods Hole Oceanographic Institution, Woods Hole, Massachusetts*

## Rates of vertical mixing, gas exchange and new production: Estimates from seasonal gas cycles in the upper ocean near Bermuda

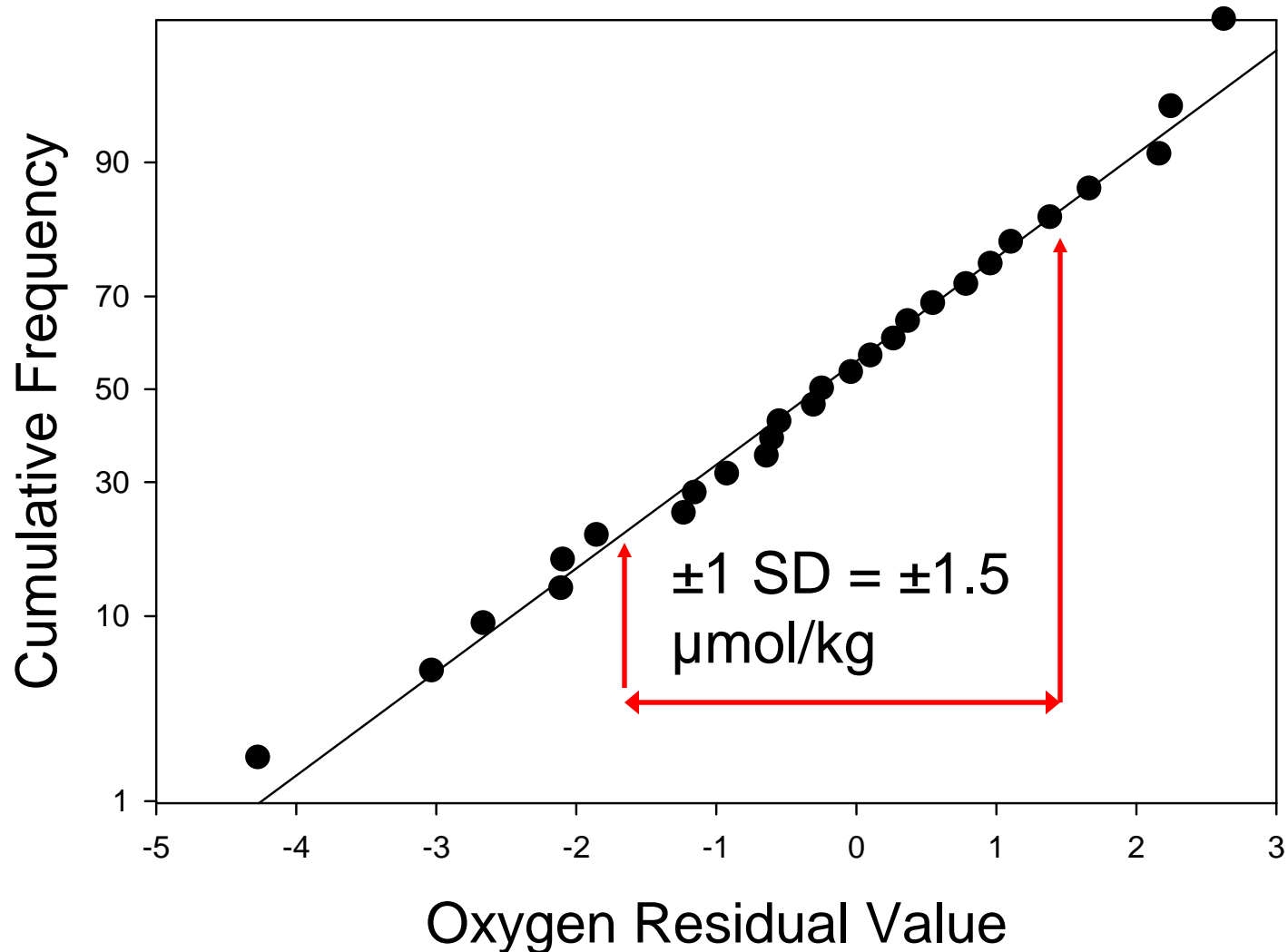
by William S. Spitzer<sup>1</sup> and William J. Jenkins<sup>1</sup>

Modeling the annual  
oxygen cycle

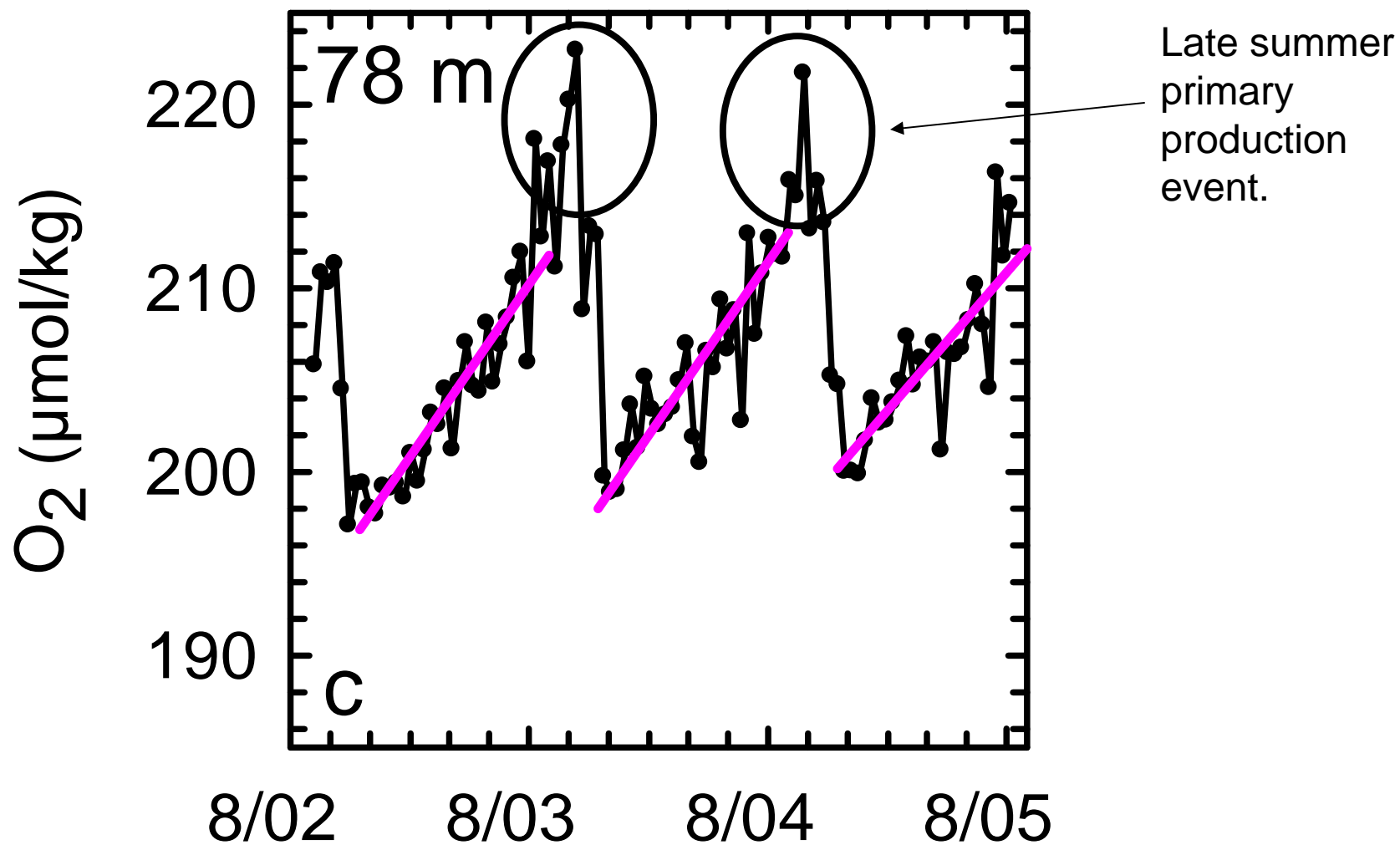


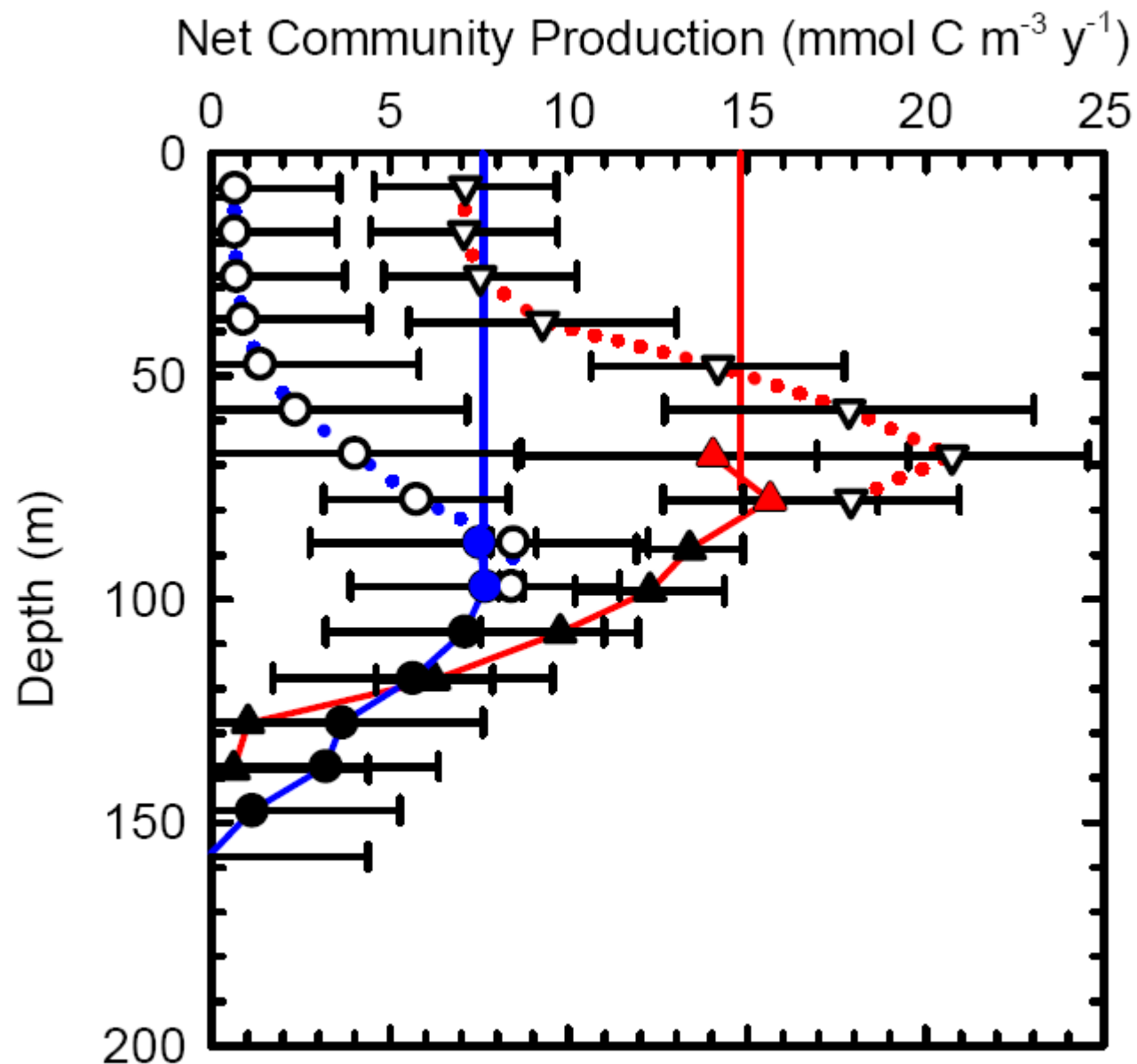
Oxygen residuals from least squares fit line at 78 m to 3/4 year of HOT data.  
A normal distribution with standard deviation =  $1.5 \mu\text{mol/kg}$ .

Random analytical error. NO EVIDENCE FOR EPISODICITY IN MOST OF  
THE YEAR!









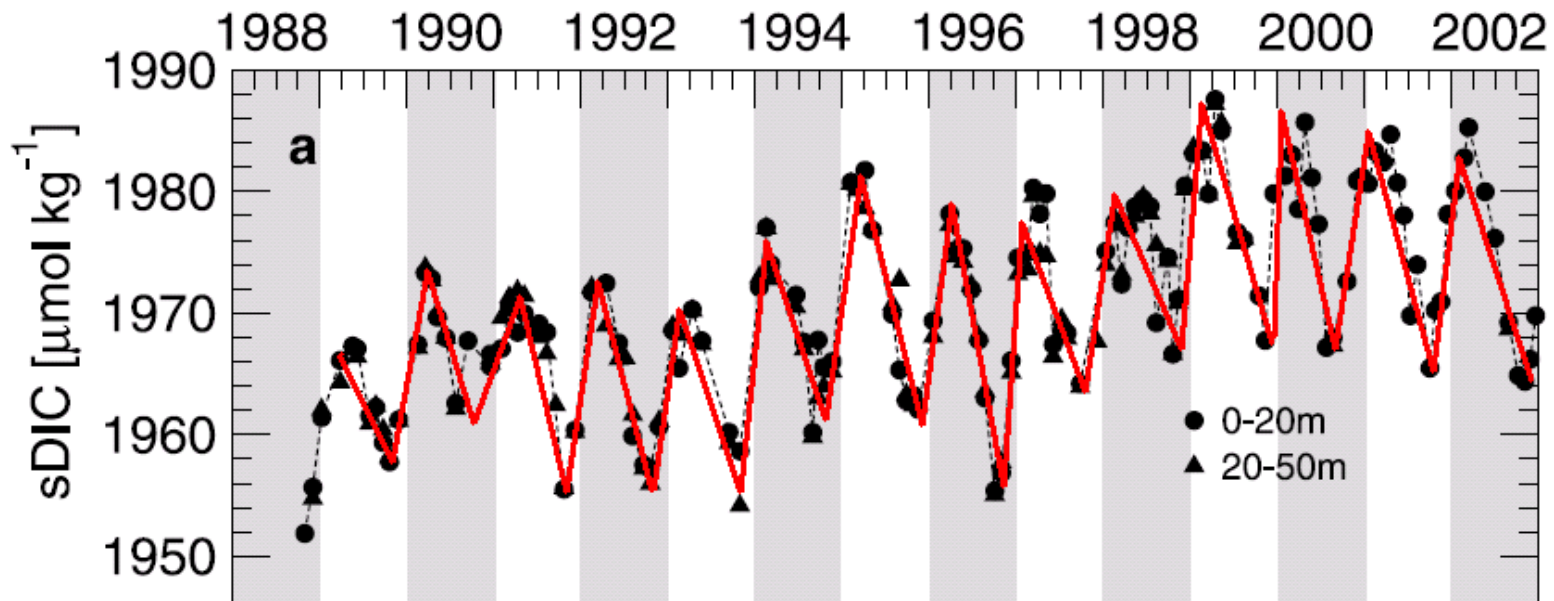
Vertically integrated  
Net Community  
Production at HOT =  
 $1.6 \pm 0.2 \text{ mol C/m}^2/\text{y}$ .

Keeling et al. (2004)  
summarized 11 other  
measurements that  
average  $1.9 \pm 0.6 \text{ mol C/m}^2/\text{y}$ .

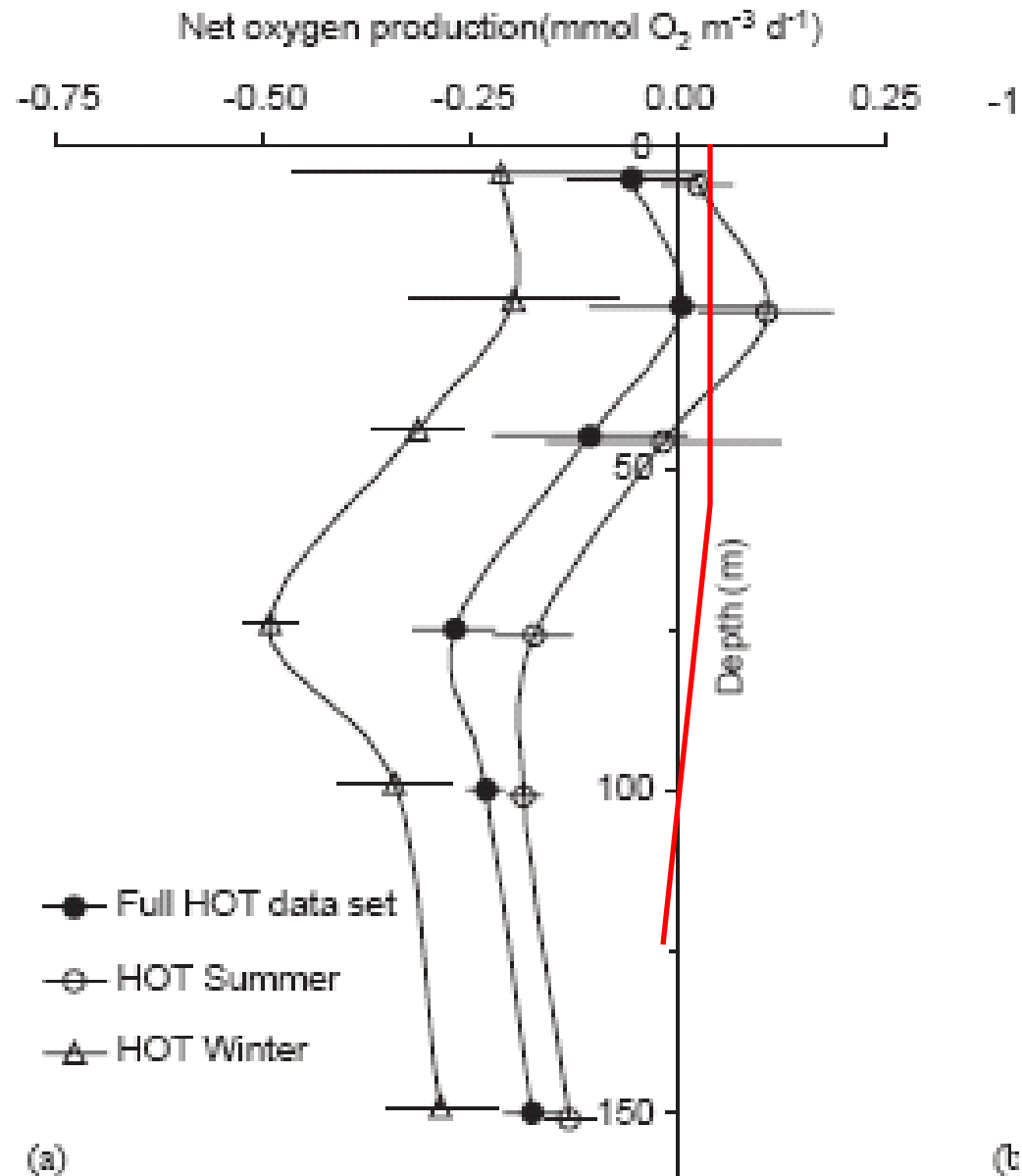
At 22 S, vertical integral  
of NCP =  $0.9 \pm 0.4 \text{ mol C/m}^2/\text{y}$ . About  $\frac{1}{2}$  the  
magnitude of NCP at  
HOT, as expected.

Cycle of Dissolved Inorganic Carbon at surface looks very similar to  $O_2$  cycle below mixed layer. DIC equilibrates with atmosphere 10x more slowly than  $O_2$ .

KEELING ET AL.: SEASONAL CYCLES AND TRENDS AT STATION ALOHA



Solution to measuring annual cycles near the surface would be a good pH sensor on a float.





# pH sensors allow TCO<sub>2</sub> and NCP to be estimated in mixed layer: Ion Selective Field Effect Transistor - ISFET

*P. Bergveld / Sensors and Actuators B 88 (2003) 1–20*

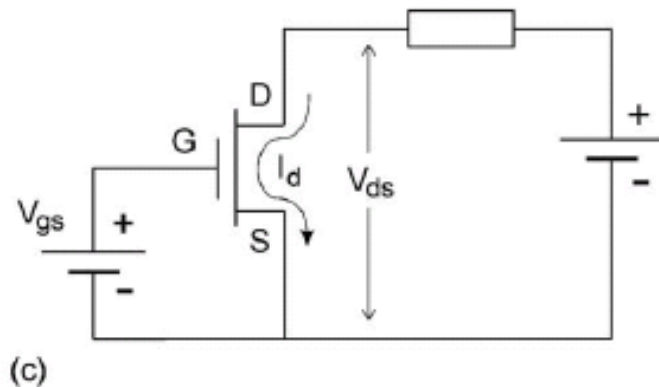
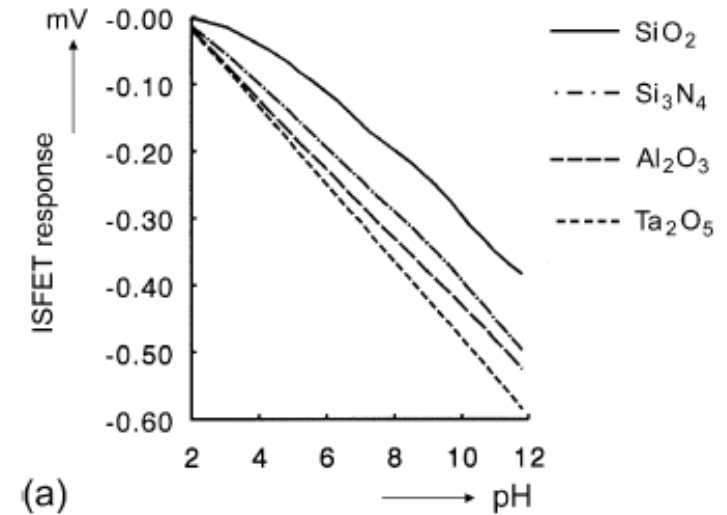
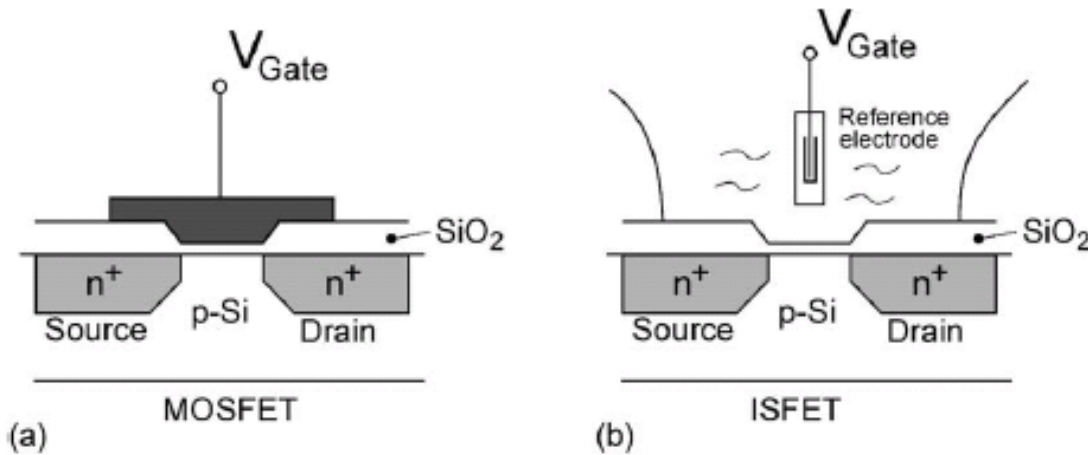
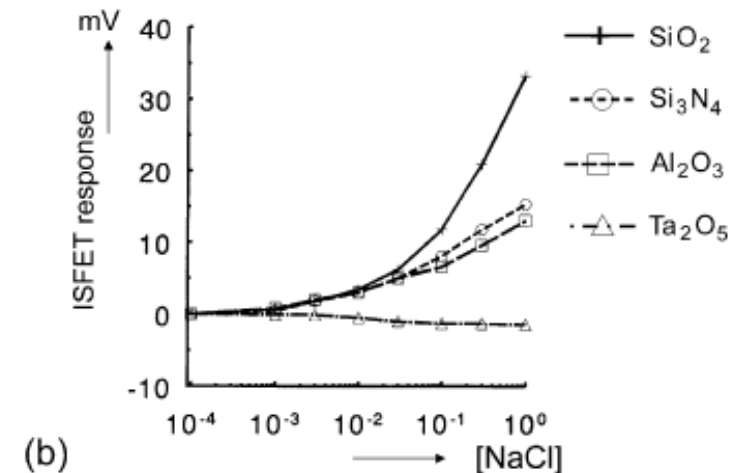
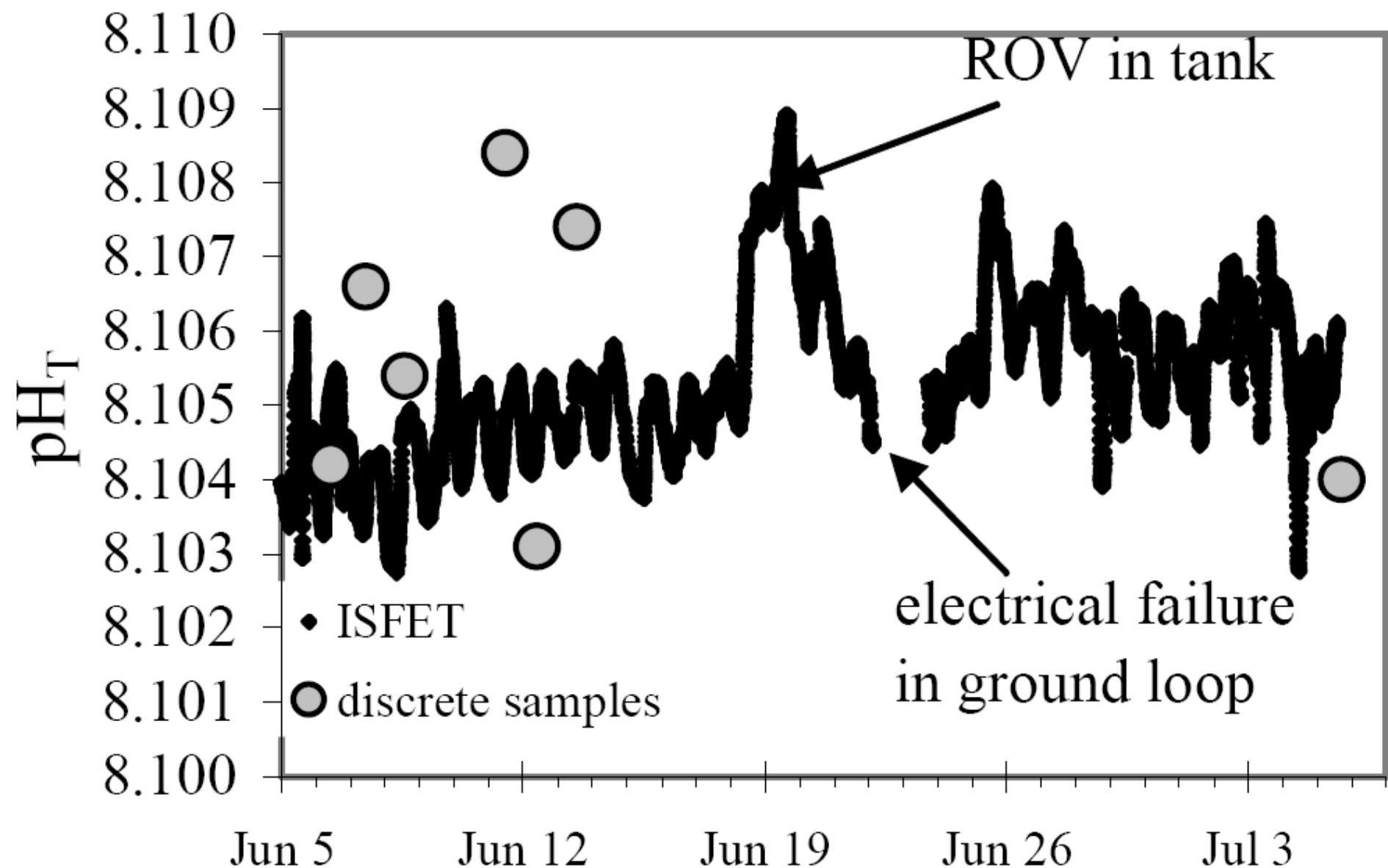
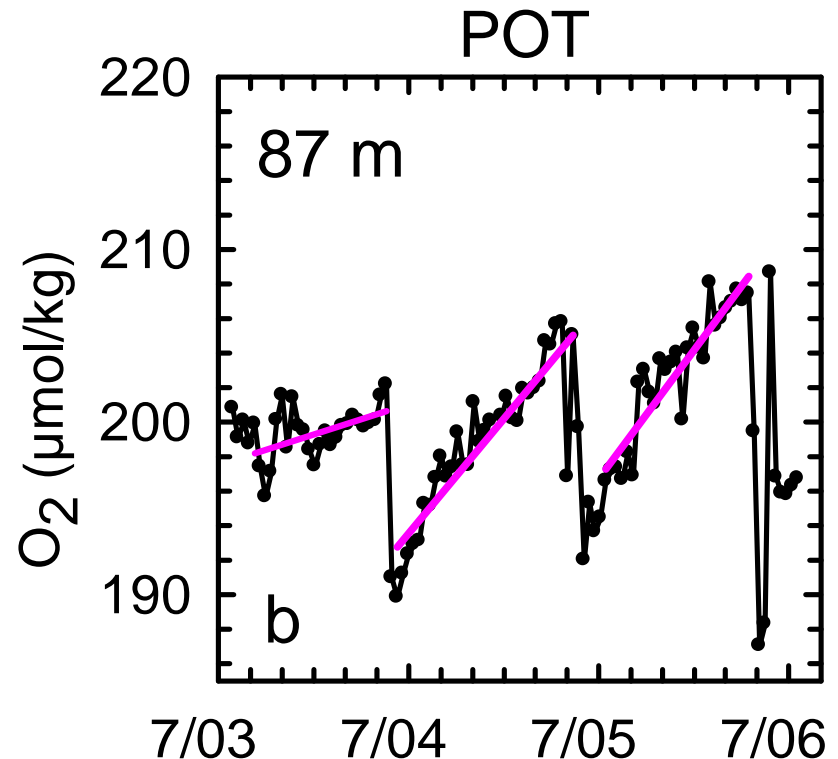
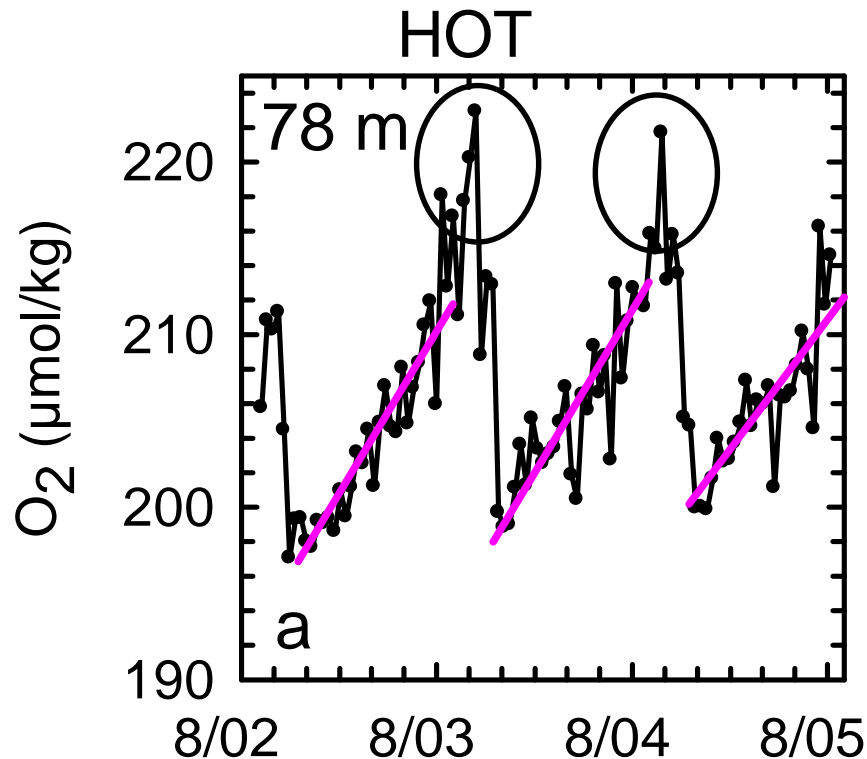


Fig. 3. Schematic representation of MOSFET (a), ISFET (b), and electronic diagram (c).

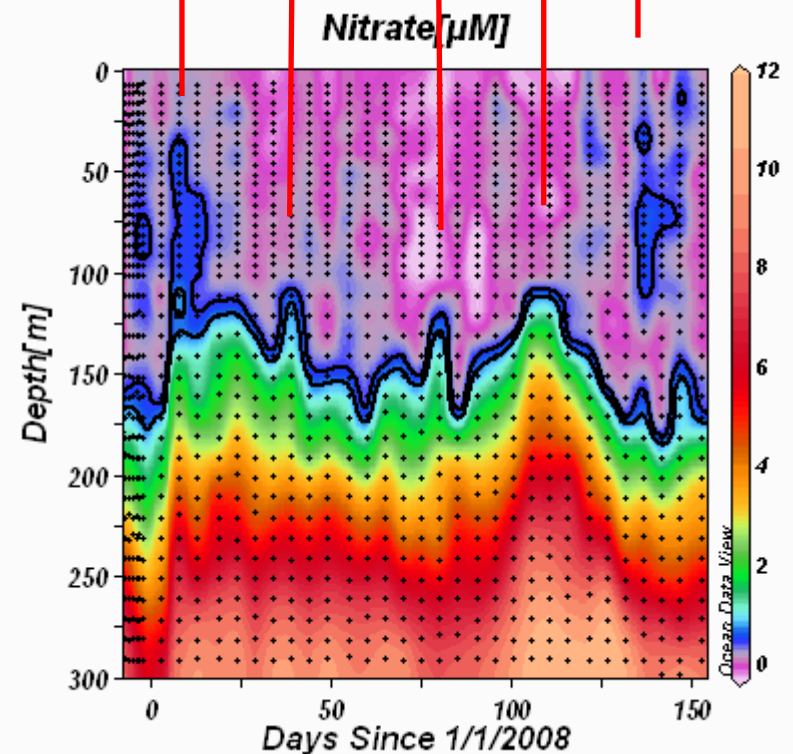
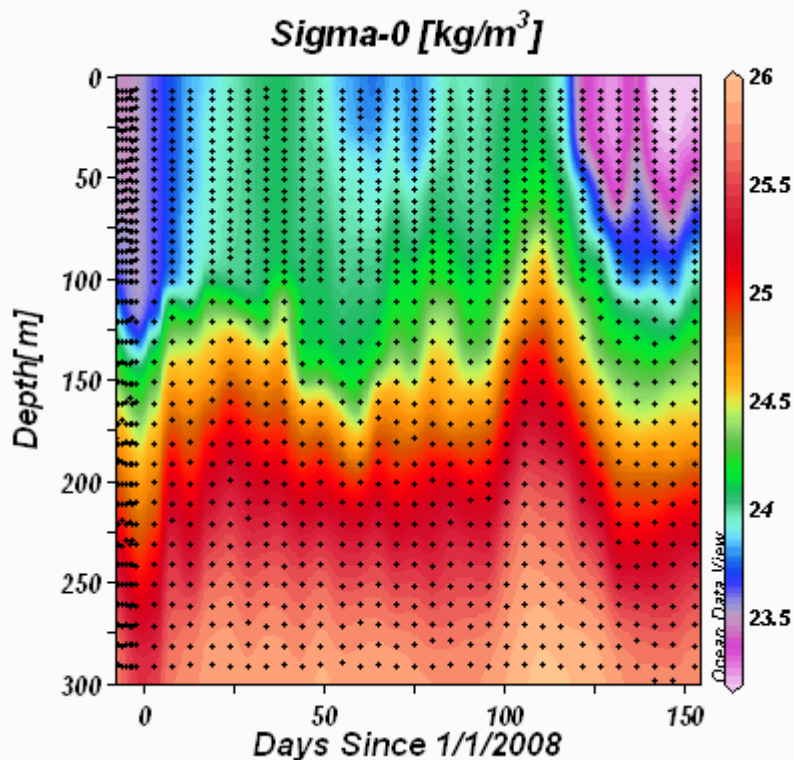
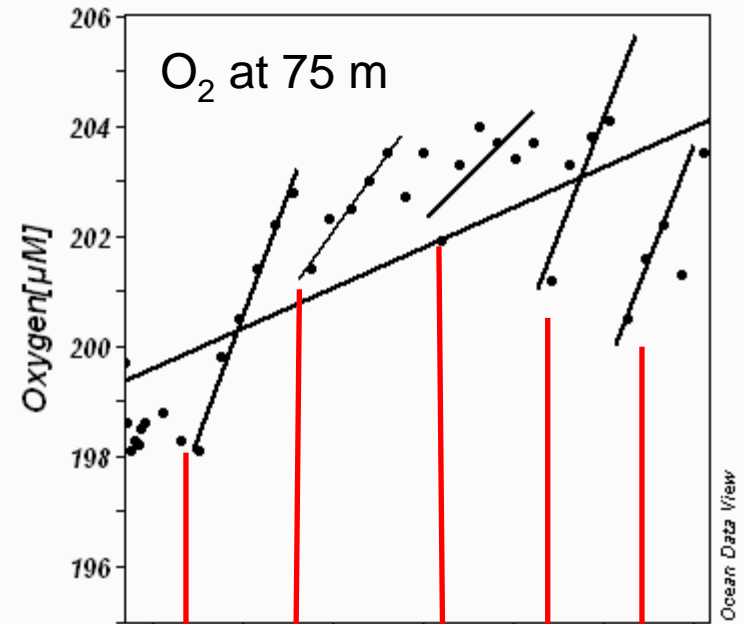




The ocean is autotrophic/has net positive oxygen and organic carbon production even in the regions with lowest concentration of plants. The real question is where do the nutrients come from that support this plant growth? Production may have episodic events, but episodes not required to sustain positive oxygen production.



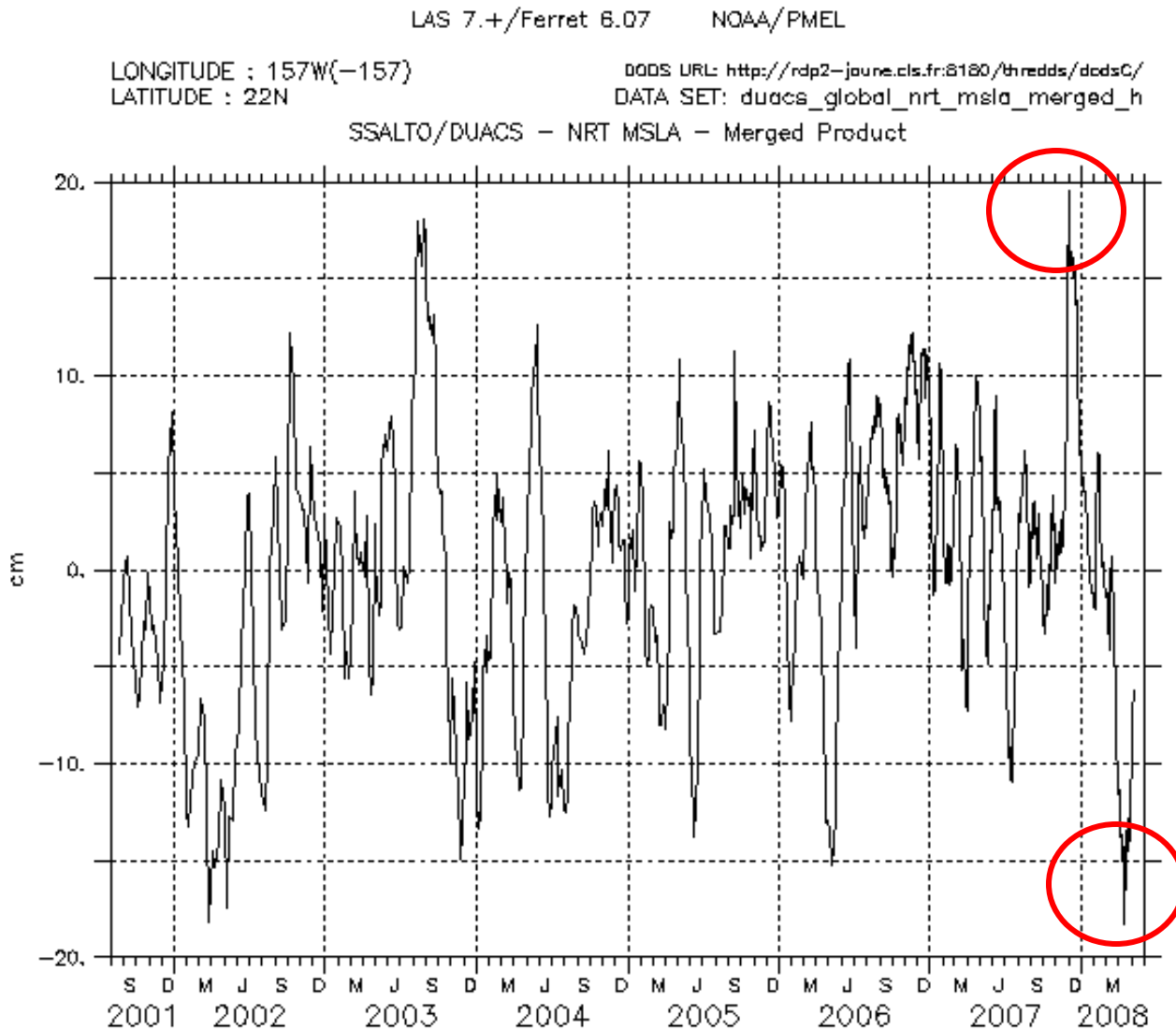
Sampling at higher frequency in 2008 (5 day cycle time versus 10 days in prior work), shows more episodic environment. Is 2008 an unusual year?





Dec 2007 to April 2008 was a fairly extreme period for mesoscale events.

Sea  
surface  
height  
anomaly  
(cm)



Maps of Sea Level Anomalies Merged (cm)