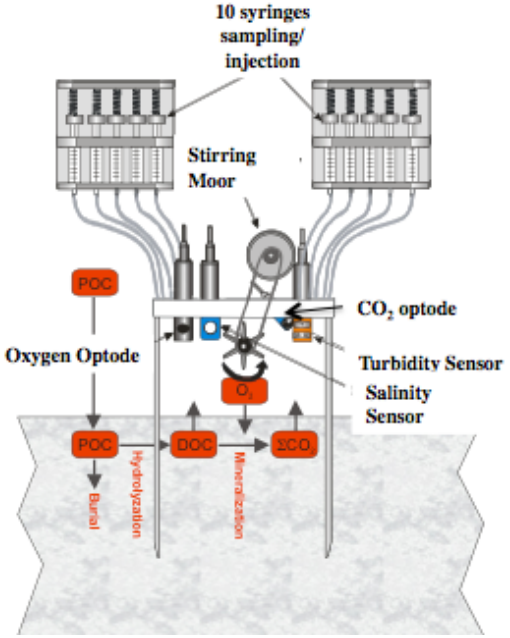
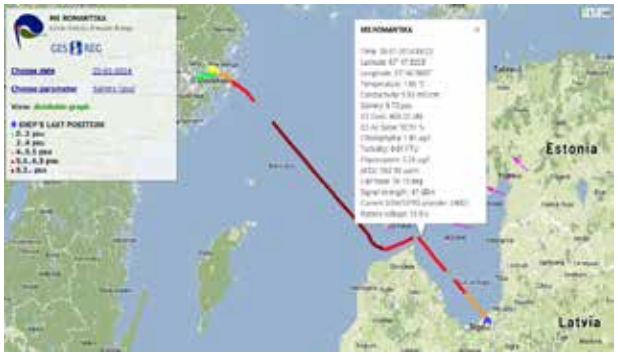
Oxygen measurements: why and when?

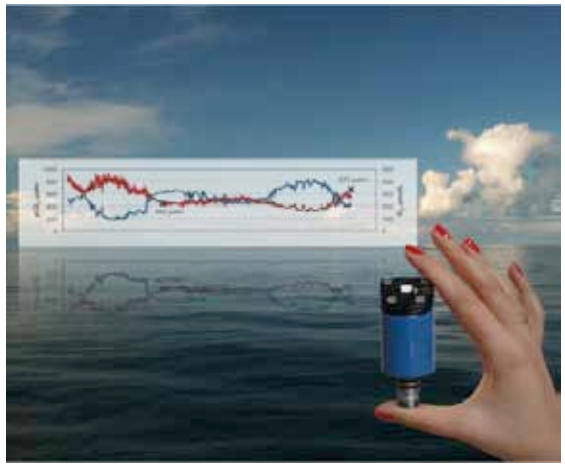
Anders Tengberg (anderste@chem.gu.se) Associate Professor at the University of Gothenburg and at the Chalmers University of Technology, Sweden, Scientific Advisor/Product Manager at Aanderaa since 1997.



Bottom

Water Column





Outline

9:00-10:30

- Why should you measure Oxygen (O_2)?
- How is O_2 related to other parameters?
- Are we measuring at the right frequencies?
- Methods to analyze and measure O_2

11:00-13:00

- What affects O_2 sensors/methods to evaluate performance?
- How good is Winkler titration?
- Field data, value of combined measurements
- Summary
- Practical Demonstration and Hands-On

Why should you measure Oxygen?

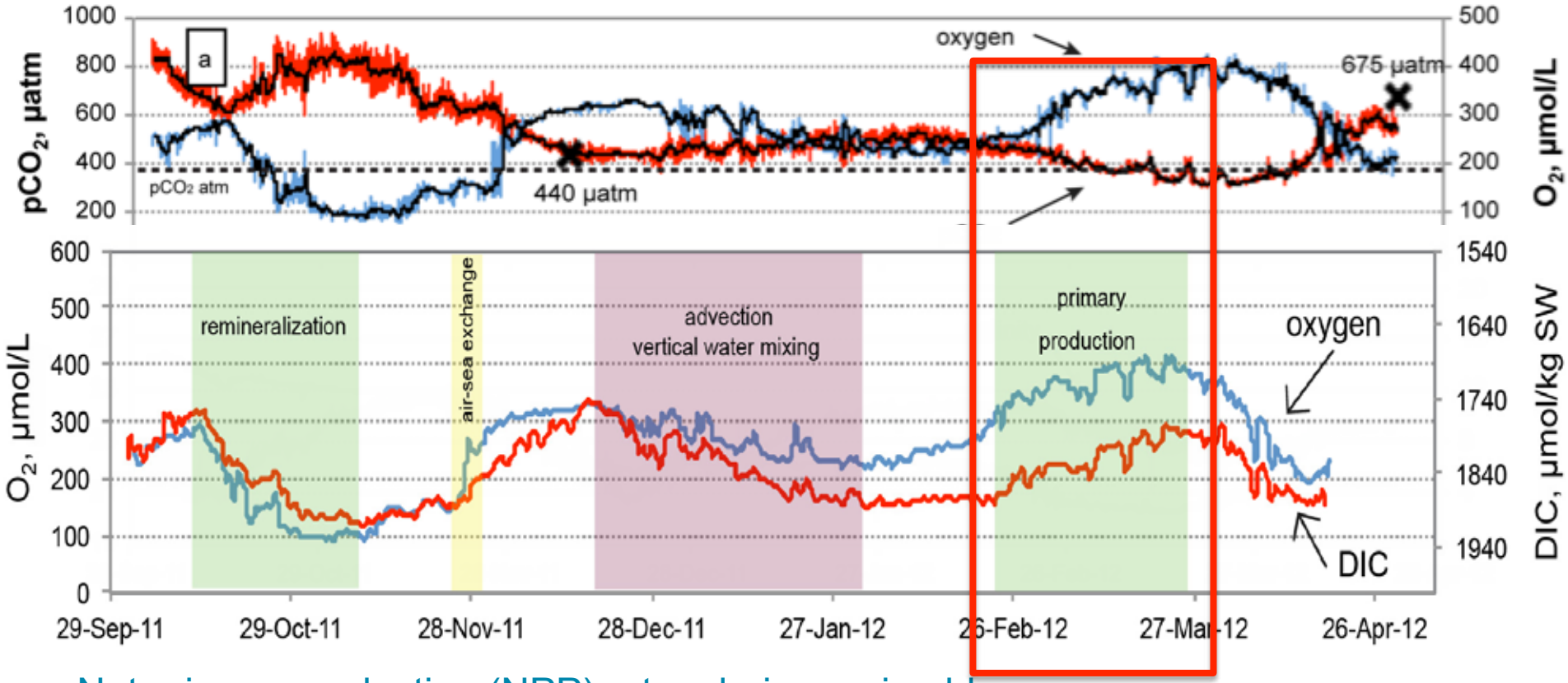
1. Most important parameter and "easy" to measure
2. Crucial for higher organisms (fish, bottom living)
3. Crucial for biological, chemical & geological processes
4. Oceanographic tracer
5. Climate related, geologically has O_2 been constant?

How is Oxygen related to other parameters?

1. Temperature: higher Temp less O_2
2. Salinity: higher Sal lower O_2
3. Currents: higher currents more turbulence/more mixing
4. pH/pCO_2: depends on process in O_2 rich conditions
   in general higher pH → lower pCO_2 → higher O_2
5. ChlA→higher O_2; Turbidity→lower O_2; CDOM→lower O_2
   Light→ higher O_2

pCO_2 optode and O_2 optode at the depth of 12.6

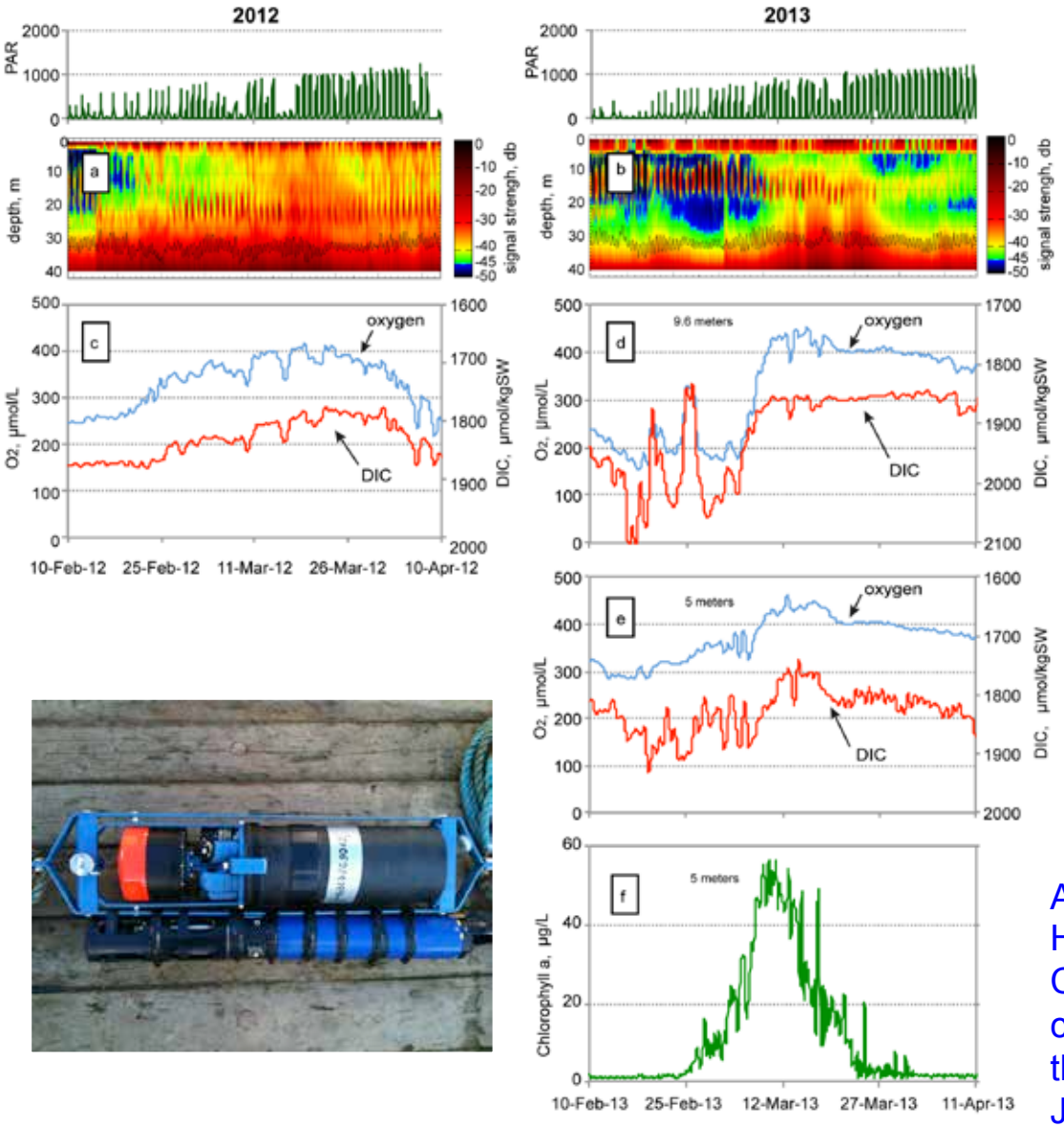
Salinity derived Alkalinity



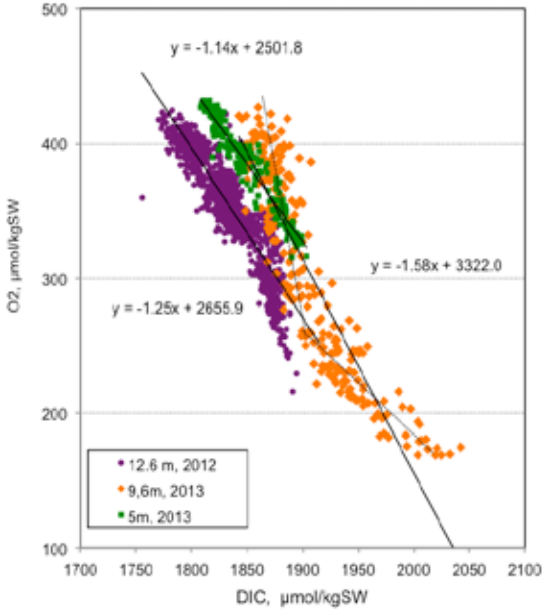
Net primary production (NPP) rates during spring bloom

- In 2012: 1.79 g C m-2
- In 2013: 2.10 g C m-2

Combining sensors gives increased understanding

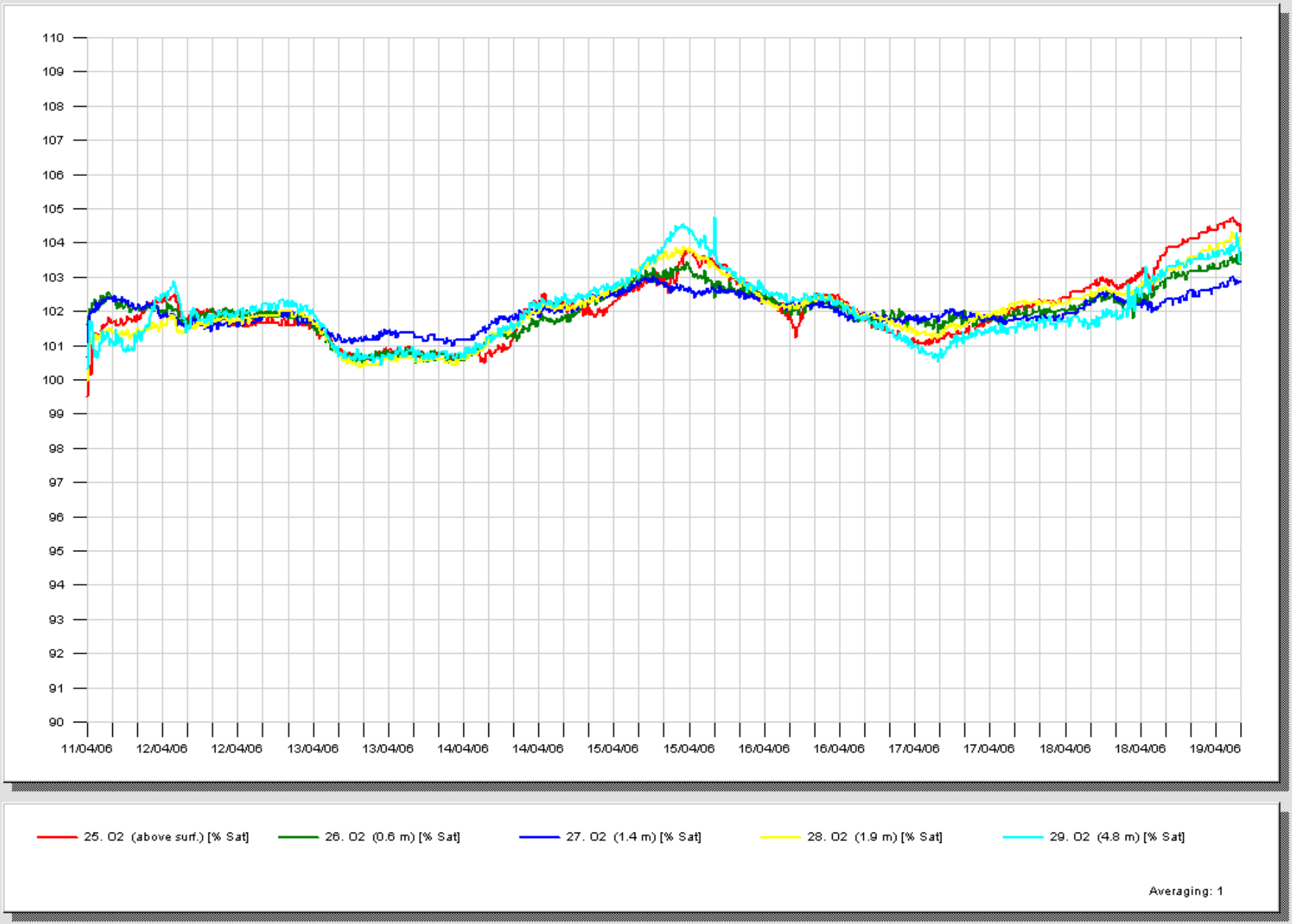


Redfield ratios
-C:O_2

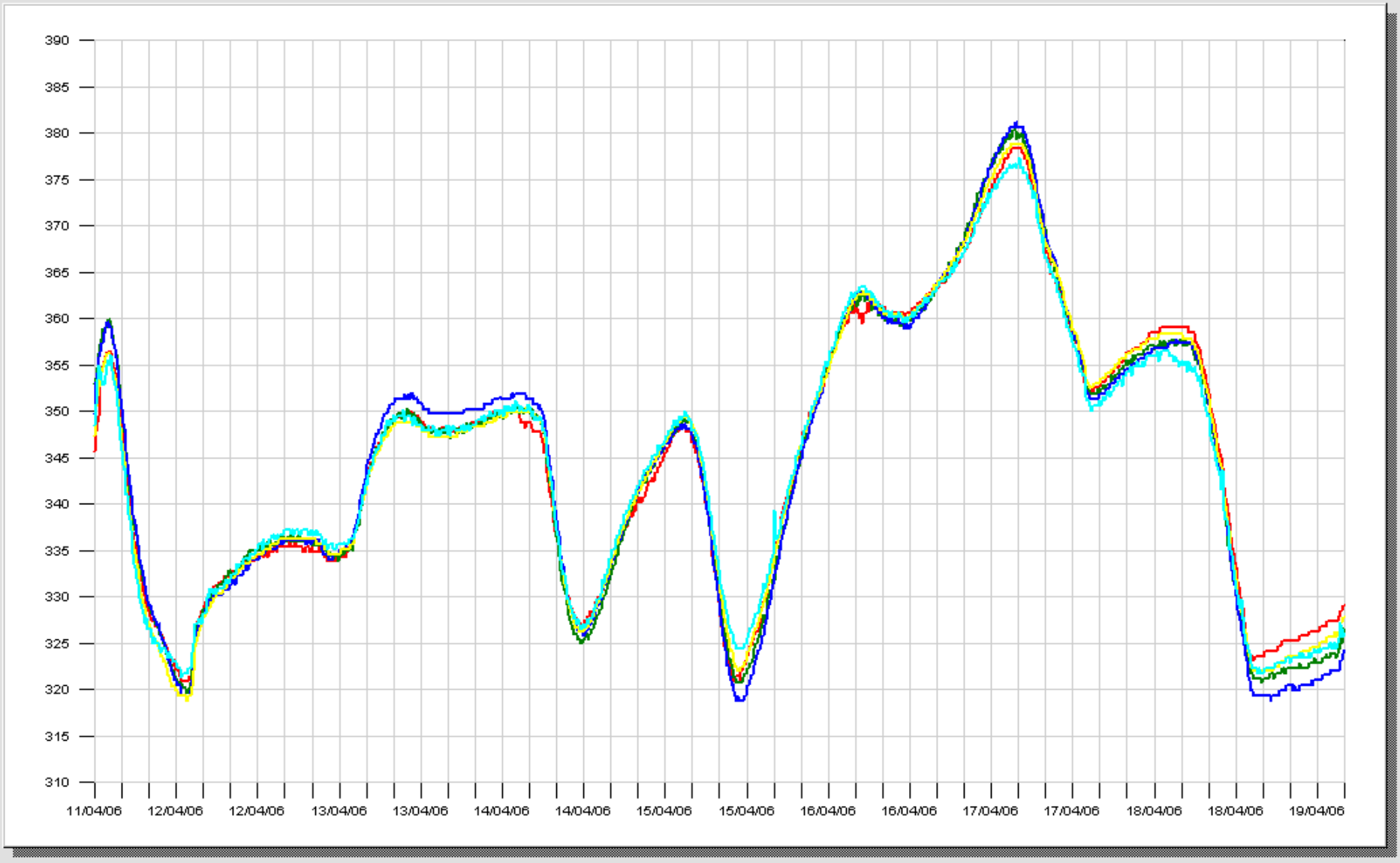


Atamanchuk, Kononets, Thomas, Hovdenes, Tengberg and Hall (2015) Continuous long-term observations of the carbonate system dynamics in the water column of a temperate fjord. Journal of Marine Systems 148, 272–284

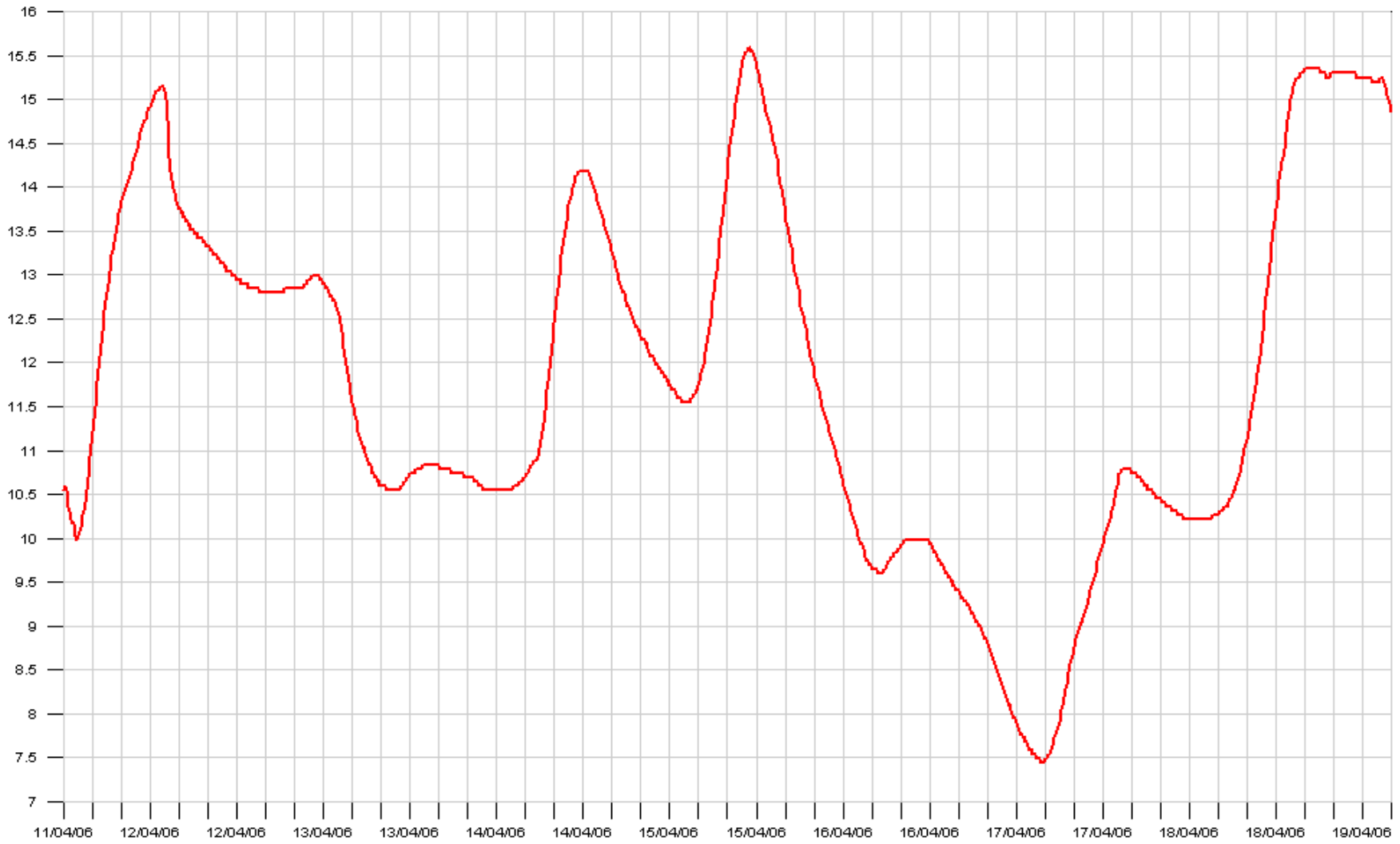
Optode postcheck in lab, airbubbled water (% saturation)



Optode postcheck in lab, airbubbled water



Optode post check in lab, airbubble water, Temperature



3. Temp. (0.8m) [deg.C]

Averaging: 1

What affects O_2 concentration?

1. Salinity and Temperature (Garcia and Gordon, 1992, L&O)
2. Primary production & bubbles, surface waters ~105%
3. Decomposition of organic matter
4. Chemical oxidation, mainly at the bottom
5. Air pressure, at surface
6. Hydrothermal vents, lower O_2

All sensors (electrochemical & optical) measure partial pressure (PO_2)

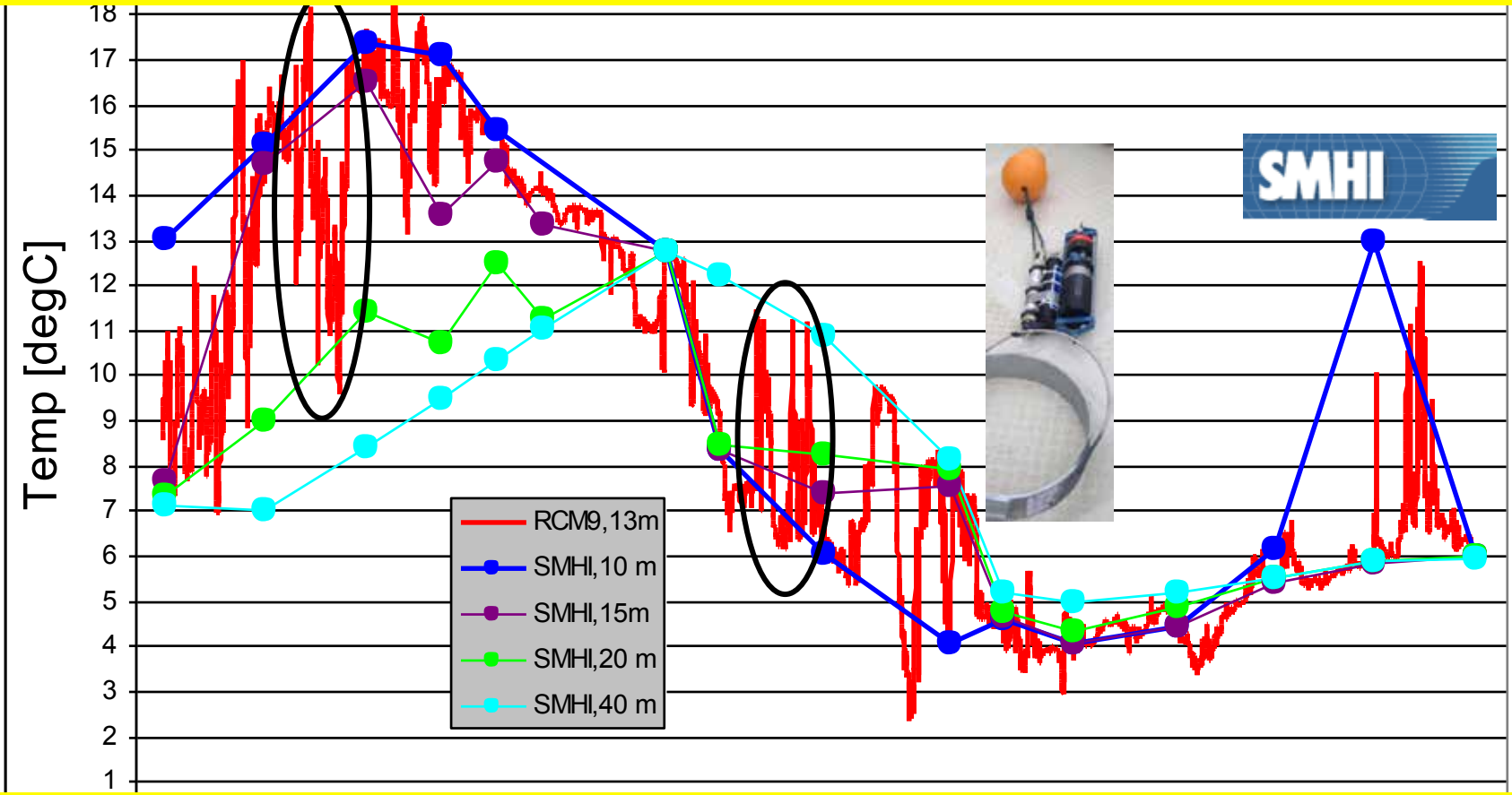
Outside the photic zone there is now known process that produce O_2

Oslo
Skagerrak
(Gothenburg)
Göteborg
Jönköping
Læsø
Ålborg
Kattegat
Anholt
Denmark
Århus
(Århus)
Öresund
Samsø
Sejerø
Endelave
Skåne Län
København
Malmö
Odense
Brandsø
Ærø

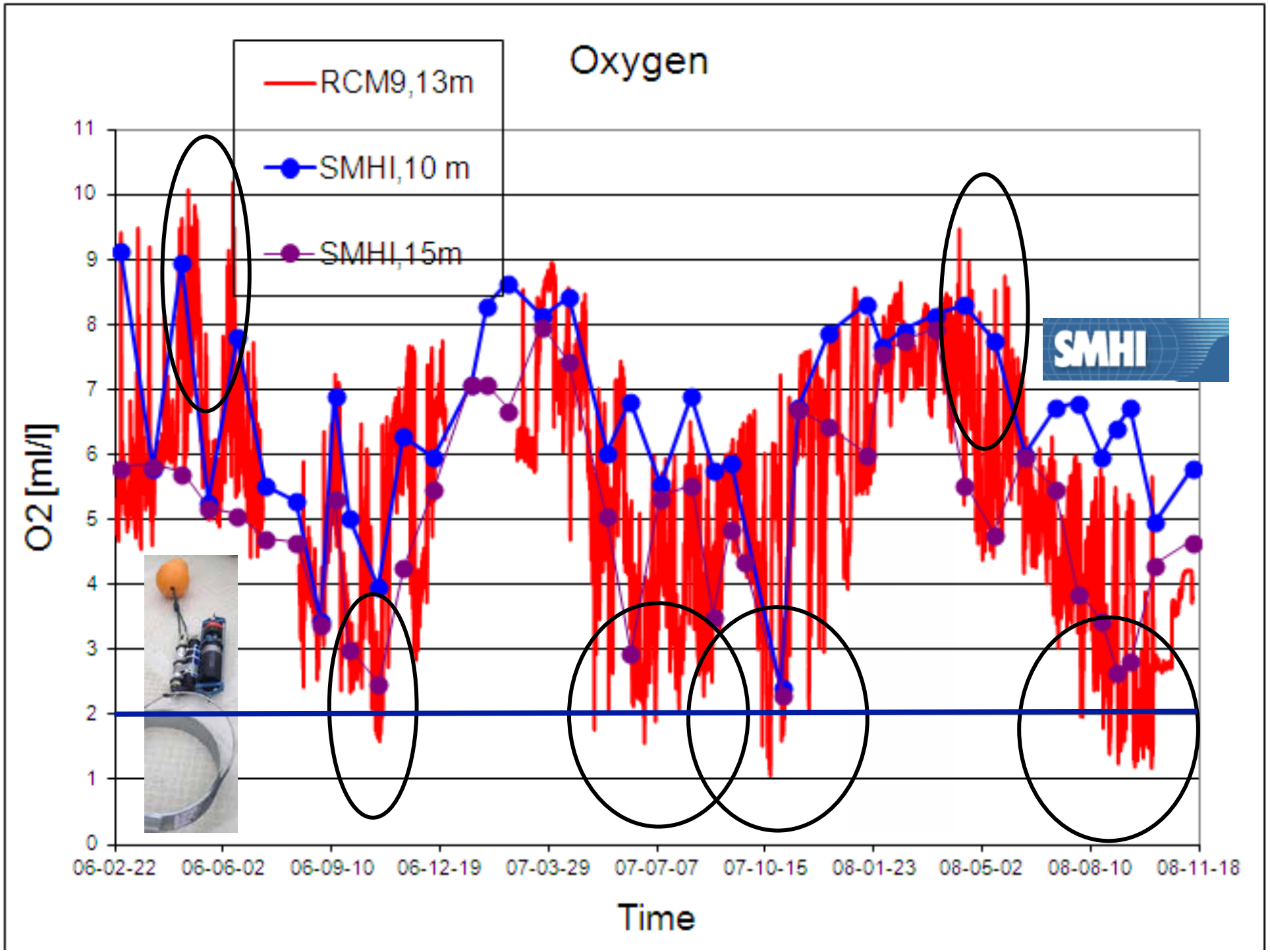
Natural variations, are we measuring at the right frequencies?

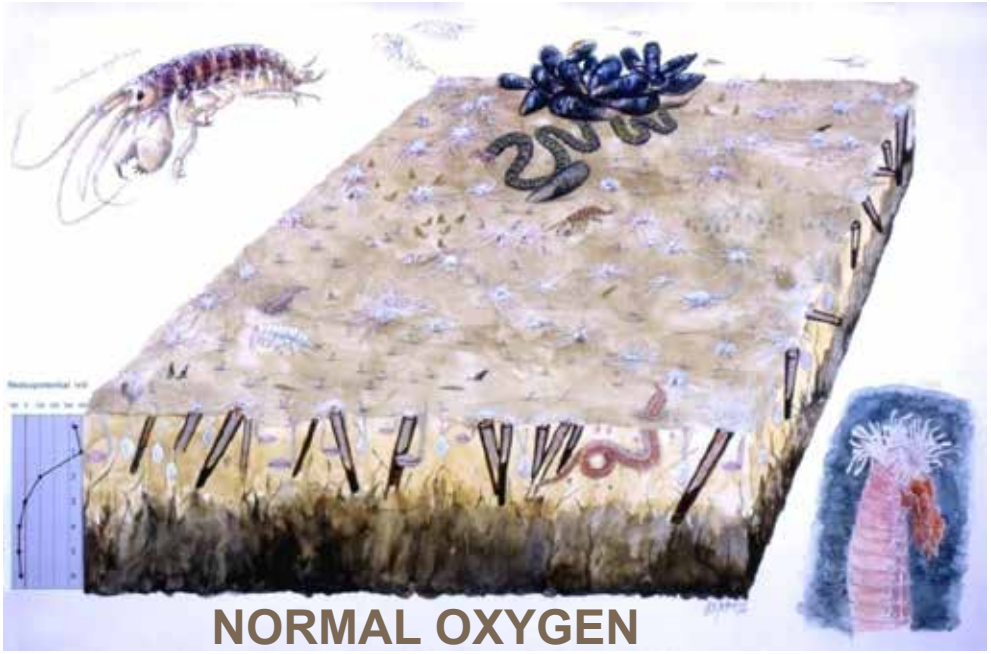
Temperature, June 12, 2007 to June 10 2008

Nyquist criteria → To understand changes Measurements should be done at twice the frequency that they occur



With weekly sampling maximal difference from one week to another was 9ºC
The average difference was 1.5ºC.
Estimated that global warming increase temp with about 0.06ºC/year

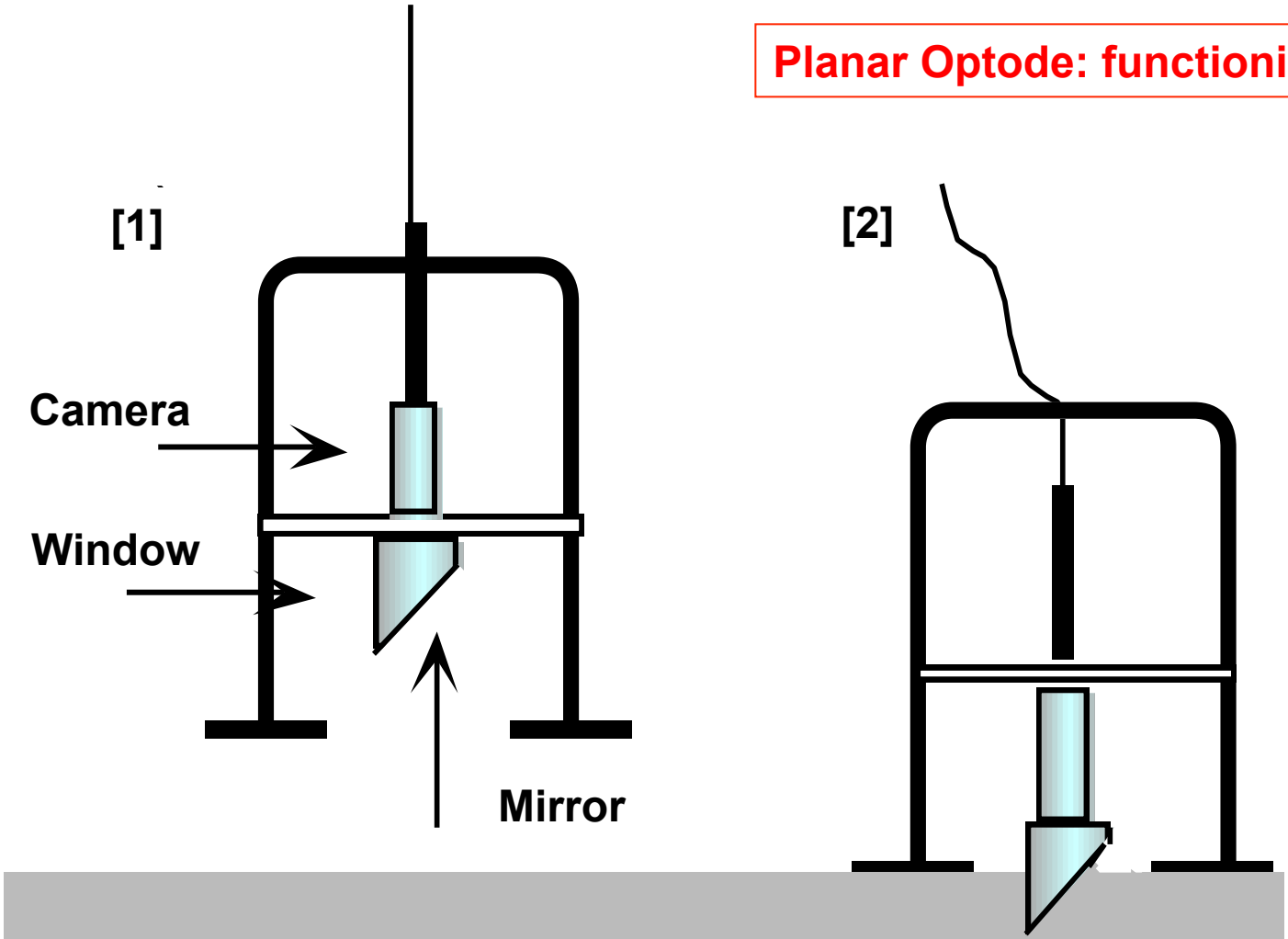

Oxygen
RCM9,13m
SMHI,10 m
SMHI,15m
O2 [ml/l]
0
1
2
3
4
5
6
7
8
9
10
11
06-02-22
06-06-02
06-09-10
06-12-19
07-03-29
07-07-07
07-10-15
08-01-23
08-05-02
08-08-10
08-11-18
Time
SMHI



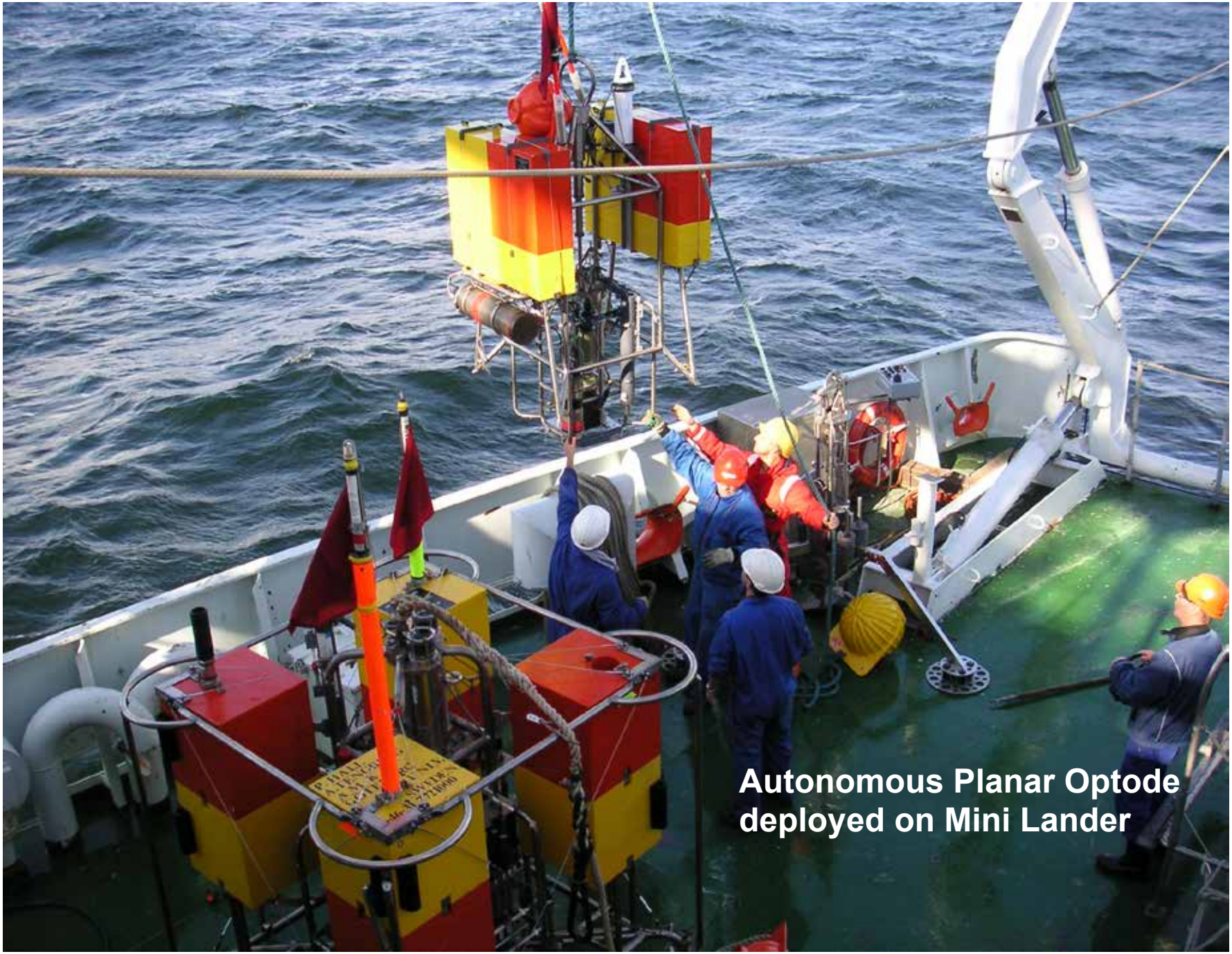
NORMAL OXYGEN

AFTER ANOXIA

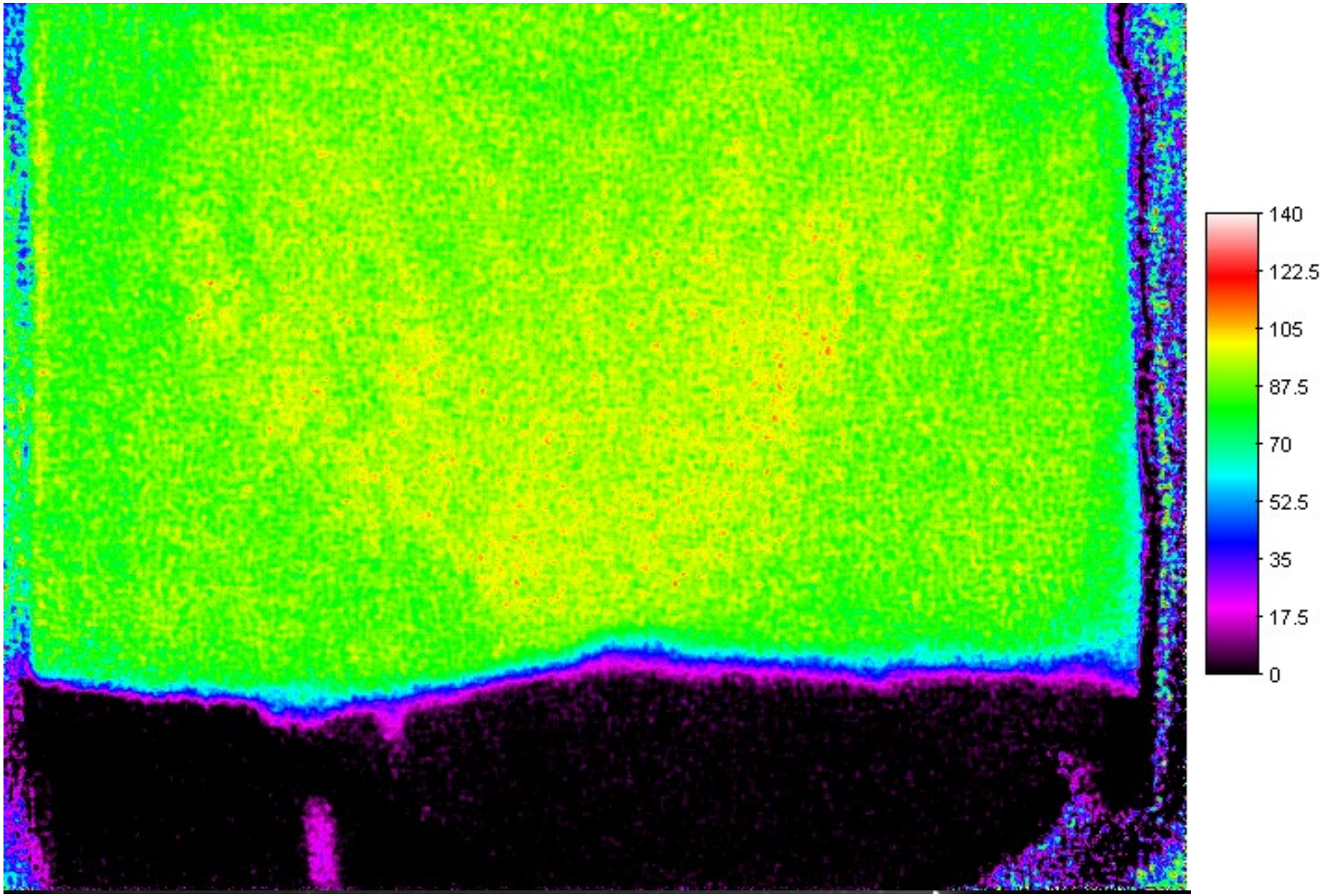
Planar Optode: functioning

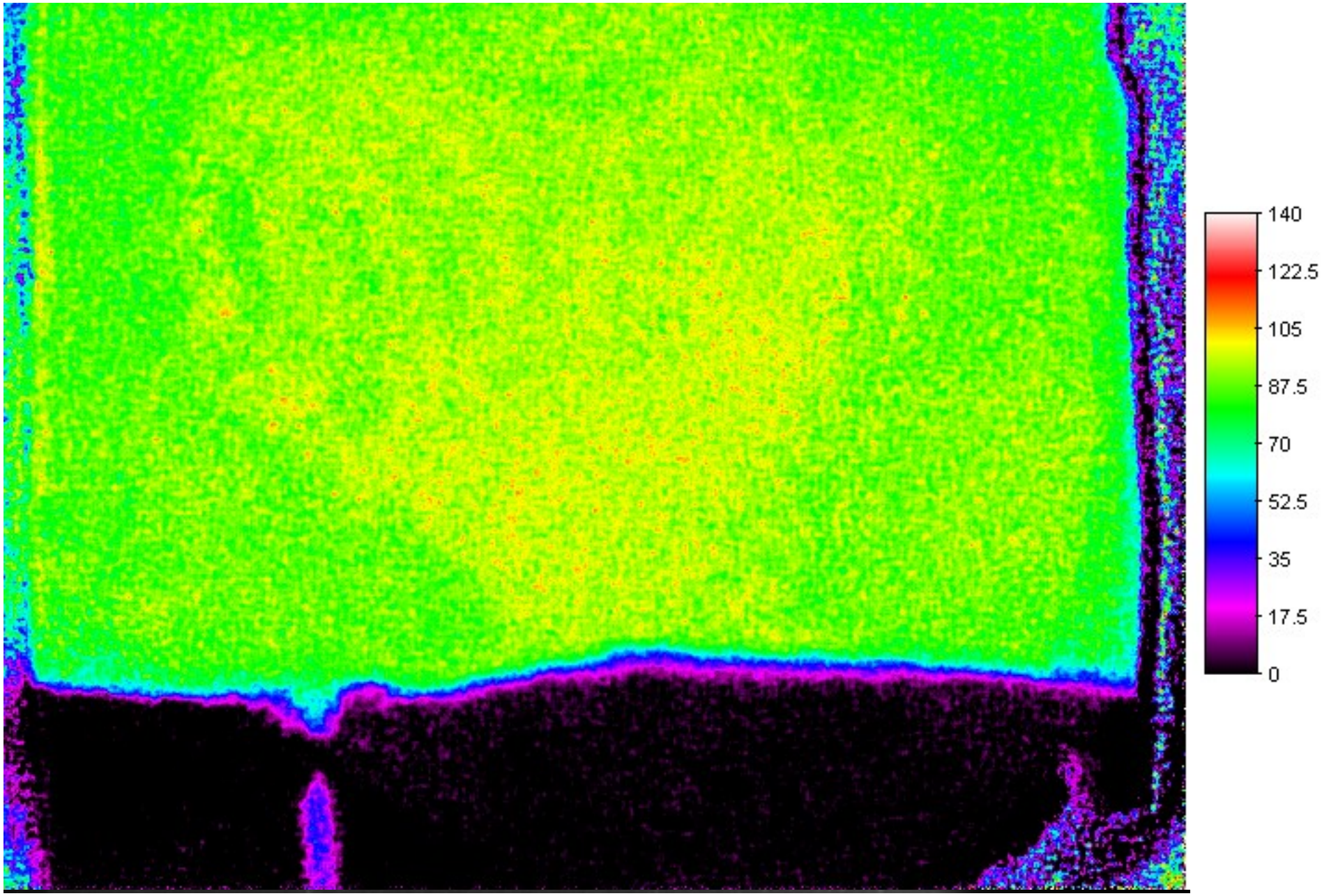


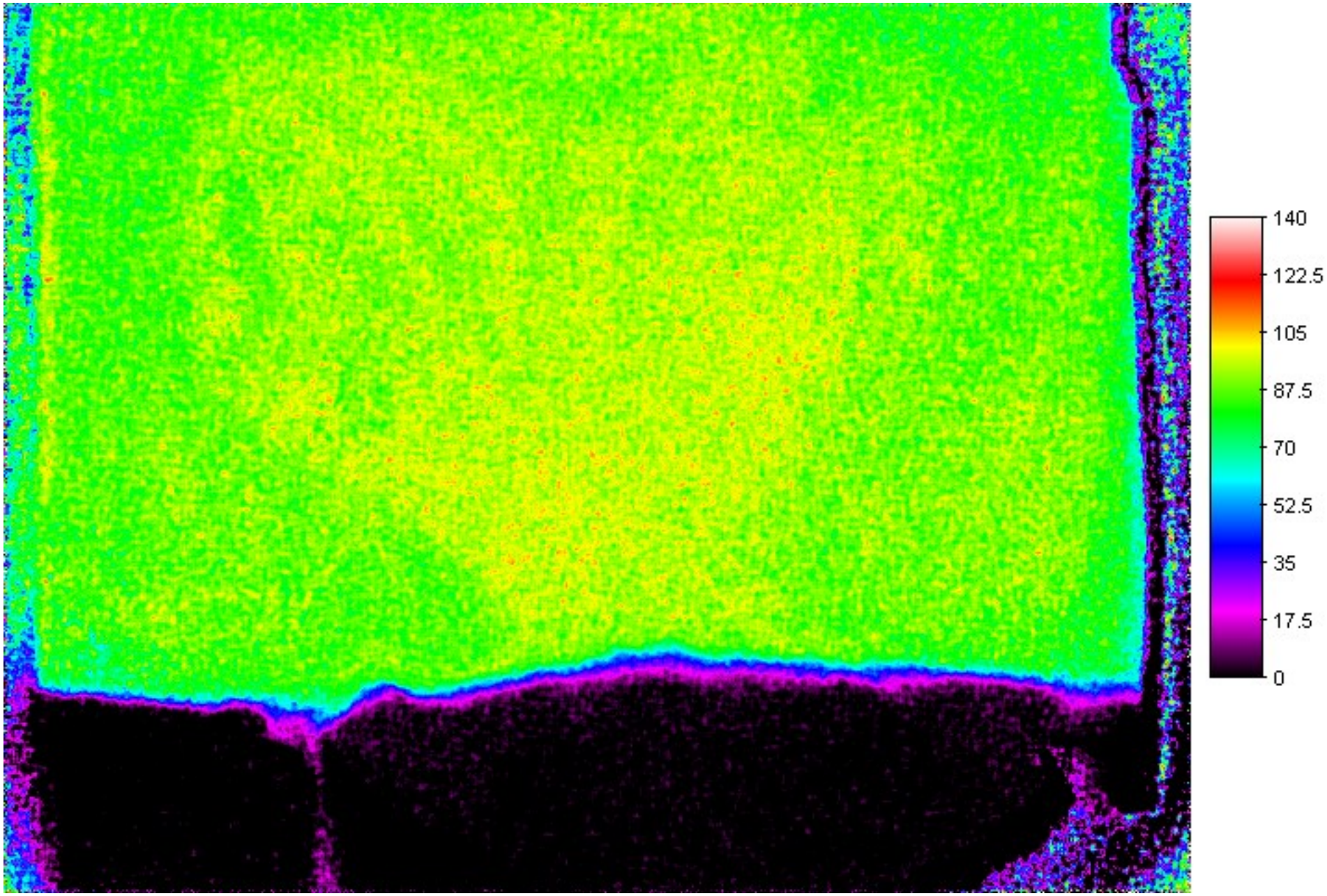
GLUD R.N, A. TENGBERG, M. KÜHL, P. HALL, I. KLIMANT and G. HOLST (2001) An in situ instrument for planar O2 optode measurements at benthic interfaces. *Limnology and Oceanography*, 46(8): 2073-2080



Autonomous Planar Optode
deployed on Mini Lander


140
122.5
105
87.5
70
52.5
35
17.5
0


140
122.5
105
87.5
70
52.5
35
17.5
0


140
122.5
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87.5
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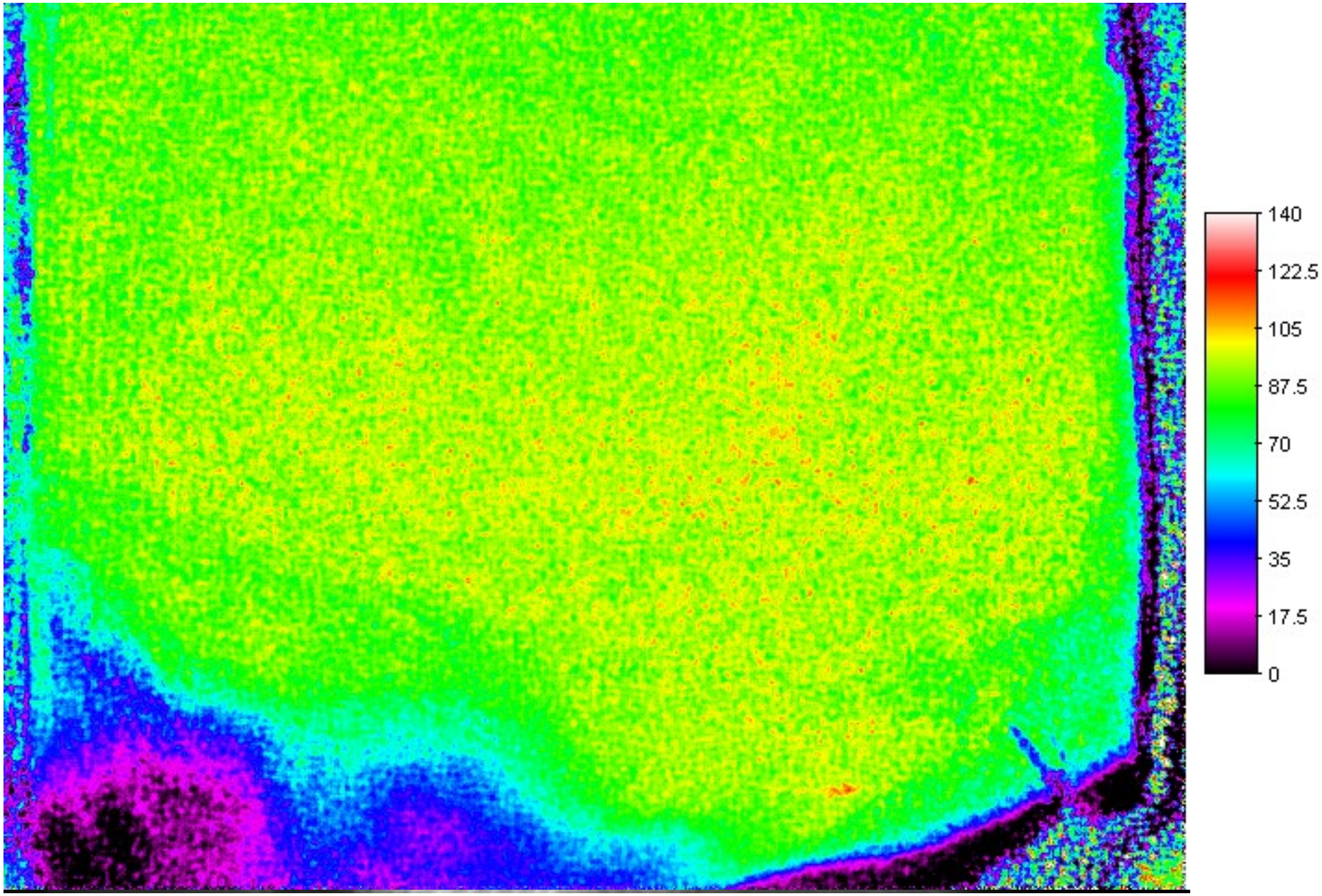
52.5
35
17.5
0

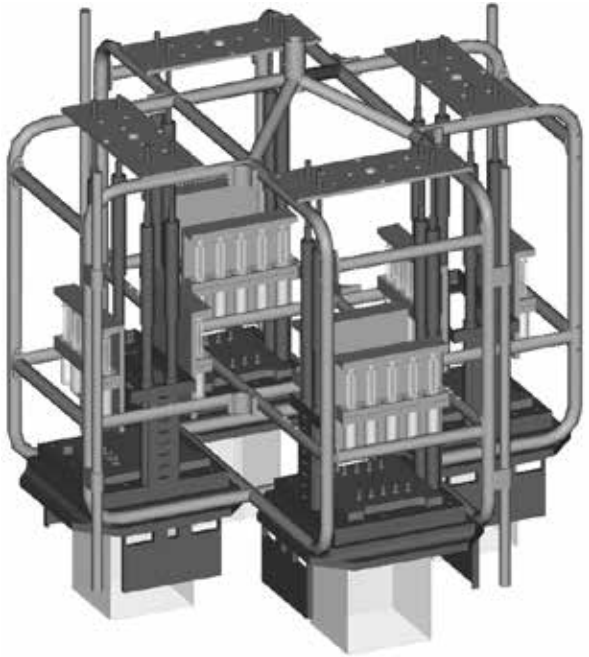

140
122.5
105
87.5
70
52.5
35
17.5
0

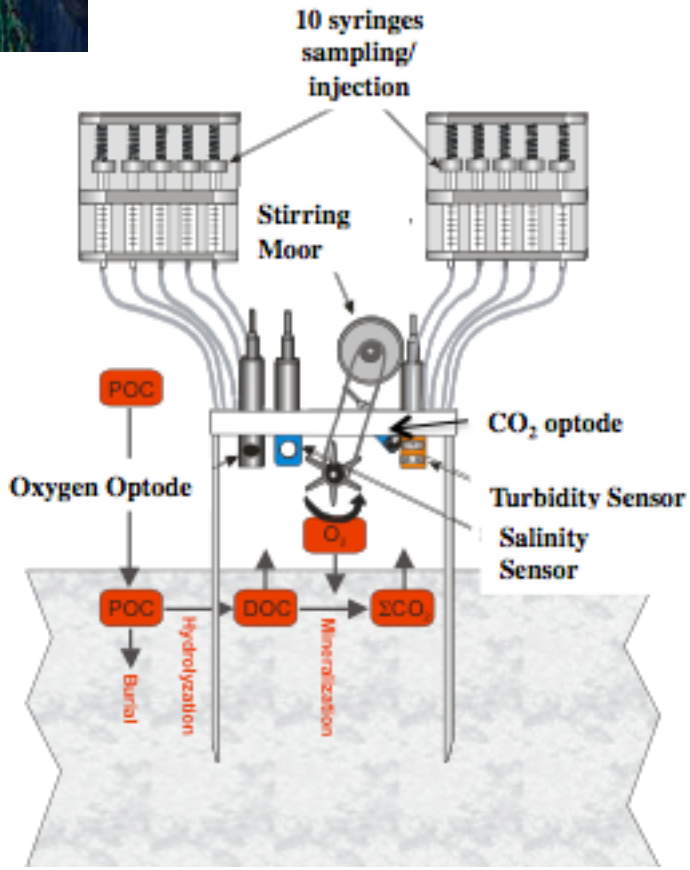
Tools: Autonomous Benthic landers

Our landers:

- 250-300 deployments
- About 800 incubations
- Deployed at 5-5600 m
- 40 water samples
- 15-25 sensors
- 95 % success rate

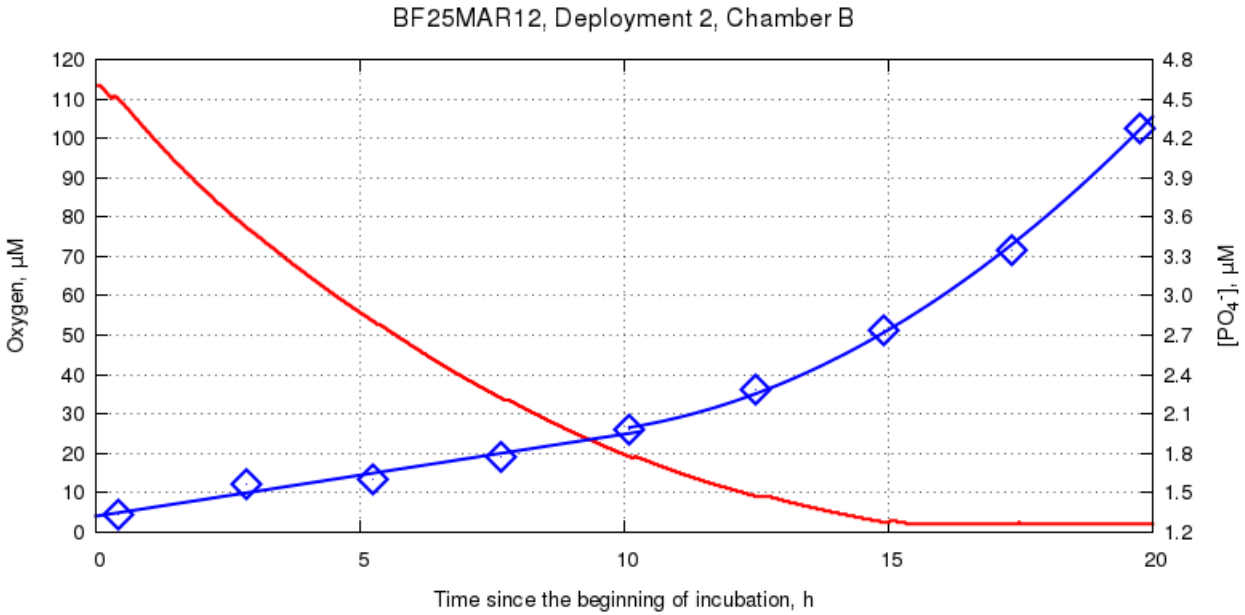
Inner frame
(4 incubations chamber modules)





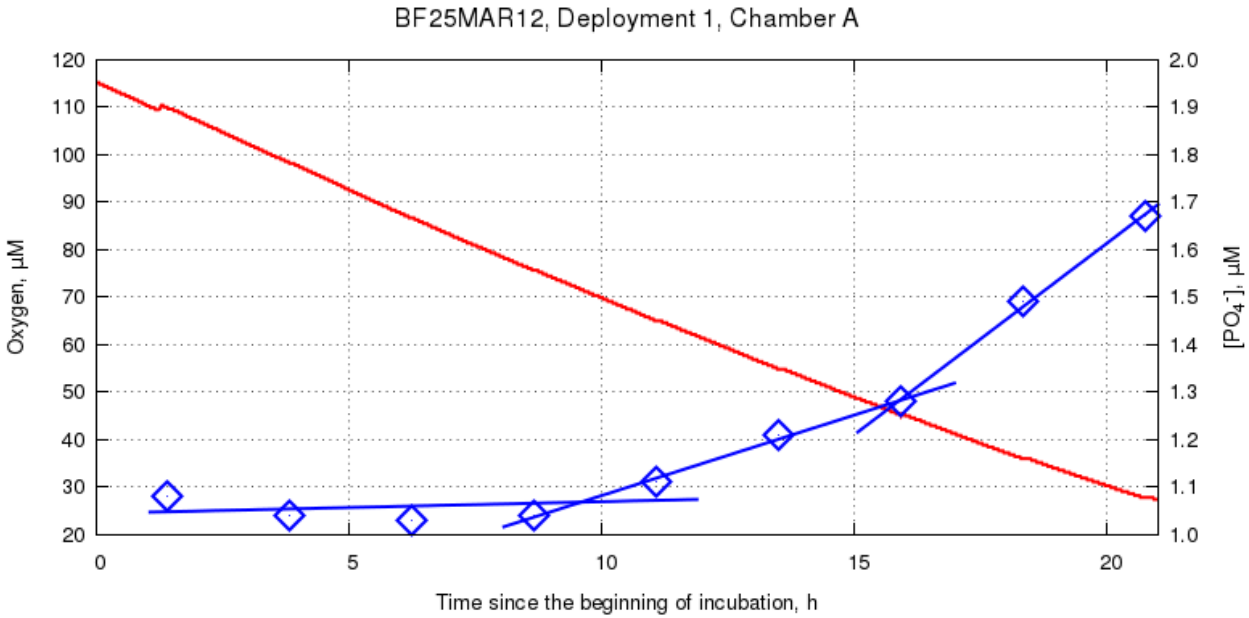
Measured Fluxes

- **Oxygen**
- Total Carbonate
- Silicate
- **Phosphate**
- Nitrate+Nitrite
- Ammonium
- DOC
- Alkalinity
- pH
- Fe and Mn
- Turbidity
- pCO_2



Red: Oxygen conc.
Blue: PO4 conc.
in benthic chambers

•For phosphate fluxes: Oxygen concentration more important than resuspension



Ways to measure Oxygen in Water

1. Chemical: Winkler titration (Winkler, 1888)
Accuracy: about 2%; Precision: about 0.5 %

Reference method

2. Electro-chemical: By sensors (Clark, 1959)
Accuracy: absolute measurements difficult, needs frequent calibration.
Precision: about 0.5 %

3A Optical: By sensors (Klimant et al., 1995)
Intensity based: Accuracy: absolute measurements difficult, needs frequent calibration.
Precision: about 0.5 %

3B. Optical: By sensors (Holst et al., 1995)
Lifetime based: Accuracy: about 1 %;
Precision: about 0.5 %

Summary

9:00-10:30

- Why should you measure Oxygen (O_2)?

Crucial parameter

- How is O_2 related to other parameters?

Related to most other parameters

- Are we measuring at the right frequencies?

Nyquist criteria: sample at twice the frequency as changes occur

- Methods to analyze and measure O_2

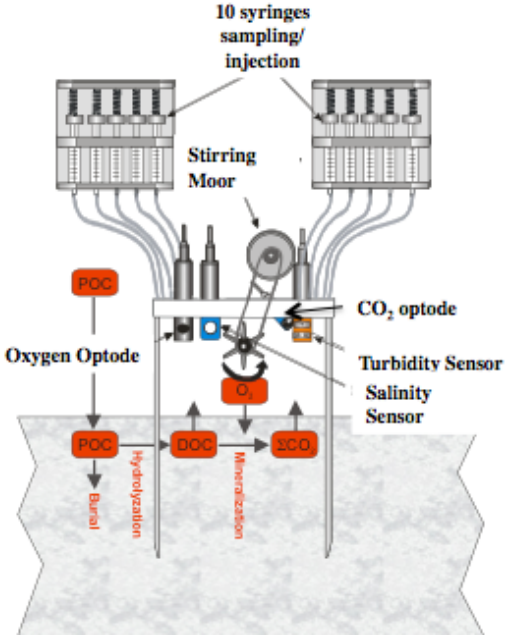
Winkler, Electrochemical sensors, Optical foil based sensors

11:00-13:00

- What affects O_2 sensors/methods to evaluate performance?
- How good is Winkler titration?
- Field data, value of combined measurements
- Summary
- Practical Demonstration and Hands-On

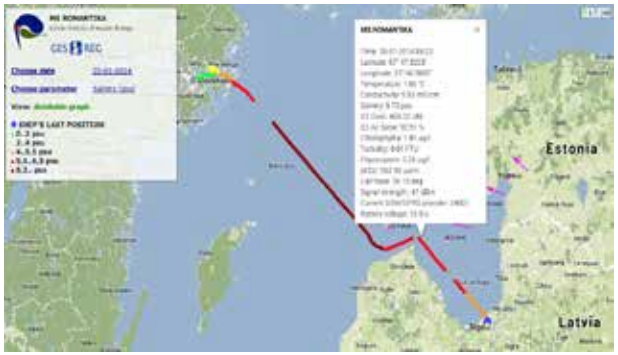
Oxygen measurements: how?

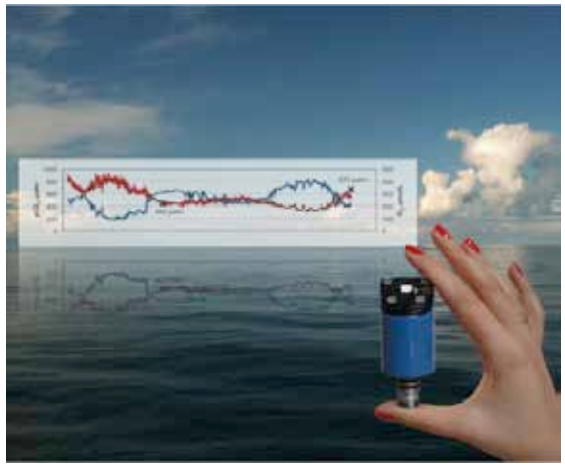
Anders Tengberg (anderste@chem.gu.se) Associate Professor at the University of Gothenburg and at the Chalmers University of Technology, Sweden, Scientific Advisor/Product Manager at Aanderaa since 1997.



Bottom

Water Column



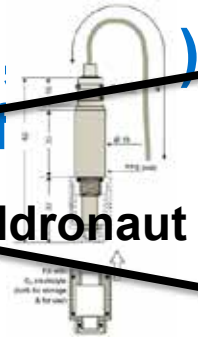


Ways to measure Oxygen in Water

1. Chemical: Winkler titration (Winkler, 1888)
Accuracy: about 2%; Precision: about 0.5 %

Reference method

~~2. Electro-chemical: By sensors (Clark)~~
~~Accuracy: absolut~~
~~Precision: about 0.~~



Careful with manufacturer specifications! Do they give field or lab specifications? Is response time for air or water? Is accuracy for the hole range of O2 Conc and Temp? Can they show data to sustain claimed accuracy/precision and response time? What about publications from independent sources?

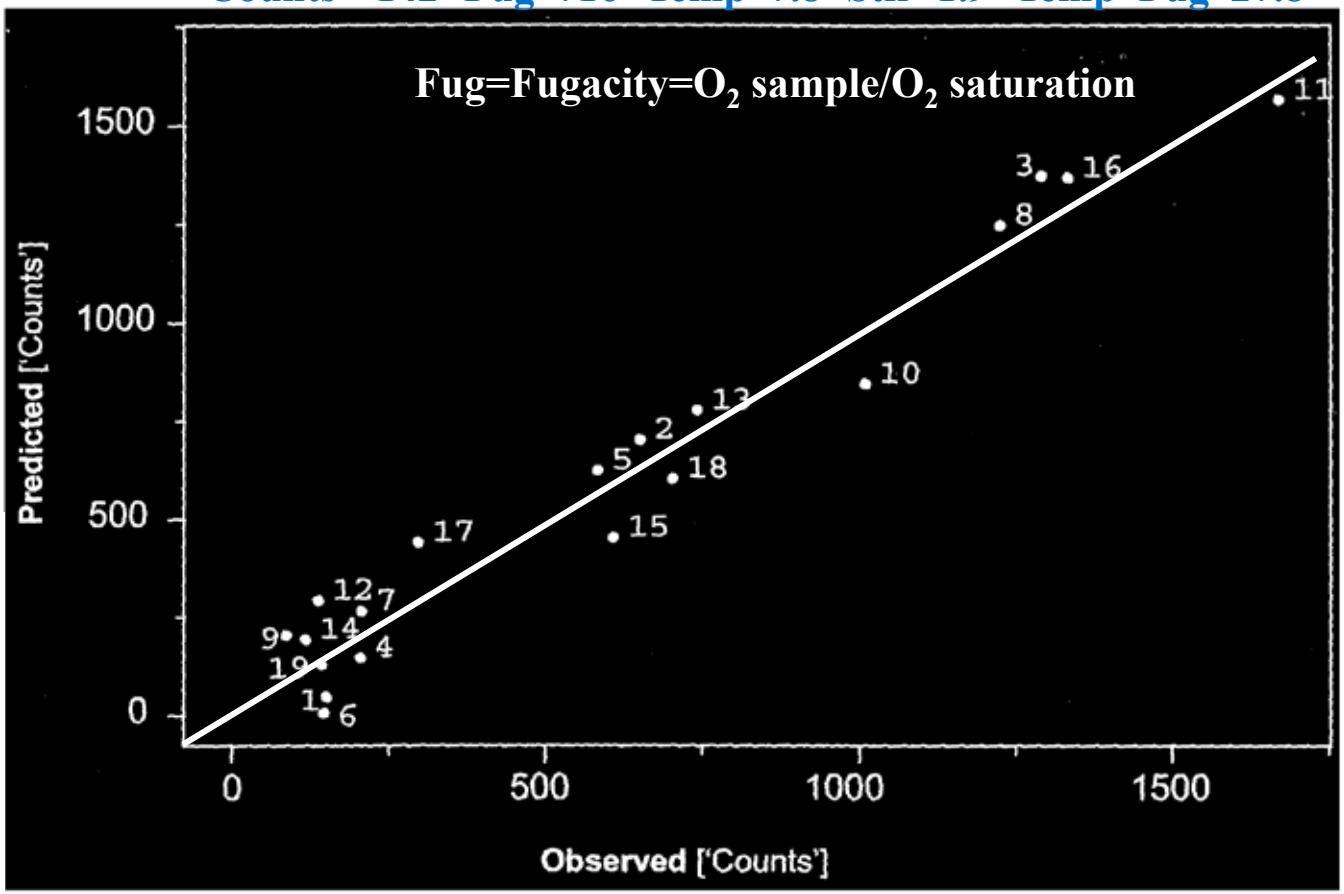
Precision: about 0.5 %

BERNTSSON, TENGBERG, HALL & JOSEFSSON (1997) Multivariate experimental methodology applied to the calibration of a Clark type oxygen sensor. Analytica and Chimica Acta, 355: 43-53

Cross-term

Counts=-142+Fug*716+Temp*7.8+Stir*1.9+Temp*Fug*27.8

Which Parameters will influence the response of an Electro-chemical sensor?



- O_2: Yes
- pH: No Effect
- Sal: Yes, cross-term
- Temp: Yes, cross-term
- Pres: Yes, not fully reversible
- Stirr: Yes
- Aging=drift: Yes, electrolyte & membrane decompose

Every sensor individual

Optode Measuring Principle Based on Fluorescence Quenching Detection of lifetime

Note: Oxygen Optodes are measuring partial pressure of oxygen.
- 100 % in sea water at 10ºC and 35 ppt corresponds to 282 µM = 9.0 mg/l = 6.3 ml/l
- 100 % in fresh water at 10ºC corresponds to 353 µM = 11.3 mg/l = 7.9 ml/l

→ **<u>If salinity variable it should be measured and compensated for</u>**

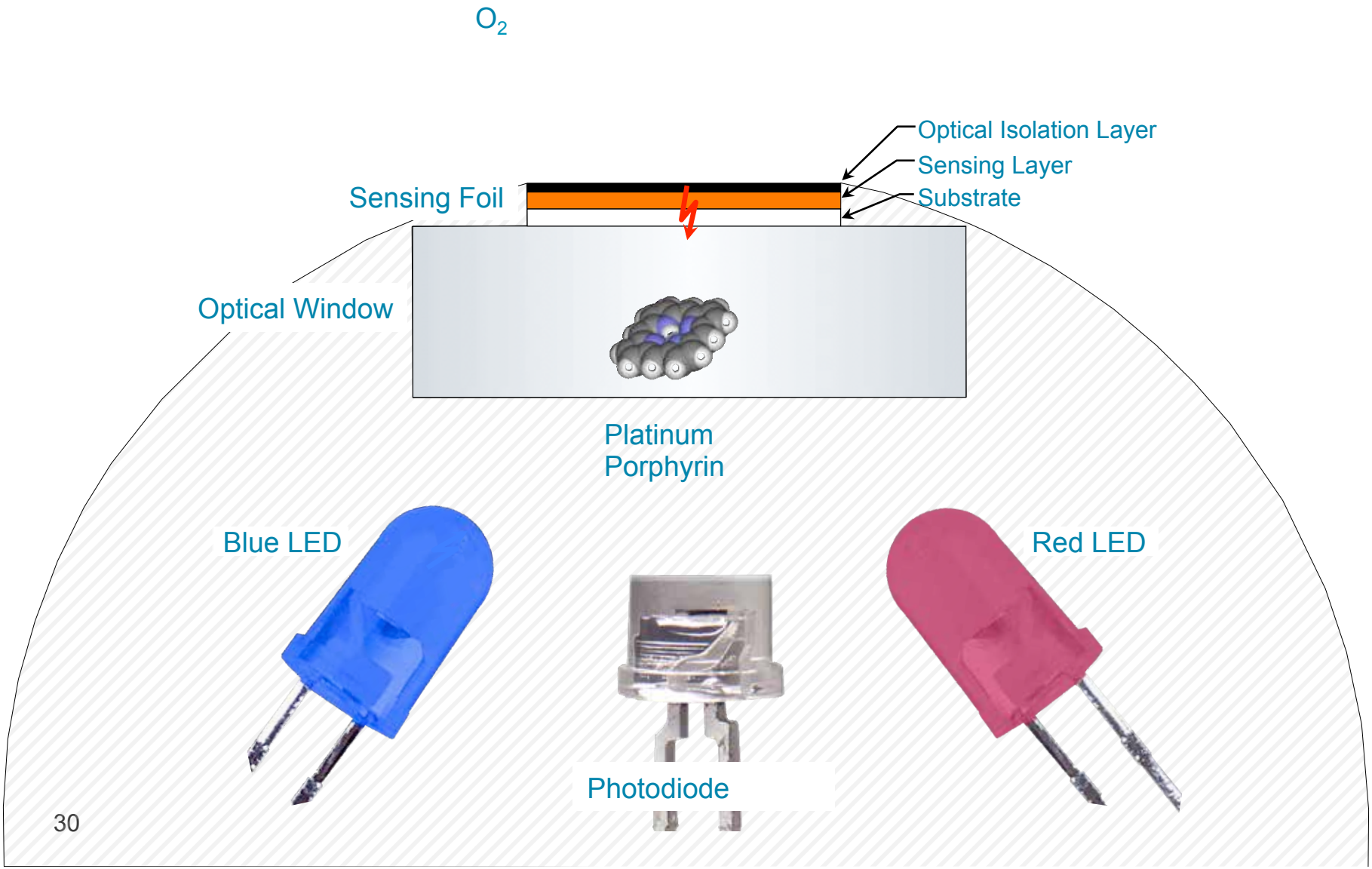
Platinum Porphyrin

Fluorescence Quenching. High O_2 gives shorter lifetime and lower intensity

Literature:

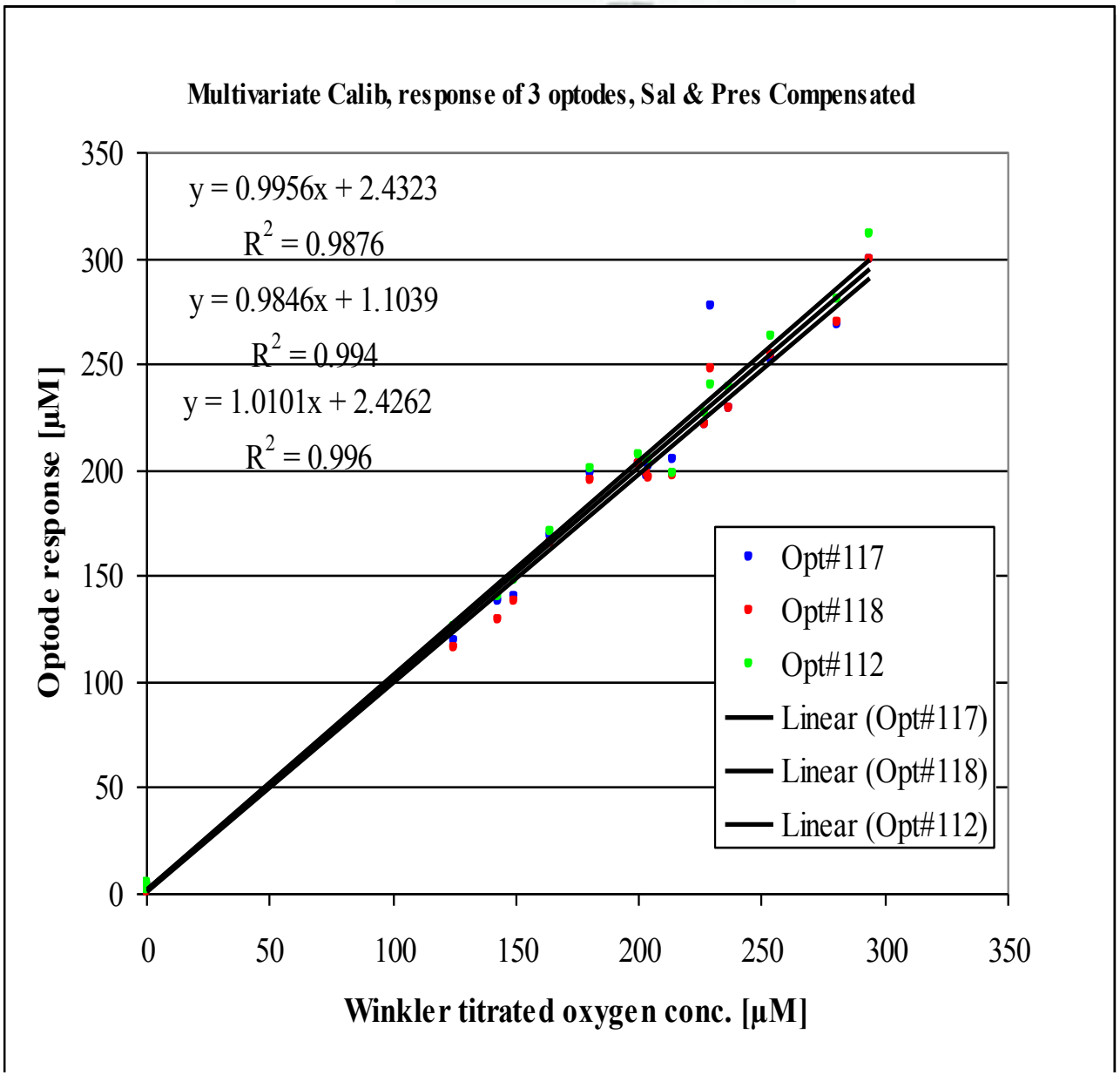
- Dynamic Fluorescence Quenching. Kautsky, 1939
- Klimant I., V. Meyer, and M. Kohls. 1995. Fibre-optic oxygen microsensors, a new tool in aquatic biology. Limnology and Oceanography 40: 1159-1165.
- Tengberg A., J. Hovdenes, J. H. Andersson, O. Brocandel, R. Diaz, D. Hebert, T. Arnerich, C. Huber, A. Körtzinger, A. Khripounoff, F. Rey, C. Rönning, S. Sommer and A. Stangelmayer (2006).Evaluation of a life time based optode to measure oxygen in aquatic systems. Limnology and Oceanography, Methods, 4, 7-17.

Optics

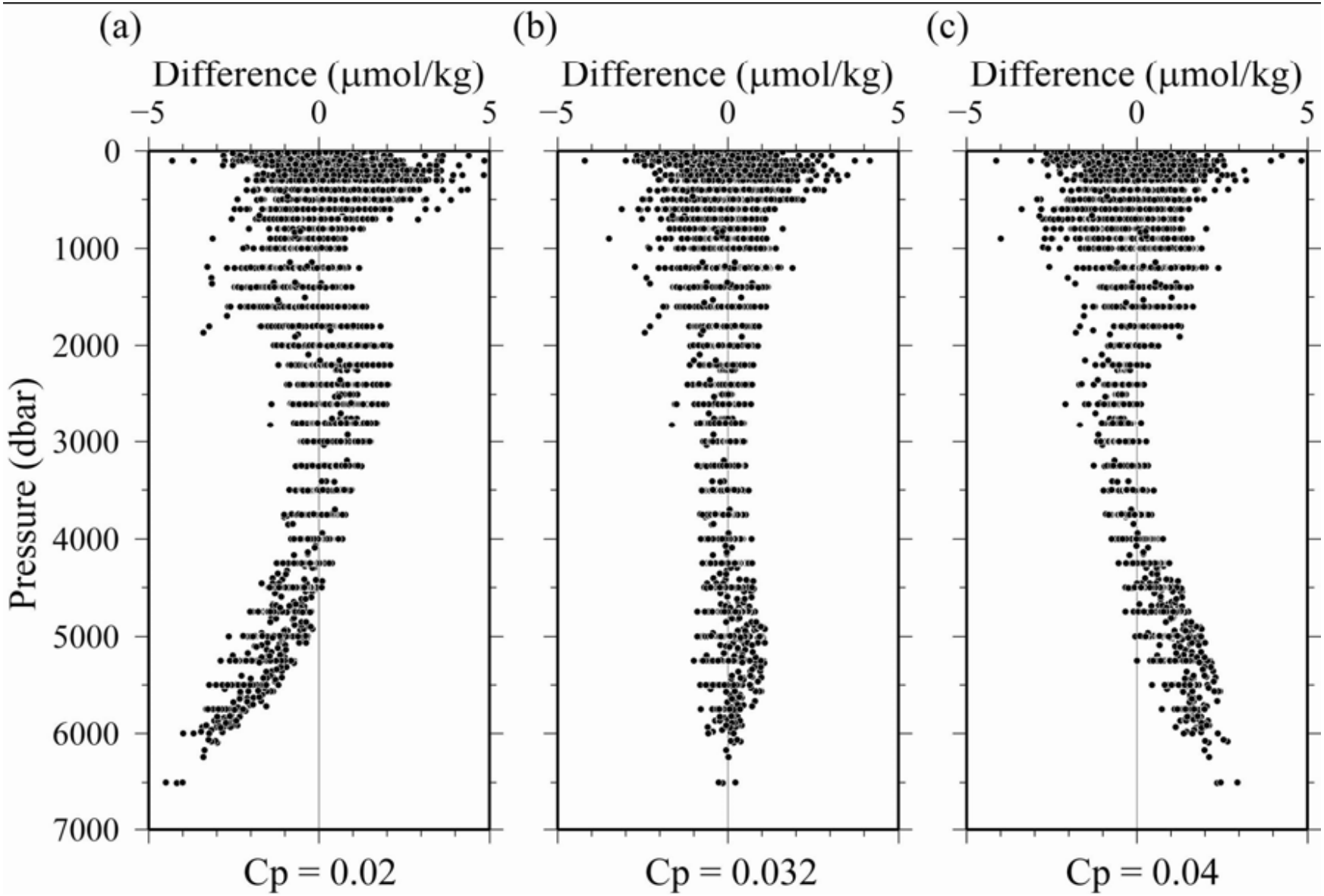

O_2
Optical Isolation Layer
Sensing Layer
Substrate
Sensing Foil
Optical Window
Platinum
Porphyrin
Blue LED
Red LED
Photodiode

Which Parameters will influence the response of an Oxygen Optode?

- O_2: Yes
- pH: No Effect
- Sal: Yes, simple formula
- Temp: No Effect
- Pres: Yes, about 4% per 1000 m, fully reversible
- Stirr: No Effect
- Aging=drift: No Effect



Tengberg, Hovdenes, Andersson, Brocandel, Diaz, Hebert, Arnerich, Huber, Körtzinger, Khripounoff, Rey, Rönning, Sommer & Stangelmayer (2006).Evaluation of a life time based optode to measure oxygen in aquatic systems. *Limnology and Oceanography, Methods,* 4, 7-17.



Uchida H., T. Kawano , I. Kaneko and M. Fukasawa (2008) In-situ calibration of optode-based oxygen sensors. Journal of Atmospheric and Oceanic Technology, 25: 2271-2281.

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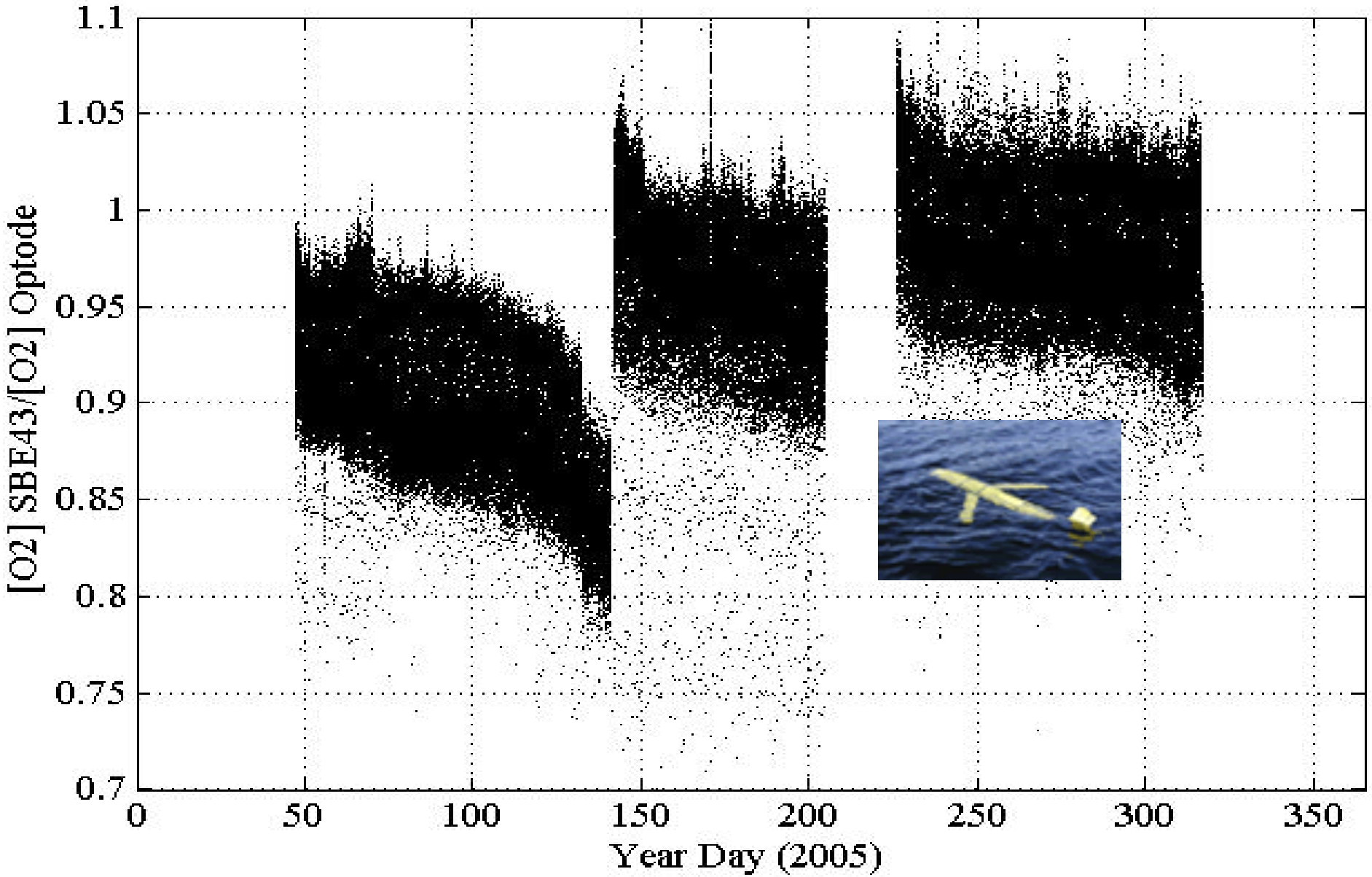
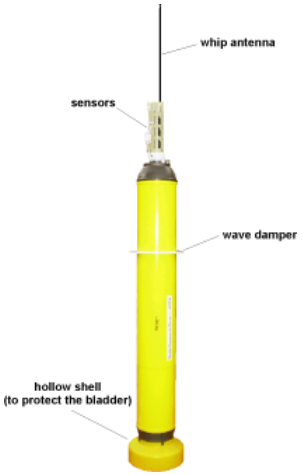


Nicholson D., S. Emerson and C. C. Eriksen (2008) Net community production in the deep euphotic zone of the subtropical North Pacific gyre from glider surveys. Limnol. Oceanogr., 53(5, part 2), 2226–2236.

Long term data from 69 Optodes on Argo floats

Yuichiro Takeshita et al., Poster presented at AGU fall meeting, San Francisco, Dec 2010.
Now published in: Takeshita et al. (2013) A climatology-based quality control procedure for profiling float oxygen data. J . Geophysical Res, Vol. 118, 1–11.



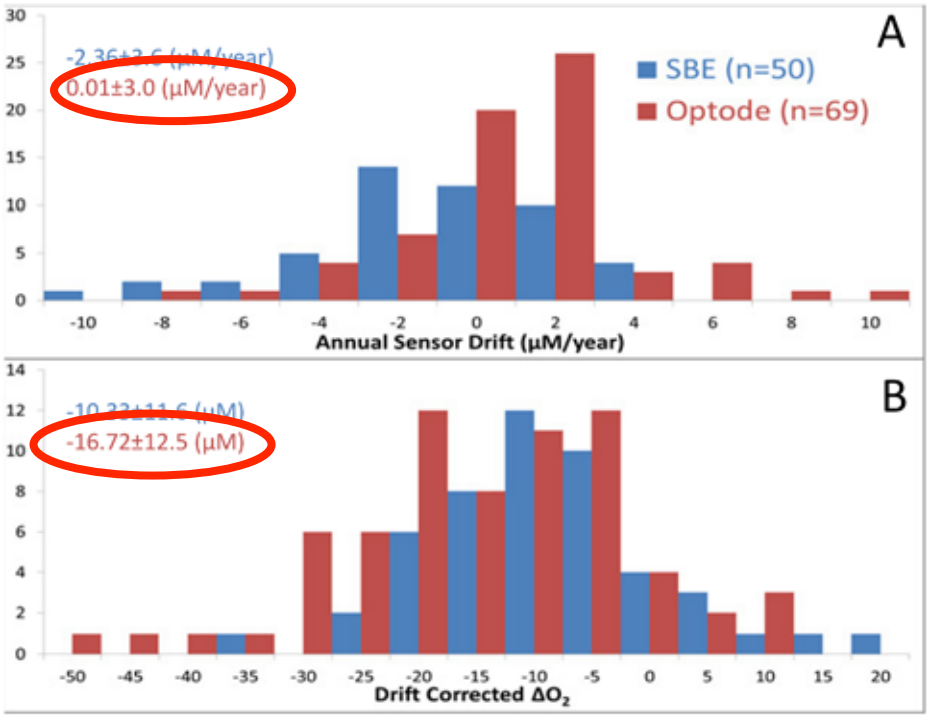
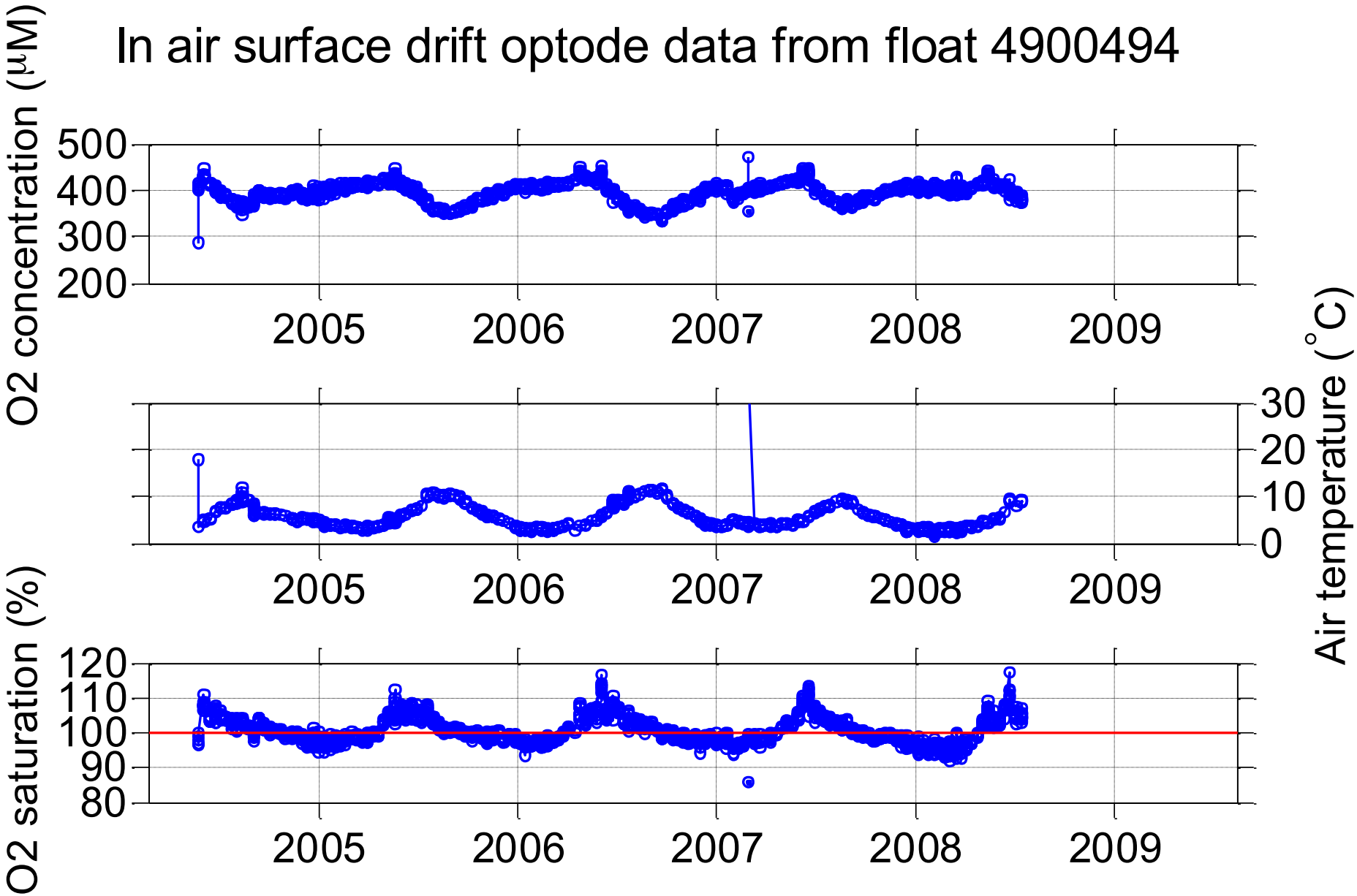


Figure 2. Histogram of sensor drift (A) and the Drift Corrected Average Deep ΔO_2 (B) for the two different types of oxygen sensors. The mean±std. dev. is labeled on the plot with its corresponding color.

- Conclusion: Optodes stable but gave lower values
- Reason: Foils bleach in ambient light (especially fluorescent) and if sampling is done at high frequency

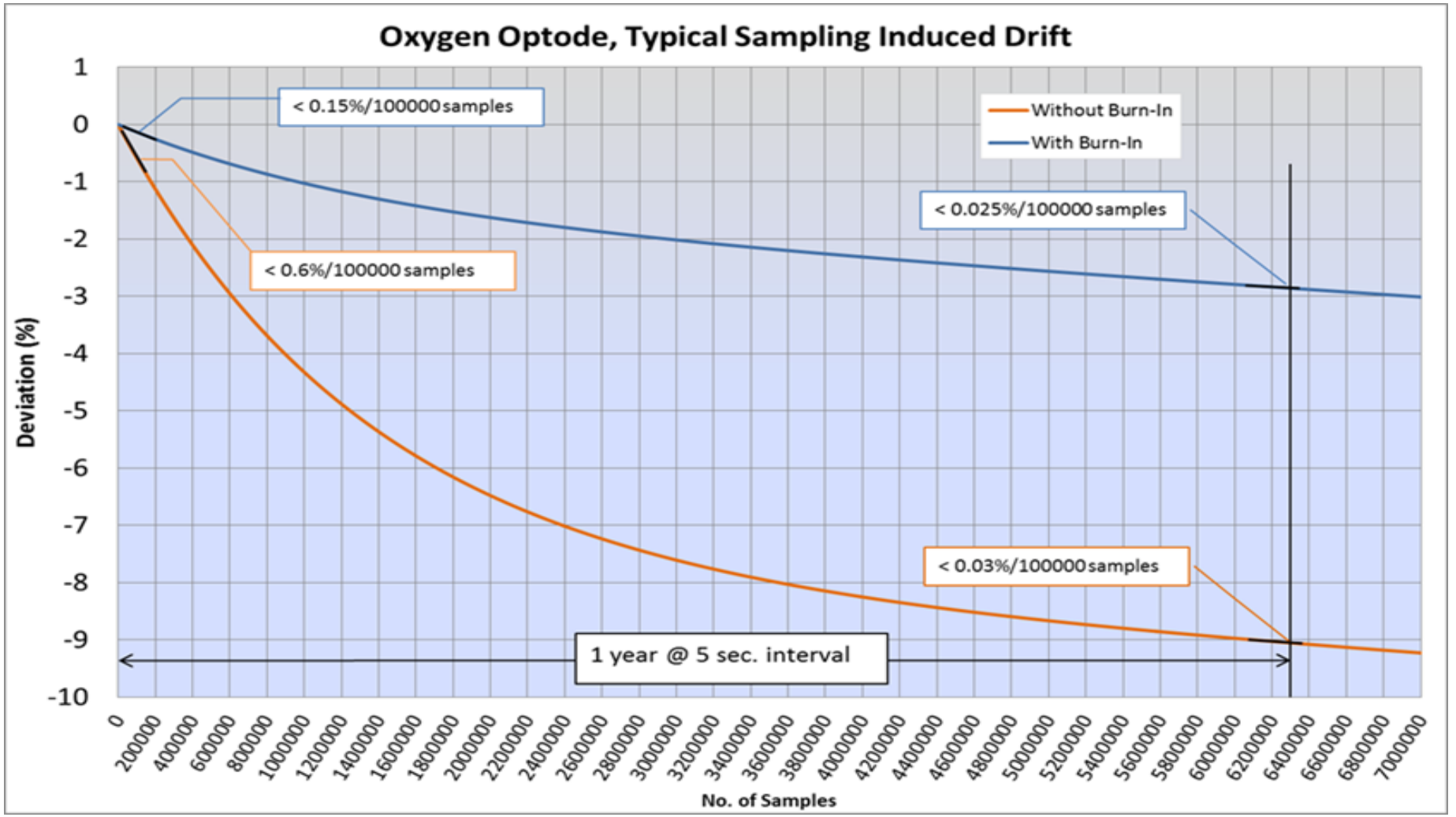
When storing sensors use black protection cap!

In air surface drift optode data from float 4900494



Denis Gilbert et al., Argo Science Workshop 3, Hangzhou, China, March 27, 2009

Optode drift in relation to number of measurements and pre-treatment (with burn-in) or not



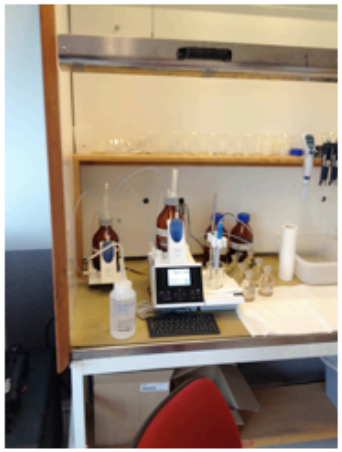
All Multipoint calibrated Foils are Pre-matured ► Better Accuracy

► Better Stability Drift < 0.15 µM/100,000 samples

If not mechanically damaged foils get better over time

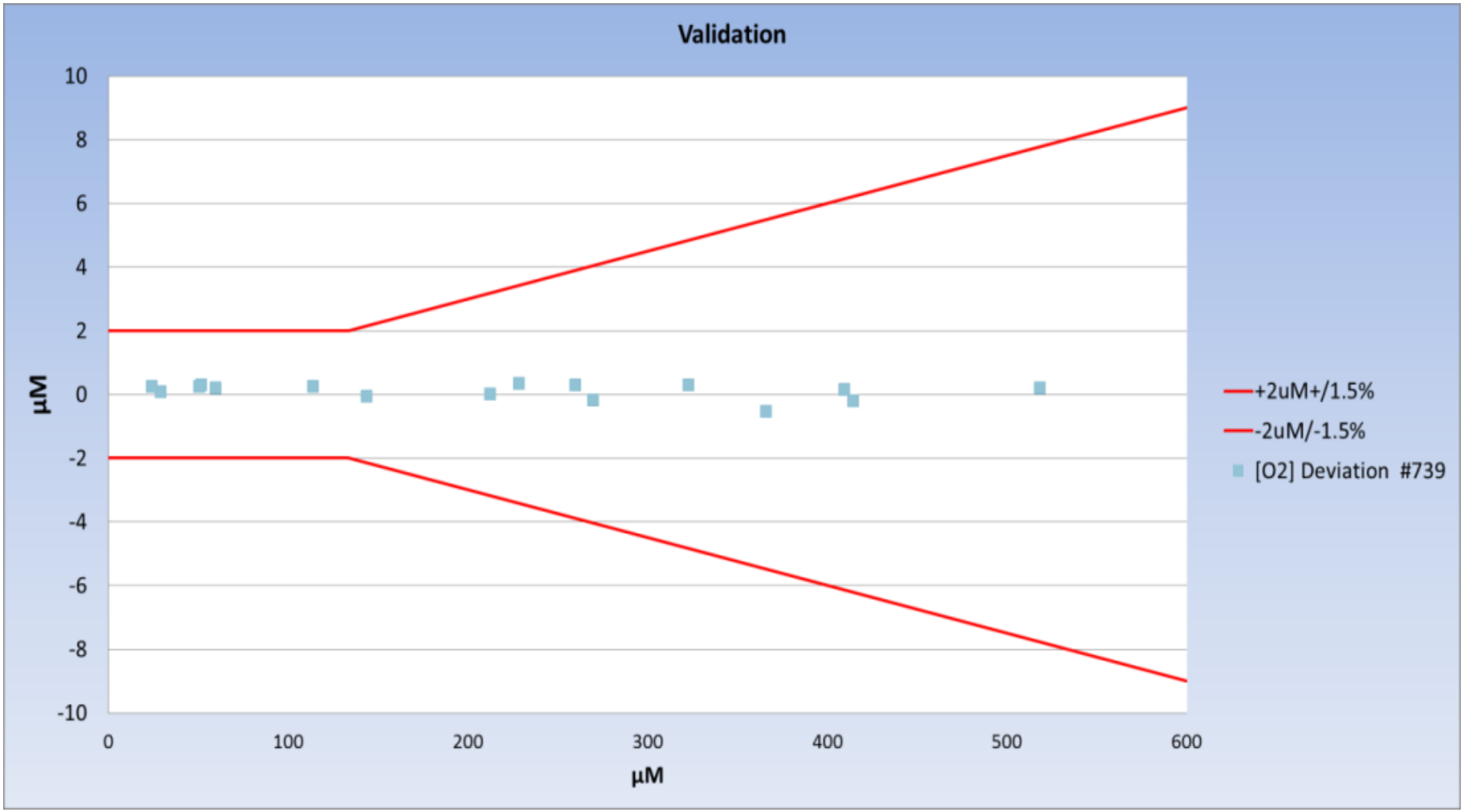
Multipoint Calibration System

- Gas injection by use of mass flow controllers
- Automatic System 40 point calibration & 20 point subsequent verification
- Operational since August 2012
- 3 parallel reference optodes in system
- Automatic Winkler system from SI Analytics for frequent verification
- International inter-comparison of calibration facilities
- Absolute accuracy better than 1.5%/±2.5 µM



Multipoint calibration only for MkII: 4330 & 4831

Validation



Accuracy over entire range of O_2 and Temp: ±2.5 µM or ±1.5%. Field resolution: ±0.2µM

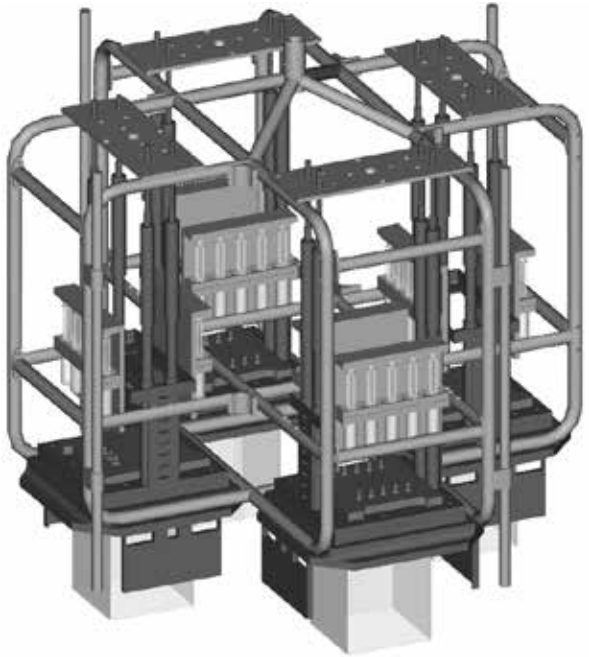
Multipoint Calibration + red LED referencing gives the highest accuracy on the market

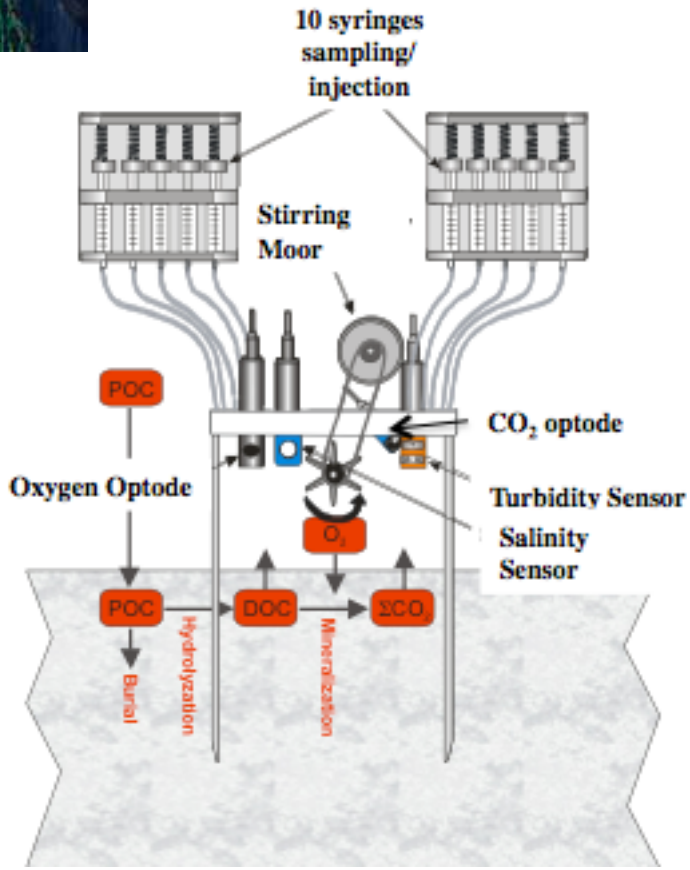
Tools: Autonomous Benthic landers

Our landers:

- 250-300 deployments
- About 800 incubations
- Deployed at 5-5600 m
- 40 water samples
- 15-25 sensors
- 95 % success rate

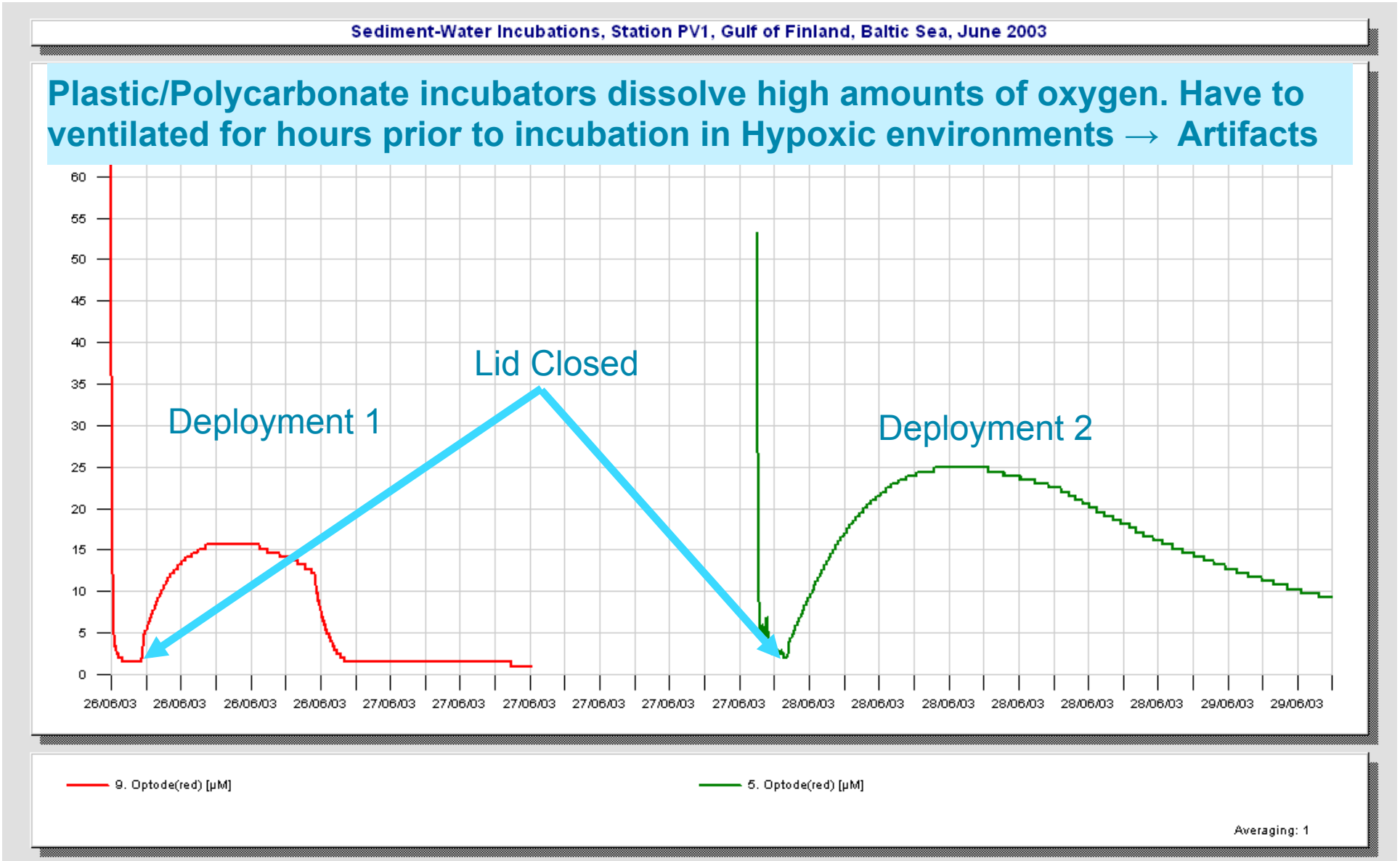
Inner frame
(4 incubations chamber modules)

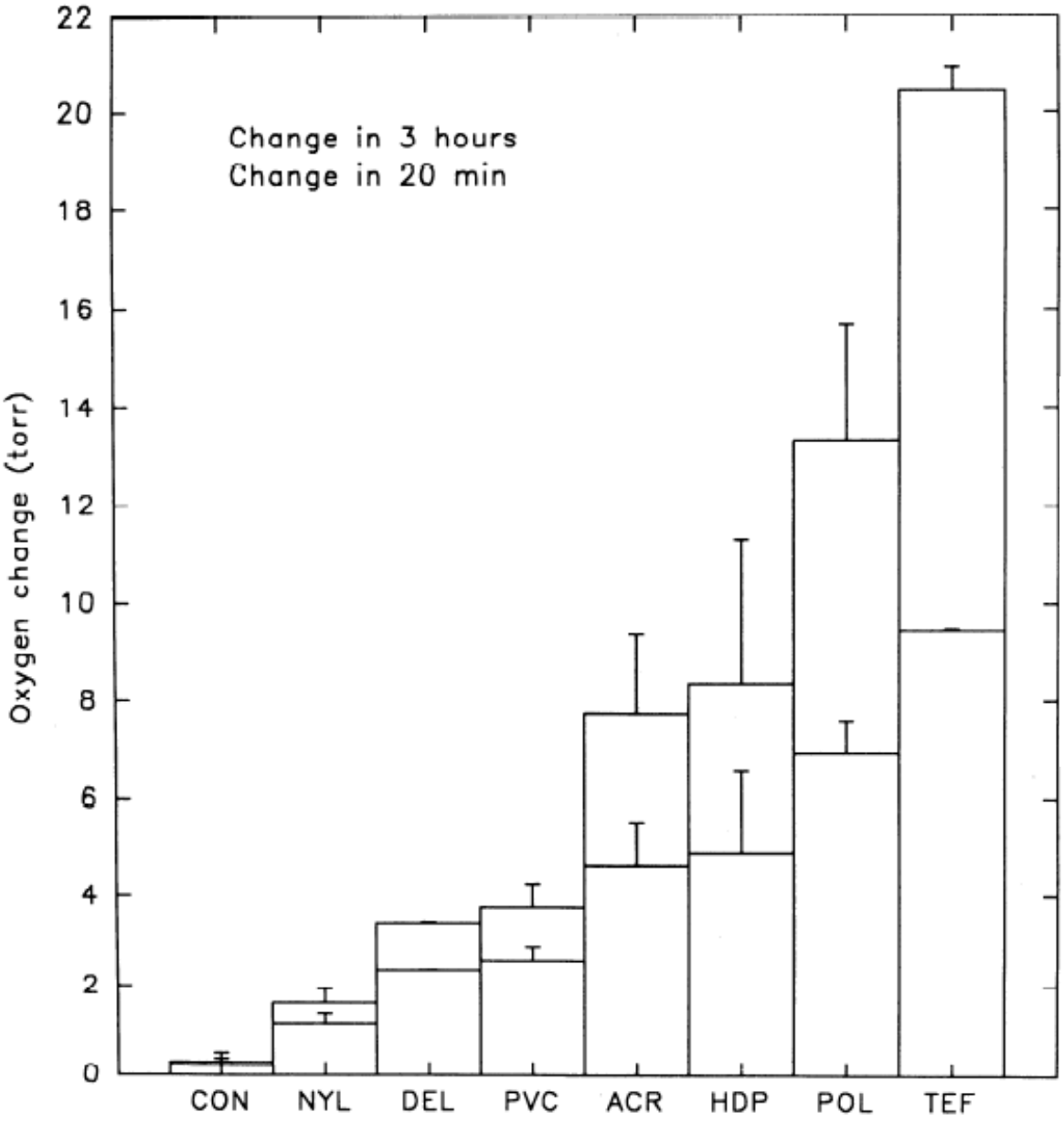




Measured Fluxes

- **Oxygen**
- Total Carbonate
- Silicate
- **Phosphate**
- Nitrate+Nitrite
- Ammonium
- DOC
- Alkalinity
- pH
- Fe and Mn
- Turbidity
- pCO_2


Sediment-Water Incubations, Station PV1, Gulf of Finland, Baltic Sea, June 2003
Plastic/Polycarbonate incubators dissolve high amounts of oxygen. Have to ventilated for hours prior to incubation in Hypoxic environments → Artifacts
Lid Closed
Deployment 1
Deployment 2
60
55
50
45
40
35
30
25
20
15
10
5
0
26/06/03
26/06/03
26/06/03
26/06/03
27/06/03
27/06/03
27/06/03
27/06/03
27/06/03
27/06/03
28/06/03
28/06/03
28/06/03
28/06/03
28/06/03
28/06/03
29/06/03
29/06/03
9. Optode(red) [µM]
5. Optode(red) [µM]
Averaging: 1

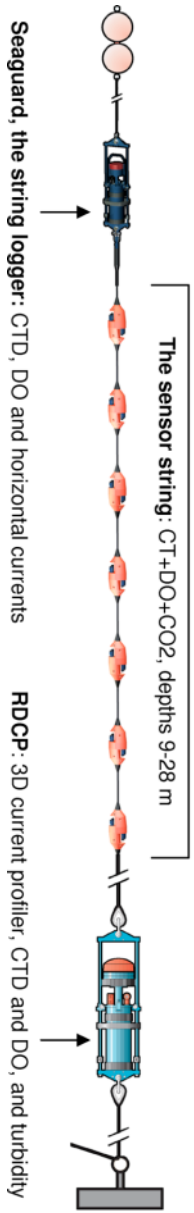


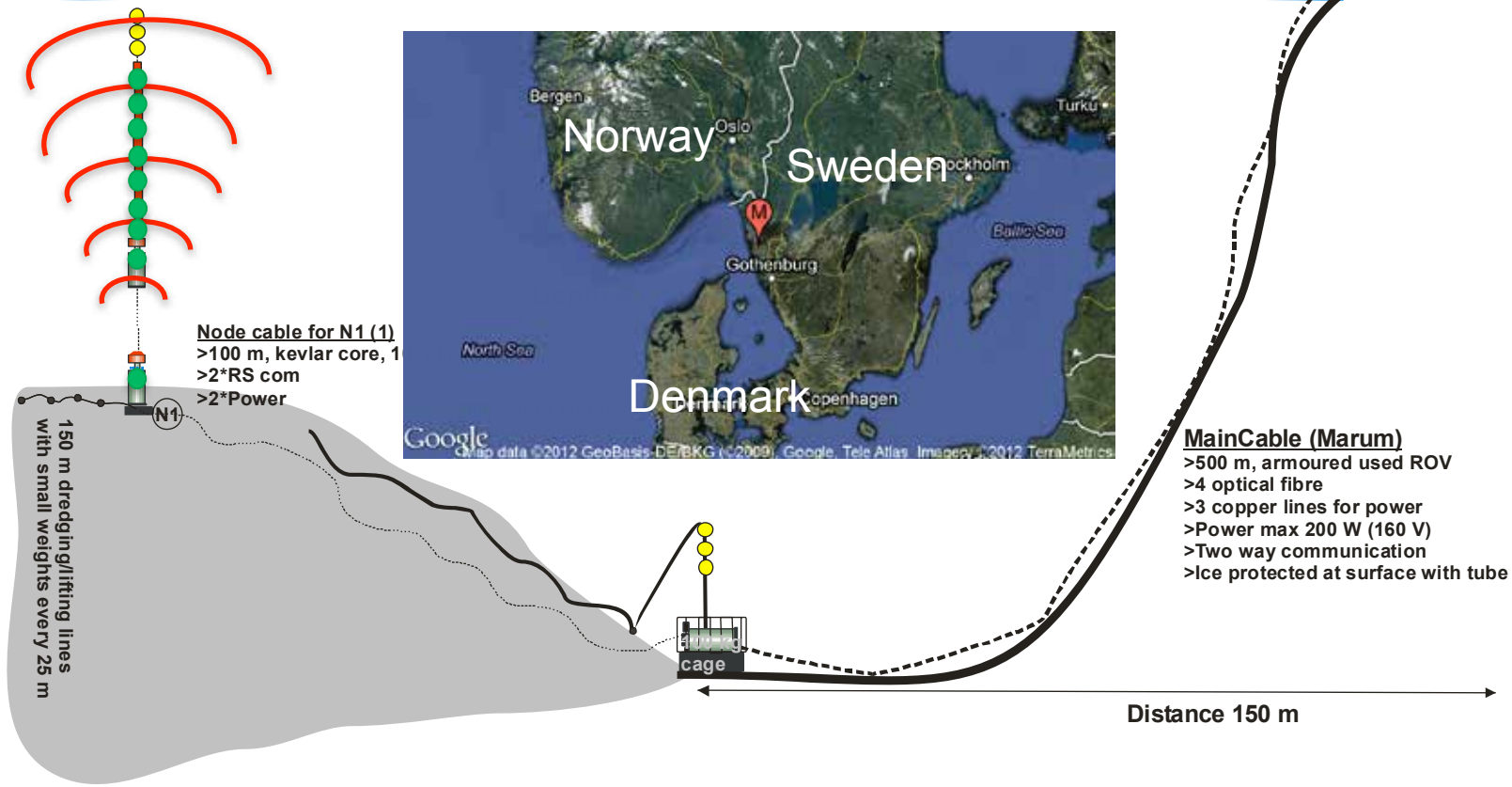
Stevens, E. Don (1992) Use of plastic materials in oxygen-measuring systems. Journal of Applied Physiology, 72(2): 801-804.

Plastic Materials have "memory" effects on O2. Plastic materials should be avoided for profiling and if high accuracy/precision is needed.

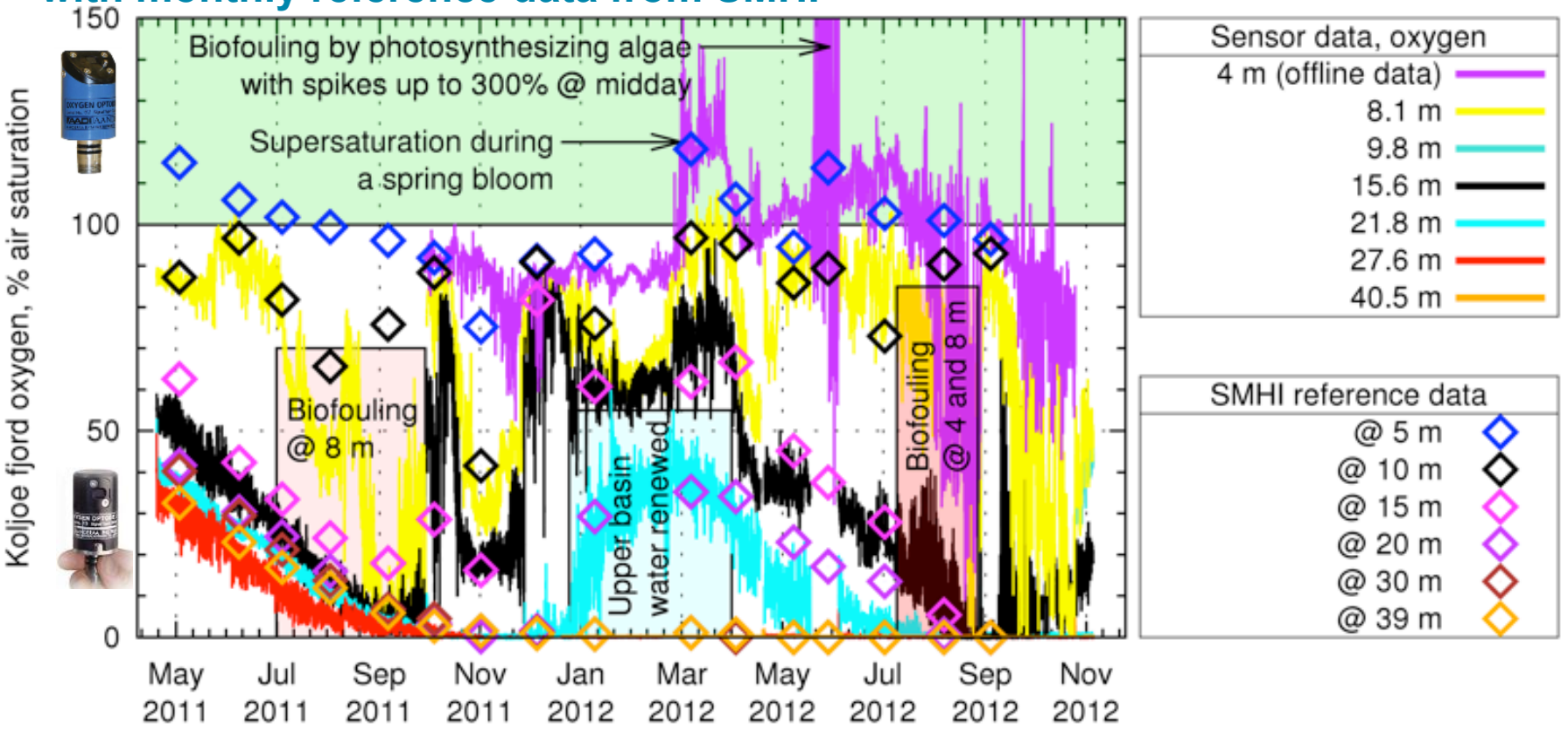
Koljoe fjord observatory

- Installed April 2011
- Real time: http://koljofjord.cmb.gu.se
- 40-50 sensors
- Quality control by monthly sampling (SMHI)

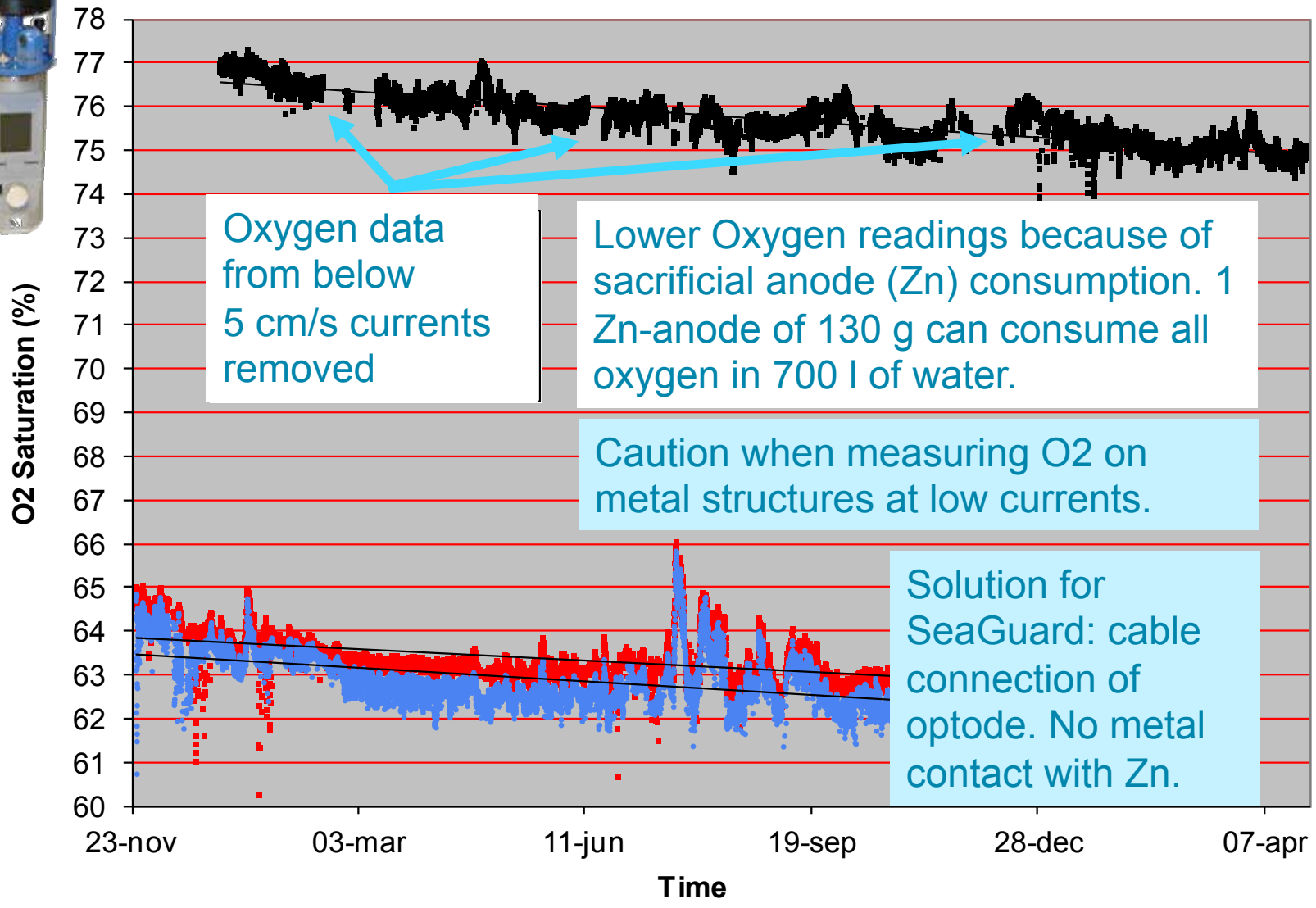




Examples of data: 18 months oxygen recordings, with monthly reference data from SMHI

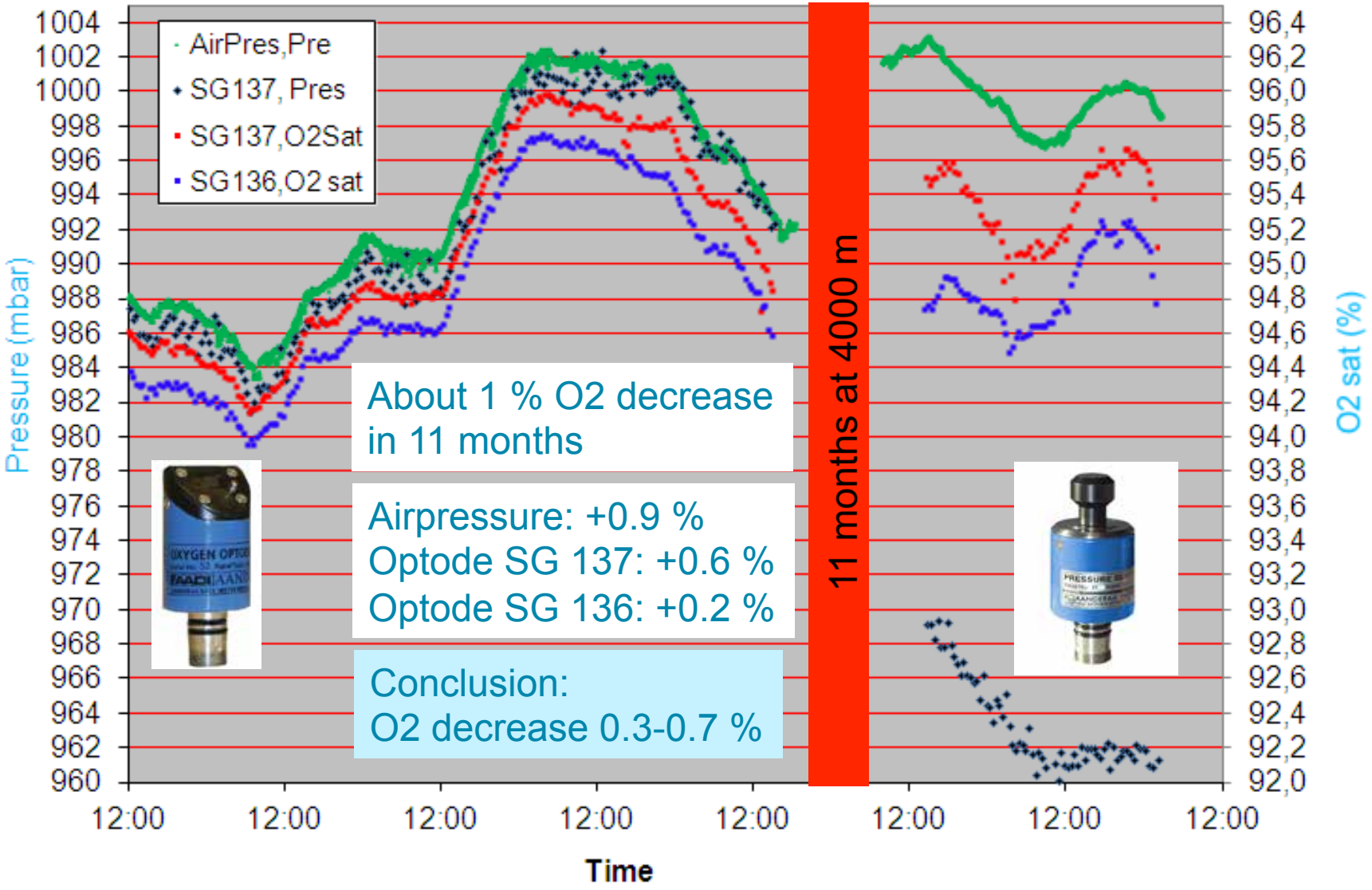


Oxygen at 4000 m



Lo Bue N. et al. (2011) Anomalies of oxygen measurements performed with Aanderaa optodes. J of Operational Oceanography. Volume 4 No. 118, 1–11.

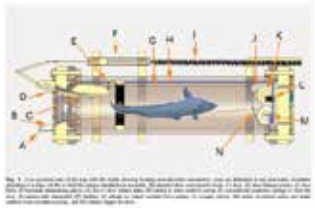
Pre & Post Deployment data. Air Pressure Ship + SG Pressure + Oxygen Saturation before and after deployment on two Seaguards



Oxygen Optodes

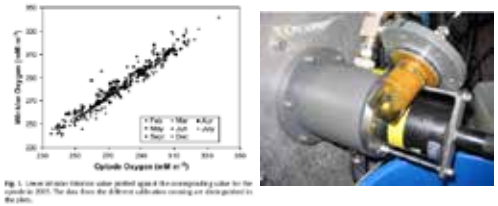
Examples of Scientific Papers

Incubators



Drazen et al (2005), Almroth et al (2012), Wikner et al (2013)

Ferry boxes



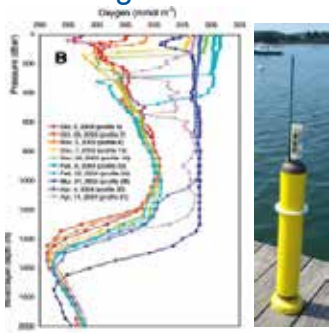
Hydes et al (2009)

Tengberg et al (2006)

Gas Exchange Chamber

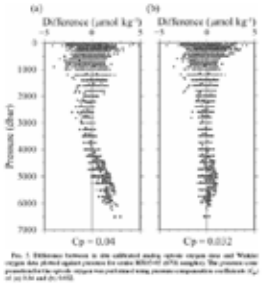
Sommer et al (2008)

Argo floats



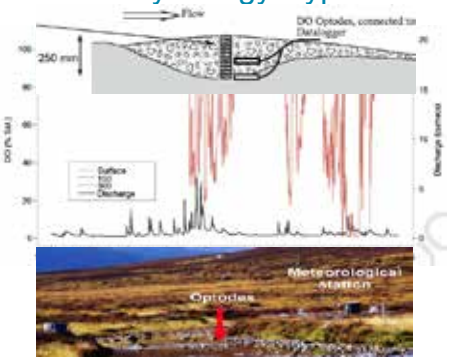
Körtzinger et al (2004, Nature)
Johnson et al (2010, Nature)
Fiedler et al (2013)
Takeshita et al (2013)

Cabled CTD



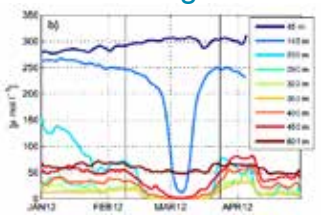
Uchida et al (2008)

Rivers/Hydrology/Hyporheic



Birkel et al (2013), Malcolm et al (2006, 2008, 2010), Soulsby et al (2008)

Moorings

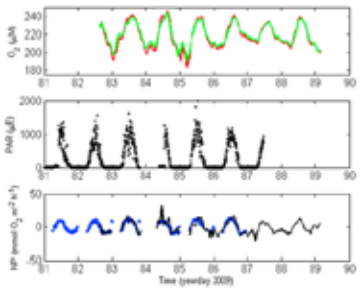


Stramma et al (2014), Viktorsson et al (2012)

Boys

Jannash et al (2008), Bushinsky & Emerson (2013)

Gradients



McGillis et al (2011), Champenois and Borges (2012)

Gliders

Nicholson et al (2008)

Oxygen Optodes

Examples of Scientific Papers

Long term stable

No O_2 consumption & Robust

Not freezing sensitive

Good for hot water monitoring

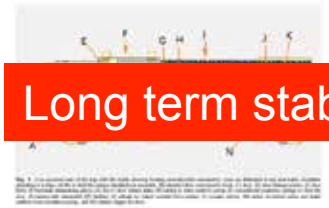
Not sensitive to H_2S and most other chemicals

High accuracy & low noise

Lower fouling sensitivity

No pressure hysteresis

Incubators



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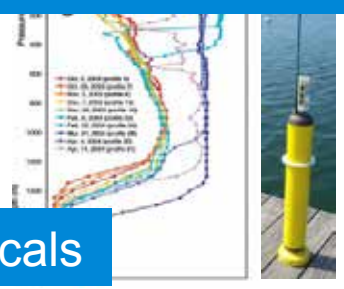

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Johnson et al (2010, Nature)
Fiedler et al (2013)
Takeshita et al (2013)

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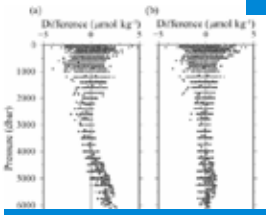
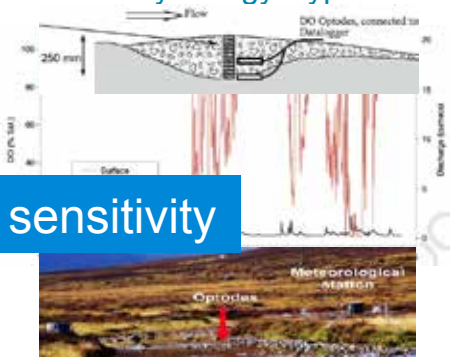


Uchida et al (2008)

Rivers/Hydrology/Hyporheic



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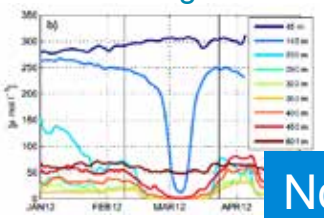

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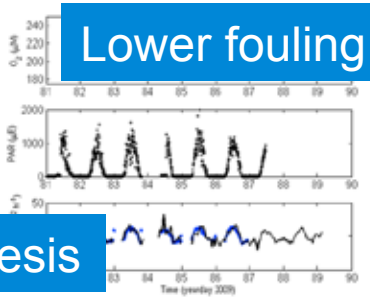
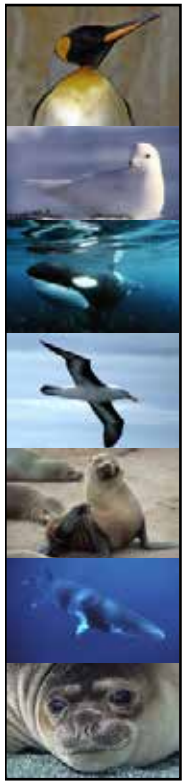


McGillis et al (2011), Champenois and Borges (2012)

Gliders

Nicholson et al (2008)

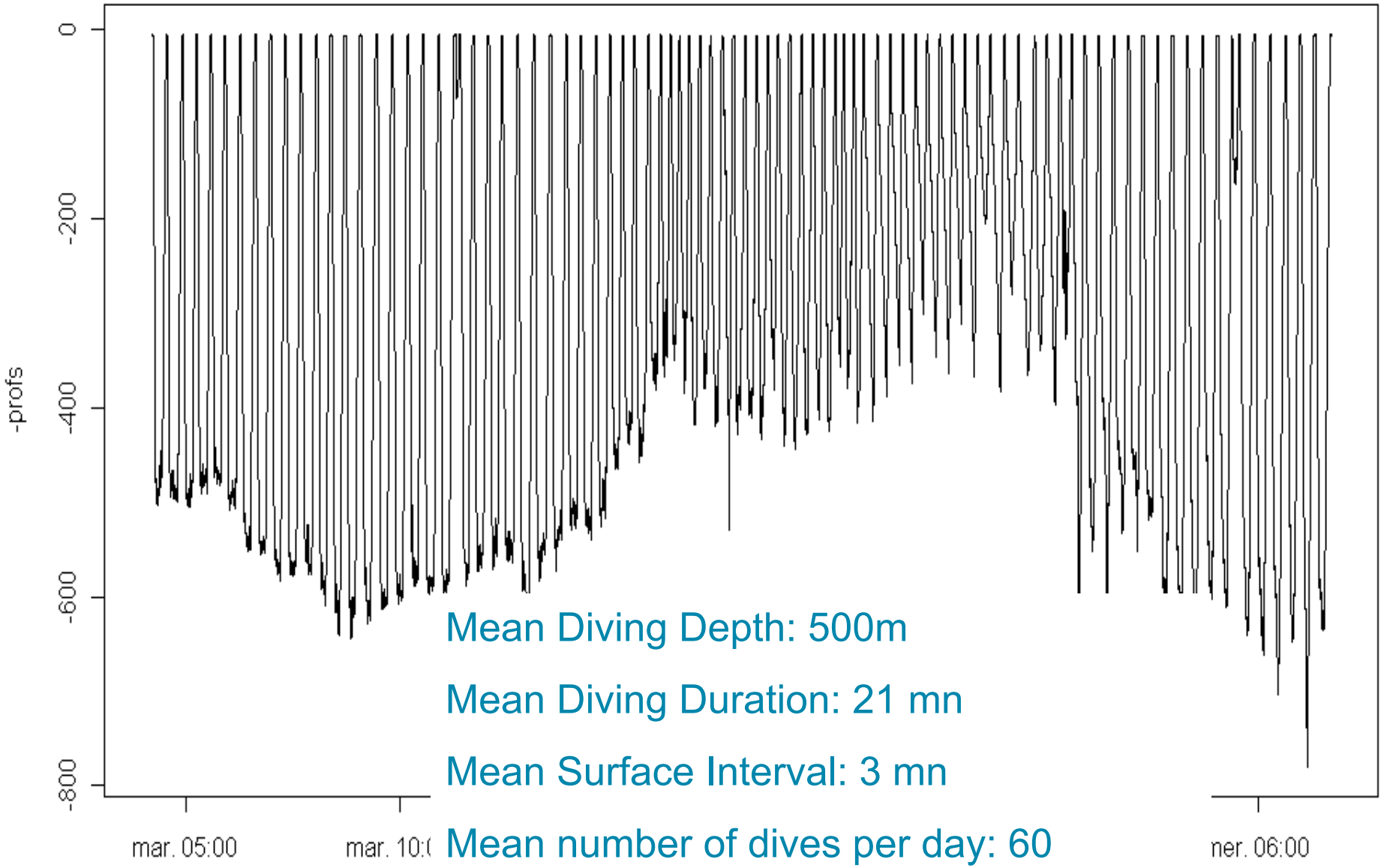
Marine Predators Team



Contribution of the Elephant Seal to monitor the oxygen content of the Southern Ocean

Christophe Guinet, CEBC-CNRS

ANR IPSOS-SEAL



Mean Diving Depth: 500m

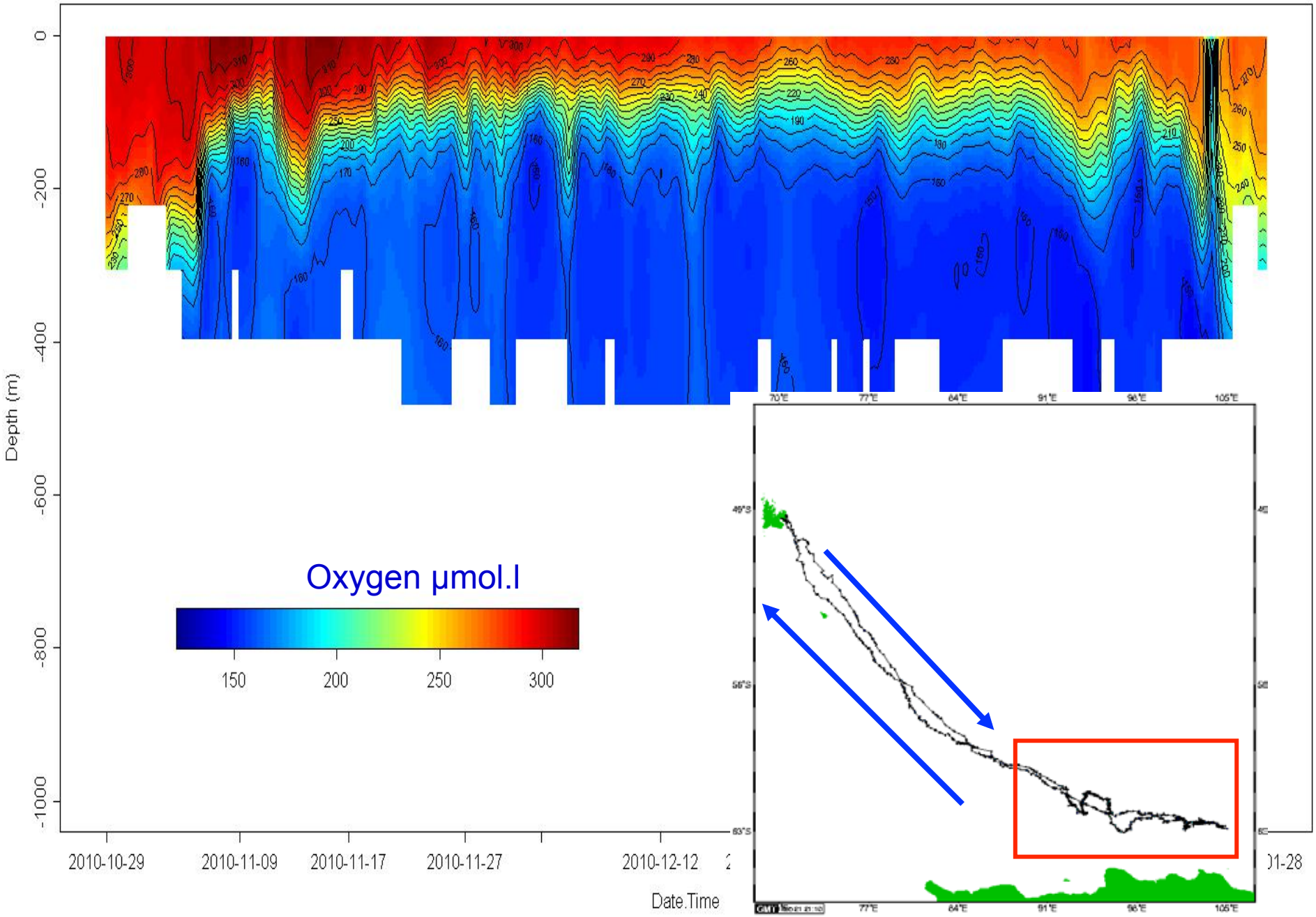
Mean Diving Duration: 21 mn

Mean Surface Interval: 3 mn

Mean number of dives per day: 60

0-2 km between dives

25 Oct -17 Nov 2010 | 17 Nov 2010 -10 Jan 2011 | 10 - 28 Jan 2011



Summary

9:00-10:30

- Why should you measure Oxygen (O_2)?

Crucial parameter

- How is O_2 related to other parameters?

Related to most other parameters

- Are we measuring at the right frequencies?

Nyquist criteria: sample at twice the frequency as changes occur

- Methods to analyze and measure O_2

Winkler, Electrochemical sensors, Optical foil based sensors

11:00-13:00

- What affects O_2 sensors/methods to evaluate performance?

Multivariate methods good tool for evaluation

- How good is Winkler titration?

Depends on person, contamination at low O_2 from plastic bottles

- Field data, value of combined measurements

Combined measurements gives better certainty, O_2 should always be combined with pCO_2, pH, ChlA

- **<u>Practical Demonstration and Hands-On</u>**