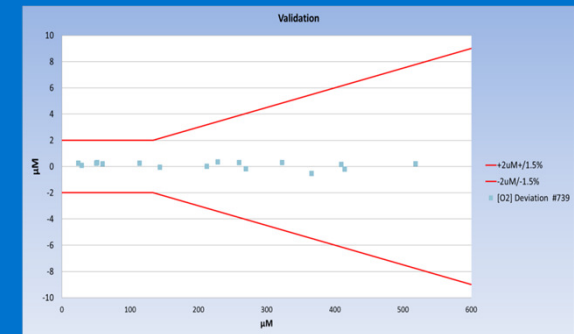
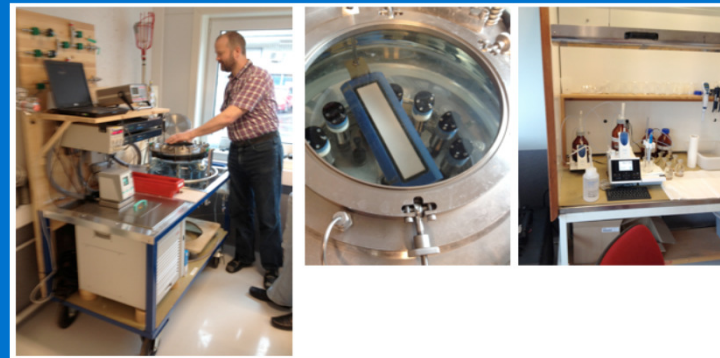


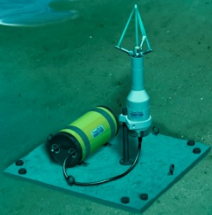
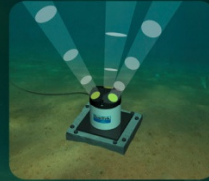
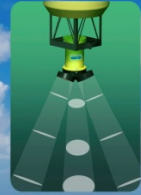
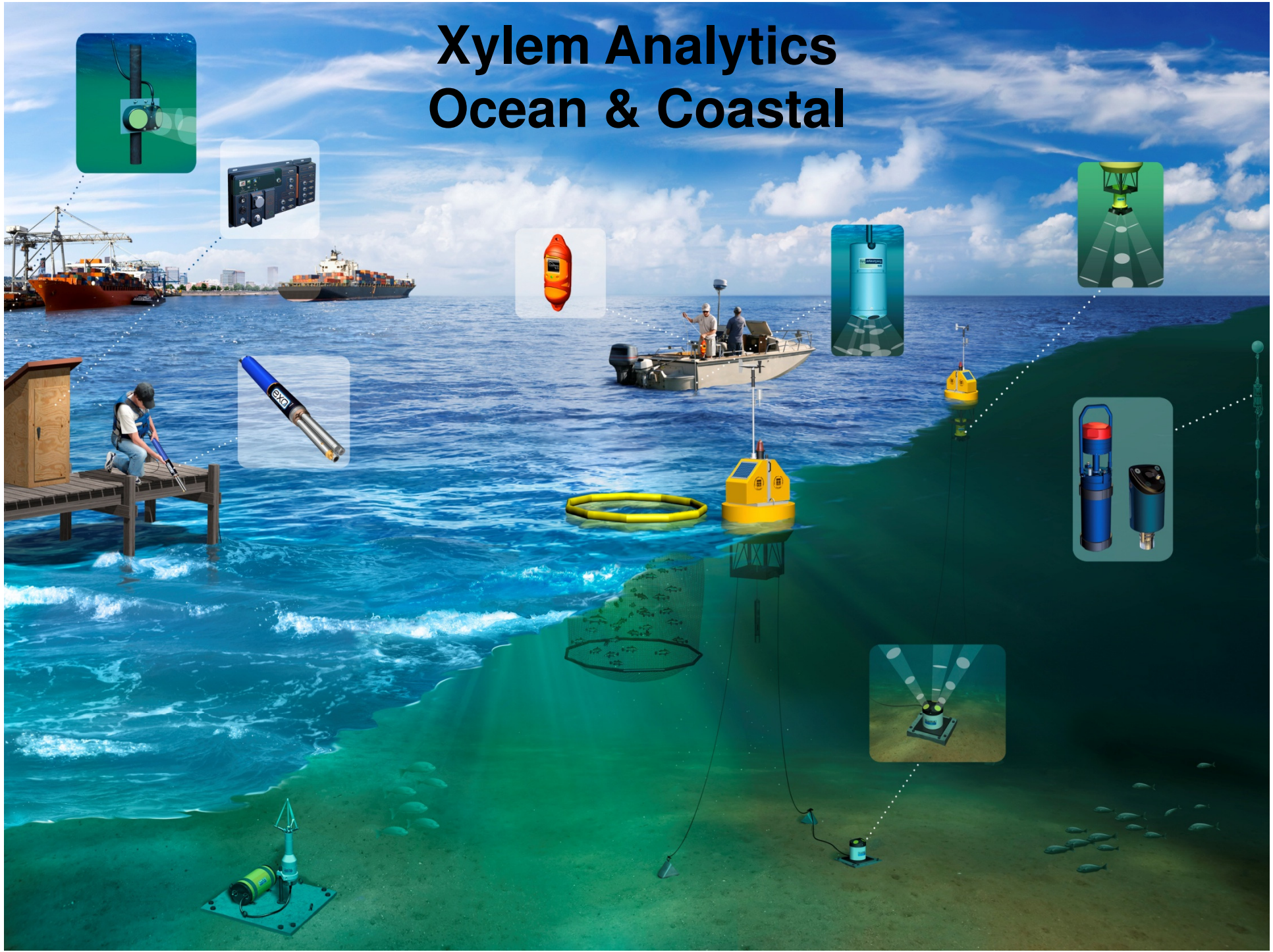
SCRIPPS, San Diego, June 12th , 2014

Improve your oxygen optode measurements: user examples, practical handling and calibrations



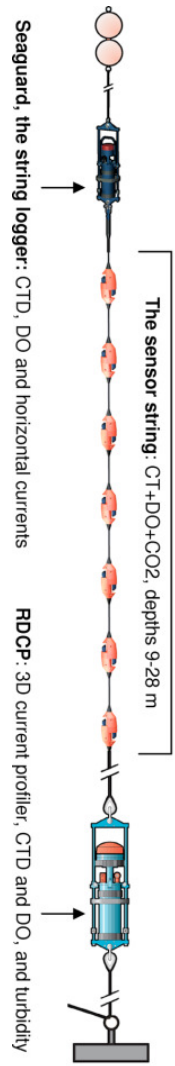
Emilie DORGEVILLE, Product Manager - emilie.dorgeville@xylem.com

Xylem Analytics Ocean & Coastal

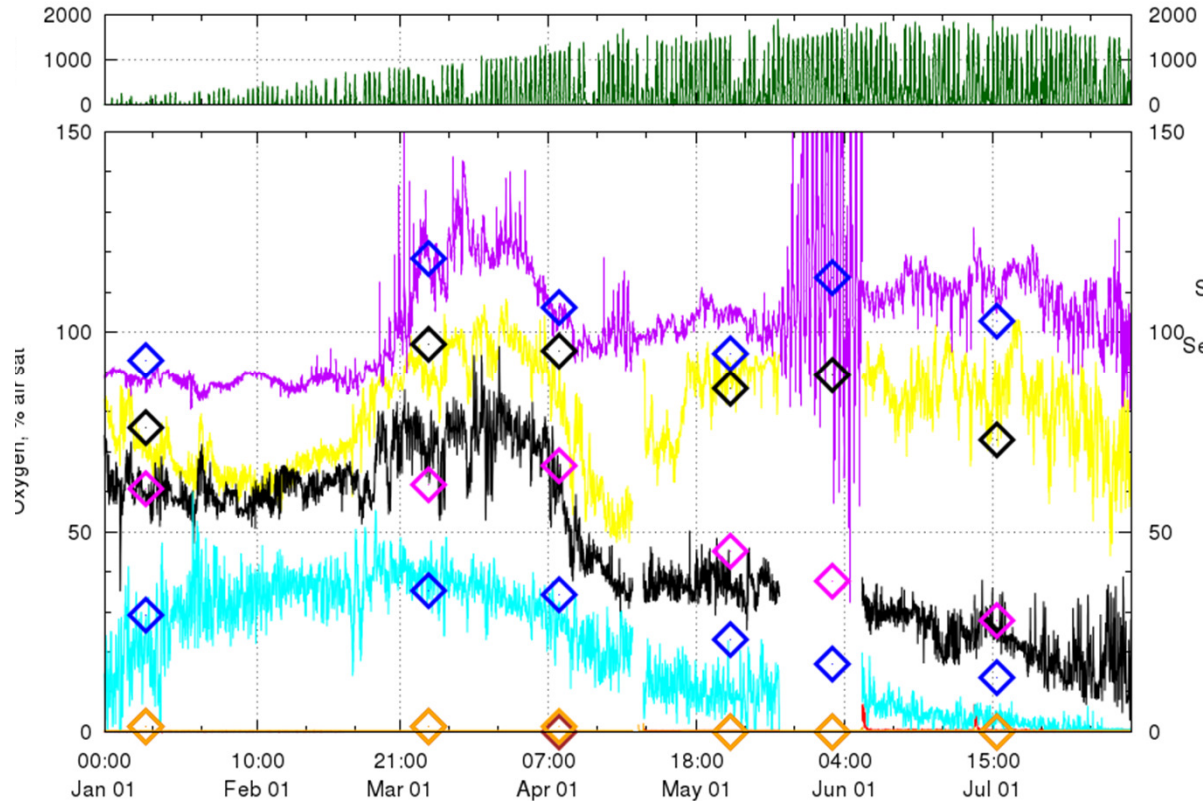


Measurement in the water column: Koljoe fjord observatory: O₂ recordings, with monthly reference data from SMHI

the Koljoe Fjord observatory, bottom depth 42 m
Seaguard with 21-m sensor string, oxygen



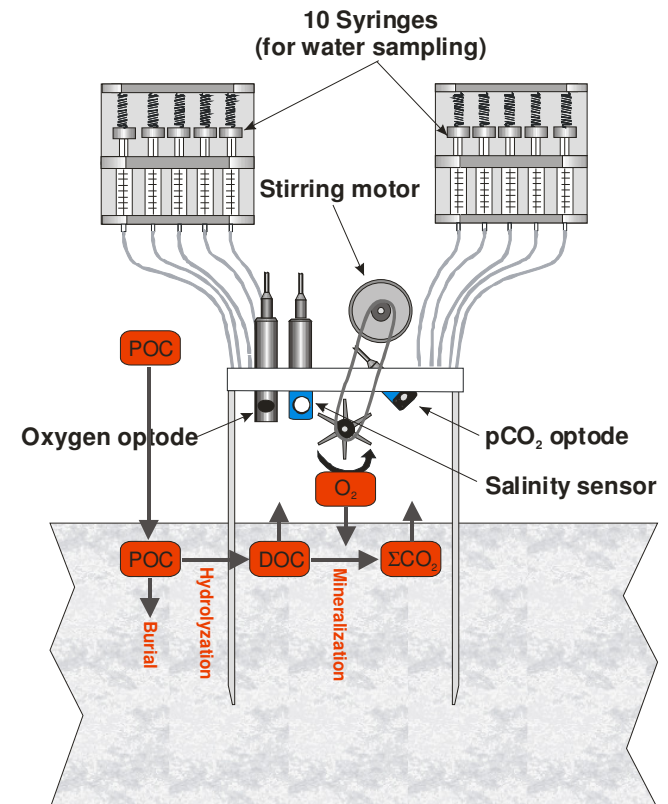
Cable for power and communication; ballast



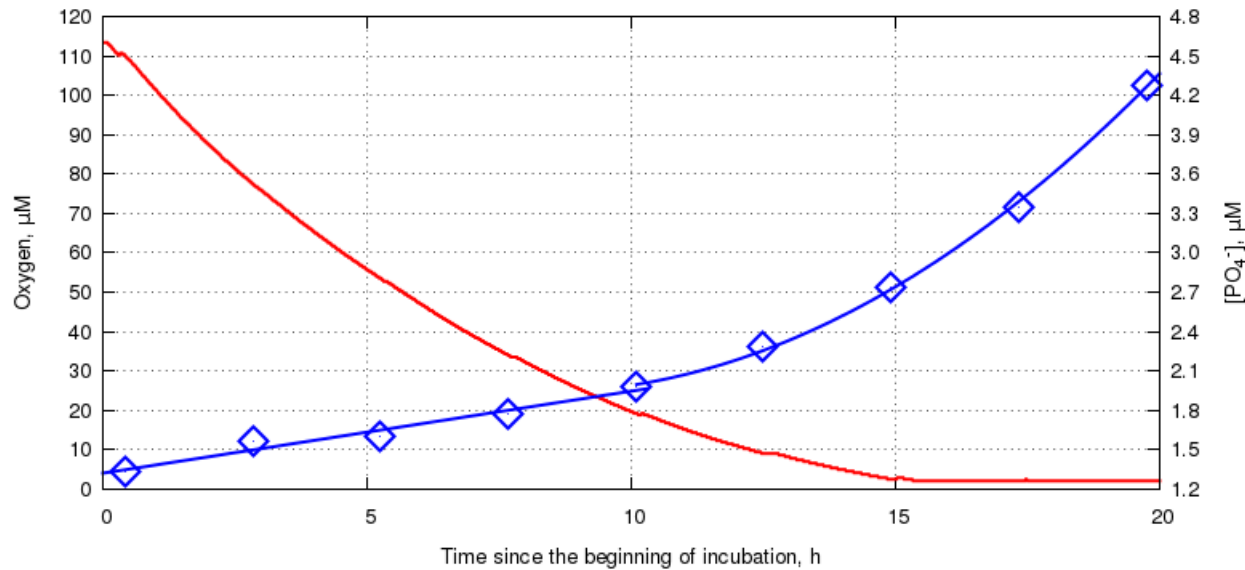
- Monthly sampling not enough
- Reference data needed for high quality sensor data
- Are plastic (PVC) bottles suitable for sampling at low O₂?



Bottom measurement: Gothenburg Autonomous Bottom Landers for Sediment-Water Incubations. Deployed ~300 times from 5-5600 m water depth



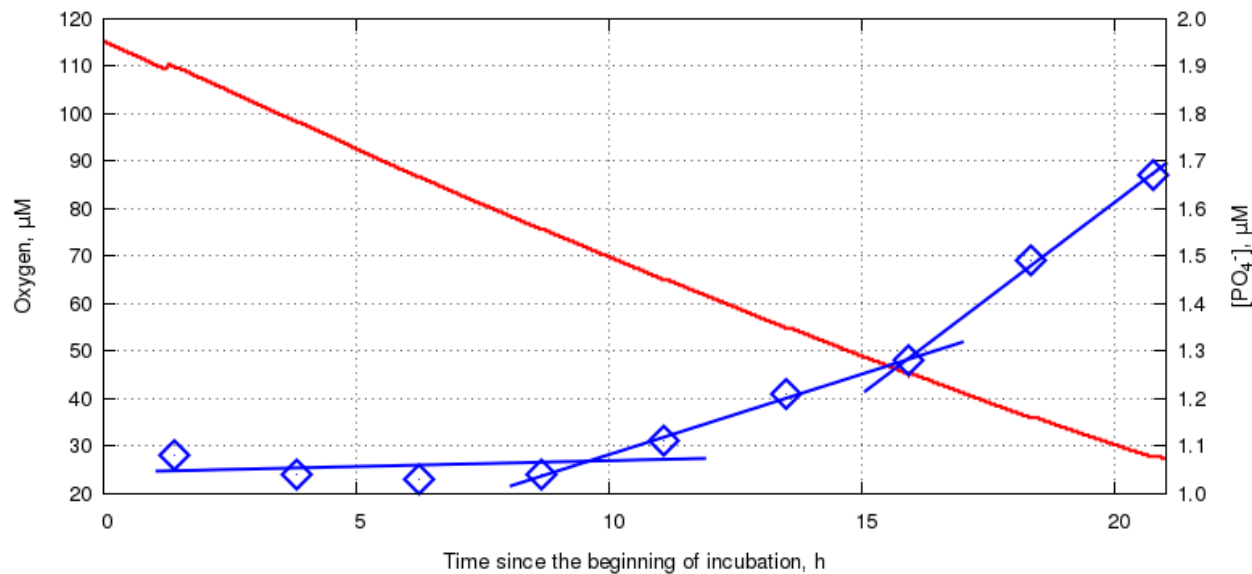
BF25MAR12, Deployment 2, Chamber B



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

• **Phosphate: Eutrophication contributor. Phosphate released from sediment when oxygen reaches values under 20-30 μM**

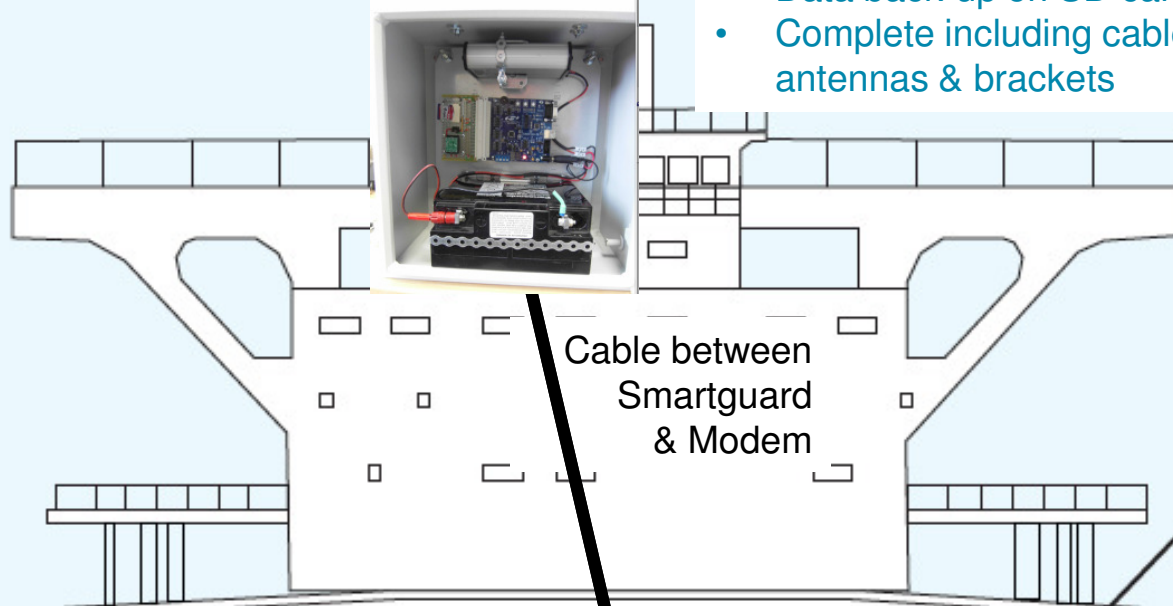
BF25MAR12, Deployment 1, Chamber A





Ambeon modem (on bridge)

- In-built GPS
- Cellphone or Iridium
- 3 serial ports for sensors
- Data back-up on SD card
- Complete including cables, antennas & brackets

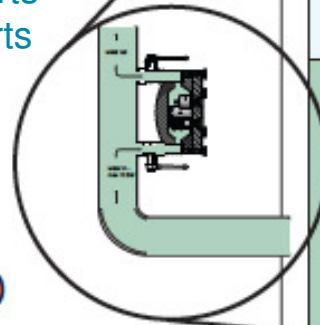


Smartguard 5300

- 20+ Aanderaa sensors
- 5 Rs-232 ports
- 6 Analog ports



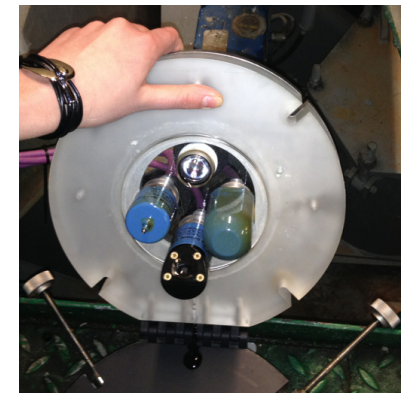
SMARTGUARD data logger



Surface measurement

SOOGuard Chamber

- Compact 30*30*20 cm
- Easy to install, brackets included
- Add extra chamber & sensors for more parameters
- 10 bar rated
- Easy to service, takes less than 10 s to open



AANDERAA

a xylem brand

AANDERAA Ambeon MSI

MS ROMANTIKA
TALLINK

Choose date: 09-03-2014

Choose parameter: Temperature [°C]

Sattelite overlay:

View: **datatable**

graph

● SHIP'S LAST POSITION

- 1,1..1,9 °C
- 1,9..2,6 °C
- 2,6..3,3 °C
- 3,3..4 °C
- 4..4,7 °C

Sweden

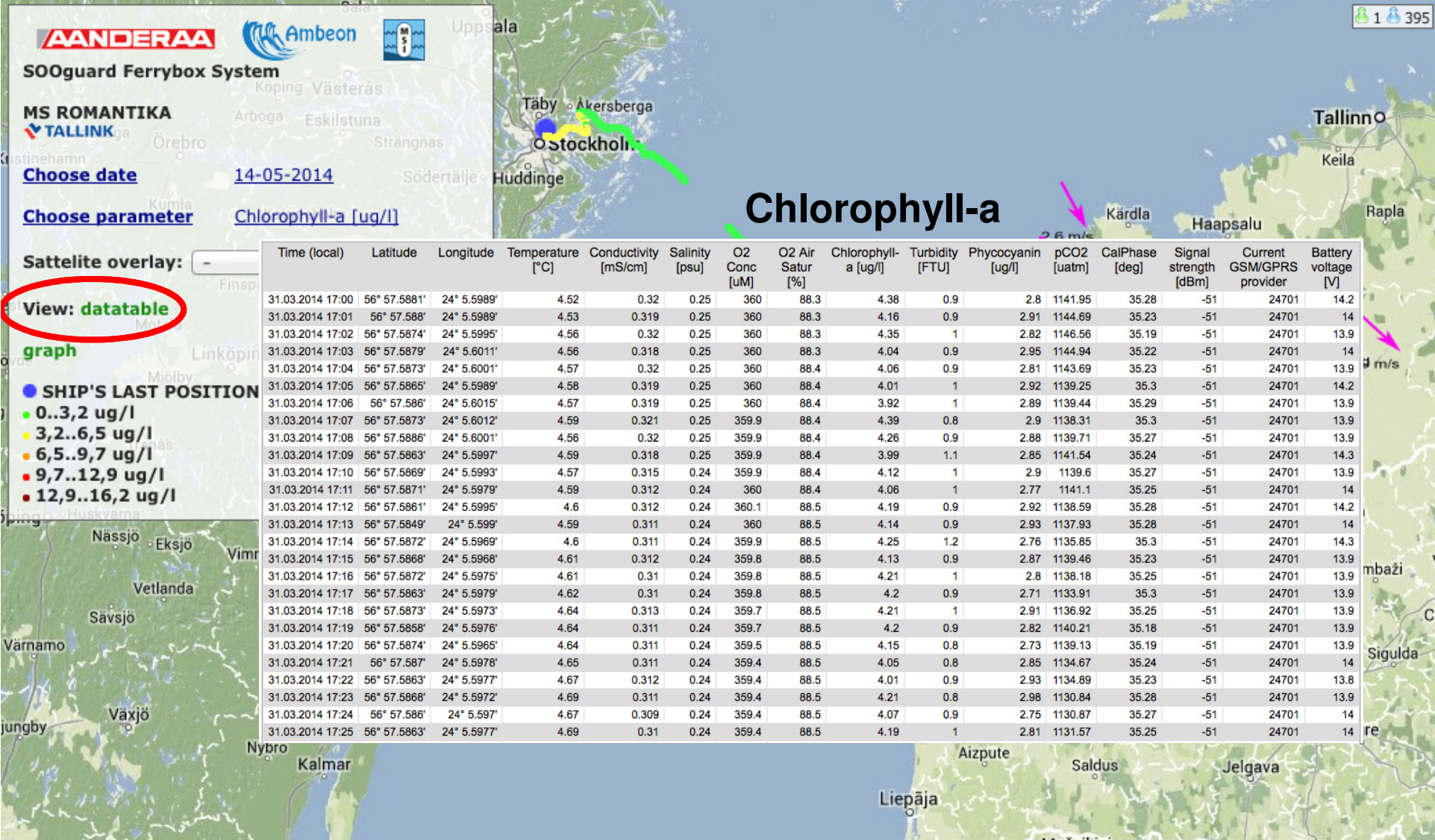
<http://on-line.msi.ttu.ee/lvferry3/?ts=1394316000¶m=salinity>

MS ROMANTIKA X

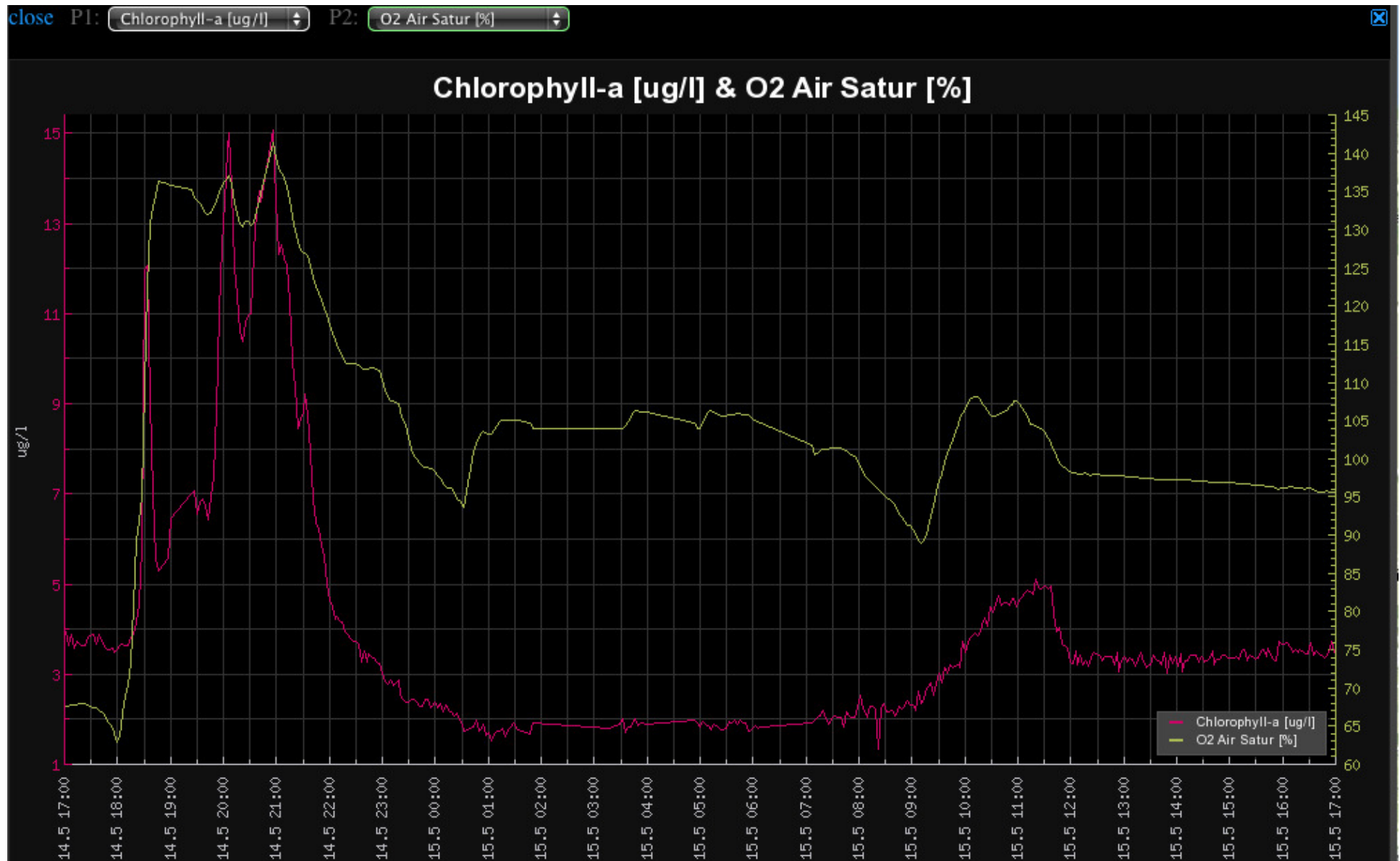
Time: 09-03-2014 23:52
 Latitude: 57° 41.8382'
 Longitude: 21° 58.6255'
 Temperature: 1.82 °C
 Conductivity: 6.39 mS/cm
 Salinity: 6.33 psu
 O2 Conc: 425.35 uM
 O2 Air Satur: 96.92 %
 Chlorophyll-a: 6.86 ug/l
 Turbidity: 0.77 FTU
 Phycocyanin: 3.29 ug/l
 pCO2: 620.18 uatm
 CalPhase: 32.74 deg
 Signal strength: -59 dBm
 Current GSM/GPRS provider: 24701
 Battery voltage: 14.3 V



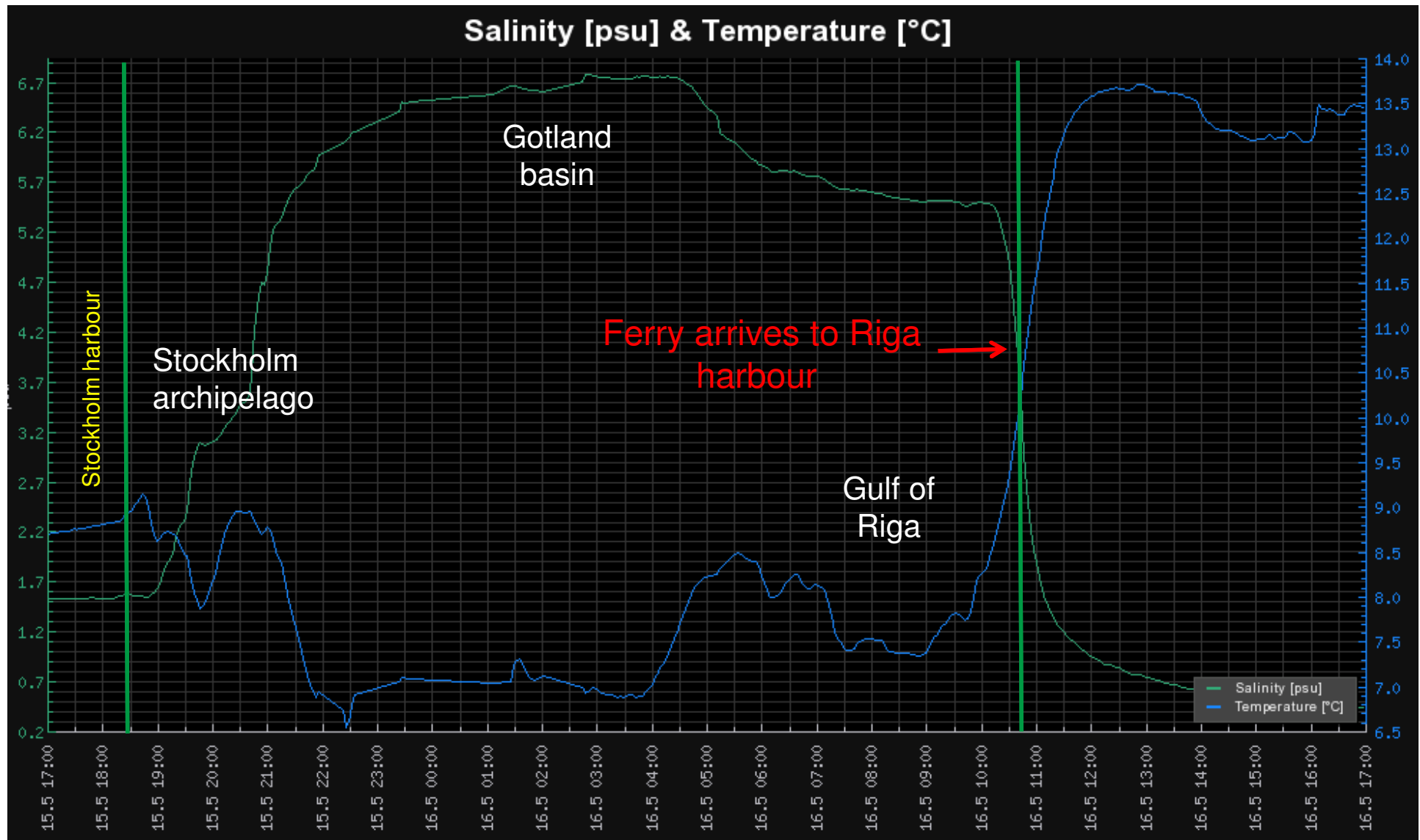
On-line data visualization tool: single property transect and datatable



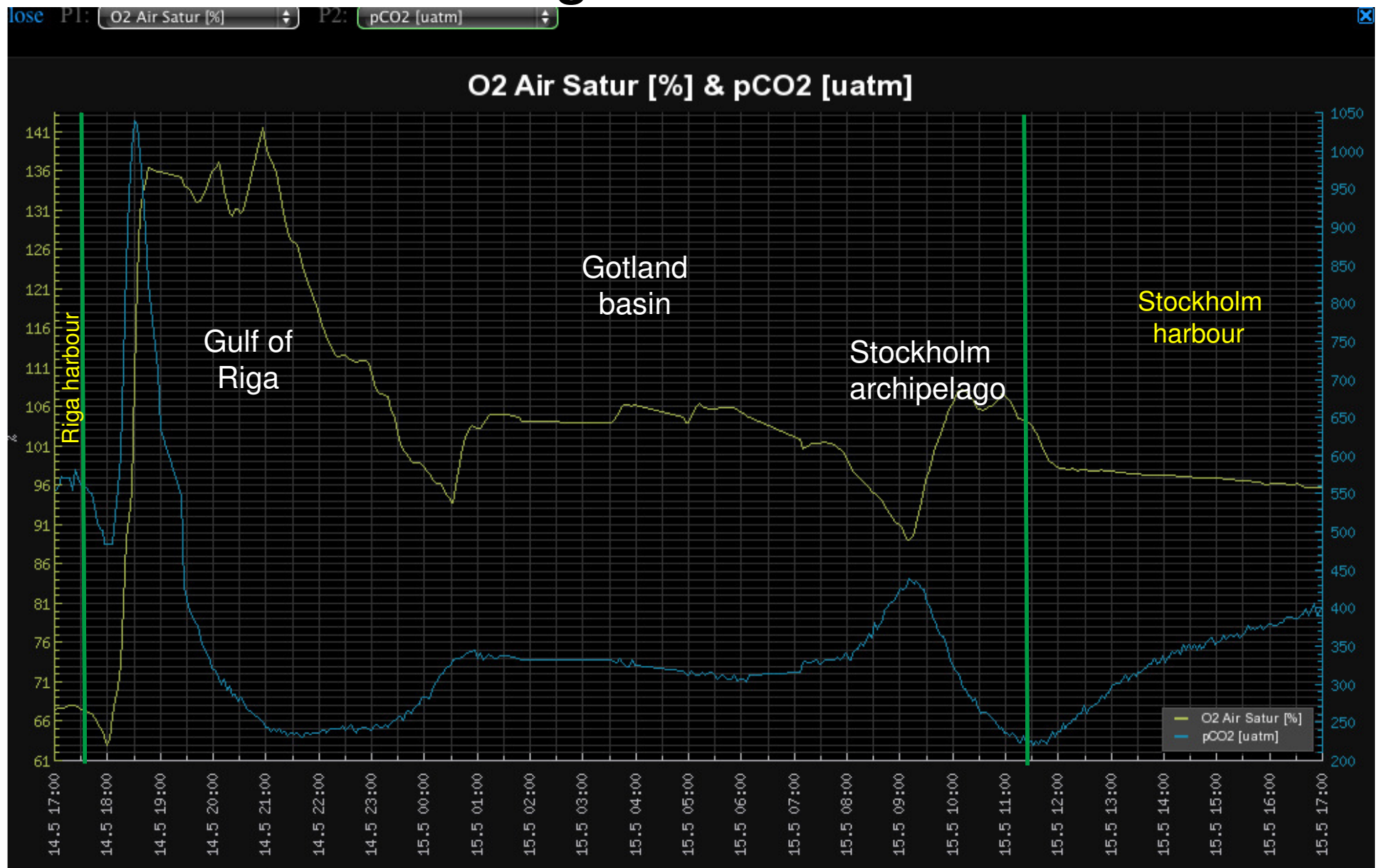
On-line data visualization tool: property vs. property

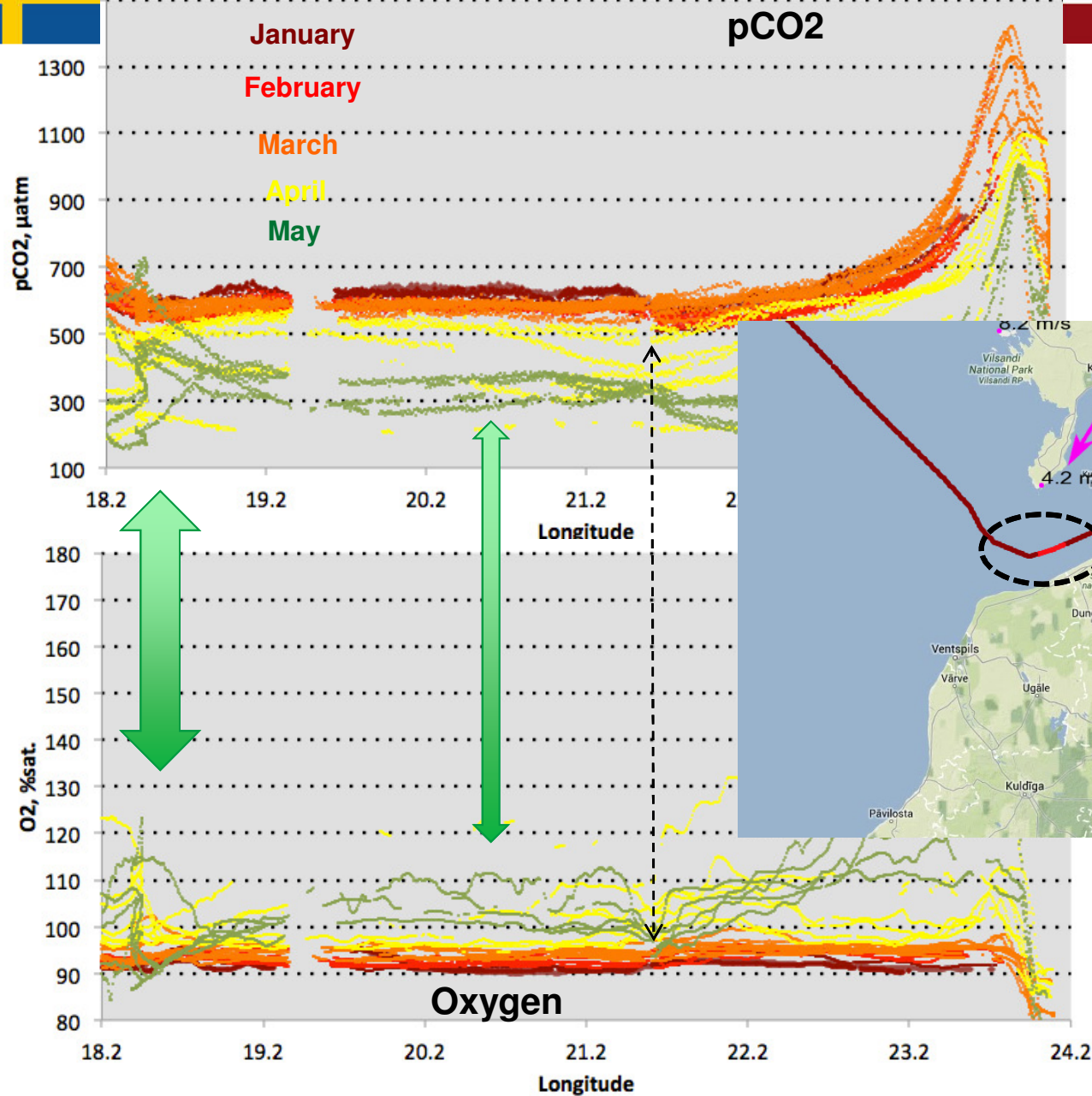


Delay in the response to in situ conditions



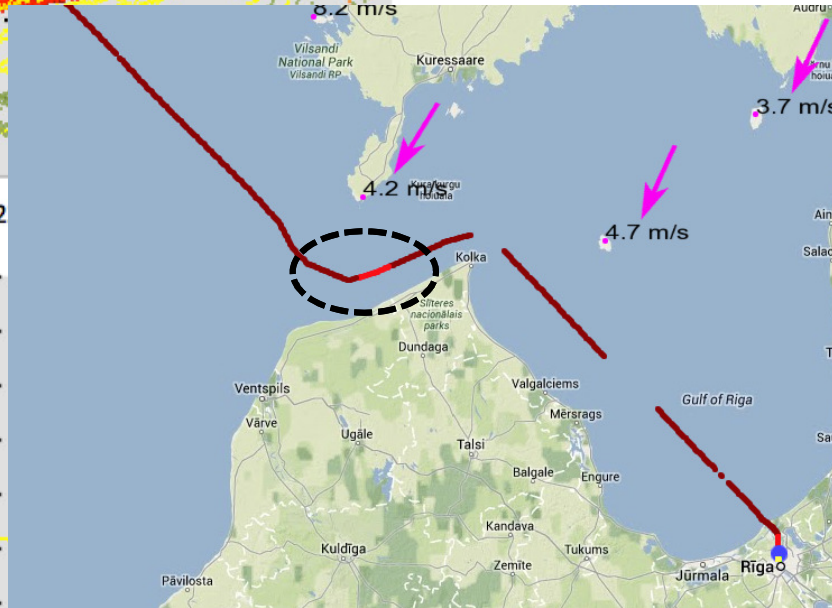
Route Riga-Stockholm





Observational period Jan-May 2014

- one-directional transect every second day



50
per

Oxygen Optodes

Examples of Scientific Papers

Incubators

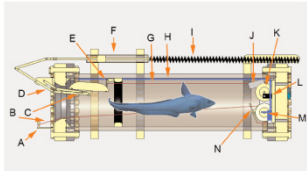


Fig. 3. Cross-sectional view of the incubator with both oxygen optodes and reference incubator. (A) Diffusion of air and water circulation. (B) Diffusion of air and water circulation. (C) Diffusion of air and water circulation. (D) Diffusion of air and water circulation. (E) Diffusion of air and water circulation. (F) Diffusion of air and water circulation. (G) Diffusion of air and water circulation. (H) Diffusion of air and water circulation. (I) Diffusion of air and water circulation. (J) Diffusion of air and water circulation. (K) Diffusion of air and water circulation. (L) Diffusion of air and water circulation. (M) Diffusion of air and water circulation. (N) Diffusion of air and water circulation.

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

Ferry boxes

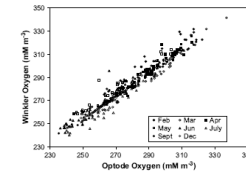


Fig. 1. Lower Winkler titration value plotted against the corresponding value for the optode in 2005. The data from the different calibration crossing are distinguished in the plot.



Tengberg et al (2006)

Hydes et al (2009)

Gas Exchange Chamber

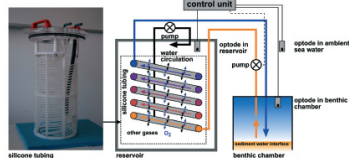


Figure 1. Schematic drawing of the gas exchange system. For explanation, see text.

Sommer et al (2008)

Cabled CTD

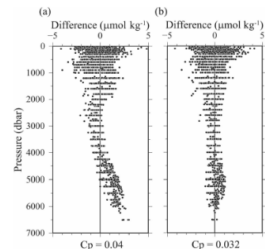
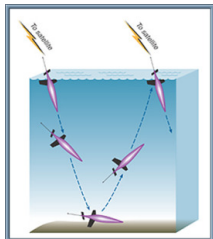


Fig. 5. Difference between in situ calibrated optode oxygen data and Winkler oxygen data plotted against pressure for cruise MB05-01 (n=76) samples. The pressure compensation for the optode oxygen was performed using pressure compensation coefficient (C_p) of 0.04 and 0.032.

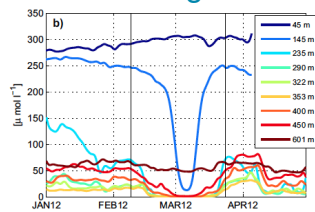
Uchida et al (2008)

Gliders



Nicholson et al (2008)

Moorings



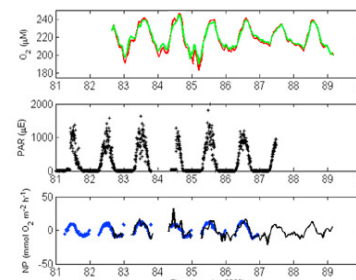
Stramma et al (2014), Viktorsson et al (2012)

Buoys



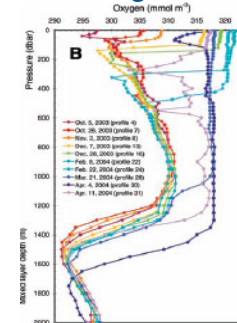
Jannash et al (2008), Bushinsky & Emerson (2013)

Gradients



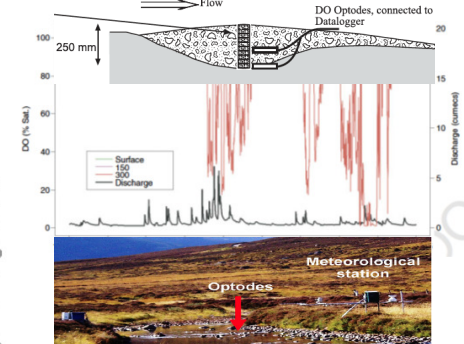
McGillis et al (2011), Champenois and Borges (2012)

Argo floats



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

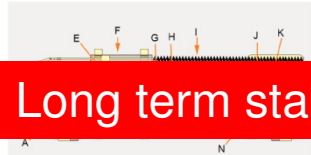
Rivers/Hydrology/Hyporheic



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

Oxygen Optodes

Incubators



Long term stable

Examples of Scientific Papers

Ferry boxes

No O₂ consumption & Robust

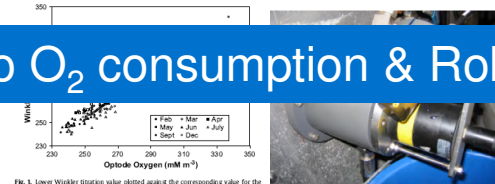


Fig. 1. Lower Winkler titration value plotted against the corresponding value for the optode in 2005. The data from the different calibration crossings are distinguished in the plot.

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

Wikner et al (2013)

Not freezing sensitive

Hydes et al (2009)

Gas Exchange Chamber

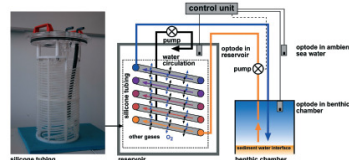
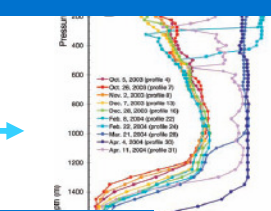


Figure 1. Schematic drawing of the gas exchange system. For explanation, see text.

Good for hot water monitoring



Argo floats

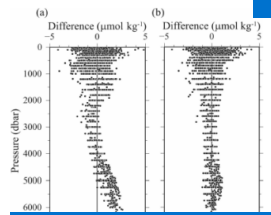


Zingler et al (2004, Nature)
Johnson et al (2010, Nature)
Fiedler et al (2013)
Takeshita et al (2013)

Sommer et al (2008)

Not sensitive to H₂S and most other chemicals

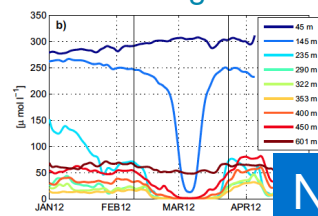
Cabled CTD



High accuracy & low noise

Uchida et al (2008)

Moorings



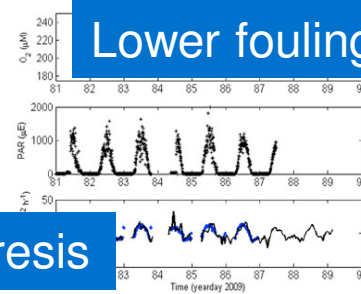
Stramma et al (2014),
Viktorsson et al (2012)

Buoys



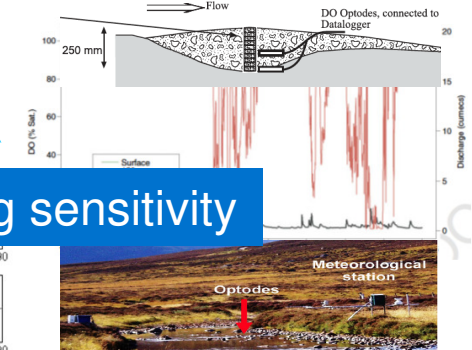
Jannasch et al (2006),
Bushinsky & Emerson (2013)

Gradients



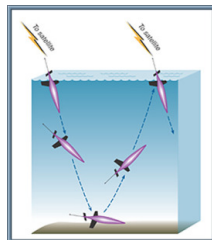
McGillis et al (2011),
Champenois and Borges (2012)

Rivers/Hydrology/Hyporheic



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

Gliders



Nicholson et al (2008)

No pressure hysteresis

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.

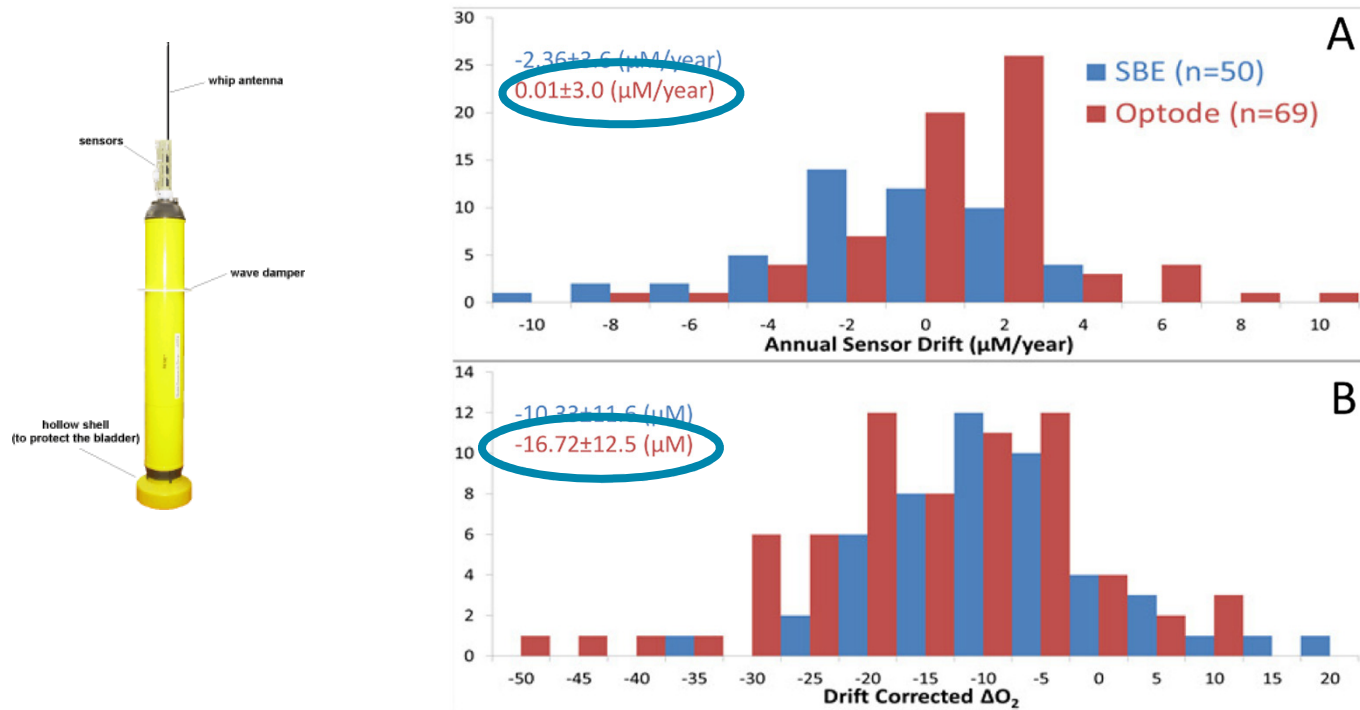
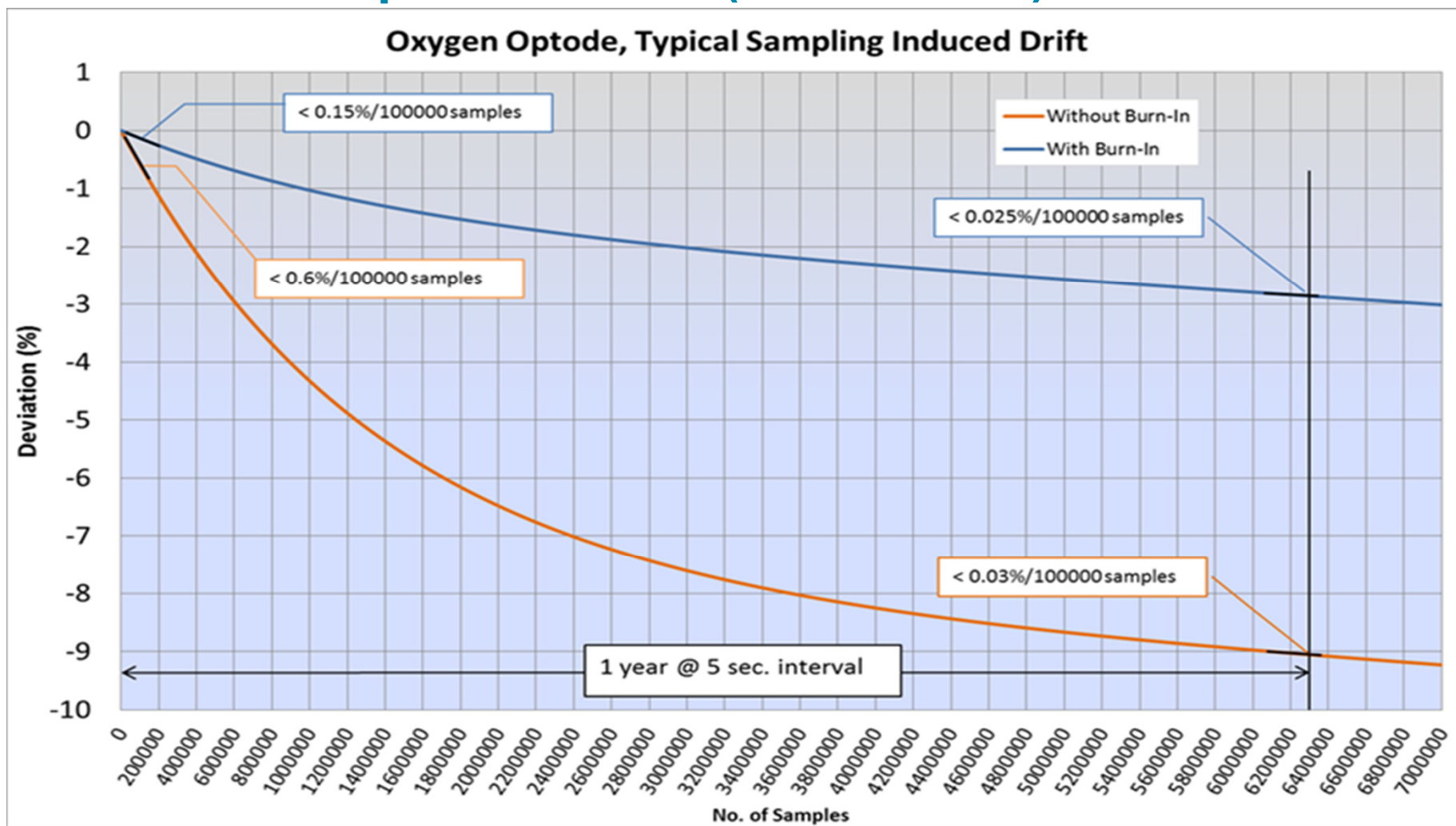


Figure 2. Histogram of sensor drift (A) and the Drift Corrected Average Deep ΔO_2 (B) for the two different types of oxygen sensors. The mean \pm std. dev. is labeled on the plot with its corresponding color.

- 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!

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 μ M/100,000 samples

If not mechanically damaged foils get better over time

Multipoint Calibration System

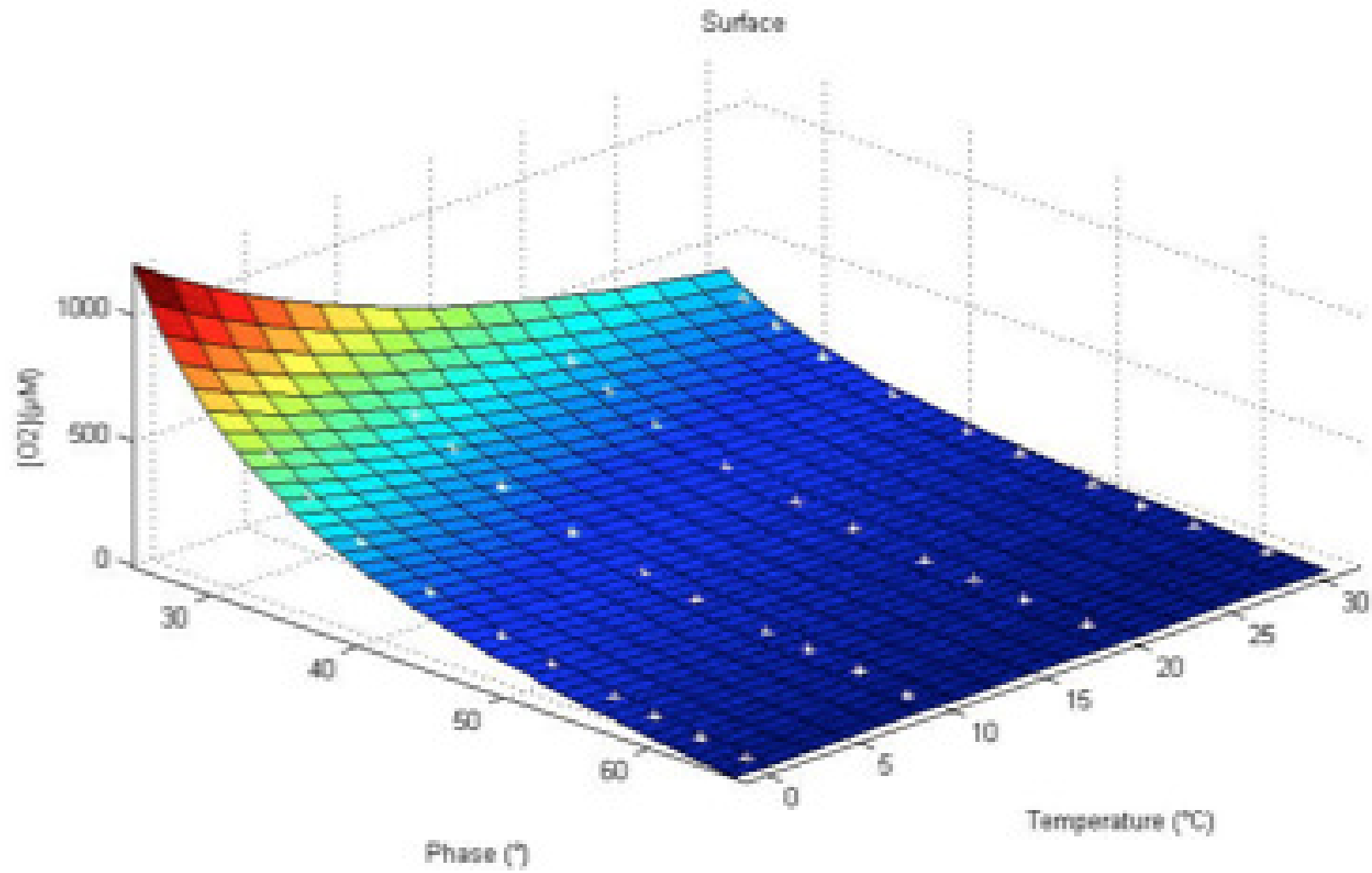
- Gas injection by use of mass flow controllers
- Automatic System 40 point calibration & 20 point subsequent verification
- Operational since August 2012
- 3 parallel reference optodes in system
- Automatic Winkler system from SI Analytics for frequent verification
- **Absolute accuracy better than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



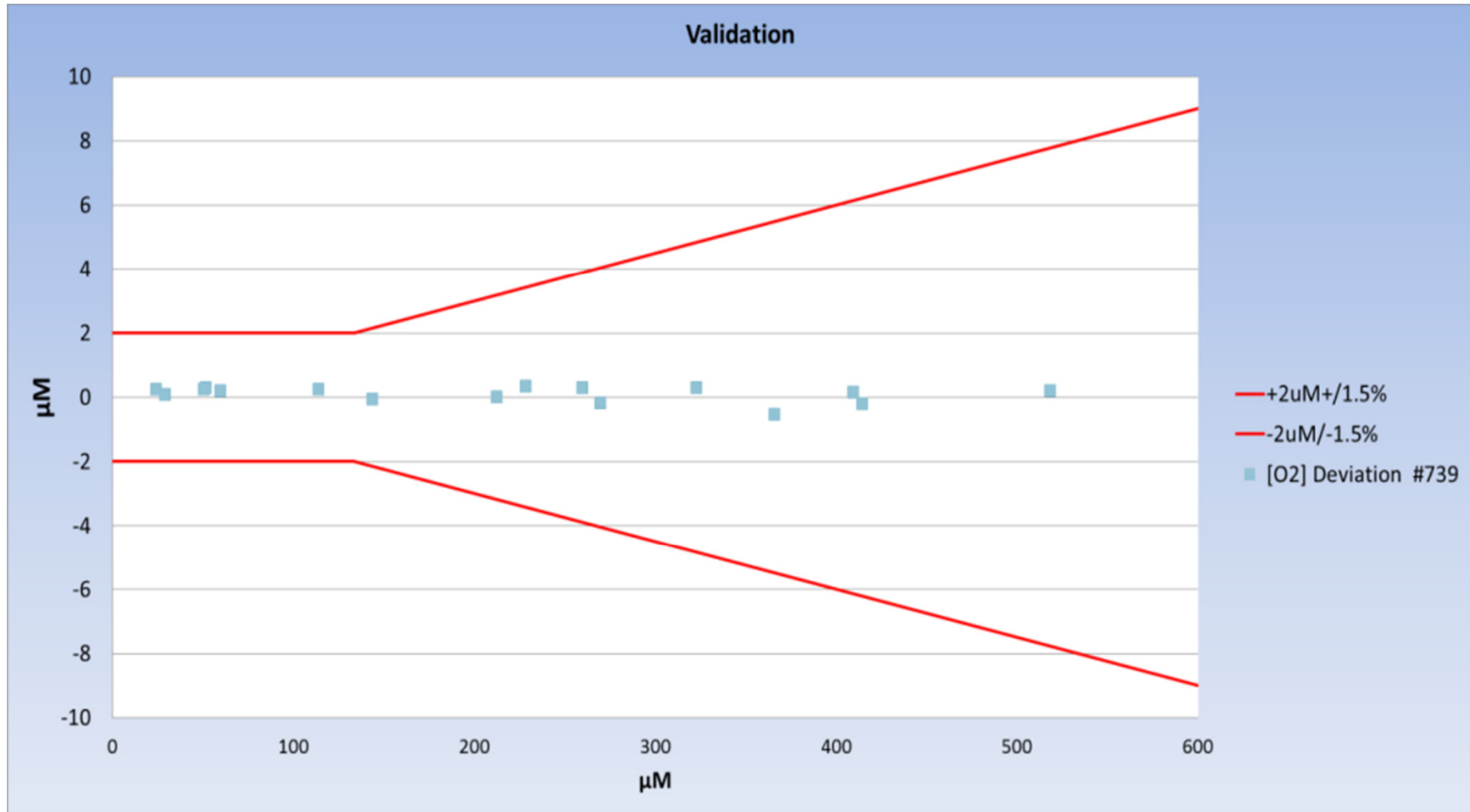
**Multipoint
calibration only for
MkII: 4330 & 4831**



Calibration plot



Validation



Accuracy over entire range of O_2 and Temp: $\pm 2 \mu\text{M}$ or $\pm 1.5\%$. Field resolution: $\pm 0.2 \mu\text{M}$

Multipoint Calibration + red LED referencing gives the highest accuracy

Sensor Development

MKI (2002)
Main models:
3830 & 3835



- Better electronics
- Better optics (faster foils)
- Red reference LED
- Better temperature compensation
- Better formulas to calculate absolute oxygen (Uchida 2008)
- Multipoint calibrations with pre-treated foils



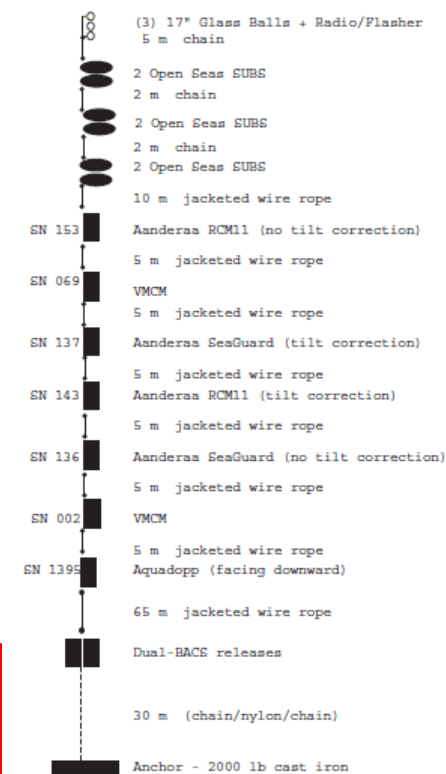
Affordable, High quality, 100 m rated
Aquaoptode 4531 introduced in 2013

MKII (2012)
Main models:
4330, 4831 &
4835



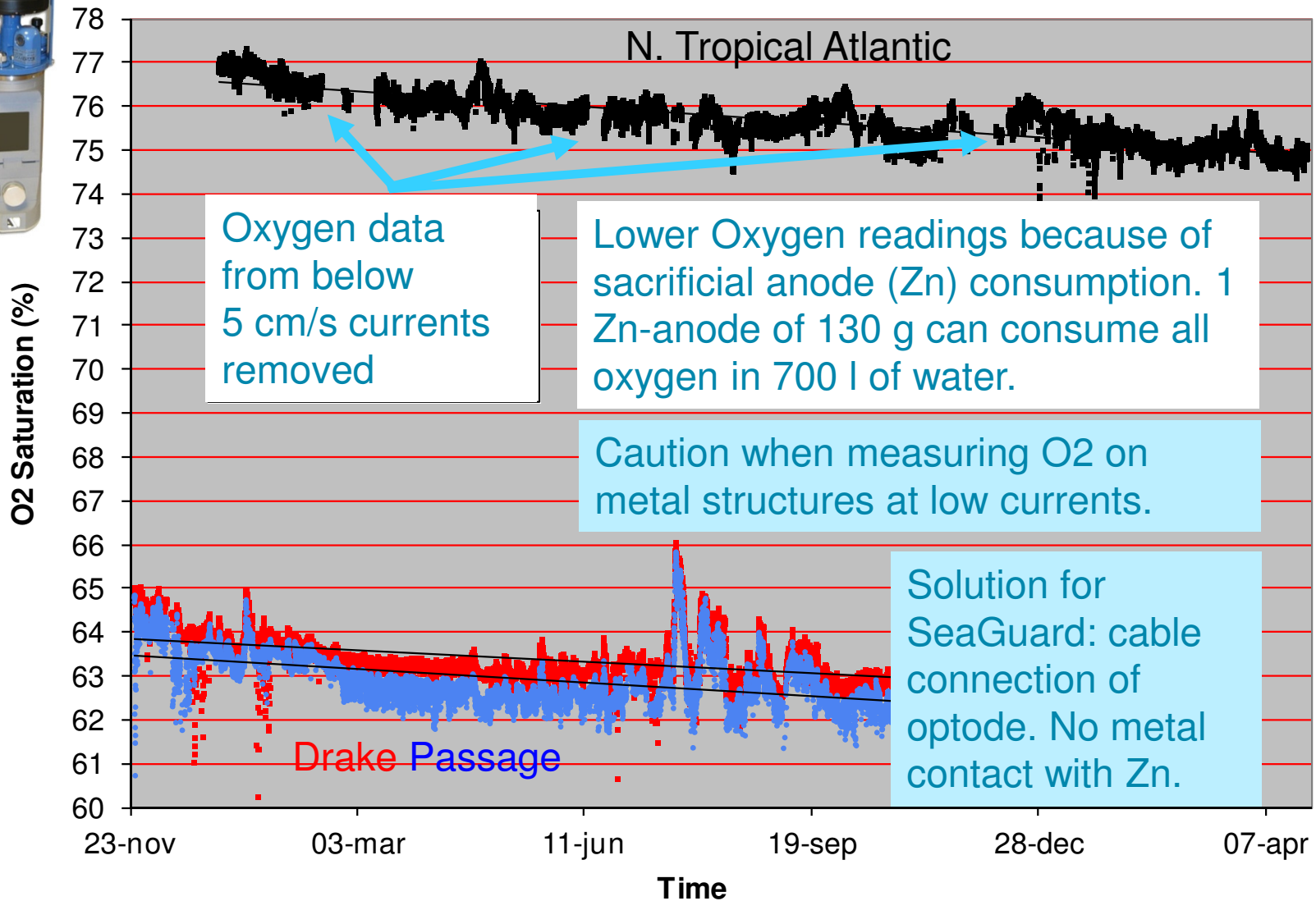
Intercomparison deployment

Year	Tester	Instruments	Duration/ Sampling	Conditions	Availability
2008	Bedford Inst, Canada	Seaguard (2), RCM8, RDI-DVS, RDI-ADCP (300)	1 month, 10 min	155 m, Nova Scotian Shelf, max speed 40 cm/s	Publication: "An intercomparison of acoustic current meter measurements in low to moderate flow regions", Drozdowski and al.
2008-2009	Bedford Inst, Canada	Seaguard (2), RCM11, RDI-ADCP (300)	12 months, 60 min	1600 m, Scotian Slope, max speed 26 cm/s	Results in paper & report, see references Upcoming peer reviewed paper
2008-2009	NOAA-PMEL, USA	Seaguard, Sontek Argonaut	9 months, 20 min	10 m, Pirata buoy, Atlantic, wave zone, max speed 60 cm/s	Results in paper, see references
2009	WSA, Germany	Seaguard (2), Nortek Aquadopp (2)	1 month, 5 min	5-10 m, Ems and Elbe rivers, max speed 120 cm/s, high tilt	Results in paper, see references
2009-2010	Univ of Rhode Island, USA	Seaguard (2), RCM11 (2), VMCM (2), Nortek Aquadopp	11 months, 30 min, low backscatter conditions	4000 m, Drake Passage, max speed 65 cm/s, downdrag	Publication: "Four Current Meter models compared in strong currents in Drake Passage", Watts and al.
2010-2011	Univ of Miami, USA	Seaguard, RDI-DVS, Nortek Aquadopp	18 months, 20 min, low backscatter conditions	4000 m, Trop Atlantic, max speed 54 cm/s, long mooring, downdrag & tilt	Will not be published



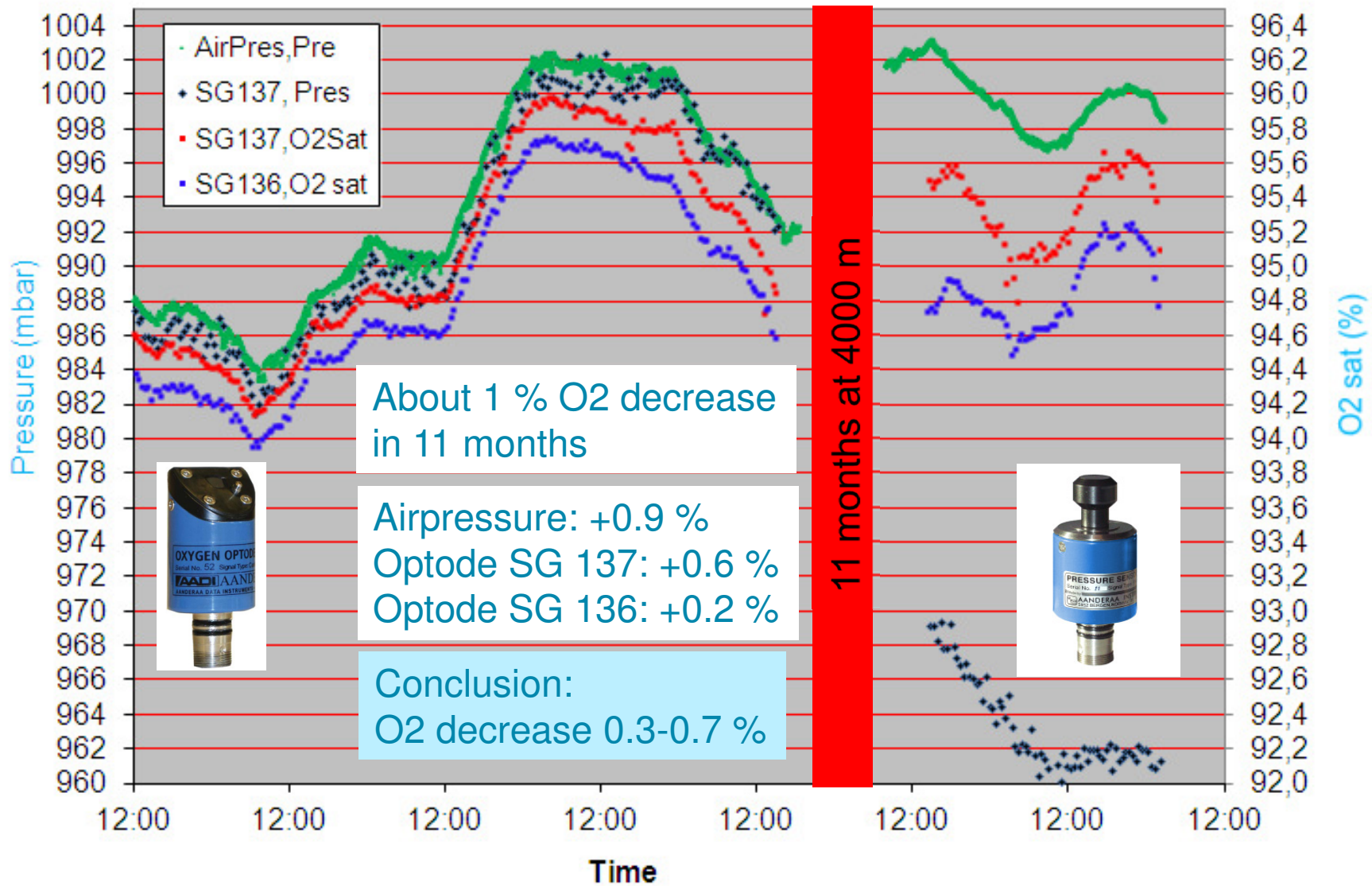


Oxygen at 4000 m



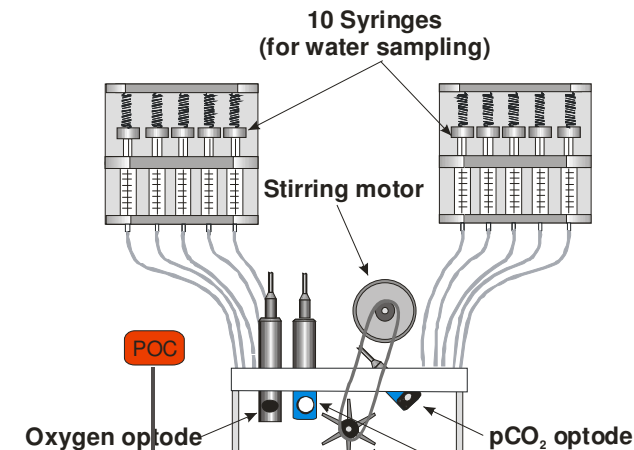
Lo Bue N. et al. (2011) Anomalies of oxygen measurements performed with Aanderaa optodes. J of Operational Oceanography. Volume 4 No. 118, 1–11.

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

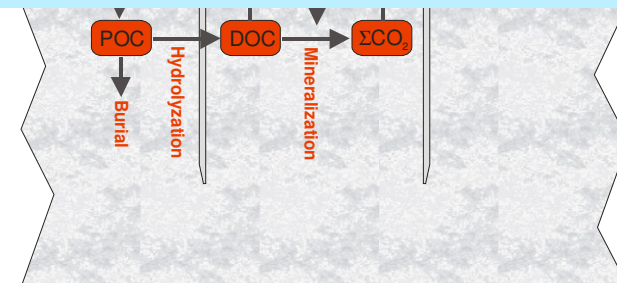


Gothenburg Autonomous Bottom Landers for Sediment-Water Incubations. Deployed ~300 times from 5-5600 m water depth

RCM Blue
in action measuring
above sediment
incubation system

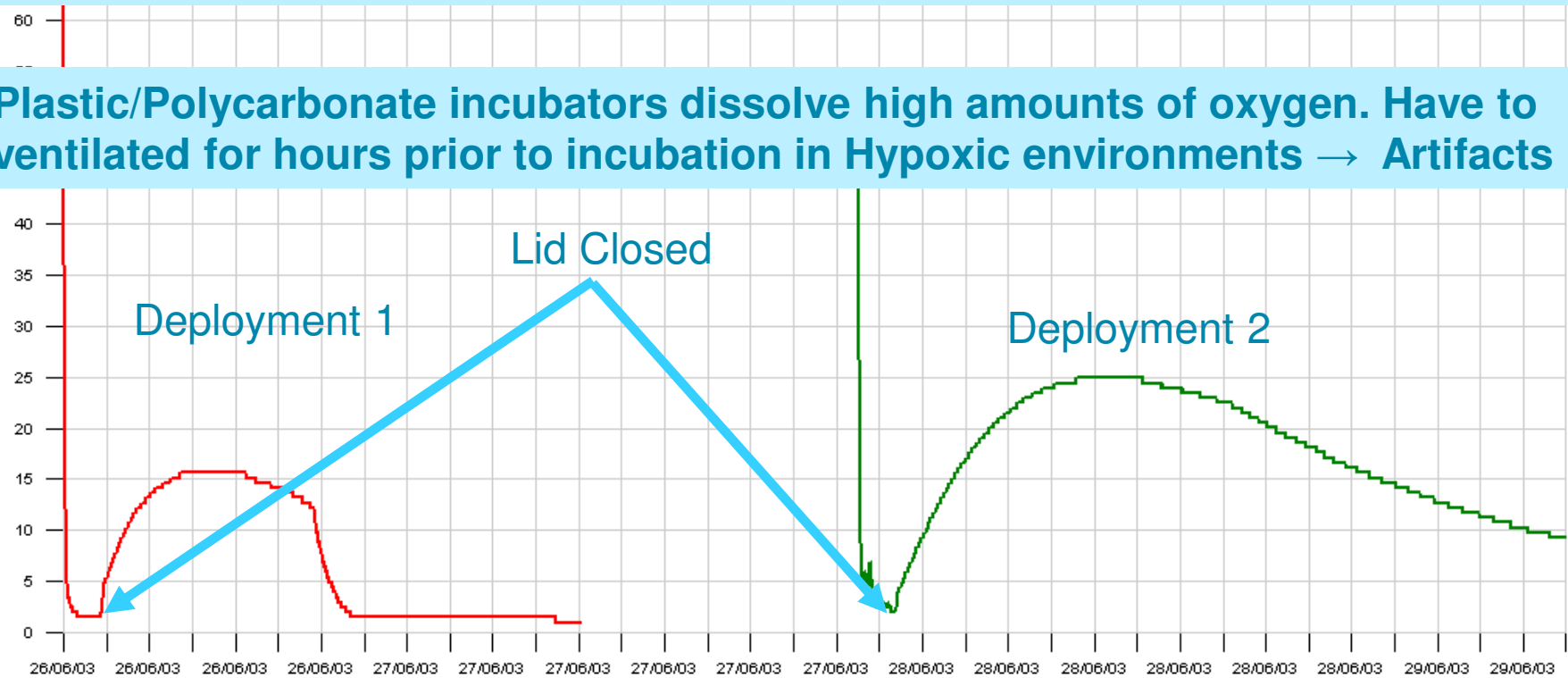


Incubation Chambers in Polycarbonate



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

Plastic/Polycarbonate incubators dissolve high amounts of oxygen. Have to ventilated for hours prior to incubation in Hypoxic environments → Artifacts

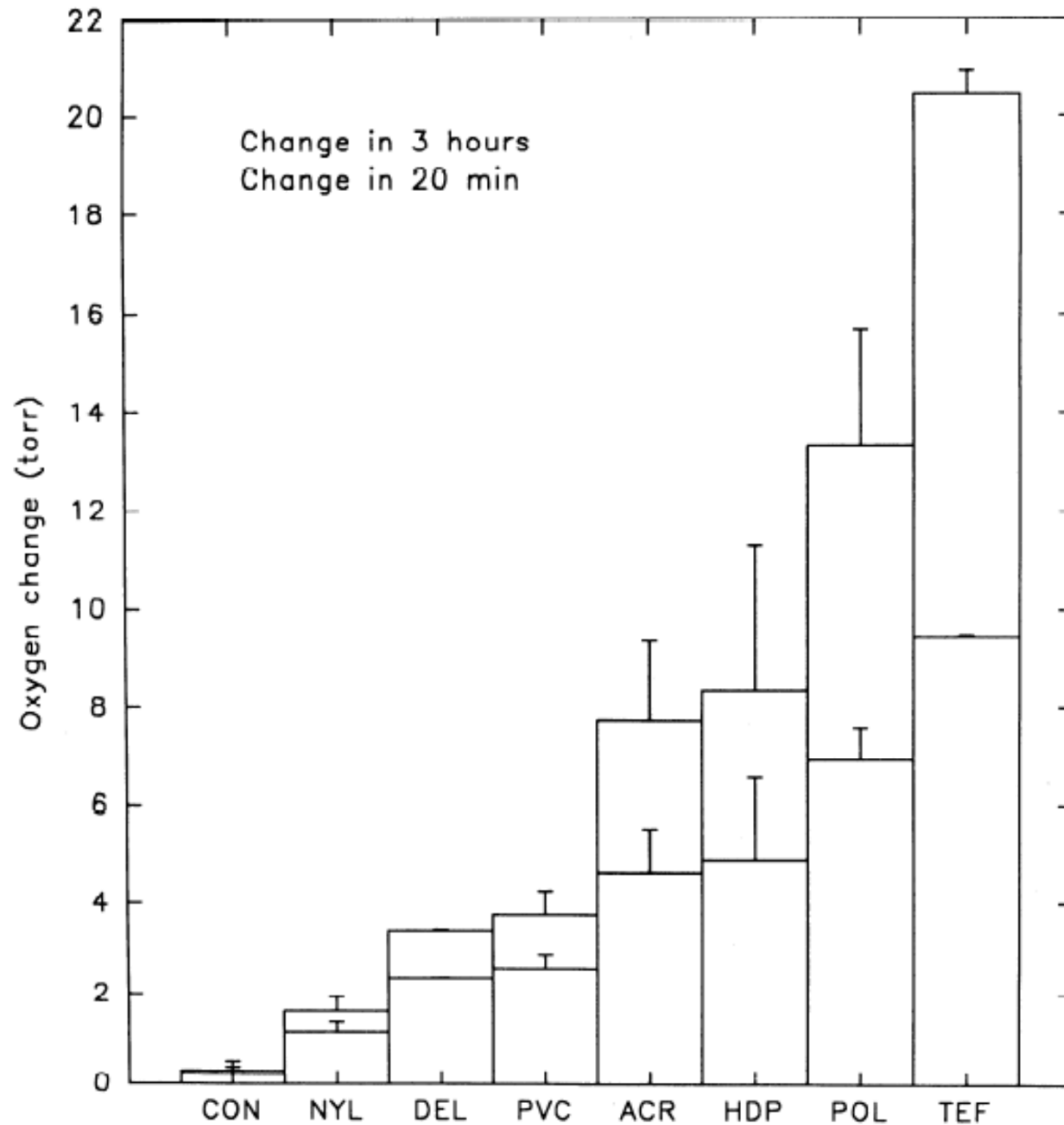


9. Optode(red) [µM]

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.



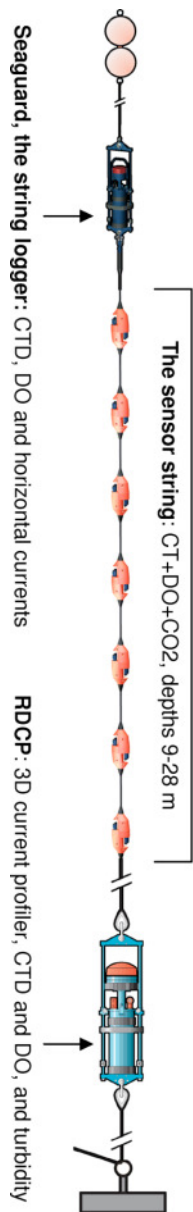
Stevens, E. Don (1992) Use of plastic materials in oxygen-measuring systems. *Journal of Applied Physiology*, 72(2): 801-804.

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

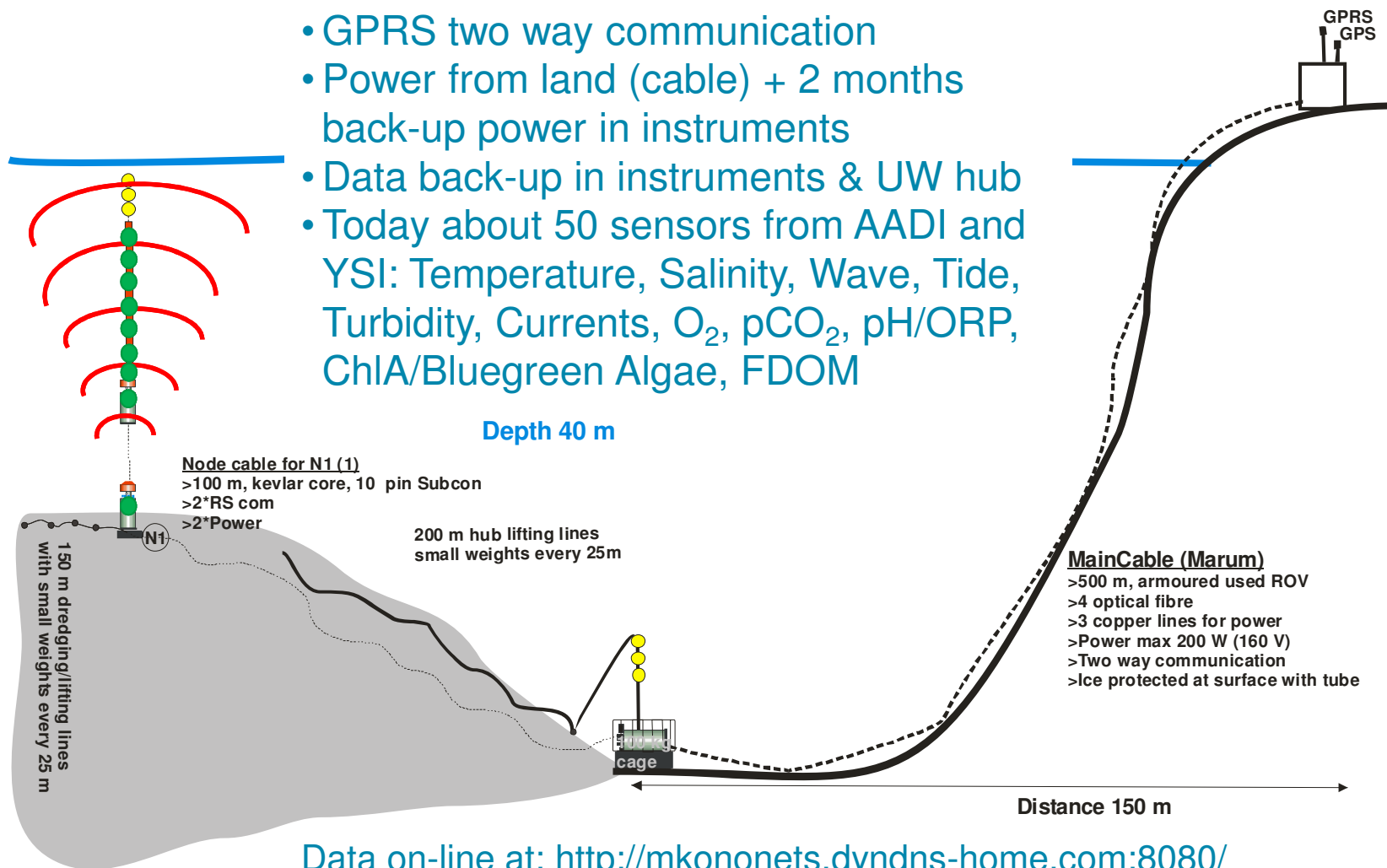
Koljoe fjord observatory: Located on the Swedish west coast in a system of fjords that suffer from frequent low oxygen conditions. In operation since April 2011



Koljoe fjord observatory: structure



- Real time 2-30 min interval
- GPRS two way communication
- Power from land (cable) + 2 months back-up power in instruments
- Data back-up in instruments & UW hub
- Today about 50 sensors from AADI and YSI: Temperature, Salinity, Wave, Tide, Turbidity, Currents, O₂, pCO₂, pH/ORP, ChlA/Bluegreen Algae, FDOM



Cable for power and communication; ballast

Data on-line at: <http://mkononets.dyndns-home.com:8080/>

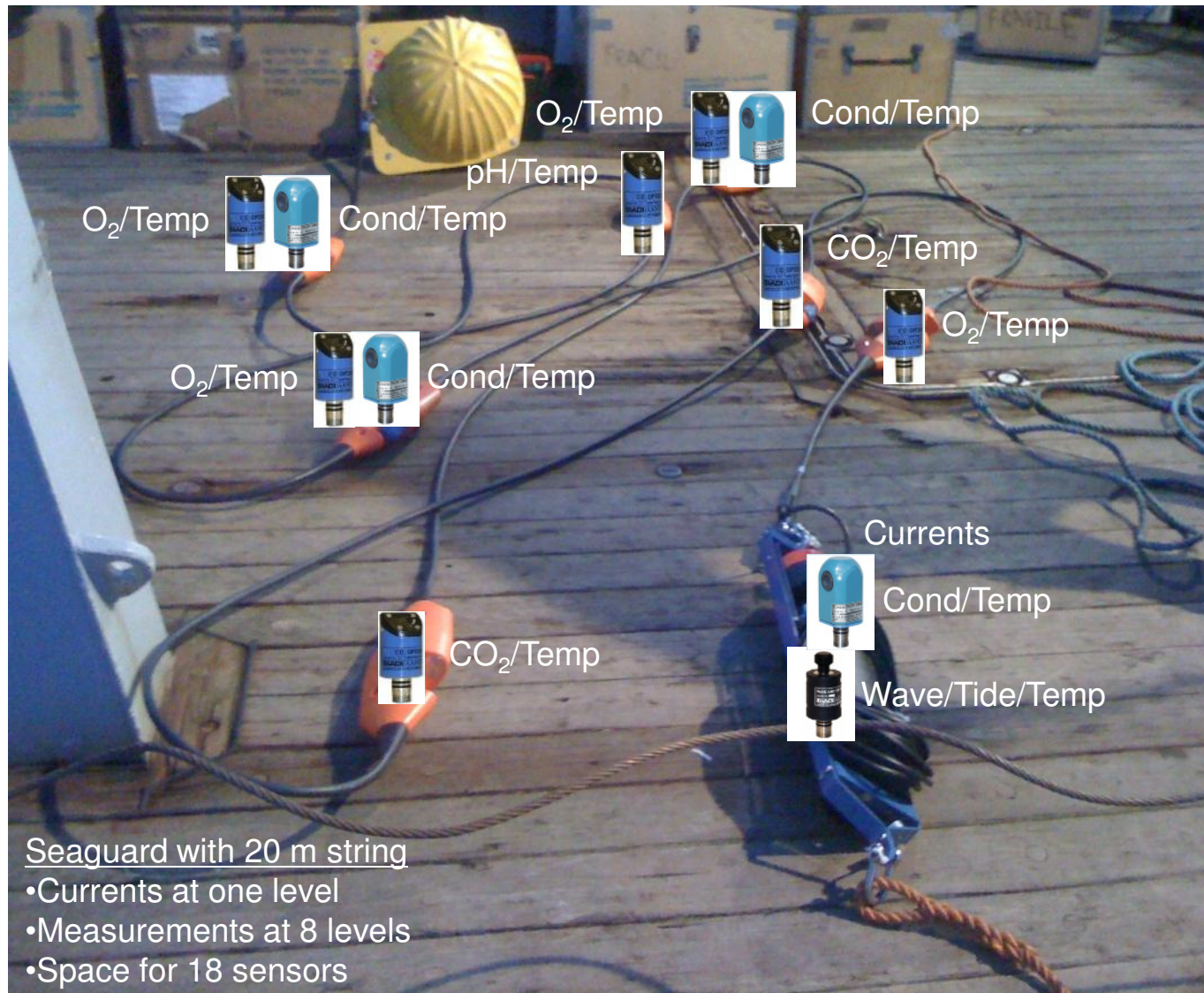


String with sensors

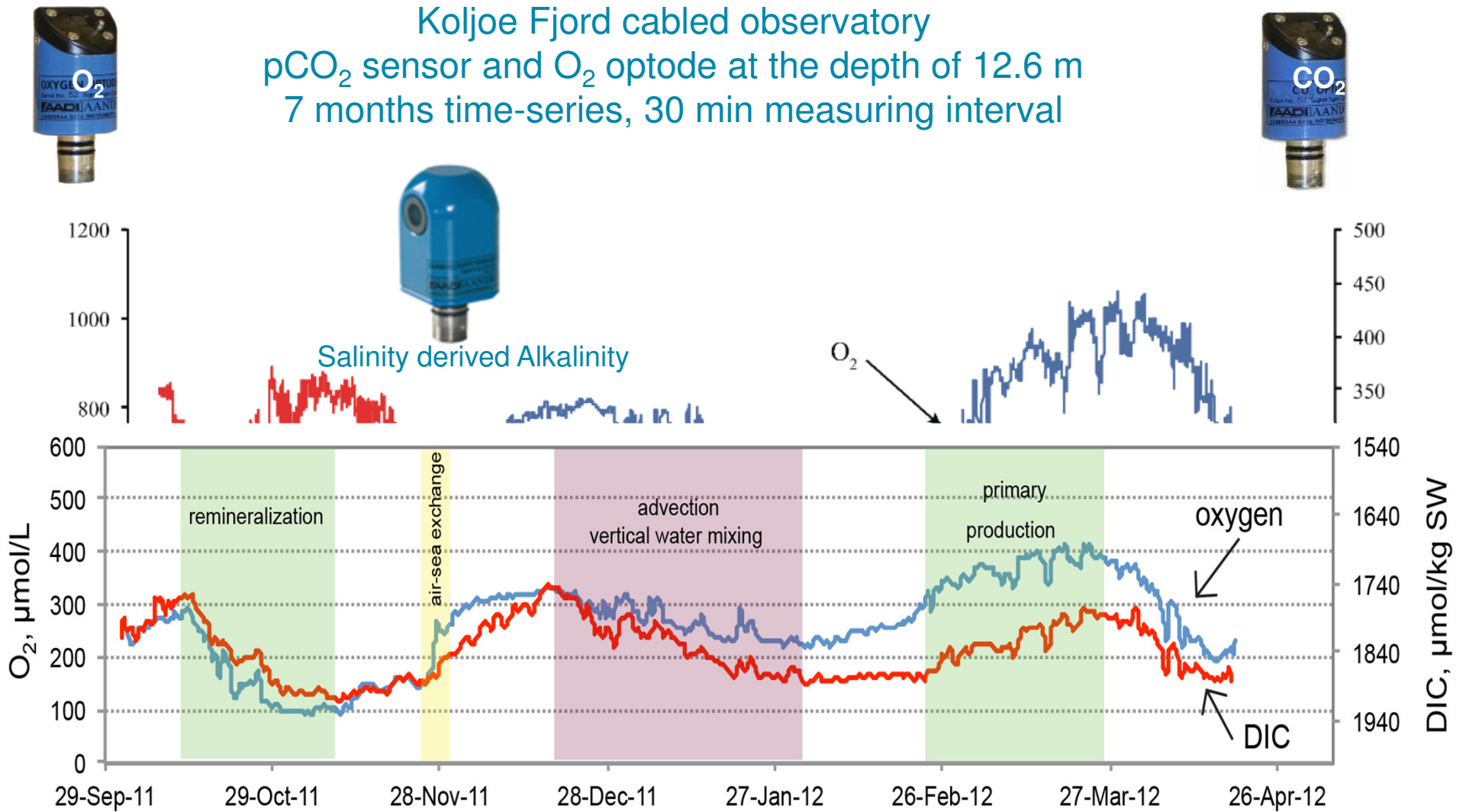
RDCP

Seaguard

Seaguard string



Koljoe Fjord cabled observatory
pCO₂ sensor and O₂ optode at the depth of 12.6 m
7 months time-series, 30 min measuring interval

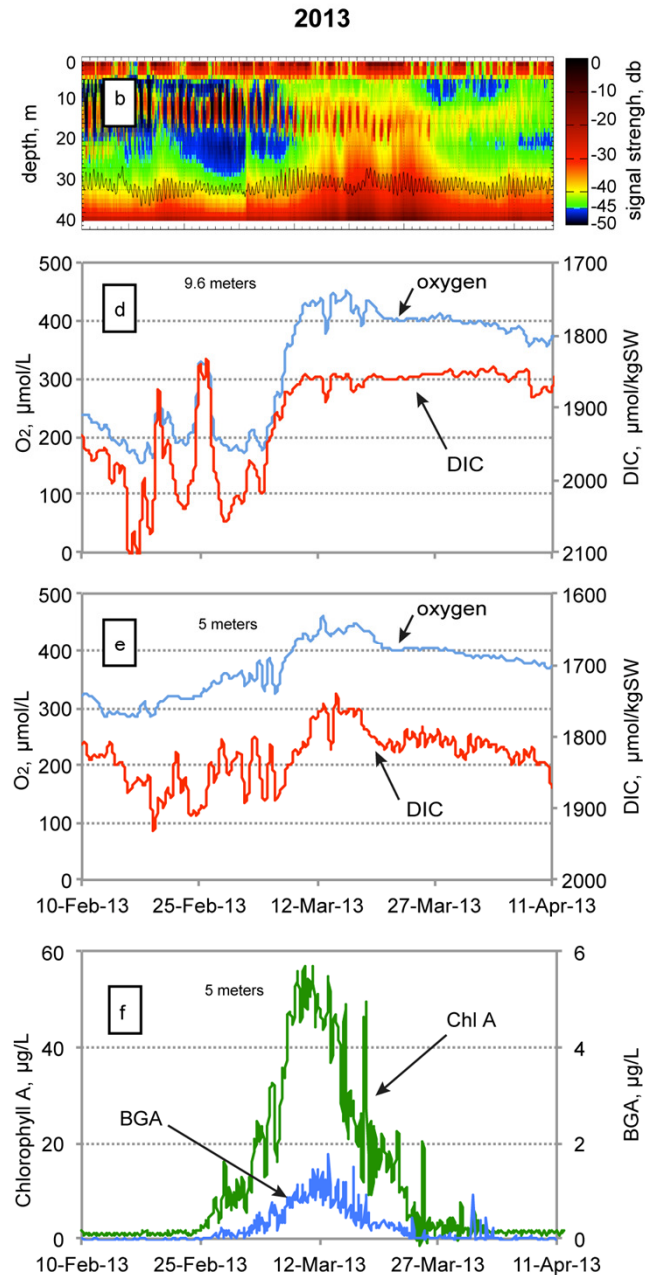


Redfield scaled plots. Atamanchuk et al. (2013)

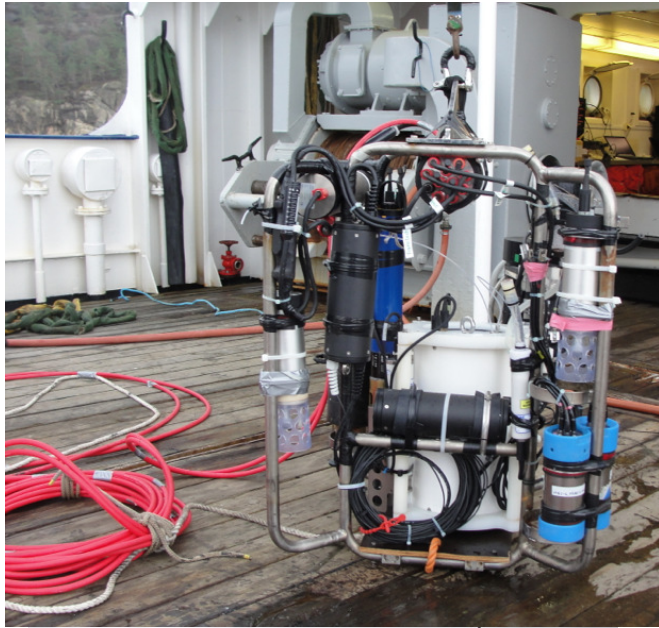
Combining Seaguard and EXO2



EXO2 sensors: C, T, D, O₂, FDOM, ChlA, pH, ORP, Cyanobact + wiper + copper antifouling
 Seaguard sensors: C, 5*T, D, Wave, O₂, 2*CO₂, Currents



Ongoing instruments tests at the Koljoeffjord observatory: pCO₂ and pH sensors inter-comparison



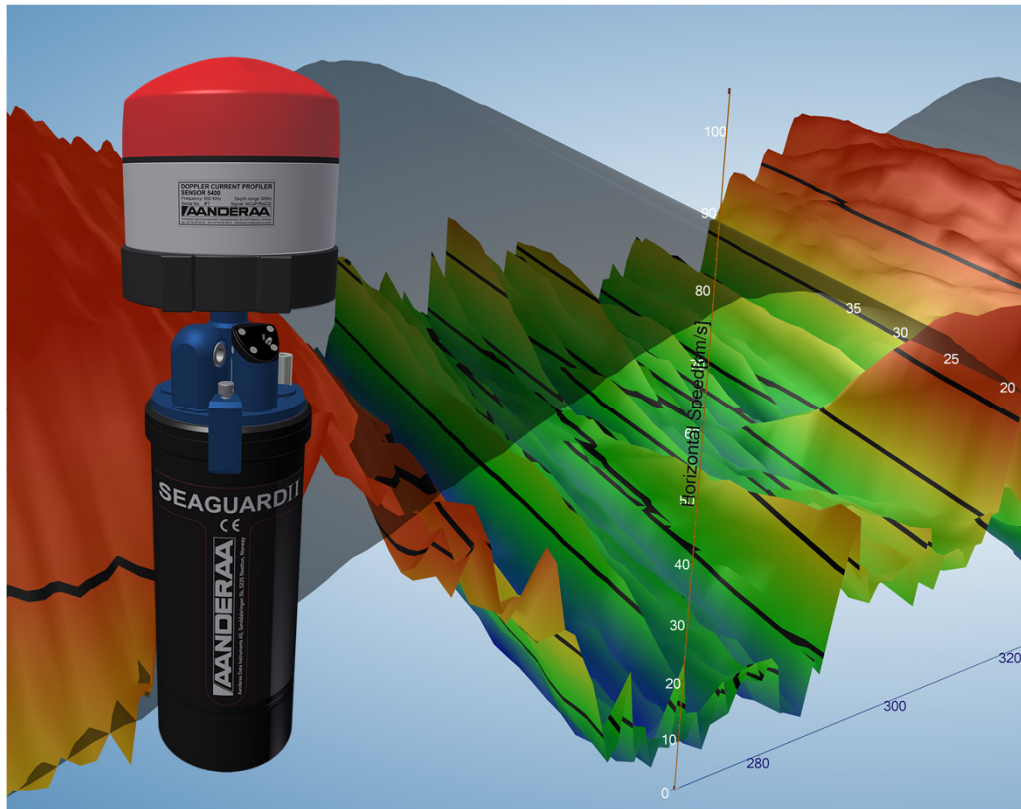
4 different pCO₂ technologies from 5 manufacturers
4 different pH technologies from 5 manufacturers

- Aanderaa Seaguard pH (optode), 2*pCO₂ (optode)
- Contros pCO₂ (IR) old
- Franatech pCO₂ (laser)
- Kimoto Electric Co 2*pH (electrochemical)
- Kyushu University 2*pH (ISFET), 2*pCO₂ (ISFET)
- PSI pCO₂ (IR) new
- PSI pCO₂ (IR) old
- Sensorlab pH (colorometric)
- YSI EXO pH (electrochemical)



- Background data from Aanderaa Seaguard (Currents, Sal, Temp, O₂ and YSI EXO with wiper and copper guard (Sal, Temp, O₂, FDOM, ChlA, Blue green algae, Turb, ORP)
- Sampling 2 times per week for pH (spectrophotometric, meta-cresol-purple, Leif Anderson), DIC (IR-Licor, with Dickson water) and Alkalinity (pH titration + Grahn)

Ongoing instruments tests at the Koljoeffjord observatory: SeaGuardII DCP – the newly released 600kHz multiparameter system current profiler



**Acoustic Doppler Current Profiling,
Broadband vs Narrowband: data
quality, range, power consumption
referencing with single point sensors**

**4 beam vs 3 beam with automatic
removal of faulty beam**

Spread mode vs burst mode

Surface current measurement

**Multi column with surface referred
capability**

Different cell sizes

Ongoing instruments tests at the Koljoeffjord observatory: Response time of new “faster” non-transparent O₂ foils, response time with improved water circulation



New non-transparent foils have about 4 times faster response time keeping the same properties and ruggedness

Better water circulation can improve response time with a factor of 4



Upcoming instruments tests at the Koljoefjord observatory: O₂ contamination from using standard Niskin bottle.



Mounting optodes inside Niskin bottles.
Mimicking typical sampling scenarios in
OMZ, in fjords, in the Black Sea and in
the Baltic Sea



SCRIPPS, San Diego, June 12th, 2014

Thanks for your attention

Conclusions

- In-situ monitoring + quality control + modeling → 3 essential components of understanding aquatic environments
- Optodes are robust, accurate, stable, flexible and have low power consumption
- Proven long-term stability + 5 years
- Used in a wide variety of applications, about 50 scientific publications
- Simple field methods can improve the absolute accuracy to $\pm 3\%$
- Multipoint calibrations improve the absolute accuracy to $\pm 1.5\%$
- Sacrificial anodes can induce artifacts
- Plastic materials have O₂ memory effects, should be avoided

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