White paper on DO measurements: sensors accuracy and scientific needs

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- Rapid ongoing changes in the world's oceans: **biogeochemical** parameters are **urgently needed** across all temporal and spatial scales
- Our ability to monitor ocean **acidification**, changes in **biogeochemical cycling** in response to climate variability, and **ocean deoxygenation** at scales is **not currently possible** !
- **Must integrate observing systems (satellite, in situ platforms, floats, moorings) with biogeochemical parameters: O2, chla, CDOM, nitrate, pCO2**

Global phytoplankton decline over the past century

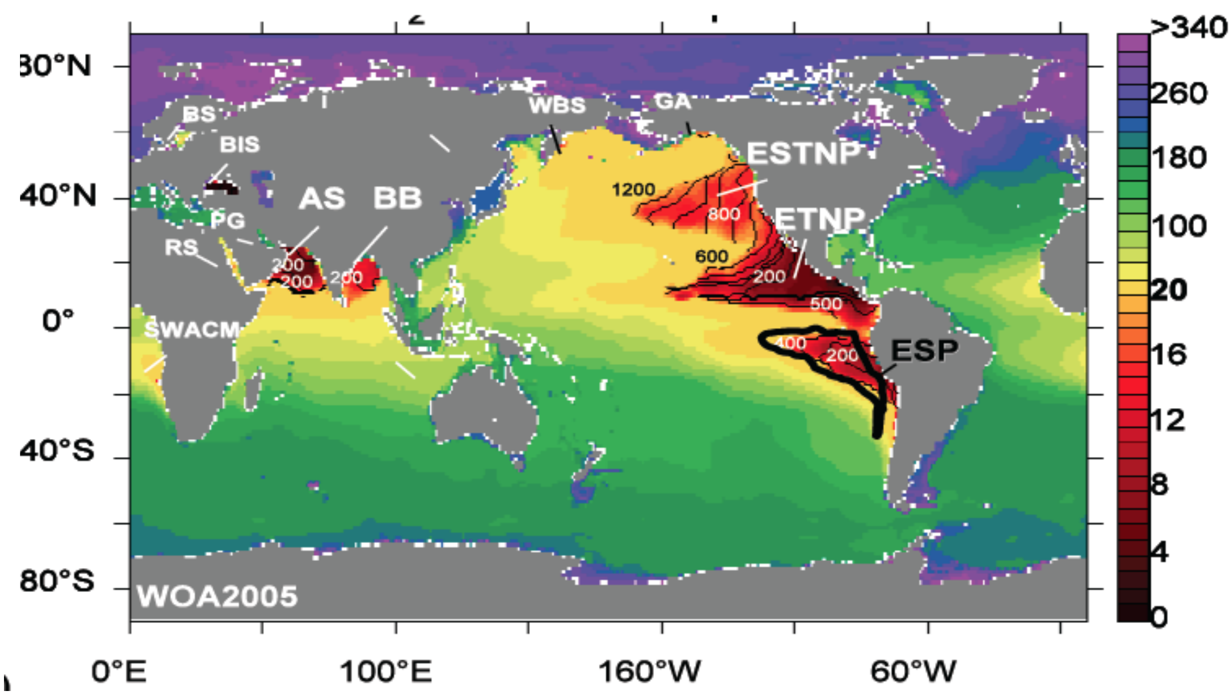
Daniel G. Boyce[1], Marlon R. Lewis[2] & Boris Worm[1]

In the oceans, ubiquitous microscopic phototrophs (phytoplankton) account for approximately half the production of organic matter on Earth. Analyses of satellite-derived phytoplankton concentration (available since 1979) have suggested decadal-scale fluctuations linked to climate forcing, but the length of this record is insufficient to resolve longer-term trends. Here we combine available ocean transparency measurements and *in situ* chlorophyll observations to estimate the time dependence of phytoplankton biomass at local, regional and global scales since 1899. We observe declines in eight out of ten ocean regions, and estimate a global rate of decline of ~1% of the global median per year. Our analyses further reveal interannual to decadal phytoplankton fluctuations superimposed on long-term trends. These fluctuations are strongly correlated with basin-scale climate indices, whereas long-term declining trends are related to increasing sea surface temperatures. We conclude that global phytoplankton concentration has declined over the past century; this decline will need to be considered in future studies of marine ecosystems, geochemical cycling, ocean circulation and fisheries.

Why are we measuring oxygen ?

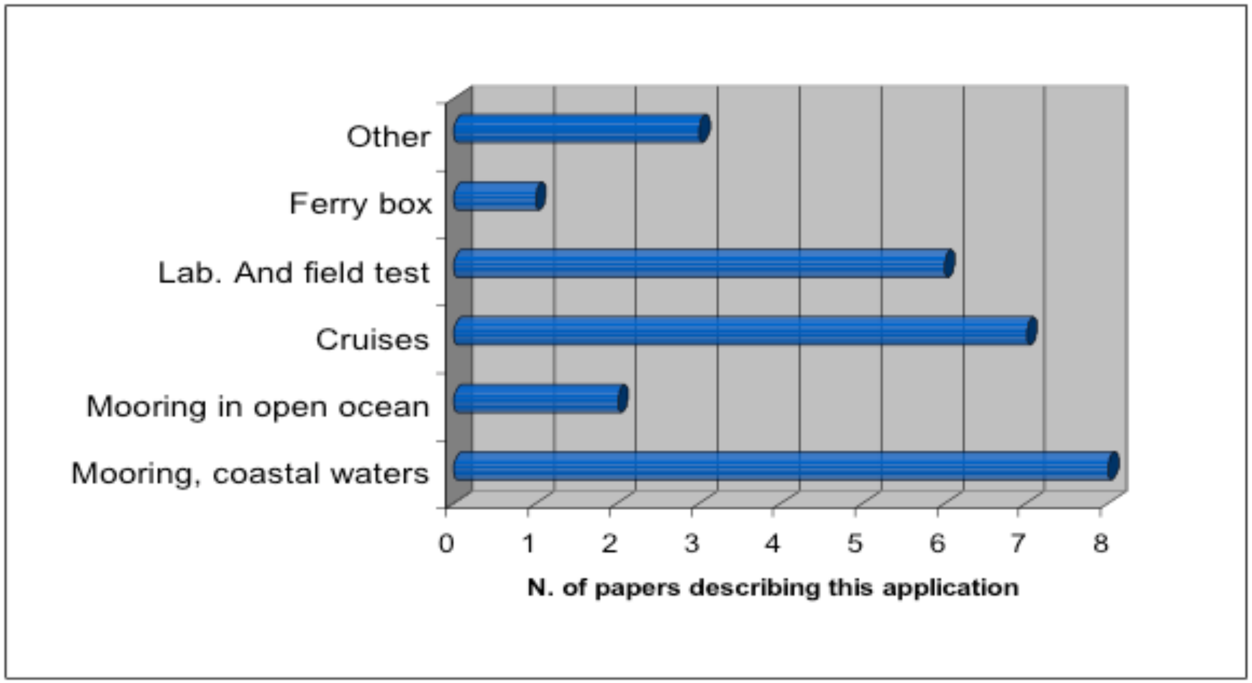
- ➢ deliver information about the biological status of the sea area
- ➢ deliver information about water exchange, circulation, water mass formation
- ➢ help to evaluate the environmental conditions for marine life
- ➢ indicate biological production/extinction

- The ocean deoxygenation is one of the most important topic
- Oxygen is one of the first measured oceanographic parameters but with a large spatio-temporal scales range : OMZs are poorly documented…



Ways of measuring oxygen (mostly used):

- Winkler Titration
- Clark-cell Sensor (electrochemical, closed system)
- Optode (chemo-optical system)



- 17 Peer-reviewed papers from 1995, independent authors
- 4 Performance Verification Statement – ACT 2004

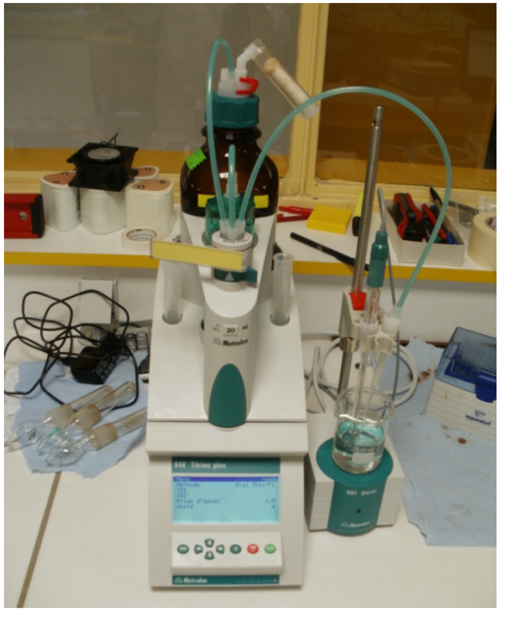
Winkler Titration:

Advantages:

- Standard measuring method
- High accuracy
- High resolution (±2µmol/l)

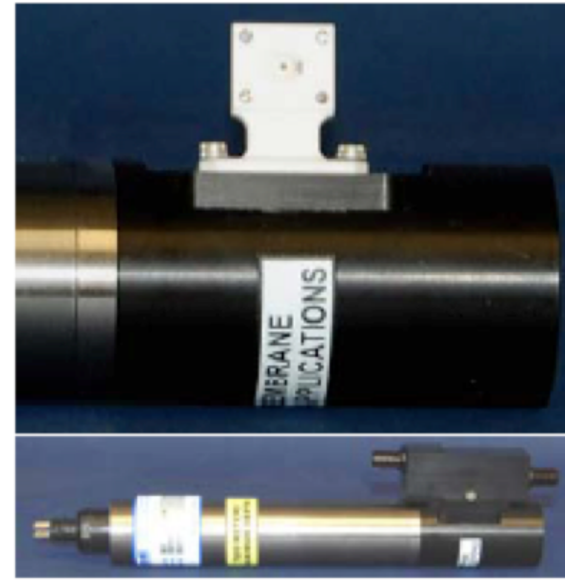
Disadvantages:

- not usable for continuous measurements
- laboratory equipment is needed



See ANALYTICA CHIMICA ACTA vol. 741
A high accuracy method for determination of dissolved oxygen. Gravimetrical Winkler method. Irja Helm, Laun Jalurse, Ivo Leito

Clark-cell Sensor (SBE43):

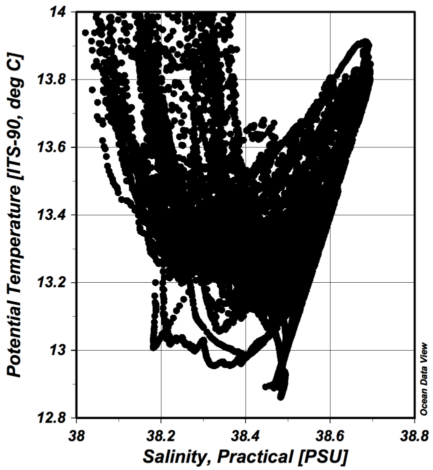


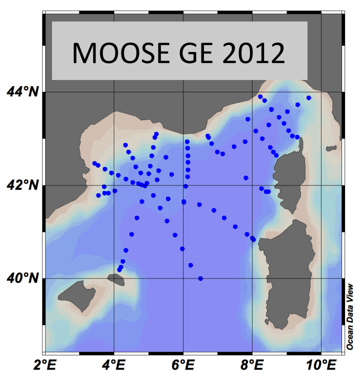
Advantages:

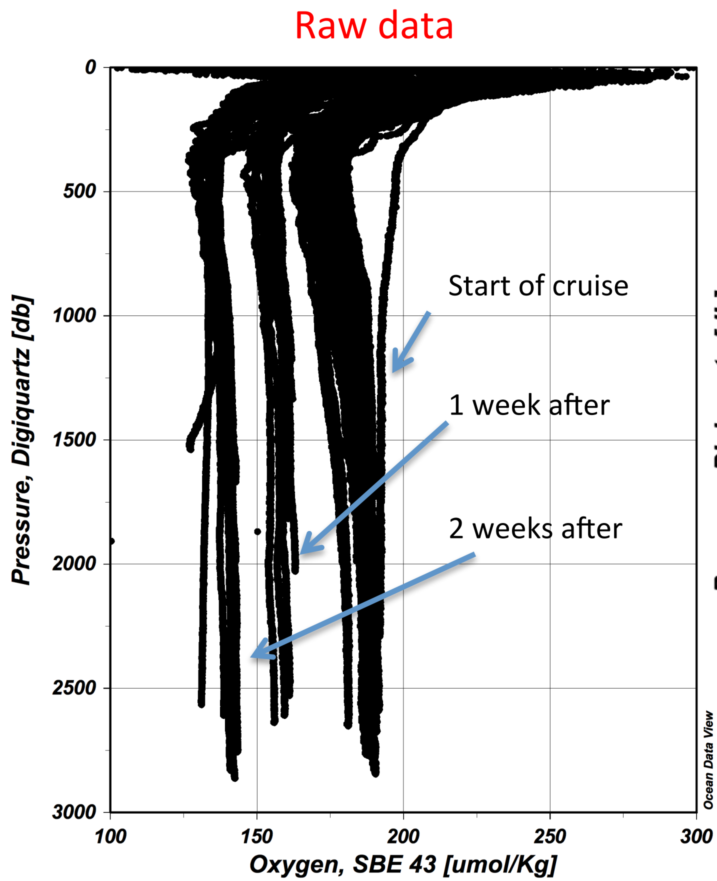
- automatic measuring system
- generating continously data
- acceptable resolution/accuracy

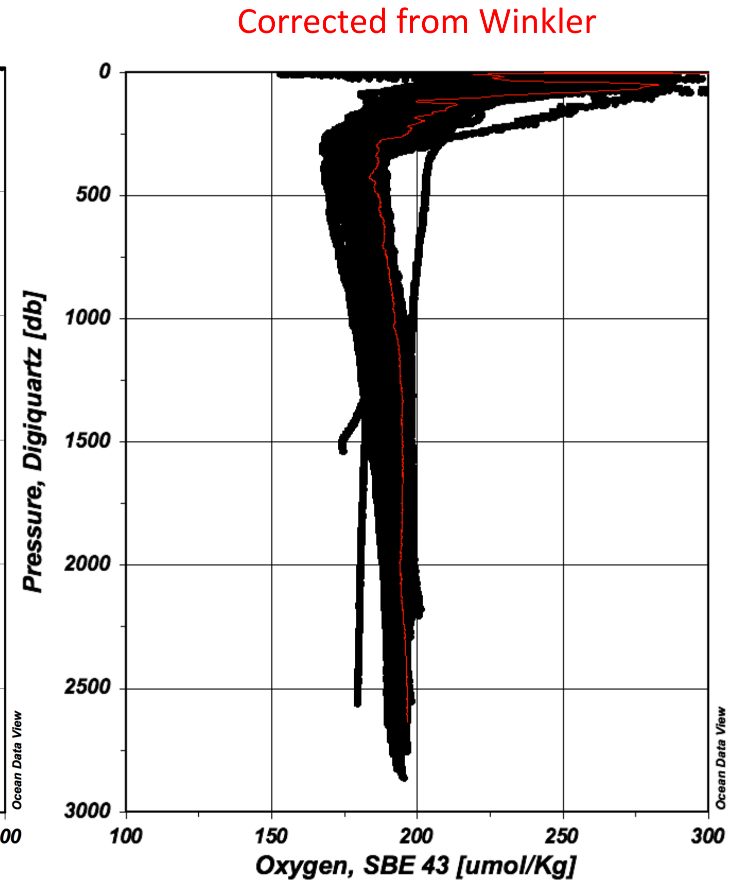
Disadvantages:

- extensive calibration/maintenance work before installation neccessary
- long-term stability is limited to the reaction of the electrolytical liquid
- fouling alters the characteristics of the membranes and they need accurate cleaning and recalibration



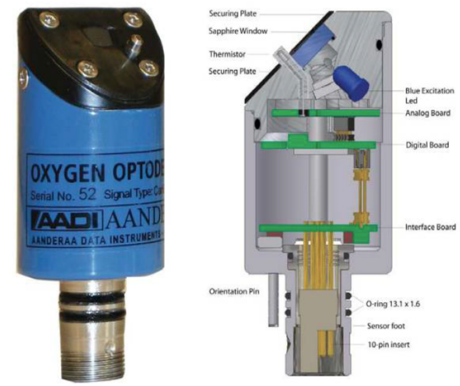






- MOOSE-GE 2012: summer cruise with 90 CTD-O2 profiles in the NW Mediterranean Sea
- Large drift from SBE43 raw data during 17 days cruise (around 50 µmol/kg !!) despite the application of the SBE cleaning procedure (Triton and bleach flushing)
- Able to correct data from O2 Winkler measurements (1 profile per day)

Optode (AADI 3835, 4330):



AADI, Bergen, Norway (www.aadi.no)

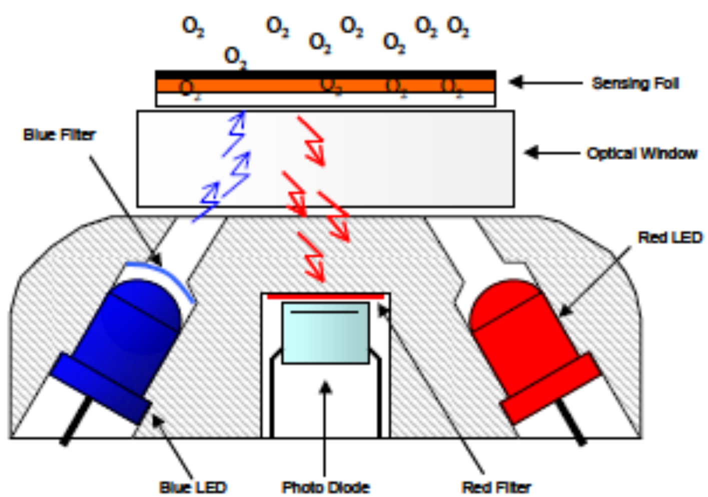
Advantages:

- compact
- easy to handle
- stable measurements up to one year: less affected by fouling
- low energy consumming

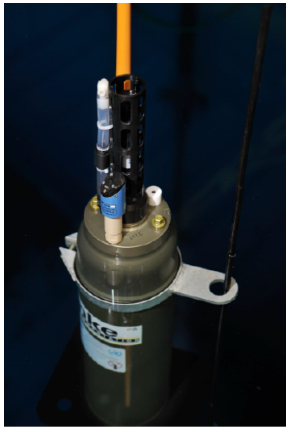
Disadvantages:

- foil cannot be treated by mechanical cleaning (windows should remains clear)
- relative long response time, not suitable for fast CTD profiles

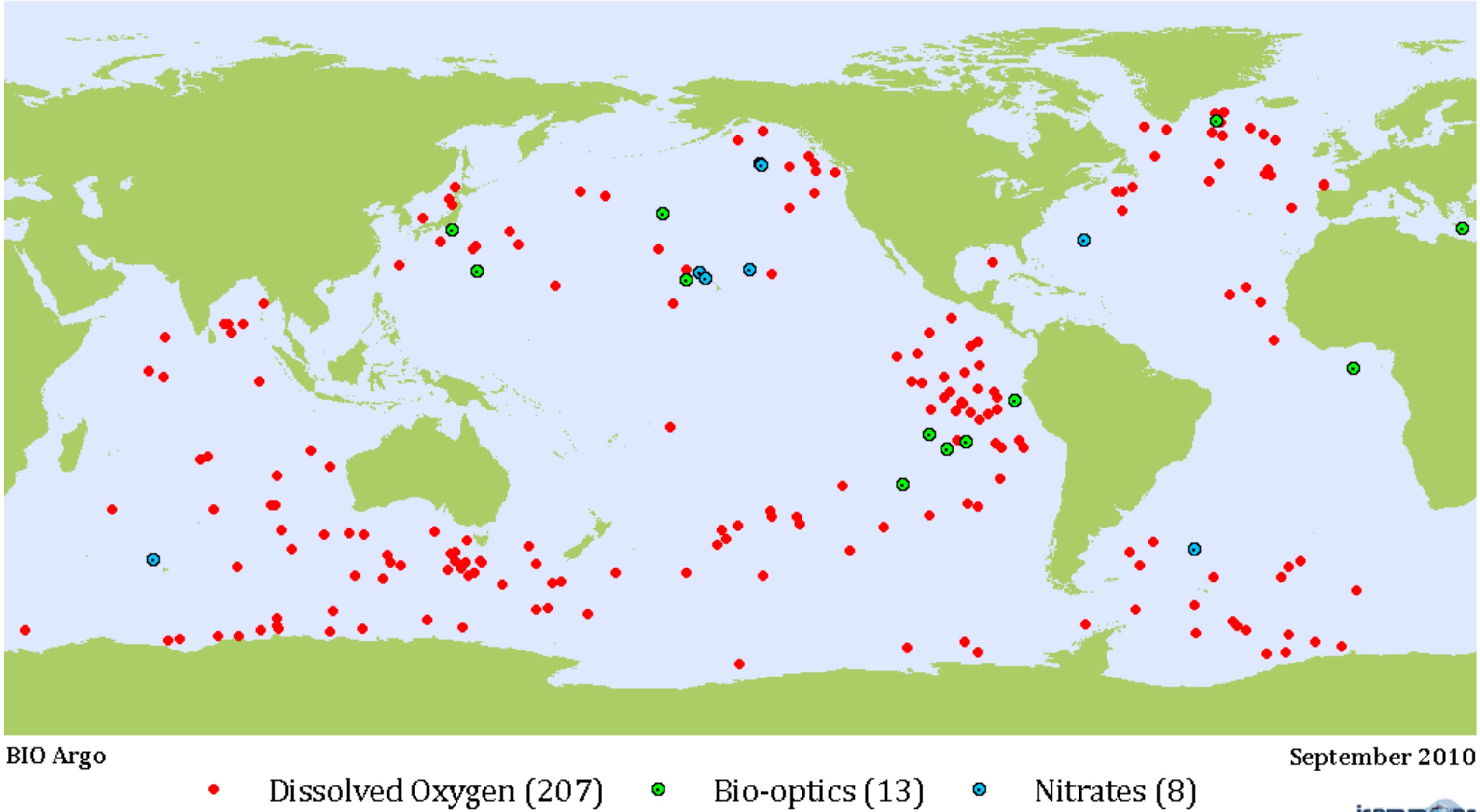
The optical design

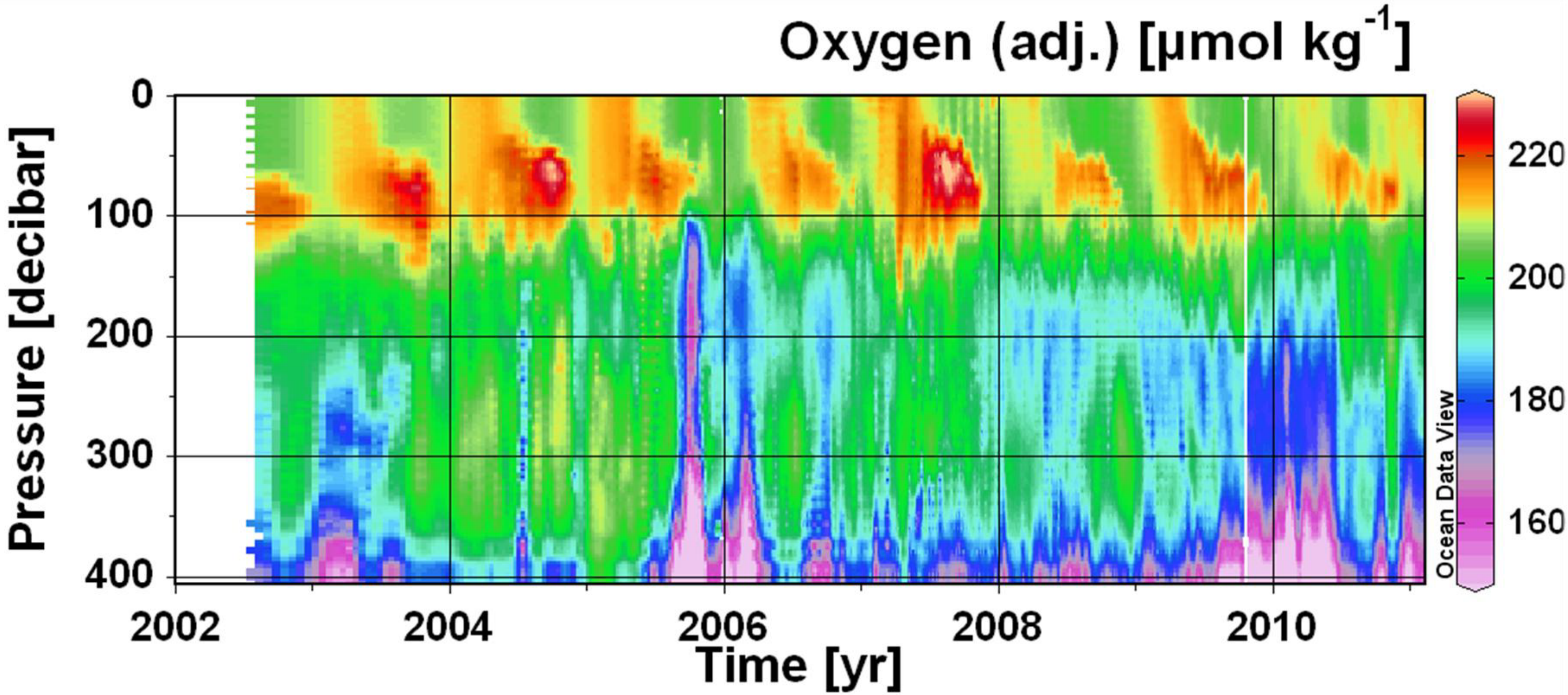


Applications with ARGO floats



Oxygen sensors have been deployed on ~ 300 Argo floats: today 200 floats are currently operating (over 3200 floats)





9 years of float-based O2 data from the HOT site show a consistent seasonal cycle, demonstrating the utility of float-based O2 optode measurements (from K. Johnson).

Sensor Comparison to gridded data in WOA 09 for 119 floats

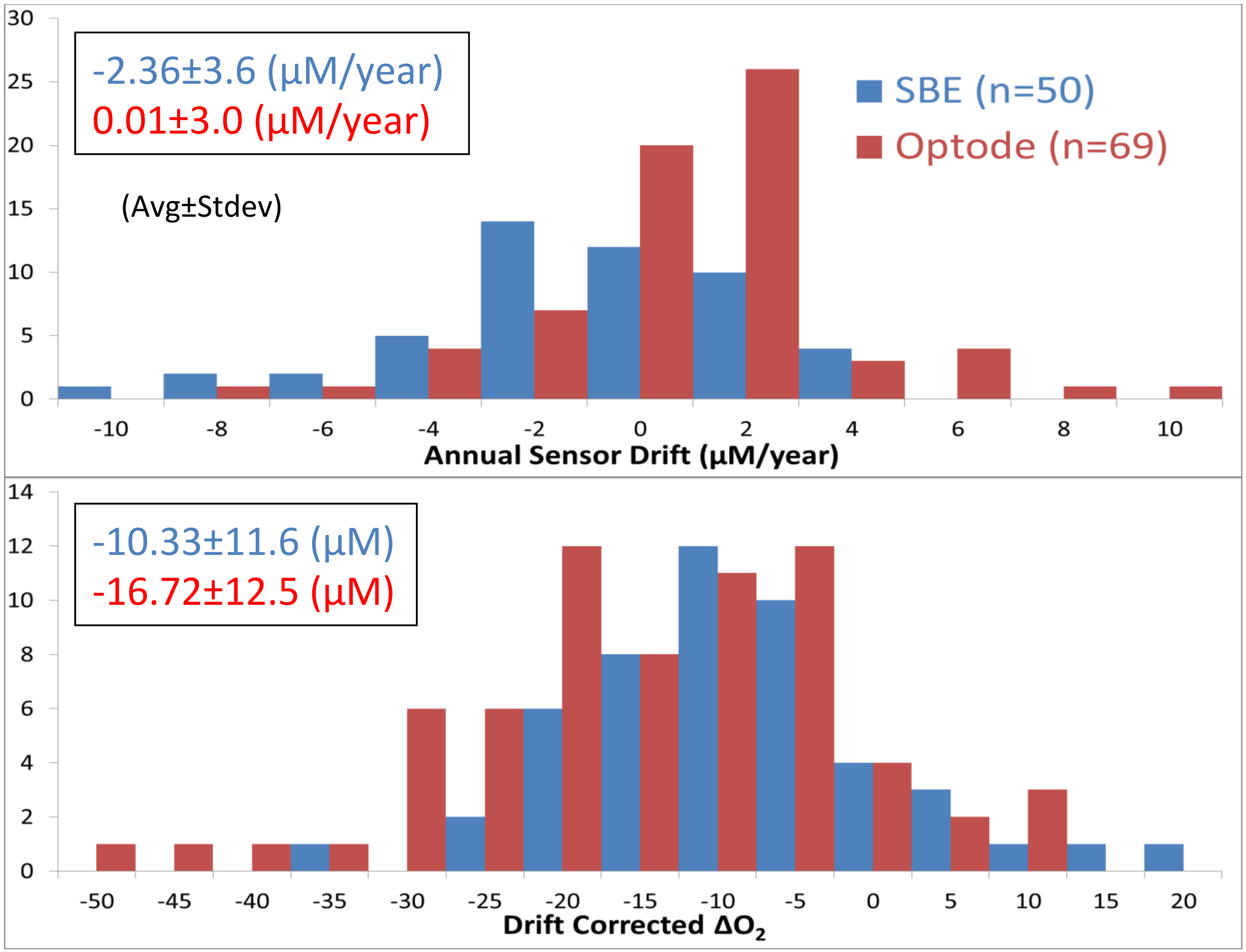
Metadata for 298 floats that include O_2 - ~21 obviously bad, ~25 record<1 yr, ~15<1000m, ~71 have only NaN in O_2 field, ~40 don't list type of O_2 sensor in metadata = 119 floats for analysis.

Drift

No drift in Optodes. Some for SBE.

Accuracy

Clear calibration offsets.



Slides from Yui Takeshita & Todd Martz, SIO

Aanderaa (AADI) calibration procedure

- Each batch of foils are characterized with respect to temperature and oxygen concentration (PreSens)
- Individual 2 point calibration (0-100%) made by AADI for correction of foil and sensor to sensor variations
- In addition each optode is temperature calibrated by AADI

but…

- **Bad initial calibration (we need 64 point calibration !)**
- **Self heating (should be >10s)**
- **Influence of the storage conditions on the data quality (light, dry air)**
- **Need to modify calibration equation**

Argo O2 meeting 2010 conclusion

➢ Recommendations for the QC of O2 data:

- Calibrate sensors before deployment
- Collect concomitant oxygen sample at deployment (Winkler)
- Compare O2 data to climatological data to estimate sensor bias or drift

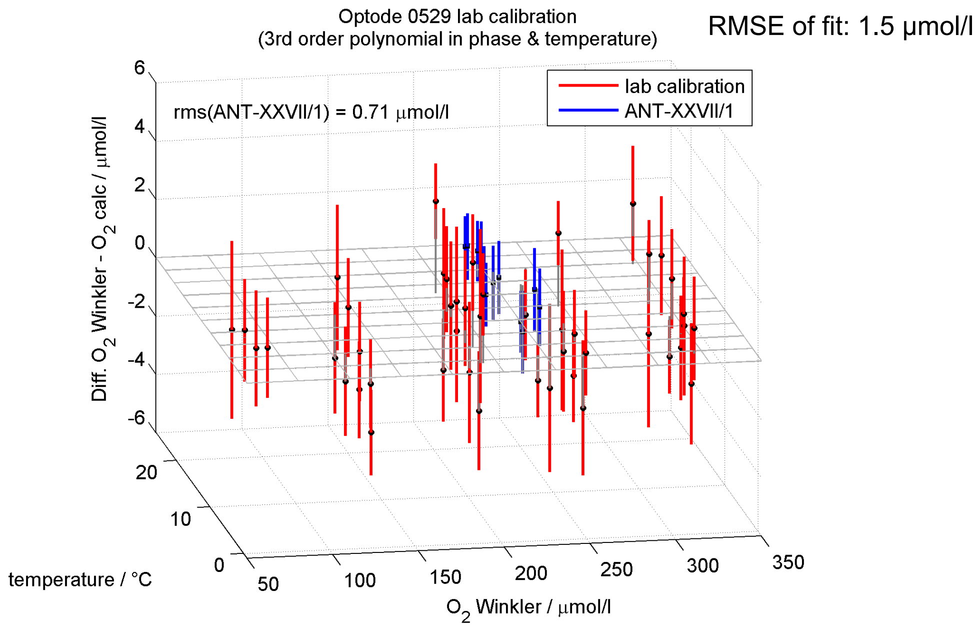
➢ Recommendation for the data management

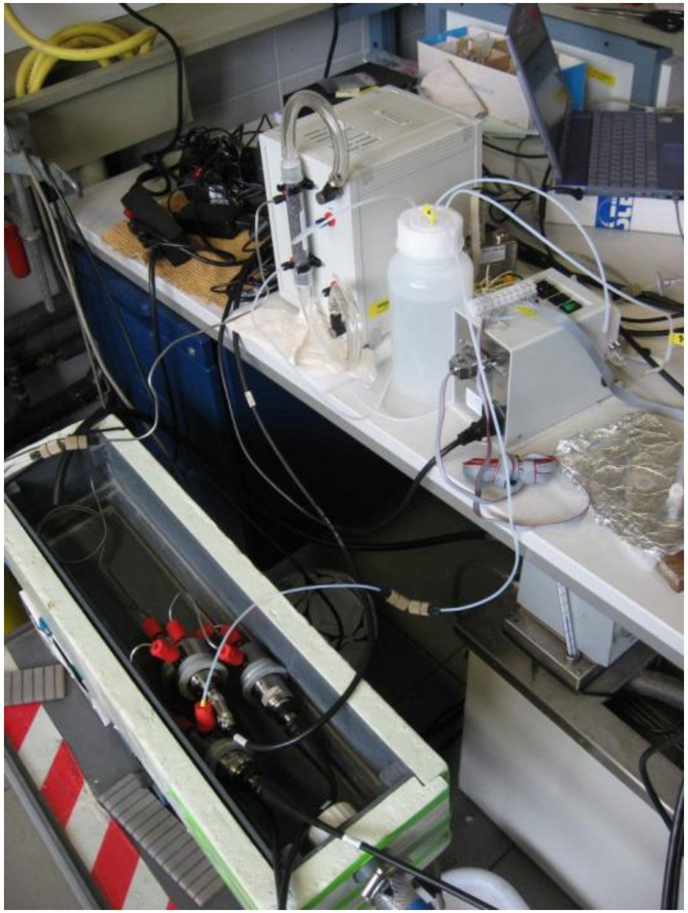
Transmit raw data and not onboard to be able to calculate O2 concentrations (C1, C2 or TCPhase)

Optode Calibration

Henry Bittig, Arne Körtzinger
IFM-GEOMAR, Kiel (and CSIRO)

- electrochemical O_2 Generator
- regulated current, flow and temp.
- triplicate Winkler samples
- several optodes in sequence
- polynomial fit in phase and temp.





Before float deployment

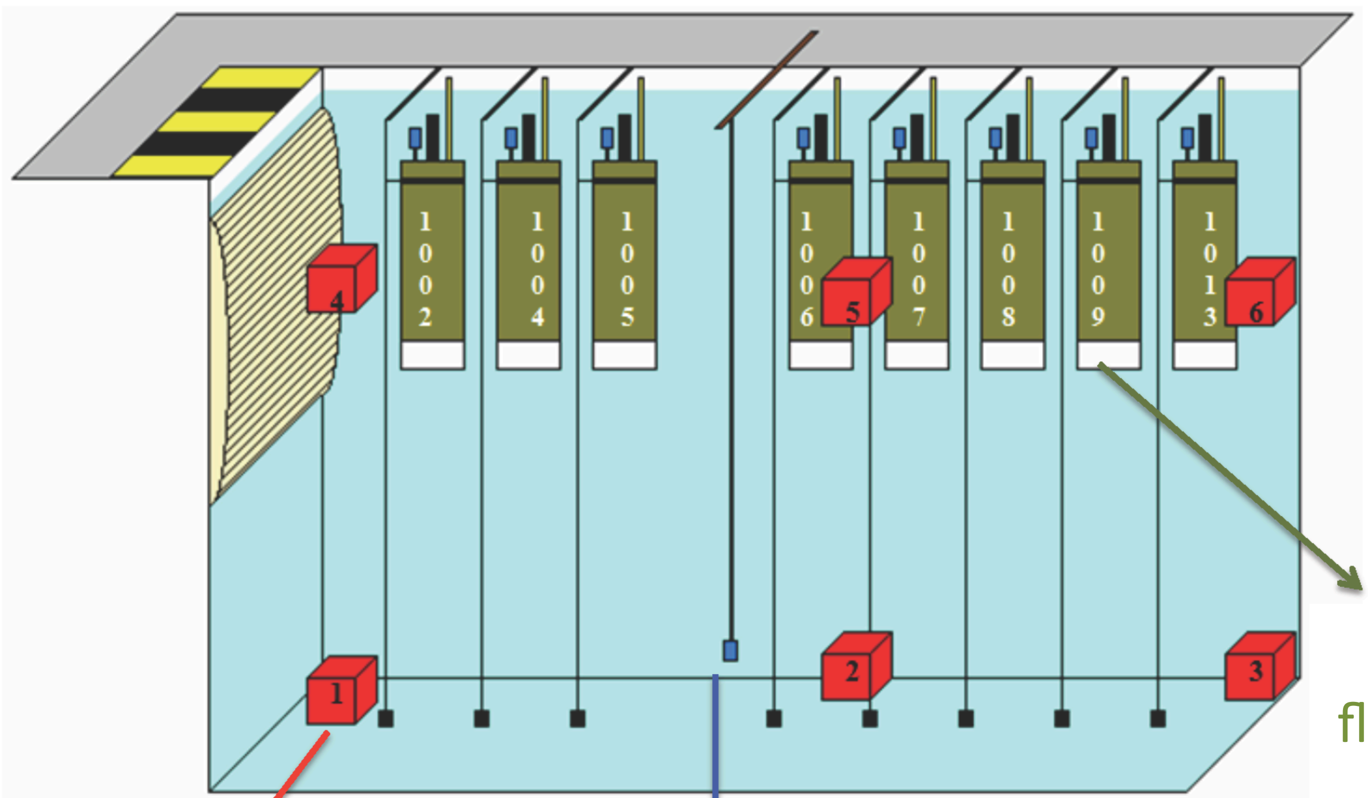
Control of the float behavior in Ifremer pool :

- 1 day cycle at 20 dbar (float at the bottom during "drift phase")
- Check sensors, Argos transmission, buoyancy control, etc
- Intercomparison between floats
- Salinity and oxygen sampling for comparison
- Free optode in between the floats (in Feb 2011 only)

- **Our initial objective was to use results from those inter-comparisons to evaluate oxygen sensors and to help correct oxygen data from floats after deployment.**
- **The experiments brought more questions than solutions !**

Can we use them anyway ?

Two experiments in 2011 and 2012 at the IFREMER pool

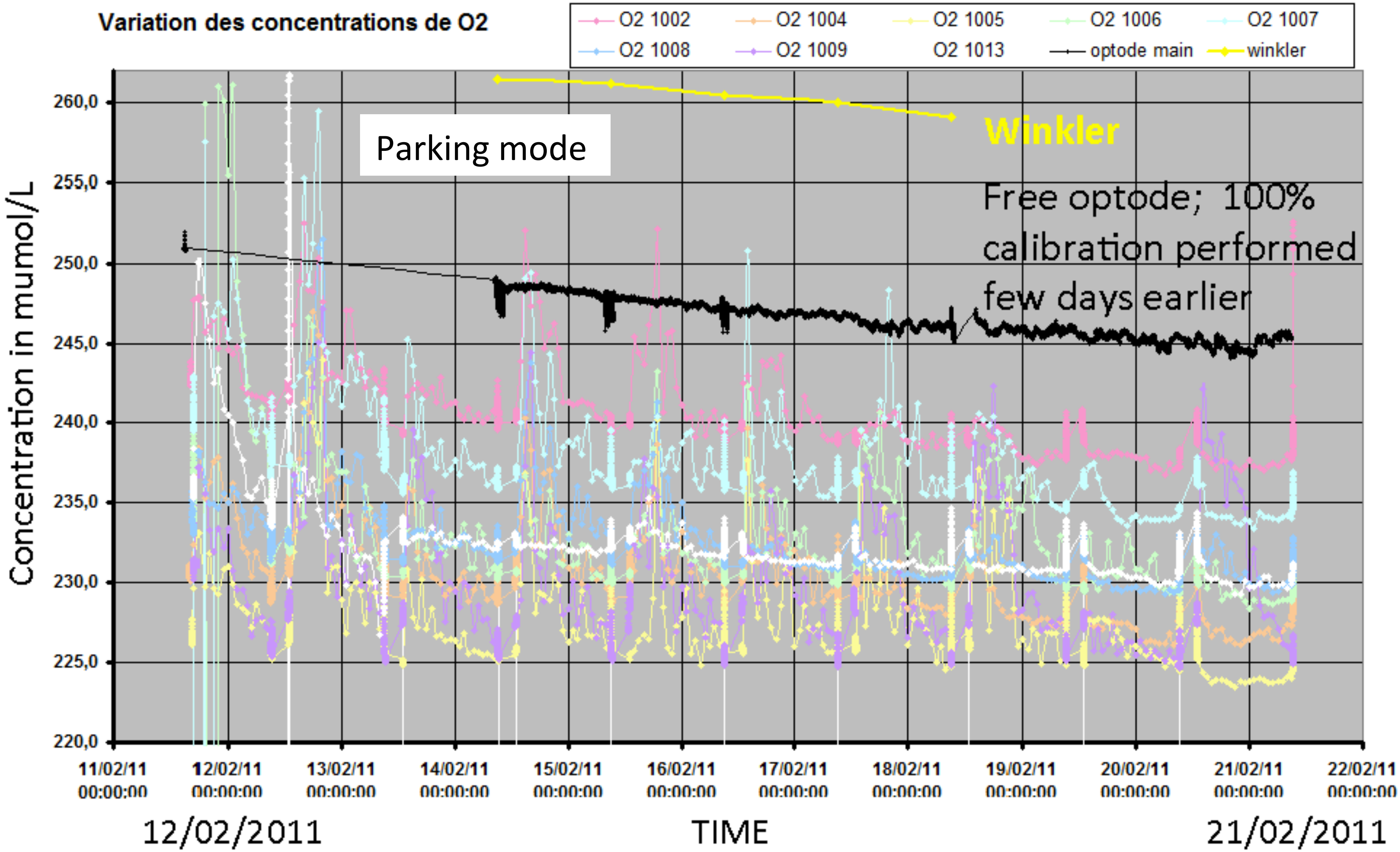


8-15 PROVOR floats with 4330 Aanderaa optode

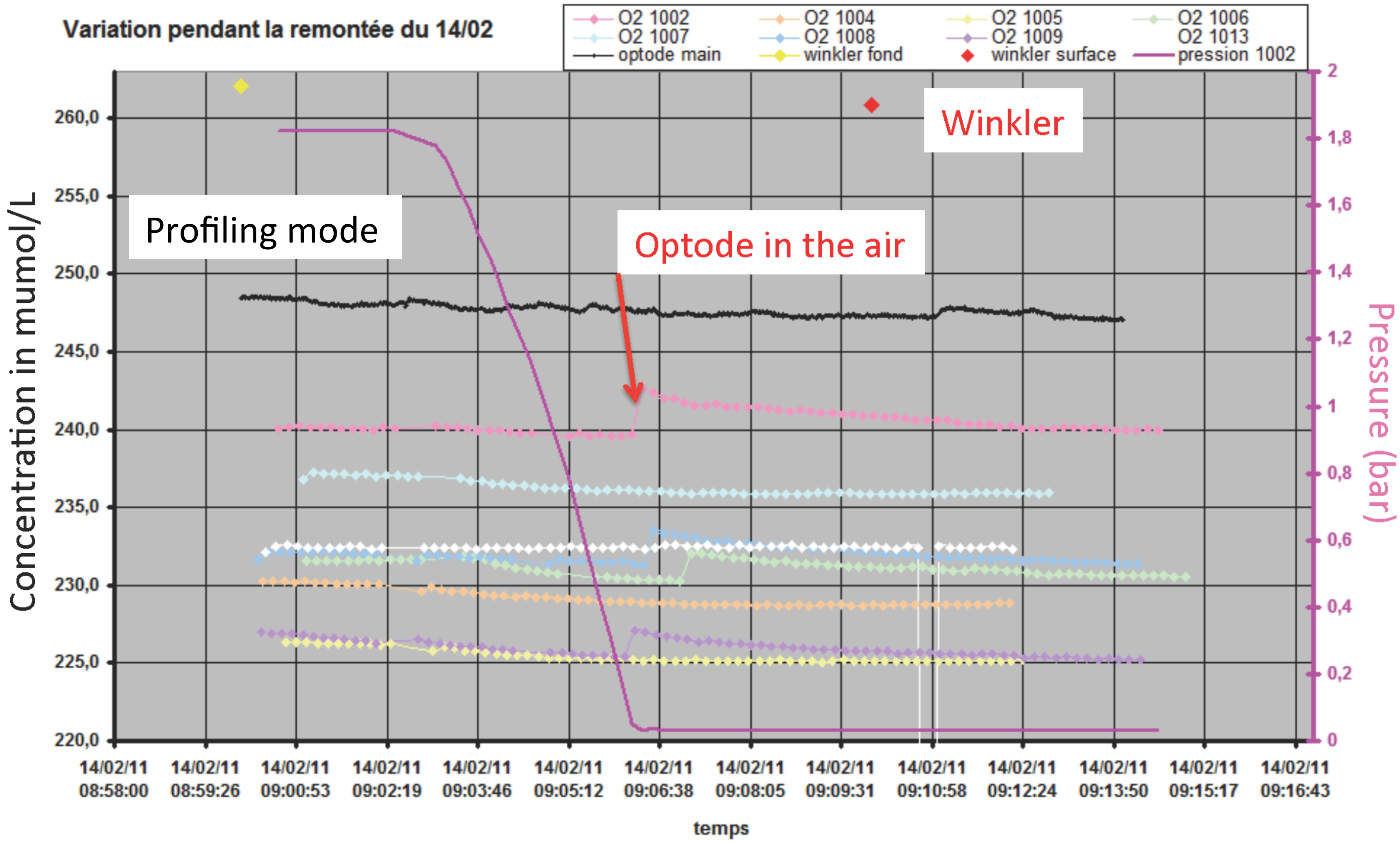
Bottle sampling and winkler titration

Free Optode

O2 concentration over 10 days at Ifremer pool : 8 floats, 1 optode, winkler titrations (2011)



Argo profiles (float ascent from 18 dbar to surface) vs winkler titration



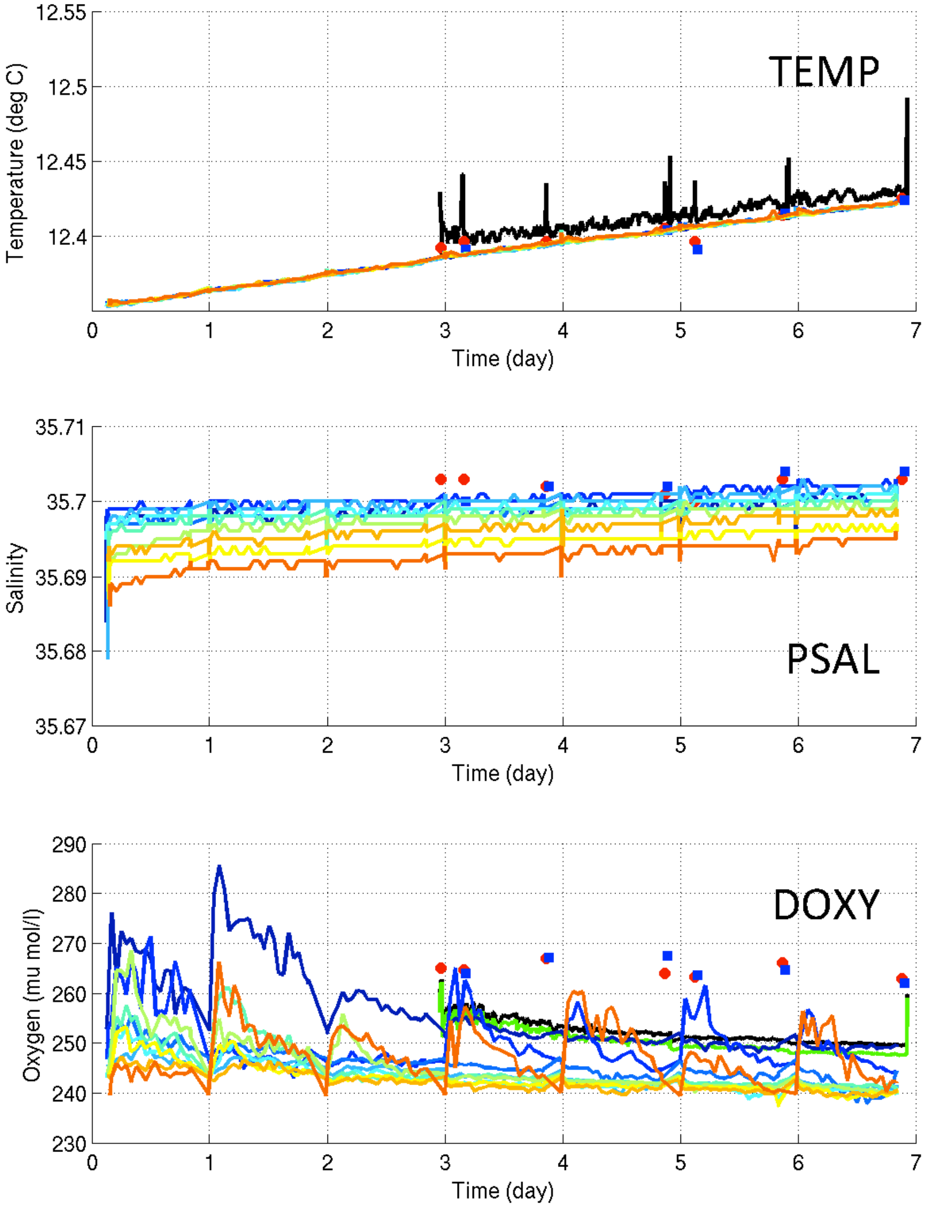
10-day experiment in March 12 at the Ifremer pool with calibrated optode

- 13 PROVOR-DO equipped with calibrated optodes and one free calibrated optodes were tested in Ifremer pool
- Calibration done in fall 2011 at CSIRO
- Calibration based on the Stern-Volmer equation (Uchida 2008)

$$[O2] = \frac{\frac{c4 + c5.T}{c6 + c7.TCPhase} - 1}{c1 + c2.T + c3.T^2}$$

✓ Use 7 calibration coefficients instead of 20
✓ Optode raw parameters to transmit: C1, C2 and TCPhase = C2-C1
✓ Use T from CTD sensor (SBE)

Main results

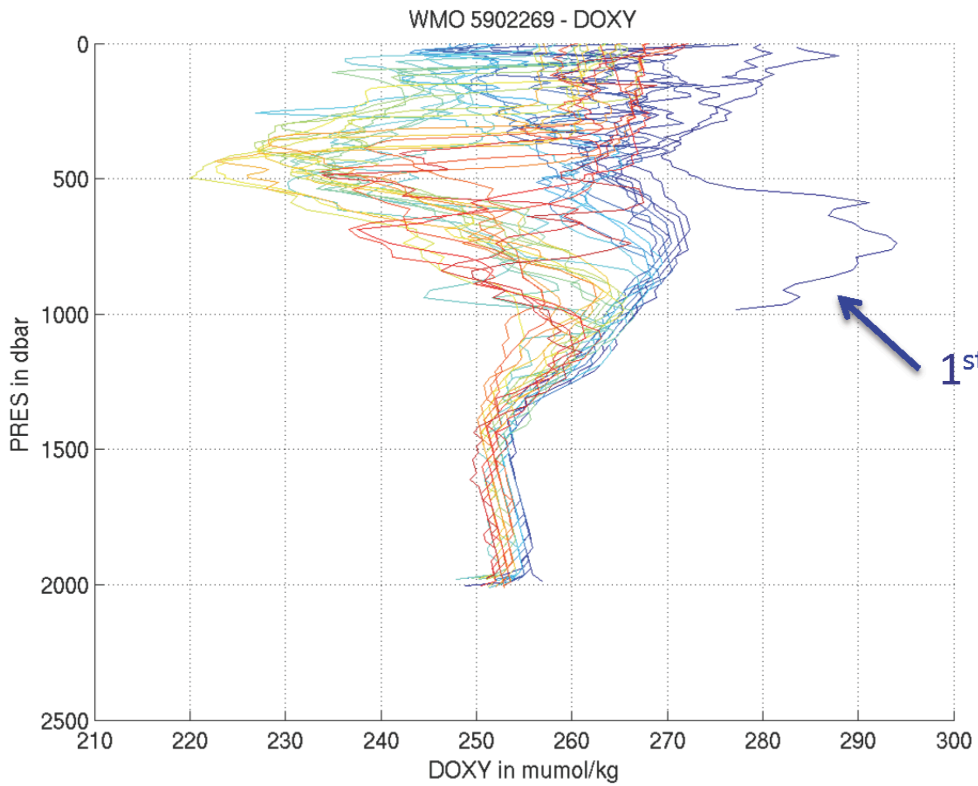


- Small vertical temperature/salinity gradient in the pool
- Despite the calibration, all optodes underestimated oxygen concentration (between 11 and 24 mumol/L)
- Large (>20 mumol/L) unexplained fluctuations during « drift » at parking depth for the floats , still no clear explanation

Unresolved questions

- Why the mean difference between the **calibrated** optodes and the Winkler titration varies between 11.7 and 23.6 mumol/L in Ifremer pool
  - Storage in dry air ?
  - Calibration in fresh water ?
  - Chlorine effect on the optode measurement and/or Winkler titration (although the chlorine was also titrated and taken into account)
  - Problem with the Winkler titration ? Solubilty of O2 in Niskin bottle ?
- Why optodes on the floats (and not the free optode) do measure large unexplained fluctuations during the drifting phase
  - Air bubbles trapped in the float ?
  - Outgassing of the some float materials (plastic) ?
  - No flow in front of the foil ?

Response of the foil after storage in dry condition

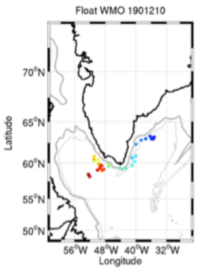


1st descending profile

- Float 5900269 deployed in the North-Atlantic in June 2010 (3830 optode)

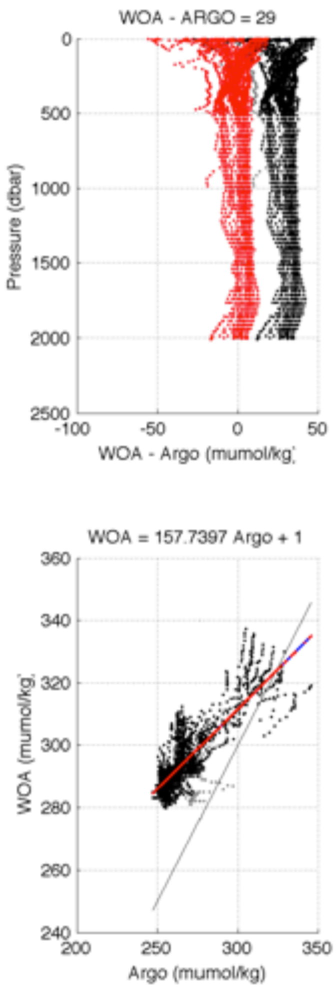
Keep the sensor wet or you will see a drift for 24hrs (high resolution mode)

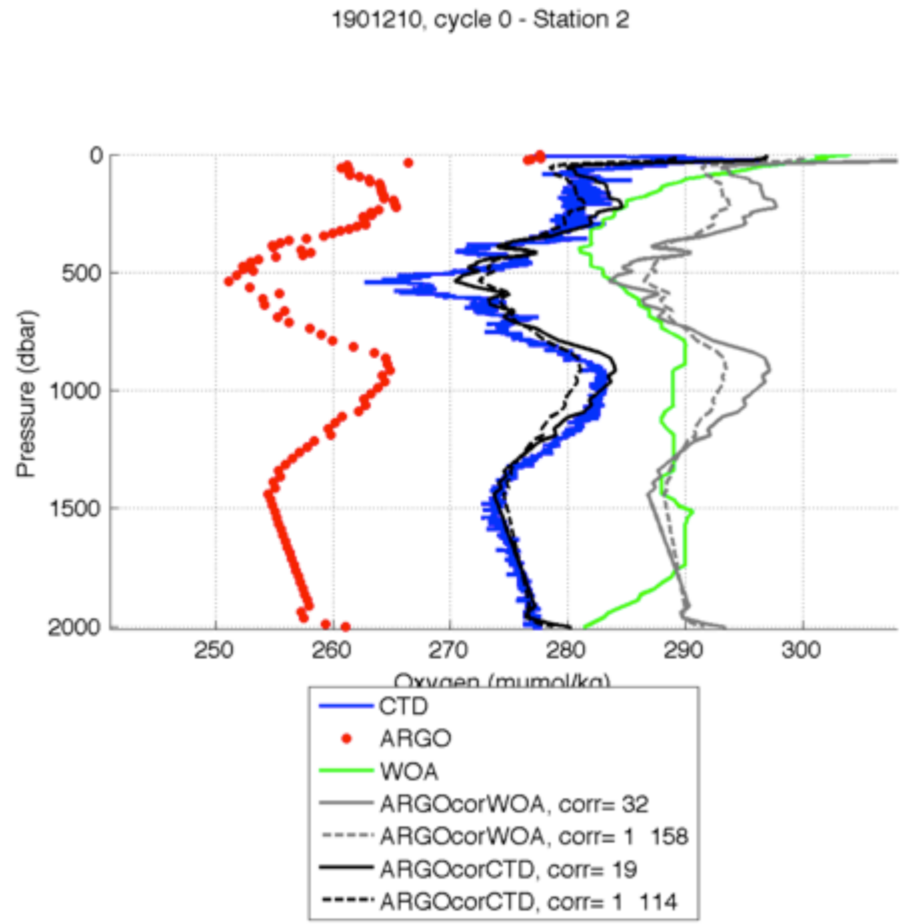
- What is amplitude of this drift ?
- Can this lead to significant bias when a 0-100% calibration is done ?
- Does the foil returns to its initial calibration after being stored in dry air ?



Post deployment correction (CTD vs data atlas)

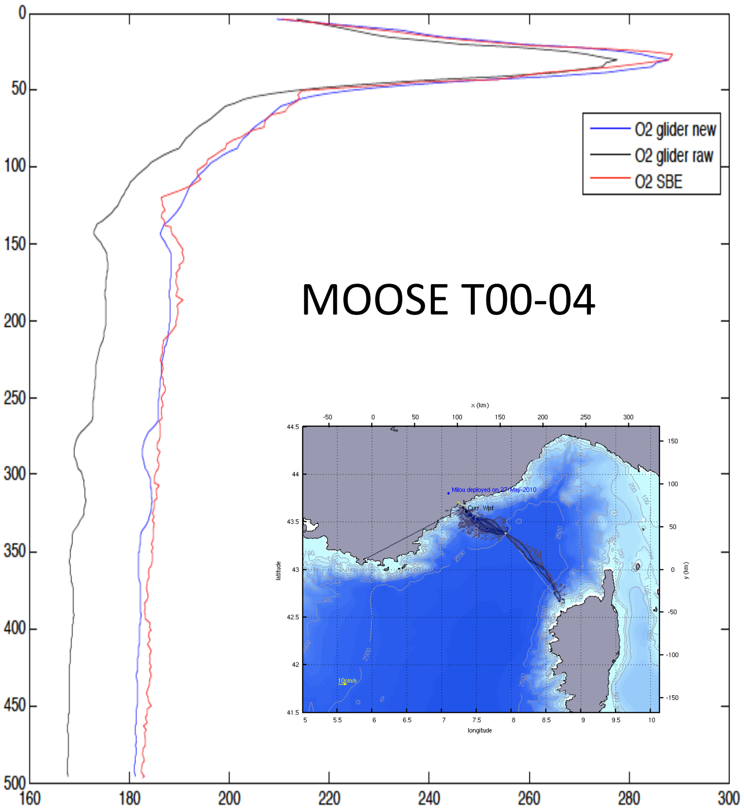
Comparison to WOA

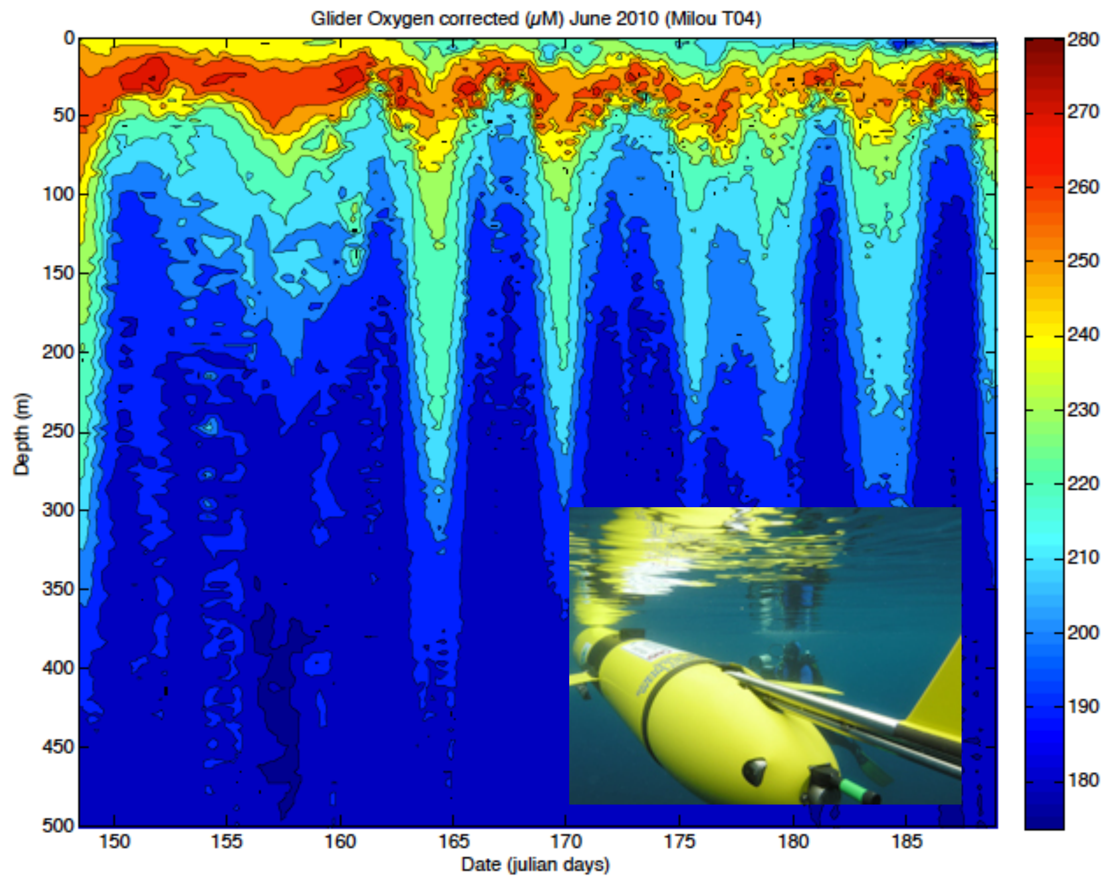




➔ Reduce difference from 20 to <10 µmol/kg

Applications with gliders: post deployment procedure



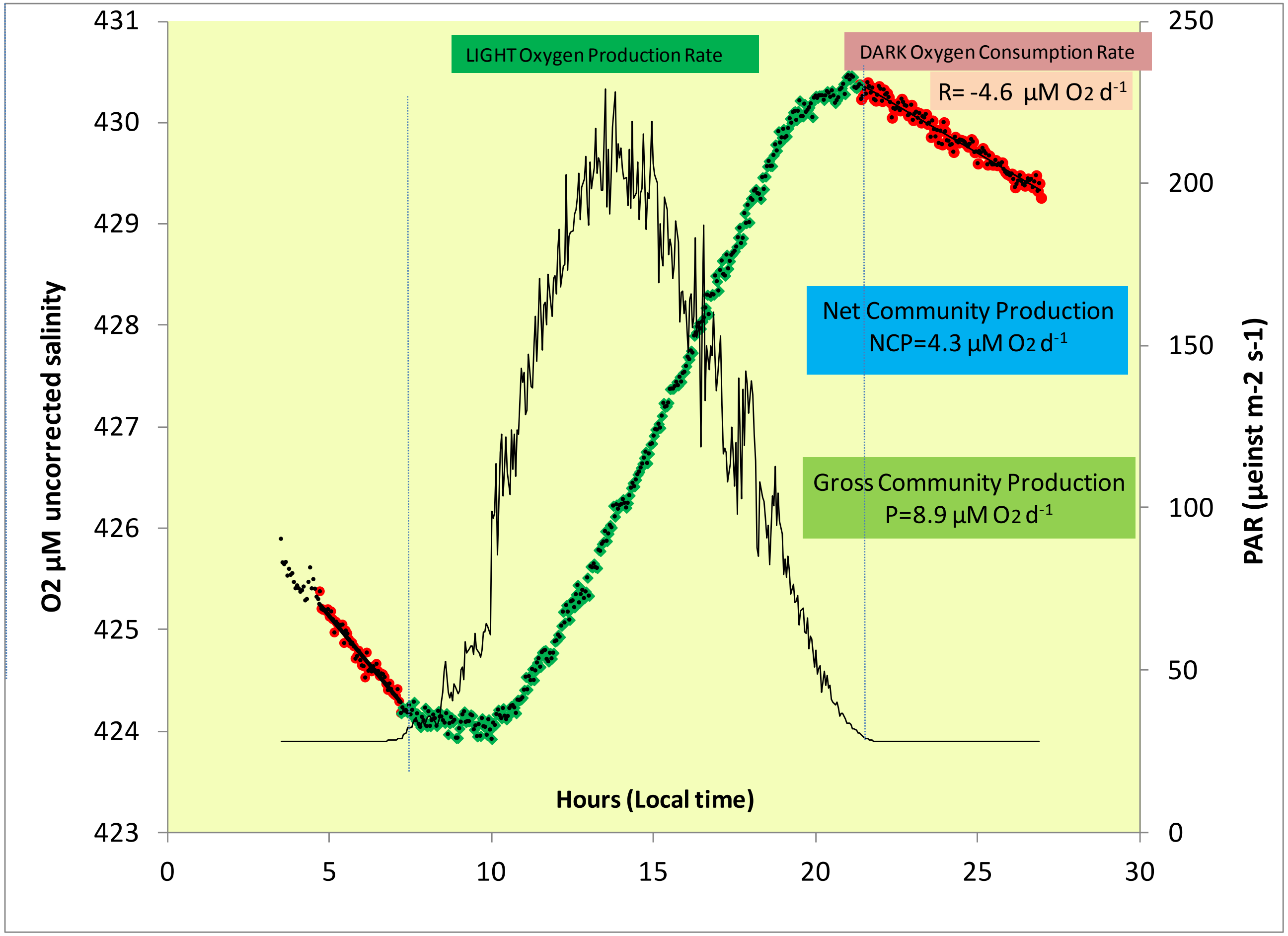


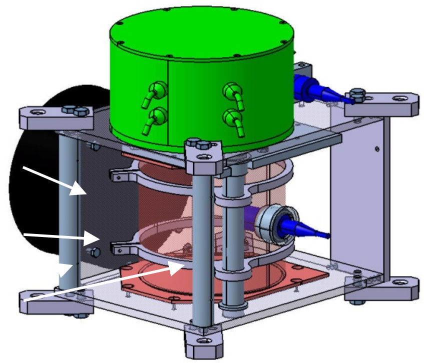
- Glider O2 measurements with optode 3835 in Ligurian Sea (July 2010)
- Drift from O2 raw data and O2 SBE_corrected @ Dyfamed = 20 umol/kg
- Possibility to correct coefficients calibrations using a polynomial fit model (Sensor Dynamics of Autonomous Underwater Gliders, Bishop, 2008) using T from CTD and after S and P correction

IODA$_{6000}$: *In situ* Oxygen Dynamics Auto-sampler

D.Lefevre (MIO and CPPM)

Incubation chamber with oxygen optode inside and outside the chamber





From Robert et al, in revision

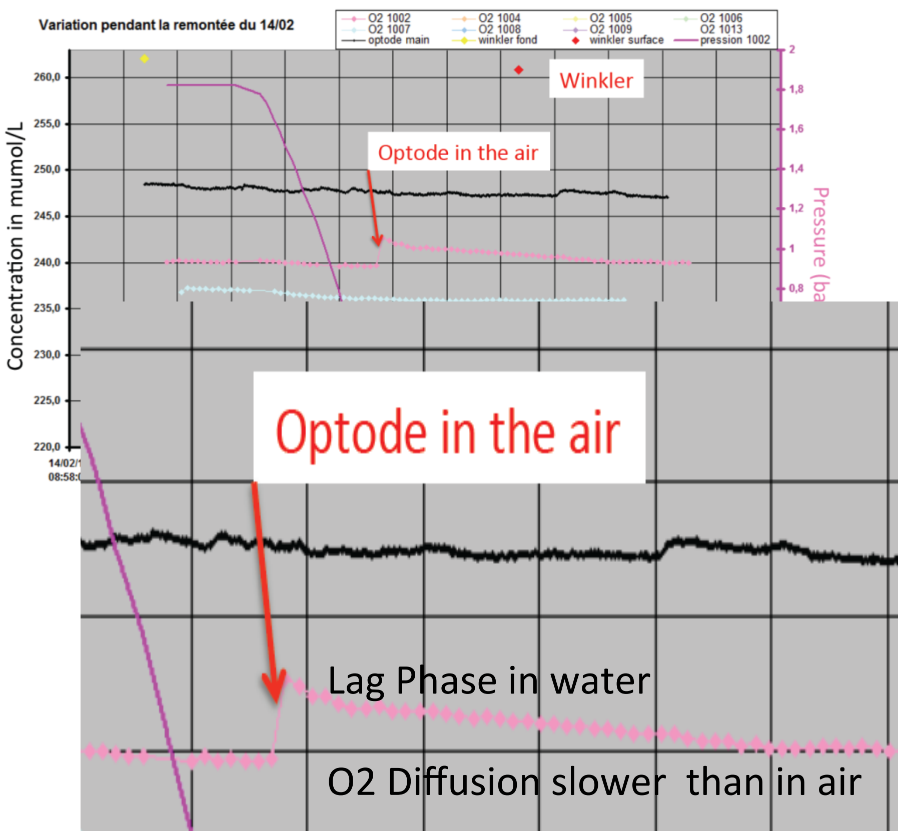
Simultaneaous In Situ determination of production and respiration

Oxygen optode and physics

The O_2 diffusion coefficient in air is 10,000 times greater than in water (20°C)

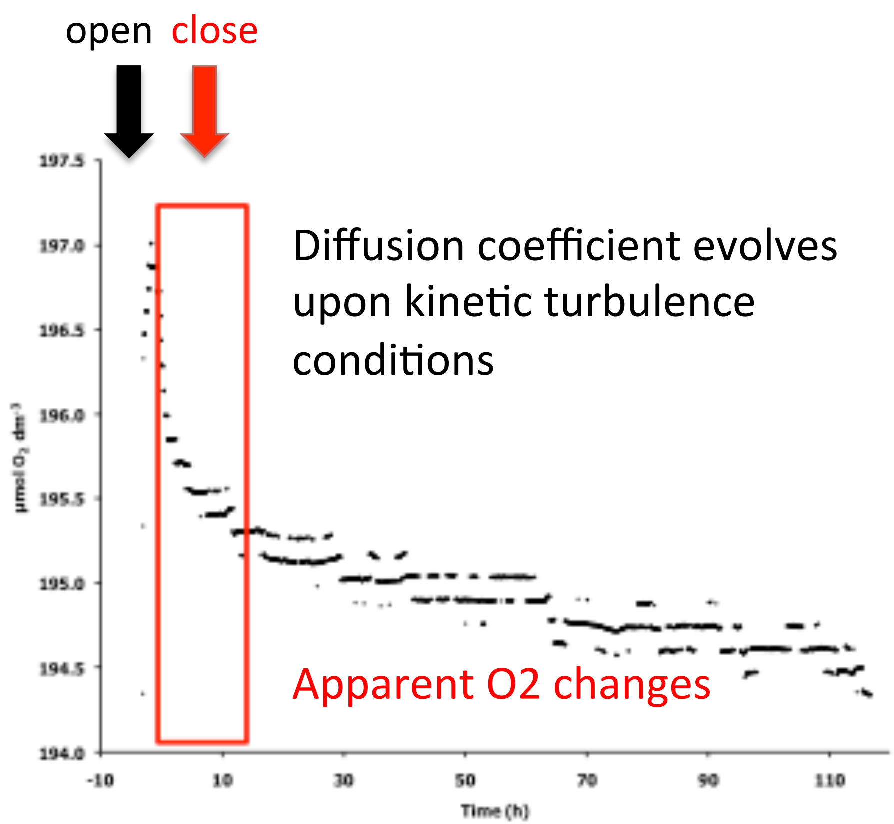
Need to know the physical conditions to interpret O2 optode data !!

ARGO: atmospheric to ocean



Virginie Thierry et al.

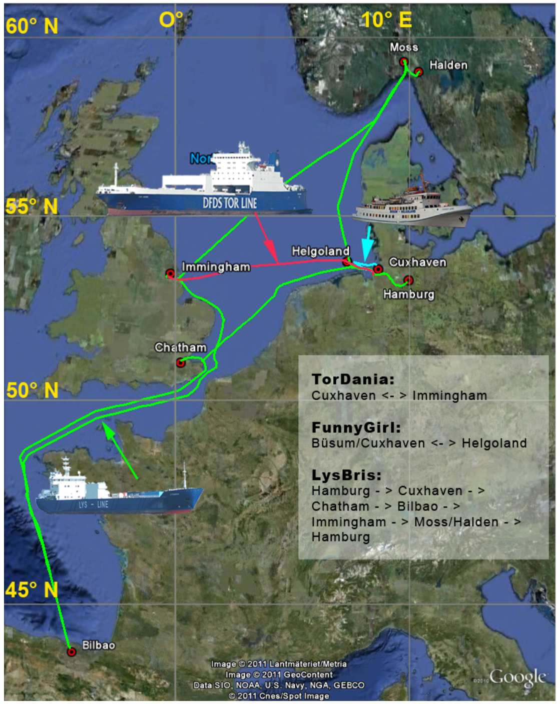
IODA: open to close environment

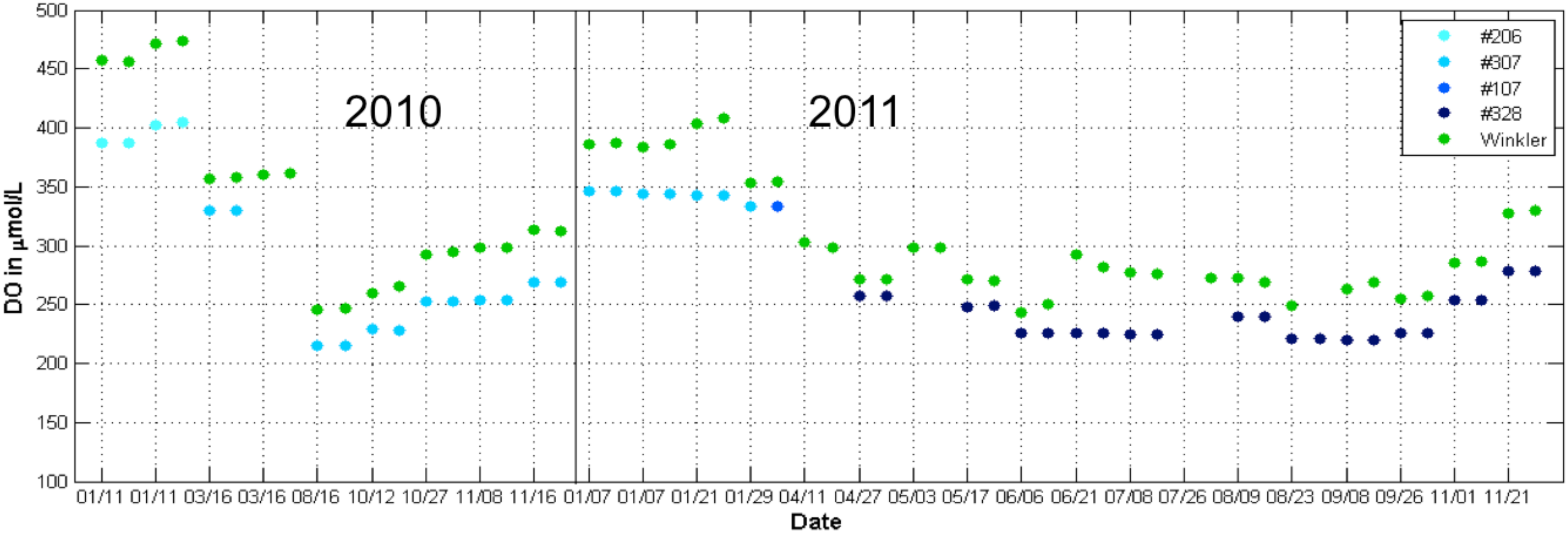


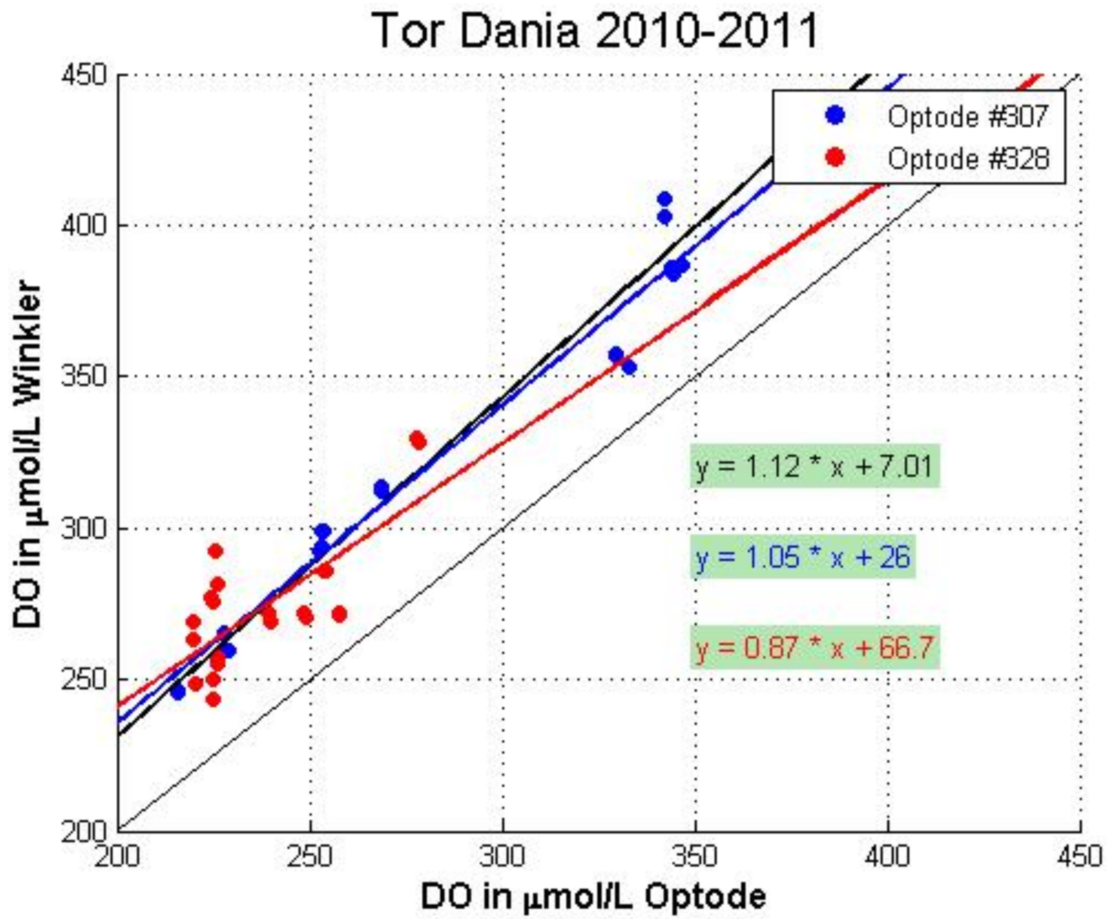
Anne Robert et al.

Applications on Ferrybox (from M.Haller, HZG)

TorDania: Dissolved Oxygen time series
2010-2011: in two years four different optodes

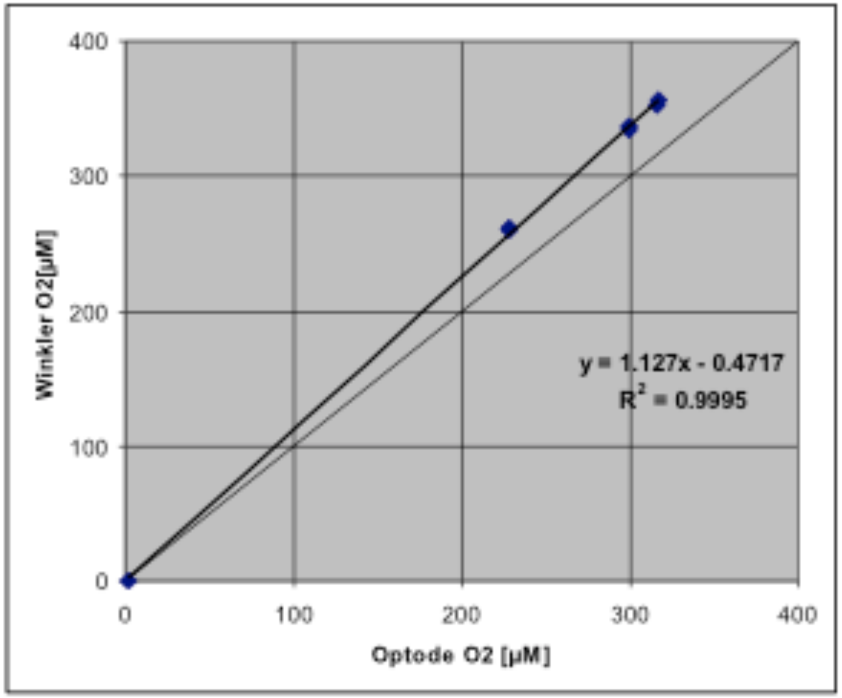


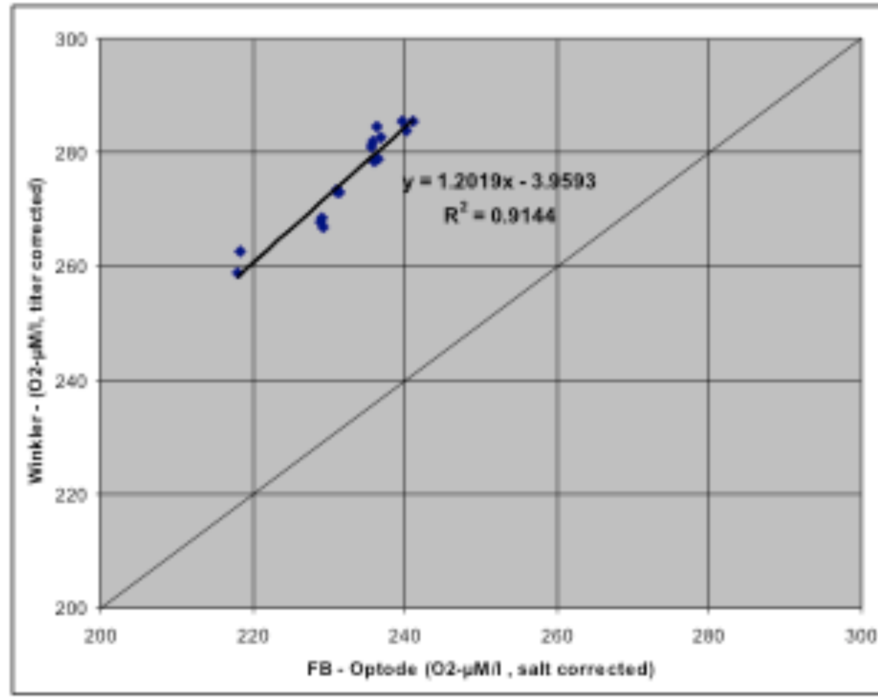




Systematic underestimation of optode measurements
Oxygen data over wide range helpful

Pre-campaign lab calibration comparison





Lab calibration Optode #205 and Winkler
9-11/06/2011

Temperature ≈ 23°C, Salinity: 0 psu
Mean ratio = **0.89**

Comparison on ship cruise R/V Heinke
Optode #205 and Winkler
17-21/06/2011

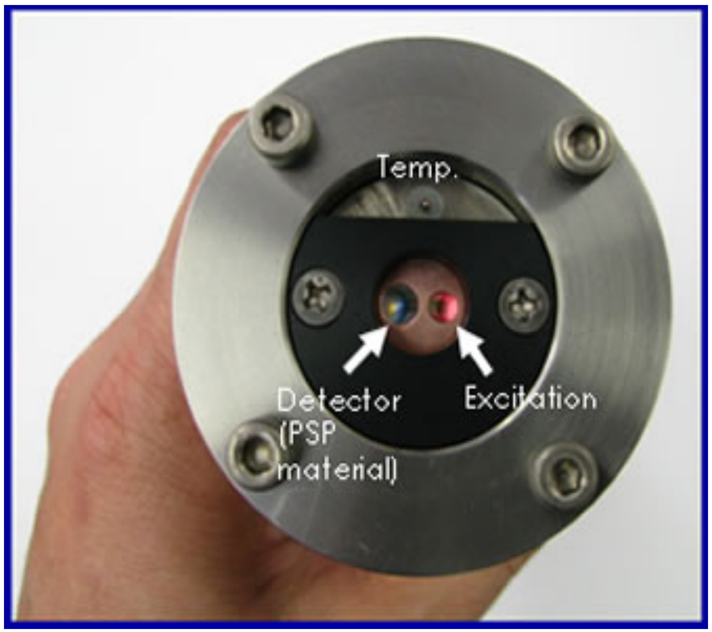
Temperature ≈ 12-15°C, Salinity: 32.3-34.8 psu
Mean ratio = **0.84**

O2-optode: conclusions and plans

- Recent results far from the **accuracy of 1 µmol/kg** required by the scientific community
- Necessary to re-calibrate optode in lab.
- ARGO: Measurements every 10s. Need to improve the NRT O2 calibration procedure: climatology comparison not always robust. Better to use O2 saturation in the air (H.Kortzinger) ??
- What about others sensors ? RINKO ? SBE63 ?

Oxygen measurements with Rinko sensor
Detlev Machoczek (BSH)

Fast response oxygen sensor



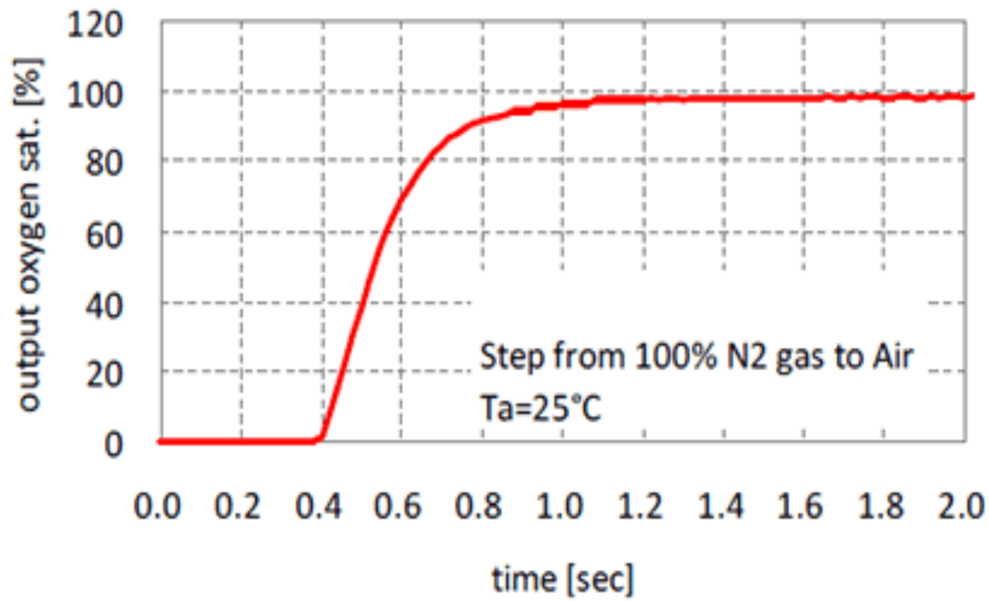
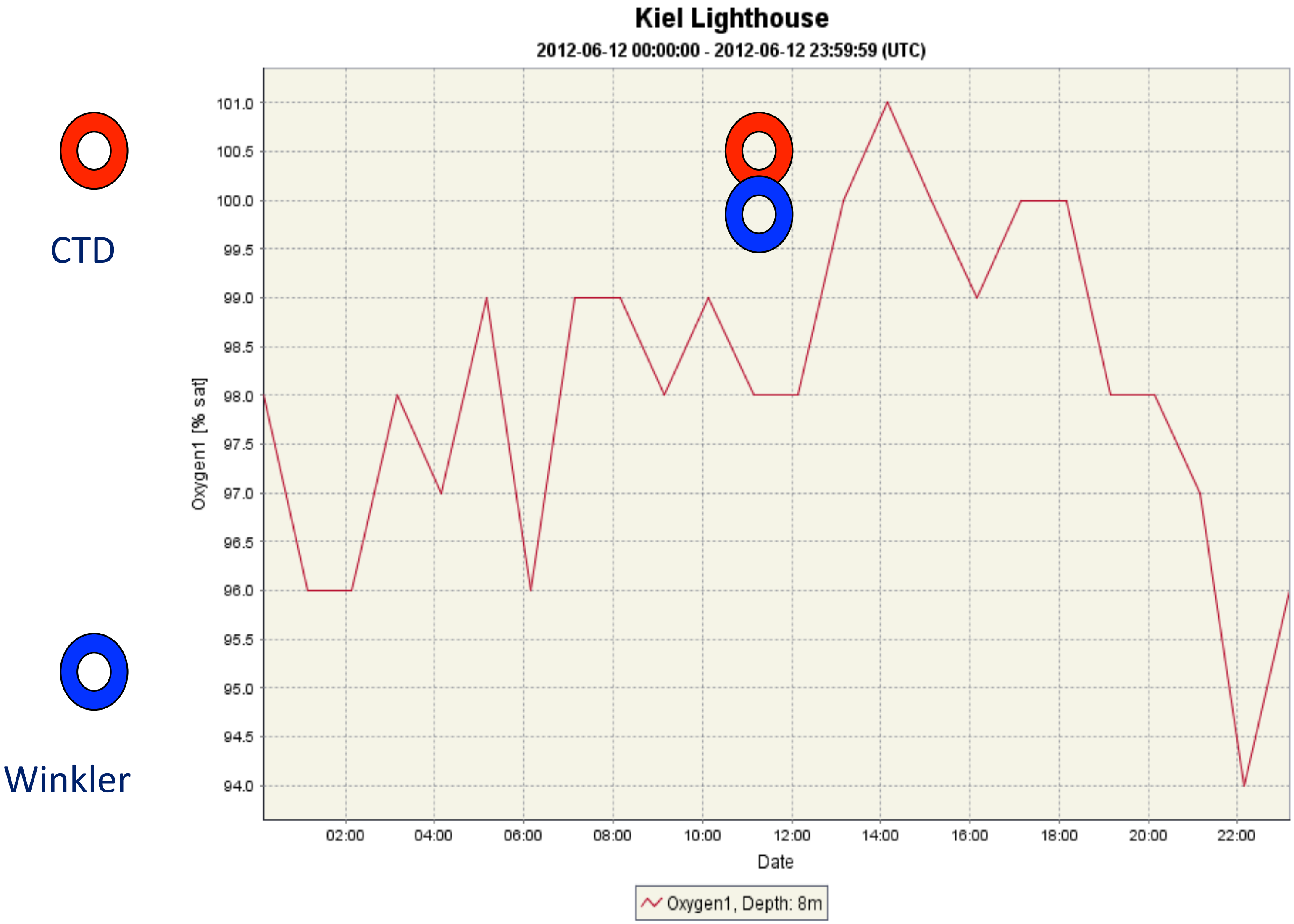


Fig.5 The response time of ***RINKO***. This figure shows that the response time which reaches to 90% value of oxygen in air is within 1second.


CTD
Winkler
Kiel Lighthouse
2012-06-12 00:00:00 - 2012-06-12 23:59:59 (UTC)
Oxygen1 [% sat]
101.0
100.5
100.0
99.5
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98.5
98.0
97.5
97.0
96.5
96.0
95.5
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94.0
02:00
04:00
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08:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
Date
Oxygen1, Depth: 8m

First results:

Calibration measurement 12. 06. 2012: CTD – Winkler-Tit.: 0.6 %

Calibration measurement 27. 09. 2012: CTD – Winkler-Tit.: 0.4 %

No calibration of the CTD – oxygen sensor between the two measurements!

Promising ?

Challenges and needs

- ✓ Recommendations: lab calibration necessary, pre and post deployment correction, improve NRT validation protocols, constrain the physical situation (optode)
- ✓ Future needs and gaps: need better accuracy and less drift, long term stability, need better calibration procedure, easy to adapt on platforms (e.g. data-logger for moorings)
- ✓ Plan some demo missions to test new and future O2 sensors in coastal waters (lab facilities, easy to access,…)
- ✓ Need summer schools to train scientists on sensors ability and data treatment (Q/C)

THANK YOU