Oxygen measurements: sensors accuracy and scientific needs

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JERICO General Assembly, October 2012

cnrs INSU Institut national des sciences de l'Univers

- Due to the relatively rapid ongoing changes in the world's oceans, biogeochemical parameters are urgently needed across all temporal and spatial scales
- Must enhance our ability to monitor ocean acidification, changes in biogeochemical cycling in response to climate variability, and ocean deoxygenation at scales not currently possible.
- **We need integrated observing systems (satellite, in situ platforms, floats, moorings), sensors and models that allow us to observe biogeochemical change**

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.

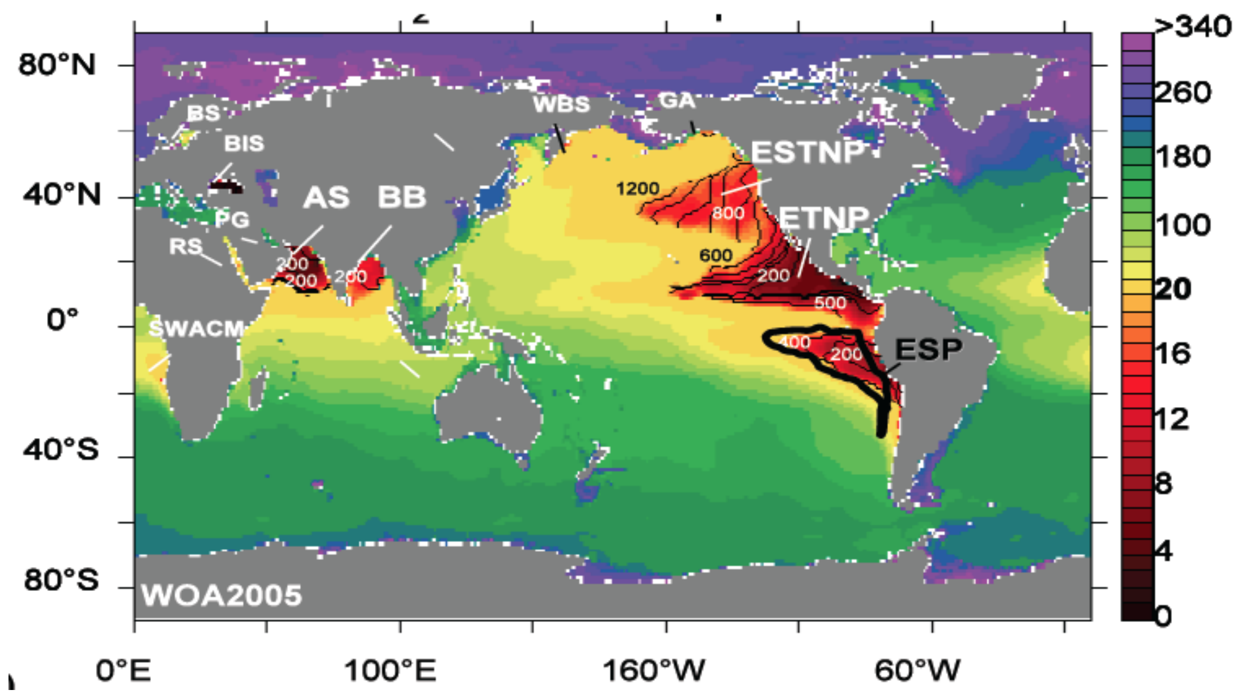
Why are we measuring oxygen ?

- Physical interests: water mass circulation, new formed deep waters, mixing depth, ventilation age, atmosphere-ocean exchange

- Biogeochemical interests: primary production estimates, remineralisation flux (consumption/production through bacteria and zooplankton)

- The ocean deoxygenation (due to global warming and human activities) is one of the most important topic (OMZ studies)

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

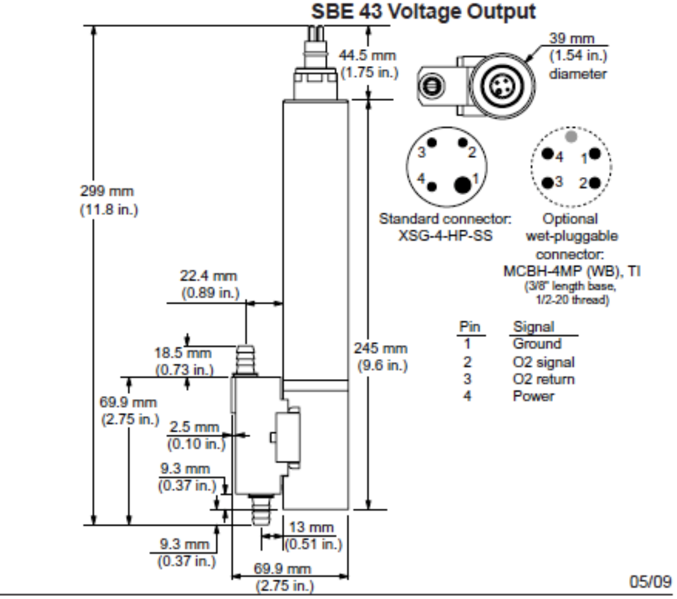


A summary of the manufacturer's stated specifications of present O2 sensors suitable for use on profiling floats

Sensor	Response Time	Accuracy	Precision	Stability
SBE 43-IDO	< 1 sec	2% of sat.	1 µmol/kg	2%/1000 hr
Optode 3830	< 25 sec	<8 µmol/kg	< 1µmol/kg	Good
Optode 4330	8-25 sec	<8 µmol/kg	< 1µmol/kg	Good
Rinko	1 sec	2%	0.1%	??
SBE 63-IDO	< 10 sec ?	1 µmol/kg ?	??	Good?

We need accuracy around 1 umol/kg to do some science !

SBE 43 Dissolved Oxygen Sensor

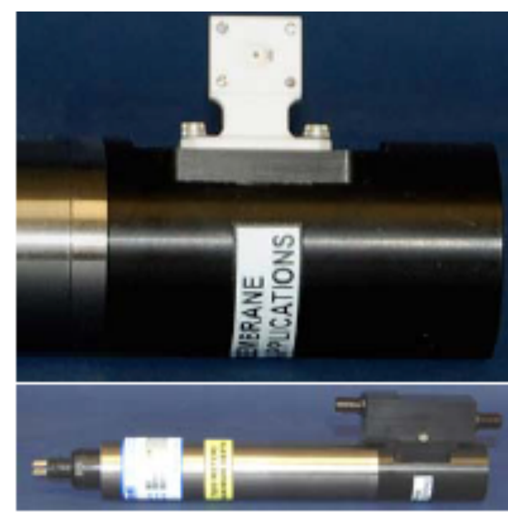


Principle of Operation:

Oxygen gas diffuses across a membrane, is converted to OH^- at the cathode (Au), 4 electrons are required, and the resulting current is converted to a voltage proportional to the number of molecules.

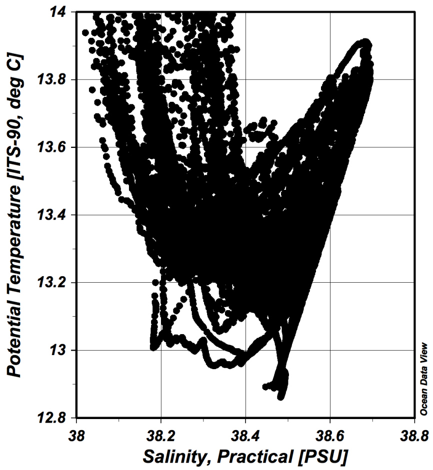
Specifications

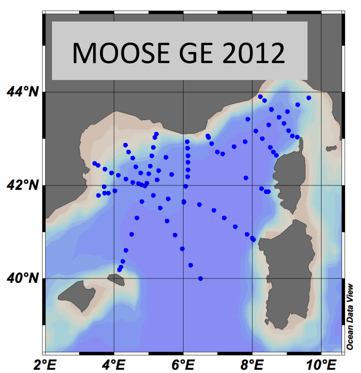
Measurement range:	120% of surface saturation in all natural waters, fresh and salt
Initial accuracy:	2% of saturation
Typical stability:	0.5% per 1000 hours (clean membrane)

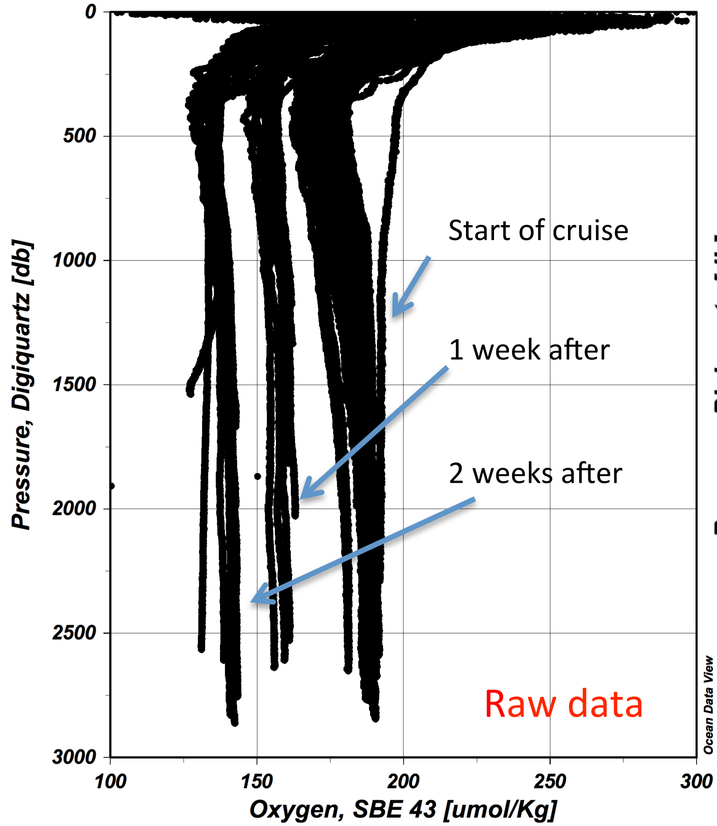


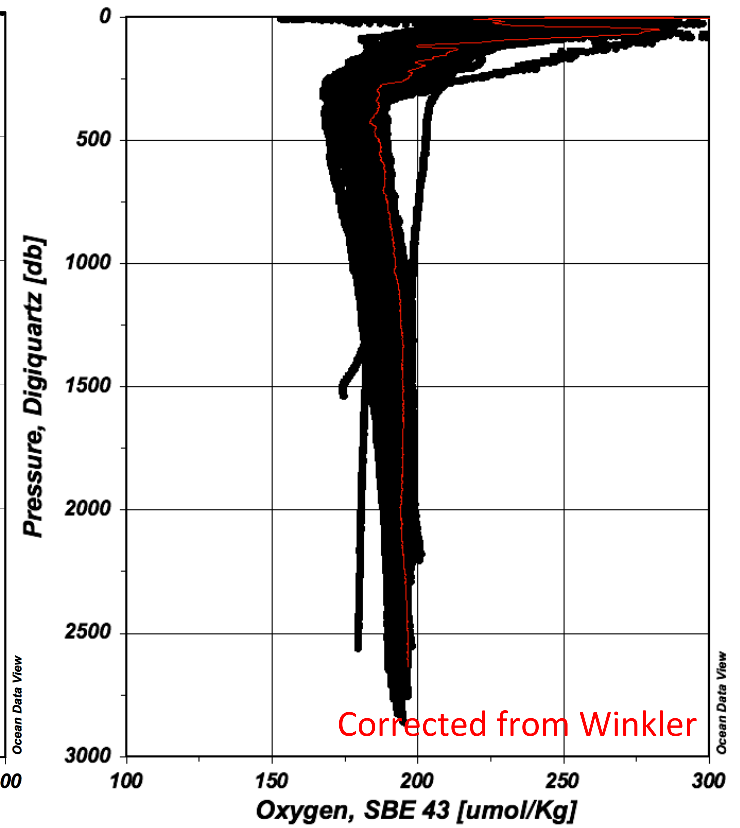
Problems with SB43:

- Sources of drift: changes in membrane tension, depletion of electrolyte, impairment of the silver anode, plating of anode metal on the cathode, and the presence of chemical contaminants in the sensor's plastic body.
- Dynamic errors leading to apparent hysteresis are caused by response-time mismatch of the compensation temperature sensor
- Membrane fouling: altering the oxygen diffusion rate through the membrane, thus reducing sensitivity. Biofouling can be particularly troublesome because the living organisms either consume or create oxygen.
- Mostly adapted for CTD profiler (very fast time response)





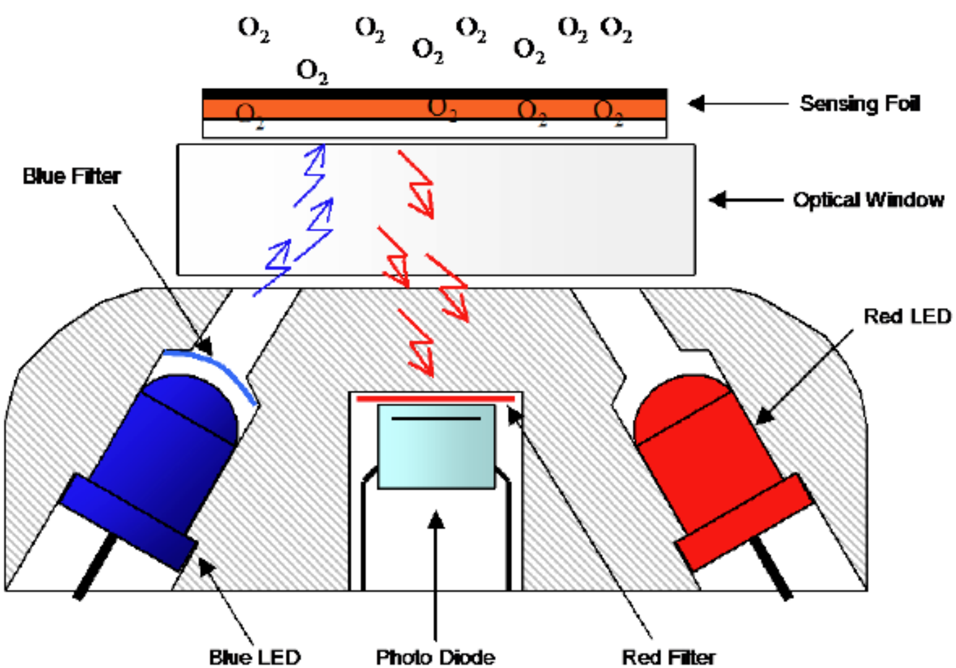


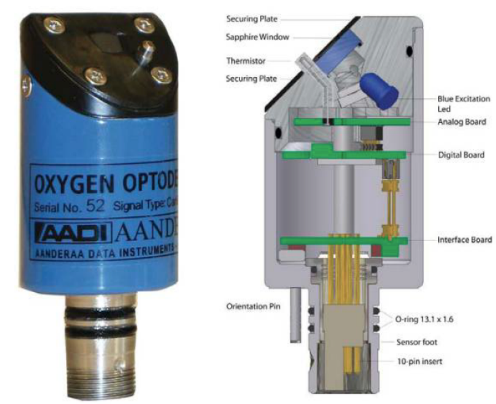


- MOOSE-GE 2012: summer cruise with 90 CTD-O2 profiles in the NW Mediterranean Sea
- Large drift from SBE43 raw data during 17 days cruise (around 50 umol/kg !!) despite the application of the SBE cleaning procedure (Triton and bleach flushing)
- Able to correct data from O2 Winkler measurements (1 profile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

Optical sensor: Aanderaa optode

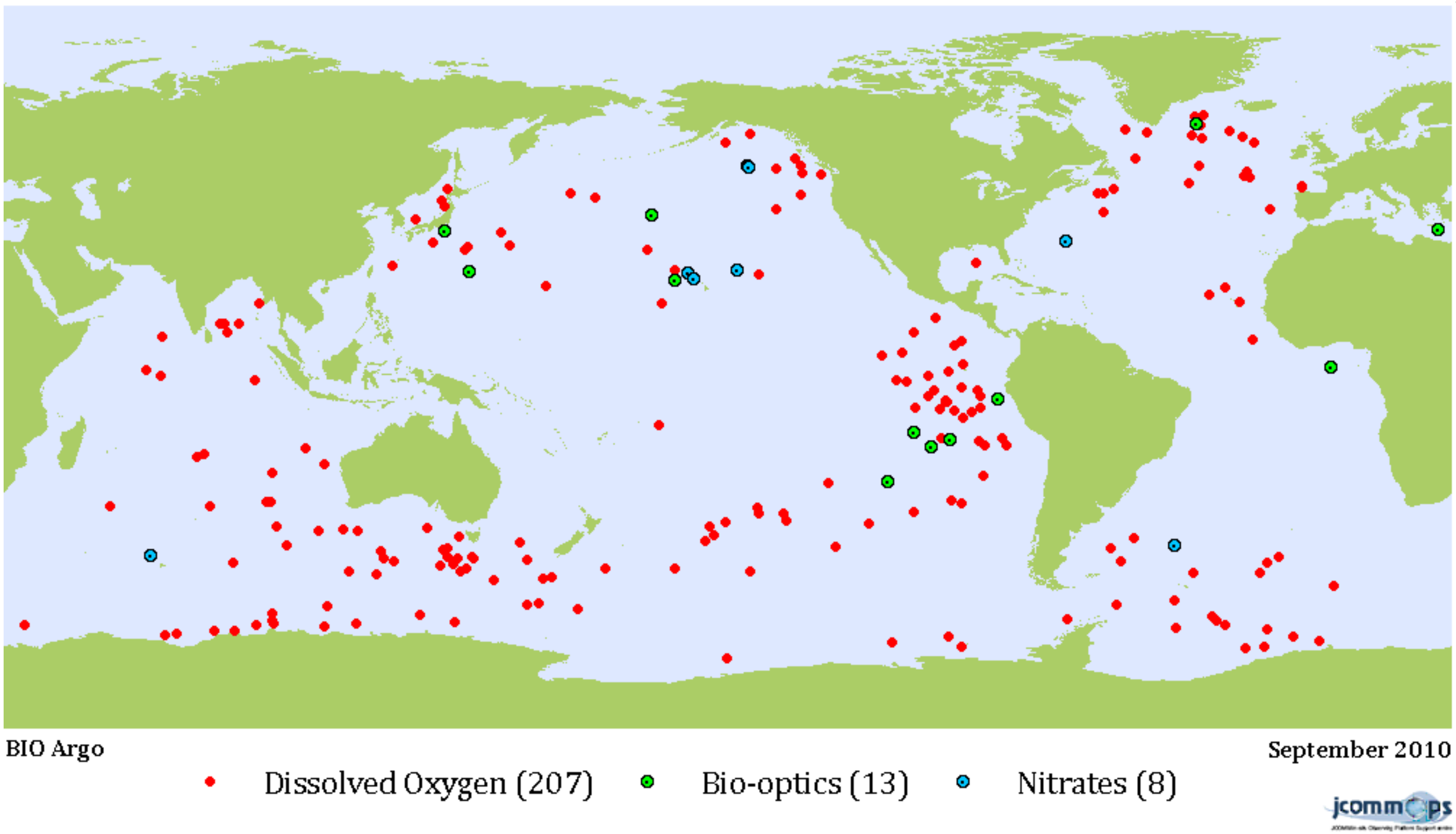
- The sensor is based on the dynamic luminescence quenching of an oxygen-sensitive fluorochrome embedded in the tip
- Long time stability, no pressure hysteresis, fast response, compact, better accuracy (accuracy <8µmol/kg, precision <1µmol/kg)
- Adapted for Argo floats, gliders, ferry boxes, moorings, plankton incubators (eg. IODA, RESPIRE,…)



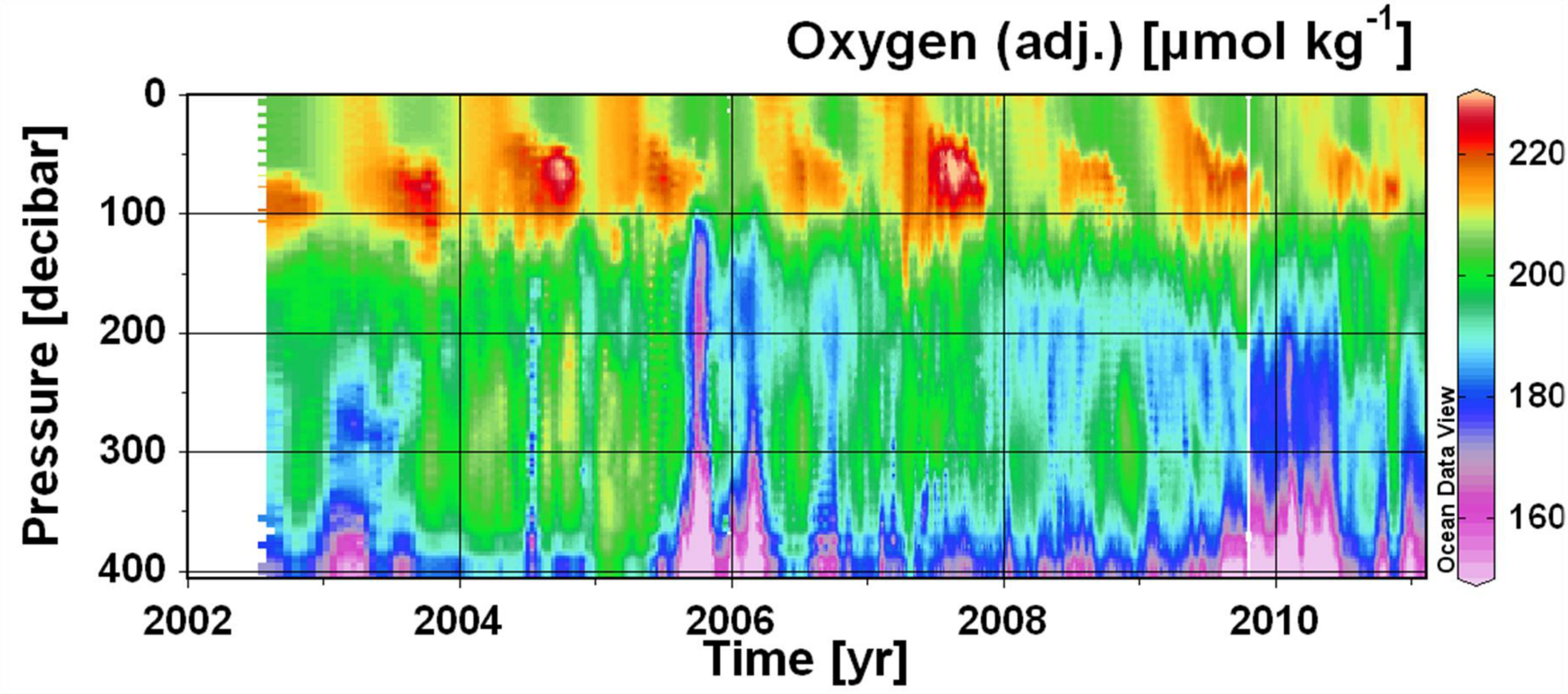


AADI, Bergen, Norway (www.aadi.no)

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



Optode on Argo 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

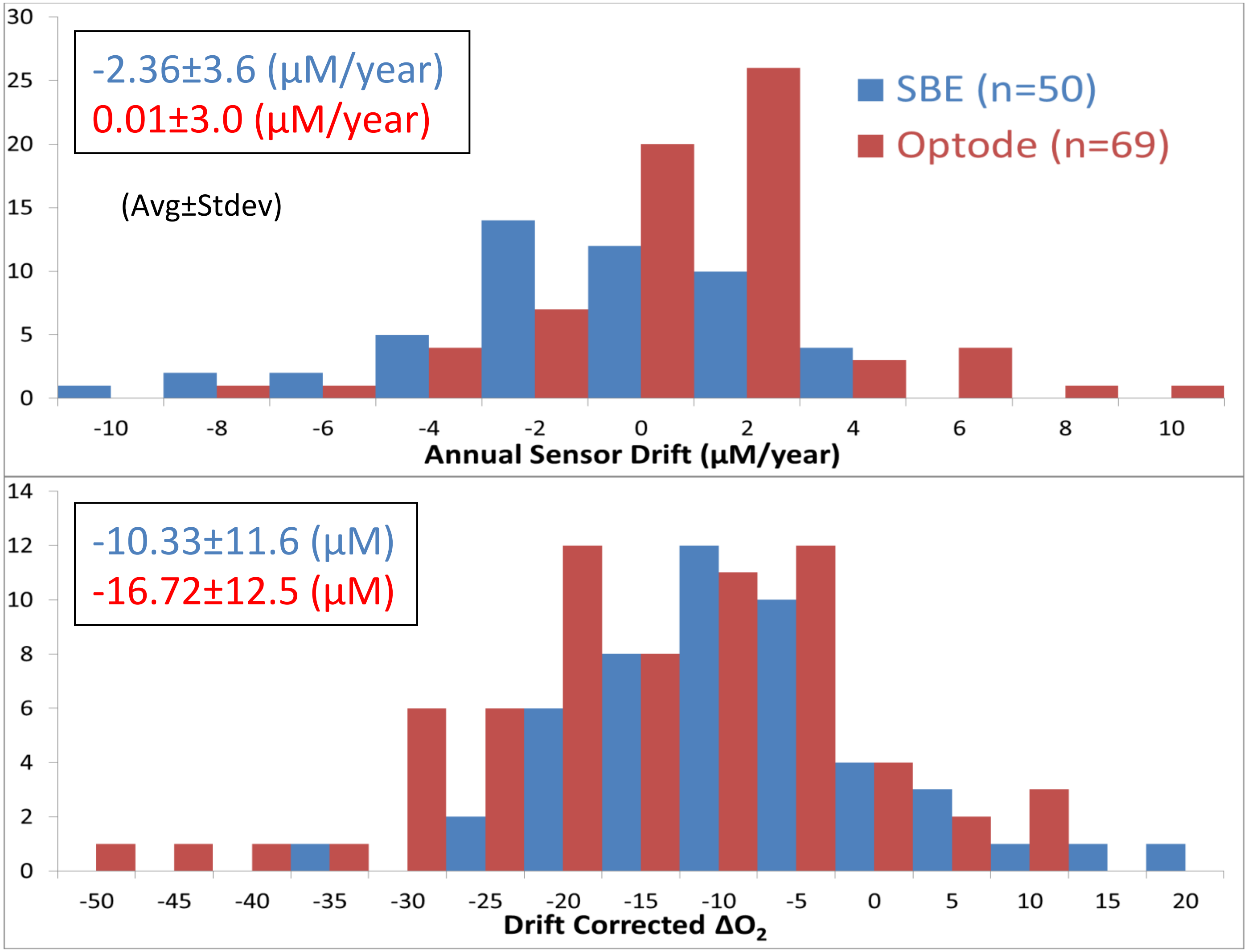
Metadata for 298 floats that include O_2 - ~21 obviously bad, ~25 record<1 yr, ~15<1000m, ~71 have only NaN in O_2 field, ~40 don't list type of O_2 sensor in metadata = 119 floats for analysis.

Drift

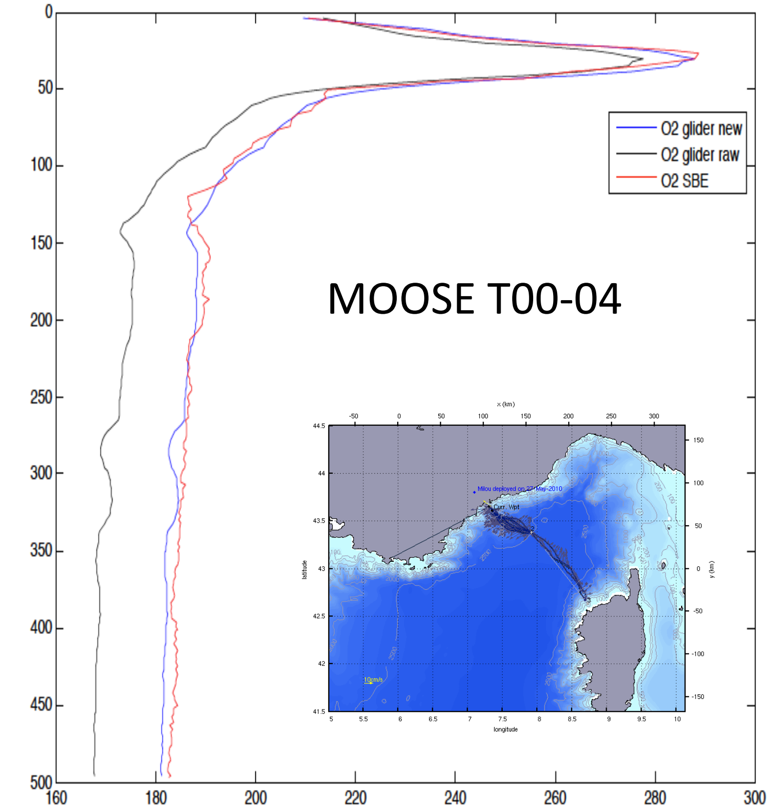
No drift in Optodes. Some for SBE.

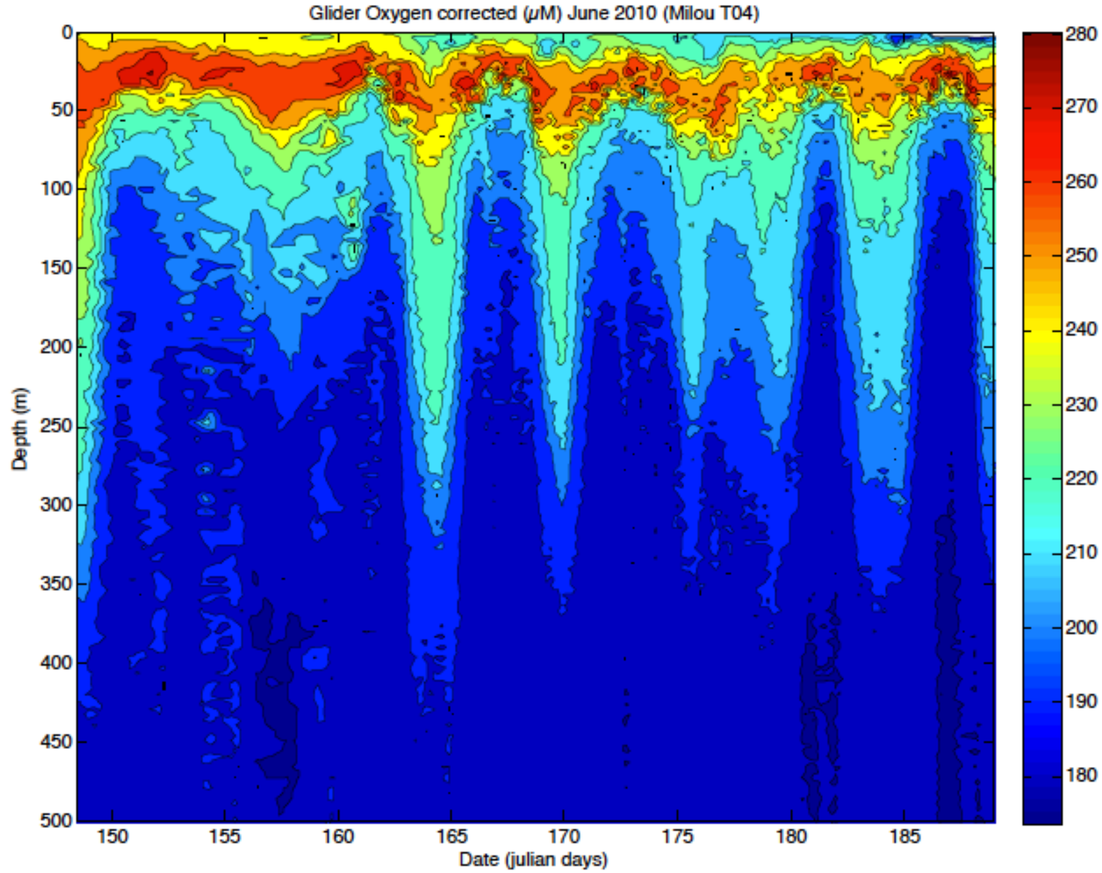
Accuracy

Clear calibration offsets.



Slides from Yui Takeshita & Todd Martz, SIO





- 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:

$$[O2] = C0Coef + C1Coef \cdot P + C2Coef \cdot P^2 + C3Coef \cdot P^3 + C4Coef \cdot P^4$$

$$CxCoef = CxCoef0 + CxCoef1 \cdot T + CxCoef2 \cdot T^2 + CxCoef3 \cdot T^3$$

New optode 4330 with better temperature compensation, faster time response (8-25s) but Aanderaa specifications are poor…

Aanderaa (AADI) calibration procedure

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

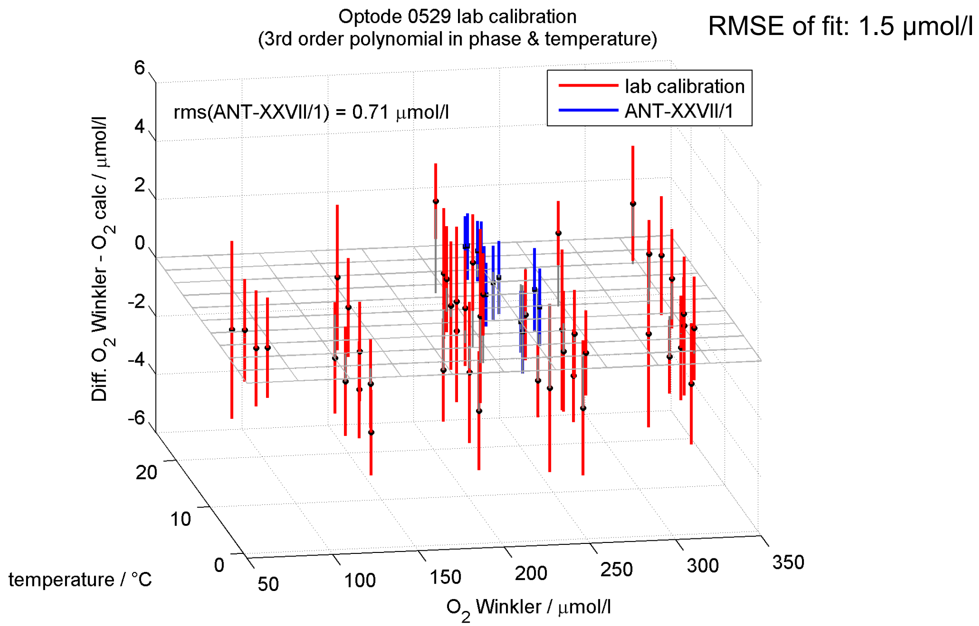
but…

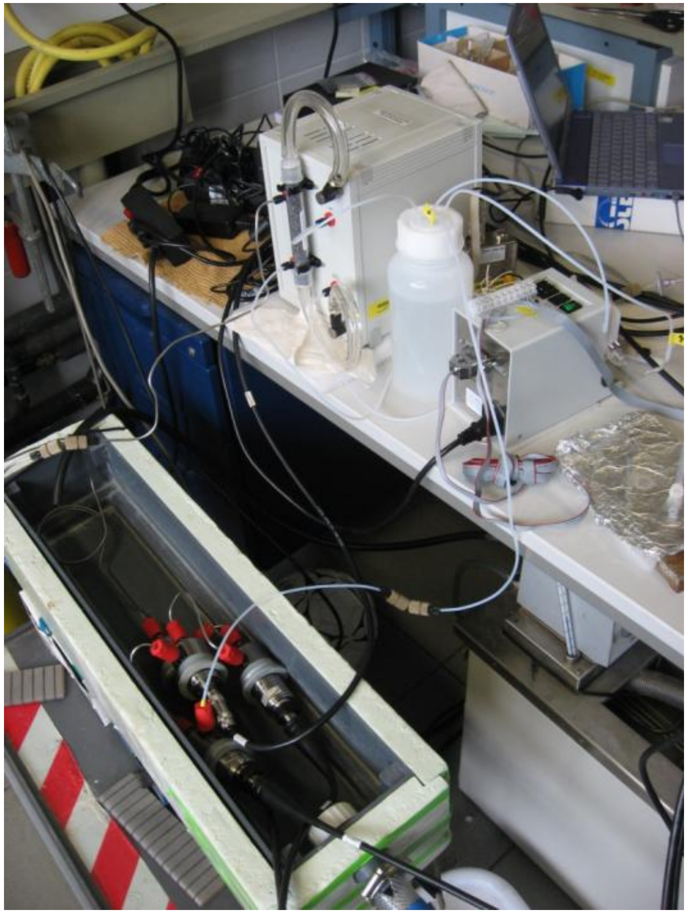
- **Bad initial calibration (we need 64 point calibration !)**
- **Self heating (should be >10s)**
- **Influence of the storage conditions on the data quality (light, dry air)**
- **Need to modify calibration equation**

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.





Argo O2 meeting 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 calculated O2 concentrations

Before float deployment

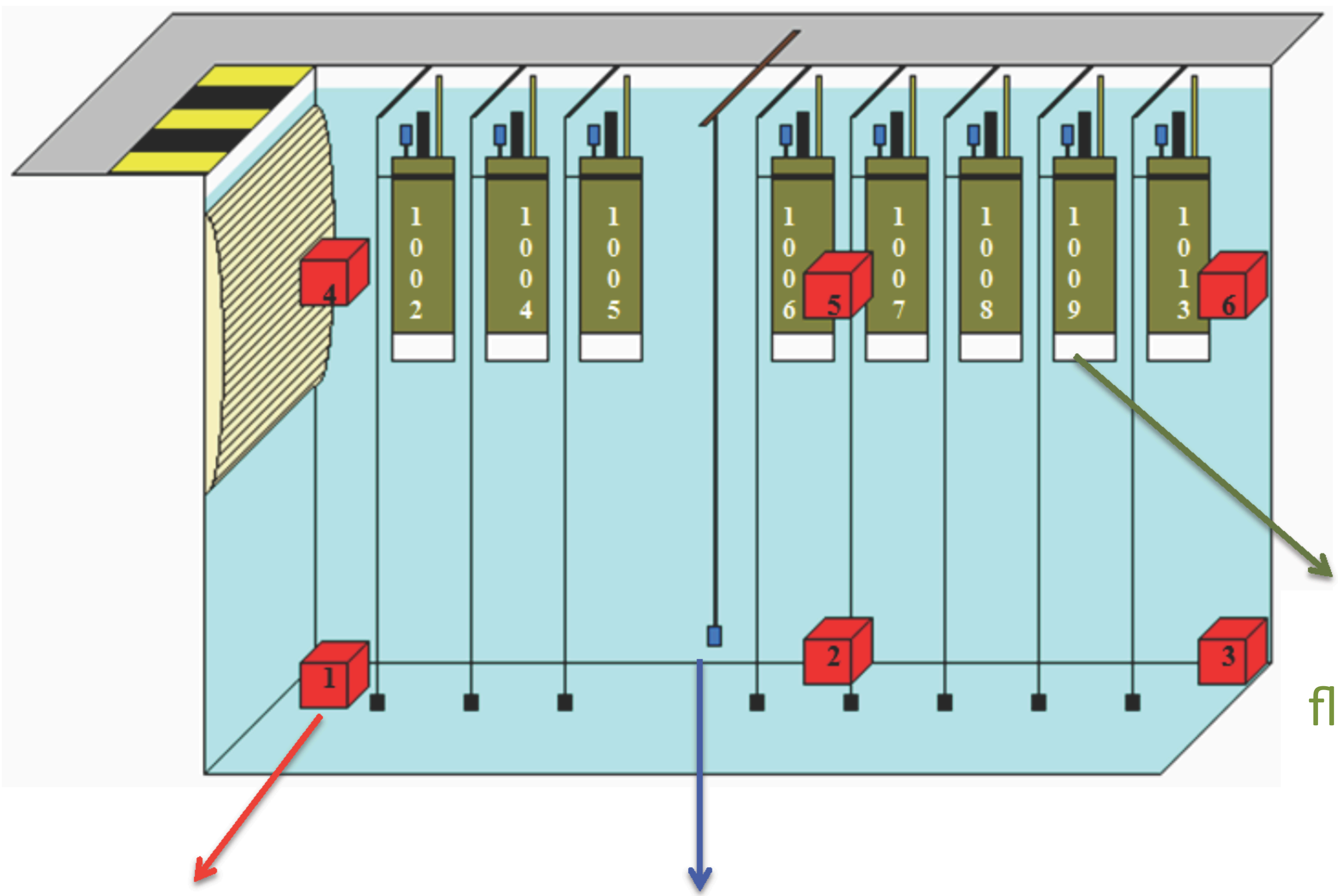
Control of the float behavior in Ifremer pool :

- 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

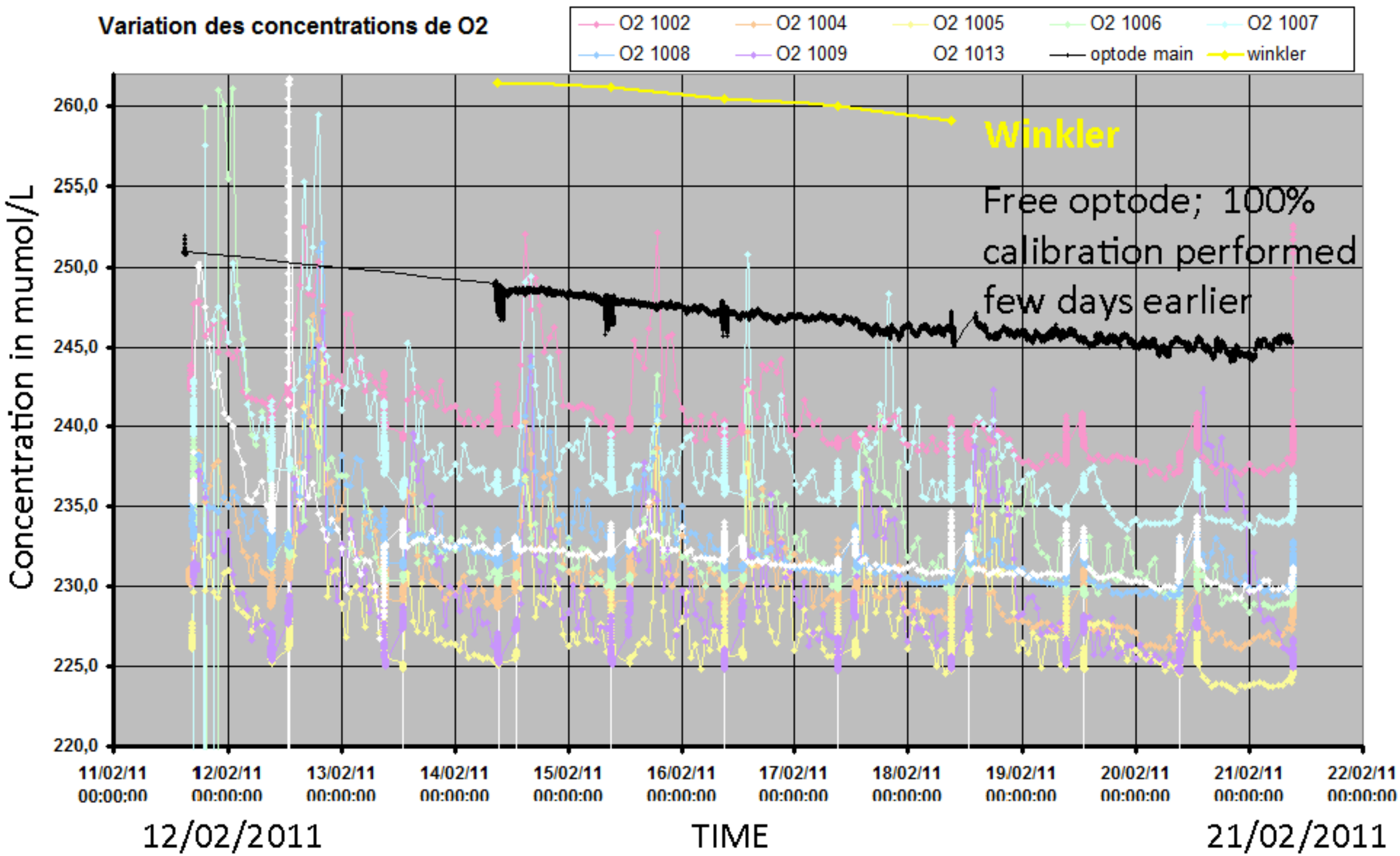


8-15 PROVOR floats with 4330 Aanderaa optode

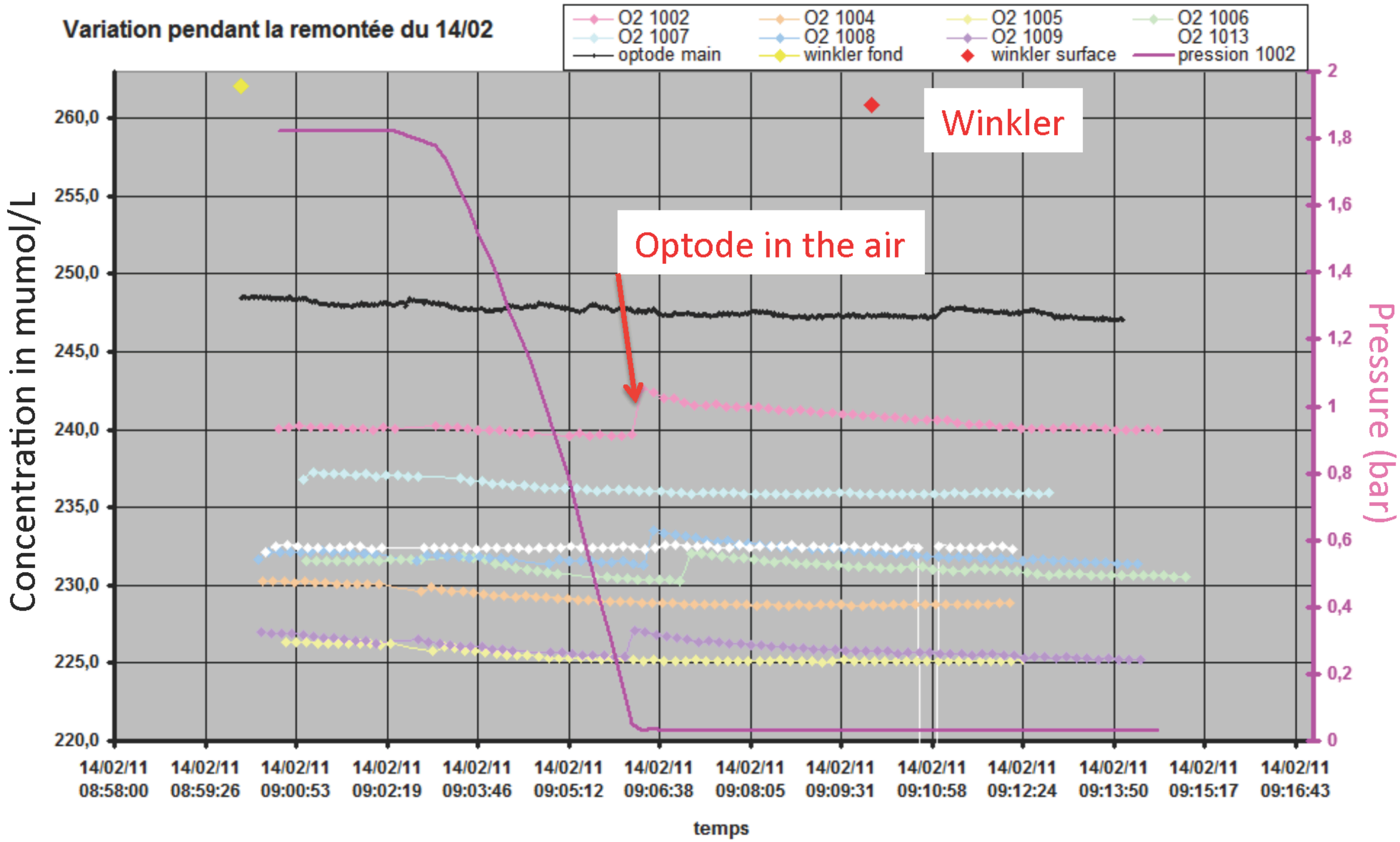
Bottle sampling and winkler titration

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



Main results

- Experiment done in winter when the pool was very homogeneous, both vertically and horizontally
- All optodes revealed the same temporal trend as the one shown by the Winkler titration over the duration of the experiment
- All optodes underestimated oxygen concentration;
- Anomalous fluctuations for the free optode : self-heating of the optode
- Large unexplained fluctuations during « drift » at parking depth for the floats , many checks, no clear explanation

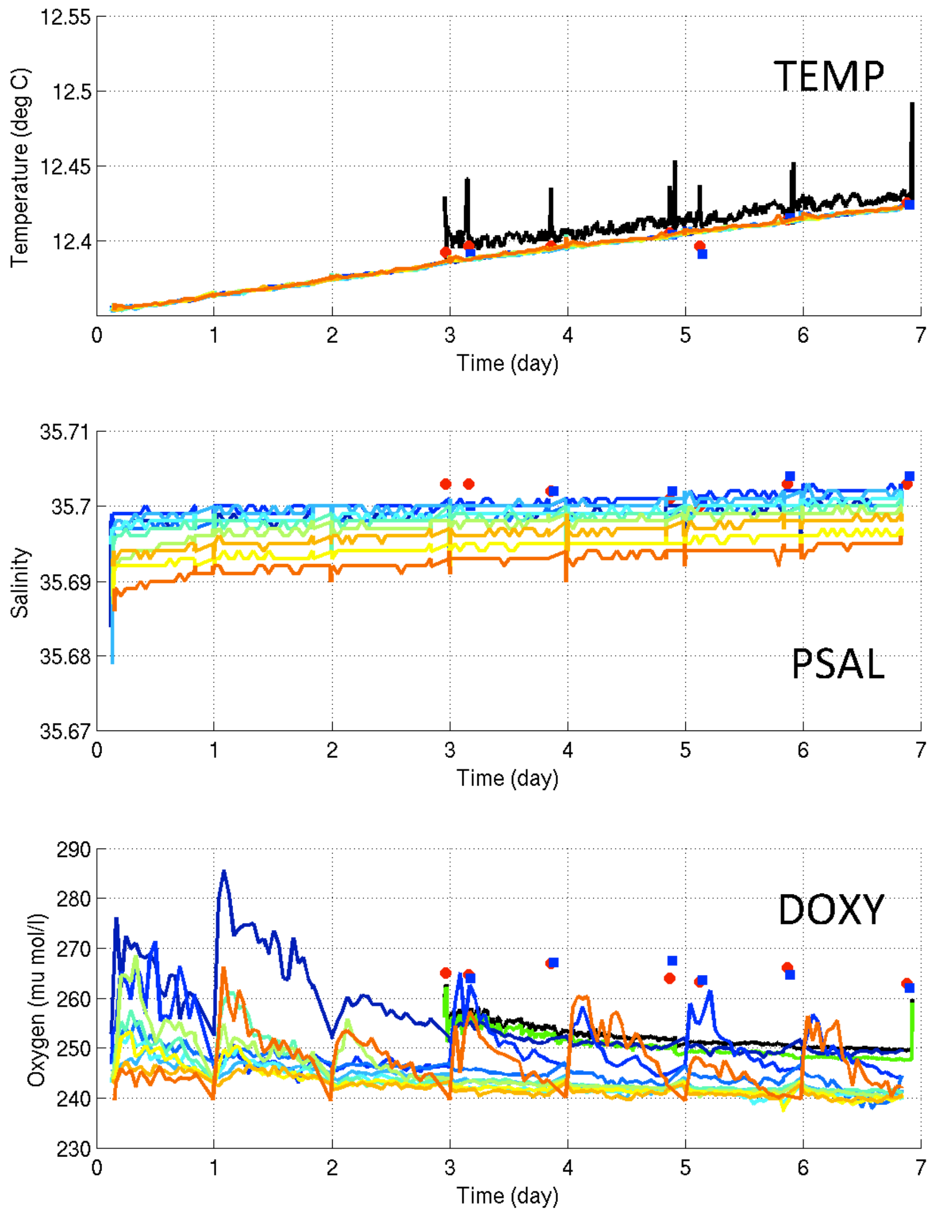
➔ **Results presented at the Argo-02 meeting**

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)



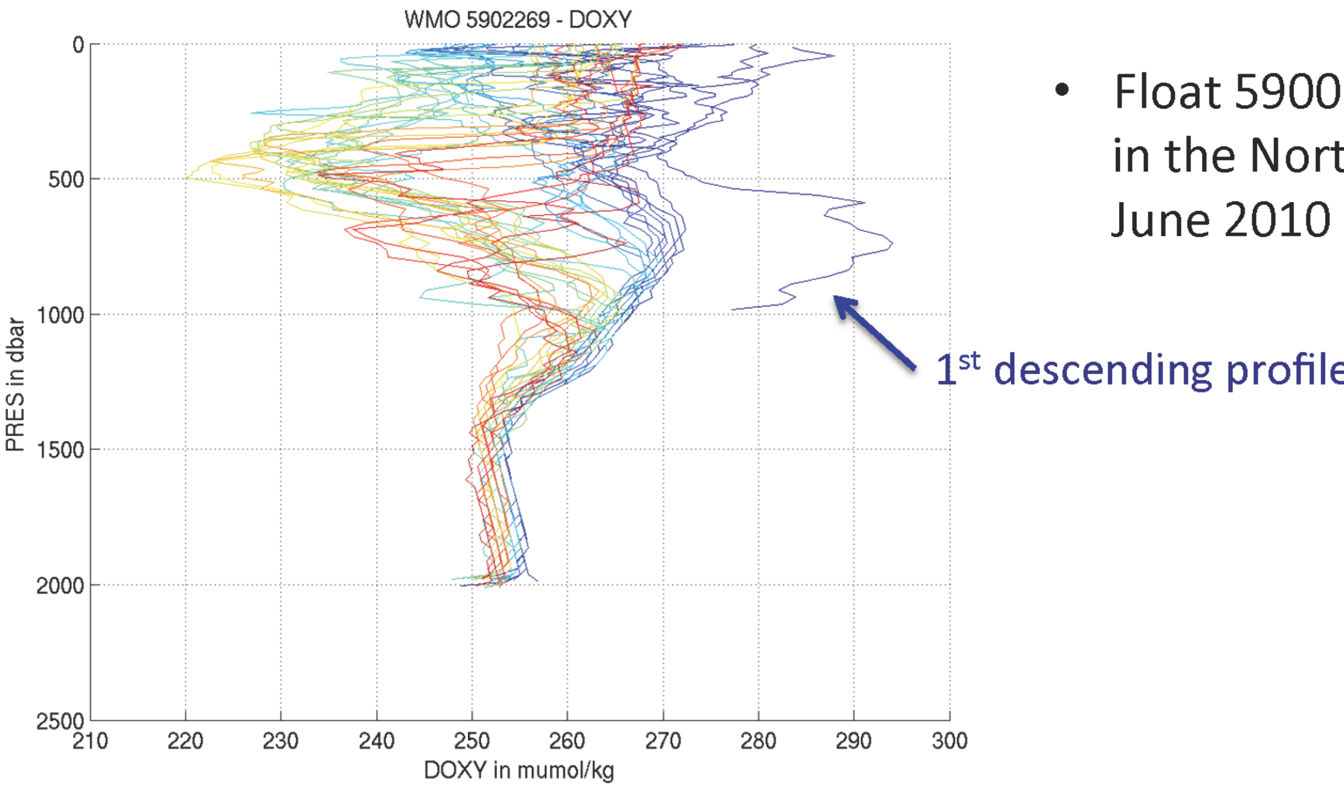
Main results

- 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

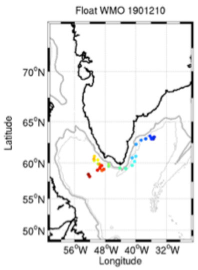
- Why the mean difference between the **calibrated** optodes and the Winkler titration varies between 11.7 and 23.6 mumol/L in Ifremer pool
  - Storage in dry air ?
  - Calibration in fresh water ?
  - Chlorine effect on the optode measurement and/or Winkler titration (although the chlorine was also 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



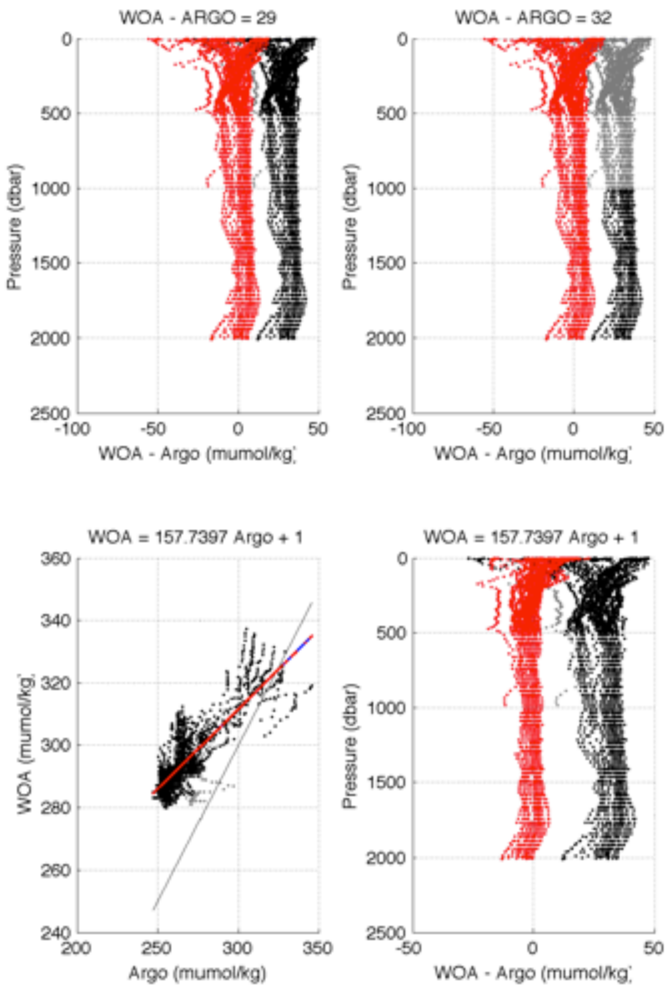
- Float 5900269 deployed in the North-Atlantic in June 2010 (3830 optode)

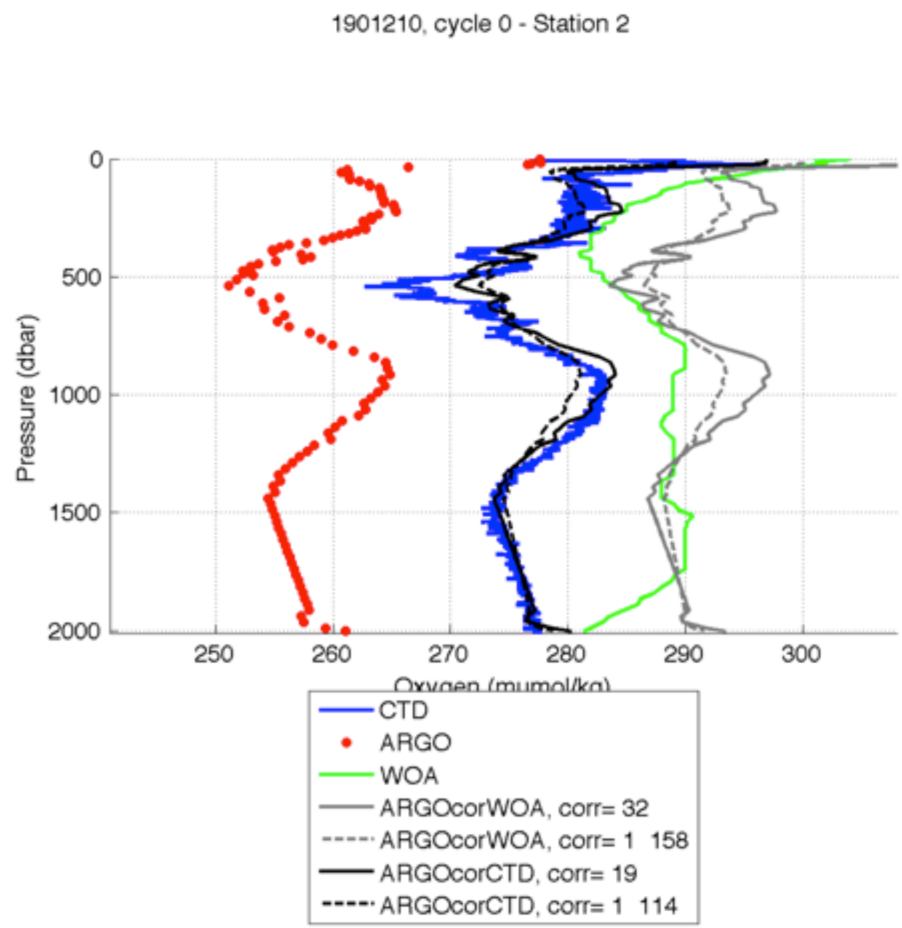
- Impact of the storage condition on the calibration ? Should we keep the optode wet ?



Post deployment correction

Comparison to WOA





➔ Reduce difference from 20 to <10 umol/kg

Response of the foil after storage in dry condition

Aanderaa's answer to a question regarding this issue:

"We recommend to store the sensor wet, or you will experience a drift the first 24 hours. This drift is exponential and will decrease after a couple of hours, but you will still see the drift after 1 day if you run with a high resolution."

- What is amplitude and sign of this drift ?
- Can this lead to a significant bias when a 0-100% calibration is done while the foil is not stabilized?
- Does it depend on the duration of the storage in dry conditions ?
- Does the foil return to its initial calibration after being stored in dry air ?

Conclusions and future strategy

- Recent results far from the accuracy of 1 umol/kg required by the scientific community
- Necessary to re-calibrate optode in lab. Excepting better calibration procedures from Aanderaa.
- What about others sensors ? RINKO ? SBE ?
- 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)
- A third ARGO test has been performed in the IFREMER pool with 10 PROVOR-DO and 5 PROVOR-DOI in Sept 2012 with free optode, Winkler titration, salinity measurements (mixing). These results are still under treatment…