Oxygen measurements: sensors accuracy and scientific needs

L. Coppola (CNRS-INSU), **E.Diamond (CNRS-INSU)**, L.Delauney (IFREMER), D.Hydes (NOC), M.Haller (HZG), J.Karstensen (IFM-GEOMAR), D.Lefevre (CNRS-INSU), D.Machoczek (BSH), R.Nair (OGS), F.Salvetat (IFREMER), S.Sparnocchia (CNR), V.Thierry (IFREMER)

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cnrs INSU Institut national des sciences de l'Univers

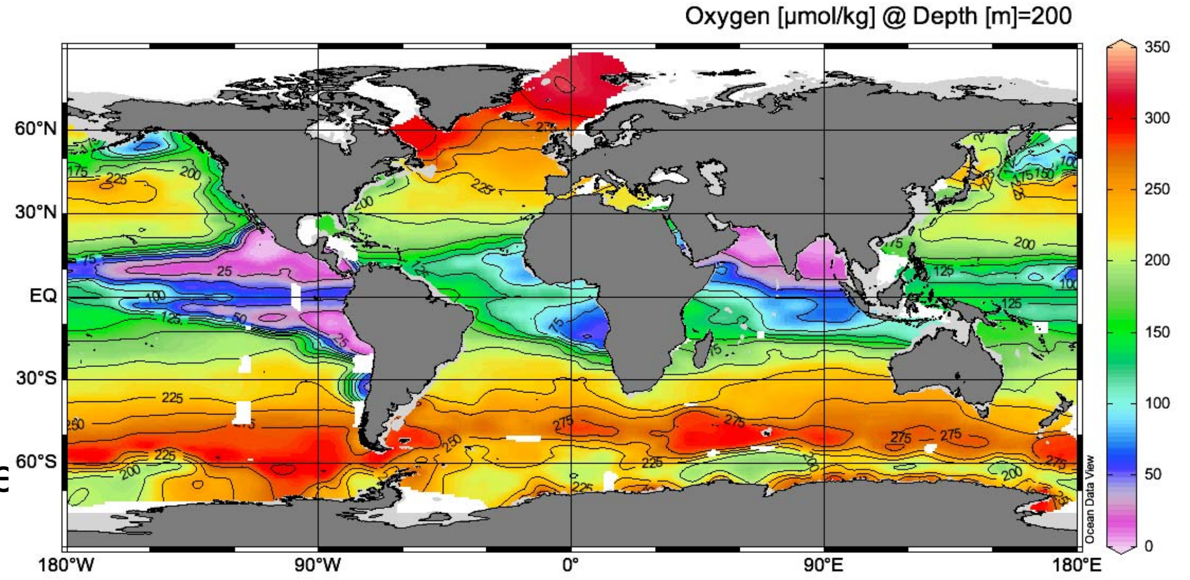
Why are we measuring oxygen ?

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

Very sensitive tracer for studying the ocean biogeochemistry response to climate variability and global climate change

- Biogeochemical interests: primary production estimates, remineralisation flux (consumption/production)

- The ocean deoxygenation is one of the most important topic (O_2<20µmol/kg)
- Oxygen is one of the first measured oceanographic parameters but with a large spatio-temporal scales range : OMZ are poorly documented…



A summary of the manufacturer's stated specifications of present O_2 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 µmol/kg to do some science !

SBE 43 Dissolved Oxygen Sensor

- Clark polarographic membrane
- Mainly used on shipboard CTD unit and moorings
- Accuracy = 2% of saturation
- Linear drift due to the biofouling issues

Oxygen(ml/l) = Soc x (V + Voffset) x φ

Possible to correct the drift with O2 Winkler analysis

Correction of the SOC term (linear slope scaling coefficient)

$$\mathbf{SOC_{new} = (DOXY_{Winkler}/DOXY_{SBE43})}$$

Experiences and problems with SBE43 sensor:

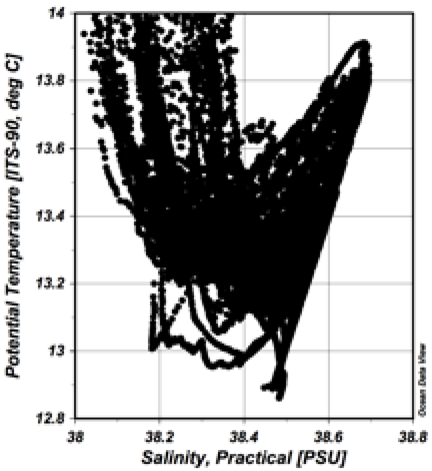
- Sources of drift: changes in membrane tension, depletion of electrolyte, impairment of the silver anode, plating of anode metal on the cathode, and the presence of chemical contaminants in the sensor’s plastic body.

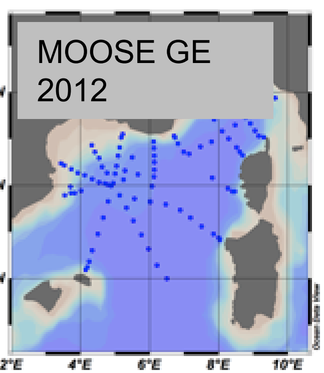
- Dynamic errors leading to apparent hysteresis are caused by response-time mismatch of the compensation temperature sensor

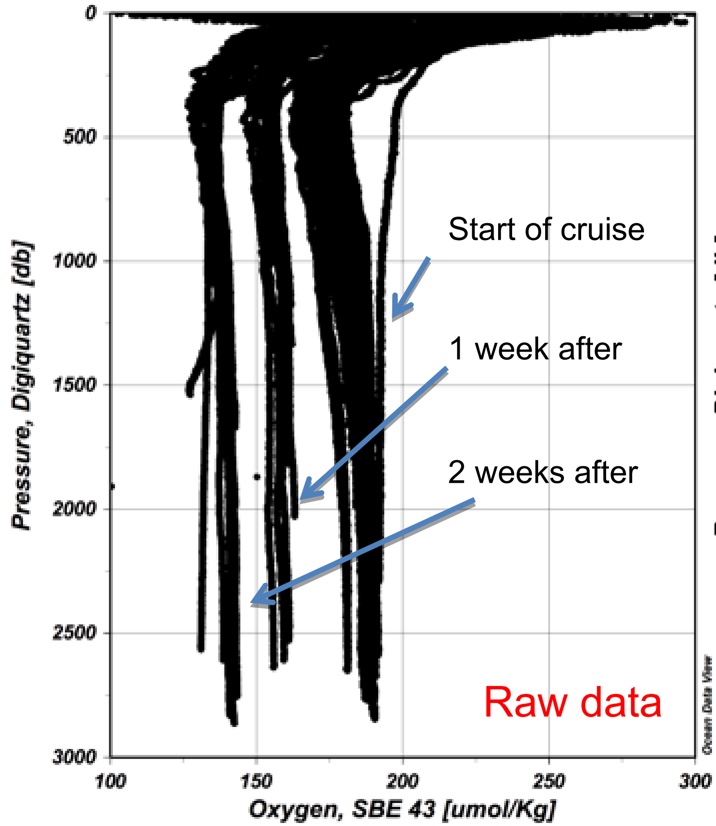
- Membrane fouling: altering the oxygen diffusion rate through the membrane, thus reducing sensitivity. Biofouling can be particularly troublesome because the living organisms either consume or create oxygen.

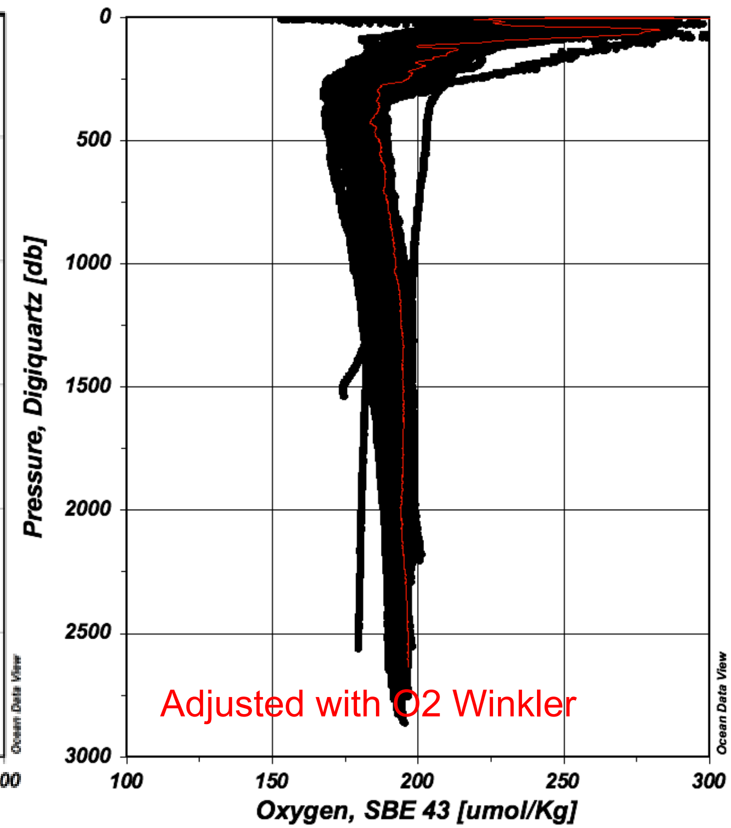
- Mostly adapted for CTD profiler (very fast time response)

Experience on field campaign (Mediterranean Sea)



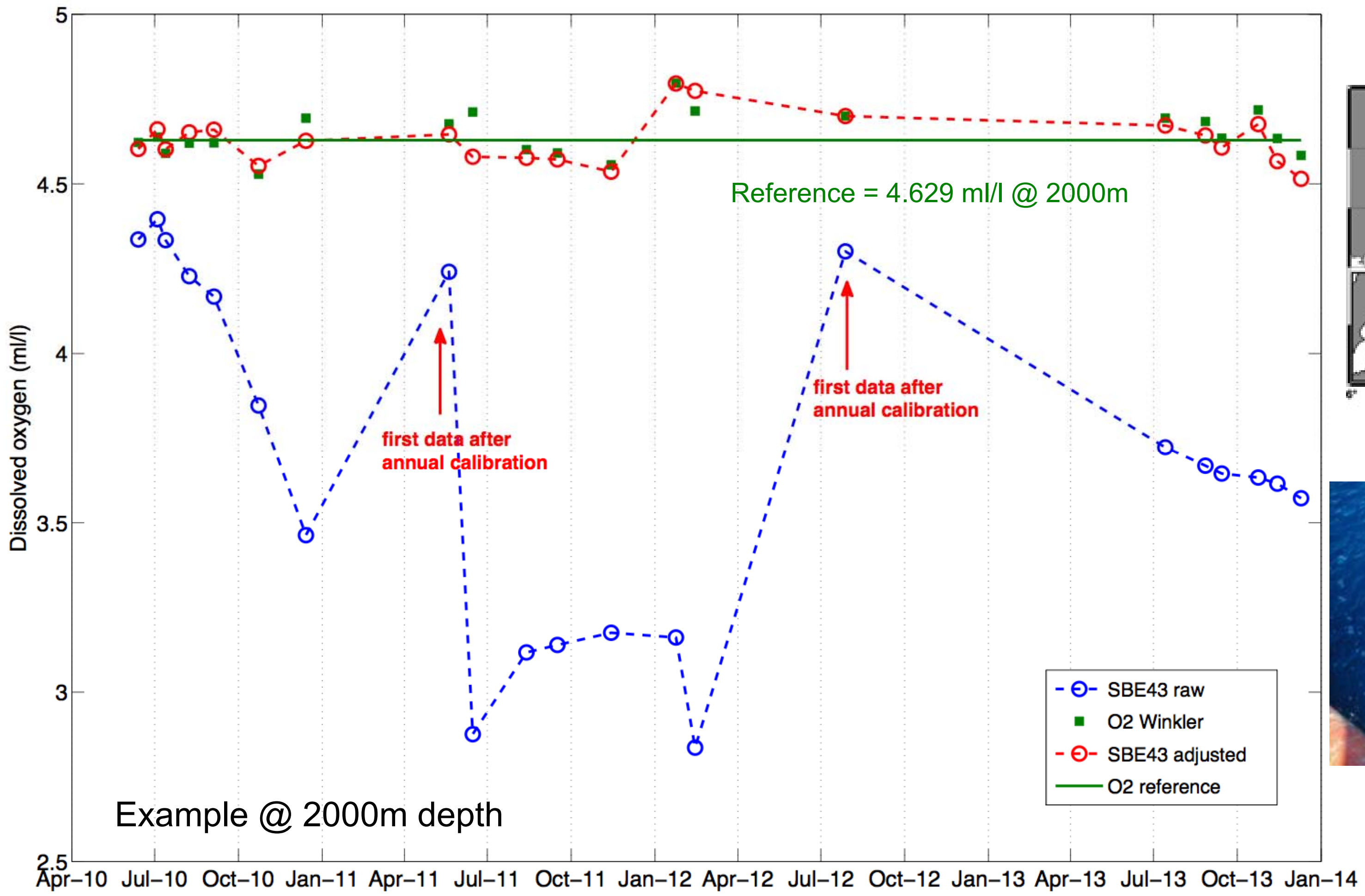


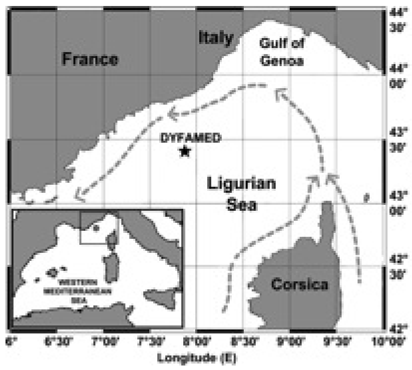


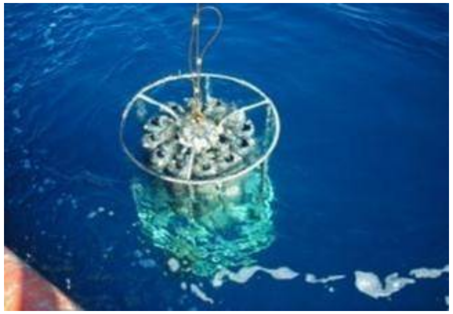


- Large drift from SBE43 raw data during 17 days cruise (around 50 umol/kg !!) despite the application of the SBE43 cleaning procedure (Triton and bleach flushing)
- Correction with O_2 Winkler analysis needed ! (1 profile per day)

Experience on time series (Mediterranean Sea)



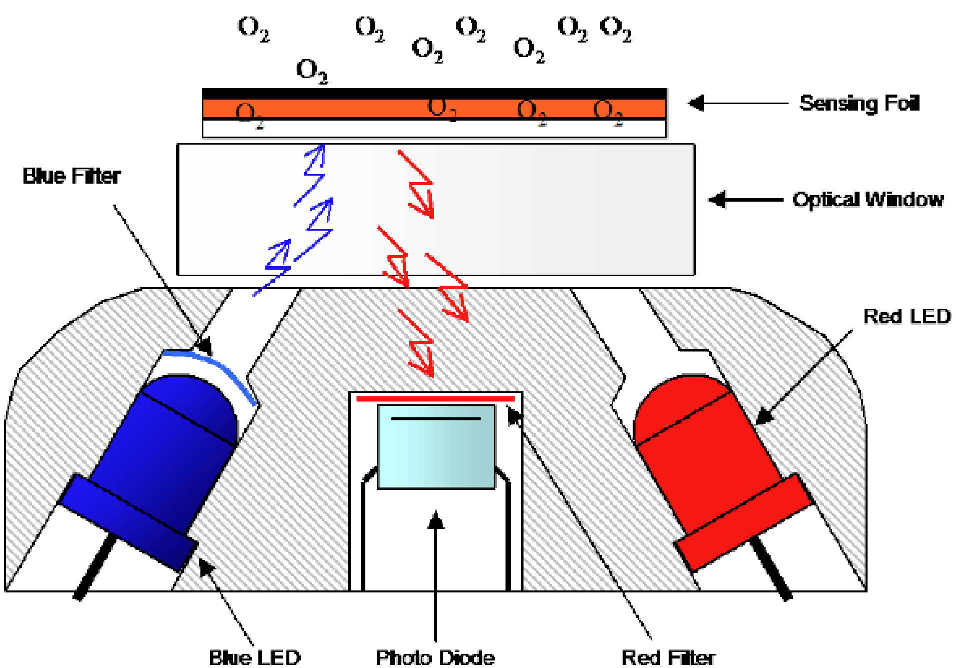




- Example with 3 years using SBE43 during monthly monitoring at the DYFAMED site
- Large differences between O_2 reference and O_2 from SBE43 after annual calibration

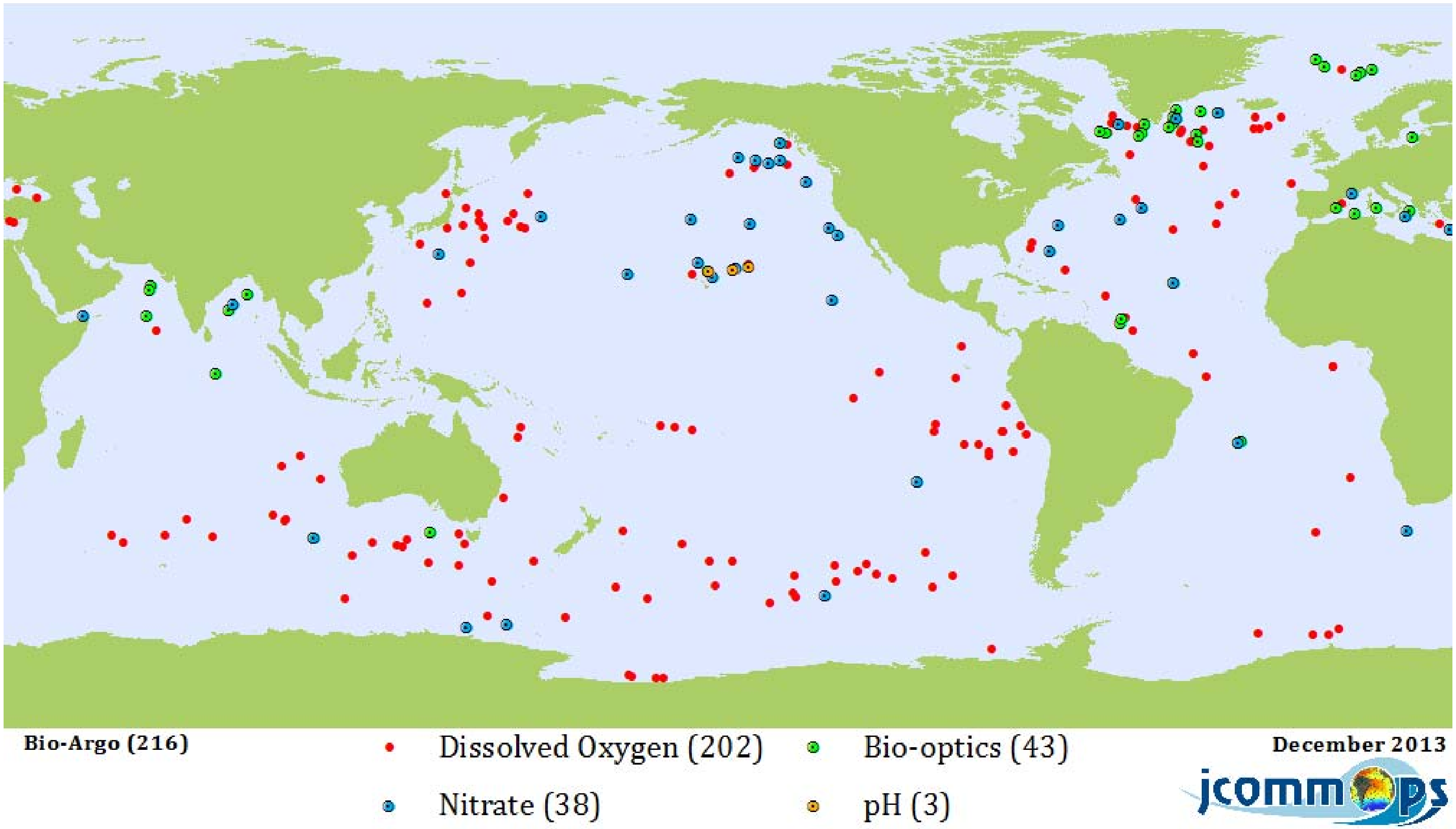
Optical sensor: Aanderaa optode

- 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 (e.g. IODA, RESPIRE,…)



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

Large interest for the Argo community



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

What about the optode accuracy ?

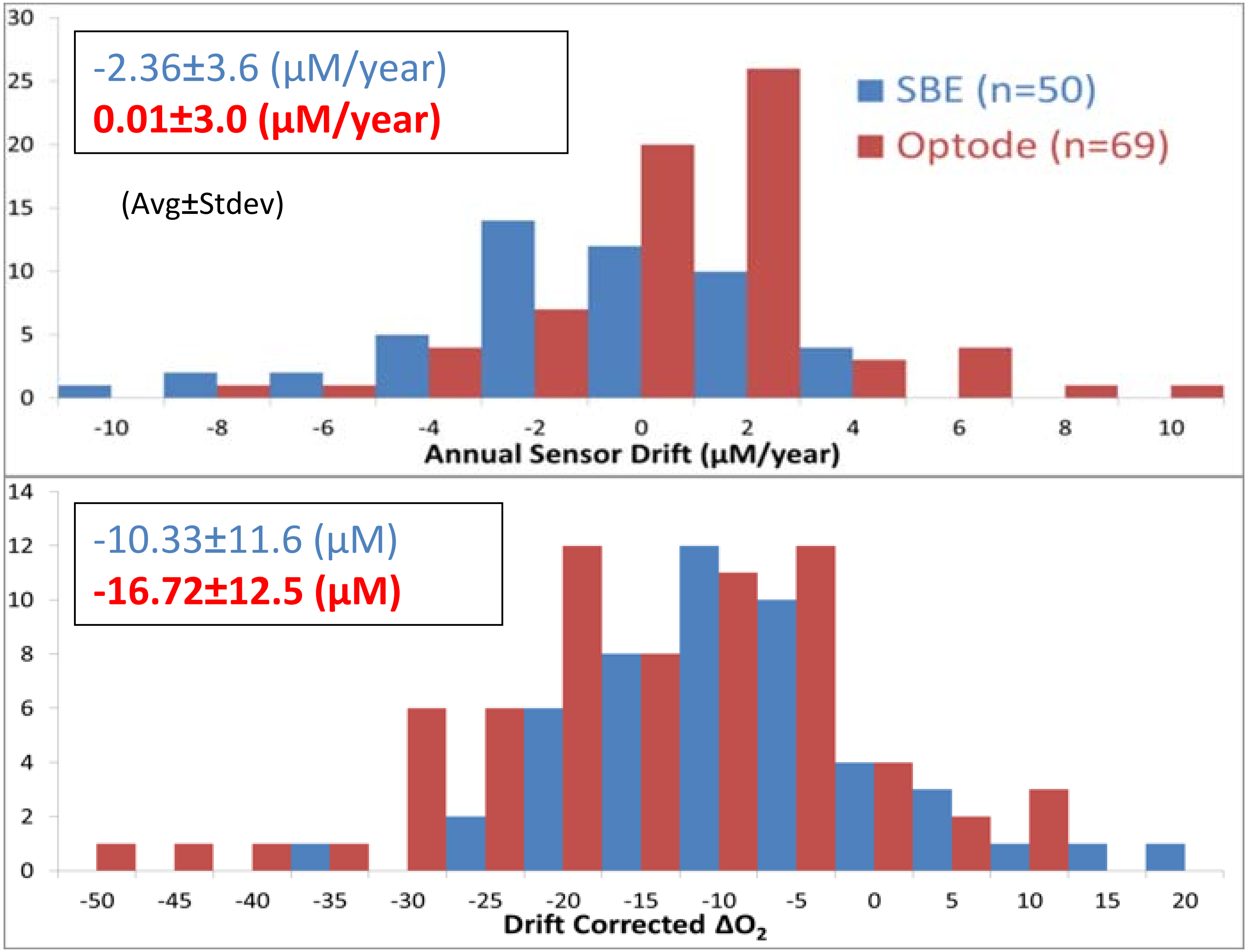
Sensor comparison to gridded data in WOA 09 for 119 floats

Drift

No drift in Optodes. Some for SBE.

Accuracy

Clear calibration offsets.

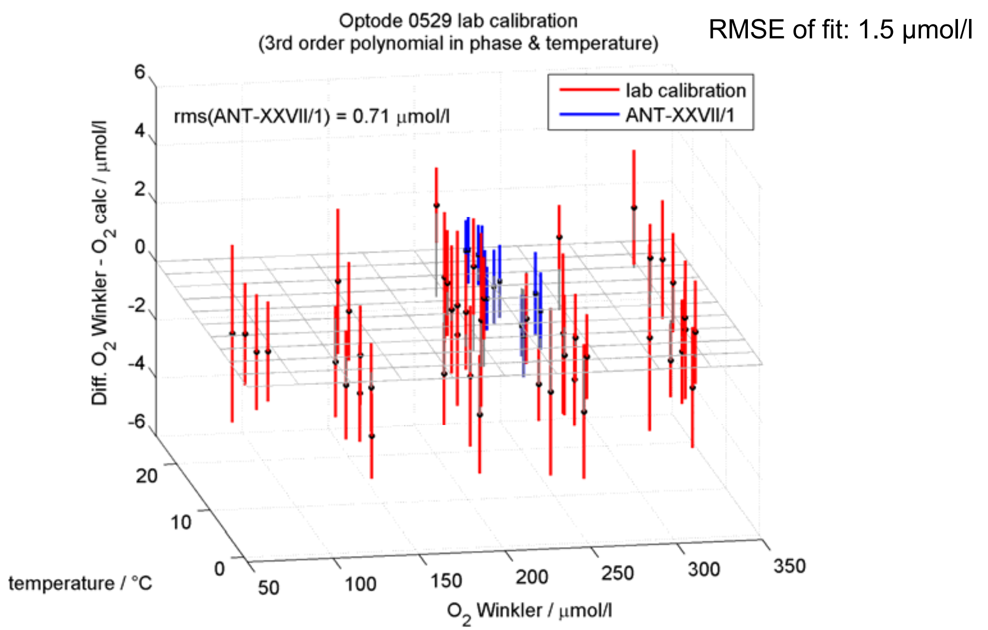


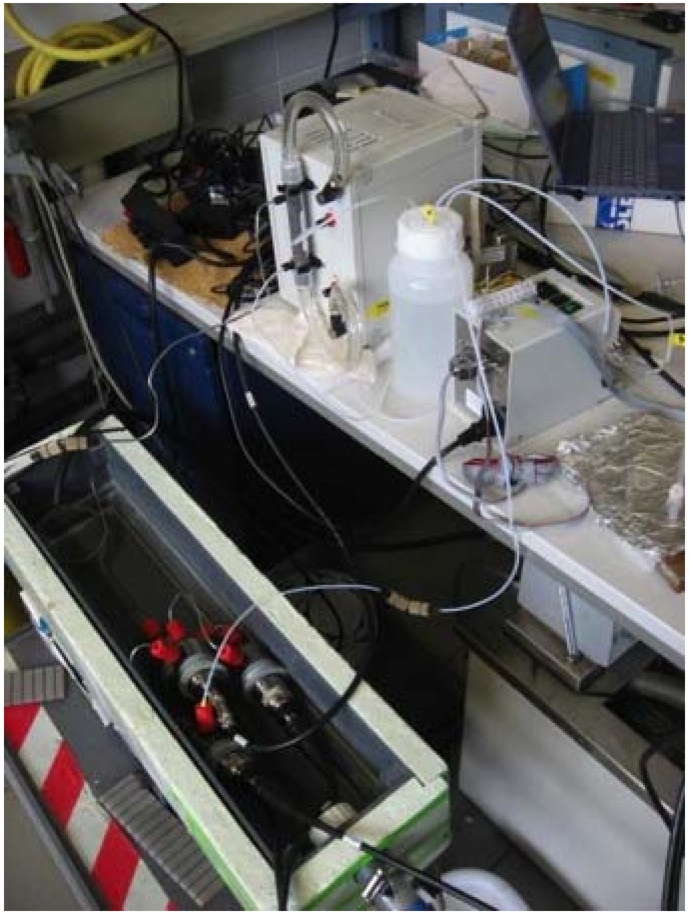
Slides from Yui Takeshita & Todd Martz, SIO

Optode: the multi-point calibration

Henry Bittig, Arne Körtzinger
(IFM-GEOMAR), Riser (CSIRO), D.Lefevre (CNRS)

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





Argo-O2 advices and calibration improvements

- Optodes were stable but gave lower values than expected

➔ Main reason : an after-curing appears in the foils during the first 1-3 months after manufacturing which typically leads to 1-4 % lower readings

➔ Storage recommendations: keep optode wet and dark at all times

- With the new optodes (4330/4835/4831), new calibration procedure:

✓ Use the Stern-Volmer equation (Uchida et al. 2008)

✓ Use a 40 multi-point calibration system (5T x $8O_2$ points)

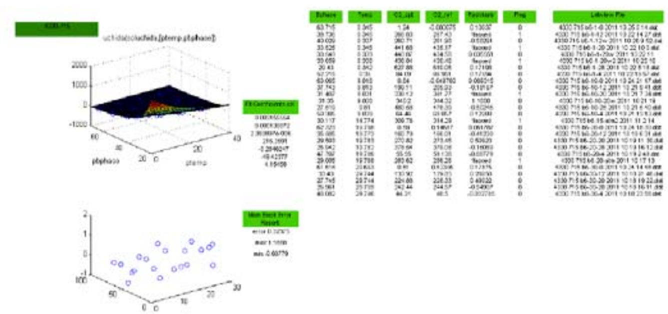
✓ Accuracy better than 1.5% (± 2 µM)

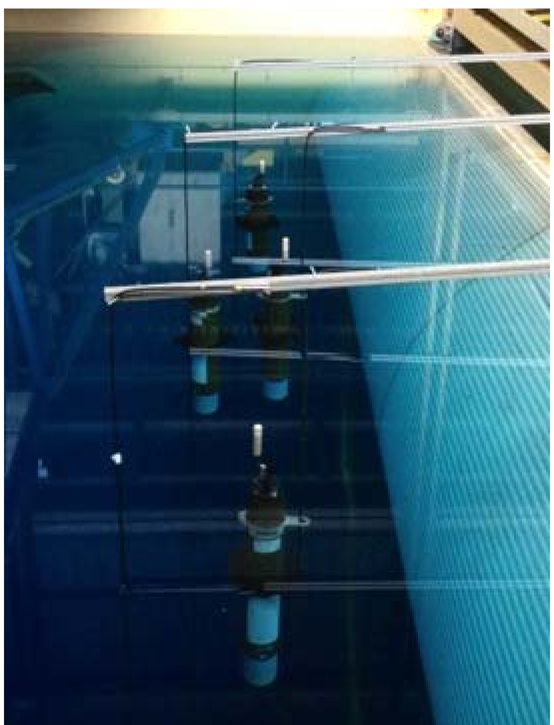
ARGO-O2 TEST PROCEDURE BEFORE DEPLOYMENT

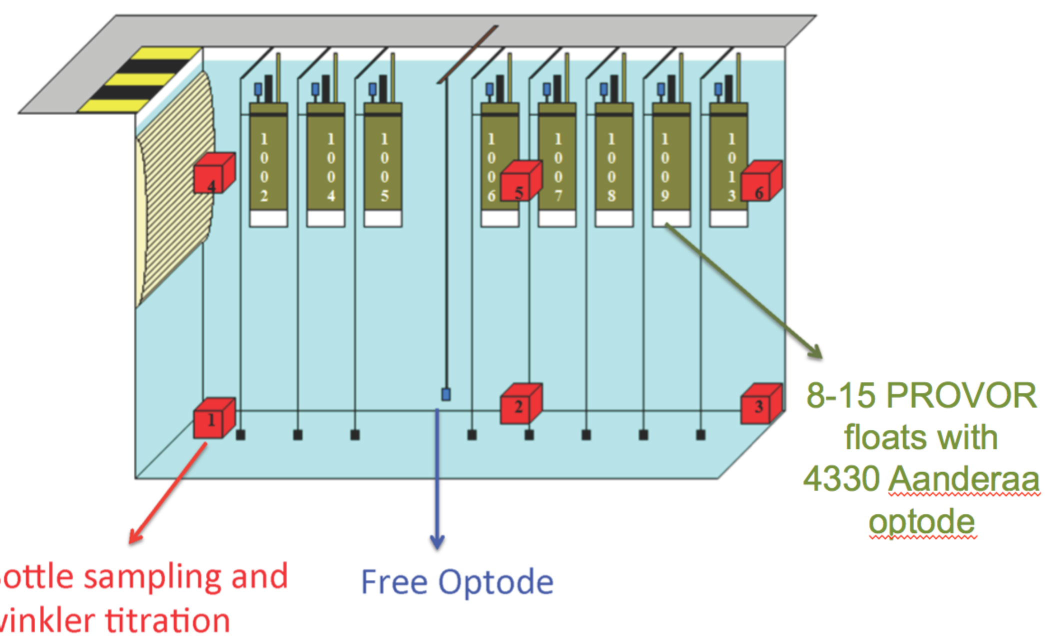
- Mixing bath (homogenization)
- Seawater with chlorine solution
- 1 profile per day (max depth 18m)
- Optode 4330 with new coefficients (CSIRO)

OPTODE 715

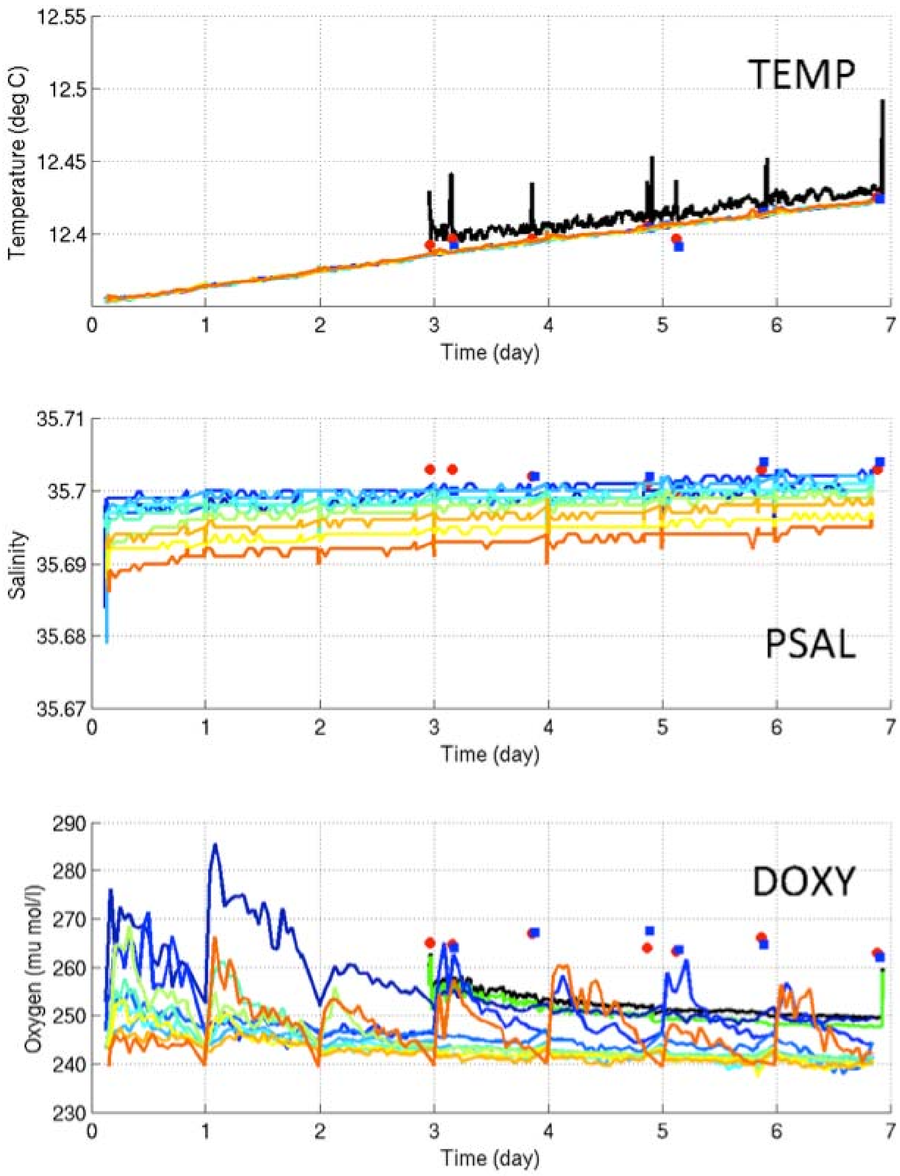
Optode serial number	PROVOR-DO	WMO	C1 to C7 coefficients	Transmission
715	OIN 11 DO 11	6901467	0.0031556 0.00013887 2.3839e-006 215.26 -0.28462 -49.424 4.1546	Iridium C1Phase and C2Phase are transmitted







Main results



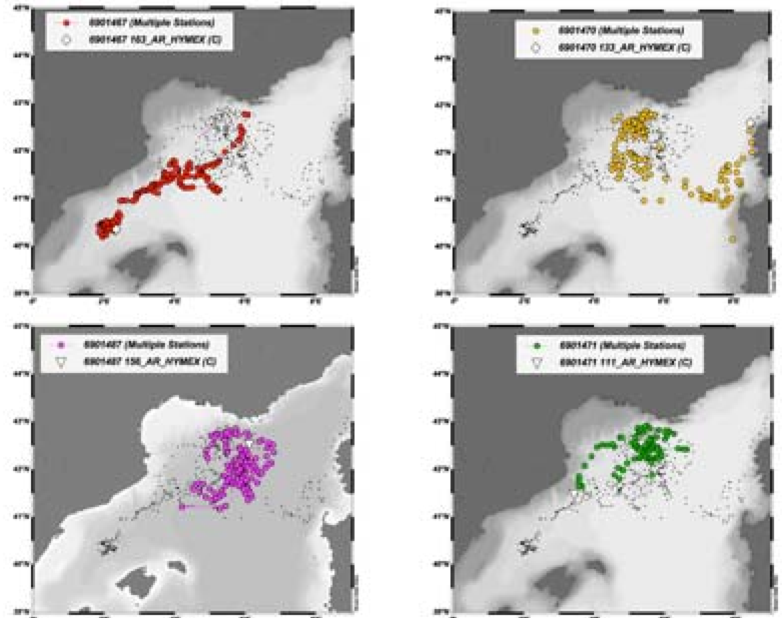
- Small vertical T/S gradient in the pool
- Despite the new calibration and the new storage, all optodes underestimated the O_2 concentrations (average 20 µmol/kg !)
- Large fluctuations during the drift at the parking depth
- No clear explanations

QUALITY CHECK DATA AT DEPLOYMENT

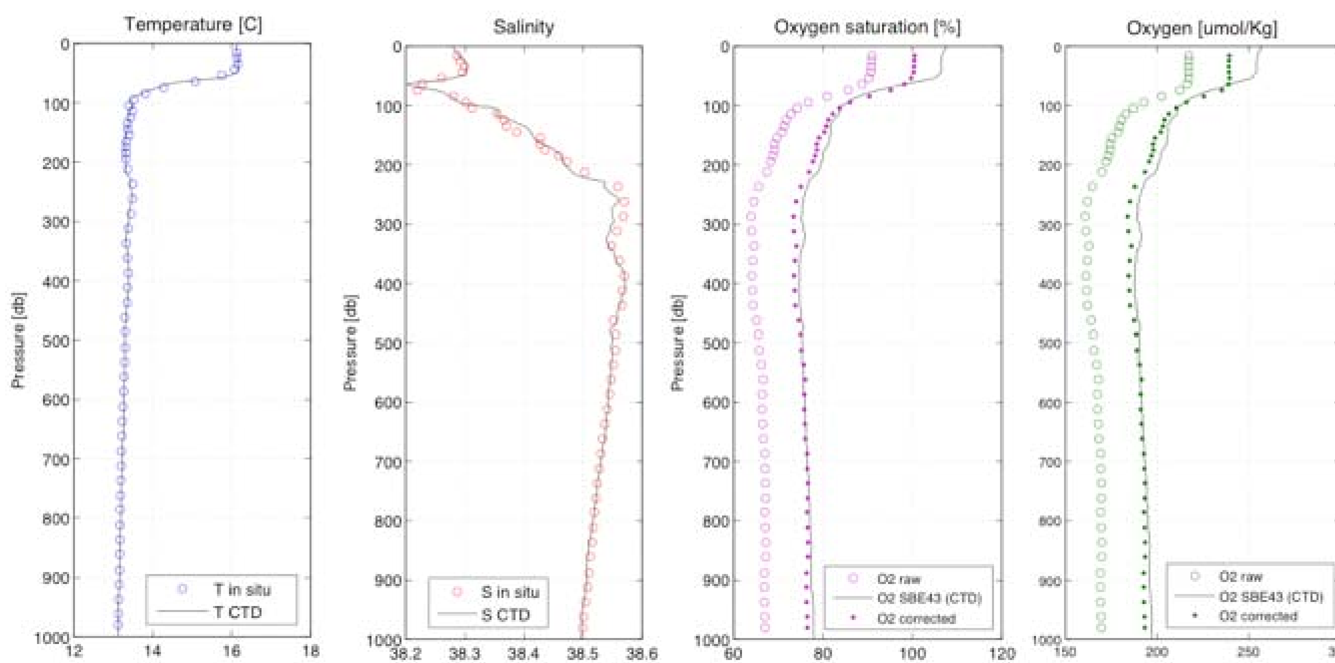
- $CTDO_2$ profile at t_0 with salinity and oxygen in situ measurements (bottles)
- Salinity and oxygen data corrected from offset
- Bittig et al. 2012 and Takeshita et al. 2013 methods (C_0=offset, C_1=gain)

$$[\mathrm{O_2}]_{\mathrm{float}}{}' = C_{0,[\mathrm{O2}]} + C_{1,[\mathrm{O2}]} \times [\mathrm{O_2}]_{\mathrm{float}}$$

$$\%\mathrm{Sat}_{\ \mathrm{float}}{}' = C_{0,\%\mathrm{Sat}} + C_{1,\%\mathrm{Sat}} \times \%\mathrm{Sat}_{\ \mathrm{float}}$$

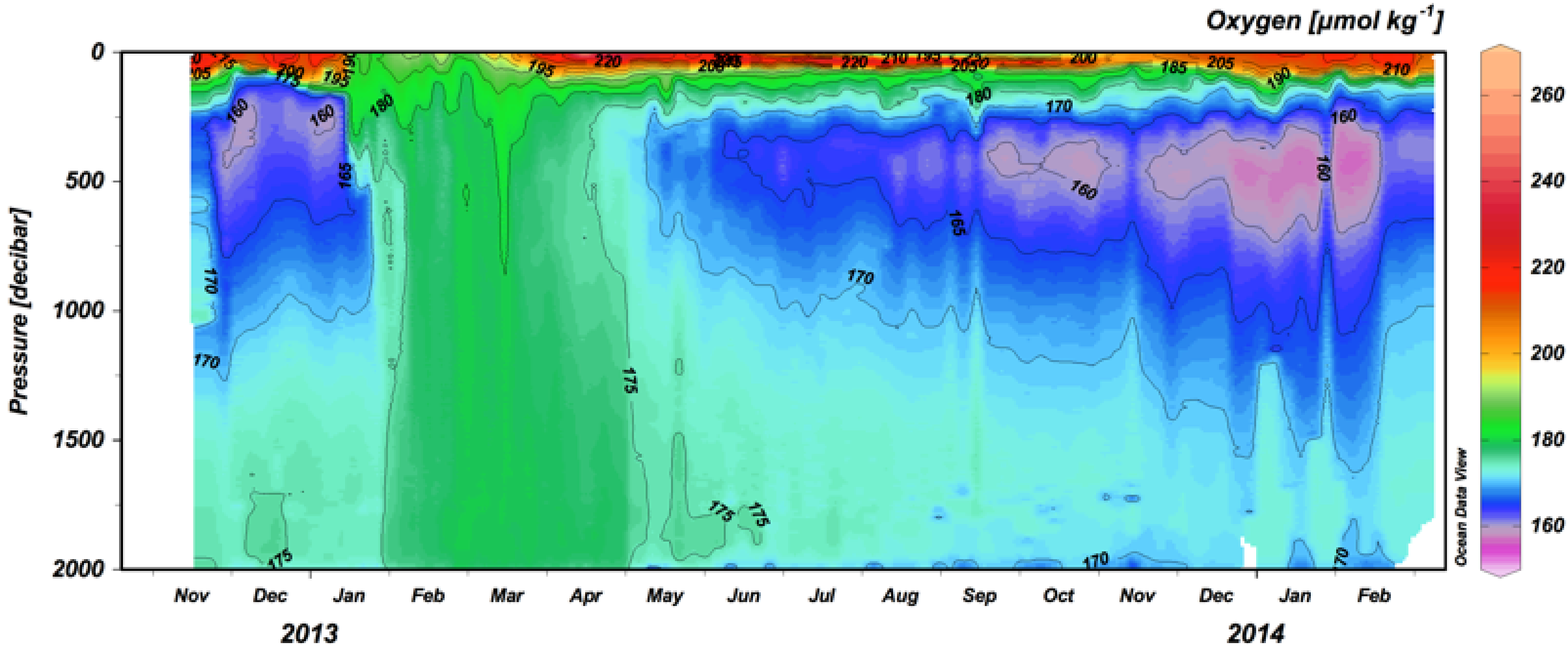


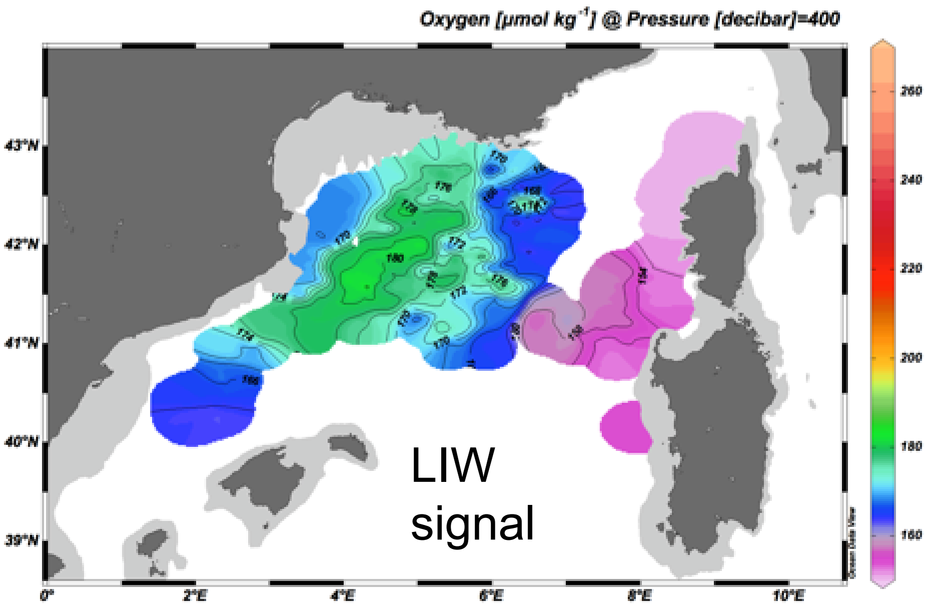
Offset O_2 conc. 10-15 µmol/kg !

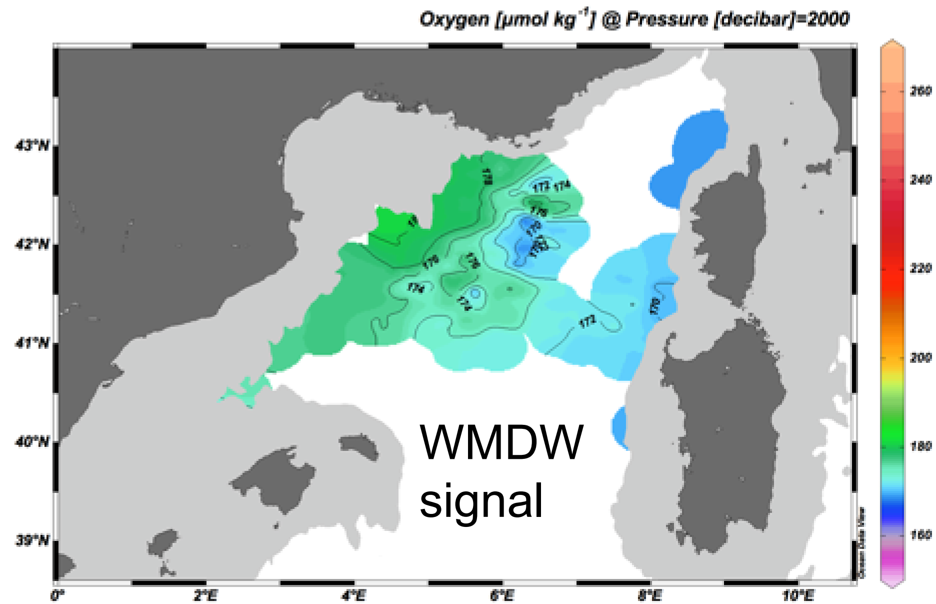


Float WMO 6901467

OXYGEN STABILITY OVER 17 MONTHS (600 O_2 profiles)







Optical sensor: SBE63

Initial accuracy = ±%2 saturation (± 3μmol/kg)

Response time < 6s

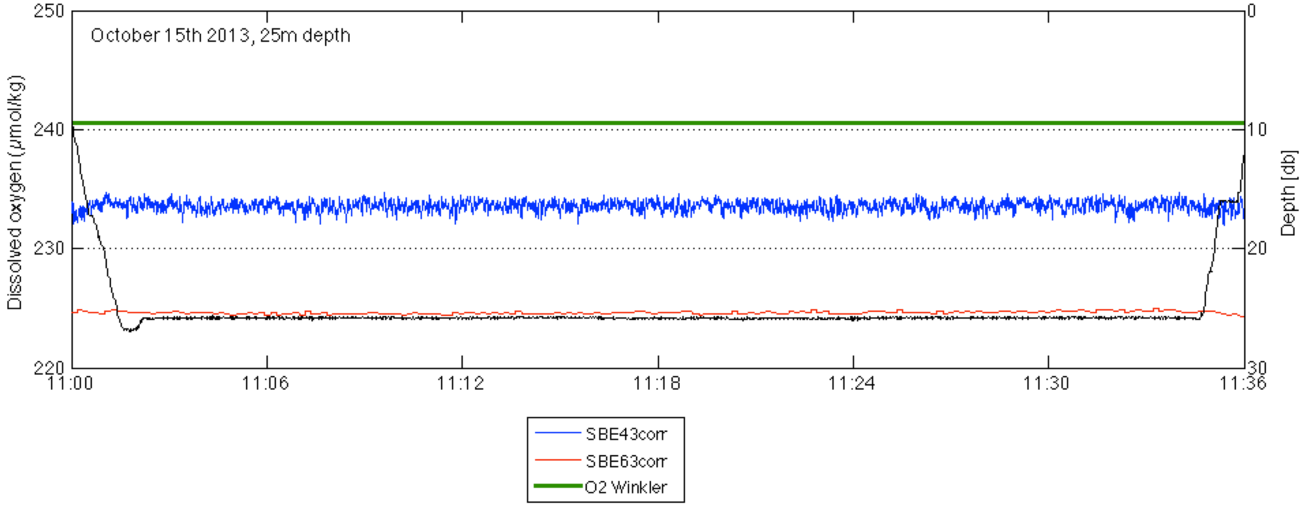
24-point calibration

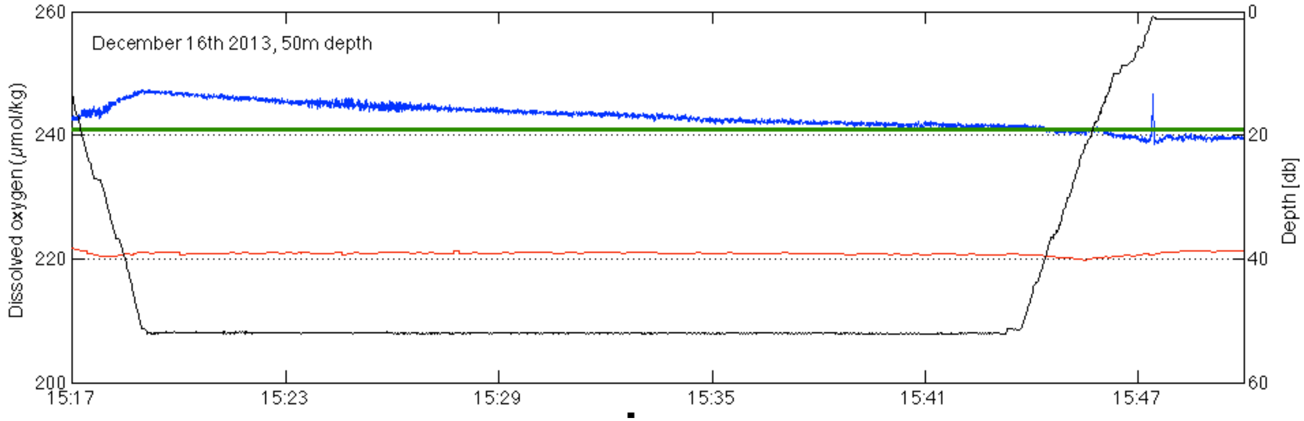
O_2 signal measured with Stern-Volmer equation

$$O_2\ (ml/l) = [\ \{\ (a_0 + a_1T + a_2V^2\ )\ /\ (b_0 + b_1V) - 1\ \}\ /\ K_{sv}\ ]\ [\ S_{Corr}\ ]\ [\ P_{Corr}\ ]$$

Mainly used on Argo floats (NAVIS) and moorings (mounted on SBE37)

FIELD EXPERIMENTS WITH SBE43 & SBE63





Sensor	Depth	DOXY [µmol/kg]	DOXYcorr [µmol/kg]	O2 Winkler [µmol/kg]	Difference	Correction
SBE43	25m	184.6	233.5	240.5 ± 1	7 ± 1	SOCnew
SBE63	25m	218.9	224.7	240.5 ± 1	19 ± 1	T, Pcorr, Scorr
SBE43	50m	190.5	243	241 ± 1	2 ± 1	SOCnew
SBE63	50m	220.9	226.8	241 ± 1	15 ± 1	T, Pcorr, Scorr

CONCLUSIONS

- SBE43: perfect for CTD profilers but need O2 Winkler to correct the membrane drift. O2 correction is quite simple
- Optode 4330: better calibration. Easier to correct (Bittig & Takeshita methods). Still a drift between lab calibration and first deployment !
- SBE63: seems more stable than SBE43. Adapted for slow profiles and moorings. O2 underestimated. Need better calibration