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Fixed Observatories and Long-time-Series of Dissolved Oxygen Measurements: *Good Quality Data is a Challenge*

Sophie Van Ganse, Laure Niclas-Chirurgien, Florence Salvetat, Caroline Le Bihan, Jérôme Blandin and Dominique Lefèvre

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hcmr ΕΛΚΕΘΕ

mio Mediterranean Institute of Oceanography

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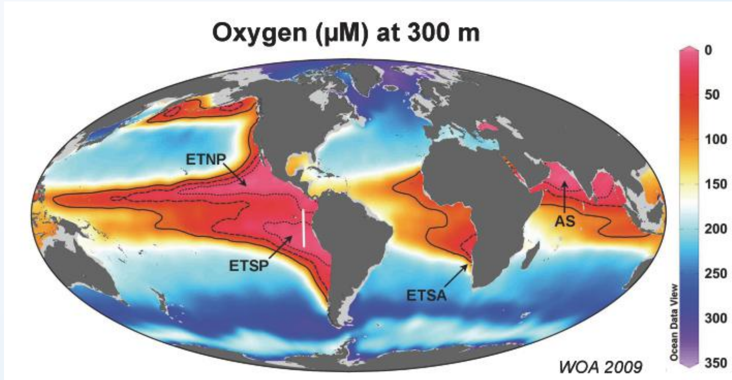
Two Minute-*Madness*

Background …

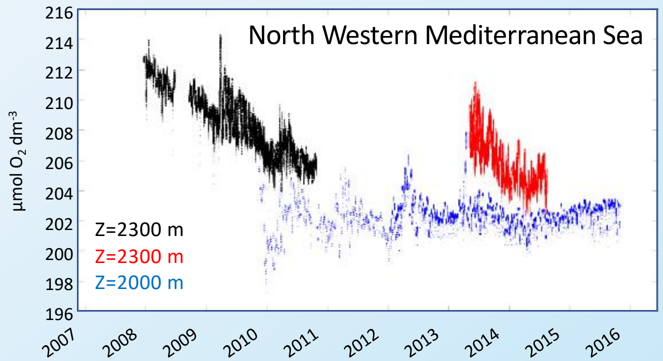
O_2 related Oceanographic research :

- Oceanic productivity
- Ocean's deoxygenation (expansion of OMZ)
- Ocean circulation/mixing
- Ocean ventilation
- …



Needs

- High quality datasets
- Long-term time-series



Tools for data acquisitions

- Autnomous Sensors
- Various types platforms (mobile & fixed)

Questions?

- Solutions to overcome drift trends?
- Is the required quality reached?

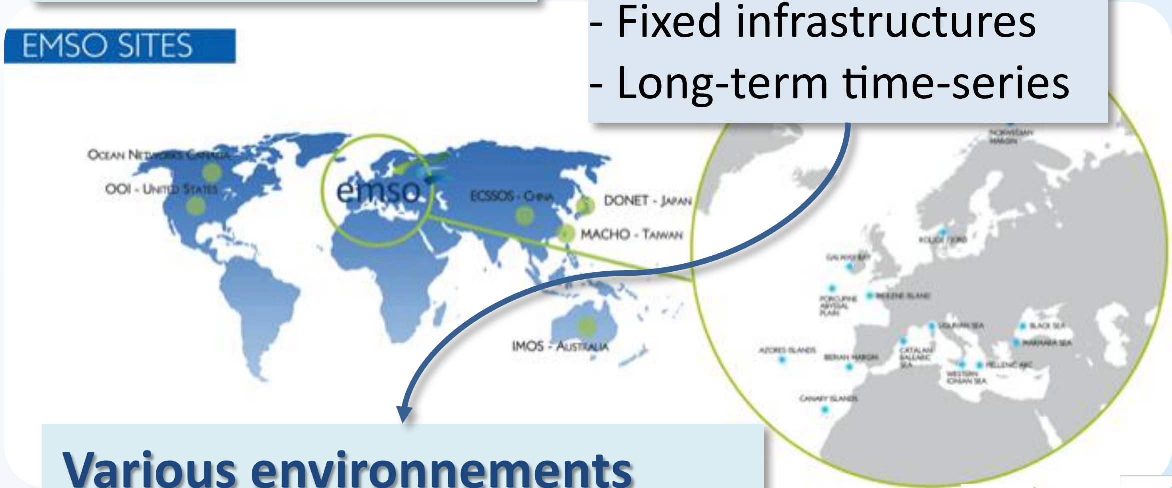
Two Minute-*Madness*

Context of the EMSO ERIC's O_2 calibration platform

Fleet of sensors

Needs of common
- Tools
- Procedures

11 Regional Facilities
- Fixed infrastructures
- Long-term time-series



Conception of a O_2 sensor calibration bench

Various environnements
- Deep sea
- Water column
- Artic to Meditarraneen sea…

Its a first step…

03/07/2019

Summary

1. Current states
   - ➔ Scientific needs
   - ➔ Tools
   - ➔ Quality requirements

2. Current strategies to overcome drift trends

3. EMSO-ERIC's O_2 Sensor Calibration Bench
   - ➔ Context & use
   - ➔ Description

4. Exemple of adjusment

5. Issues

1.1 Current states: Scientific needs for long-time-series O_2 measurements

Required level of accuracy depends of :

➔ Scientific objectives

- Seasonal to decadal variation?
- Event detection?

➔ Open Ocean or Coastal waters?

Open Ocean	Coastal waters
• NCP and export production • Ocean's deoxygenation (expansion of OMZ) • Ocean circulation/mixing • Ocean Interior ventilation • Biogeochemical processes	• Water quality index • Biomass indicator • Seasonal variations • Anoxic events • …
≈ 1 µmol/l	**≈ 5 to 6 µmol/l**

Variability range in open ocean :

- Observed seasonal variability range in the upper thermocline:

✓ 10 to 20 µmol/kg *(Najjar & Keeling ,1997)*

- Expected long term trend of oxygen in the upper ocean

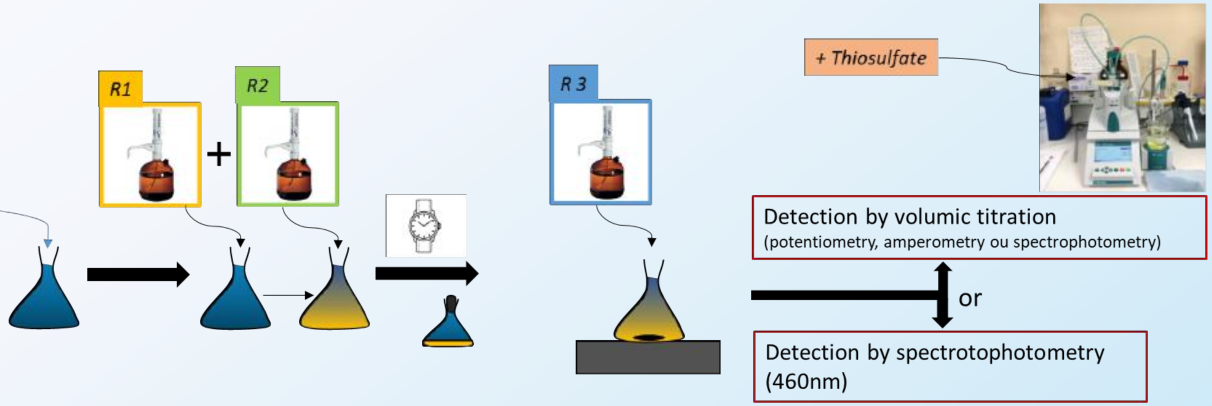
✓ 5 to 20 µmol/kg *(Keeling, Kôrtzinger & Gruber 2009)*

Tools for dissolved oxygen (O_2) measurements:

➔ Reference measurements = Winkler titration analysis

- ❑ accuracy ≈ **0.2 µmol/kg**
- ❑ manual sampling
- ❑ laboratory analysis

- ❑ discrete samples
- ❑ low frequency
- ❑ time consuming



➔ O_2 sensors

- ❑ accuracy **IF WELL USED** ≈ **2-3 µmol/kg**
  - ❑ **Calibrated**
  - ❑ **Appropriate data processing**
  - ❑ **Appropriate deployment procedure**
  - ❑ **…**
- ❑ autonomous
- ❑ high frequency

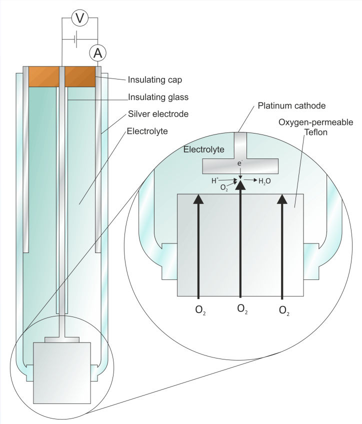
1.2 Current states: Tools for long term timeseries of O_2 measurements

➔ **Two different type of sensors**

Clark electrode: Redox reaction

$O_2 + 4\,e + 4\,H+ \rightarrow 2\,H_2O$

$4\,Cl^- + 4\,Ag \rightarrow 4\,AgCl + 4\,e$

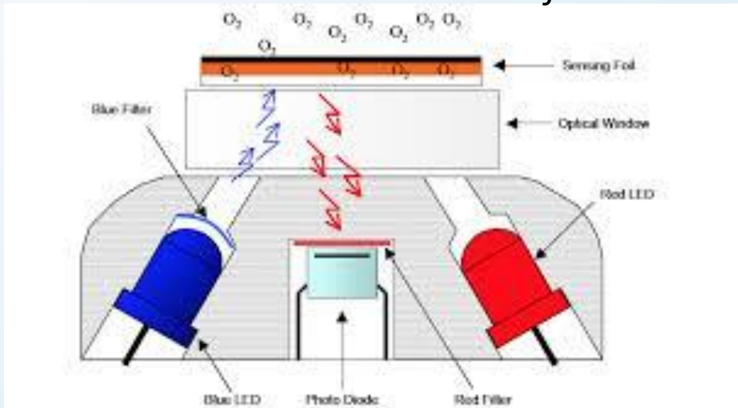


- ✓ Fast response-time
- ✓ O_2 consumption
- ✓ Require regular maintenance
- ✓ Commonly used on CTDs profiling (SBE43)

Optode: Luminescence quenching

$$\frac{I_0}{I} = \frac{\Lambda_0}{\Lambda} = 1 + K'_{SV} \cdot a^M_{O_2} \approx 1 + K'_{SV} \cdot c^M_{O_2}$$

Modified Stern Volmer Equation



- ✓ Longer response-time
- ✓ Commonly used for long term timeseries
- ✓ No O_2 consumption

➔ Measurements influenced by temperature, pressure, salinity

➔ Changes of performance over time (drift trends)

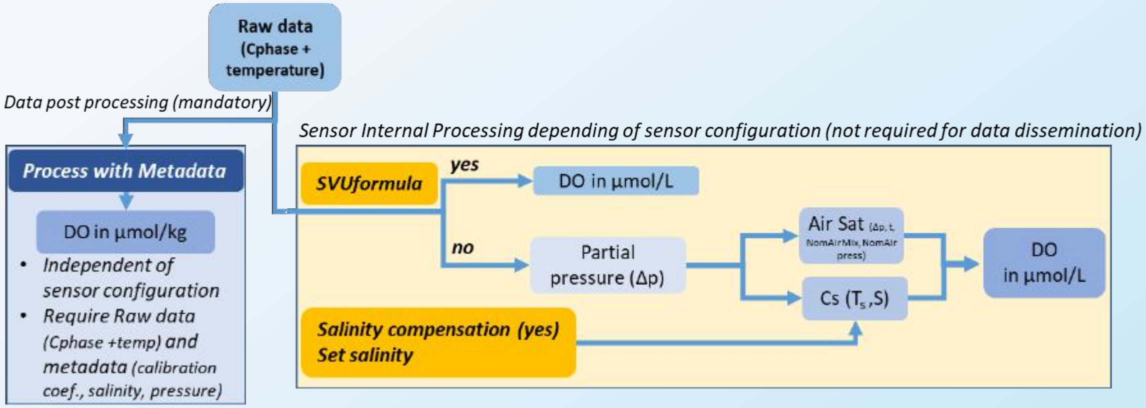
Requirements for quality measurements:

➔ KNOWLEDGE OF YOUR SENSOR

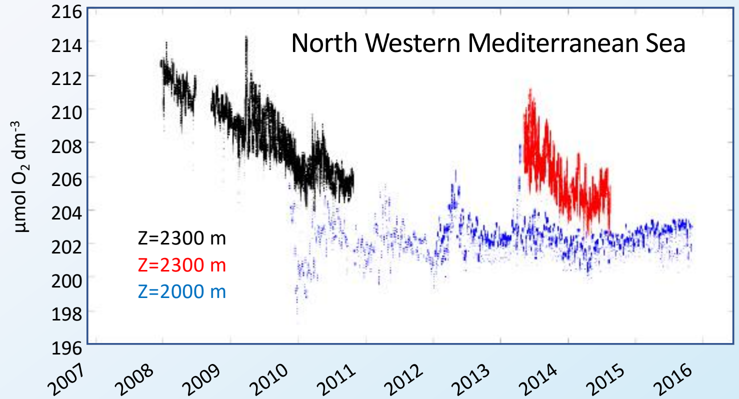
- ❑ O_2-temperature response (coefficients)
- ❑ Pressure compensation
- ❑ Salinity compensation (yes/no)

➔ Post processing raw data instead of direct reading (internal processing)

Exemple of Aanderaa optode internal processing (type 4330):



➔ Drift adjustment solutions?



Exemple of O_2 measurements over a 8 years on a deep sea fixed observatory in the North Western Medietrranean Sea @ 2000 and 2300 m depth.

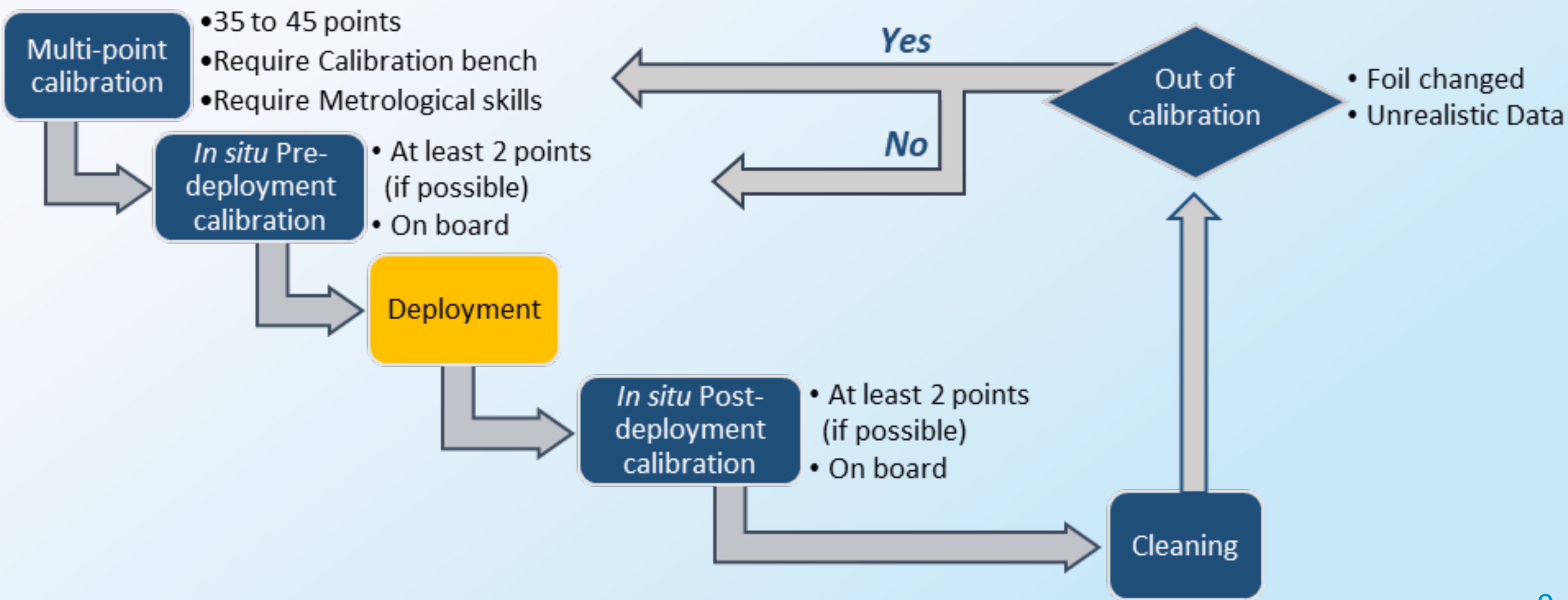
2. Current strategies to overcome drift trends

Mobile observatories (profilers and gliders)**:**

- ✓ Pre-deployement measurement
- ✓ Routine adjustment with **in air measurements** *(SCOR WG 142)* and atmospheric O_2 data (https://www.nodc.noaa.gov/OC5/woa13/woa13data.html)

Fixed observatories (long term time series):

- ❑ Different stages of adjustments required

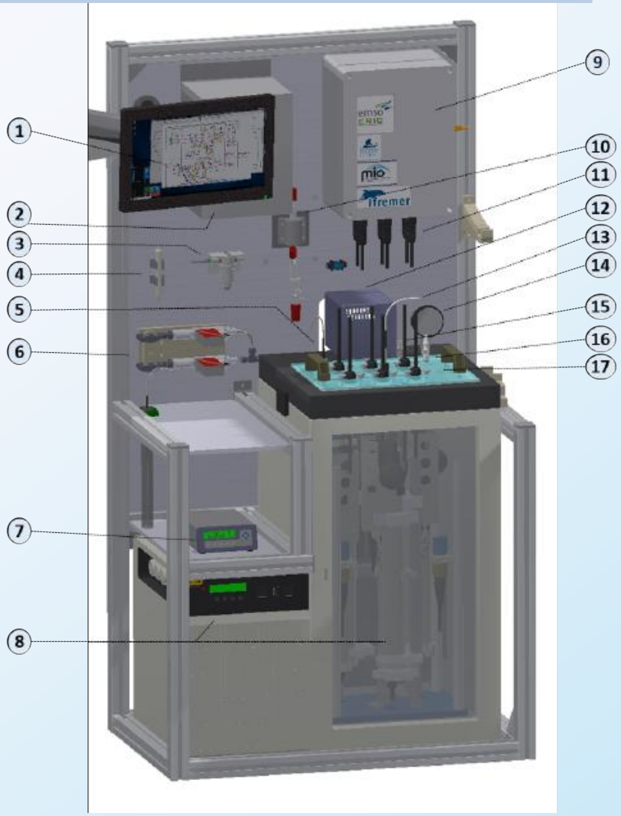


EMSO-ERIC context

- ✓ multiple fixed observatories (11 sites)
- ✓ Diversity of environments
- ✓ measurements of O_2 on every regional facility

➔ Harmonisation of O_2 measurements

➔ Conception of a O_2 sensor calibration bench + good practices recommandations



Use of the bench

- ❑ Common calibration setup
- ❑ Different types of sensors (stand alone or multiparameter sensors)
- ❑ Multipoint calibration
  - ➔ Characterisation of O_2-T response
- ❑ Sensor investigations
  - ➔ Current impact, drift trends…

Dissolved Oxygen	Temperature 2.5°C	10°C	15°C	20°C	30°C
0%	✓	✓	✓	✓	✓
10%	✓	✓	✓	✓	✓
25%	✓	✓	✓	✓	✓
50%	✓	✓	✓	✓	✓
75%	✓	✓	✓	✓	✓
90%	✓	✓	✓	✓	✓
100%	✓	✓	✓	✓	✓

3.2 EMSO-ERIC's Dissolved Oxygen Sensor Calibration Bench: Description

Automated Control :
- ✓ O_2 concentration
  - → stability ≈ 0.1µmol/L
  - → Levels of ratio of O_2/N_2
- ✓ Temperature
  - → stability ≈ 0.001°C

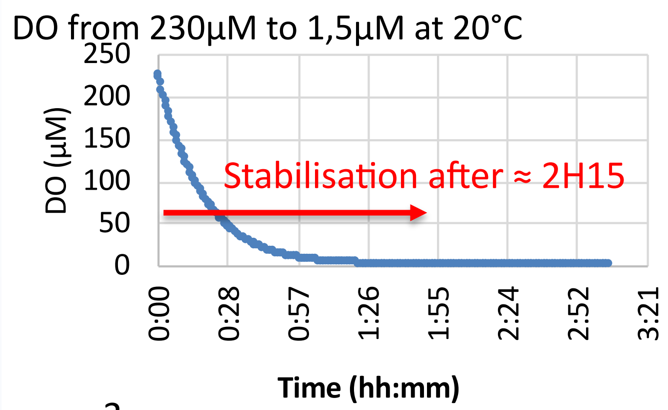
Automated Record :
- ✓ O_2 Sensors outputs
- ✓ Reference temperature
- ✓ Gaz input & output
- ✓ Internal atm. pressure

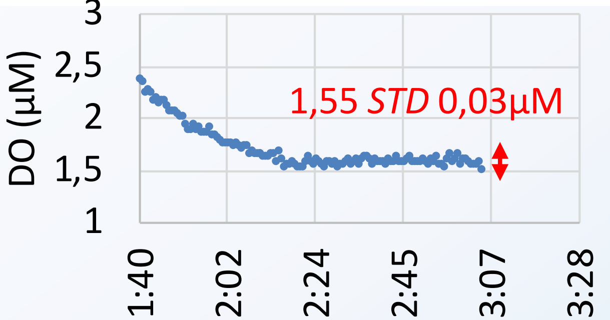
Power supply
- ✓ O_2 Sensors
- ✓ Mass flow valves

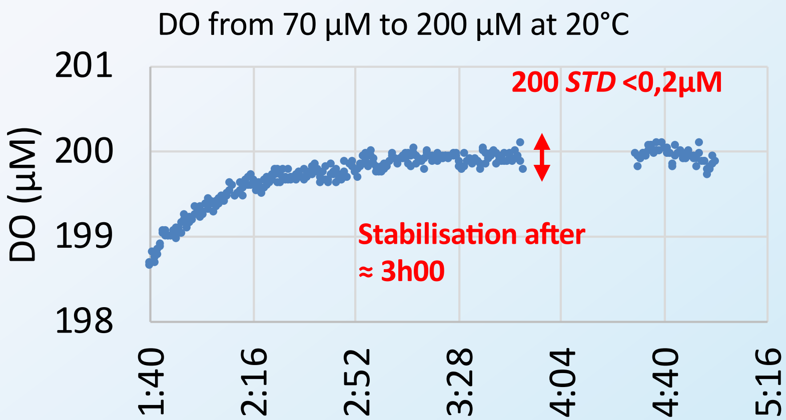
Reference measurements :
- ✓ **O_2:** Winkler titration
  - →Manual sampling
- ✓ **°C:** Reference thermometer

3.2 EMSO-ERIC's Dissolved Oxygen Sensor Calibration Bench: description

O_2 stability (approx 10000 data)

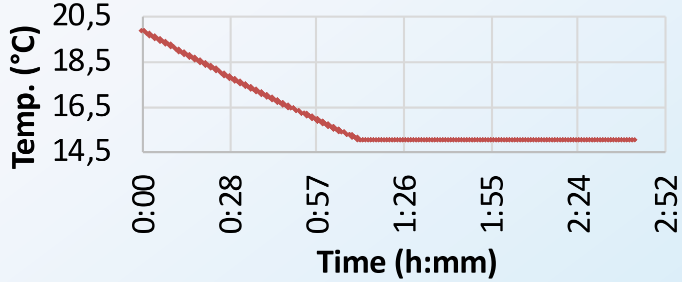


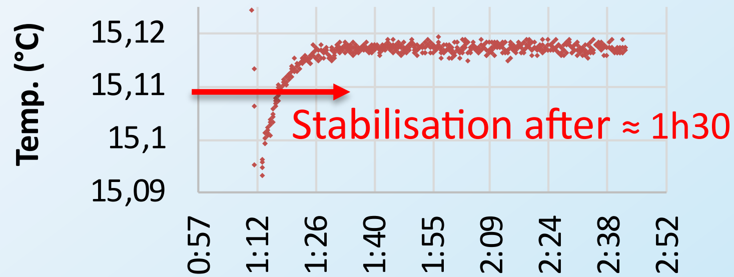


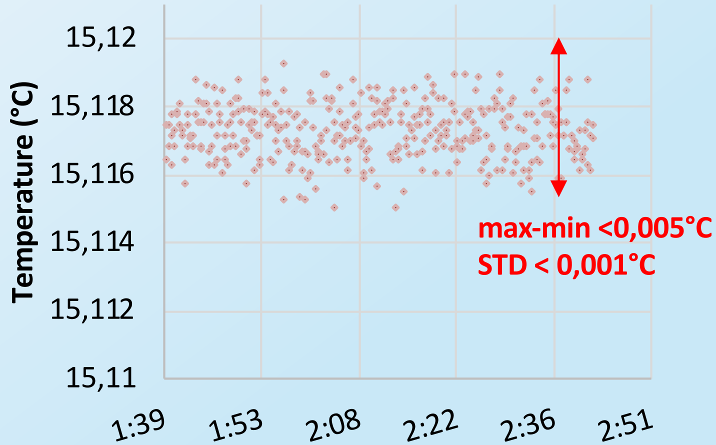


Temperature stability

(approx 10000 data)



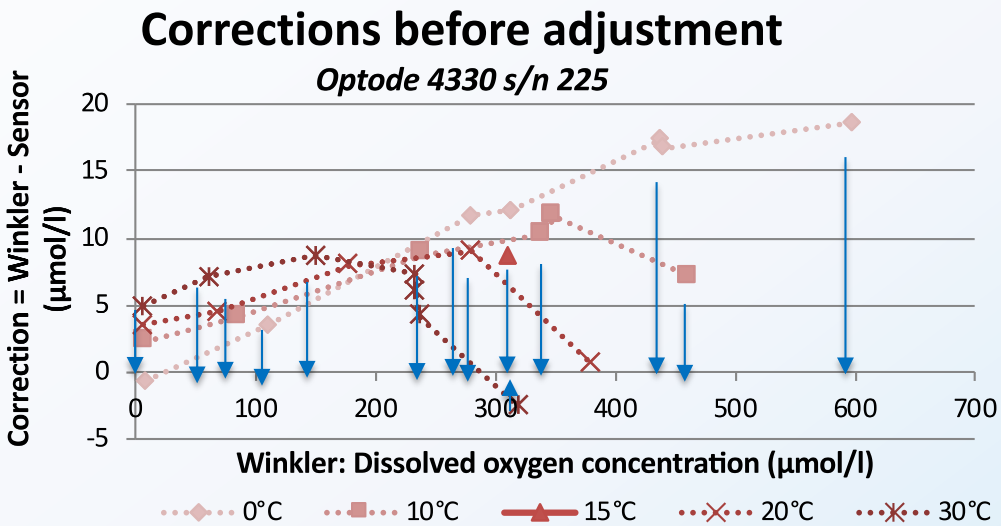




4. Example of adjusment using « Uchida et al. (2008) »

Example of Multipoints calibration

- 5 temperatures + 4 DO ➔ 26 points
- Characterisarion of O_2-Temperature-response of the sensor

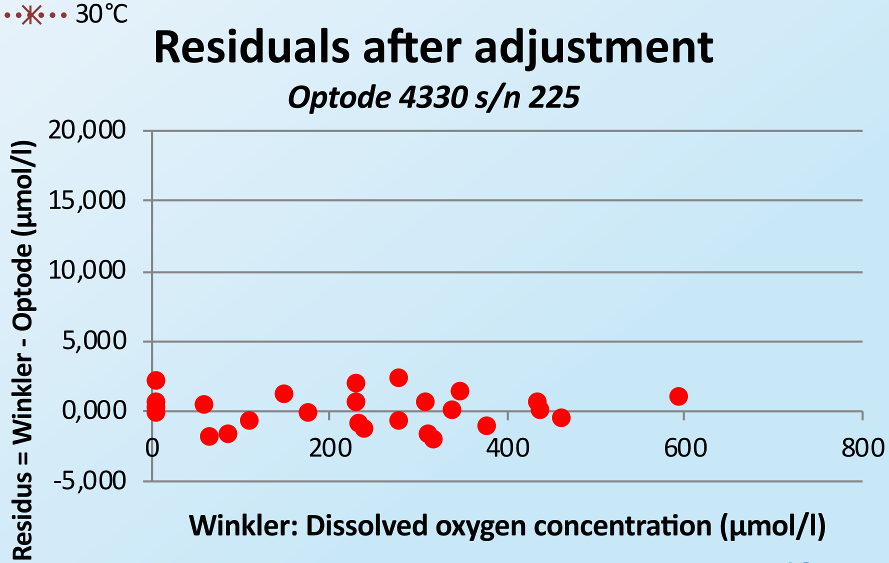


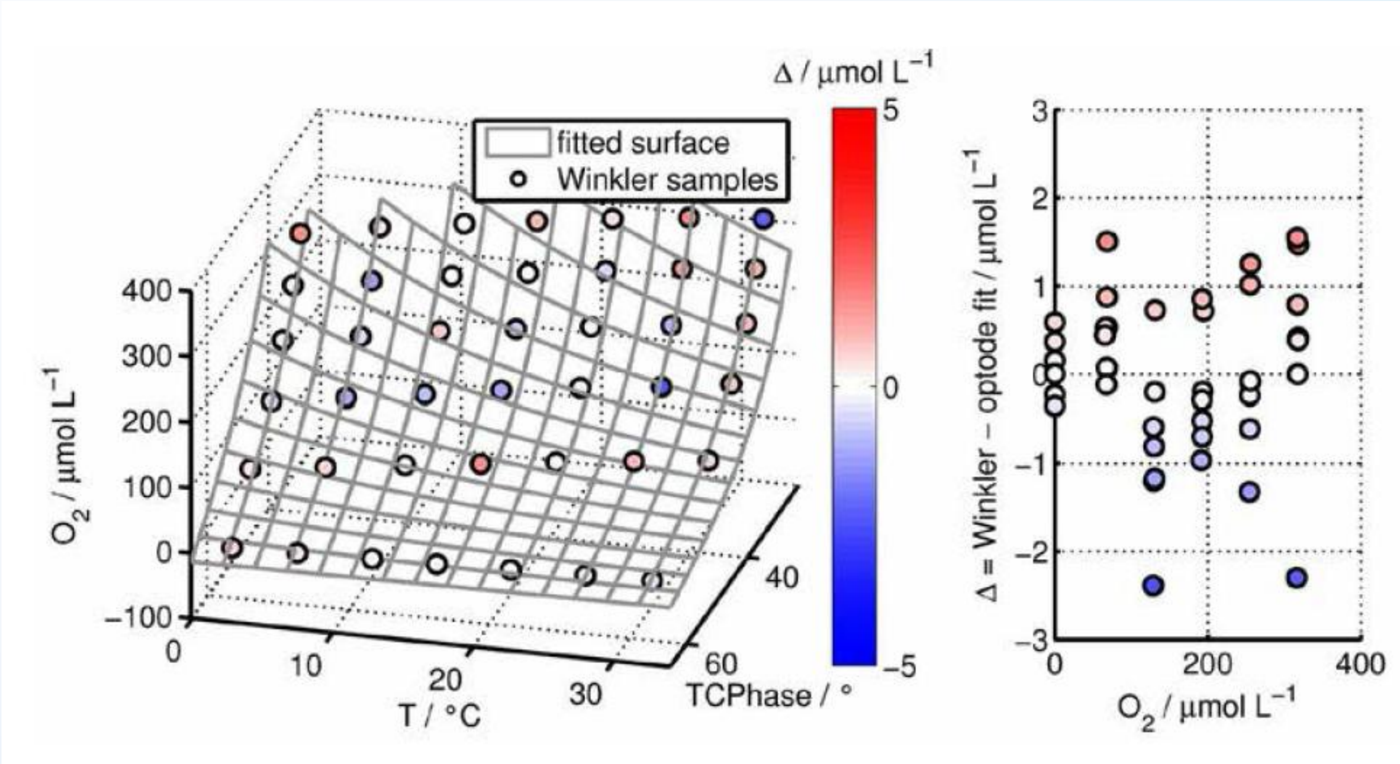
$$[O_2]\mu mol/l = \frac{\frac{P_0}{P_c} - 1}{K_{sv}}$$

$$K_{sv} = c_0 + c_1 t + c_2 t^2$$
$$P_0 = c_3 + c_4 t$$
$$P_c = c_5 + c_6 CalPhase$$

Uchida et al. (2008)

Solver which calculates the Uchida coefficients for the lowest $\sum residuals^2$

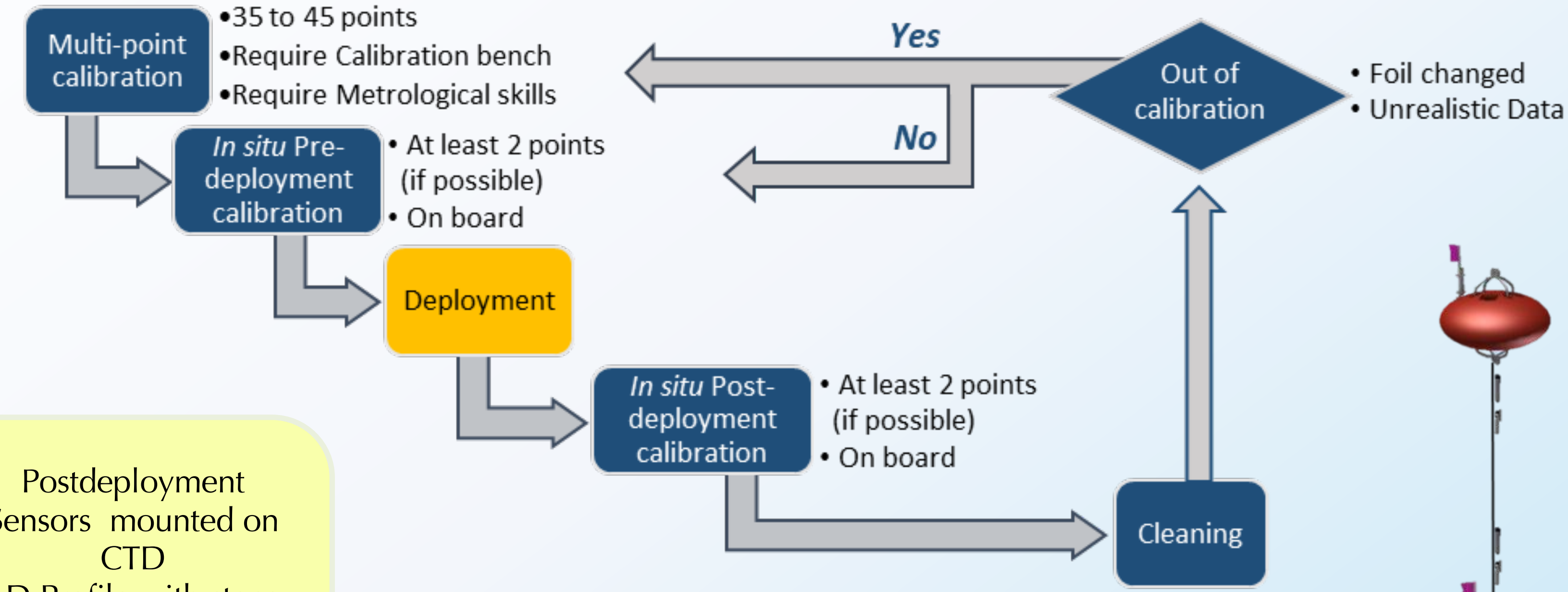


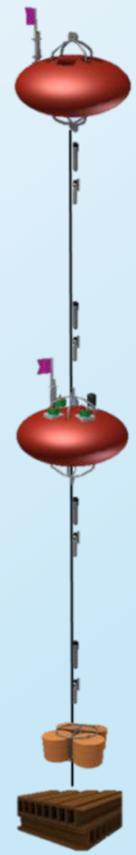


From Bittig et al. 2012

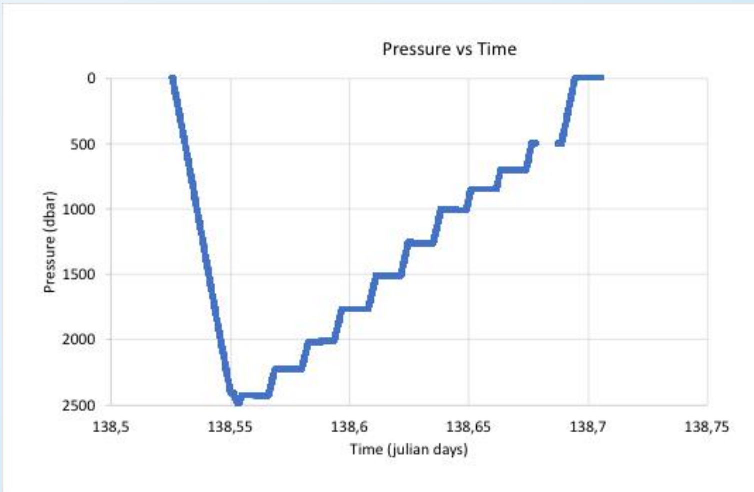
Provides → **Accuracy** (at the time of the calibration)
→ **Robustness to non linear variability of Temperature & O_2 levels**

5. Fixed observatories (long term time series)





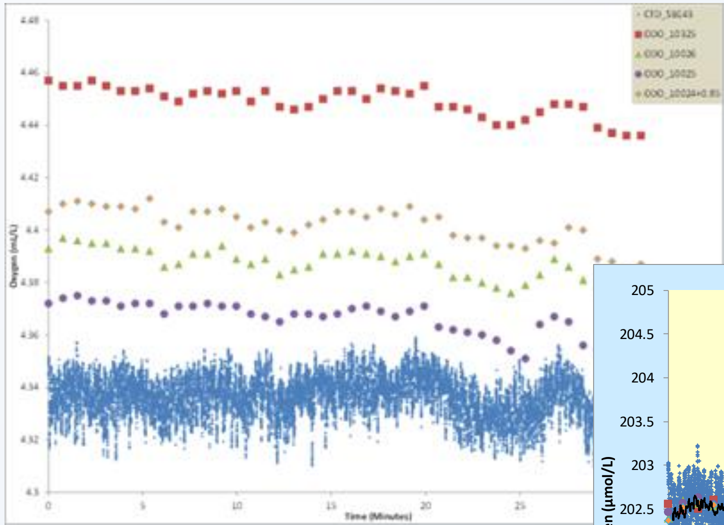
Postdeployment
Sensors mounted on CTD
1D Profile with steps
30 points required encompassing depth of time series

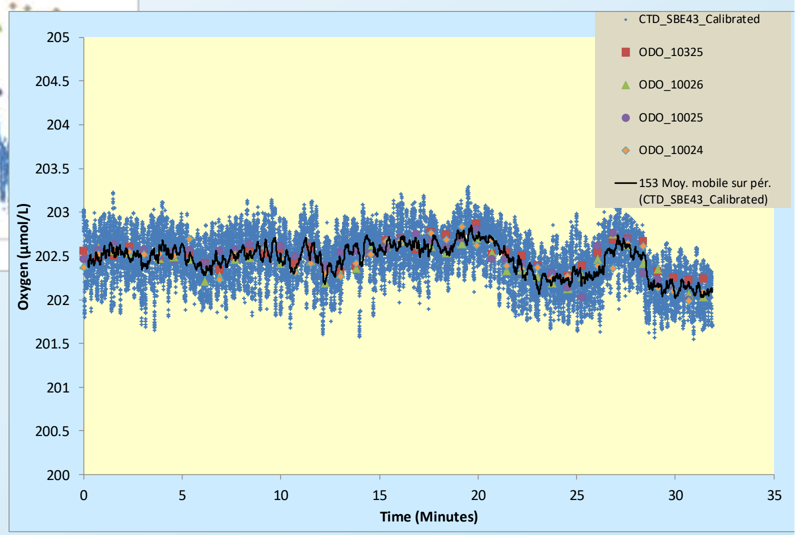


4. In Situ Example : Complementarity of bench calibration and pre-post deployment procedure

Data acquisition CTD
Sensors @ 2 depths (5 and 2000 m)
30-45 mins

Time series of available parameters (Oxygen)



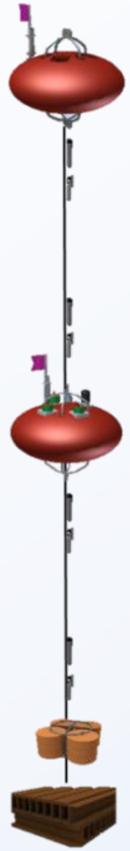


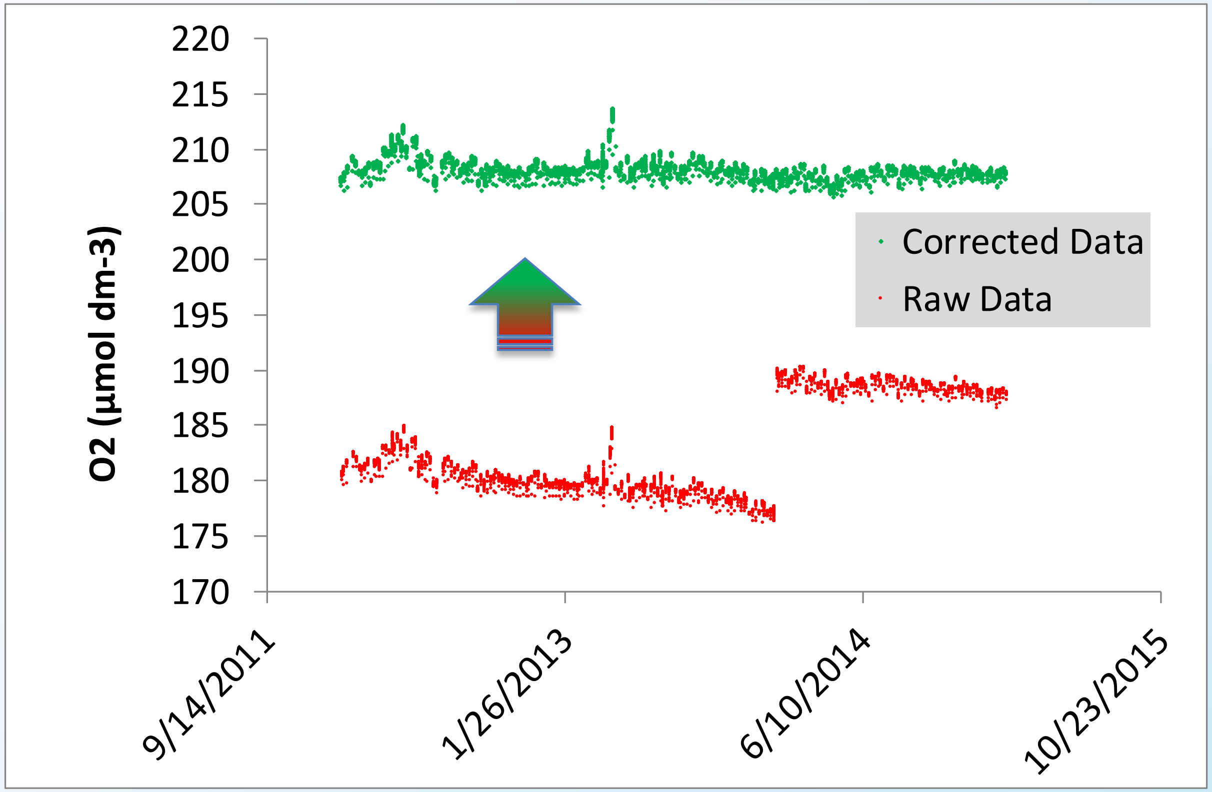
Microcat mounted on CTD caroussel

Co variability, **offset** → correction pre-deployment
→ correction post-deployment

and then drift correction to apply on acquired data =set

4. In Situ Example : Complementarity of bench calibration and pre-post deployment procedure





Allows assessment of sensor drift and miss behaviour during deployment

Conclusion & Prospective

➔The calibration bench & fixed long-term-time-series

- It is a first step…
- pre and post deployment measurements are essential

➔ Considering uncertainties

- desired level of accuracy (1µM) not reached
- estimated uncertainty of calibration result ≈ 6 to 8µM
- estimation of *in-situ* measurement probably > 6 to 8µM

➔ Prospective

- progress in *in-situ* calibration to qualifying data