SOERE CTDO2
Labellisé Allenvi

The case of very low [O_2] area

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Thanks to: Mélanie GIRAUD, Jesus LEDESMA, Jacques GRELET, François BAURAND, Dominique LEFEVRE

Workshop on Interoperability Technologies and Best Practices in Environmental Monitoring
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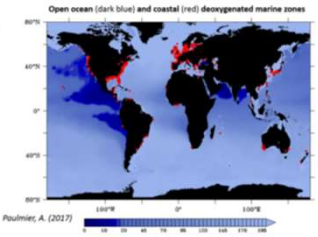
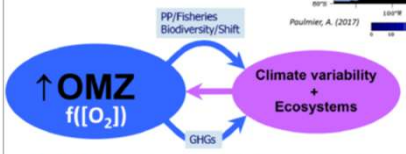
The very low [O_2] areas



Why?



→ Key-role on: - climate (CO_2, N_2O, CH_4, DMS, ...);
- ecosystems («Respiratory barrier», nitrogen loss)

→ Sensitive to changes of the:
- climate (warming; ENSO); environment (fertilizations)

Outline:

*I. **WINKLER**: analyses of the O_2 measurement quality in a Oxygen Minimum Zone (OMZ): detection limit, reproducibility*

*II. **O_2-CTD ADJUSTMENT** WITH WINKLER: the OMZs issues*

*III. **ULTRA-LOW [O_2] ADJUSTMENT**: O_2-CTD using 0-STOX reference*

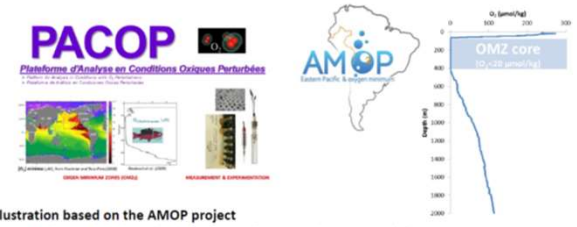
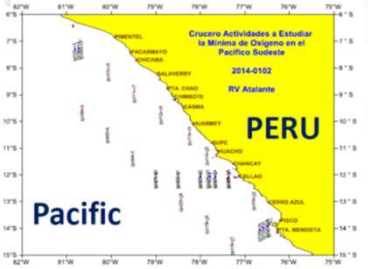
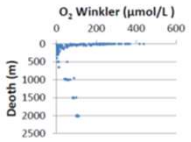


Illustration based on the AMOP project
(Activities of research dedicated to the Minimum of Oxygen in the eastern Pacific):
www.legos.obs-mip.fr/recherches/projets-en-cours/amop

AMOP: PROJECT DEDICATED TO LOW O_2



157 profiles with a sampling focussed on the O_2 parameter, >5000 measurements:
- **5 platforms** with O_2: CTD (2), FR-CTD (1), drifting line (9), **Argo-floats** (3), **mooring** (5), on board from Niskin (3);
- **4 measurement techniques**: Winkler (potentiometry, photometry), electrochemistry (SBE43, SE63, STOX), optodes.
- Focus on the OMZ (Core & Oxicline).



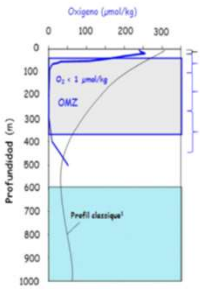
Chemical method of reference with indirect standard (O_2 fixation, and titration, blanks & titration of the NaS_2O_3 (Winkler, 1888)). Use of automatic titrator.

> 1800 measurements with systematical triplicates for all the stations and incubations.

I. WINKLER: analyses of the O_2 measurement quality in an OMZ

- **Goal:** to analyze the Winkler method quality for the specific O_2 distribution in an OMZ

1) Limit of Detection (LOD)
2) Reproducibility



Surface *(supersaturation)*
OXYCLINE *(extreme gradient)*
CORE *(O_2<limit of detection)*
LOWER O_2 GRADIENT (LOG)

I.1) Limit Of Detection (LOD)

WHICH CONTAMINATION AT THE NISKIN SAMPLING?

➢ ***Experiments with 15 replicates***

1) WINKLER SAMPLING & FIXATION

2) REFERENCE FOR LOW [O_2]

STOX (Switchable Trace Oxygen sensor with nano-/pico-molar LOD) AS "0"

Revsbech NP, Larsen LH, Gundersen J, Dalsgaard T, Ulloa O, Thamdrup B. Determination of ultra-low oxygen concentrations in oxygen minimum zones by the STOX sensor. Limnol Oceanogr Methods. 2006; 7: 371–381.

II. O_2-CTD ADJUSTEMENT WITH WINKLER

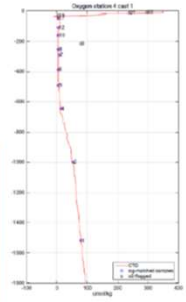
❖ Collaborations with GLAZEO from 2015 to 2018 in 2 steps:

1) Classical approach and OMZs issues;

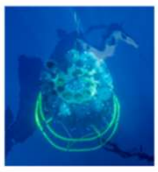

Calibration des données CTD-Oxygène de la campagne AMOP 2014

Rapport final – Avril 2014

Carole Saout-Grit
GLAZEO



2) Improvement



III. ULTRA-LOW [O_2] ADJUSMENT: O_2-CTD using 0-STOX reference

❖ **After the adjustment with the Winkler reference** (out of the core), **USE of a REFERENCE for the ULTRA-LOW [O_2] in the OMZ core**
(e.g. STOX/LUMOS with nano-/pico-molar detection limit)

TAKE HOME MESSAGE:

1) WINKLER MEASUREMENT

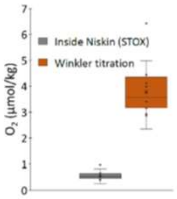
a) In the OMZ core, not relevant as a reference

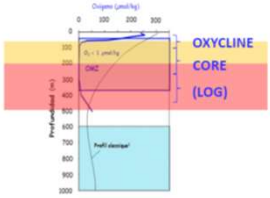
Limit of detection > 4 µM due to:

- O_2 release by the polymers in the Niskin bottle: 0.3<1 µM;
- Winkler sampling and fixation process: 2<7 µM

b) Reproducibility affected in the upper highest OMZ O_2 gradient (oxycline-core interface):

Lower core & LOG: ~80% better reproducibility compared to the lower oxycline & upper core





TAKE HOME MESSAGE:

1) WINKLER MEASUREMENT
- a) In the OMZ core, not relevant as a reference
  Limit of detection > 4 µmol/kg
- b) Reproductibility affected in the upper highest OMZ O_2 gradient (oxycline-core interface):
  Lower oxycline & upper core: ~80% higher reproducibility compared to the lower core and LOG

2) ADJUSTEMENT OF O_2-CTD WITH WINKLER
- a) Presence of very localized outliers, at the:
  - surface → strong natural temporal variability
  - oxycline → negative concentrations
- b) Focus on the upcasts, & on the calibration parameters for downcasts
  (without Tau20 → smoothed profiles)

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3) ADJUSTMENT OF O_2-CTD FOR LOW [O_2]
- **a) Requirement of a «anoxic» reference:** STOX/LUMOS, historical
- **b) Limit of detection x~50 better than with Winkler**: ~60 nmol/kg

NEXT:

1) **Proposition to write a Paper of Recommendations according to the protocols of O_2 sampling, measurements and adjustment in O_2-perturbated regions (e.g. OMZs) in order to:**
   - share the results of those **methodological studies**;
   - allow **inter-comparisons** between data, **assessing** and **increasing** the **quality** of the global datasets
   - improve **key-observations** in terms of **low O_2 concentrations** and **variability**;

NEXT:

2) Importance to have connections between our communities and the international initiatives:

- **GO_2NE** (***Global Ocean Oxygen Network***), IOC-Unesco WG;
- **IOCCP** (***International Ocean Carbon Coordination Project***), SCOR/IOC-Unesco;
- **VOICE project** (***Variability in the Oxycline and its Impact on the Ecosystems***), outcome of IMSOO (*Implementation of Multi-disciplinary Sustained Ocean Observations*)/GOOS (*Global Ocean Observing System*), IOC-Unesco, WMO (*World Meteorological Organization*), UN Environment, ISC (*International Science Council*)

http://www.ioccp.org/oxygen

Variability in the Oxycline and Its Impacts on the Ecosystem (VOICE) Science Plan Workshop, 13-15 September 2017, Monterey, CA, USA

http://mel.xmu.edu.cn/summerschool/go2ne/

Application closes: November 15, 2018