Détermination de l'O_2 ultra-faible: incertitudes et solutions

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

LEGOS — Observatoire Midi-Pyrénées OMP — glazeO oceanography & environment — UCA Universidad de Cádiz — AARHUS UNIVERSITY — cnrs INSU Observer & comprendre — IRD Institut de recherche pour le développement — Instituto del Mar del Perú Ciencia y Tecnología

Virtual Meeting ODATIS-CES-OXYGENE (November 23th, 2020)

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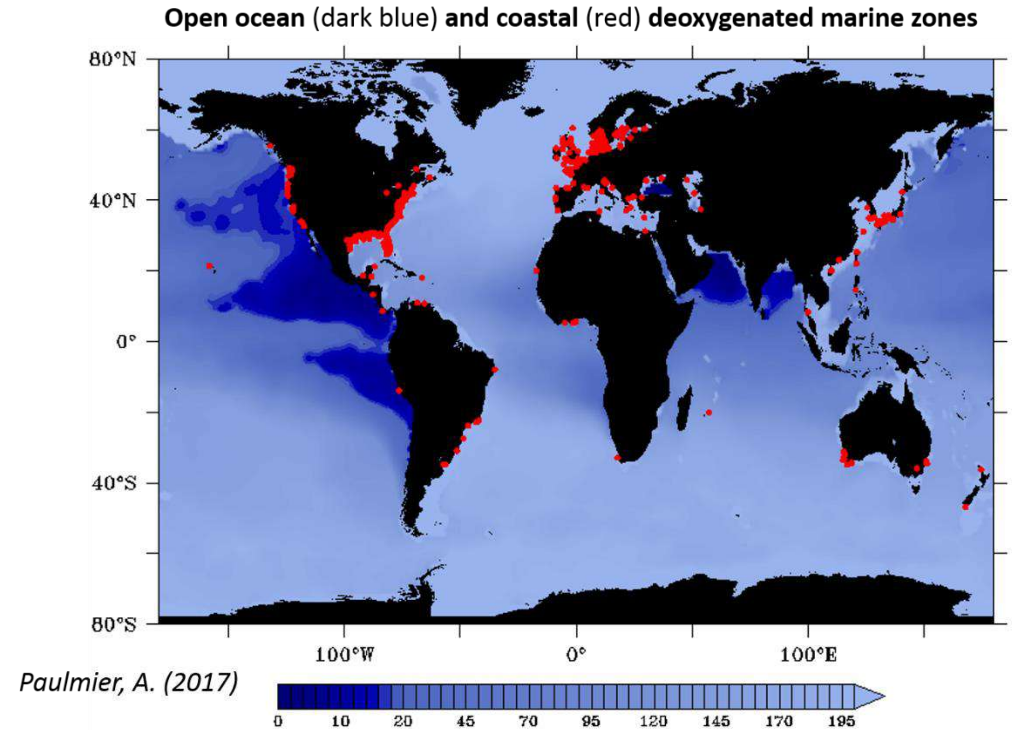
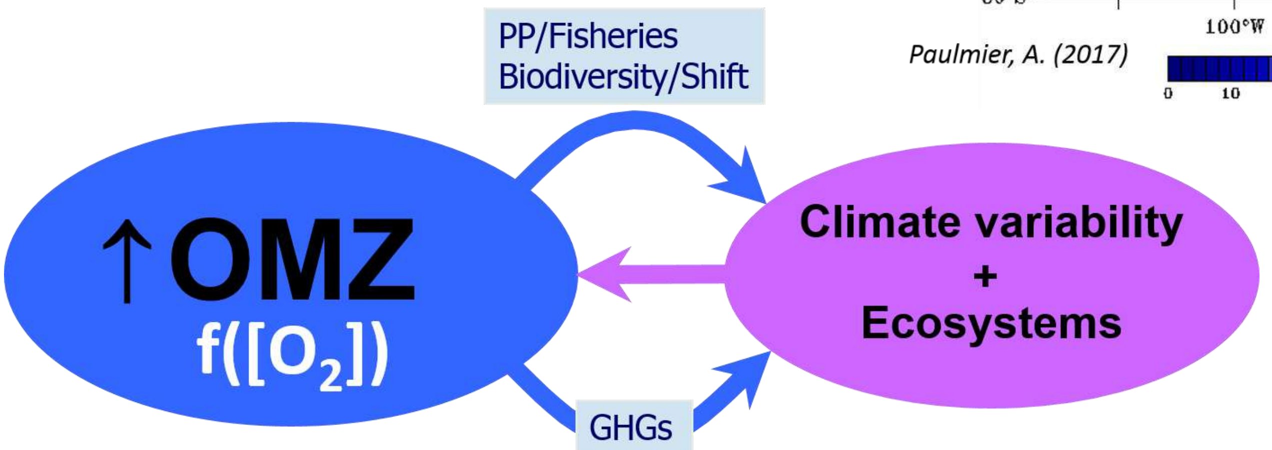
Les Zones à très faible $[O_2]$

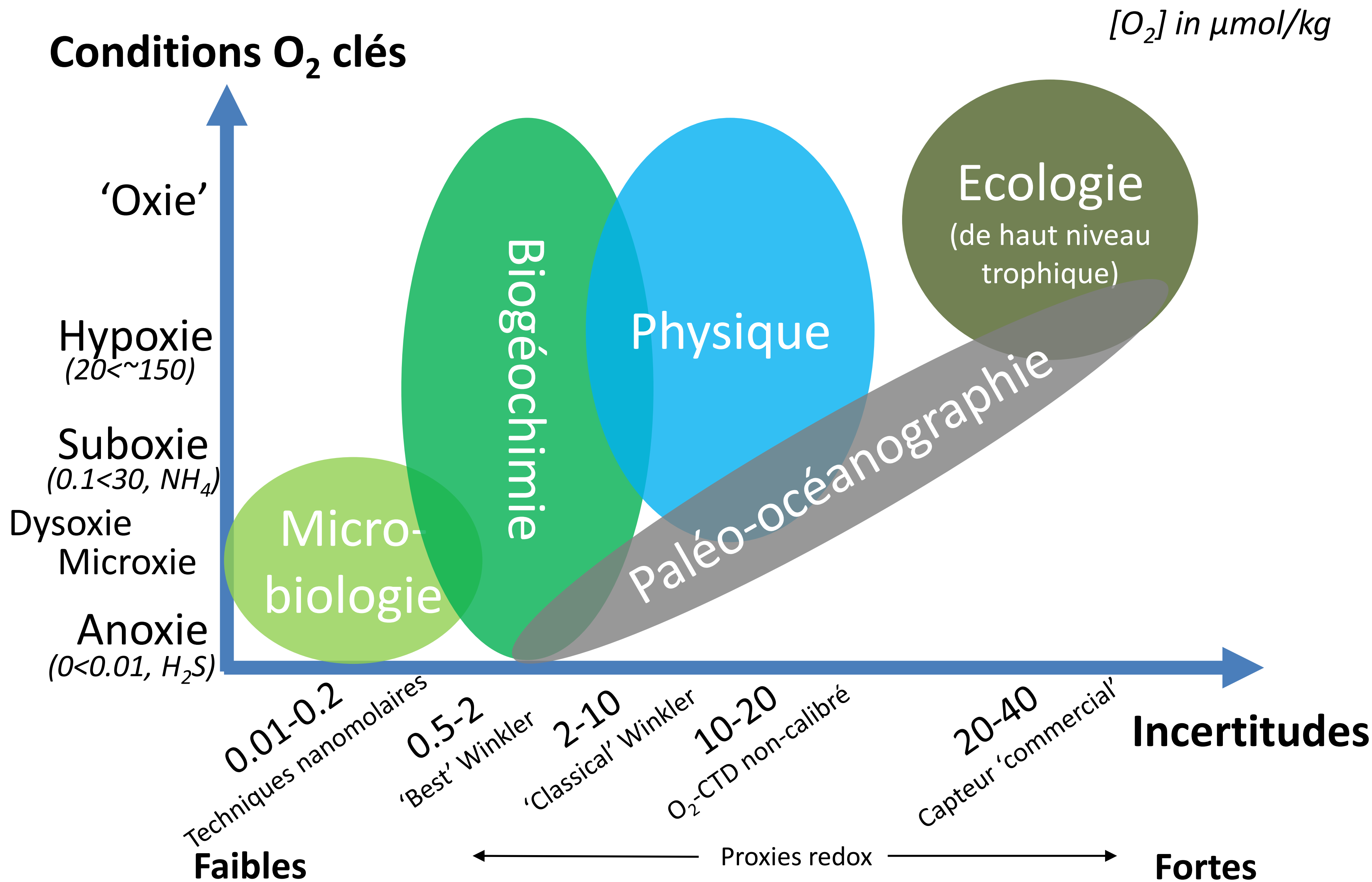


Pourquoi?



Impliquant des besoins en qualité de $[O_2]$ différents

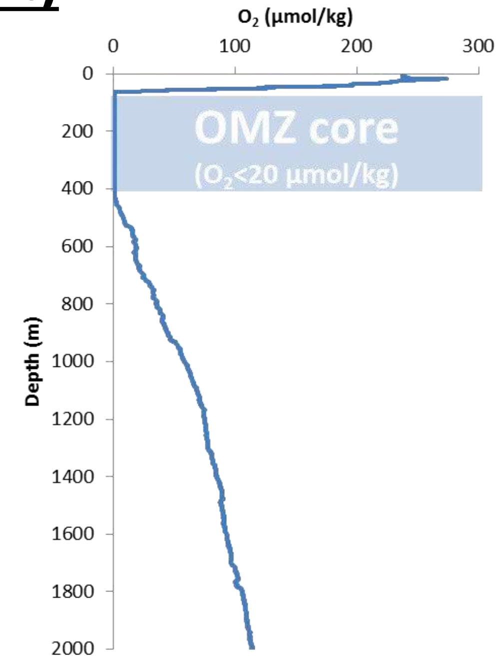
Des besoins différents en qualité dans les zones O_2-perturbées:



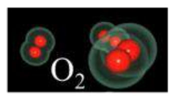
Outline: focalisée sur les OMZs (low O_2, high gradient)

I. Mesure de référence ***WINKLER***

II. ***Ajustement*** *des profils haute résolution* ***O_2-CTD***

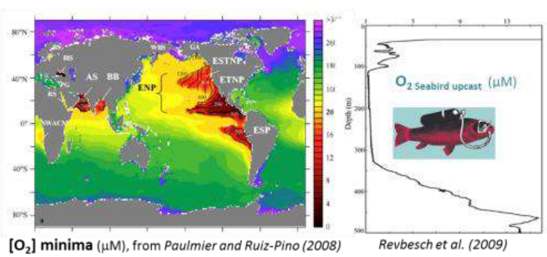


PACOP



Plateforme d'Analyse en Conditions Oxiques Perturbées

- Platform for Analysis in Conditions with O_2 Perturbations
- Plataforma de Análisis en Condiciones Oxicas Perturbadas



[O_2] minima (µM), from Paulmier and Ruiz-Pino (2008) — Revbesch et al. (2009)

OXGEN MINIMUM ZONES (OMZs)

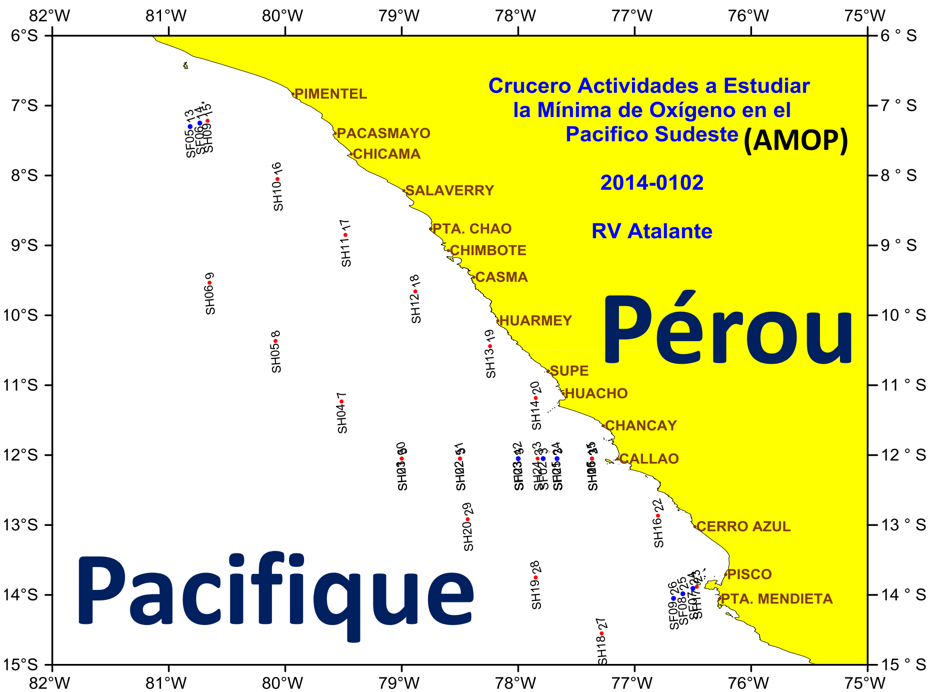
MEASUREMENT & EXPERIMENTATION

LEGOS/OMP

AMOP
Eastern Pacific & oxygen minimum

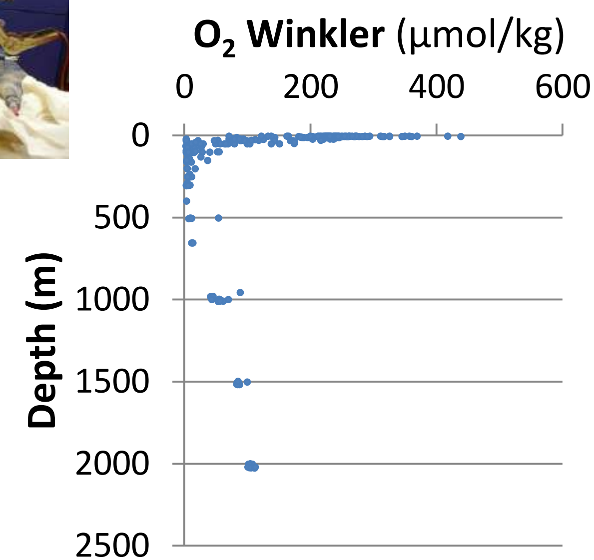
Activités de recherche dédiées au Minimum of d'Oxygen dans le Pacifique oriental:
www.legos.obs-mip.fr/recherches/projets-en-cours/amop

AMOP: support idéal pour l'analyse de la détermination des concentrations en conditions ultra-faibles (OMZ Core & Oxycline)



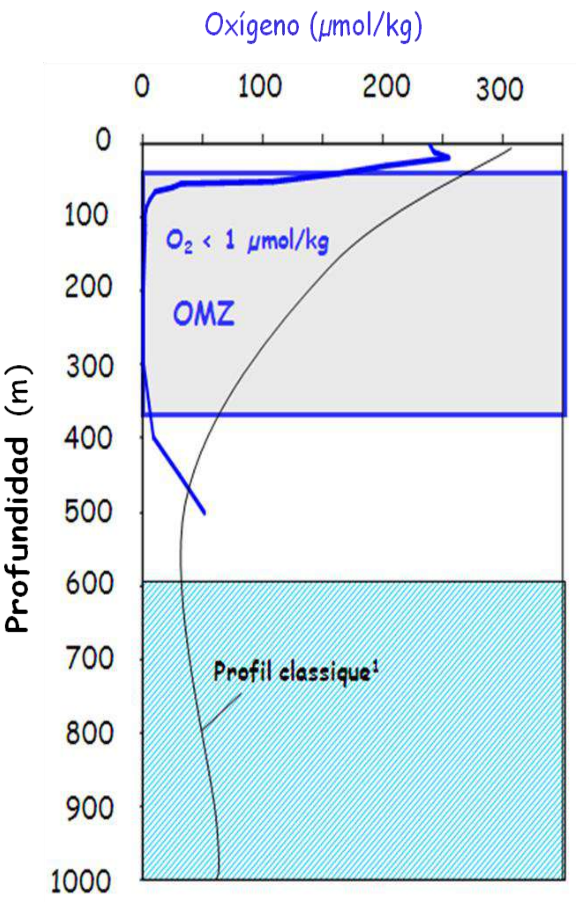
157 profiles avec échantillonnage focalisé sur le paramètre O_2, >5000 mesures:

- **5 platformes** avec O_2: CTD, Niskin-rosette à bord, FR-CTD, drifting line, Argo-floats, mooring;
- **4 techniques de mesures**: Winkler (potentiométrie, photométrie), électrochimie (SBE43, SE63, STOX), optodes.



> 1800 mesures Winkler avec triplicats systématiques pour toutes les stations et incubations.

1) Limite de Détection (LOD) ⇒ caractérisation du core de l'OMZ
2) Reproductibilité ⇒ sensibilité aux faibles variations, position des forts gradients

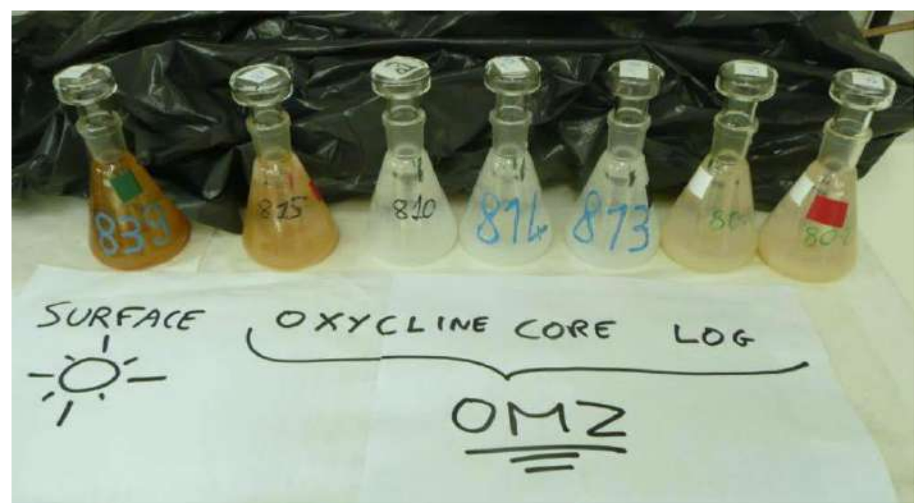


Surface *(supersaturation)*

OXYCLINE *(gradient extrême)*

CORE *(O_2<limite de détection)*

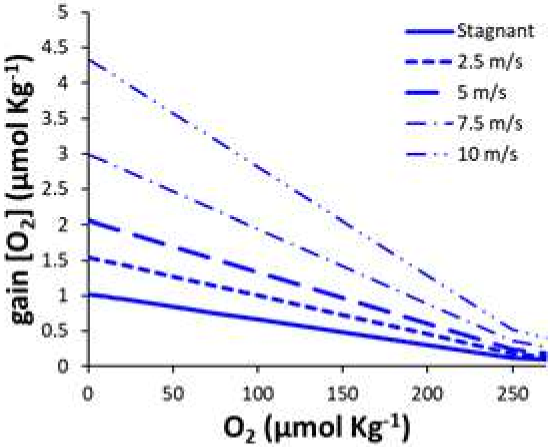
LOWER O_2 GRADIENT (LOG)



1) Limite de Détection (LOD) ⇒ caractérisation du core de l'OMZ

1) ECHANTILLONNAGE & FIXATION WINKLER

➢ CONTAMINATION PAR O_2 ATMOSPHERIQUE



Estimation de la contamination par l'O_2 atmosphérique en fonction de la [O_2] initiale en 1 min pour flacon Winkler de 150 ml et d'ouverture de 26 mm

Garcia-Robledo E, Paulmier A, Borisov S, Revsbech NP. 2020. Sampling in Oxygen Minimum Zones: the deviation from anoxic conditions. In preparation.

I. La mesure de référence WINKLER: incertitudes/problématiques, solutions

1) Limite de Détection (LOD) $\Rightarrow$ caractérisation du core de l'OMZ

➢ ***Expériences avec 15 réplicats***

1) ECHANTILLONNAGE & FIXATION WINKLER

2) REFERENCE POUR LES LOW [O_2]

STOX (Switchable Trace Oxygen sensor with nano-/pico-molar LOD) → "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. 2009; 7: 371–381.

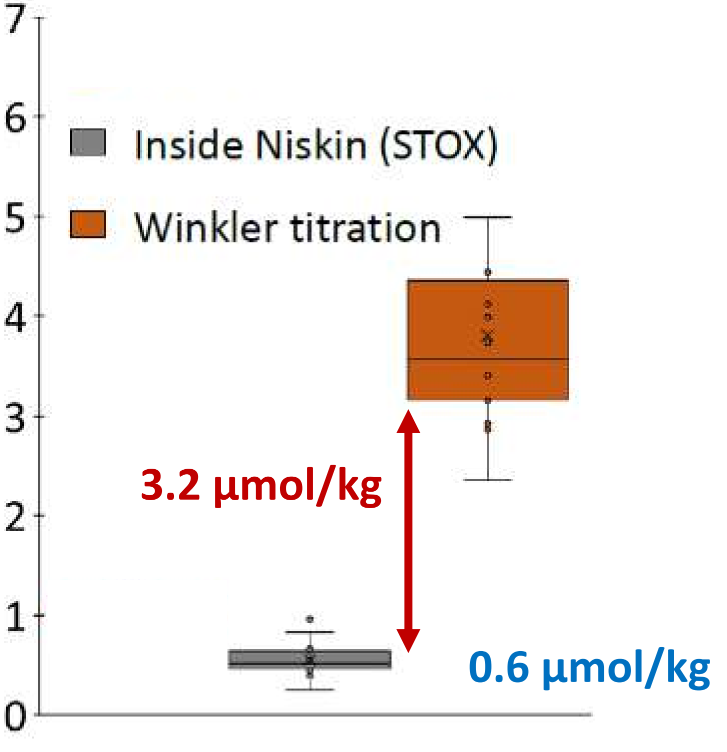
I. La mesure de référence WINKLER: incertitudes/problématiques, solutions

1) Limite de Détection (LOD) ⇒ caractérisation du core de l'OMZ

➢ Expériences avec 15 réplicats

1) ECHANTILLONNAGE & FIXATION WINKLER

2) REFERENCE POUR LES LOW $[O_2]$



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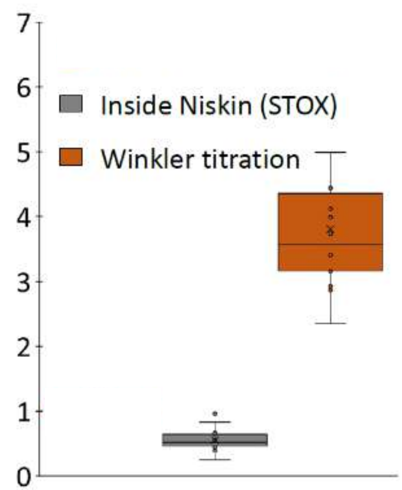
I. La mesure de référence WINKLER: *incertitudes/problématiques*, solutions

1) Limite de Détection (LOD) ⇒ caractérisation du core de l'OMZ

➢ *Expériences avec 15 réplicats*

1) ECHANTILLONNAGE & FIXATION WINKLER

2) REFERENCE POUR LES LOW [O_2]



➢ Mesure Winkler: **pas représentative dans le core sous ~4 µmol/kg!!!**

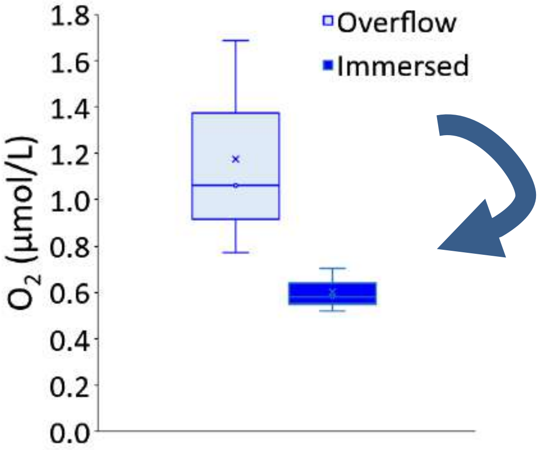
❖Contamination durant l'**échantillonnage** par **$O_{2\ atm}$** ***(~3 µmol/kg)***
+ **Relargage de O_2 par les polymères** de la Niskin ***(~0.5 µmol/kg)***

I. La mesure de référence WINKLER: incertitudes/problématiques, solutions

1) Limite de Détection (LOD) ⇒ caractérisation du core de l'OMZ

➢ Solutions:

1) Remplissage et fermeture des flacons Winkler immergé dans un récipient (e.g. 1 L) **avec la même eau**



Diminution en $[O_2]$ d'un facteur ~2

Garcia-Robledo E, Paulmier A, Borisov S, Revsbech NP. 2020.
Sampling in Oxygen Minimum Zones: the deviation from anoxic conditions. In preparation.

2) Utilisation de bouteilles de prélèvement moins contaminantes que les Niskin (HPSS, *Bianchi et al., 1999*?)**, hotte 'artisanale' avec gaz 'neutre'** (e.g. N_2)

2) Reproductibilité

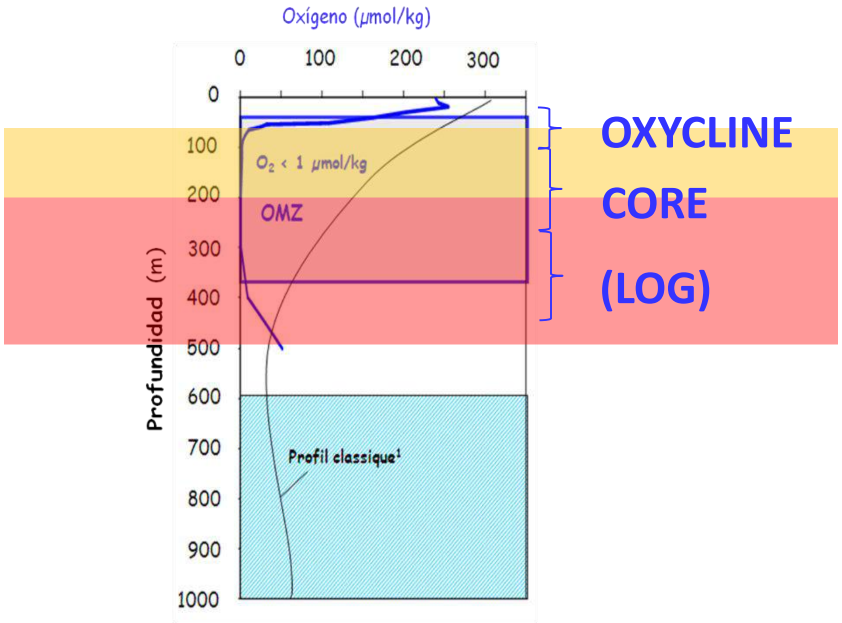
➢ Hypothèse:

<u>remplissage hétérogène</u> de la <u>Niskin</u> dans l'<u>OMZ supérieure</u>

⇒ ↑ **reproductibilité** (de ~80%) **dans les couches plus stables** (lower core, LOG)

par rapport à celles plus soumises à une dynamique de O_2

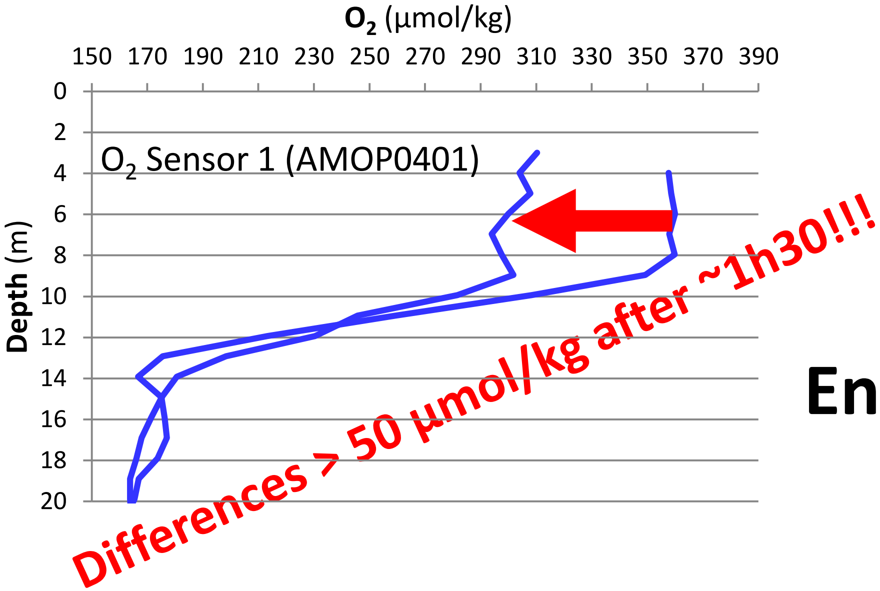
(upper high O_2 gradients, exposé aux effets d'«upwelling/mélange»)**?**



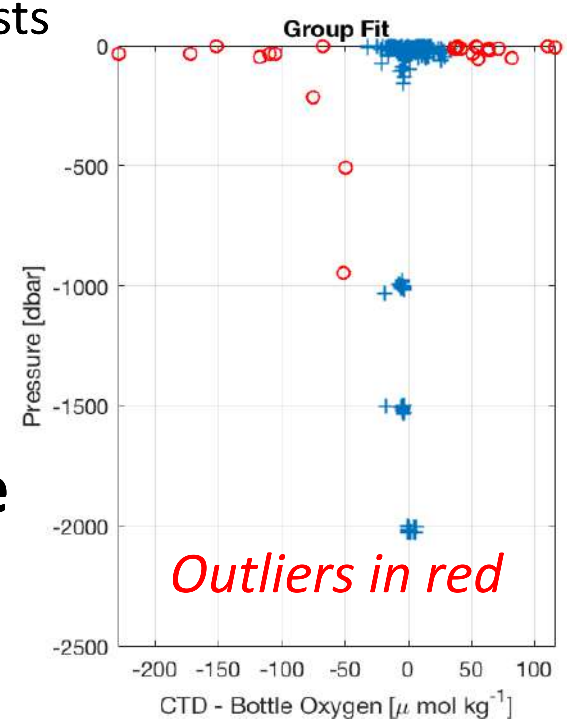
➢ Solutions: Privilégier un échantillonnage dans les couches profondes

II. Ajustement O_2-CTD: incertitudes/problématiques, solutions

1) 'Classical' O_2 ⇒ down- versus up-casts



En surface



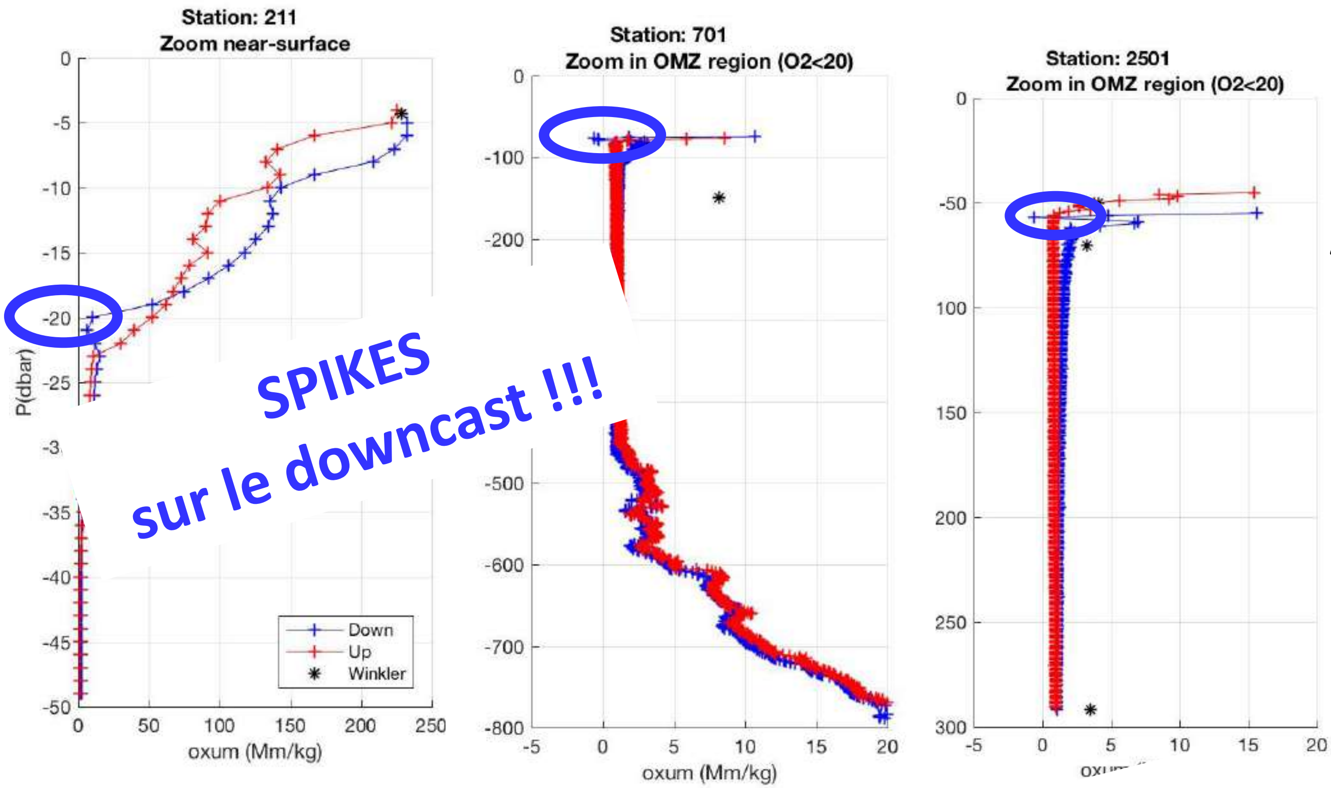
➢ **Spécifique aux régions d'OMZ?**

C. Soaut. Amélioration de la calibration des données CTD-O2 de la campagne océanographique AMOP 2014. GLAZEO. Rapport Juin 2018

❖ **Zones à forte dynamique verticale (upw, mix/strat), variabilité temporelle extrême, lié au fort gradient vertical de O_2**

II. Ajustement O_2-CTD: incertitudes/problématiques, solutions

1) ‘Classical’ O_2 ⇒ down- versus up-casts



SPIKES sur le downcast !!!

A l’oxycline

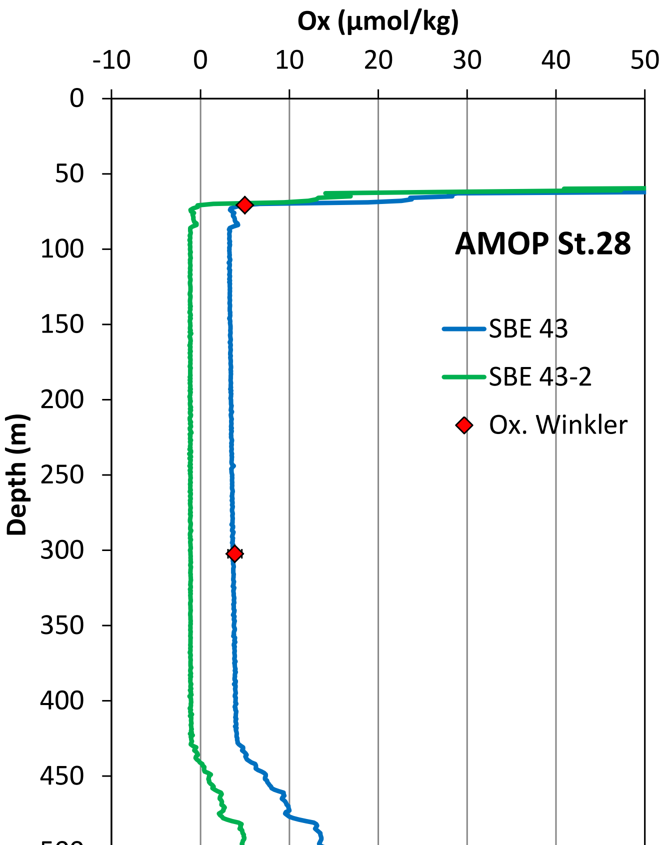
Concentrations négatives !!!

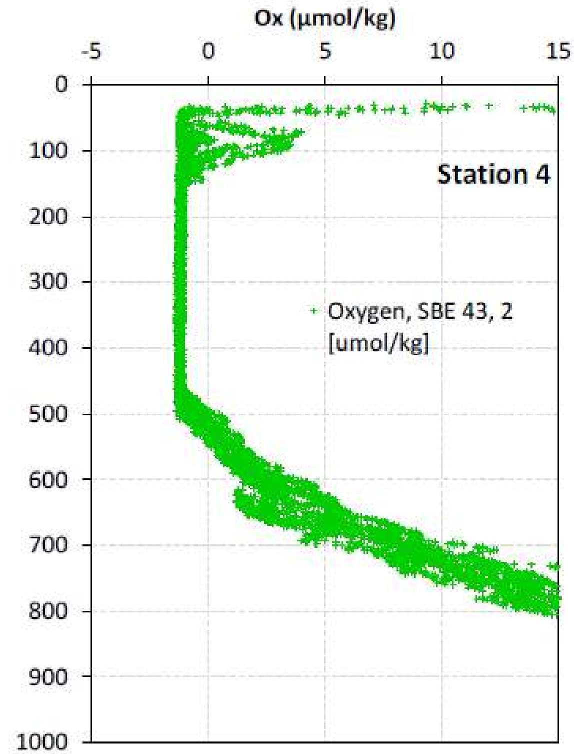
Oxycline non-représentée de manière optimale

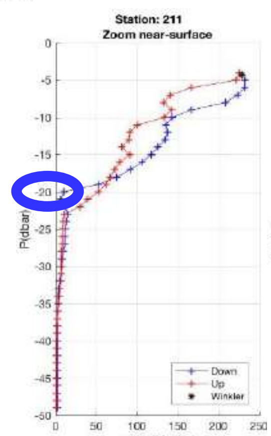
C. Soaut. Amélioration de la calibration des données CTD-O2 de la campagne océanographique AMOP 2014. GLAZEO. Rapport Juin 2018

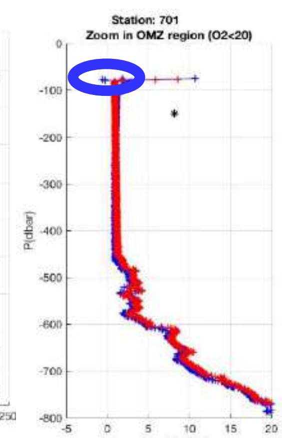
II. Ajustement O_2-CTD: incertitudes/problématiques, solutions

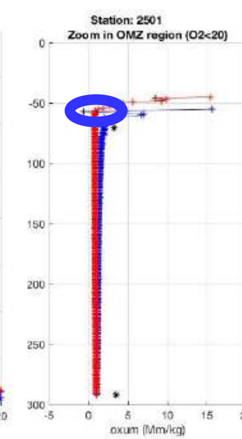
1) 'Classical' O_2 ⇒ down- versus up-casts
2) Low O_2 - core ⇒ anoxie







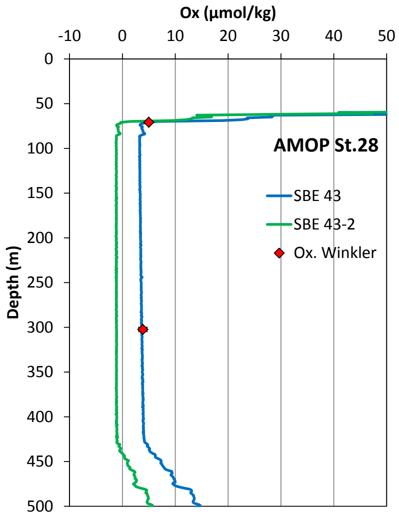


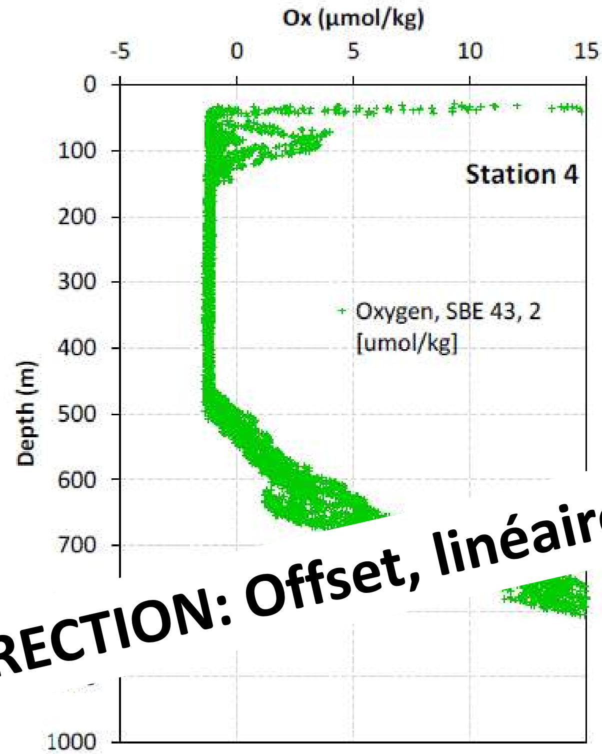


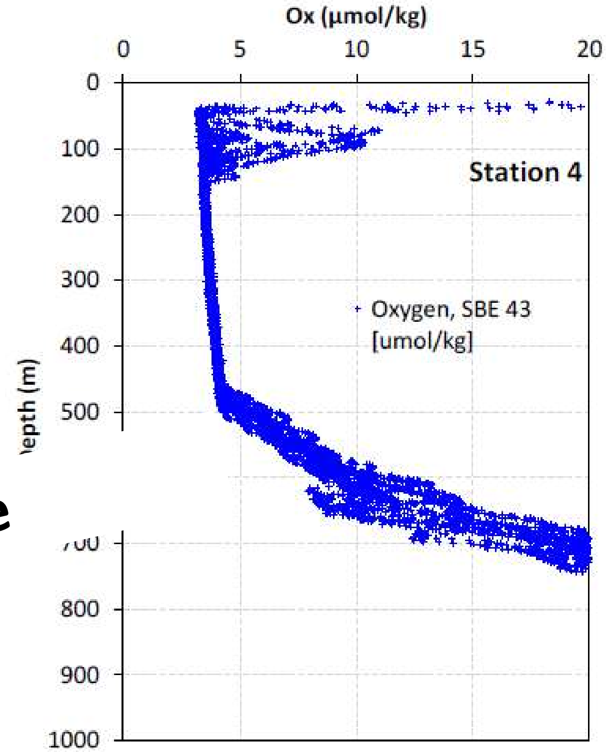
- **Off-set significatif**

II. Ajustement O_2-CTD: incertitudes/problématiques, solutions

2) Low O_2 - core







CORRECTION: Offset, linéaire

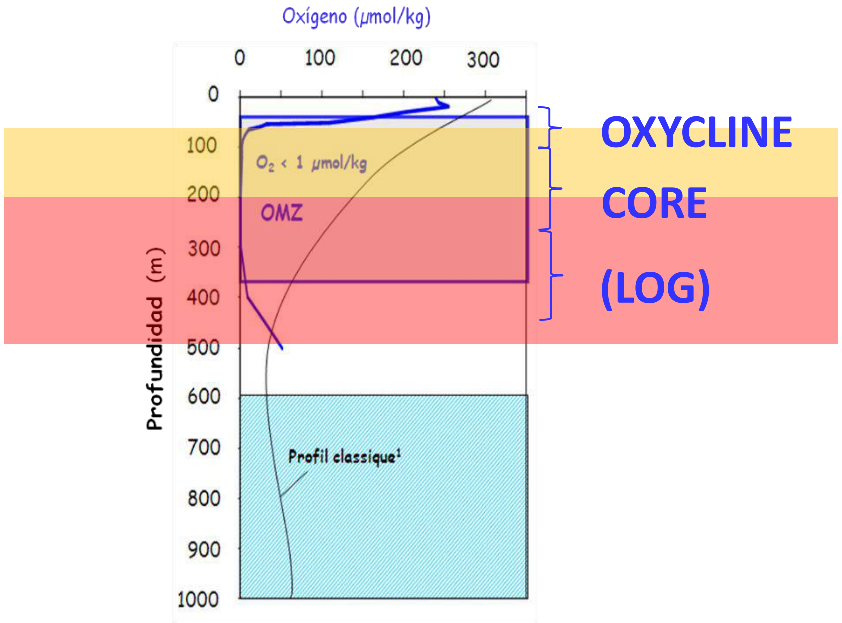
→ **LOD~60 nmol/kg**
(3*SD; ↓~2 ordres de grandeurs)

- Off-set significatif
- **Drift dû au relargage de O_2 par les polymères**

TAKE HOME MESSAGE dans l'OMZ:

INCERTITUDES

- ***Mesure Winkler de référence:***
  ⇒ Non adapté pour oxycline&core de l'OMZ



- ***Ajustement O_2-CTD downcast:***
  ⇒ ≠ upcast prélèvement bouteille

Ocean Deoxygenation: Drivers and Consequences · Past · Present · Future ·

INTERNATIONAL CONFERENCE KIEL GERMANY

3 – 7 September 2018

SFB 754

Kiel Declaration on Ocean Deoxygenation

Participants of the international conference
"Ocean Deoxygenation: Drivers and Consequences – Past – Present – Future",
3 – 7 September 2018 in Kiel, Germany organized by:
Kiel Collaborative Research Center SFB 754 and Global Ocean Oxygen Network (GO_2NE – IOC-UNESCO)

The ocean is losing its breath

Oxygen in the ocean supports the largest ecosystems on the planet. It is alarming that the ocean is losing oxygen, termed ocean deoxygenation, primarily due to global warming by greenhouse gas emissions, and pollution by nutrients and organic wastes particularly in coastal waters. We call on all nations, societal actors, scientists and the United Nations to:

(a) Raise global awareness about ocean deoxygenation through local, regional and global efforts, including interdisciplinary research, innovative outreach, and ocean education.

(b) Take immediate and decisive action to limit pollution and in particular excessive nutrient input to the ocean.

(c) Limit global warming by decisive climate change mitigation actions.

Both the Paris Agreement addressing Climate Change and the United Nations' 2030 Agenda for Sustainable Development demand conservation and sustainable use of the ocean, seas and marine resources in order to safeguard ocean ecosystems and their current and future societal benefits. These are severely threatened by ocean deoxygenation.

Scientists assembled at the conference and from around the world agree that:

1. During the past 50 years oxygen-depleted waters have expanded four-fold. Some areas of the ocean have lost up to 40% of their oxygen.
2. The ongoing loss of oxygen from the ocean is a rapidly increasing threat to marine life, the ocean's ecosystems and coastal communities.
3. Global warming impacts ocean oxygen in two ways: the capacity to hold oxygen decreases in warming waters, whilst warming reduces ocean mixing and circulation limiting the supply of oxygen from the atmosphere. Pollution by nutrients and organic waste enhances oxygen demand by increasing biological production and oxygen consumption during decomposition.
4. Deoxygenation disrupts marine ecosystems, affects fish stocks and aquaculture and leads to loss of habitat and biodiversity. It can, in extreme cases, lead to the production of toxic gases when all oxygen in the water has been lost.
5. Deoxygenation can accelerate global warming via enhanced marine production of greenhouse gases under low oxygen conditions.
6. The problem of deoxygenation is predicted to worsen in the coming years under continued global warming and increasing nutrient input to coastal regions as human populations and economies grow.
7. Expanded observation is immediately required for accurate documentation and prediction of ocean oxygen changes, and for improved understanding of its causes and consequences.
8. Strategies to slow and eventually reverse deoxygenation and its ecological impacts need to be co-developed between science and societal actors. This will contribute to the UN Decade of Ocean Science for Sustainable Development.

Conference Chair, Executive Board & Conveners

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QUESTIONS

AMOP cruise on RV L'Atalante in the OMZ off Peru, January-February 2014

http://www.legos.obs-mip.fr/recherches/projets-en-cours/amop


150
125
100


SF2