# Novel Oxygen Optode Sensor for Profiling Ocean Observation Platforms: Extensive Characterization and In-Depth Assessment of its Fast Response Time

[WP6, Task 6.1: Sensors and new instrumentation]

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## Introduction

Data show a decline in the global oceanic $O_2$ content of more than 2% since 1960 (Schmidtko et al., 2017). Quantifying changes of $O_2$ levels improves the understanding of chemical, biological and physical processes in the global ocean, especially in Oxygen Minimum Zones (OMZ).

The faster response time of the novel optical oxygen sensor (optode) KM Contros HydroFlash® $O_2$ compared to other optodes is promising to observe various processes with higher spatial and temporal data resolution. The sensing principle is based on dynamic fluorescence quenching (DSQ) and described by the Stern-Volmer-Equation ($\frac{I_0}{I} = \frac{\Lambda_0}{\Lambda} = 1 + K_{SV} \cdot pO_2$).

## Motivation

Integrated characterization of the CONTROS HydroFlash® $O_2$ optode is aimed regarding oxygen, temperature, salinity and pressure dependence, long-term stability and drift, response time and air-calibration compatibility.

## Methods

Calibration procedures follow the laboratory setup described in Bittig et al. (2012). Bittig et al. (2018) suggest a functional model for partial pressure $pO_2$ and low root-mean-square errors (RMSE) to determine the behaviour of the optode. The fit equation for the exponential response time $\tau$ is given by Bittig et al. (2014).



0–1,200 m    1,200 m–sea floor

DO change [µmol kg⁻¹ decade⁻¹]
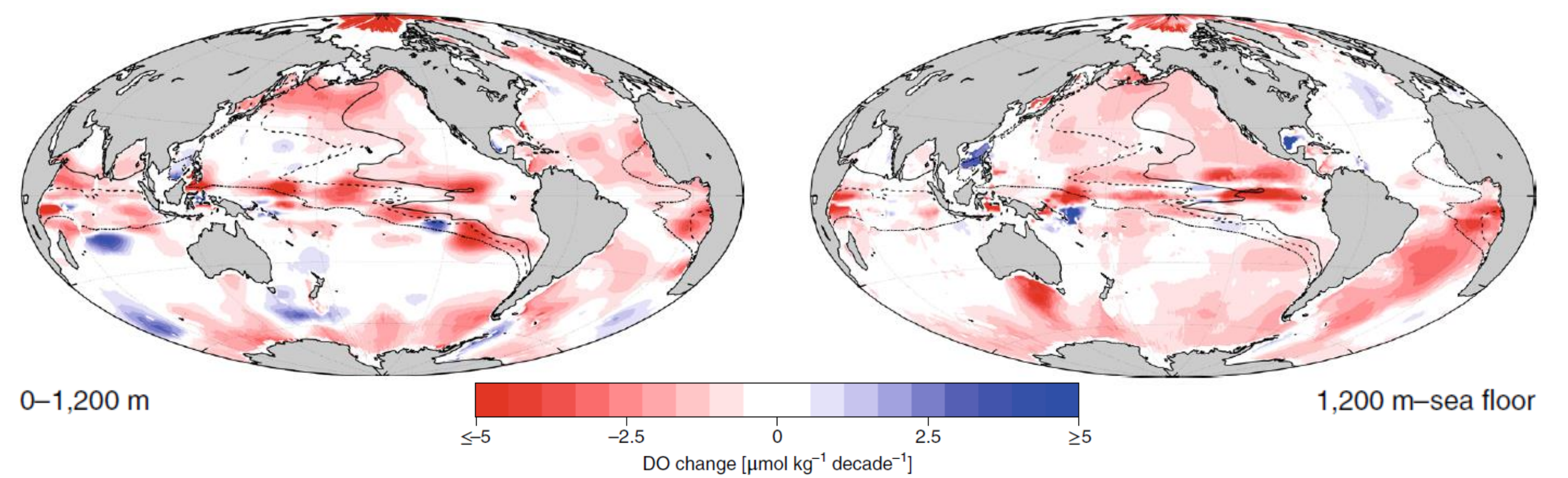≤-5   -2.5   0   2.5   ≥5

**Fig. 1: Oxygen change in the ocean. Observational estimate of the 50-year (1960 to 2010) oxygen change in the upper and deep ocean (from Oschlies et al., 2018).**
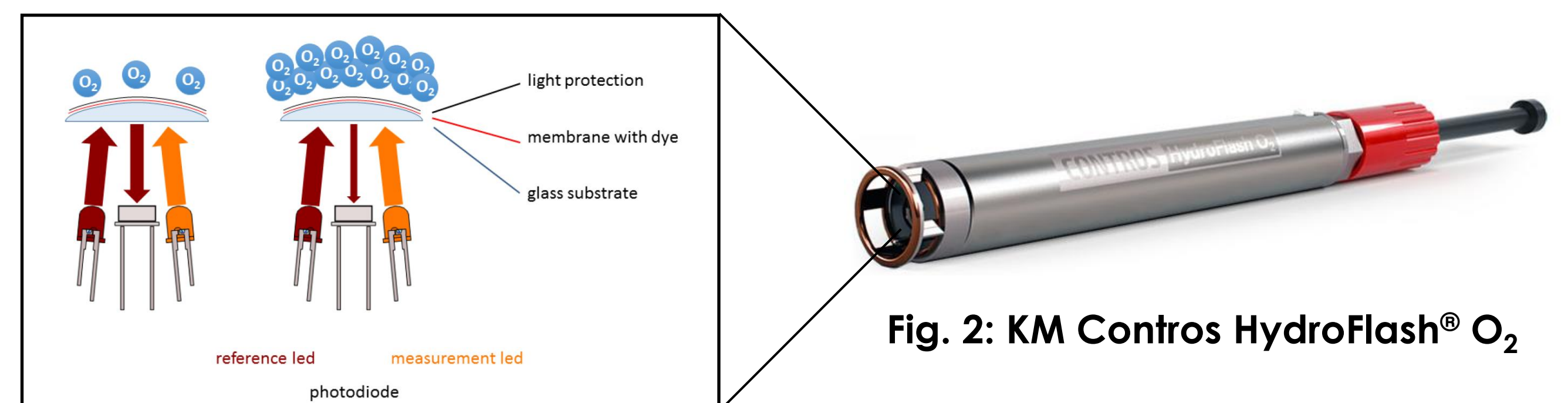
light protection
membrane with dye
glass substrate
reference led    measurement led
photodiode

**Fig. 2: KM Contros HydroFlash® $O_2$**

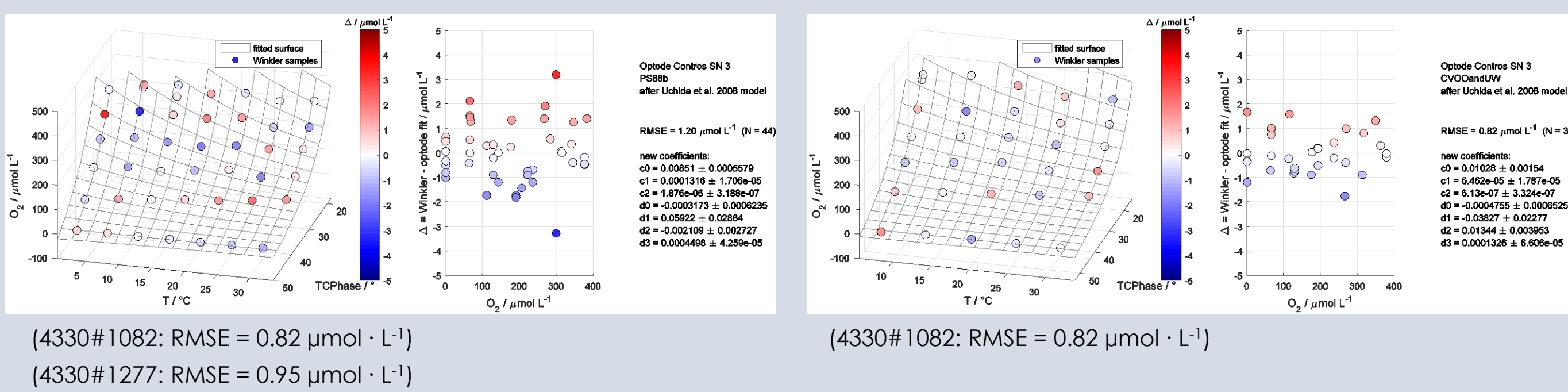$$pO_{2,adj} = \frac{\frac{1 + c_4 \cdot \vartheta}{c_5 + c_6 \cdot \varphi_{adj} + c_7 \cdot \varphi^2_{adj}} - 1}{c_1 + c_2 \cdot \vartheta + c_3 \cdot \vartheta^2}$$

$$h(t) = A \cdot \left(1 - e^{-\frac{t-t_0}{\tau}}\right)$$

φ: phase shift / °  ||  $c_1 - c_7$: cal. coefficients  ||  θ: temperature / °C

h(t): step response curve  ||  A: amplitude
t: elapsed time  || $t_0$: time offset  || τ: response time

## Results

Applied model is most promising and shows robust fitting results for CONTROS HydroFlash® $O_2$ optodes. **Lab calibrations** yield **accuracies with RMSE < 1 µmol · L⁻¹**.

(4330#1082: RMSE = 0.82 µmol · L⁻¹)
(4330#1277: RMSE = 0.95 µmol · L⁻¹)

(4330#1082: RMSE = 0.82 µmol · L⁻¹)



Step Response drift–like setup
Optode Contros SN 1
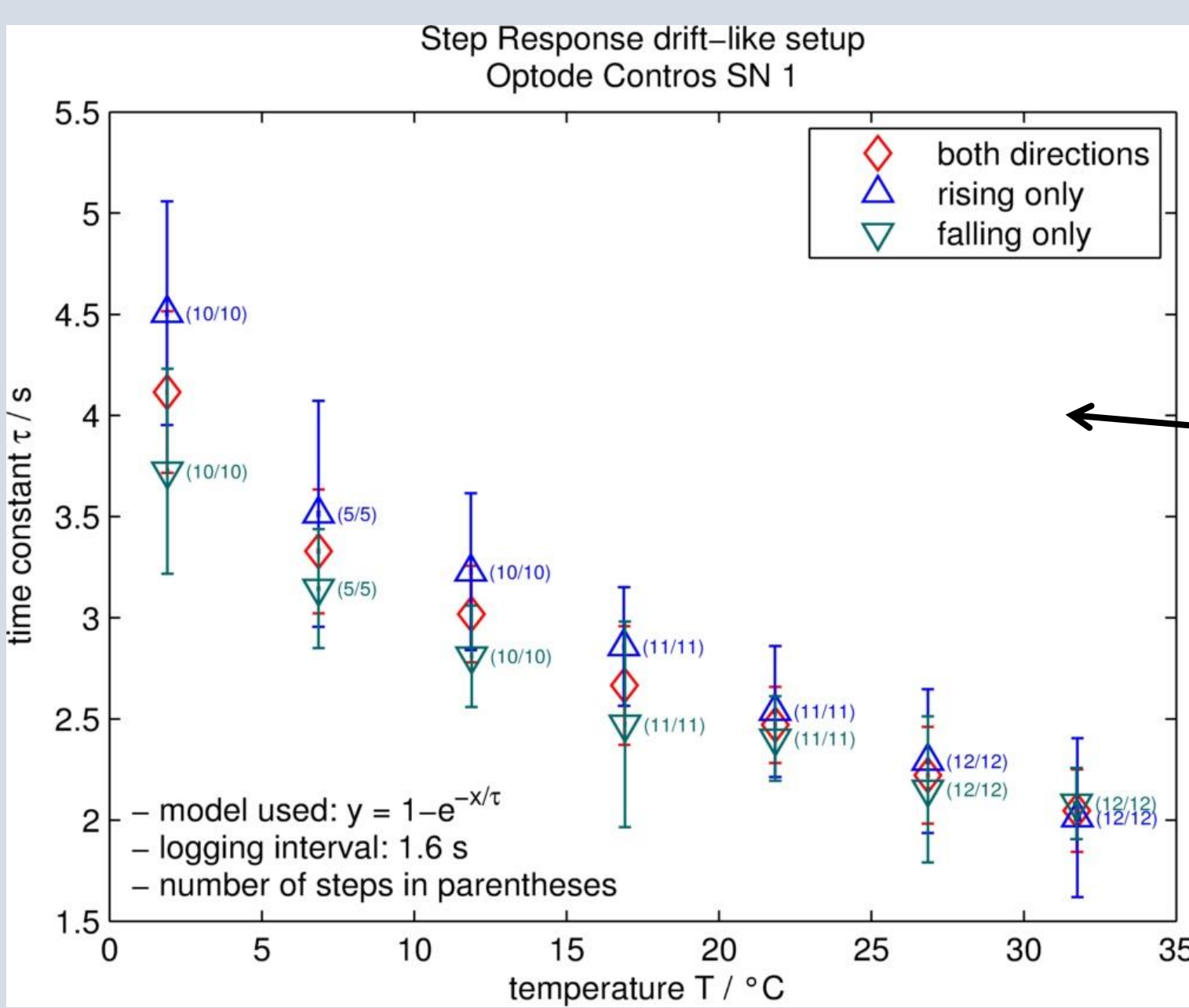
The **response time** of $\tau_{63\%} = 3 - 4 s$ is ~50% faster compared to other optodes (weak-turbulent flow).

– model used: y = 1−e^{-x/τ}
– logging interval: 1.6 s
– number of steps in parentheses
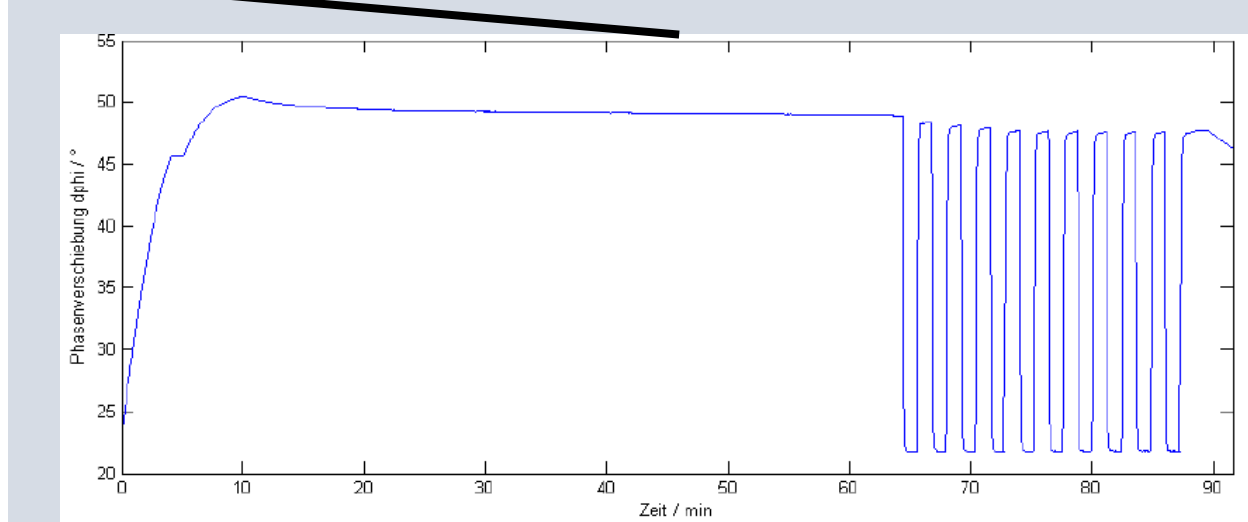
**Applications of HydroFlash(R) $O_2$ Optode**

(chronological order)
— PS88b (Nov 2014): UW & CTD-profiles
— M116 (May-Jun 2015): UW & CTD-profiles
— M119 (Sep-Oct 2015): UW & CTD-profiles
★ CVOO mooring (2015-2016,2016-2018,2018-2019)
● Argo-Float Dual-Oxygen optode tests (Jun 2016)
M133 (Dec 2016-Jan 2017): UW package
— (incl. pCO₂, chl a/turbidity/phycocyanin)

**Implementation on Argo-Float**

(figures provided by LOV)

**8+ months mooring data**

CVOO Mooring 2016-2017 at 120m: KM HydroFlash O2 DO-0216-005

(expected temperature offset between 0.2 to 0.3 °C)

**Underway (UW) measurements:**
100+ days

**Performance on CTD-casts:**
80+ profiles (up to 6000m)

## Discussion

This novel and significantly faster optode promises high quality observations including fast oxygen level changes. A float test revealed an issue with the sun-shading (direct solar irradiation exposure), while for the rest of the profiles data was successfully recorded without peculiarities. Mooring deployments qualitatively show the utility for long-term ocean observations.
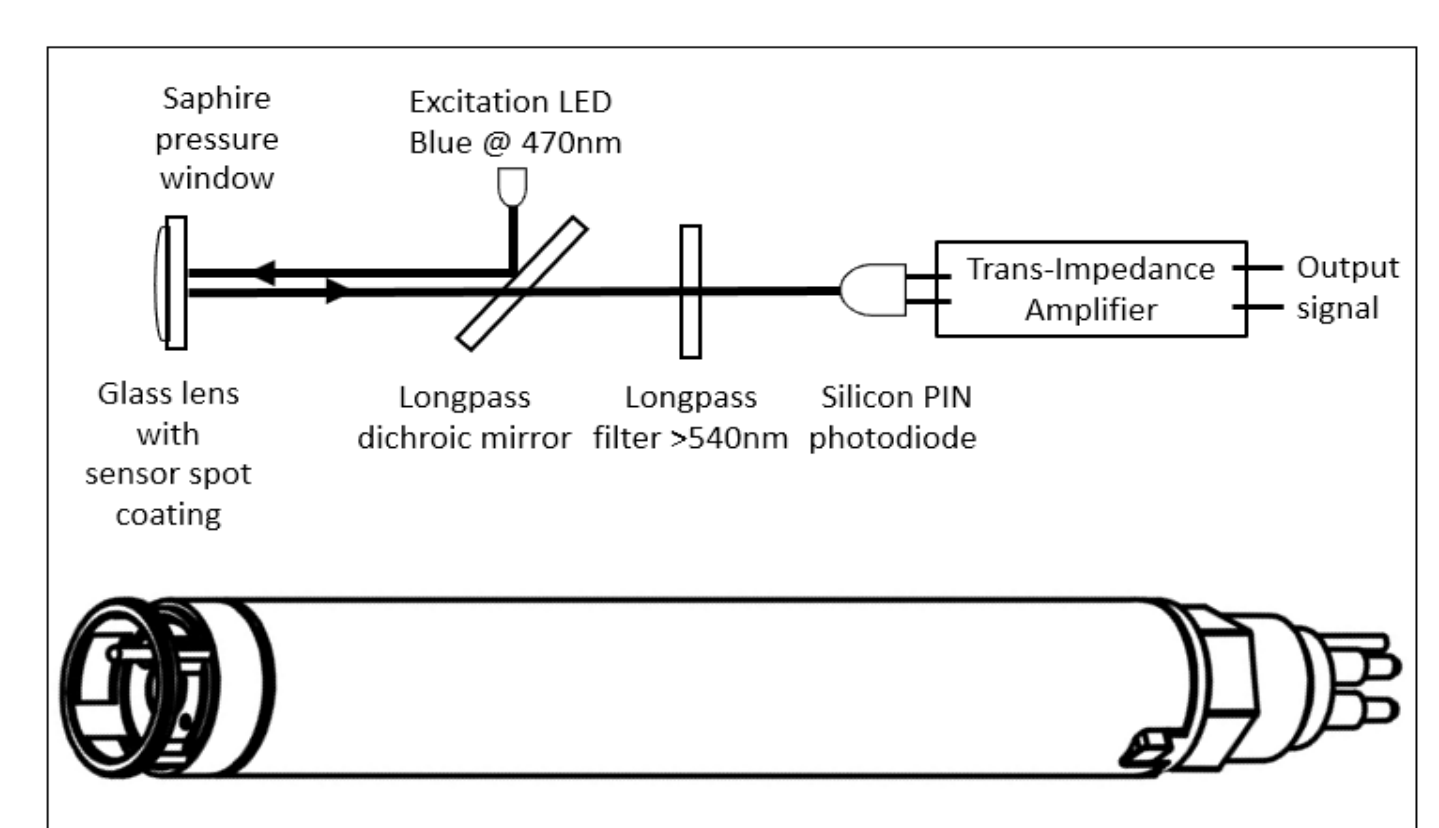
## Outlook

Methodological paper with full characterization & best practices of this optode is in preparation. Biogeochemical analysis of observational data will follow soon.

## Optode outlook for pH and $CO_2$

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Universal opto-electronics for pH and $CO_2$ measurements based on the fluorescence quenching detection principle have been developed with low power consumption and a small form factor (15*60 mm). Precision and response time are constrained by the chemical dyes on the spots.

While the new compact and low-power hardware allows for expanding the range of optode sensors, the measuring quality is not yet in the range of most scientific requirements.

Future development work will focus on further miniaturization, improved accuracy and enhanced characterization of the sensors.

Saphire pressure window
Excitation LED Blue @ 470nm
Glass lens with sensor spot coating
Longpass dichroic mirror
Longpass filter >540nm
Silicon PIN photodiode
Trans-Impedance Amplifier
Output signal

**References:**
Bittig et al. (2012). A novel electrochemical calibration setup for oxygen sensors and its use for the stability assessment of Aanderaa optodes. Limnology and Oceanography: Methods 10, pp. 921-933. [doi:10.4319/lom.2012.10.921].
Bittig et al. (2014). Time response of oxygen optodes on profiling platforms and its dependence on flow speed and temperature. Limnol. Oceanogr.: Methods 12, 2014, pp. 617-636. [doi:10.4319/lom.2014.12.617].
Bittig et al. (2018). Oxygen Optode Sensors: Principle, Characterization, Calibration, and Application in the Ocean. Frontiers in Marine Science 4.429, pp. 1-25. [doi:10.3389/fmars.2017.00429].
Oschlies et al. (2018). Drivers and mechanisms of ocean deoxygenation. Nature Geoscience, 11, pp. 467-473. [doi:10.1038/s41561-018-0152-2].
Schmidtko et al. (2017). Decline in global oceanic oxygen content during the past five decades. Nature 542., p. 335. [doi:10.1038/nature21399].

**– Note –**
You will find me at my poster

**Tuesday, 26.3
12:30 – 13:30**