

# ***Interactive comment on “Technical Note: Oxygen Optodes on Profiling Platforms: Update on Response Times, In-Air Measurements, and In-Situ Drift” by Henry C. Bittig and Arne Körtzinger***

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We want to thank the three reviewers for their time and effort to review our manuscript and for the positive reviews. Below are our responses to their helpful and constructive comments.

My only concern, which relates not to this publication specifically, but to the recent body of work on this topic is that I feel that the Bittig et al. papers (2014, 2015a, 2015b and this one) would have been much more valuable as a cohesive whole, or two papers, rather than broken down in these smaller

"technical note" units. It becomes difficult to follow the overall narrative and the inexperienced reader is likely to be lost in a collection of different parameterisations. Despite this, the authors must be commended for providing a clear, concise overview in the appendix of this manuscript; it is just a shame it is relegated to the end of a technical note that likely will not be perceived as the definitive body of work due to the title.

We see the point being made and actually agree that the recent oxygen optode literature is relatively scattered, which may discourage curious readers to go through the works. However, the different "smaller units" in fact testify to the learning process we had on our side, too, and actually helped evolve both others' (e.g., SCOR WG 142, Johnson et al. 2015) and our knowledge (e.g., this work) about oxygen optodes. This learning process includes the presentation and is far from finished and we will consider the reviewers comment for our future work.

Regarding the appendix, our initial feeling was (while being important and a core aspect of the present work) that this part is essentially a revised, improved presentation of the results of Bittig et al. 2014 and as such does not belong into the main body of a publication. We hope that the concise (and separate) presentation of the algorithm will facilitate its application.

The authors may consider changing the title to avoid a series of colons, maybe something like "Update on response times, in-air measurements, and in-situ drift for oxygen optodes on profiling platforms".

Agreed and changed.

Page 1, Line 1-2: "are or eventually run out of calibration" – a bit awkward – maybe just say that the sensors experience significant drift?

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We don't think there is a common understanding of the term "drift": Here, does drift mean that the calibration coefficients are simply off (i.e., a change in sensor response ("drift") happened sometime after the calibration but before the deployment) or does it mean that there is a continuous change in the calibration coefficients during the deployment from one profile to the next one (i.e., the sensor drifts in situ), or does it refer to the apparent in situ conditioning during the first couple of pressure cycles? There is abundant evidence for the first, a slowly growing body of data that suggests the second, and only a few hints for the third. Moreover, the magnitudes of pre-deployment or "storage" drift (i.e., the first) and in situ drift (2nd) are an order of magnitude apart, and they potentially follow different mechanisms (see following question on linear vs. exponential). Given that ambiguity, we rephrased the statement to "various sources of drift in the calibration coefficients".

Abstract lines 4 and 5. The sentence beginning with "Also: : :" could be combined with the previous one.

Fixed.

P1, L12: Time frame over which that drift occurred would be helpful since there is still uncertainty about whether in situ drift rates are constant or variable.

We added the deployment duration, 2 and 3 years, respectively. D'Asaro and McNeil (2013) give an exponential time constant of ca. 2 years for the optode bias at 100 % saturation, i.e., of our slope factor  $m_i$ . This is for 3 optodes that were used only intermittently and were stored at laboratory conditions otherwise. Given that there is an order of magnitude difference in the drift amplitude ( $\approx 5 \% \text{ yr}^{-1}$  in their case vs.  $\approx 0.5 \% \text{ yr}^{-1}$  in our and other in-situ cases), one can speculate that the time evolution of in-situ drift might be different from "storage" drift, too. Even if  $m_i$  followed a 2-year exponential decay, a 2 or 3 year time series is likely too short to distinguish from a linear

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trend (see manuscript figure 5). We might not be able to tell until a few years from now when a certain number of  $\geq 5$ -year in-air timeseries are available, and then for practical purposes a constant in-situ drift rate might just be adequate enough. However, this assumes that there are no other effects on the in-air measurements, like, e.g., an optode in-situ conditioning during the first 40 profiles (manuscript figure 6). This obviously can bias interpretations of a constant or variable in-situ drift rate.

One very minor comment- in the last line of the abstract it is unclear whether the accuracy is better or worse than 1  $\mu\text{mol}/\text{kg}$ .

Fixed.

P1L20: "they" cannot refer to oceanic oxygen measurements.

Fixed.

1 Introduction, the first paragraph is one long sentence that is poorly structured.

P1L21: I would suggest splitting the sentences at the colon. The final sentence beginning with "Also: : ." is also awkward.

Fixed.

2 Instrument description, line 16, parenthesis within parenthesis are discouraged. I may have missed it, but the authors do not specify which type of foil and whether these are pre-aged or not for the AA4330.

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Fixed. Our observation is that the transparent foils did not catch on for float or glider deployments due to little characterisation of the behaviour in the presence of sunlight. Instead, all float and glider deployments known to us use the "standard foils" with black optical coating. The Aanderaa optodes were factory multi-point calibrated and as such pre-aged.

P10, L9: Could the differences between Aanderaa and SBE optodes be due to differences in calibration? Do you have a way of differentiating uncertainties in the temperature dependency from uncertainty in the pressure dependency? Surface data at the same temperature as deep data would work.

Thank you for bringing up the calibration, we added the missing information. Aanderaa and Sea-Bird optodes were calibrated in the same calibration run at GEOMAR before deployment. Moreover, seasonal temperature variations at the surface, combined with the in-air measurements for the Aanderaa optodes, suggest that the temperature parameterisation of the optode response is adequate between 20 and 30 °C (see lower left panel in figure 1 below) and Aanderaa and Sea-Bird optodes show a constant difference (not shown). We therefore have no reason to suspect a temperature-induced difference between the two sensors at 4 °C at depth, but rather attribute this to the different pressure coefficients., which have been shown to be variable within the observed range ( $\approx 0.6\%$  uncertainty at 2000 dbar for *each* optode, Bittig et al. 2015). (Figure 1 below gives the relation between in-air correction slope expressed as  $1 - m_i$  and sea surface temperature for float 6900890.  $1 - m_i$  shows no dependence on SST (lower left panel) whereas there is a continuous drift between early  $1 - m_i$  (blueish) and late  $1 - m_i$  (yellowish).)

P2, L27: I think this paragraph continue to refer to Bittig et al. 2014, but that is unclear until several sentences into the paragraph.

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Fixed.

3 Time response, P2L30 Are the authors able to quantify the error that was introduced by relying on "nearby" profiles?

In Bittig et al. 2014, the criterion used to match a glider dive with a CTD profile was within 8 hours and within a distance of 10 nm of the CTD profile. The Argo-floats used there only measured their first profile 10 days after deployment. Based on these constraints, we obtained boundary layer thicknesses  $l_L$  of  $110 \pm 86 \mu\text{m}$  for downcast dives and  $71 \pm 60 \mu\text{m}$  ( $\pm 1\sigma$ ) for upcast dives of a glider at similar ocean conditions to the two floats reported here. For the floats deployed in polar waters, we got an average  $l_L$  of  $210 \pm 230 \mu\text{m}$  (i.e., response times  $\tau$  around  $190 \pm 230$  s).

In this work, the constraints are much tighter and our estimates of  $l_L$  much more reliable (mean  $111 \pm 19 \mu\text{m}$ ; However, remember that  $l_L$  is a function of vertical velocity!).

P3L9: How well is "well-defined"?

$\pm 3$  s. Information added.

P4, Paragraph1: Any thoughts on the breakpoint in the boundary layer thickness vs. float vertical velocity relationship? Presumably this is due to a sensor design choice, like foil recess. Is it worth speculating on changes that could be made to make this function more linear? Presumably that would help with the time response corrections you are making.

A (very) preliminary look at fluid dynamics can give a hint: The Reynolds number  $Re = \rho \cdot v \cdot L / \mu$  gives the ratio between inertial and viscous forces. The transition between turbulent and laminar flow occurs somewhere around  $Re \approx 2000$ . A back-of-the-envelope calculation (viscosity  $\mu$  and density  $\rho$  at  $10^\circ\text{C}$  and a salinity of 35, velocity

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$v$  of  $0.1 \text{ m s}^{-1}$ ) gives a characteristic length scale  $L$  of  $\geq 3 \text{ cm}$  to have turbulent flow. This is in the same order of magnitude as the size of the optode and as suggested very likely related to the recess of the foil, i.e., the breakpoint likely reflects the transition between laminar flow (slower than  $0.095 \text{ dbar s}^{-1}$ ) and turbulent flow.

More details of the breakpoint's location and its relation to the foil window's design would need to be established with proper fluid dynamics simulations, which is beyond the scope of this manuscript and our expertise.

Also, please note that the simple two layer model used in Bittig et al. 2014 assumes molecular transport in the liquid boundary layer (with associated  $\text{O}_2$  diffusion constant). The diagnosed breakpoint in our model  $l_L$  therefore reflects the transition between turbulent/molecular transport and not necessarily a step-transition in the actual liquid boundary layer thickness.

While a better understanding of the fluid dynamics can certainly help to improve the time response of the sensor, we think it is less relevant to our time response correction, as long as the regime/behaviour is properly characterized.

P5L6: missing a word between "It is" and "to note".

Fixed.

Have the authors observed any bias due to the thermal inertia of the sensor itself affecting the sample (primarily on the AA4330)?

We think the community consensus is that thermal inertia was an issue for Aanderaa 3830 models but is no longer a concern with Aanderaa 4330 models (e.g., Thierry et al. 2016, chap. 4.1.3). As an illustration, the median differences between Aanderaa 4330 optode temperature and CTD temperature show a maximum mismatch of  $0.06 \text{ }^\circ\text{C}$  when crossing the surface thermocline. This translates to a  $\text{O}_2$  difference of ca.  $0.2 \text{ } \mu\text{mol kg}^{-1}$ . Considering that the optode time response effect is an order of magnitude more important ( $13 - 17 \text{ } \mu\text{mol kg}^{-1}$  difference between uncorrected and corrected

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Aanderaa 4330 data, with  $2 - 3 \mu\text{mol kg}^{-1}$  difference between Aanderaa and Sea-Bird optode both after correction), the thermal inertia can be neglected.

Interestingly, the SBE63 optode shows a similar mismatch ( $0.04 \text{ }^\circ\text{C}$ ) to the CTD temperature.

Was the vertical offset in sensors taken into account? By that I mean, the authors specify the floats were modified to return a specific timestamp for the oxygen probes.

Was that a time stamp for each, or did the float run on a single thread processor collecting sequential measurements of P, time and oxygen with a single timestamp for both oxygens, in which case vertical spacing needs to be accounted for?

The floats provide one time stamp per pressure level (i.e., CTD and optode data together). As such, both optodes had the same time stamp. The Aanderaa optode was located close to the CTD's pumped path intake (about the same height for 6900889 and max. 10 cm below for 6900890) which is why we did not add a pressure and/or time offset. This information is added to the text.

Question about the time stamp: Since most Argo data (that I know of) does not include the time stamp for each measurement, would it be at all useful to estimate a time response correction based on typical ascent speed and the pressure of each sample? I recognize that due to changes water density the ascent speed will not remain constant (as pointed out in the text and figure 3b), but perhaps that can be estimated as well, given knowledge about the float's volume and mass. My point is, you have convincingly demonstrated the need to adjust optode oxygen to account for response times, but is there a way to correct data that does not have a measurement-specific time

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stamp and what would be the increase in uncertainty? This might be of great value to other researchers if it is possible.

You are right, Argo focussed on profiles and originally did not see their data as time series. The quick answer therefore is that access to the original, float-transmitted files is currently the most promising way to get (some) timing information. For the long answer, one needs to check the Argo files in detail. Argo float data are split into individual profiles and trajectory. In its current format version 3.1 there exists a "core" profile with the CTD data, a "bio" profile with Biogeochemical-Argo intermediate (e.g., phase shifts) and final parameters (e.g., DOXY), and a "merge" profile with both the CTD and the final biogeochemical parameters. The primary variable of these profile files is pressure, which is used to provide the link between each of them. Each profile has a single time stamp, JULD, when the float is at the surface. The trajectory files (again split into "core" and "bio") contain information of the float deployment in one single file for the entire deployment in the order of their occurrence. Information contained are, e.g., profile or ascent start and end times, park pressure measurements during the drift phase, but also optode in-air measurements. Each observation can have both an own pressure and a JULD, i.e., time stamp. To our knowledge, most floats report some timing information for certain pressure levels in their log file, that are likely to end up in the trajectory file (depending on the float decoder). However, assignment to a specific sensor observation may not always be possible if not the entire data string is stored in the trajectory file (e.g., if only pressure is recorded along with the JULD but there exist multiple sensor observations with the same pressure). However, putting the entire data string into the trajectory file effectively replicates the entire profile if all observations are timed as in our case, which is not the intention of the trajectory data structure.

To mend this situation, the Argo Data Management Team recently (Sept. 2016) approved the creation of an optional intermediate variable "MTIME" in the bio profile files that gives the time stamp for each measurement relative to the profile time (JULD). For floats with abundant timing information (i.e., all measurements are timed as in our

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case), the timing information should go into that variable "MTIME". For floats with scarce timing information (i.e., only some measurements are timed), it should stay in the trajectory file (i.e., its natural place). The implementation of "MTIME", however, is optional to the different data centres.

To assess whether an estimated time is helpful, we took the start and end time of the profile observations and assumed a constant ascent velocity to "re-estimate" the Aanderaa optode 4330 time stamps. The result is shown below in figure 2 (Same as manuscript figure 3 but assuming a constant ascent velocity between profile start and end time (panel b) and recalculating the Aanderaa 4330 optode time stamps accordingly.). The main difficulty we see is less in the estimation of the response time but in the lack of knowledge when a specific measurement was actually taken (assuming pressure-initiated sampling, not frequency-based). In our experiment, the slow down near the pycnocline is not adequately taken into account (i.e., optode samples are estimated closer in time together than they actually are and the response time is estimated to be faster). Both effects are somewhat compensating, so that the median difference between both optodes in the strongest gradients is around  $7 - 8 \mu\text{mol kg}^{-1}$  (compared to  $2 - 3 \mu\text{mol kg}^{-1}$  with proper time stamps and  $13 - 17 \mu\text{mol kg}^{-1}$  without any time response correction). Moreover, we see a consistent over-correction in our case, that can cause a significant bias (90-percentile reaches up to  $35 \mu\text{mol kg}^{-1}$ ).

Given these caveats incl. the potential for serious bias, the results are still surprisingly promising. With a more advanced estimation of the ascent speed, e.g., through some sparse timing information from the log / trajectory file, such time response corrected data appear more adequate than uncorrected data.

Figure 1: Figure title is wrong, and the N above the colorbar unclear.

Fixed and the N removed. (N gave the number of data points per  $0.002 \text{ dbar s}^{-1}$  and  $4 \mu\text{m}$  bin and is adequately described by "data density".)

Figure 2: I feel that replacing density with temperature (or adding another

subplot) would be much more useful. Salinity has little to no effect here, whereas temperature does.

We tend to disagree. What is most important for the time response is the density structure. It is the density profile/stratification that determines the vertical velocity of the float and the depth(s), at which the float slows down significantly (e.g., the pycnocline). This not only has a direct effect on the response time (lower  $v$  means higher  $l_L$  means higher  $\tau$ ), but also indirectly on the actual data (and the spacing of the data if pressure-triggered) since the float spends more time in the density gradient regions, giving the (slow) sensor more time to adjust (i.e., lower dynamic bias) and thus counteracting the higher  $\tau$ . Temperature, in contrast, has a smaller impact on  $\tau$  than the density's effect via modification of  $l_L$  and  $\Delta t_i$  and we relegated the temperature profile therefore to figure 3.

We therefore keep figure 2 as before. The density's importance is now emphasized in the discussion of figure 3.

Figure 3b/c – What causes the wavelike fluctuations in ascent speed and response time of the Aanderaa optode between 100 and 1500 db?

The wavelike fluctuations in ascent speed are caused by the float operation: To ascent, the float increases its buoyancy by moving its piston and thus increasing the volume of its external oil bladder. When the ascent speed falls below a certain threshold, the buoyancy is re-adjusted by moving the piston again, causing the float to re-accelerate. Some Argo Data Centers do record these piston buoyancy actions in the respective float tech files. This feedback cycle repeats itself about half a dozen times between 1800 and 300 dbar in our case, see an individual profile of float 6900890 below in figure 3 (same as manuscript figure 2 but to full depth).

In fact, the intermediate and deep density structure seems to be so stable, that these buoyancy actions occur at similar depths for all profiles, which causes them to appear

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as said wavelike structure in the median velocity profile.

As for the response time, a fluctuation in  $v$  translates directly into a fluctuation in  $l_L$  (manuscript figure 1), which translates directly into a fluctuation in  $\tau$  (Bittig et al. 2014 or Appendix, respectively). The seemingly flat side of the 10-percentile originates from the discontinuity of  $l_L$  vs.  $v$  around  $0.095 \text{ dbar s}^{-1}$ : Float data slower than  $0.095 \text{ dbar s}^{-1}$  show a pronounced  $l_L$ - (and  $\tau$ -)  $v$ -dependence (median and 90-percentile portion) while float data faster than  $0.095 \text{ dbar s}^{-1}$  have essentially a "fixed"  $l_L$  around  $100 - 110 \mu\text{m}$  (10-percentile portion).

We added the velocity for the regime transition in eq. 1 as vertical line in panel 3b and added the above information to the discussion.

Figure 3f: What causes the discrepancy between Aanderaa and SBE optodes in deep water?

We believe this discrepancy to be due to uncertainties in the pressure corrections of both optodes as stated in the manuscript text, with explicit reference to figure panel 3f (P5L12f).

P7L2: Purely a question of preference, but I would replace "their" by "the" (or even "our") since it is essentially the authors' work. "Their" comes across as a bit artificial.

Fixed.

Variable carry over slope? I think from equations 7 and 9,  $mt=0$  is constant, and based on the carry over slope determined from the entire deployment. The carry over slope must vary seasonally and potentially interannually, if the float moves far enough. Is it possible to split the deployment into periods of time with different carry over slopes or fit the carry over slope to some type of function of season or time?

To clarify the equations, the carry over slope is only an intermediate fitting parameter to account for secondary effects of the float "in air" measurements (equation 8). The carry over slope  $c$  is not used to correct the data. Data are corrected by the oxygen correction factor  $m_i$  for each profile  $i$  (equations 7 and 9). However, the reviewer is insofar correct that requiring a constant carry over slope  $c$  imposes some implicit constraints on the other fit parameter (equation 8), i.e., both the initial oxygen correction factor  $m_{t=0}$  and the drift rate  $a$  (equation 7). In our data, we have no indication of a variable carry over slope (e.g., figure 4 below).

While both our floats stayed within few 100 km of their deployment in the Eastern Tropical North Atlantic, we assume the height of the optode above the sea surface to be the main factor on  $c$  (see also Bushinsky et al. 2016 and Johnson et al. 2015 comment on Argo Canada floats) and less likely the region.

P10, lines 3-4: While they authors may [not] have found a significant drift, I believe they also had fewer measurements and the floats were not raised out of the water as high.

P10L4: It would be interesting to verify this; however, this is likely out of the authors' hands. If the authors get the chance, having this verified (or simply getting a pers. comm. from Johnson et al.) would provide a much greater level of credibility. Otherwise, this comes across as purely speculative and out of place.

In fact, this paragraph needed revision. Johnson et al. 2015 did not filter their data but used only floats where they had at least one full seasonal cycle of float data. While they did observe a similar carry over effect, they argued that it is negligible on annual and longer time scales since surface  $O_2$  supersaturations are typically small ( $<3\%$ ) for most of the year. Over their set of floats, they did find individual floats that drifted significantly. However, that drift occurred both positive and negative and on average

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they concluded to have no statistical drift. In our view, properly accounting for the carry over may change the distribution/histogram of their drift rates. We assume that the Johnson et al. 2015 data would then more likely resemble the distribution of Bushinsky et al. 2016 (who also observed some individual positive drift rates), i.e., a distribution skewed towards / with a mean at slightly negative drift rates (order of  $-0.5$  to  $0$  %  $\text{yr}^{-1}$ ). Still, this remains speculation and we removed it from the manuscript.

The floats of Johnson et al. 2015 were APEX floats with an air bladder, similar to our Navis floats. Also, their optodes were typically mounted on 10 cm stalks above the CTD top cap, so that the height above the water should be comparable. It is true that they only had a few data ( $\geq 1$ ) per surfacing.

P10, last paragraph. This is an interesting and important point. Are the environmental conditions significantly different between the two floats? If environmental factors control the in situ drift rate, then one would expect all 4 optodes on both floats (which seem to be deployed in the same location) to drift similarly. Instead one float has two optodes drifting twice as fast as the other float. But different manufacturer's optodes drift at similar rates on the same floats. And one optode is housed, the other is not. I'm not sure you can necessarily answer many questions here, but it might be worth expanding on this point for a few sentences, because this comparison gets at some of the central questions surrounding in situ drift in oxygen optodes

We do agree with this point and added this to the text: Concerning the different in situ drift rate between the two floats, the only obvious difference is that the second pair of optodes was deployed a year later and subjected to a second laboratory calibration before deployment. Otherwise, they were from the same batch, treated the same, and the floats were deployed in comparable field conditions.

P12L17: rephrase "easier accessible"

Removed.

In addition to the changes noted here, we updated the analyses to include new float data until December 2016.

Thierry V., H. Bittig, D. Gilbert, T. Kobayashi, K. Sato, C. Schmid, 2016: Processing Argo OXYGEN data at the DAC level, v2.2, <http://dx.doi.org/10.13155/39795>

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Interactive comment on Ocean Sci. Discuss., doi:10.5194/os-2016-75, 2016.

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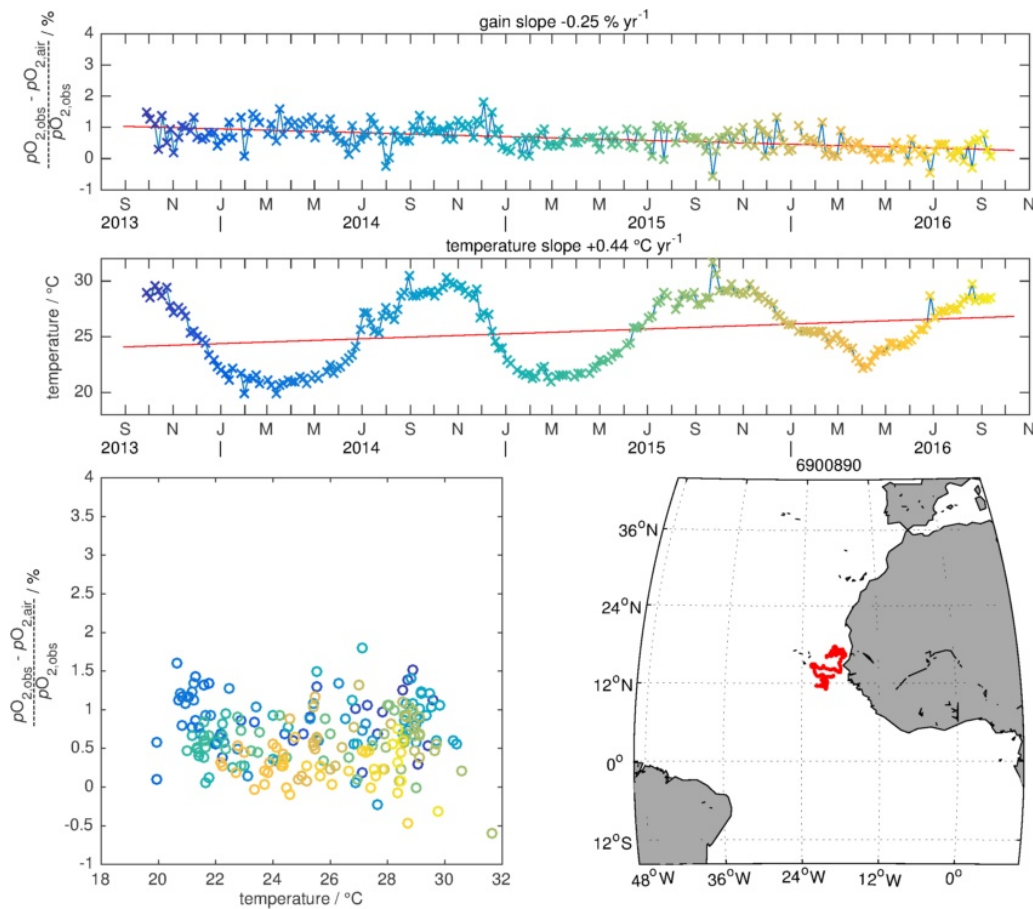


Fig. 1.



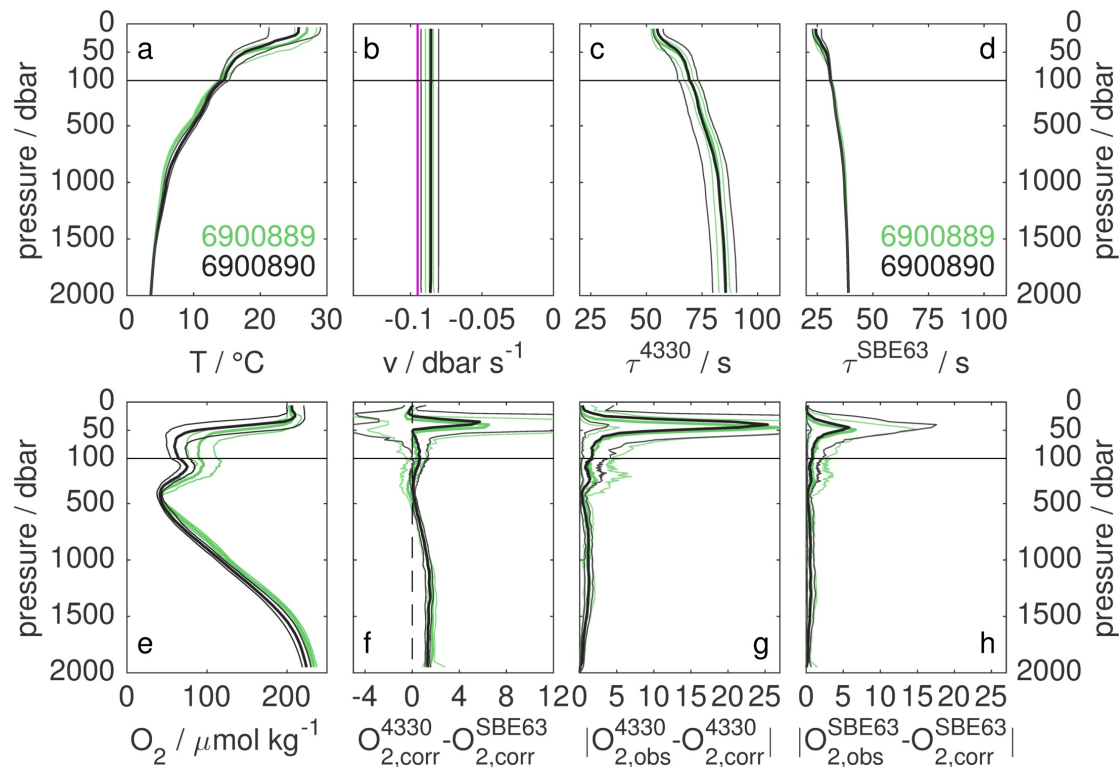


Fig. 2.

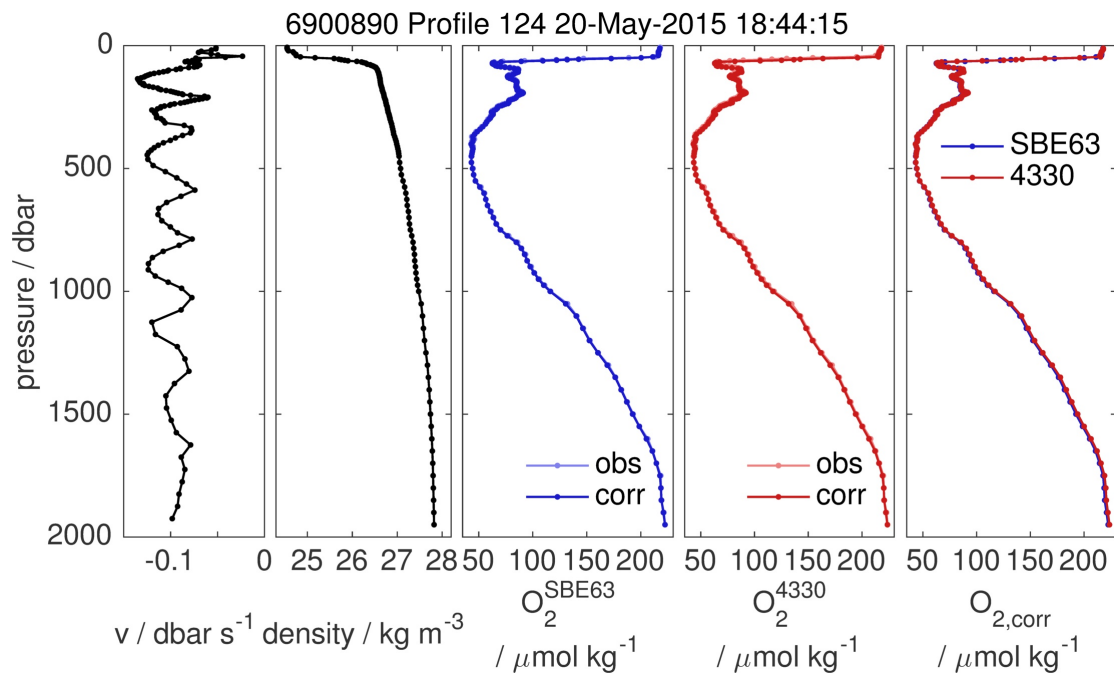


Fig. 3.

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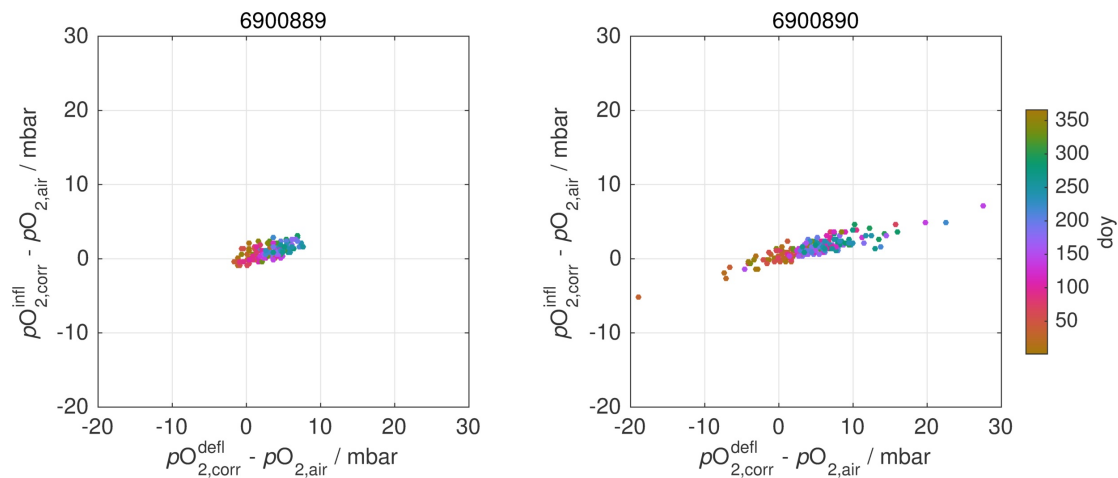


Fig. 4.

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