frontiers (submitted)

Oxygen Optode Sensors: Principle, Characterization, Calibration and Application in the Ocean.

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Outline

Sensor Principle

Sensor Characterization

- O_2 and temperature
- Salinity
- Hydrostatic pressure
- Time #1: Sensor time response
- In-air calibration approaches (avg. gain, carry-over, what’s water/air)
- Time #2: Optode drift behaviour (“storage” and in-situ; pO_2 correction)

Accuracy estimates

- Foil batch / multi-point calibration accuracy; two-point adjustments

Argo updates

- Update of scientific part of cookbook
- In-air data storage in traj files: What’s in water, what’s in air?

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Accuracy estimates

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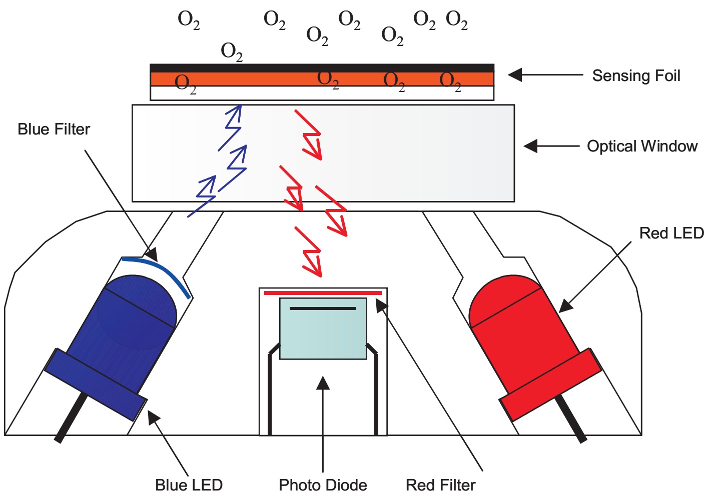
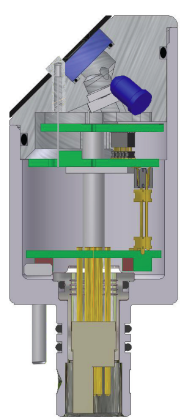
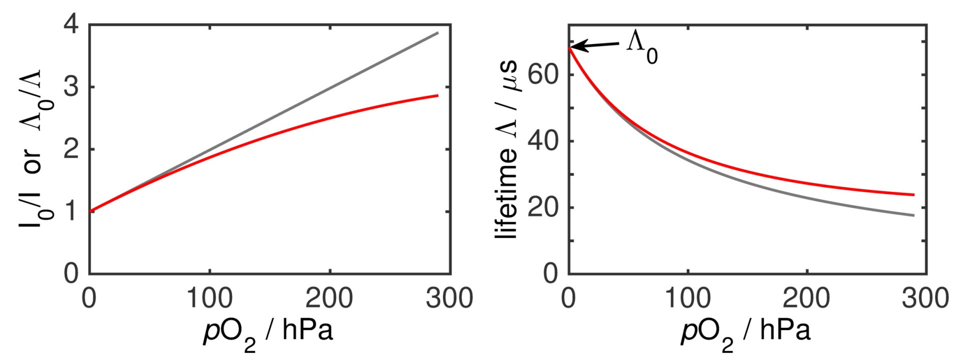
Sensor Principle

- Dynamic luminescence quenching → $c(O_2)^M$ inside sensing foil
- Immersed inside sensing foil → Equilibrium between sensing foil & seawater: equal pO_2!
- Non-linear Stern-Volmer behaviour **O_2 optodes are pO_2 sensitive**



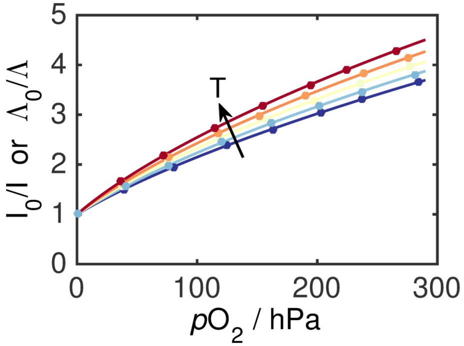


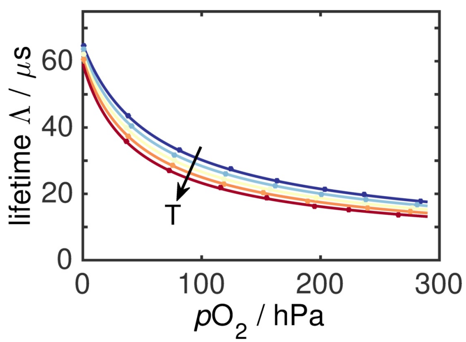
$$\frac{I_0}{I} = \frac{\Lambda_0}{\Lambda} = 1 + K_{SV} \cdot pO_2$$ linear Stern-Volmer

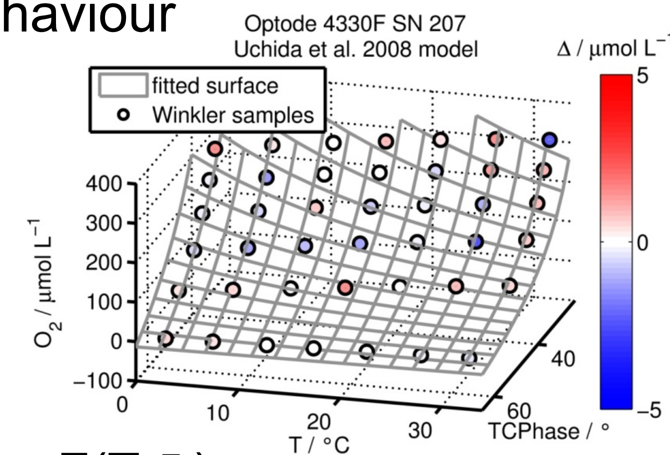


O_2 and Temperature

Non-linear Stern-Volmer (& non-linear O_2) behaviour







Number of (parametric) functional models $O_2 = F(T,\Phi)$

e.g., AADI polynomial, Uchida et al. 2008, Uchida et al. 2010, Sea-Bird ~2013, McNeil and D'Asaro 2014, Bittig et al. subm., ...

Salinity

No salinity influence: Salinity-impermeable sensing foil.

"Salinity correction" comes only from pO_2 c(O_2) conversions:

c(O_2) pO_2 "freshwater c(O_2)"

$$c_{O_2,\mathrm{adj}}\big|_S = \frac{1013.25\,\mathrm{hPa} - p\mathrm{H_2O}(\vartheta, S\!=\!0)}{1013.25\,\mathrm{hPa} - p\mathrm{H_2O}(\vartheta, S)} \cdot \mathrm{S_{Corr}} \cdot c_{O_2,\mathrm{adj}}\big|_{S=0}$$

O_2 conversions?

SCOR WG 142: Recommendations on O_2 quantity conversions (incl. Matlab functions) google or DOI:10.13155/45915

```
function pO2=O2ctoO2p(O2conc,T,S,P)
%function pO2=O2ctoO2p(O2conc,temp,sal,pres)
%
% convert molar oxygen concentration to oxygen partial pressure
%
% inputs:
%   O2conc - oxygen concentration in umol L-1
%   T      - temperature in ∞C
%   S      - salinity (PSS-78)
%   P      - hydrostatic pressure in dbar (default: 0 dbar)
%
% output:
%   pO2    - oxygen partial pressure in mbar
%
% according to recommendations by SCOR WG 142 "Quality Control Procedures
% for Oxygen and Other Biogeochemical Sensors on Floats and Gliders"
%
% Henry Bittig
% Laboratoire d'OcÈanographie de Villefranche-sur-Mer, France
% bittig@obs-vlfr.fr
% 28.10.2015

% set input default
if nargin<4, P     = 0;       end

xO2     = 0.20946; % mole fraction of O2 in dry air (Glueckauf 1951)
pH2Osat = 1013.25.*(exp(24.4543-(67.4509*(100./(T+273.15)))-(4.8489*log(((273.15+T)./100)))-0.000544.*S)); % saturated water vapor in mbar
sca_T   = log((298.15-T)./(273.15+T)); % scaled temperature for use in TCorr and SCorr
TCorr   = 44.6596.*exp(2.00907+3.22014.*sca_T+4.05010.*sca_T.^2+4.94457.*sca_T.^3-2.56847e-1.*sca_T.^4+3.88767.*sca_T.^5); % temperature correction part from Garcia and Gordon (1992), Benson and Krause (1984) refit mL(STP) L-1; and conversion from mL(STP) L-1 to umol L-1
Scorr   = exp(S.*(-6.24523e-3-7.37614e-3.*sca_T-1.03410e-3.*sca_T.^2-8.17083e-3.*sca_T.^3)-4.88682e-7.*S.^2); % salinity correction part from Garcia and Gordon (1992), Benson and Krause (1984) refit ml(STP) L-1
Vm      = 0.317; % molar volume of O2 in m3 mol-1 Pa dbar-1 (Enns et al. 1965)
R       = 8.314; % universal gas constant in J mol-1 K-1

pO2=O2conc.*(xO2.*(1013.25-pH2Osat))./(TCorr.*Scorr).*exp(Vm.*P./(R.*(T+273.15)));
```

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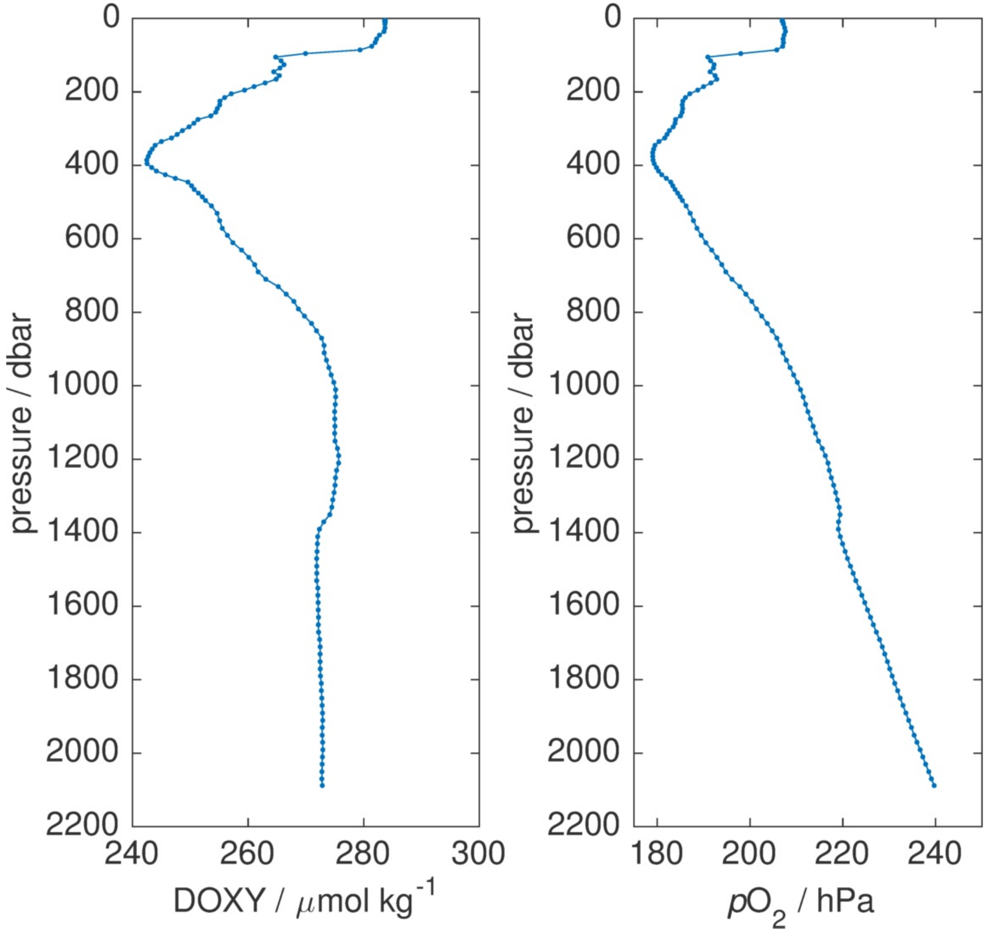


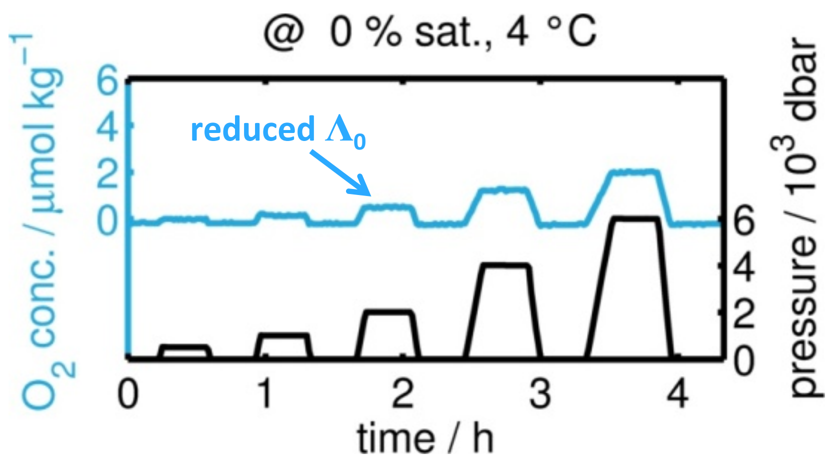
O_2 solubility changes with hydrostatic pressure:

pO_2 ~+14 % per 1000 dbar

Hydrostatic pressure

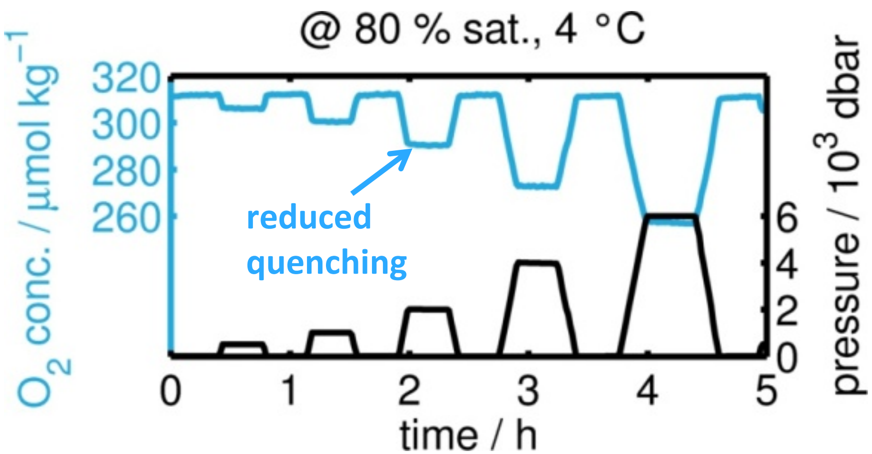
(1) Effect on luminophore:

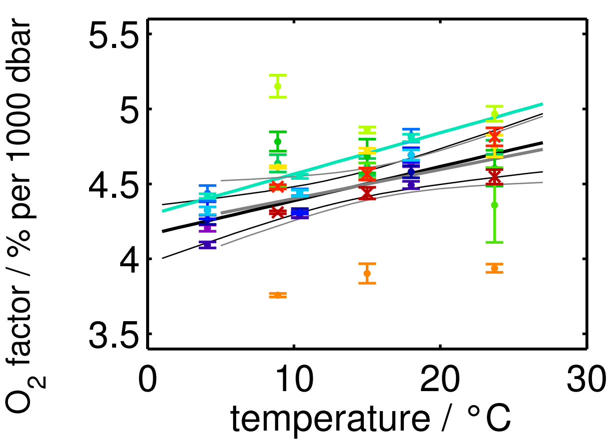
- always there, even at 0 % O_2
- O_2- and T-independent
- Offset on phase shift
- Different for SBE63 & AADI



(2) Effect on O_2 luminescence quenching:

- O_2- and T-dependent
- Same for SBE63 & AADI
- ~4.3 % (±0.3 %) per 1000 dbar





Hydrostatic pressure: Last minute addition

2 Floats with 2 O_2 optodes: Difference between both optodes

Pressure conditioning effect during first ~40 cycles?

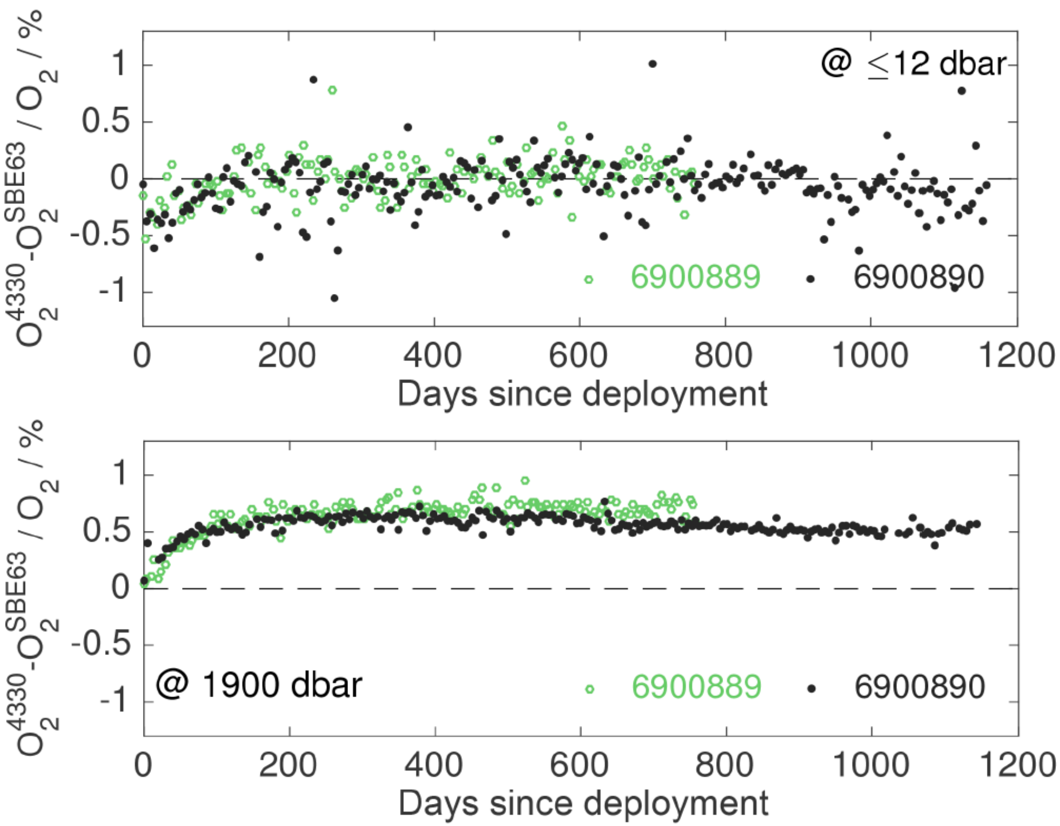


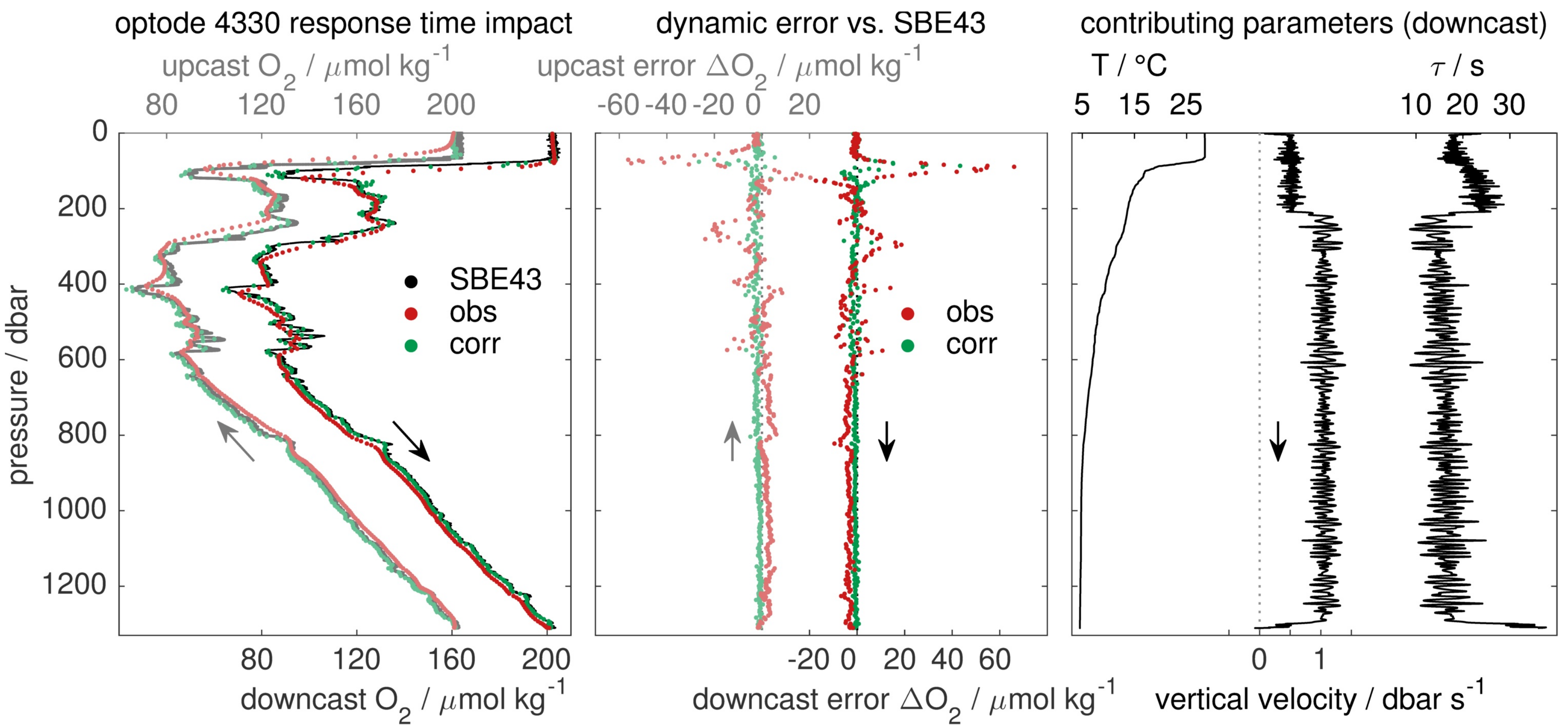
Figure 6. Percent difference between O_2 from the Aanderaa 4330 optode and the SBE63 optode using time response corrected data (top) near the surface and (bottom) at depth for floats 6900889 (green) and 6900890 (black). There seems to be a conditioning effect on either one or both optodes during the first half-year / ≈ 40 profiles, after which differences between optodes are stable.

Time #1: Sensor time response

O_2 molecules need time to diffuse in/out of sensing foil. Causes “lag” and “smearing”. Reasonably-well understood 🎭 Corrections possible.

Time response is faster:

- at higher T (diffusivity & solubility T-dependence)
- with faster flow in front of foil (liquid boundary layer)



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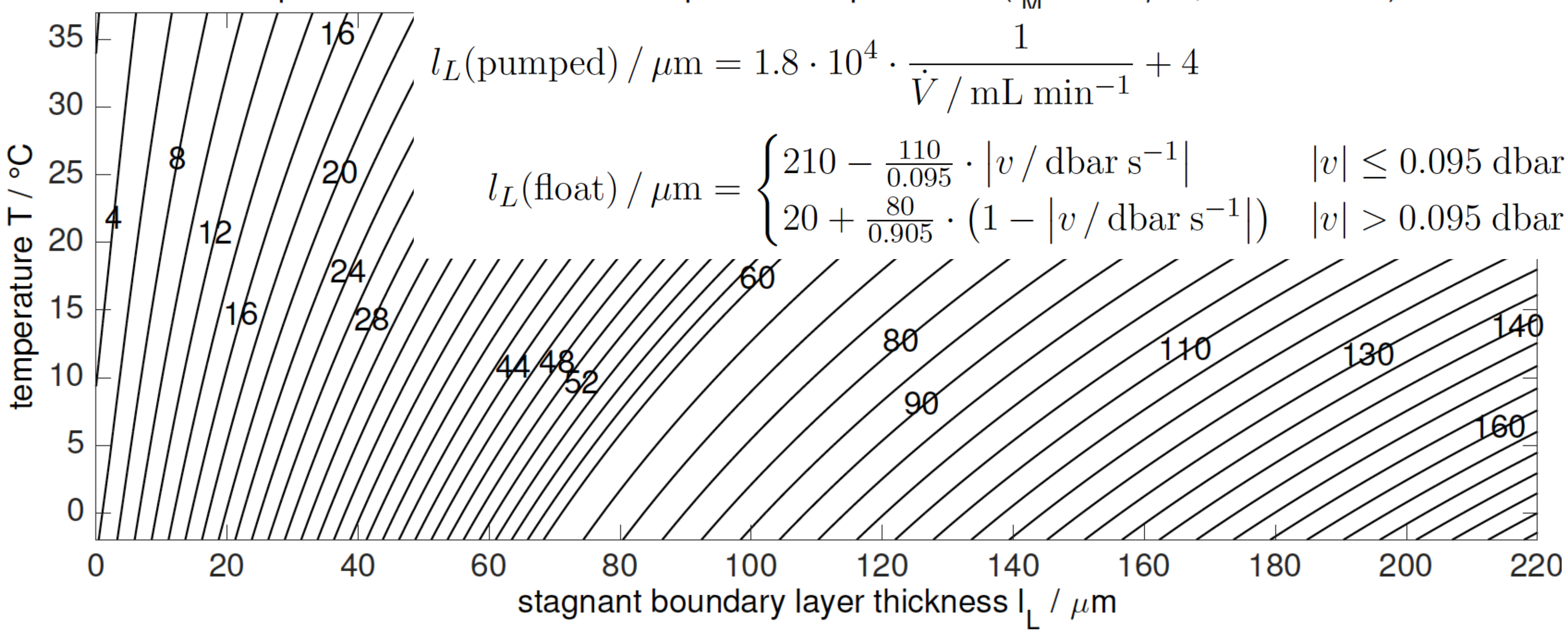
response time τ / s - flow & temperature dependence (l_M = 100 μm, standard foil)



$$l_L(\text{pumped}) / \mu\text{m} = 1.8 \cdot 10^4 \cdot \frac{1}{\dot{V} / \text{mL min}^{-1}} + 4$$

$$l_L(\text{float}) / \mu\text{m} = \begin{cases} 210 - \frac{110}{0.095} \cdot \left|v / \text{dbar s}^{-1}\right| & |v| \leq 0.095 \text{ dbar s}^{-1} \\ 20 + \frac{80}{0.905} \cdot \left(1 - \left|v / \text{dbar s}^{-1}\right|\right) & |v| > 0.095 \text{ dbar s}^{-1} \end{cases}$$

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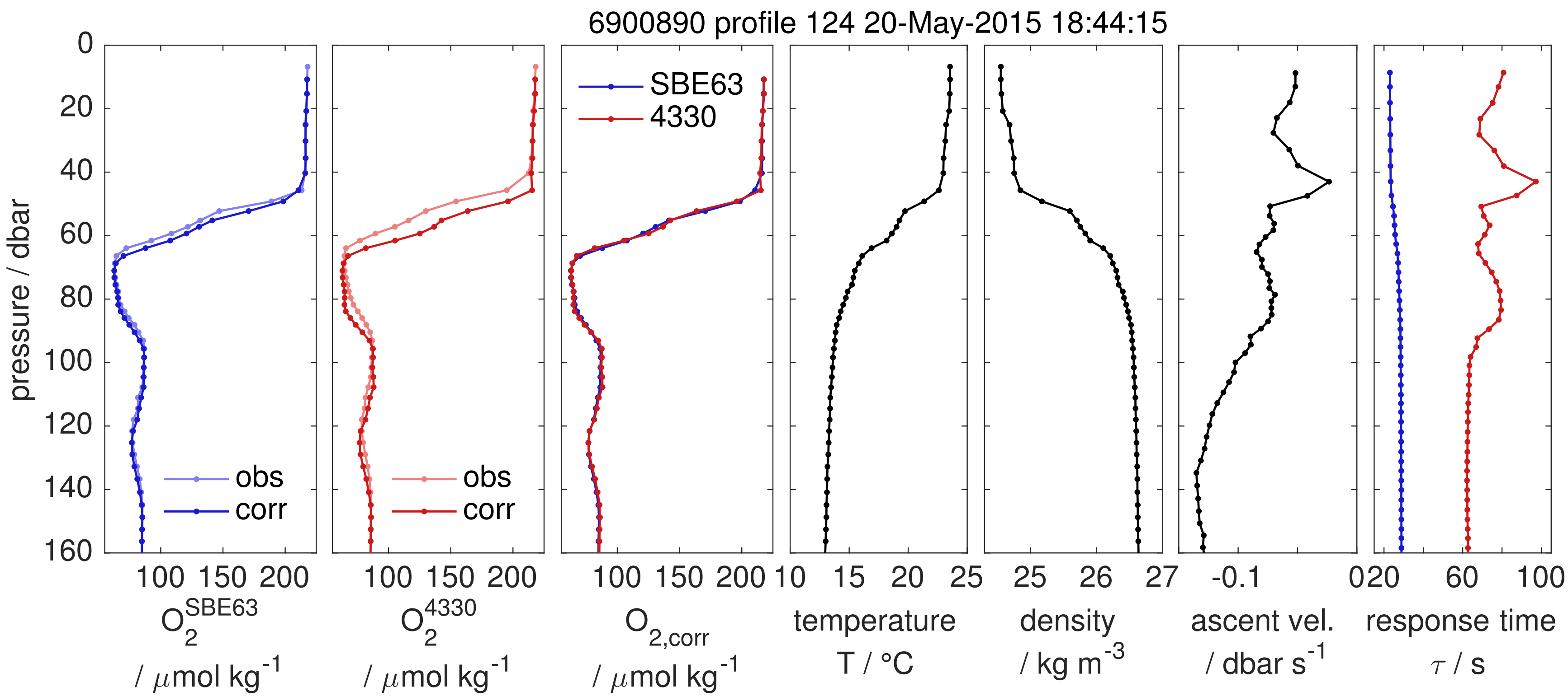


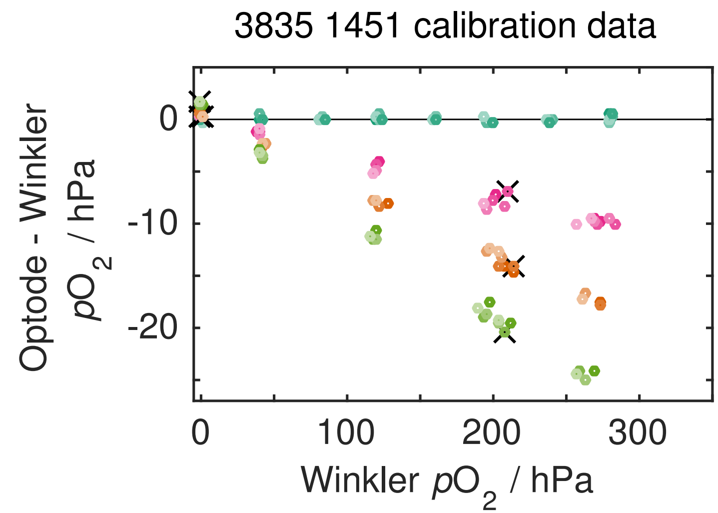
Time #2: Optode drift behaviour

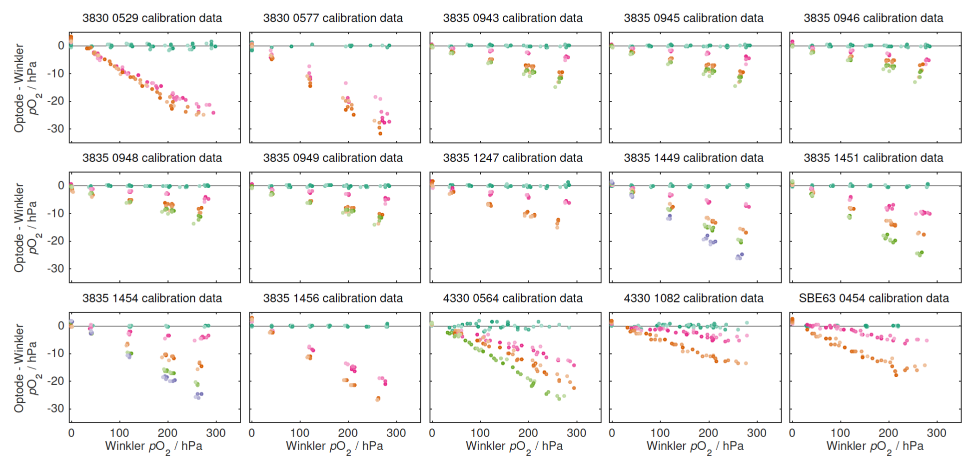
(1) “Storage” drift: Character

- Considerable drift between calibration and later deployment/recalibration
- Order ~5 % per year
- O_2 sensitivity loss
- Linear with O_2
- (Small zero-O_2 intercept)

> Correct with factor on O_2 (!)

> preferably on pO_2
(because of sensing principle)





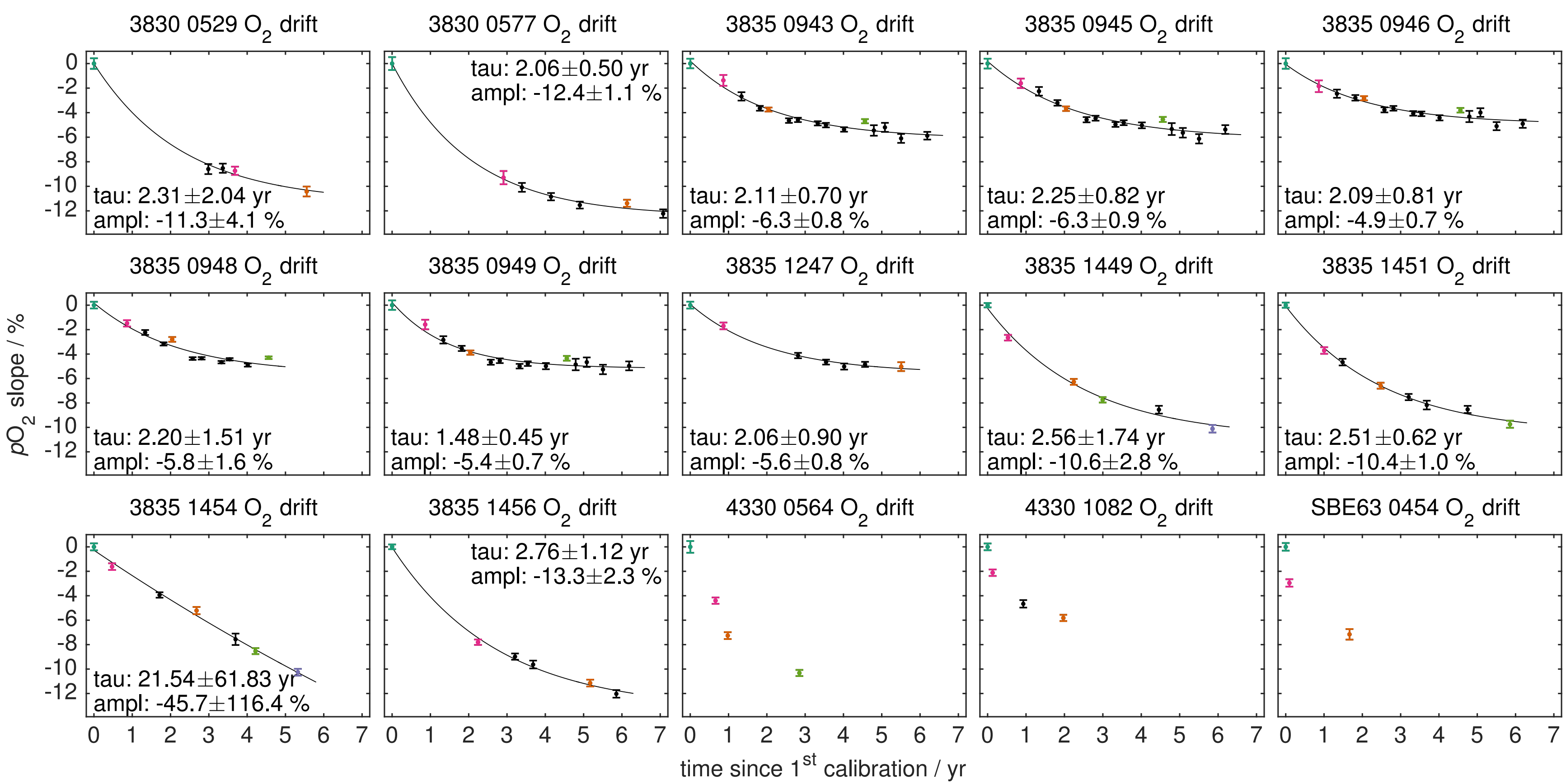
Time #2: Optode drift behaviour

(1) "Storage" drift: Time evolution

Old foils drift less than new foils. 🎭 Unless damaged, don't change foils.

d'Asaro and McNeil (2013): ~2 years exponential time constant

Bittig et al. (subm.): 2.2 ± 0.6 years



In-air calibration

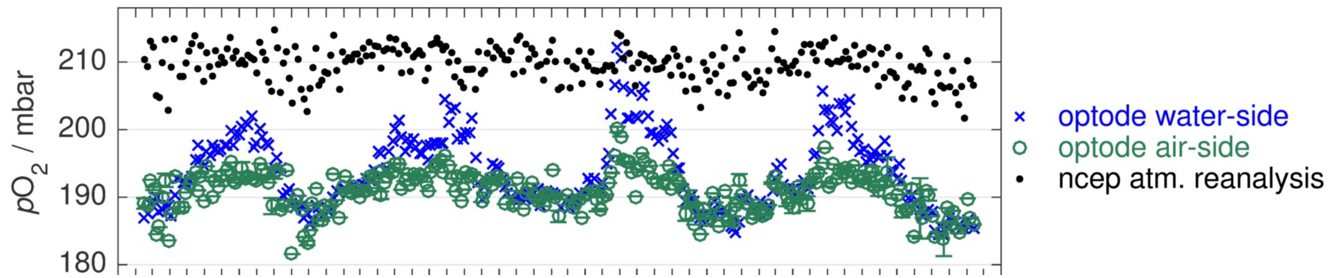
Thanks to simple “storage” drift character!

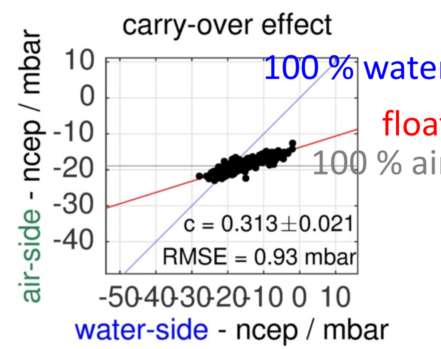
> 1-point correction of O_2 sensitivity loss @ ~205 mbar pO_2

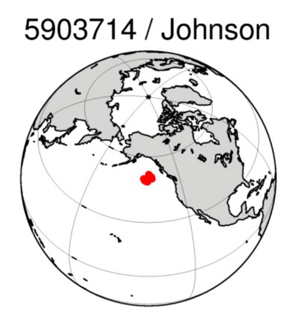
(1) Johnson et al. (2015): mean ratio $pO_{2,\text{optode in-air}}$ / $pO_{2,\text{reference in-air}}$ > simple

(2) Bittig and Körtzinger (2015): linear regression *(i.e., >20 surfacings?)* > robust
$\Delta pO_{2,\text{surface in-air}}$ vs. $\Delta pO_{2,\text{surface in-water}}$ to remove ‘carry-over’ bias

‘Carry-over’ bias can be negligible or present.



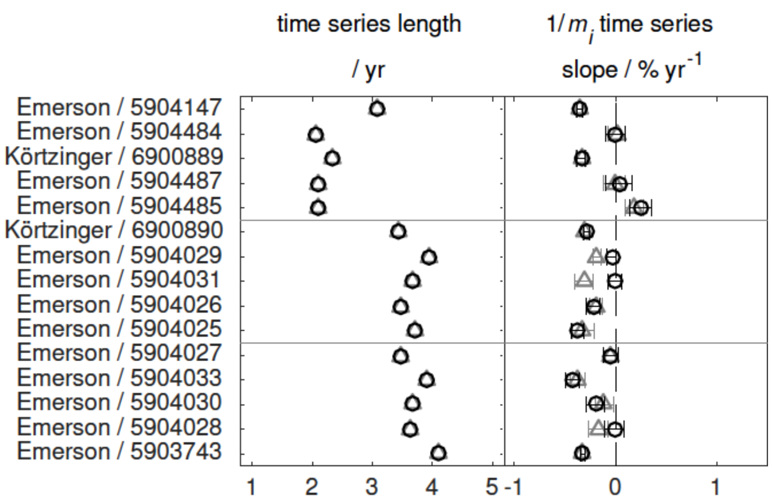


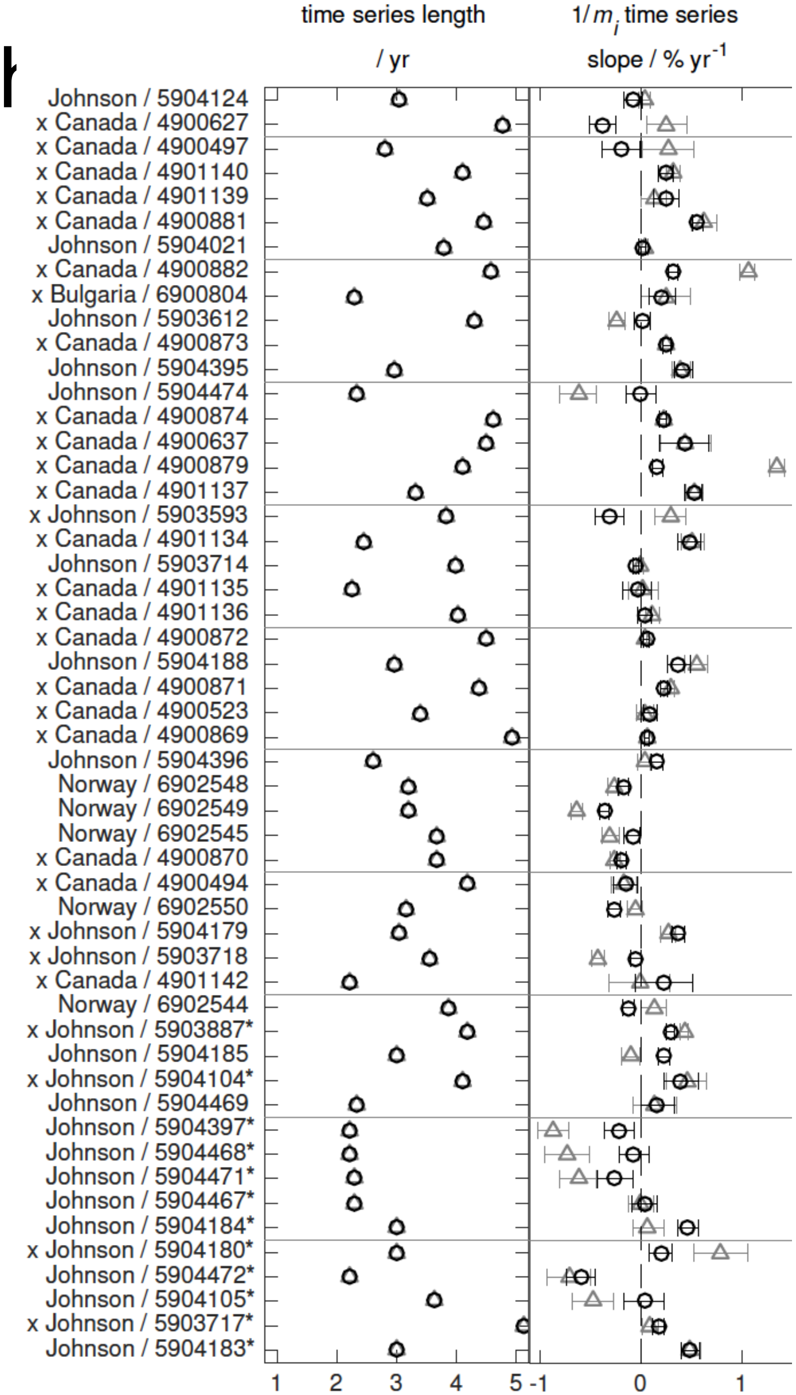


Time #2: Optode drift bel

(2) In-situ drift: Float in-air references

- Order magnitude smaller than “storage” drift
- 15 floats with multi-point > 2 yr & 52 floats with foil batch cal. > 2 yr
- Mixed results: individual optodes can drift significantly (i.e., needing corrections), but average ±0





Accuracy estimates for O_2 adjustments

>150 multi-point (re-)calibrations

- How good are foil batch calibrations?
- How good are multi-point calibrations?
- What is a good way to adjust calibrations?
- What accuracy is realistic for which option?

Adjustment: What’s due to (good/bad) calibration, what’s drift?

(a) Multi-point calibrations

- O_2 response drift of sensing foil between multi-point and re-calibration

(b) Foil batch calibrations

- Variability within the sensing foil batch
- O_2 response drift of sensing foil between multi-point and re-calibration
- Differences between the reference and sensor phase measurements

Accuracy estimates: Method

- 3 approaches (= data density):

i: 2-points at 0 % O_2 sat. (20 °C) & 100 % O_2 sat. (10 °C) (=AADI)

ii: 2x4 points at 0 % & 100 % O_2 sat. (4 – 36 °C)

iii: full re-calibration data

- Refit equations (= How?):

2 degrees of freedom equations; all combinations of slope and/or offset on T, phase and/or O_2

- Assessed by 90-th percentiles of $|\Delta pO_2|$

Accuracy estimates: Multi-point adjustments

Model	N_{Opt}	N_{Cal}	90-th percentile of refit $\lvert\Delta p O_2\rvert$-90-th percentiles / hPa 2 degrees of freedom refits a	b	c	d	e
3830	14	121	4.7 / 2.5 / 1.9	2.0 / 1.7 / 1.1	1.6 / 1.3 / 1.0	1.4 / 1.3 / 1.0	2.6 / 1.9 / 1.5
4330	11	26	4.8 / 2.1 / 1.7	1.8 / 1.9 / 1.7	1.9 / 1.9 / 1.8	2.1 / 2.0 / 1.8	2.7 / 1.8 / 1.7
4330F	2	5	1.3 / 1.2 / 0.6	1.1 / 0.9 / 0.7	1.2 / 0.9 / 0.7	1.1 / 0.9 / 0.6	1.2 / 1.0 / 0.6
SBE63	4	12	2.9 / 2.2 / 1.5	3.5 / 2.3 / 1.4	1.2 / 1.3 / 0.9	1.1 / 1.2 / 0.9	1.9 / 2.0 / 1.5
all	31	164	4.6 / 2.4 / 1.8	2.1 / 1.9 / 1.5	1.7 / 1.5 / 1.3	1.7 / 1.5 / 1.3	2.6 / 1.9 / 1.7

refit equations: (a) $\mathcal{F}_{\mathrm{batch}}(\vartheta, c_1 \cdot \varphi + c_2)$ (b) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + c_2)$ (c) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, c_2 \cdot \varphi)$ (d) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi) + c_2$ (e) $\mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + c_1) + c_2$

- Adjustment approaches: i / ii / iii

i: 2-points at 0 % O_2 sat. (20 °C) & 100 % O_2 sat. (10 °C) (=AADI)

ii: 2x4 points at 0 % & 100 % O_2 sat. (4 – 36 °C)

iii: full re-calibration data

- Most-suitable refit equations: (b) – (d) 🎭 slope on O_2

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- Order ~5 % per year
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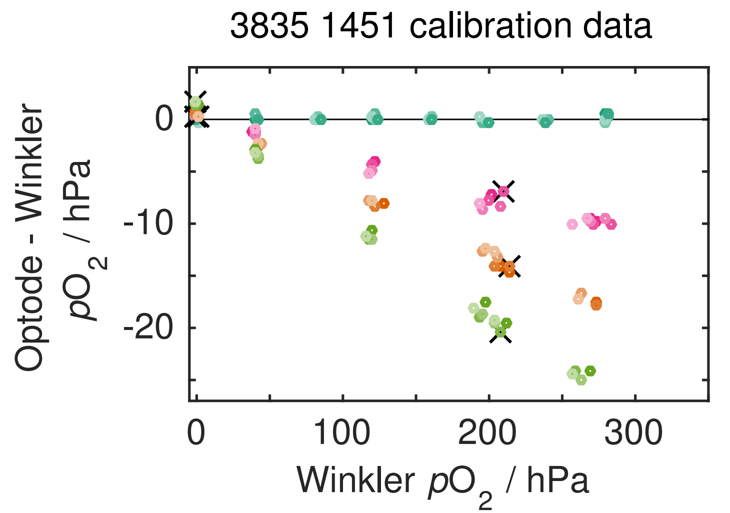
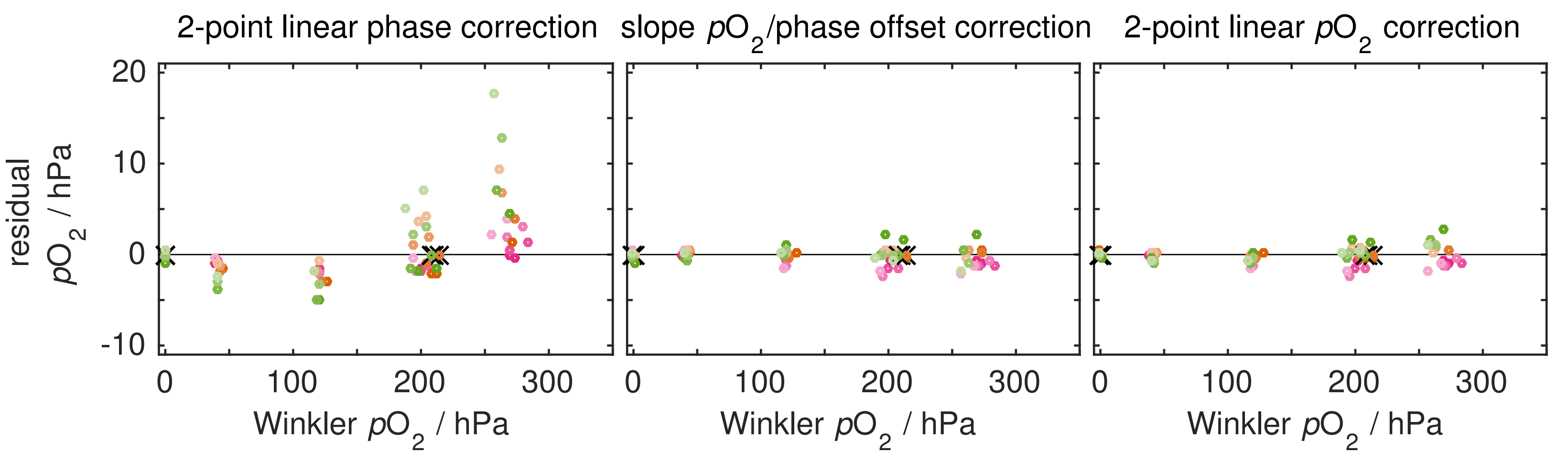
- Linear with O_2
- (Small zero-O_2 intercept)

> Correct with factor on O_2 (!)

> preferably on pO_2
> (because of sensing principle)





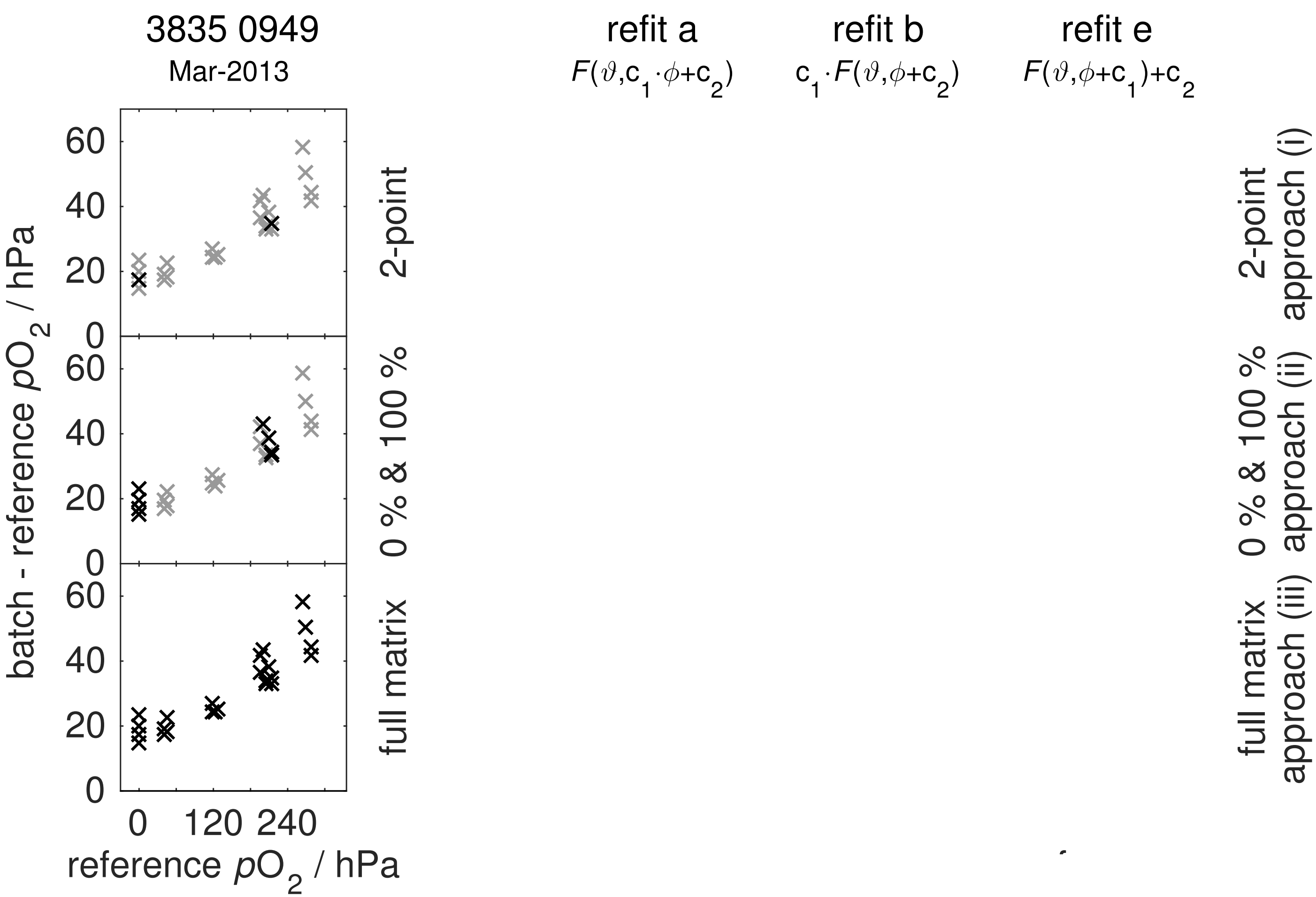
Accuracy estimates: Foil batch adjustments

Model	FoilID	N_{Opt}	N_{Cal}	2 degrees of freedom refits		
				a	b	e
3830	1707	5	11	12.9 / 5.2 / 4.5	9.8 / 7.3 / 6.7	5.2 / 4.8 / 4.6
	2408	1	7	15.9 / 6.2 / 6.0	7.4 / 7.8 / 6.8	5.0 / 3.3 / 2.9
	4807	15	83	20.5 / 9.0 / 7.9	8.2 / 7.8 / 6.3	6.8 / 4.1 / 4.2
	5009	4	27	15.0 / 6.9 / 6.3	9.1 / 8.5 / 8.3	3.5 / 3.7 / 2.9
	all	25	128	20.5 / 8.9 / 7.8	9.1 / 8.3 / 7.7	6.7 / 4.1 / 4.2
4330	1023E	21	28	7.0 / 7.1 / 3.9	6.1 / 4.0 / 4.1	5.6 / 5.5 / 3.7
	1206E	11	12	5.5 / 6.6 / 4.1	6.6 / 4.0 / 4.2	6.0 / 5.1 / 4.2
	all	32	40	6.5 / 7.1 / 4.0	6.5 / 3.9 / 4.1	6.0 / 5.3 / 4.1
4330F	2808F	2	5	17.6 / 8.6 / 7.0	4.3 / 2.5 / 2.6	8.8 / 8.0 / 6.2
all	all	59	173	17.7 / 8.1 / 6.8	8.6 / 7.7 / 6.6	6.6 / 5.3 / 4.3

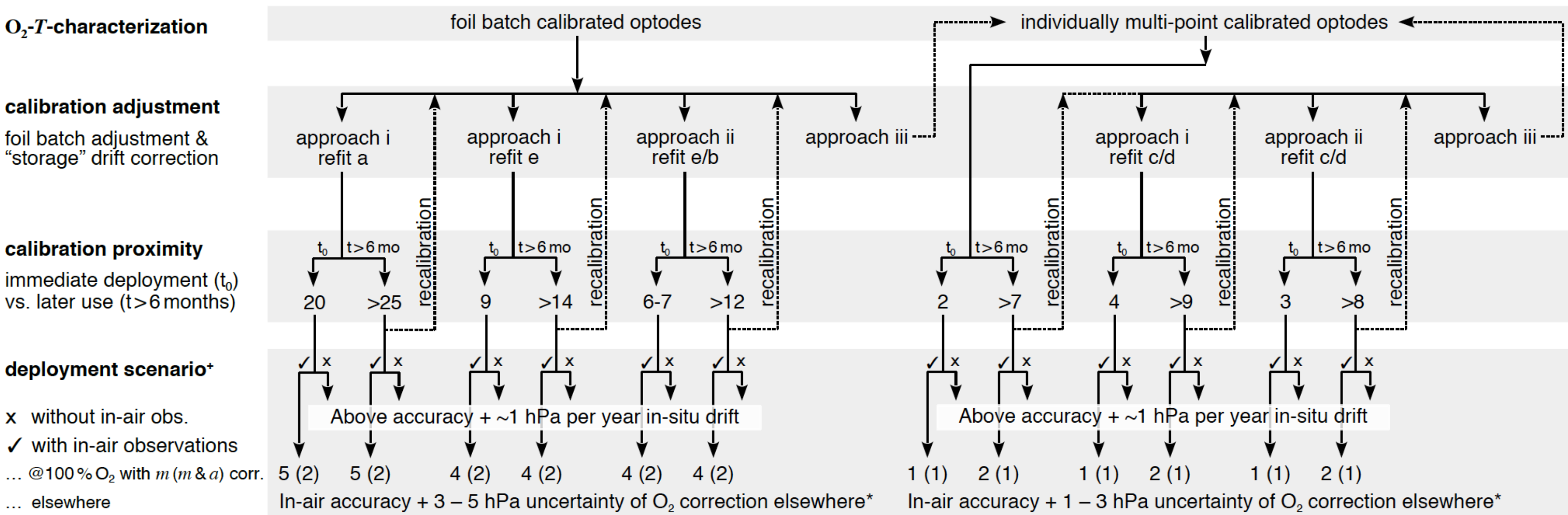
refit equations: (a) $\mathcal{F}_{\mathrm{batch}}(\vartheta, c_1 \cdot \varphi + c_2)$ (b) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + c_2)$ (c) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, c_2 \cdot \varphi)$
(d) $c_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi) + c_2$ (e) $\mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + c_1) + c_2$

- Most-suitable refit equation: (e/b) offset on phase, offset/slope on O_2
- Least-suitable refit equation: (a) offset on phase, slope on phase

Accuracy estimates: Foil batch adjustments



Accuracy estimates: Guidance



* O_2 drift correction applies a slope *m* (or *m* & *a*) on pO_2, based on reference data only at 100 % O_2. Accuracy at other O_2 levels depends on the validity of such a slope-only correction, which relies on an adequate O_2-*T*-characterization.

\+ Accuracies valid at the hydrostatic pressure of the reference. The hydrostatic pressure corrections adds an uncertainty of ca. 0.3 % of the O_2 value per 1000 dbar (from the pressure level of the reference).

adjustment approaches:
(i) two-point adjustment (0 % O_2, 20 °C and 100 % O_2 sat., 10 °C) (Aanderaa standard)
(ii) 0 % and 100 % O_2 sat. adjustment at 4 temperature each (between 4 – 36 °C)
(iii) full multi-point calibration matrix in O_2 and T (20 – 45 points)

refit equations:
(a) $\mathcal{F}_{\mathrm{batch}}(\vartheta, \mathrm{c}_1 \cdot \varphi + \mathrm{c}_2)$ (b) $\mathrm{c}_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + \mathrm{c}_2)$ (c) $\mathrm{c}_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \mathrm{c}_2 \cdot \varphi)$
(d) $\mathrm{c}_1 \cdot \mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi) + \mathrm{c}_2$ (e) $\mathcal{F}_{\mathrm{batch}}(\vartheta, \varphi + \mathrm{c}_1) + \mathrm{c}_2$

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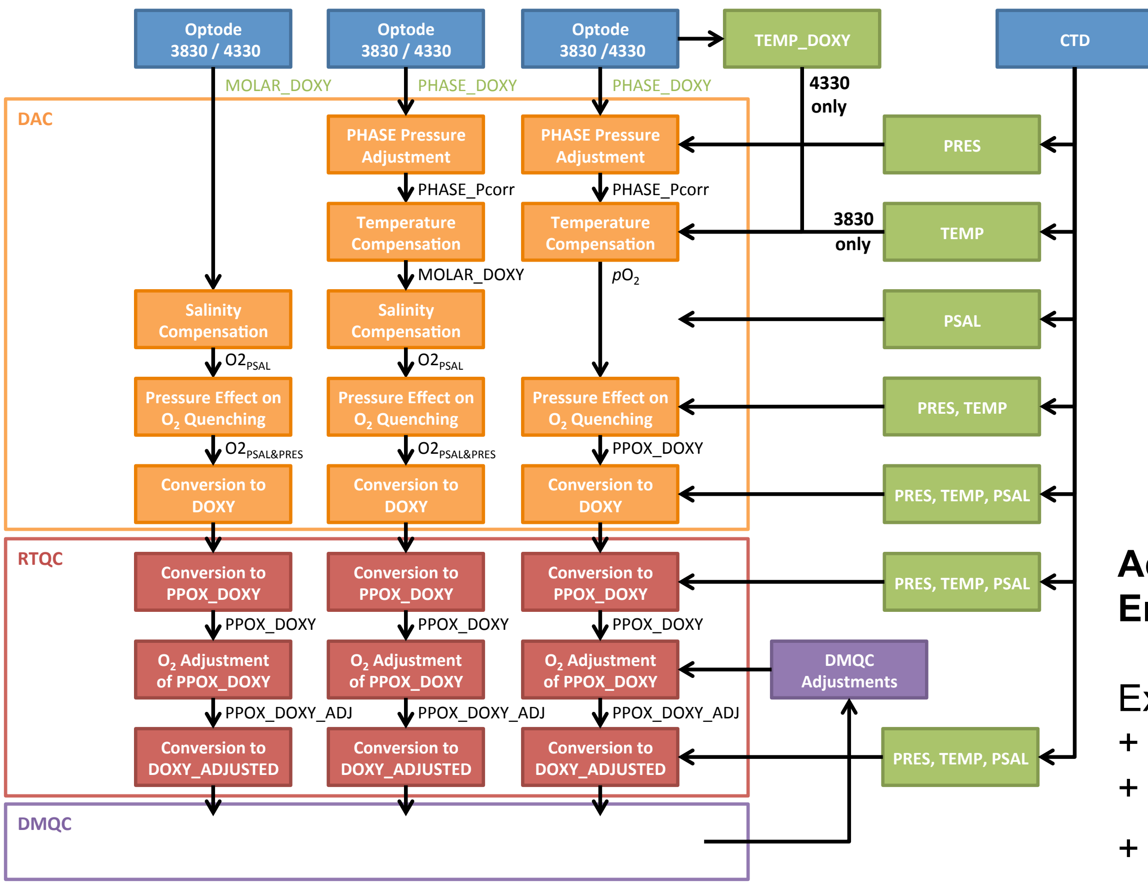
- Time #2: Optode drift behaviour (“storage” and in-situ; pO_2 correction)

Accuracy estimates

- Foil batch / multi-point calibration accuracy; two-point adjustments

Argo O_2 Processing / QC updates

- Update of scientific part of cookbook
- Guidance on adjustment process and adjusted error estimation to reflect adjustment uncertainty in data



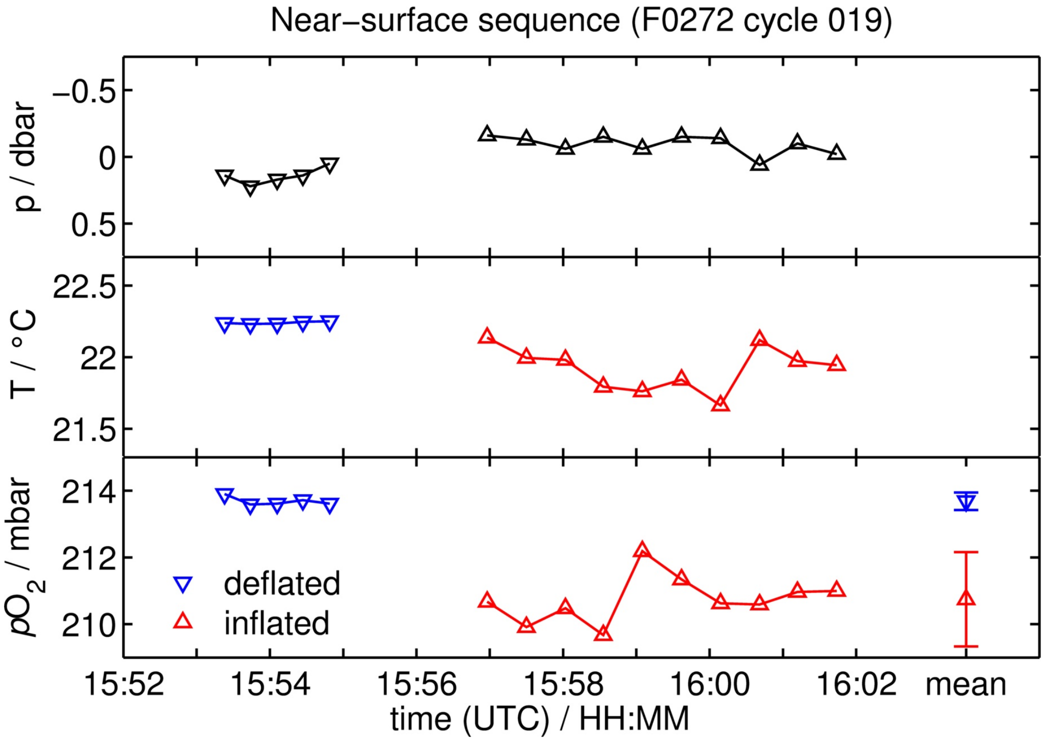
Optode 3830	Case 201_201_301	Cases 201_202_20x and 201_203_20x	No case specified yet. Option for DMQC.
Optode 4330	Case 202_201_301	Cases 202_204_30x and 202_205_30x	No case specified yet. Option for DMQC.

Adjustment on PPOX_DOXY
Error estimate on PPOX_DOXY

Example uncertainty w. in-air calibr.:
+ 95 % CI of in-air gain (@205 mbar)
+ ~2 or ~4 mbar for O_2/T-calibration
+ 0.3 % per 1000 dbar for P correction

Storage of surface data (in-water/in-air)

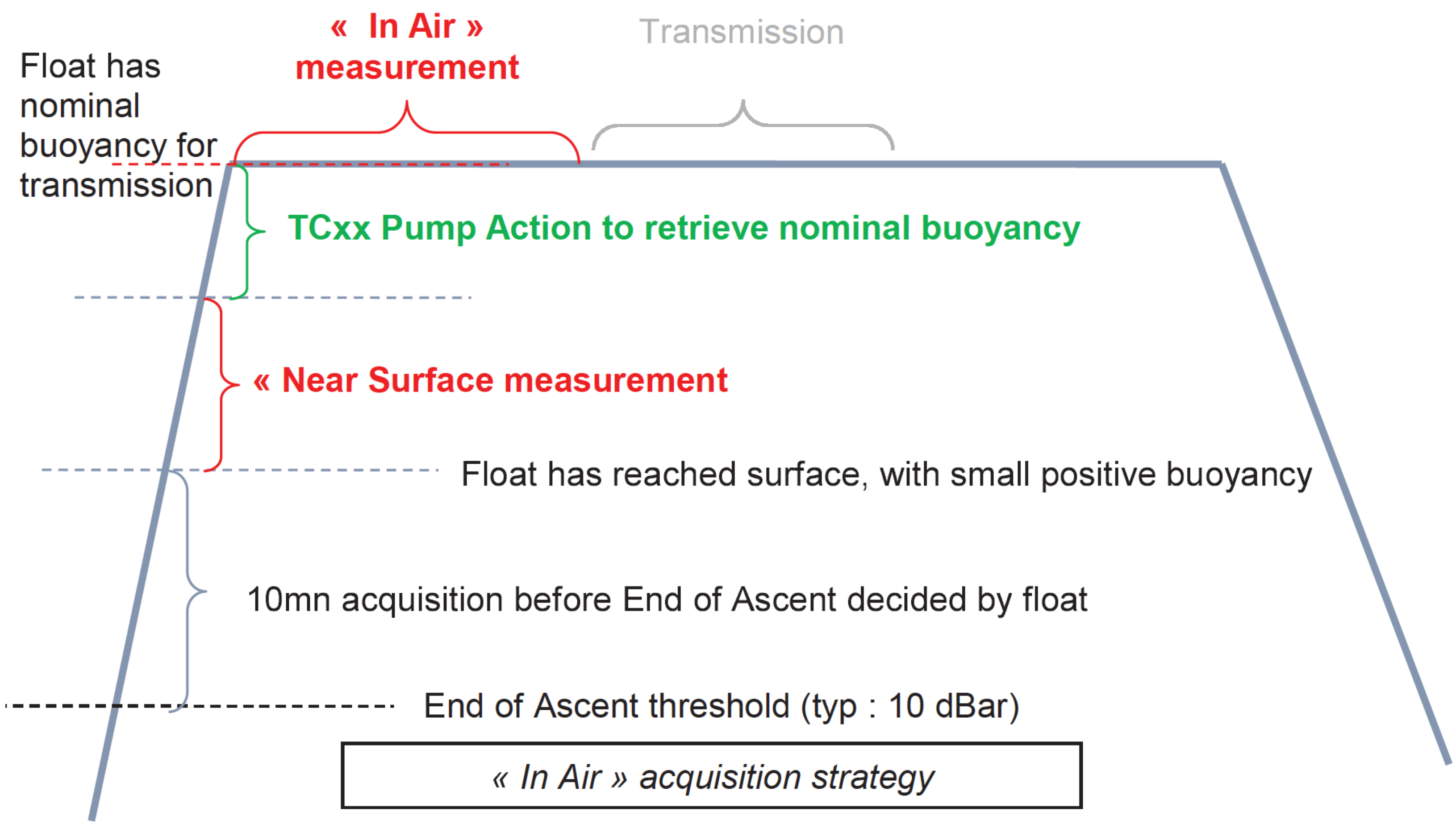
- How to know what's in-air, what's at the surface but in water and what's in water (near the surface)
- How to label it and how to store it (in the b-traj)



- 5 samples @ 20 s before air bladder inflation
- 10 samples @ 30 s after air bladder inflation
- at end of every profile

Storage of surface data (in-water/in-air)

- How to know what's in-air, what's at the surface but in water and what's in water (near the surface)
- How to label it and how to store it (in the b-traj)



Still open issue: ‘Hook’ at base of profile

- First profile (purple): Float outgassing?
- Remaining profiles: Start of profile always lower than “expectation”
- Pronounced with Provor floats
- Cause: In-situ O_2 consumption at base of profile? Relation with bbp spikes when float starts to ascent? → Unknown...

→ QC test necessary !