Oxygen session

8th BGC-Argo, 20th ADMT, Villefranche-sur-Mer, France

Henry Bittig (IOW)

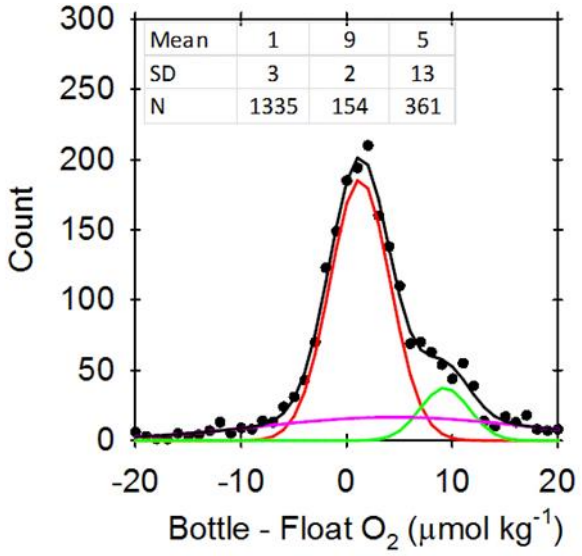
Ken Johnson, Josh Plant, Tanya Maurer (MBARI)

Virginie Thierry (Ifremer), Catherine Schmechtig (CNRS)

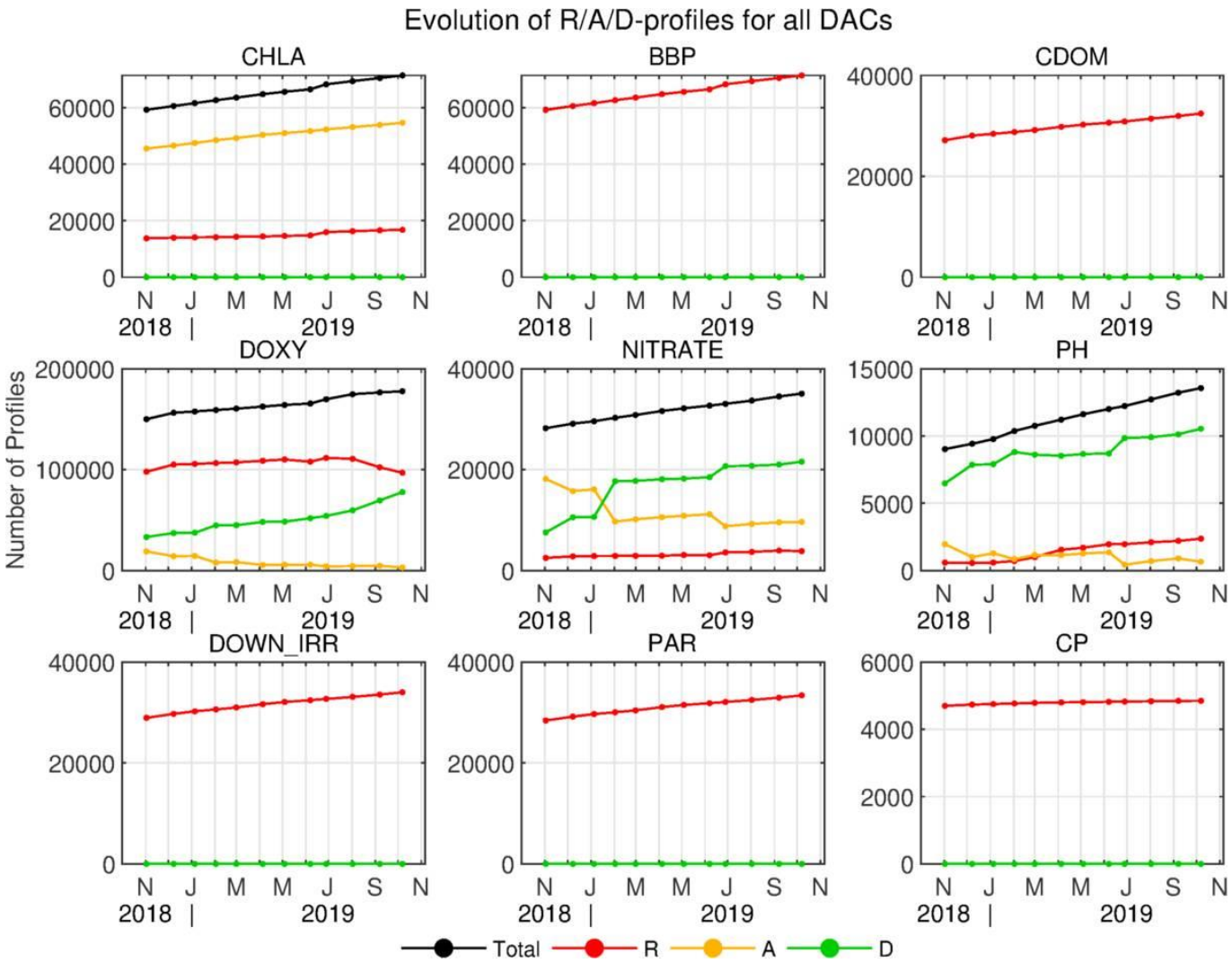
et al.

Good news first: We already came quite some way! ☺

- 180k profiles with DOXY, of which 80k have received DMQC
- Well documented processing and quality control
- Approaching Winkler Quality in the best cases !

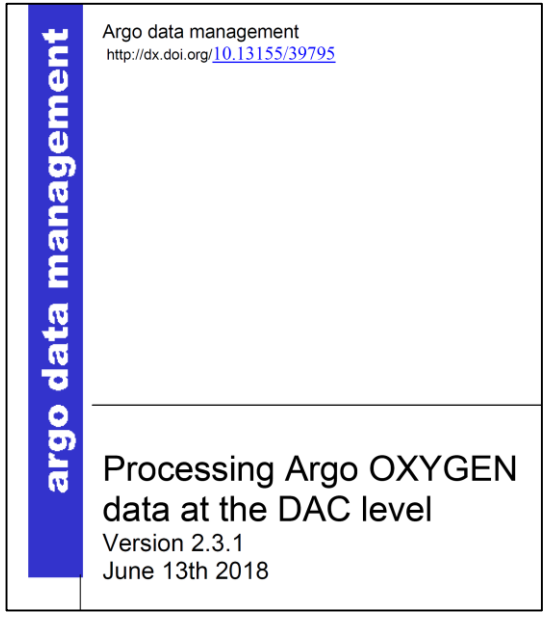


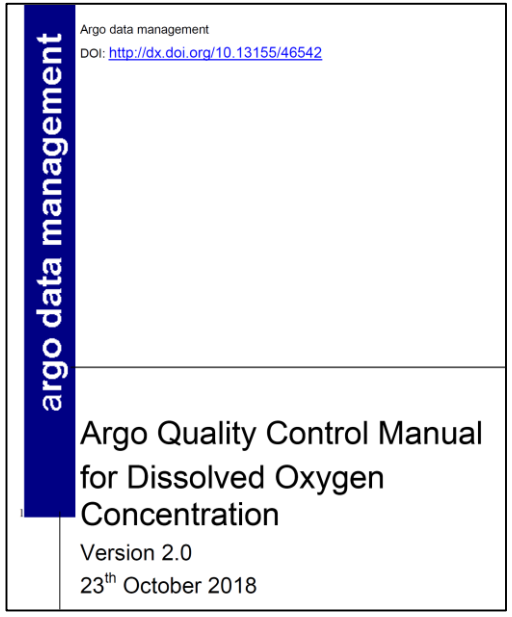
by MBARI / SOCCOM, May 2018

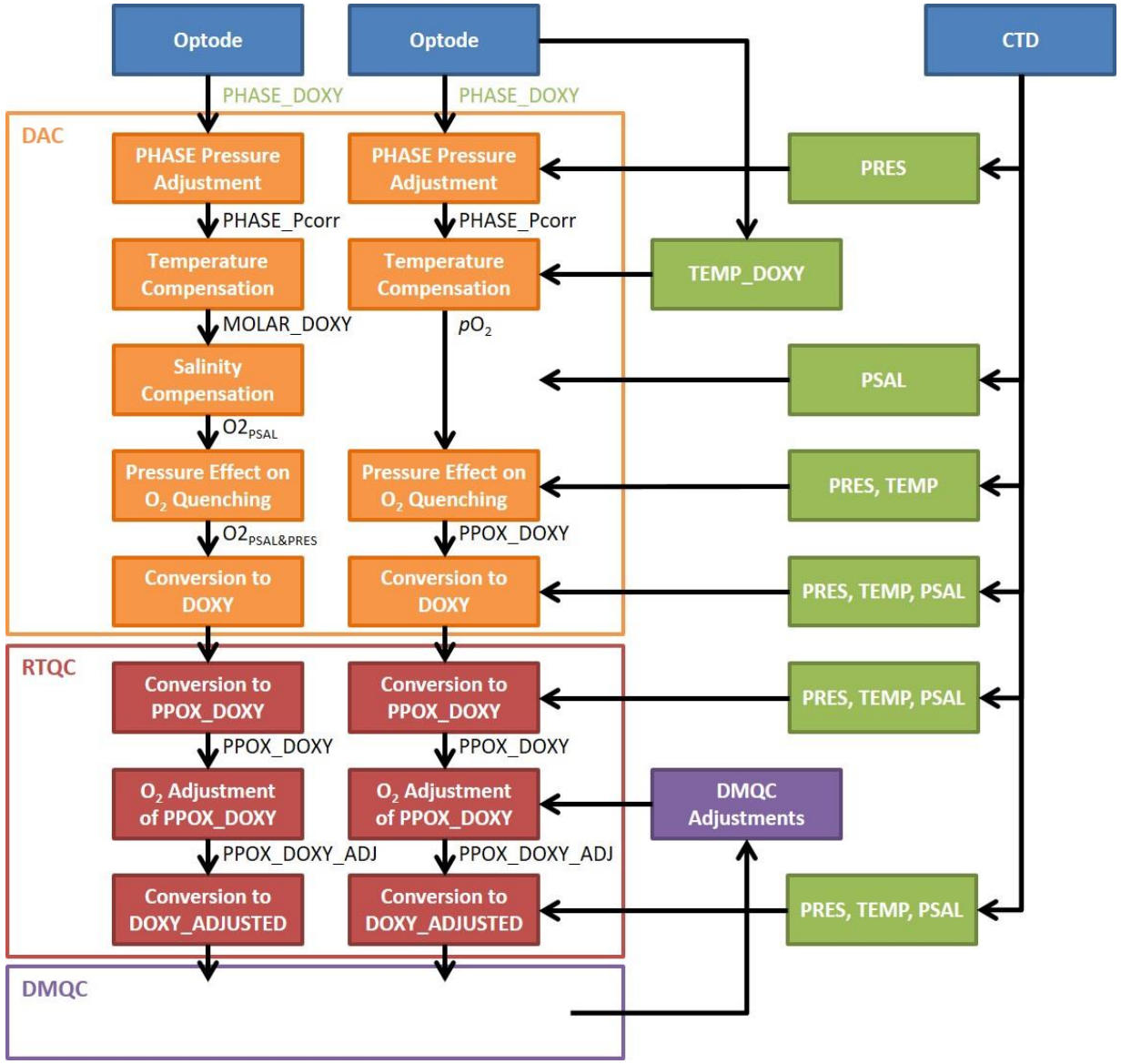


Processing: State of the art

- BGC-Argo DAC cookbook:
  stable; tiny, ca. yearly amendments
- BGC-Argo QC manual:
  essentials present (simple RTQC tests, data adjustment), future refinements expected (finer QC tests, adjusted error estimation, ...)

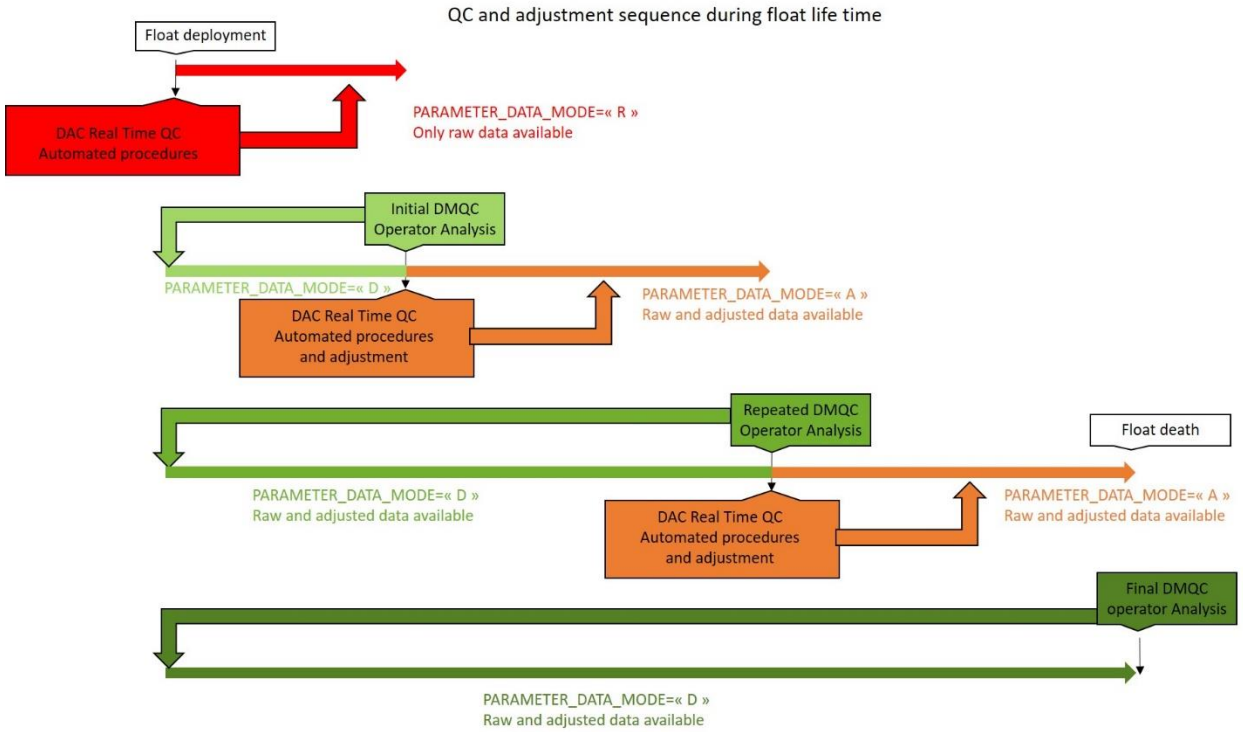


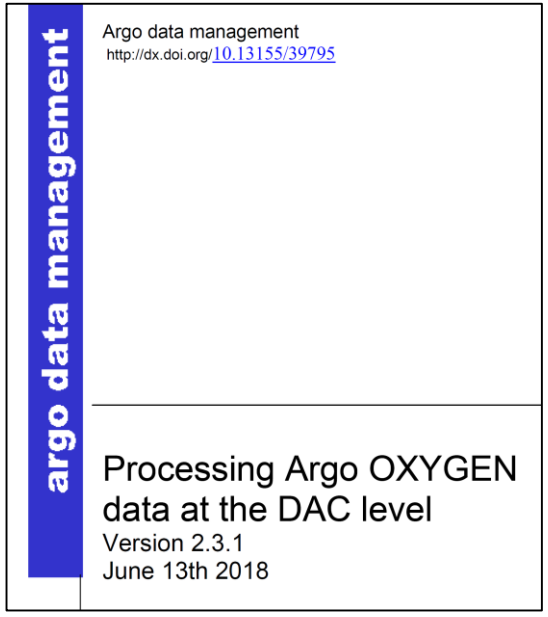


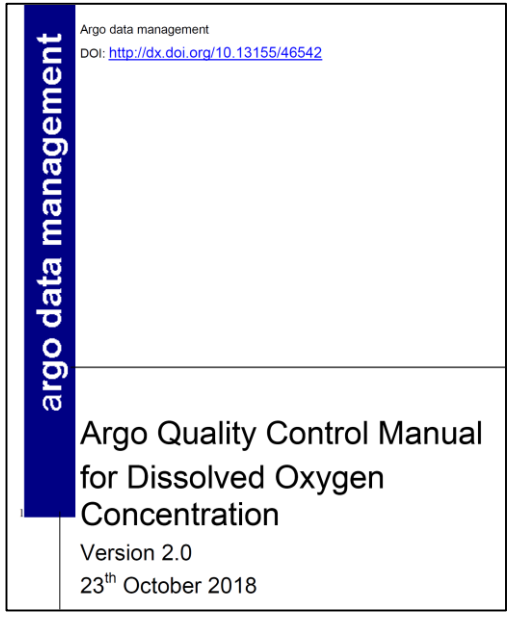


Processing: State of the art

- DAC: Processing raw data -> DOXY
- DAC: RTQC DOXY -> DOXY_ADJUSTED
  (after PI DMQC feedback)
- PI: Quick first DMQC for RT adjustment
- PI: Repeat DMQC in regular intervals







Bittig et al. (2019) A BGC-Argo guide: Planning, deployment, data handling and usage. Front. Mar. Sci. 6:502. doi: 10.3389/fmars.2019.00502

Agenda of refinements

Processing

- PhaseCoef0 issue

RTQC

- Quick biofouling with rapid daily cycling during day
- Need faster ways to filter out (probably) bad data quickly:
  Regional Range Tests, Surface Saturation Test

Adjustments

- Adjustment maths, adjusted error estimate
- Workflow
- Time response correction (DM), MTIME variable

Follow-up: PhaseCoef0 issue

Following modification of cal. procedures after Apr. 2017, not all calibration coefficients were stated on Aanderaa 4330 calibration sheets. Fixed ~Sept. 2018.

Optode 4330 SN range ~2400 - ~3000

-> AO 103, IF 88, IN 10, HZ 7, JA 1 float

New deployments with 4330 optodes in this SN range need checking!

Betreff: [argo-bio] Processing Argo O2 Data and Argo O2 QC
Von: Henry Bittig <bittig@obs-vlfr.fr>
Datum: 14.06.2018 15:05
An: Argo Bio <argo-bio@jcommops.org>, argo-dm <argo-dm@jcommops.org>

Dear Argo-bio and Argo-dm lists,

please find attached the updated O2 cookbook and QC manual with modifications according to the last ADMT meeting and with the request for comments within the next three weeks (until July 5), after which they will be posted on the ADMT website.

Modifications to the versions distributed before ADMT18 in Hamburg are
O2 cookbook:
- There was a typo in the O2 solubility's B2 factor: Its value is -1.0341e-2, not -1.0341e-3.
The impact is minor and probably doesn't merit a full DOXY reprocessing in its own, but should be corrected for new data (all DACs).
- Aanderaa 4330 optode multi-point calibrations after Apr. 2017 may include a PhaseCoef0 different from 0. This is included in the optode internal config, but it is not stated on the calibration certificates. If the calibration certificates are used by a DAC, PhaseCoef0=0 or PhaseCoef0~=0 must be verified by re-calculation of the calibration data. The value of PhaseCoef0 is retrievable from the calibration certificates (I can share Matlab code if needed).
- PARAMETER_ACCURACY gives realistic values for different optode calibrations. *They state the "plug & play" accuracy, not the accuracy attainable after adjustment.*

Follow-up: PhaseCoef0 issue – pre

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-> AO 103, IF 88, IN 10, HZ 7, JA 1 float

New deployments with 4330 optodes in this SN range need checking!

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CALIBRATION CERTIFICATE
Form No 830, Juli 2012

Certificate no: 4330_2903_00137192
Foil batch no: 1517M

Product: 4330
Calibration date: 13.11.2017

Serial no: 2903
Page 1 of 2

Index	Temperature reference(°C)	[O2] Reference(µM)	Temperature raw data(mV)	Phase reading(°)
0	29.911	0.75	-203.320	60.49
1	20.131	0.28	112.613	61.64
2	10.326	0.47	438.340	62.47
3	0.836	1.42	737.447	63.18
4	0.913	22.62	735.167	60.27
5	0.987	44.02	732.920	57.63
6	1.016	65.31	732.040	55.27
7	1.034	106.92	731.513	51.33
8	1.064	149.42	730.620	48.00
9	1.083	213.13	730.027	43.97
10	1.119	317.20	728.947	39.06
11	1.149	421.85	728.027	35.48
12	1.172	527.65	727.380	32.73
13	10.315	15.63	438.667	59.45
14	10.199	34.09	442.473	56.28
15	10.134	50.90	444.573	53.76
16	10.107	83.81	445.487	49.57
17	10.092	117.59	445.980	46.08
18	10.082	168.06	446.293	41.96
19	10.074	250.83	446.573	37.05
20	10.100	334.30	445.707	33.52
21	10.086	418.92	446.187	30.88
22	20.071	12.03	114.600	58.28
23	19.970	26.68	117.933	54.80
24	19.933	40.15	119.173	52.06
25	19.916	66.41	119.767	47.62
26	19.912	93.37	119.900	44.01
27	19.914	133.60	119.800	39.83
28	19.925	199.94	119.447	34.94
29	19.931	267.71	119.213	31.50
30	19.940	336.41	118.947	28.95
31	29.963	9.40	-204.920	57.09
32	29.966	21.33	-205.047	53.31
33	29.998	32.35	-206.007	50.37
34	30.024	53.86	-206.827	45.72
35	30.042	75.83	-207.380	42.03
36	30.054	108.90	-207.773	37.81
37	30.063	163.33	-208.027	33.02
38	30.068	219.35	-208.207	29.69
39	30.071	277.09	-208.287	27.24

Page 1

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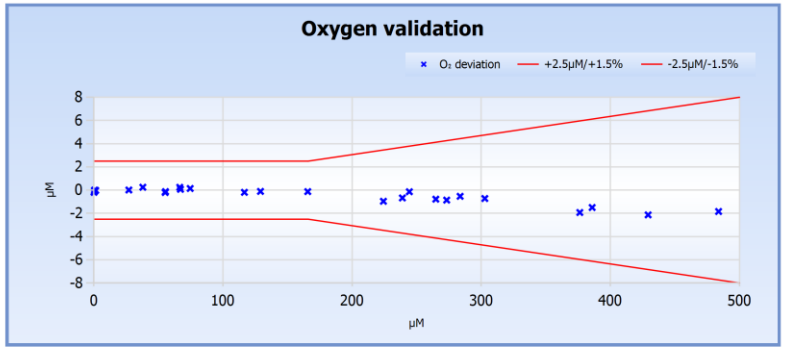
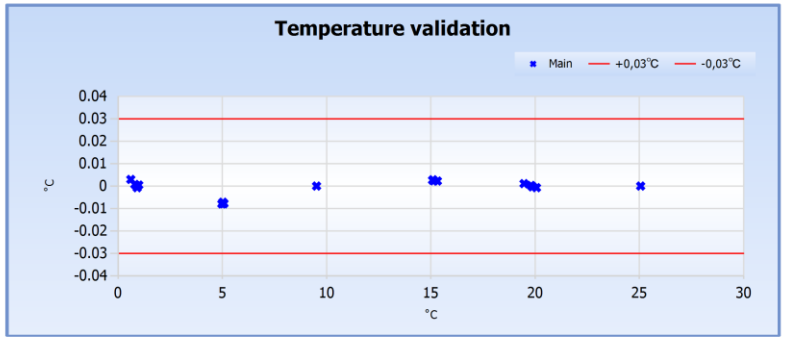
Page 2 of 2

Index	0	1	2	3	4	5	6
SVUFoilCoef	2.80898E-03	1.17750E-04	2.39215E-06	1.25352E02	-2.27661E-01	-3.14673E01	2.48711E00
TempCoef	2.35445E01	-3.05747E-02	2.77781E-06	-4.16717E-09	0.00000E00	0.00000E00	





Date:13.11.2017

Tor-Ove Kvalvaag

Tor-Ove Kvalvaag, Calibration Engineer

Page 2

Follow-up: PhaseCoef0 issue – post

Following modification of cal. procedures after Apr. 2017, not all calibration coefficients were stated on Aanderaa 4330 calibration sheets. Fixed ~Sept. 2018.

Optode 4330 SN range ~2400 - ~3000

-> AO 103, IF 88, IN 10, HZ 7, JA 1 float

New deployments with 4330 optodes in this SN range need checking!

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CALIBRATION CERTIFICATE

Form No 830, Juli 2012

Certificate no: 4330_3023_00151937 | Product: 4330 | Serial no: 3023
Foil batch no: 1517M | Calibration date: 26.09.2018 | Page 1 of 2

Index	Temperature reference(°C)	[O2] Reference(µM)	Temperature raw data(mV)	Phase reading(°)
0	30.457	2.65	-205.107	58.97
1	20.174	2.04	124.520	60.07
2	10.189	2.16	453.520	60.80
3	0.837	2.57	745.127	61.41
4	0.896	20.94	743.373	58.92
5	0.956	43.15	741.613	56.25
6	1.003	64.78	740.220	53.91
7	1.049	107.52	738.893	49.92
8	1.083	151.55	737.847	46.52
9	1.106	216.26	737.187	42.48
10	1.113	319.46	736.993	37.66
11	1.122	427.86	736.673	33.97
12	1.172	532.18	735.220	31.26
13	10.775	16.96	434.447	57.80
14	10.694	34.14	437.073	54.84
15	10.626	50.50	439.273	52.38
16	10.558	83.55	441.467	48.16
17	10.517	117.85	442.840	44.61
18	10.479	169.61	444.060	40.39
19	10.457	254.02	444.753	35.39
20	10.433	335.26	445.540	31.98
21	10.421	420.22	445.927	29.31
22	20.308	13.66	120.080	56.84
23	20.305	27.58	120.200	53.56
24	20.307	41.32	120.093	50.76
25	20.313	67.73	119.900	46.29
26	20.321	94.62	119.633	42.68
27	20.330	135.99	119.400	38.36
28	20.335	202.15	119.200	33.49
29	20.343	269.13	118.907	30.06
30	20.349	338.33	118.733	27.49
31	30.331	11.28	-201.247	55.83
32	30.322	22.29	-200.967	52.40
33	30.322	34.12	-200.993	49.25
34	30.326	55.51	-201.093	44.64
35	30.333	78.37	-201.300	40.79
36	30.335	112.72	-201.387	36.43
37	30.350	166.83	-201.813	31.69
38	30.359	222.92	-202.100	28.36
39	30.363	281.13	-202.207	25.89

Page 1

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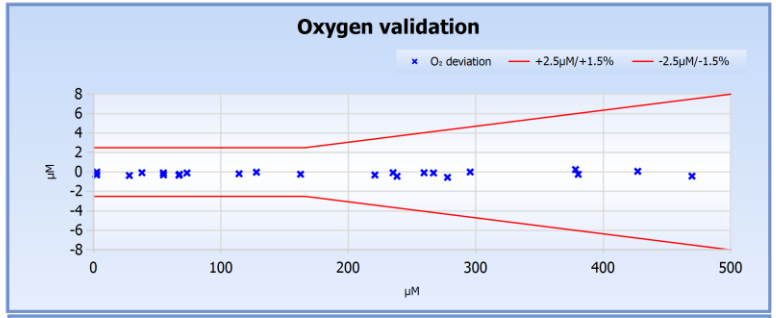
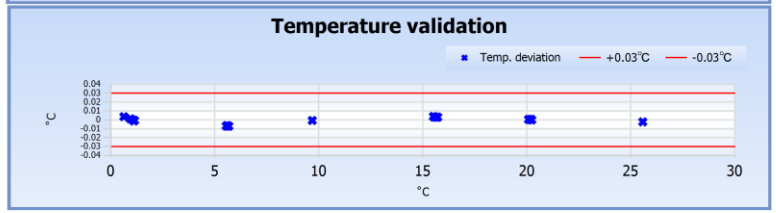
Foil batch no: 1517M | Calibration date: 26.09.2018 | Page 2 of 2

Giving these coefficients

Index	0	1	2	3	4	5	6
SVUFoilCoef	2.72541E-03	1.20870E-04	2.08391E-06	1.65032E02	-1.95740E-01	-3.55476E01	3.26582E00
TempCoef	2.39762E01	-3.08300E-02	2.86136E-06	-4.23999E-09	0.00000E00	0.00000E00	





With following settings

Index	0	1	2	3
PhaseCoef	-4.12000E-01	1.00000E00	0.00000E00	0.00000E00

Index	0 (Offset)	1 (Slope)
ConcCoef	0.00000E00	1.00000E00
Salinity	0.00	

Date:26.09.2018

Tor-Ove Kvalvaag

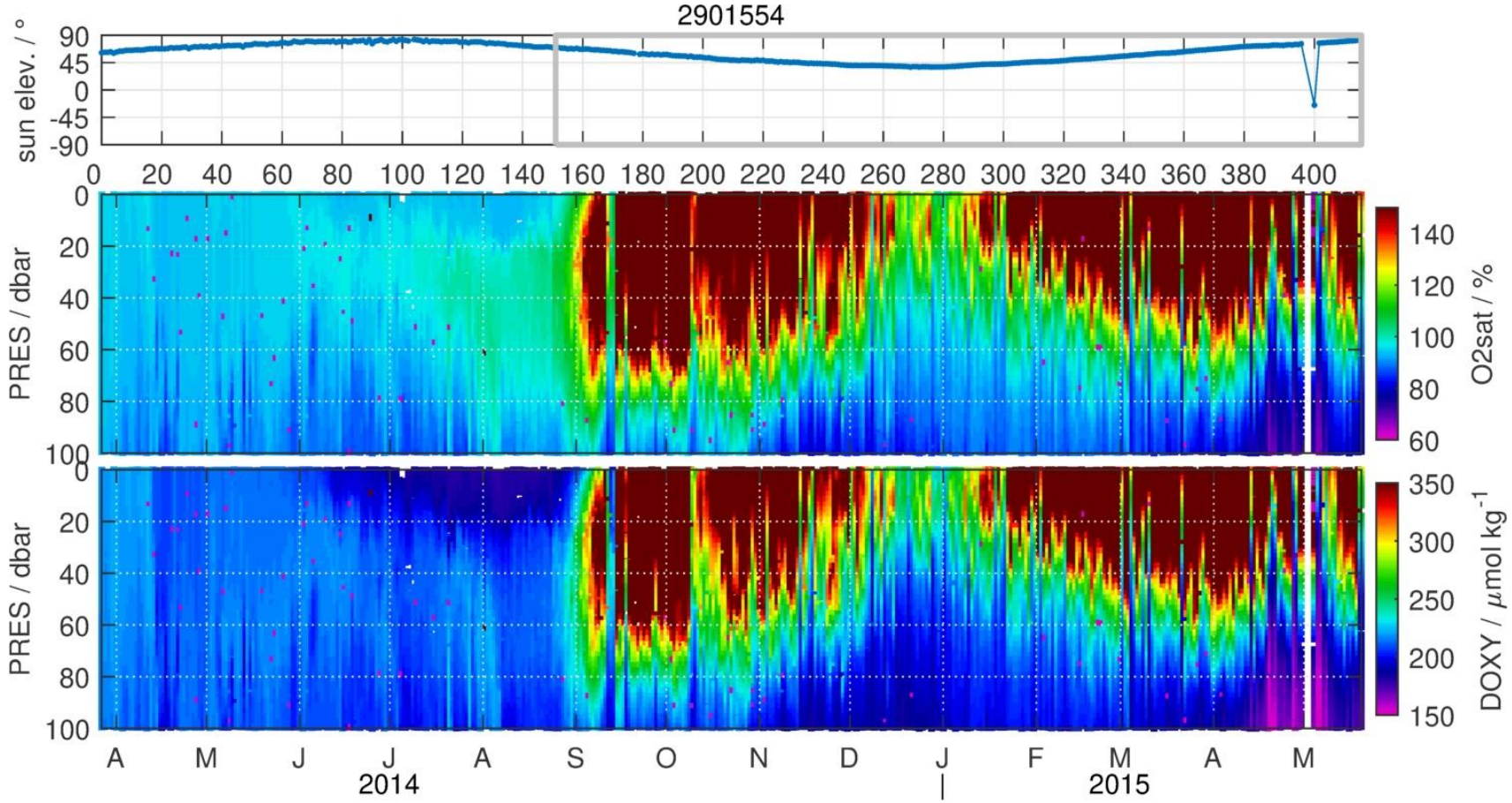
Tor-Ove Kvalvaag, Calibration Engineer

Page 2

Optode biofouling

Avoid continuous daily surfacing during the day in warm areas!
Risk of severe biofouling

- daily during noon



Optode biofouling

Avoid continuous daily surfacing during the day in warm areas!
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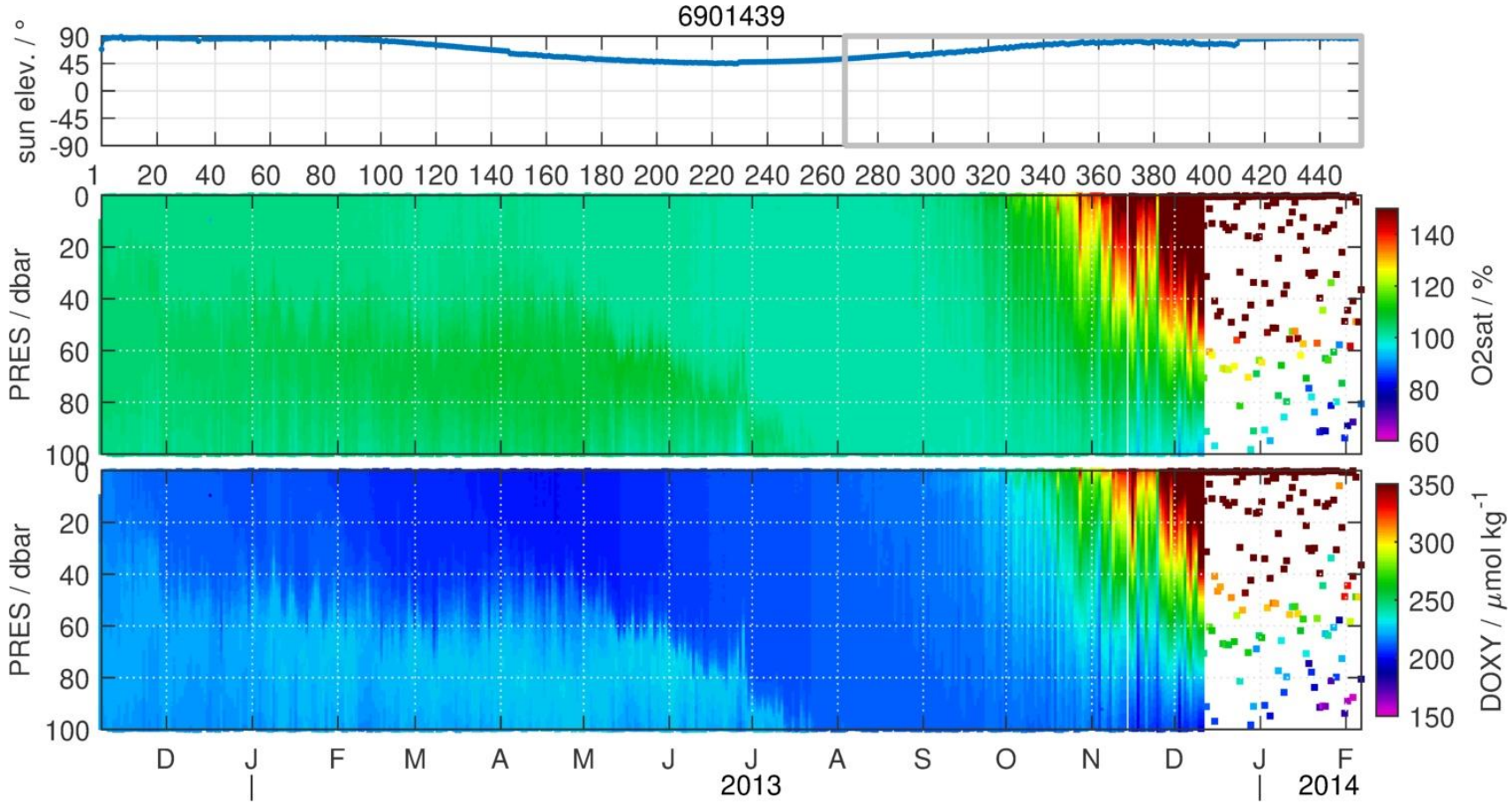
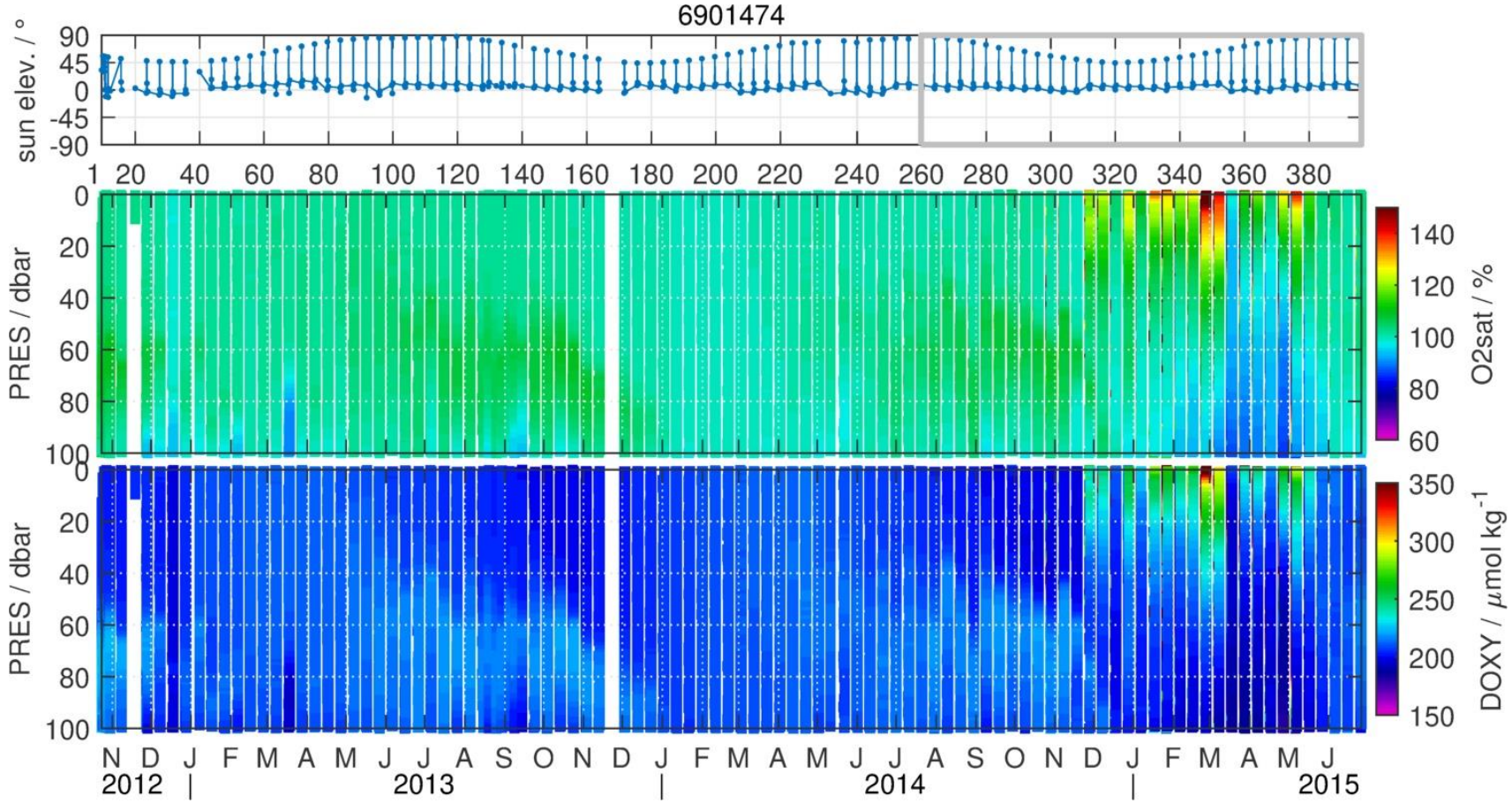
- daily during noon
- daily during noon



Optode biofouling

Avoid continuous daily surfacing during the day in warm areas!
Risk of severe biofouling

- daily during noon
- daily during noon
- 4 rapid cycles at 10 d interval



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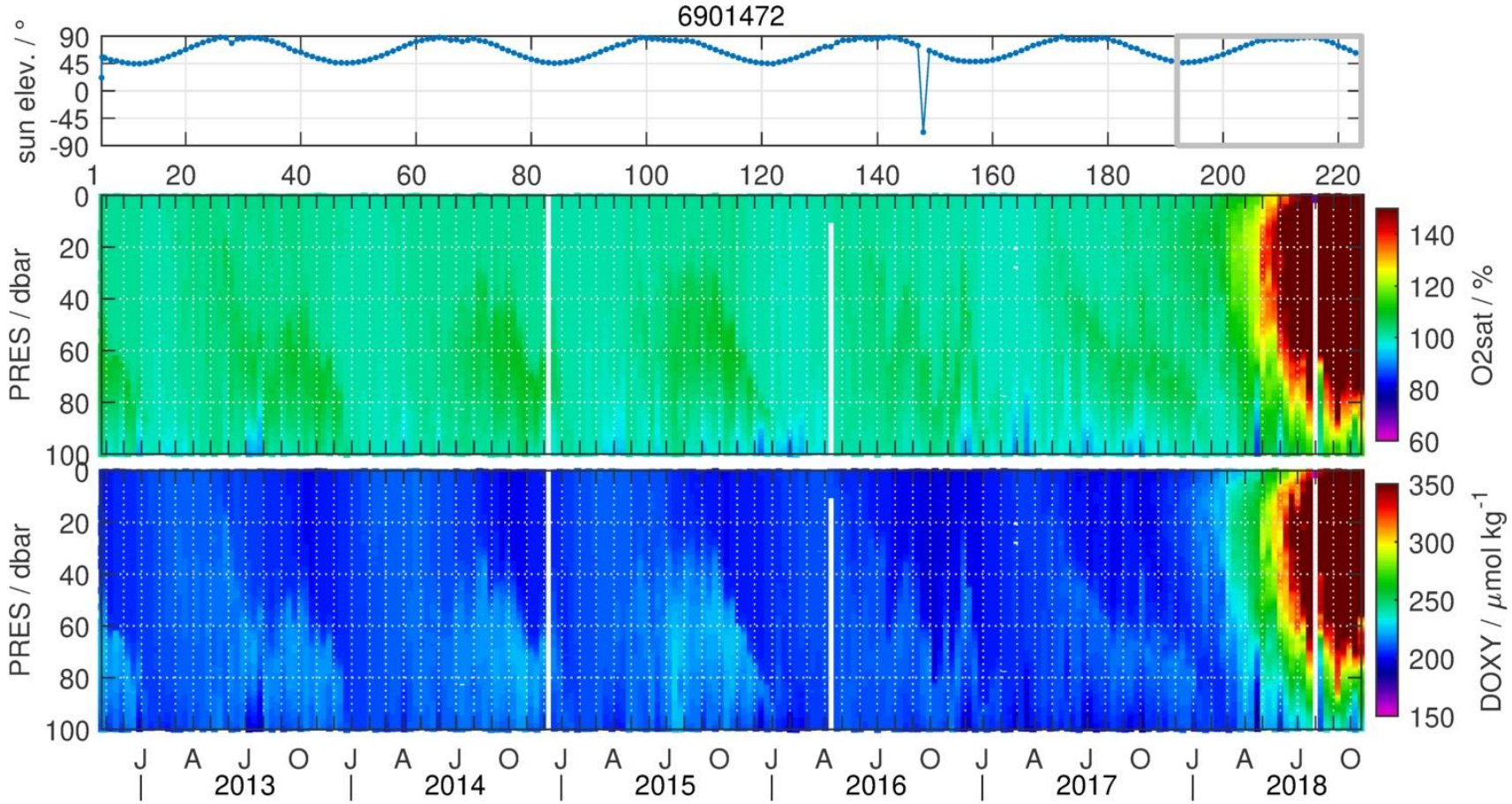
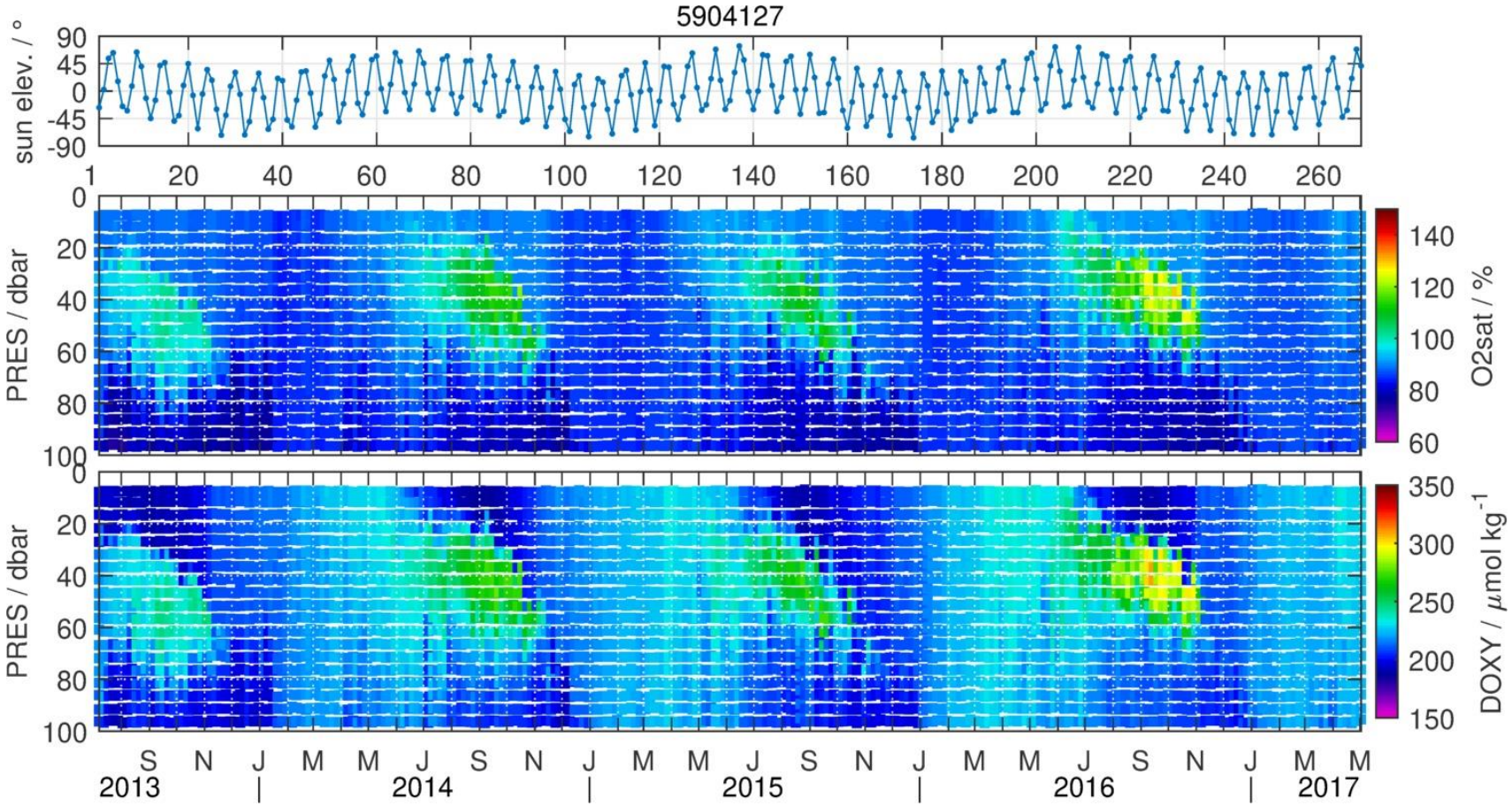


Optode biofouling

Avoid continuous daily surfacing during the day in warm areas!
Risk of severe biofouling

- daily during noon
- daily during noon
- 4 rapid cycles at 10 d interval
- 10 d during noon
- 5 d interval



Improve RTQC: Proposal to add Surface Saturation test

Test Definition

⇒ Convert DOXY into DOXY saturation

⇒ Mean in the first 10 meters (without levels with QC=4 at range test)

⇒ If mean(DOXY_sat >= 150): QC = 4 for the whole profile

⇒ If triggered for 10 consecutive profiles: Put float on greylist with QC = 4

Evaluation

This test was run on the entire Coriolis DOXY fleet on the raw DOXY values (neglecting DOXY_QC)

⇒ 29 Coriolis floats trigger the saturation test

Comparison with DM and inputs from greylist yields:

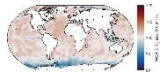
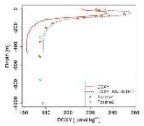
⇒ 22 floats were already greylisted by operators with QC = 4
(with a date prior the trigger => test tends to be conservative)

⇒ 3 floats trigger the test but with DOXY_QC = 4 already set by the range test
(the saturation test should be performed after the range test)

⇒ 4 floats trigger the test intermittently: Expert feedback confirmed weird sensor behaviour and probably bad, uncorrectable data; or biofouling shortly before float death

DM methods for DOXY adjustment

Sources of reference data:

 Direct in air measurements	• Most accurate reference • Can remove bias and drift • No reliance on gridded O_2 fields • SCOR WG 142 recommendation	• SBE63 optodes not capable of in air measurements • Requires good DAC decoding (b-traj) • Artefacts with bad O_2-T-calibration
 Surface O_2 saturation climatology	• Possible with all sensors • Can remove systematic bias (and drift) but less accurate • Possible option for RT	• Reliance on match with gridded field
 Winkler-calibrated CTD-O_2 deployment profile	• Possible with all sensors • Can only remove initial bias • May cover range of O_2 / T	• Spatio-temporal match • Only one profile; bad statistics
 Deep O_2 concentration climatology / stable layer	• Complement to surface O_2	• Requires stable deep layer • Reliance on match with gridded field • High uncertainty (esp. for surface O_2)

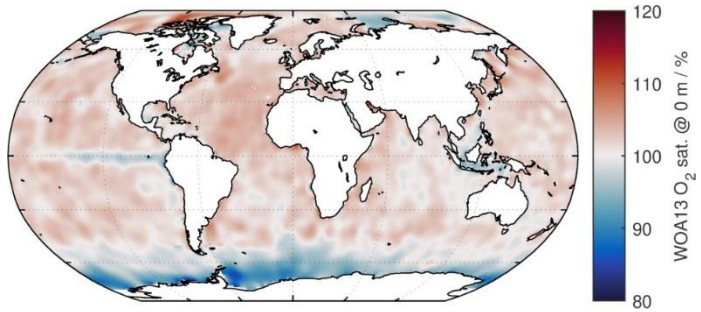
Bittig et al. (2018), Johnson et al. (2017), Bushinsky et al. (2015), Johnson et al. (2015), Bittig and Körtzinger (2015), Takeshita et al. (2013), Tengberg et al. (2006)

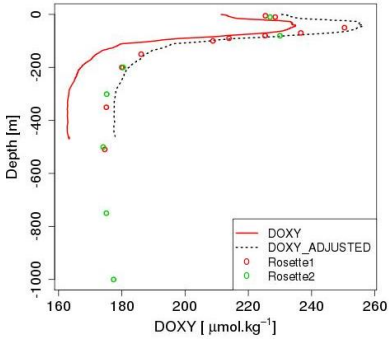
DM methods for DOXY adjustment

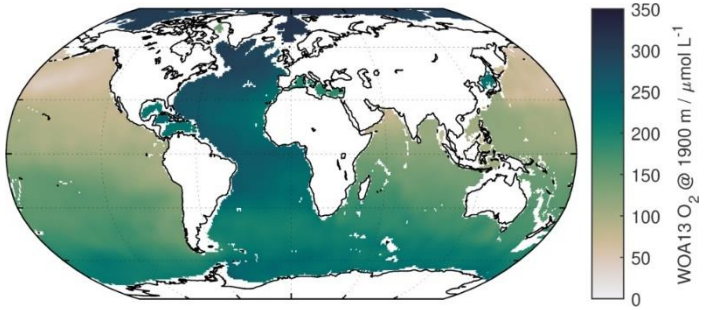
Ways to adjust sensor data:

Optodes (Aanderaa, SBE63, JAC, ...)	• gain factor on PPOX_DOXY (+small zero offset if warranted; order 5 hPa max.)	• Follows sensing principle • Reliance on O_2-T-calibration (multipoint !)
Electrodes (SBE43)	• gain factor and offset on DOXY	• Follows sensing principle

No matter where the reference data come from!







Bittig et al. (2018)

DOXY adjustments: Math (Bullet-proof version)

Oxygen optodes sense the O_2 partial pressure *inside* the sensing membrane.
-> Correction must be done *on PPOX_DOXY* at *inside membrane conditions*!

```
% convert DOXY into DOXY_in_molar_units units convertion (micromol/kg to micromol/L)
rho = potential_density(presValues, tempValues, psalValues);
molarDoxyValues = doxyValues .* rho;

% pressure effect un-correction:
% at presValue, optode quenched by different pO2 inside membrane than pO2 outside in seawater due to re-equilibration effect
% translate already corrected value (outside conditions) back to sensed value (inside membrane)
oxygenPresUncomp = calcoxy_presuncomp(molarDoxyValues, presValues, tempValues, pCoef2, pCoef3);

% convert DOXY_in_molar_units_and_inside_conditions into PPOX_DOXY units convertion (micromol/L to hPa)
ppoxDoxyValues = O2ctoO2p(oxygenPresUncomp, tempValues, psalValues, presValues);

% adjust PPOX_DOXY
ppoxDoxyAdjValues = ppoxDoxyValues * a_slope + a_offset;

% convert PPOX_ADJUSTED into DOXY_ADJUSTED_in_molar_units_and_inside_conditions units convertion (hPa to micromol/L)
oxygenAdjPresUncomp = O2ptoO2c(ppoxDoxyAdjValues, tempValues, psalValues, presValues);

% pressure effect re-correction:
% at presValue, optode quenched by different pO2 inside membrane than pO2 outside in seawater due to re-equilibration effect
% translate adjusted sensed value (inside membrane) to adjusted corrected value (outside conditions)
molarDoxyAdjValues  = calcoxy_prescomp(oxygenAdjPresUncomp, presValues, tempValues, pCoef2, pCoef3);

% convert DOXY_ADJUSTED_in_molar_units into DOXY units convertion (micromol/L to micromol/kg)
doxyAdjValues = molarDoxyAdjValues ./ rho;
```

apply a small zero offset only if warranted (batch calibrated optodes?)
order 5 hPa max.

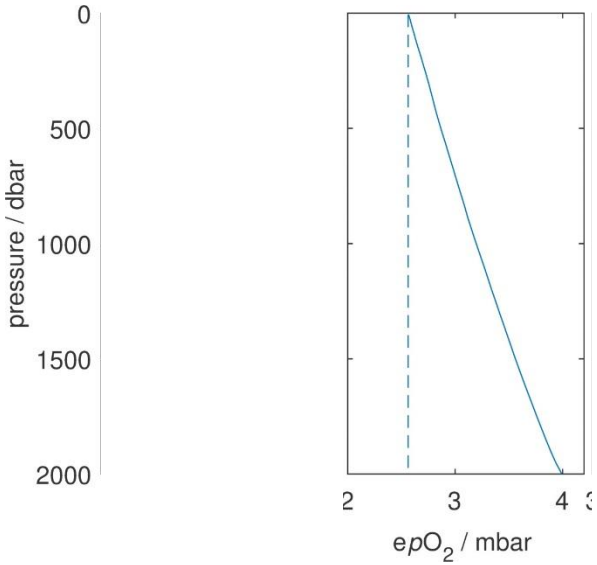
DOXY adjustments: Error estimate

Oxygen optodes sense the O_2 partial pressure *inside* the sensing membrane.
-> Error should be expressed as PPOX_DOXY converted back to DOXY

QC manual recommendation:

Error should be a constant PPOX_DOXY on entire profile, not a fraction of the value

(Work in progress: Complete error budget for DOXY)

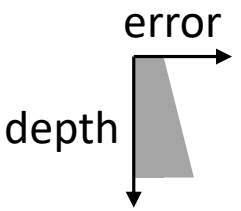



```
% convert PPOX_ADJUSTED into DOXY_ADJUSTED_in_molar_units_and_inside_conditions units convertion (hPa to micromol/L)
oxygenAdjPresUncomp = O2ptoO2c(ppoxDoxyAdjValues, tempValues, psalValues, presValues);

% pressure effect re-correction:
% at presValue, optode quenched by different pO2 inside membrane than pO2 outside in seawater due to re-equilibration effect
% translate adjusted sensed value (inside membrane) to adjusted corrected value (outside conditions)
molarDoxyAdjValues  = calcoxy_prescomp(oxygenAdjPresUncomp, presValues, tempValues, pCoef2, pCoef3);

% convert DOXY_ADJUSTED_in_molar_units into DOXY units convertion (micromol/L to micromol/kg)
doxyAdjValues = molarDoxyAdjValues ./ rho;
```

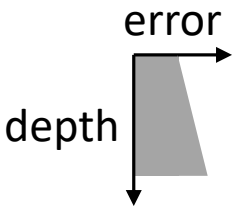
DOXY adjustments: Error estimate, 2nd level

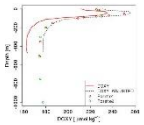
- Only one DM method: Following sensing principle
- Accuracy depends on reference data accuracy and character

Direct in air measurements

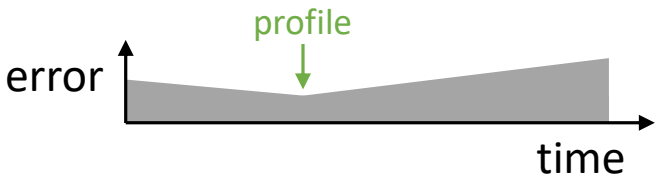


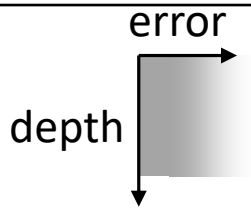
Surface O_2 saturation climatology

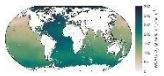




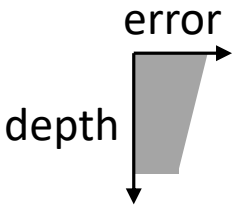
Winkler-calibrated CTD-O_2 deployment profile







Deep O_2 concentration climatology / stable layer



Adjustment workflow

Bittig et al. (2019) A BGC-Argo guide: Planning, deployment, data handling and usage. Front. Mar. Sci. 6:502.
doi: 10.3389/fmars.2019.00502

Float PI

- coordinates with a DAC on upcoming float deployment
- notifies float with AIC
- deploys float

Float

transmits raw data

DAC

- processes raw data in real-time and
- sends 'R'-files to GDAC within 24 h

GDAC

- performs higher-level aggregation and
- makes files available for users

Users

may incorporate DMQC results for adjustments into real-time data stream

DAC

- checks format conformity to Argo rules with file checker
- sends 'D'-files to GDAC to replace real-time 'R' files

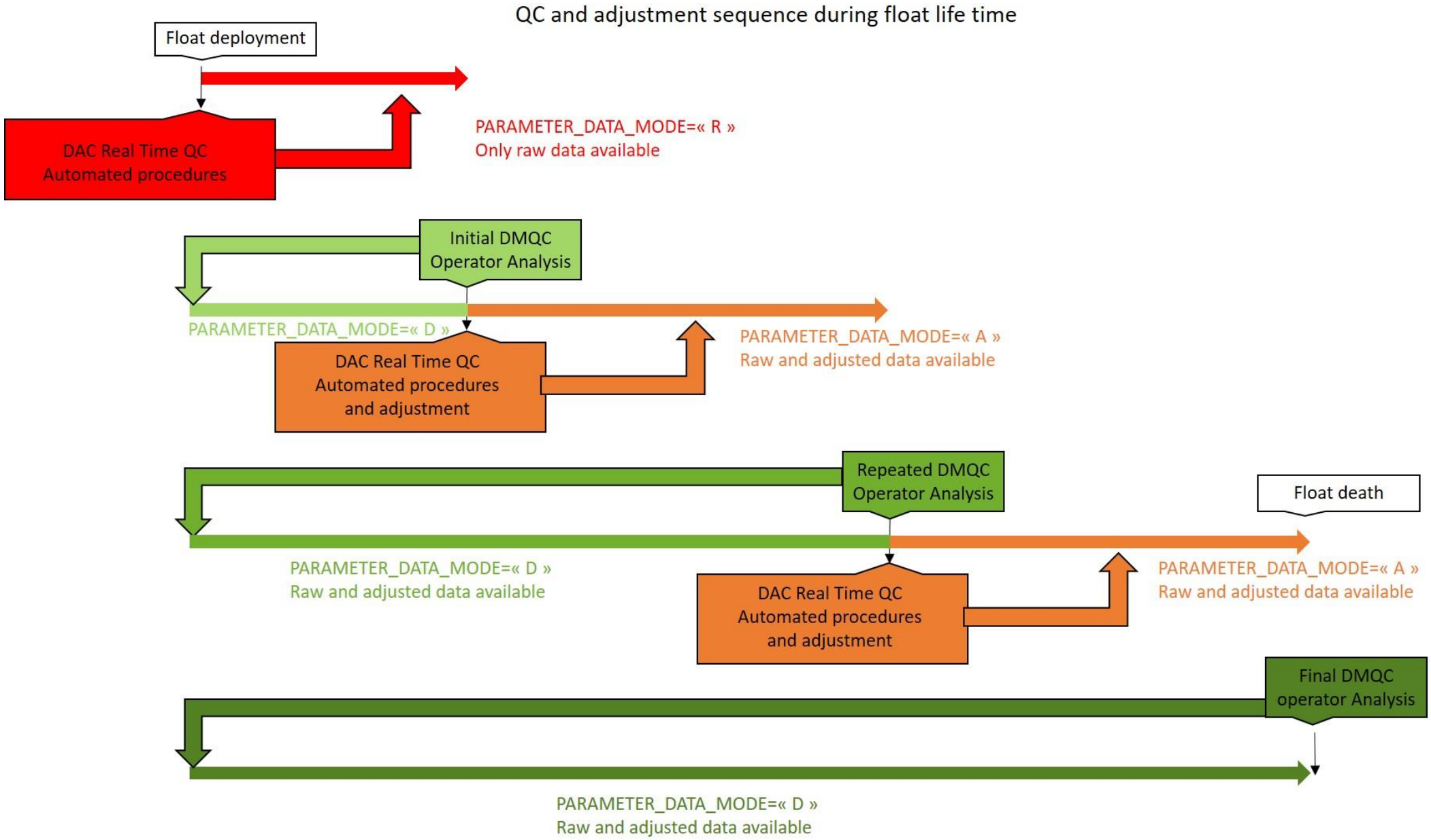
Float PI / DMQC expert

'Operator analysis':

- assesses float data and
- provides DMQCed and adjusted data files to DAC (1 or more parameters)

Adjustment workflow

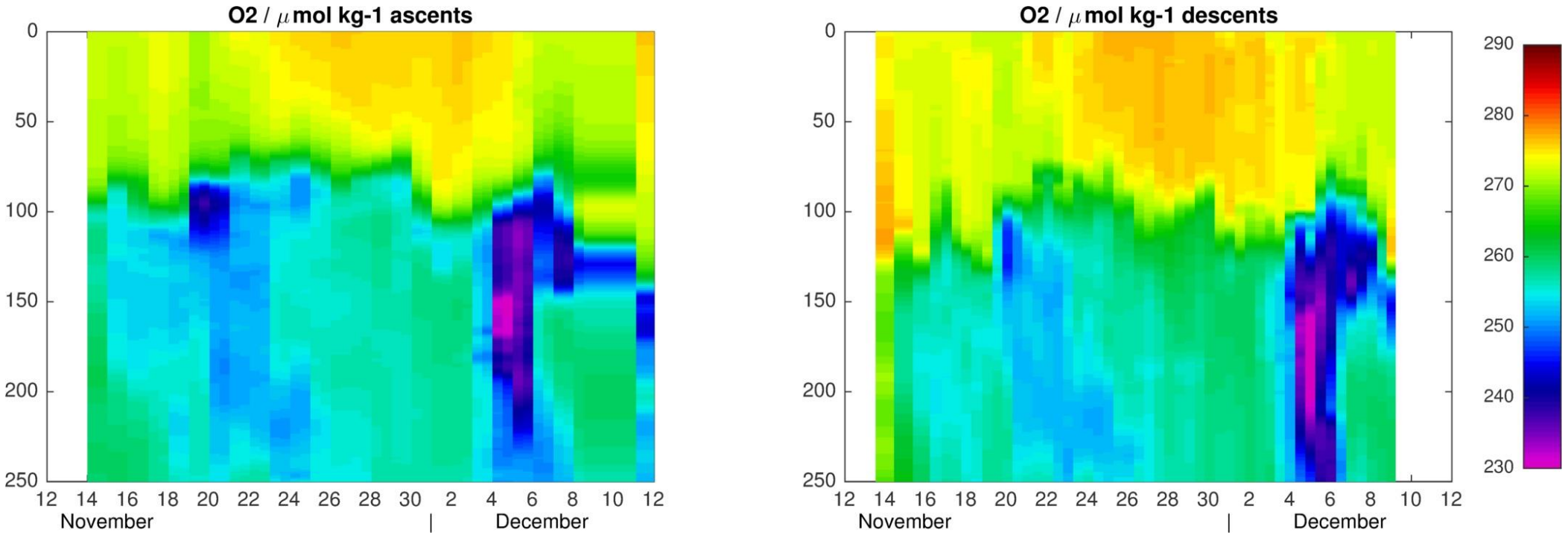
Bittig et al. (2019) A BGC-Argo guide: Planning, deployment, data handling and usage. Front. Mar. Sci. 6:502.
doi: 10.3389/fmars.2019.00502



Time response correction

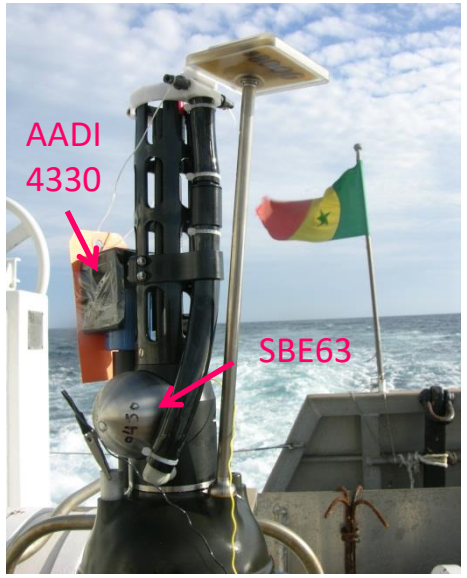
- Requires expert knowledge / sensor understanding

6901180

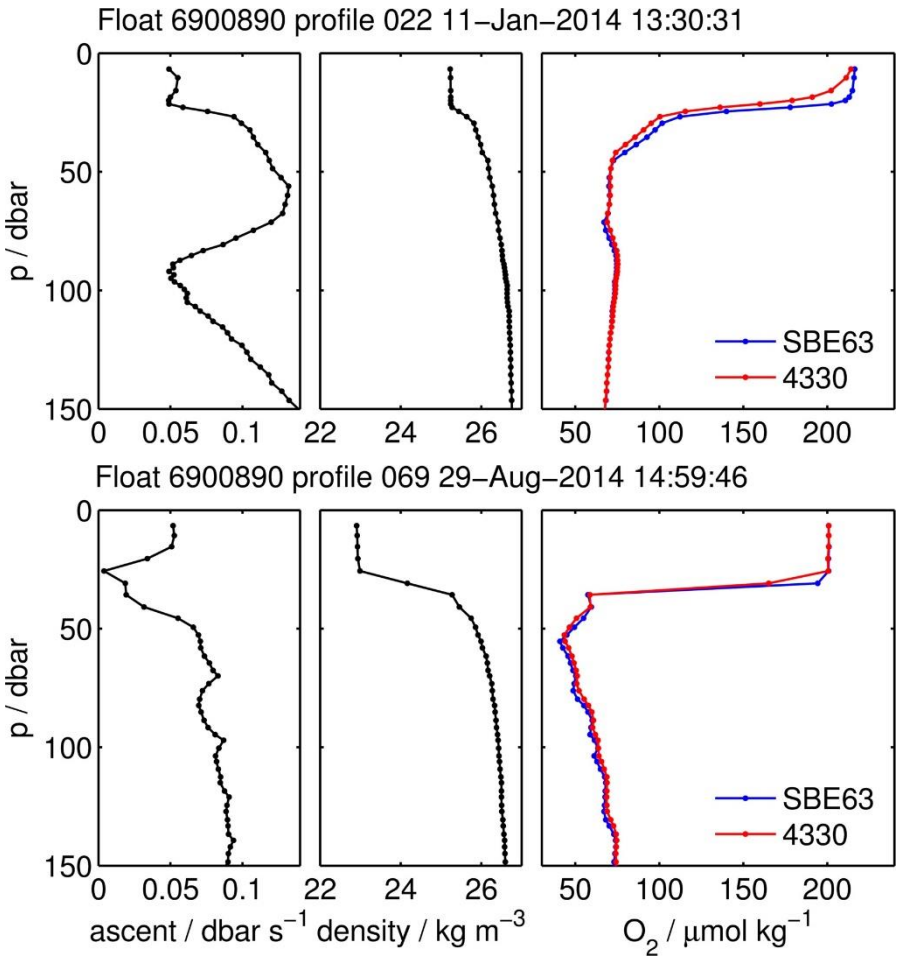


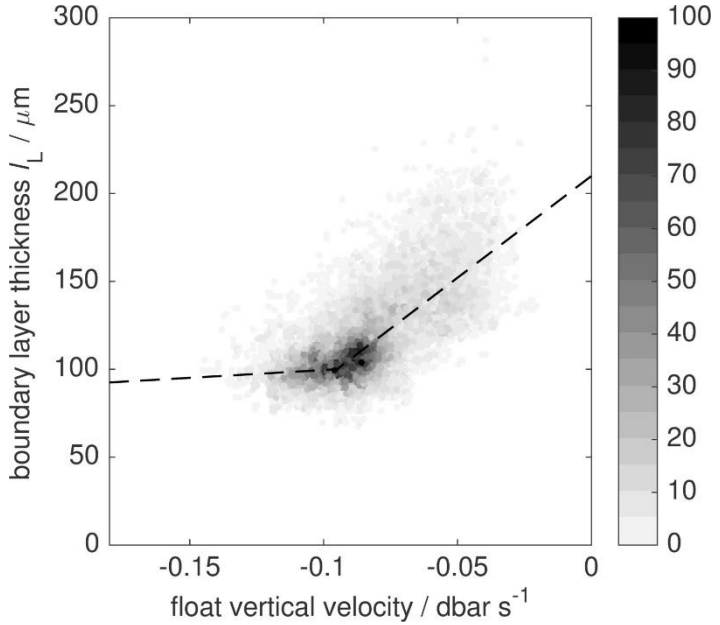
Time response correction

- Requires expert knowledge / sensor understanding



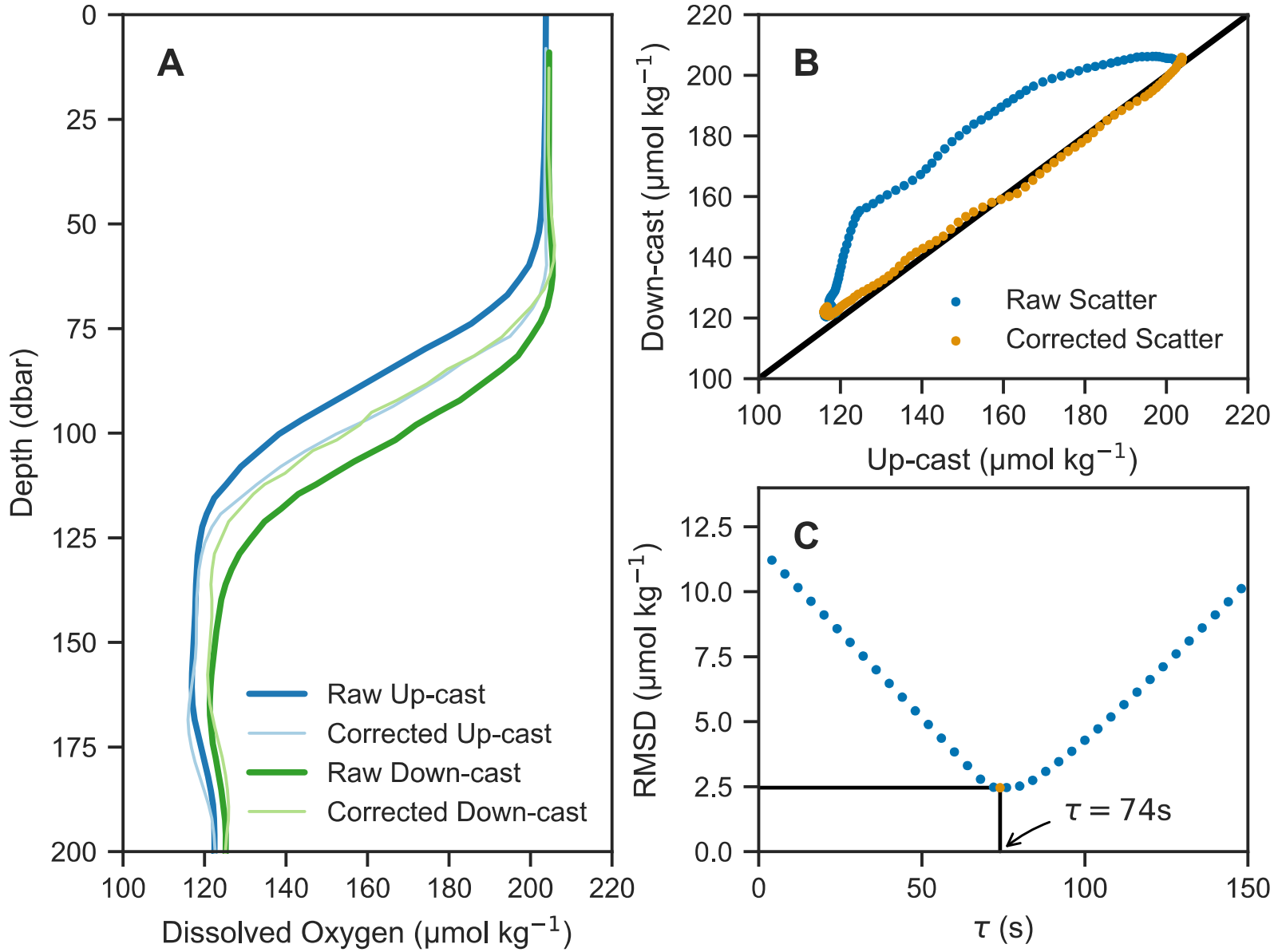
Bittig and Körtzinger (2017) Technical note: Update on response times, in-air measurements, ... Ocean Sci.





Determining Sensor Response-time *in-situ*

- Upon deployment, floats were programmed to profile continuously, recording data including timestamps on both up- and down-casts.
- Optode response time is determined by performing the correction for a range of τ values on pairs of time-adjacent up- and down-casts.
- The value of τ that minimizes the mismatch (Root Mean Square Deviation, RMSD) between the two casts is taken to be the effective sensor response time.



by Chris Gordon, Dalhousie University

Determining Sensor Response-time *in-situ*

- Median values of effective response times are around 70 s with standard deviations up to 20 s (see Table)
- Large standard deviations in response times likely due to environmental factors rather than changes to the inherent sensor response time – this method determines the effective response time which is highly dependent on the flow at the sensor interface.
- Results are on the low end or just outside the estimated range of response times for autonomous floats provided in Bittig and Körtzinger (2017) of 70-140 seconds, using boundary layer estimates based on float profiling velocity.

Float ID	τ (s)	σ_τ (s)
f7939	76.5	8.5
f7940	69	15.5
f7941	67	16.9
f7942	64.5	14.9
f7943	75	16.5
f7944	76	13.9
f7945	73.5	13.3
f8081	68	16.0
f8082	73	18.8
f8083	66.5	20.4
Average	70.9	15.5

by Chris Gordon, Dalhousie University

Time response correction

- Requires expert knowledge / sensor understanding
- Currently a DM task

4.6 Further delayed-mode tasks for DOXY

In addition to O2 adjustment as suggested above and general visual QC, delayed-mode QC for DOXY should try to address:

- Correction of the oxygen optode time response if time stamps are available (see e.g., Bittig and Körtzinger 2017, Bittig et al. 2014).

- If no time stamps are available, correction of the oxygen optode time response may still be feasible using a mean float ascent velocity as input (see figures 2/3 of https://dx.doi.org/10.5194/os-13-1-2017 and https://dx.doi.org/10.5194/os-2016-75-AC1, respectively).

- The presence of a so-called 'O2 hook' at the base of the profile (first ~50 dbar), i.e., significantly lower O2 observations as suggested by the O2 gradient at slightly shallower depths / as indicated from climatological data

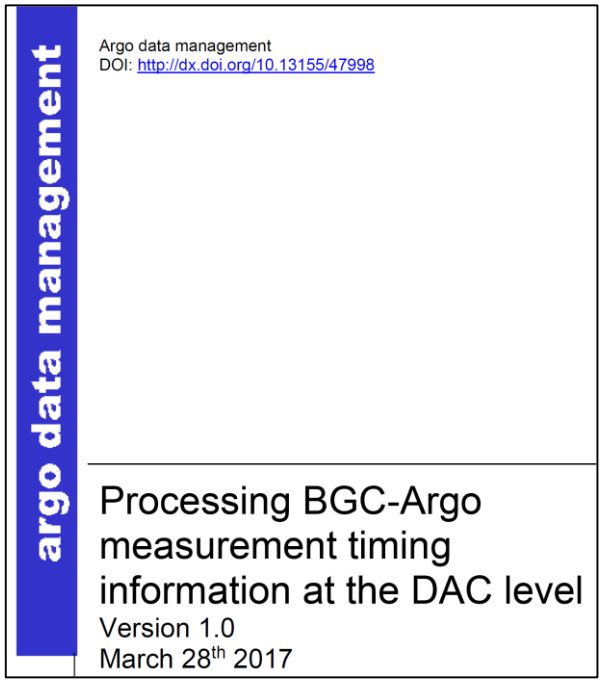
Time response prerequisite: Time!

1. Float does not transmit timestamps

   Need to get creative (~ascent speed) -> Ken

2. Float transmits timestamps

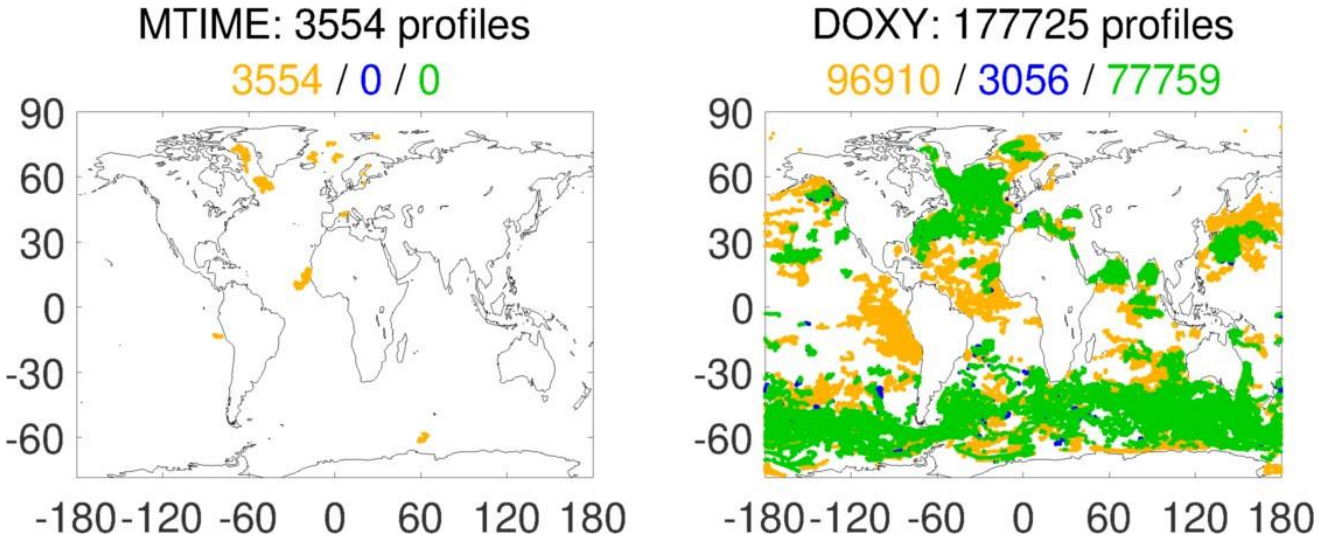
   (a) intermittently (-> traj), or
   (b) at all points (-> traj and profile "**MTIME**")

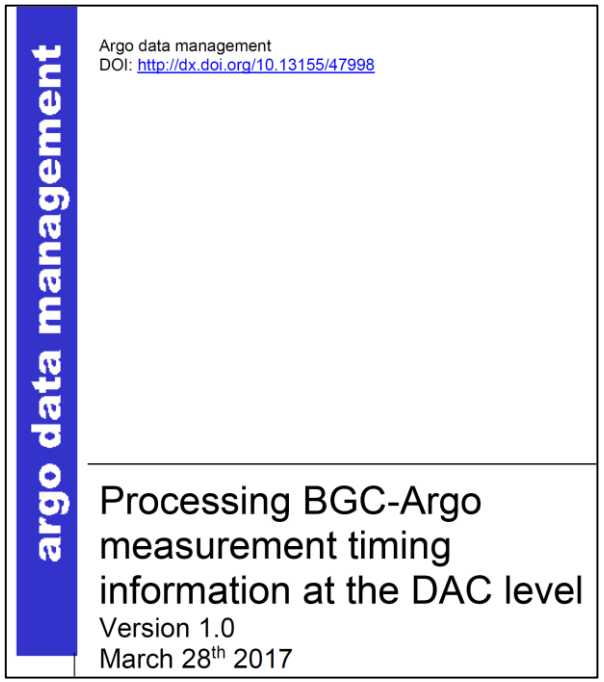


saw a need to be able to store timing information in the float's profile file. Following discussions at ADMT16, AST17, and ADMT17 it was concluded that timing information associated with each measured parameter of the profile is scientifically useful for Biogeochemical-Argo, but does not seem necessary for core Argo. Sparse timing data should remain in the trajectory file – it was designed to handle this data and keeps QC of timing information mostly to one file. Abundant timing information (i.e., timing information for all profile observations), however, are stored in the i-parameter "MTIME" in the b-profile files.

Time response prerequisite: Time!

Very few floats with (optional) MTIME in profile





- Presently only filled by Coriolis (41 floats)
- Makes time response correction by an (expert) user very hard!!

Please check your BGC float decoders: Is there timing information that could / should be stored in “MTIME” ?

The most plausible explanation would be an effect of turbulence on the foil of the optode

Tests in lab with 3 optodes (from D.Lefevre M.I.O.):

Thermal conditions are stable (+/- 0.5°C) and the O2 forcing condition is maintained at +/- 0.1 µM.

The rotation of the blades at 120 rpm is obtained from the start

<u>We can observed:</u>

- The transition from 0 to 120 rpm and 120 to 0 rpm results in a concentration change of 0.8 µM with almost no thermal evolution

- ”Equilibrium" is found after about a hundred minutes

- There is symmetry in the optode response

Turbulent regime changes near the optode can therefore impact a large part of the DOXY profile

How to correct the bottom DOXY profiles ? How to qualify this part of the profile in a rigorous way (and not only visually) ? How could we reduce the deviation between up & downcasts ?