



Oxygen concentration in the South Adriatic Sea: the gliders measurements.

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Introduction

In this report we explored the oxygen data recorded by 4 different gliders (2 Slocum SN 402 and 403 and 2 SeaGlider SN SG554 and SG661) in the South Adriatic Pit. A first comparison with other available oxygen data (from floats, CTDs profiles or Winkler samples) in the area evidenced a large difference of the glider oxygen values with respect to the other data. Moreover, a detailed analysis demonstrated that the SeaGlider data seem to overestimate the floats/CTDs/Winkler data, while the Slocum data underestimate them.

The data analysis pointed out two main issues:

- the need of compensate the glider oxygen data for the depth and salinity;
- the need of in-situ correct/calibrate the glider oxygen data.

These issues were investigated throughout the report and a final homogeneous dataset with validated, corrected and compensated oxygen values were obtained for all the glider missions.

Preliminary comparison of Glider data with Oceanographic campaigns in South Adriatic Sea

The Adriatic Sea is an elongated basin, with its major axis in the northwest–southeast direction, located in the central Mediterranean Sea, between the Italian and the Balkan peninsula. Countries with coasts on the Adriatic Sea are Albania, Bosnia and Herzegovina, Croatia, Greece, Italy, Montenegro and Slovenia. Being located at mid latitudes, the Adriatic Sea is characterized on one hand by a strong seasonal variability and on the other hand by synoptic weather variations, which are in turn modulated by the seasonal signal (Gacic et al., 2001). The southern part is characterized by a large depression that reaches more than 1200 m depth. The water exchange with the Mediterranean Sea takes place through the Otranto Channel, whose sill is about 800 m deep.

Generally, the whole Adriatic Sea is a well-oxygenated basin. During spring and summer a subsurface maximum is formed in the euphotic zone, between approximately 10 and 50 m, due to biological activity that results in a net production of oxygen near the pycnocline after the density stratification of the water column has become established. In autumn and winter ventilation at the surface and water column mixing create a more homogeneous oxygen distribution. The average basin value of dissolved oxygen is approximately 5.5 ml l^{-1} (Artegiani et al., 1997, Vilibic et al. 2002).

Methods for measuring dissolved oxygen concentration

Oxygen measurements can be obtained directly with an analytic analysis and indirectly by means of electrochemical measurements. The Winkler titration is the most accurate and widely adopted method to estimate the oxygen concentration in the water from punctual samples. The oxygen concentration that is obtained by the Winkler method allows to calibrate oxygen measurement obtained with oxygen probes that sample continuously all along the water column. There are different kind of sensors which derive the oxygen concentration using different physical principles/characteristics as the electrochemistry (Clark electrode or polarographic system) or the optic.

Winkler

The chemical determination of oxygen concentrations in seawater is based on the method proposed by Winkler (1888) and modified by Strickland and Parsons (1968).

The Winkler analysis of dissolved oxygen has different steps. A seawater sample, that hasn't been exposed to additional oxygen source, is "fixed" by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound. The amount of neutralizing agent required to neutralize the acid with titration indicates the amount of oxygen present in the original sample. The procedure is particularly delicate and susceptible to human error.

Optical sensors

Optical sensors mounted on CTD or autonomous profiling instruments provide direct in-situ measurements of oxygen. Among all the different kind of sensors on the market, we would consider the Seabird SBE 43 usually mounted on CTD and Floats and the Aanderaa Oxygen Optode usually mounted on Gliders and Floats.

The SBE 43 is a high-accuracy oxygen sensor which determines the dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane from the ocean environment to an electrode. At the electrode, the oxygen gas molecules are converted to hydroxyl ions (OH⁻) in a series of reaction steps. The reaction is then completed by the electrode which supplies four electrons per molecule. The sensor counts oxygen molecules by measuring the electrons per second delivered to the reaction. At another electrode, silver chloride is formed and silver ions (Ag⁺) are dissolved into solution. As a result, the chemistry of the electrolyte changes continuously as oxygen is measured, which leads to a slow but continuous loss of sensitivity that produces a continual, predictable drift in the sensor calibration over time.

The SBE 43 is designed to be used in a CTD's pumped flow path, providing optimal correlation with CTD measurements (<http://www.seabird.com/sbe43-dissolved-oxygen-sensor> & <http://www.seabird.com/document/an64-sbe-43-dissolved-oxygen-sensor-background-information-deployment-recommendations>).

The Aanderaa oxygen Optodes are based on the ability of selected substances to act as dynamic fluorescence quenchers. The luminous indicator is a special platinum – porphyrin complex set inside a gas permeable foil that is exposed to the surrounding water. The foil is excited by modulated blue light, and the Optode measures the phase shift of a returned red light. The sensor

has an incorporated temperature thermistor that enables linearization and temperature compensation of the phase measurements in order to provide the absolute O₂ concentration.

The Seaglider and the Slocum gliders considered in this report are equipped with the Oxygen Optode 4330/4330F and the Oxygen Optode 4831/4831F, respectively (<http://www.aanderaa.com/media/pdfs/oxygen-optode-4330-4330f.pdf> & http://www.xylemanalytics.co.uk/media/pdfs/4330-4330f-oxygen-optode_dec12.pdf, <http://www.xylemanalytics.co.uk/media/pdfs/aanderaa-oxygen-optode-4831-4831f.pdf>).

Yearly oxygen data comparison

The oxygen concentration obtained from the Winkler method and from different optical sensors mounted on several platforms such as Argo floats, Gliders and CTDs were compared using all the available data collected in the South Adriatic Sea between 2013 and 2017 (Figs 1 and 2).

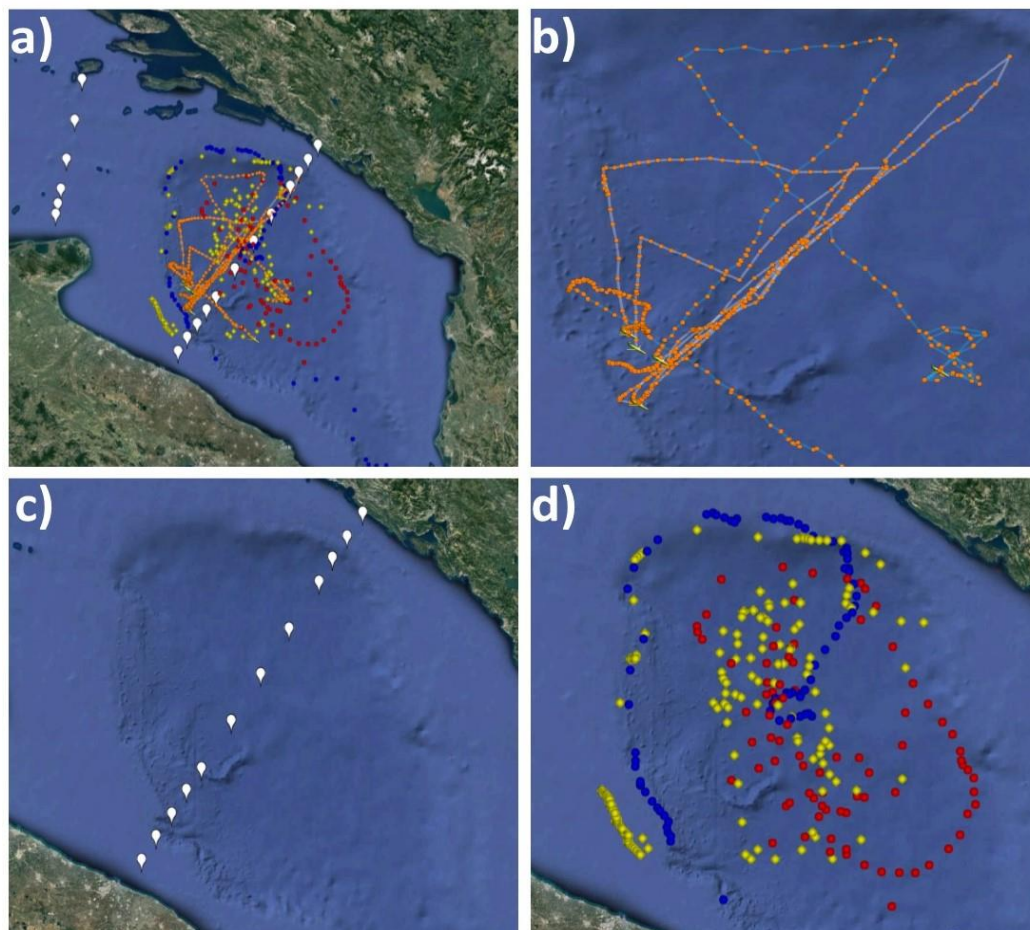


Fig. 1: Geographical position of the different measuring platform (a), glider surfacing during different glider mission (b), CTD/Winkler stations during oceanographic cruises (c) and float profiles (d) in the South Adriatic Sea (6901865 blue circles; 6903178 yellow circles and 6903197 red circles).

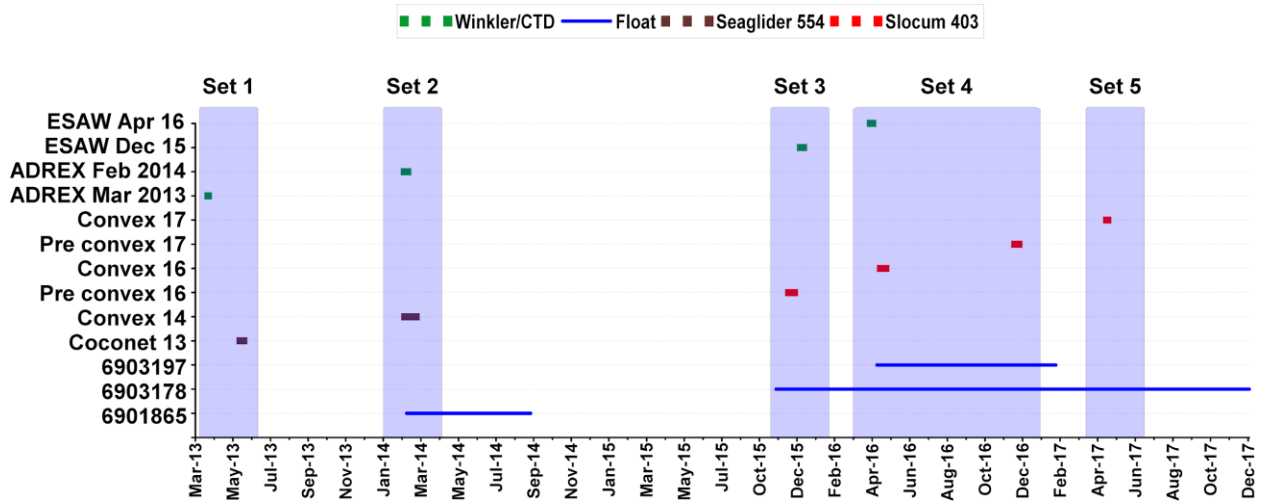


Fig. 2: Time intervals of the available oxygen data; y axis reports the platform/cruise/mission name.

Data were grouped by year, without considering the spatial variability, obtaining five distinct cases (Table 1).

		2013	2014	2015	2016	2017
Float	WMO 6901865		█			
	WMO 6903178			█	█	
	WMO 6903197				█	█
Glider	Coconet 2013	█				
	Convex 14		█			
	Pre convex 16			█		
	Convex 16				█	
	Pre convex 17				█	
	Convex 17					█
Survey	ADREX Mar 13	█				
	ADREX Feb 14		█			
	ESAW Dec 15			█		
	ESAW Apr 16				█	
		Set1	Set2	Set3	Set4	Set5

Table 1: Available oxygen data divided by platform and year. The black slots indicate the platforms considered in the 5 selected cases.

Before the comparison, the oxygen data were all converted to same units (ml/l). In particular, the float oxygen data are usually provided in $\mu\text{mole/Kg}$ and were converted to ml/l following Bittig et al. (2016):

$$[\mu\text{mole/kg}] = [\text{ml/l}] * 44660 / (\sigma_{\theta}(P=0, \theta, S) + 1000)$$

where:

- σ_{θ} is the density of a water parcel if it was raised adiabatically to the sea surface, keeping the salinity stable.
- P = Pressure = 0
- θ is the potential temperature
- S = Salinity

The oxygen data comparison of the 5 cases are presented in Figs from 3 to 7. The data collected with gliders, floats, CTD and the data obtained from Winkler samples are plotted in green, purple, red and blue, respectively.

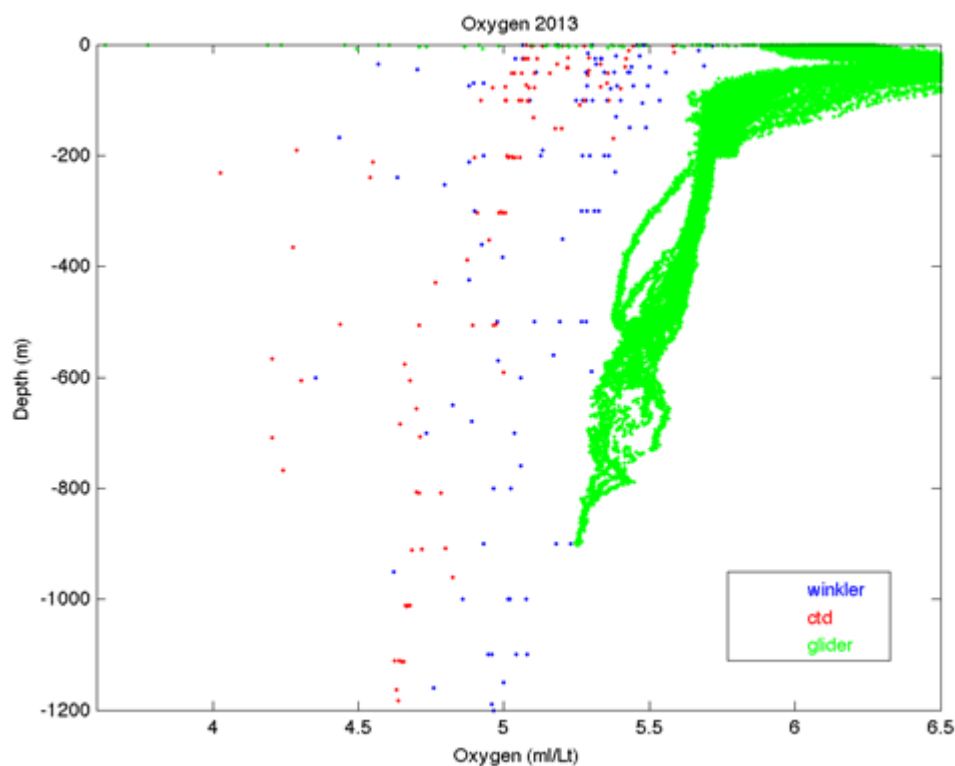


Fig. 3: Profiles of oxygen concentration obtained by the different platforms for case 1 in 2013 (Winkler, CTD and Glider).

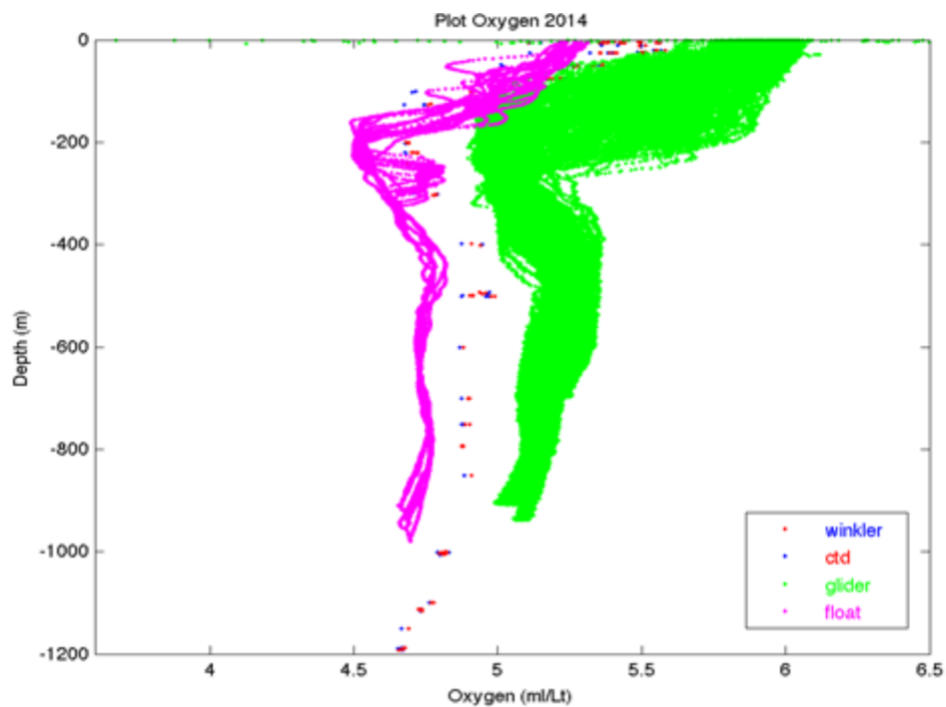


Fig. 4: Same as Fig. 3 for case 2 in 2014 (Winkler, CTD, Glider and Float).

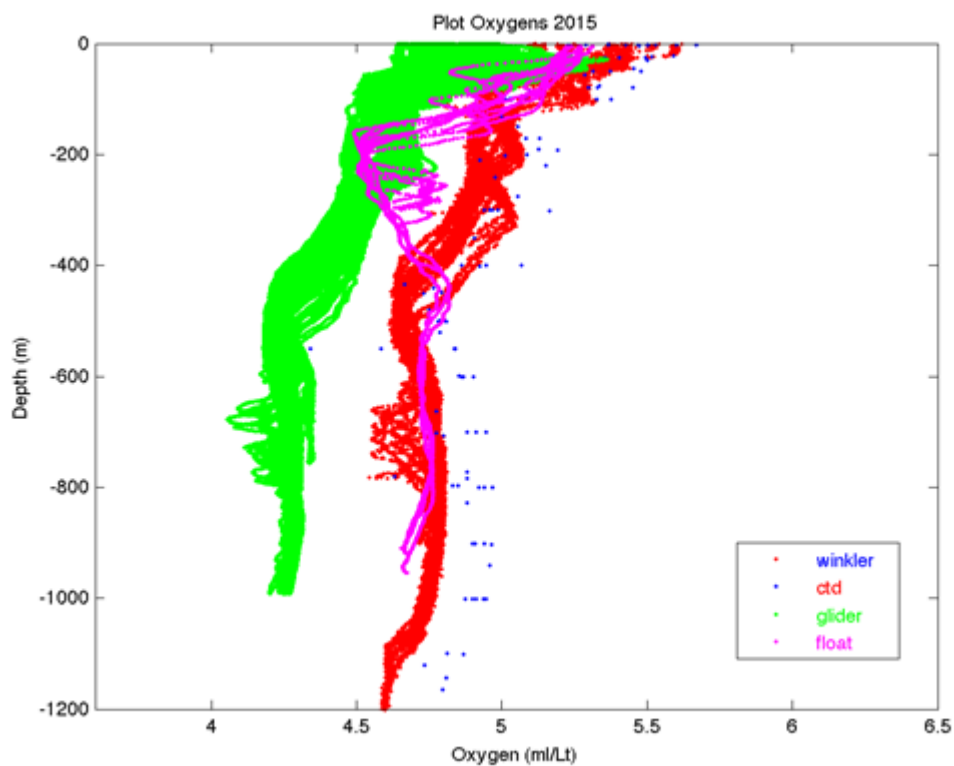


Fig. 5: Same as Fig. 3 for case 3 in 2015 (Winkler, CTD, Glider and Float).

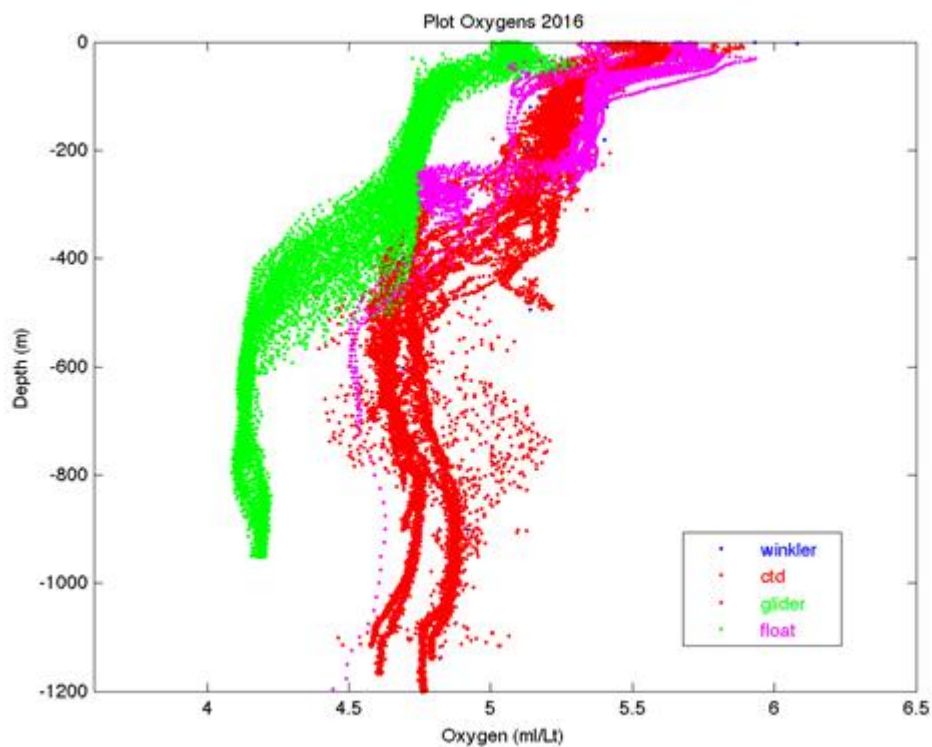


Fig. 6: Same as Fig. 3 for case 4 in 2016 (Winkler, CTD, Glider and Float).

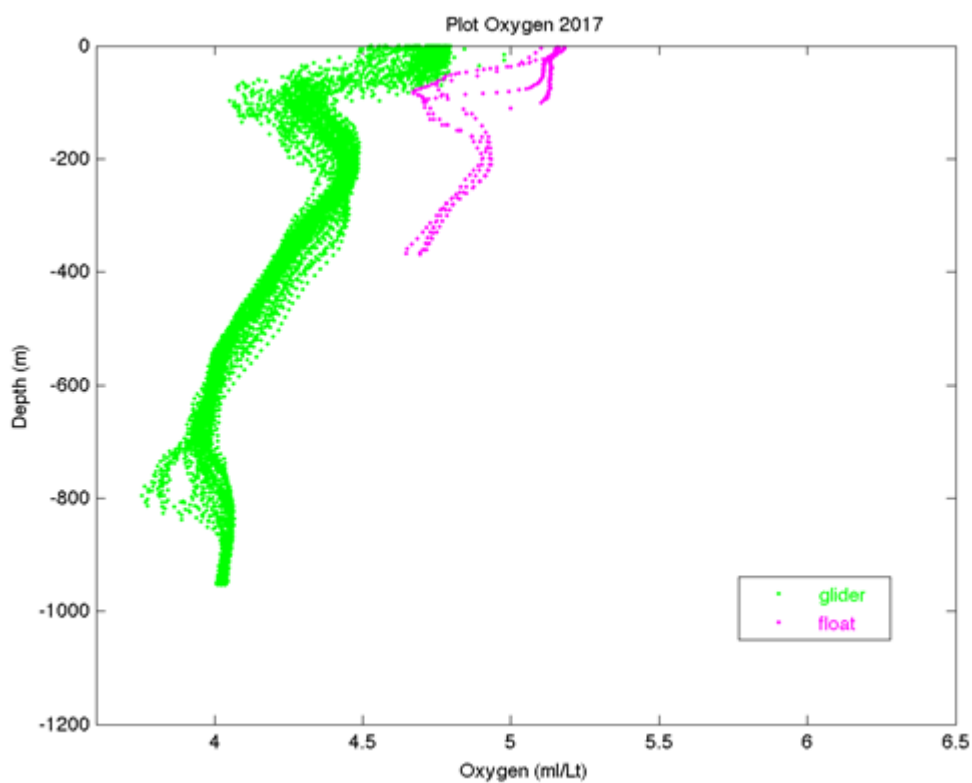


Fig. 7: Same as Fig. 3 for case 5 in 2017 (Glider and Float).

The comparison of all oxygen measurements shows the same oxygen shape along the water column. The maximum concentration is measured in the surface layer and a second oxygen maximum is observed between 200 and 400 m depth. At deeper layers, the oxygen remained almost stable. The oxygen concentration varied from 4.4 to 5.8 ml/l for the floats, from 4.5 to 5.8 ml/l for the CTDs and the Winkler samples and between 3.8 and 6.2 ml/l for the gliders.

The oxygen profiles obtained from the floats, CTDs and Winkler data seems to be in a better agreement than the one measured with the glider. In 2013 and 2014, the oxygen concentrations from gliders are overestimated, while in 2015, 2016 and 2017 concentrations are underestimated. In the first case, the measurements were performed by the SeaGlider SG554, while in the second case by the Slocum glider 403, both equipped with Aanderaa Optode oxygen sensor.

The possible reason for the observed difference may be due to hardware and/or software problem. No evident hardware issues were detected, therefore we investigate the possible software problems considering a wrong and/or different sensors calibration or possible differences in the computing of the oxygen concentrations from the raw (phase) data.

Evaluation of the temperature as measured by the oxygen sensor

The Oxygen Aanderaa Optode sensor use the temperature recorded by itself for computation of the oxygen concentration.

The old Optode model (3835) recorded inaccurate temperature data due to the stagnancy of the water in the glider tail cone where the sensor was positioned (the temperature probe of this oxygen sensor is located on the back of the sensor, pointing towards the inside of the glider tail cone). For this specific model the temperature recorded by the glider CTD must be used to compute the correct oxygen concentration.

The temperature measured by the Optode sensors mounted on our gliders instead is coherent with the CTD values as demonstrated in Fig.8 and, therefore, the observed differences of the glider oxygen data with respect to the other oxygen data are not due to an inaccurate temperature in the computation.

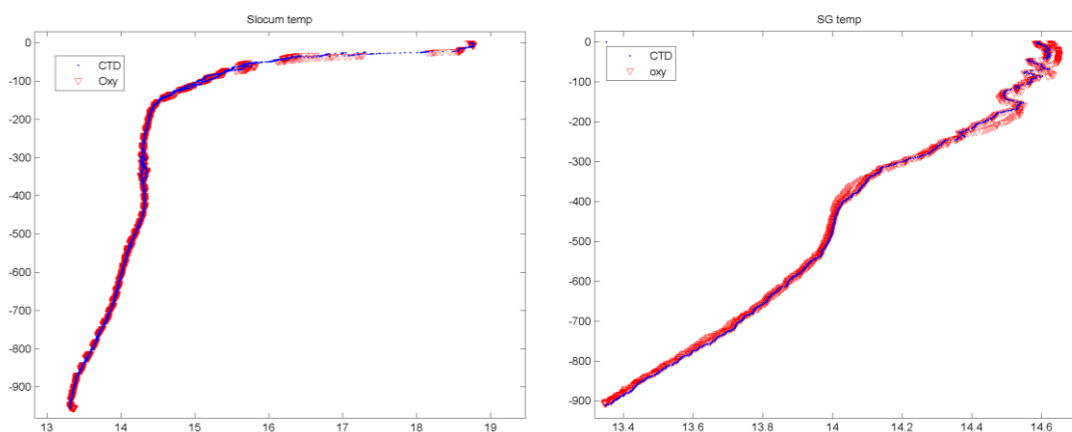


Fig.8 Temperature profiles recorded by the CTD (blue) and by the Oxygen sensor (red) mounted on the Slocum 403 and the SeaGlider SG554 (left and right, respectively)

Oxygen computation from phase data

The Aanderaa Optode oxygen sensor is influenced by temperature, salinity and pressure that modify the hardware response of the sensor. As a consequence, a compensation is needed.

A check of the computational steps was performed following the Aanderaa TD269 Oxygen optode operating manual (2017).

From the raw data the difference between the phase obtained with blue (C1Phase) and red light (C2Phase) excitation is calculated as:

$$TPhase = A(t) + (C1Phase - C2Phase) \cdot B(t)$$

The $A(t)$ and $B(t)$ are temperature-dependent 3rd order polynomials that give a temperature compensation of the measured phase. Usually, as in our case, this compensation is not performed and $A(t)=0$, $B(t)=1$.

Thus the CalPhase is computed as:

$$CalPhase = PhaseCoef0 + PhaseCoef1 \cdot TPhase + PhaseCoef2 \cdot TPhase^2 + PhaseCoef3 \cdot TPhase^3$$

Based on the $CalPhase$ and the temperature, the partial pressure of O_2 is calculated using a two dimensional polynomial:

$$\Delta p = C0 \cdot t^{m0} \cdot ph^{n0} + C1 \cdot t^{m1} \cdot ph^{n1} + C2 \cdot t^{m2} \cdot ph^{n2} + \dots + C27 \cdot t^{m27} \cdot ph^{n27}$$

where the polynomial coefficients $C0$ to $C13$ are recorded in the property $FoilCoefA$ and $C14$ to $C27$ are stored in $FoilCoefB$. The temperature exponents are stored as $FoilPolyDegT$ and the phase exponents are recorded as $FoilPolyDegO$.

The air saturation is then calculated as:

$$AirSaturation (\%) = \left(\frac{\Delta p \cdot 100}{NomAirPress - Pvapour(t) \cdot NomAirMix} \right)$$

with:

$NomAirPress = 1013.25$ hPa,

$NomAirMix$ is the nominal O_2 content in air, by default 0.20946 and

$Pvapour(t) = e(52.57 - (6690.9 / (t + 273.15)) - 4.681 \cdot \ln(t + 273.15))$

If the property Enable HumidityComp is set to 'No' the $Pvapour(t)$ will be set to zero.

The oxygen concentration is finally computed as:

$$O_2 \text{ Concentration } (\mu M) = \left(\frac{C^* \cdot 44.614 \cdot AirSaturation}{100} \right)$$

where C^* is the oxygen solubility (cm^3/dm^3) calculated from the Garcia and Gordon equation of 1992:

$$\ln(C^*) = A0 + A1 T_s + A2 T_s^2 + A3 T_s^3 + A4 T_s^4 + A5 T_s^5 + S (B0 + B1 T_s + B2 T_s^2 + B3 T_s^3) + C0 S^2$$

where:

$$T_s = \text{scaled temperature} = \ln\left(\frac{298.15 - t}{273.15 + t}\right)$$

t = Temperature, °C

S = Salinity, configurable property, default set to zero

$A0 = 2.00856$	$B0 = -6.24097e-3$
$A1 = 3.22400$	$B1 = -6.93498e-3$
$A2 = 3.99063$	$B2 = -6.90358e-3$
$A3 = 4.80299$	$B3 = -4.29155e-3$
$A4 = 9.78188e-1$	$C0 = -3.11680e-7$
$A5 = 1.71069$	

A possibility for linear correction of the O_2 Concentration is also introduced (and used by the Slocum gliders):

$$O_2 \text{ Concentration } [\mu M] = \text{ConcCoefb} + \text{ConcCoefa } [O_2]'$$

For our Slocum gliders only the ConCoefs (determined by the factory) are:

$$\begin{aligned} \text{ConcCoefa} &= 6.200611e-1; \\ \text{ConcCoefb} &= 1.018849; \end{aligned}$$

Optode configuration coefficients in gliders

The Optode configuration coefficients can be retrieved from the Slocum glider by sending to the glider the **u4stalk 4 9600 34** command (syntax from the Aanderaa TD269 Oxygen optode operating manual (2017)) and then:

- Stop (enter)
- Get All (enter)

This will NOT work using glider terminal, the operator should use minicom or teraterm configured to send either Line Feed (Ascii Code 10) or Line Feed + Carriage Return (Ascii Code 10 + Ascii Code 13).

After these commands, the Aanderaa Optode coefficients are displayed.

In the case of the SeaGlider, the Aanderaa Optode configuration coefficients can be retrieved from the “show configuration” option of the sensor interactive menu.

From the obtained outputs, the fundamental difference between the Optode configuration coefficients of the Slocum and of the SeaGlider is that the salinity reference is set to 35 for the Slocum glider and to 0 for the SeaGlider.

Salinity compensation of data

The O₂ concentration is the partial pressure of dissolved oxygen in the water. Since the foil is only permeable to gas and not to water, the Optode cannot sense the effect of salt dissolved in the water. Hence the Optode works as if it is immersed in fresh water. In the case of the in-situ salinity variation less than ± 1 ppt, the O₂ concentration can be compensated in real-time inside the sensor by setting the internal property 'Salinity' (i.e. the salinity reference) to the average measured salinity. If the salinity varies significantly it is mandatory to perform a salinity compensation afterward.

The compensated O₂ concentration (in μM) is calculated from the following equation:

$$O_{2c} = [O_2]e^{S(B_0+B_1T_S+B_2T_S^2+B_3T_S^3)+C_0(S^2-S_0^2)}$$

where:

S = measured salinity in psu

$T_S = \text{scaled temperature} = \ln\left(\frac{298.15 - t}{273.15 + t}\right)$

t = temperature, °C

$B_0 = -6.24097\text{e-}3$

$C_0 = -3.11680\text{e-}7$

$B_1 = -6.93498\text{e-}3$

$B_2 = -6.90358\text{e-}3$

$B_3 = -4.29155\text{e-}3$

$S_0 = \text{salinity reference.}$

NOTE: Salinity compensation is not performed within the Optode, neither by the glider software.

Depth compensation of data

The Optode sensing foil response decreases with water pressure (3.2% lower response at 1000 m depth; more details in Uchida et al., 2008.). This effect is the same for all AADI oxygen Optodes and is totally and instantly reversible and easy to compensate for.

The depth compensated O₂ concentration, O_{2c}, is calculated from the following equation:

$$O_{2c} = O_2 \left(1 + \frac{0.032 d}{1000}\right)$$

where:

d is depth in meters or pressure in dbar.

O_2 is the measured Oxygen concentration in either μM or % and the unit of the compensated concentration, O_{2c} , depends on the unit of the O_2 input.

NOTE: Depth compensation is not performed within the Optode, neither by the glider software.

Compensated oxygen concentration

The uncompensated oxygen concentrations recorded by the Optode, with the configuration coefficients set by the manufacturer, were corrected using the pressure (depth) and salinity measured by the glider CTD to obtain the compensated values of the oxygen. The compensation led to a decrease of the oxygen values of about 1 ml/l and 0.1 ml/l in the SeaGlider and the Slocum, respectively.

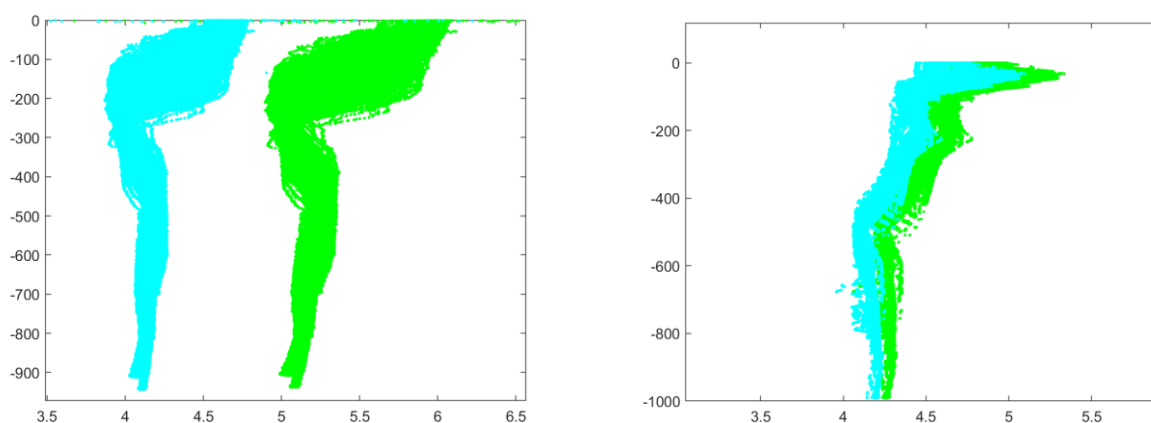


Fig.9 Compensated oxygen data of the SeaGlider (Convex14 mission) and of the Slocum (PreConvex16 mission) (left and right, respectively). Original data are depicted in green and compensated values in cyan.

After the compensation, glider oxygen concentrations show similar values, especially in the deepest layers (Fig.10).

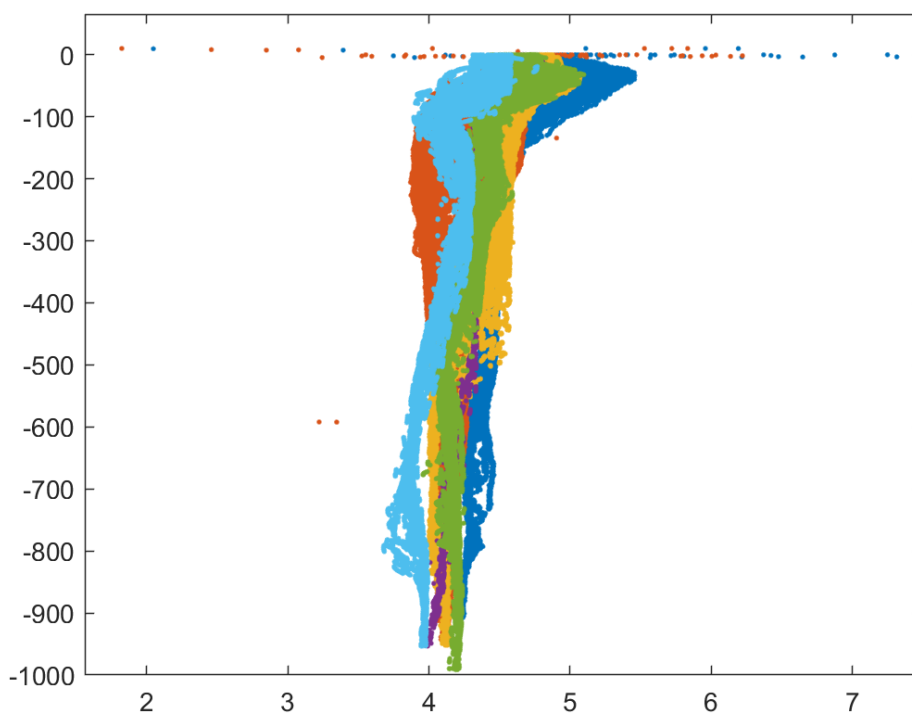


Fig.10 Compensated oxygen during all the glider mission between 2013 and 2017.

The contribution of the salinity to the oxygen compensation has a larger weight (Fig. 11) with respect to the contribution of the depth (or pressure; Fig. 12).

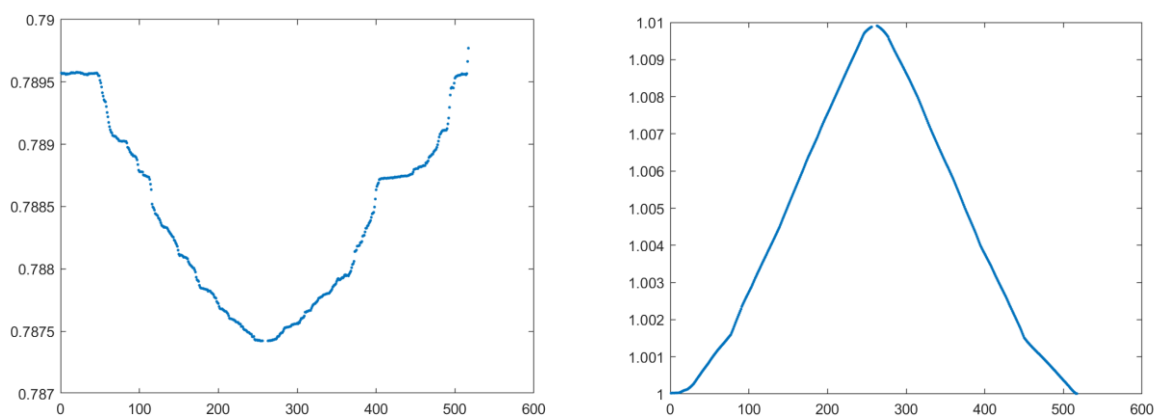


Fig.11 Multiplicative salinity and depth factors (left and right, respectively) for dive 11 of the Convex14 glider mission.

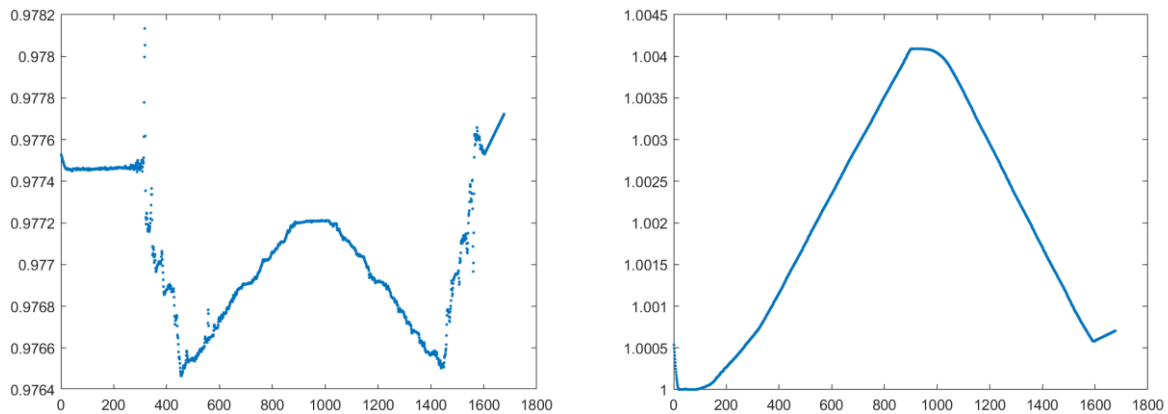


Fig.12 Multiplicative salinity and depth factors (left and right, respectively) for dive 30 of the PreConvex16 glider mission.

The compensation procedure is very important, contributing largely in the correction of the data, but a difference with respect to the Winkler/CTD/float values still remain (underestimation of about 0.5-0.8 ml/l; compare the blu, red and magenta lines of Figs from 3 to 7 with the compensated values of Fig. 10).

Lab tests

To further investigate the gaps between the glider oxygen data and the data from Winkler/CTD/float, some lab tests were run at the OGS wet laboratory to compare the measurement of the gliders with a reference sensors and Winkler samples.

In October 2017 the Slocum gliders 402 and 403 were immersed in a salty water tank along with a reference sensor (Aanderaa 4330F) and two 4531A sensors (brand new).

The reference sensor recorded values around 248 $\mu\text{mol/l}$ (5.55 ml/l) with salinity reference of 0 (corresponding to 202 $\mu\text{mol/l}$ (4.52 ml/l) with salinity reference 35; the brand new sensors recorded almost identical values). The 4831 sensors mounted on the two Slocum gliders instead underestimated the oxygen with mean readings of 185 (4.14 ml/l) and 192 $\mu\text{mol/l}$ (4.3 ml/l) for the glider unit 402 and unit 403, respectively (with salinity reference of 35). The underestimation is therefore 17 and 10 $\mu\text{mol/l}$ (corresponding to 0.38 and 0.22 ml/l).

In September 2018 the Aanderaa oxygen sensor on the SeaGlider SG554 was compared with the reference sensor 4330F. The readings of the glider Aanderaa ranges between 249 (5.57 ml/l) and 253 $\mu\text{mol/l}$ (5.66 ml/l), with a mean value of 251 (5.62 ml/l), while the measurements of the reference sensor were between 239 and 241 $\mu\text{mol/l}$ (5.35 and 5.4 ml/l) (Table 2; these last values were confirmed by Winkler samples). Since both the instruments were set to a salinity reference

of 0, it results that the Aanderaa mounted on the SeaGlider overestimates the oxygen of about 11 $\mu\text{mol/l}$ (0.25 ml/l).

DATE	TEMPERATURE	DISSOLVED OXYGEN	
		Uncompensated (S = 0)	Compensated (S = 39)
	(°C)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)
9/6/2018	22,37	241,93	192,92
9/6/2018	22,37	241,51	192,58
9/6/2018	22,37	241,34	192,45
9/6/2018	22,37	240,91	192,10
9/6/2018	22,37	240,54	191,81
9/6/2018	22,37	240,17	191,51
9/6/2018	22,37	239,68	191,12
9/6/2018	22,37	239,51	190,99
9/6/2018	22,37	239,20	190,73

Table 2: Measurements performed with the Aanderaa 4330F reference sensor (s/n 1474) during the second test.

The tests demonstrated that the oxygen values measured with the Slocum gliders is underestimated for about 0.2-0.4 ml/l with respect to the value obtained by the reference instrument, while the SeaGlider measurements seems to overestimate it by about 0.2 ml/l.

Unfortunately, it was not possible to run the single point “calibration” in the under-control tank in the same time for the two kind of gliders (about one year of gap), moreover, the gliders were submerged in the tank without wetting the foil for 48 hours prior to test the sensors (as indicated in the Aanderaa TD269 Oxygen optode operating manual, 2017) and therefore the tests do not provide good and consistent results that allow for a sensor correction and a different approach was taken.

In-situ “calibration” of the glider oxygen data

The oxygen dataset, was extended including the years 2018-2020 (not available at the beginning of the writing of this report; Fig.13). The Preconvex19 mission was performed with the SeaGlider 661 which is equipped with an unpumped CTD; these data were corrected for the thermal lag following (Garau et al., 2011). Data were compensated for salinity and depth and then compared with the oxygen dataset collected and validated by dr. Garić and dr. Batistić at P-1200 L-term station in the South Adriatic Pit (SAP; Fig. 14).

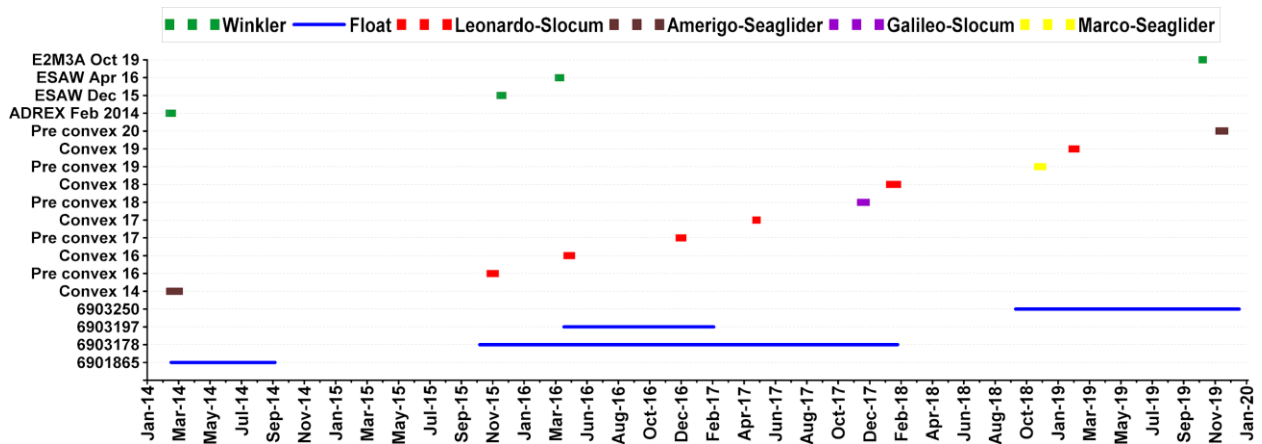


Fig. 13: Timing of the Winkler samples, profiling floats and glider missions in the South Adriatic Sea.

Platform/mission/cruise	Deploy date	Last date	Mission days*
WMO_6901865	18/02/2014	14/09/2014	209
WMO_6903178	30/10/2015	14/02/2018	839
WMO_6903197	16/04/2016	10/02/2017	301
WMO_6903250	09/10/2018	31/12/2020	815
Convex 14	15/02/2014	06/03/2014	20
Pre convex 16	20/11/2015	30/11/2015	11
Convex 16	22/04/2016	01/05/2016	10
Pre convex 17	03/12/2016	10/12/2016	8
Convex 17	06/05/2017	08/05/2017	3
Pre convex 18	02/12/2017	13/12/2017	12
Convex 18	29/01/2018	14/02/2018	17
Pre convex 19	22/11/2018	02/12/2018	11
Convex 19	30/01/2019	07/02/2019	9
Pre convex 20	21/11/2019	02/12/2019	12
ADREX_2014	14/02/2014	20/02/2014	7
ESAW_DEC_15	10/12/2015	15/12/2015	6
ESAW_APR_16	05/04/2016	09/04/2016	5
E2M3A Fix 19	18/10/2019	20/10/2019	3

*Mission days are considered until 31/12/2019

Table 3: Deploy and recovery/last dates and number of days at sea of the platform/mission/cruise performed in the south Adriatic Sea and depicted in Fig. 13.

Glider data were also compared with the dissolved oxygen distribution recorded at the P-1200 L-term station in the SAP (Fig. 14). During the late winter, the average concentrations is about 5.2 ml/l; the surface layer oxygen presents values of 5.5 ml/l while in the bottom layer oxygen the dissolved oxygen decreases to about 5 ml/l. This trend was also observed in previous studies conducted in the SAP (Artegiani et al, 1997; Zavatarelli et al., 1998; Manca et al., 2004 and Šantić et al., 2019). The mean oxygen values measured by the glider during the same period (Fig. 15a),

vary between 4.5 ml/l at the surface and 4 m/l at the bottom. The difference between the highest and the lowest values along the water column measured by the glider or at the station is coherent and is about 0.5 ml/l, while the gap between the two datasets is about 1 ml/l (the glider underestimate).

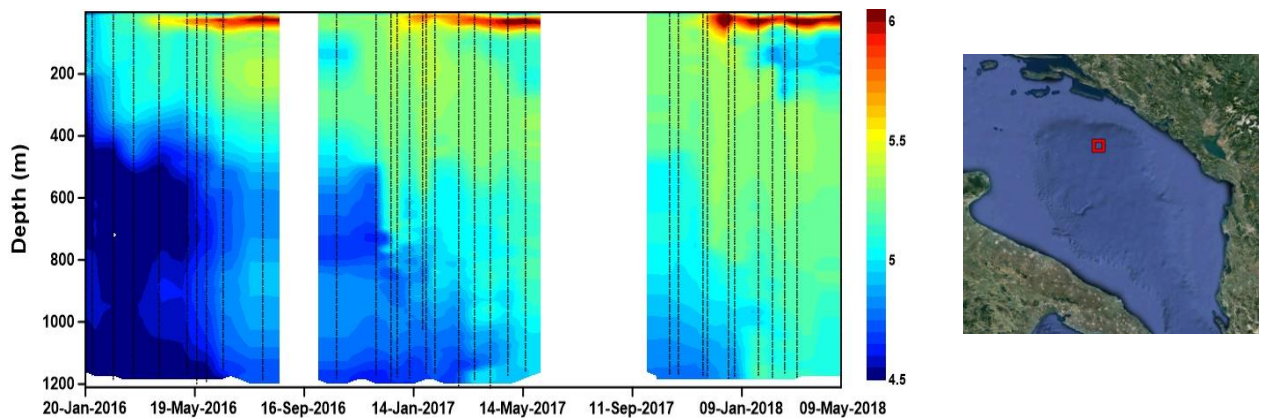


Fig. 14: Dissolved oxygen time series recorded at P-1200 L-term station (left panel; courtesy of dr. Garić and dr. Batistić) and the geographic position of the station in the SAP (right panel).

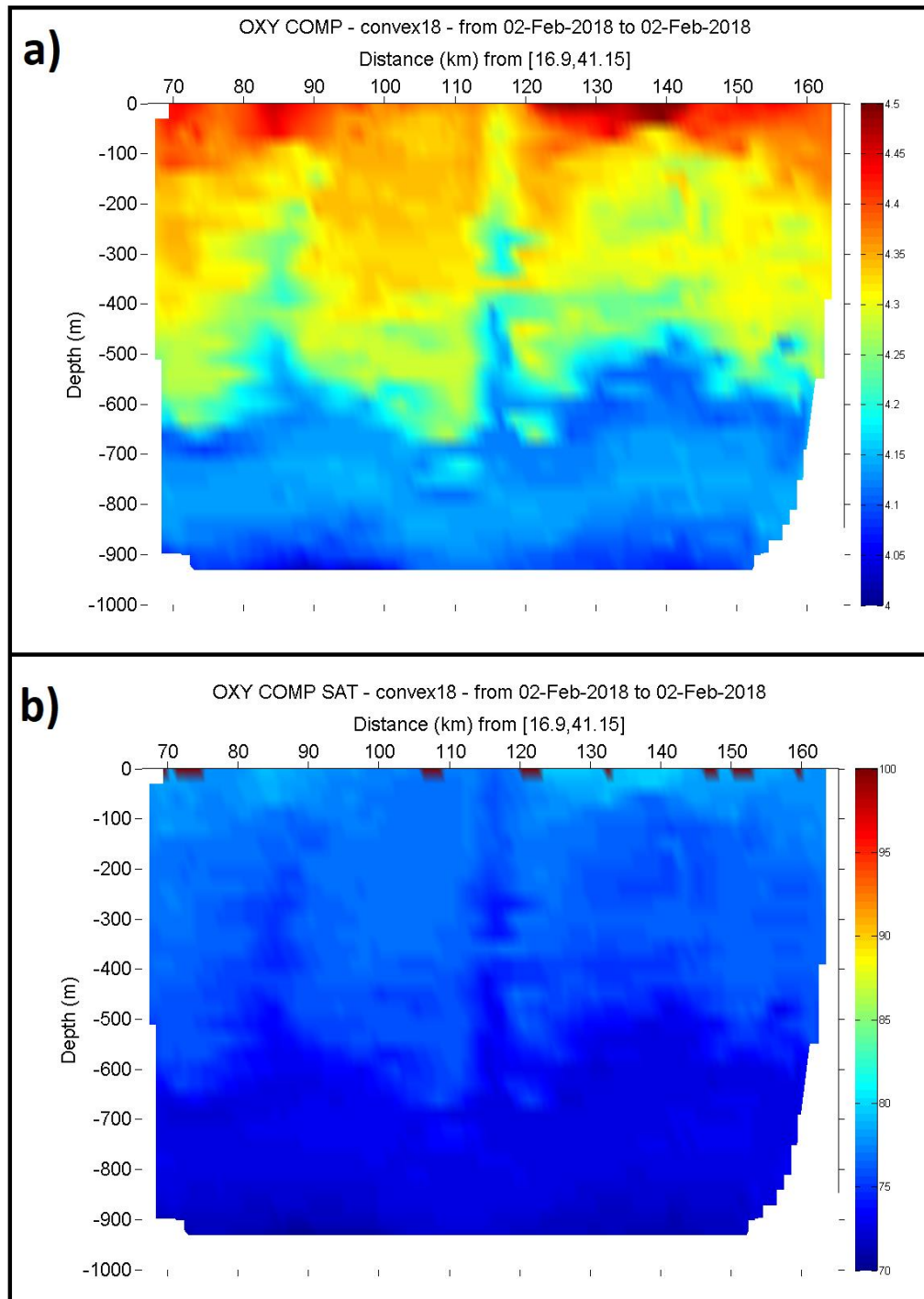


Fig. 15: Dissolved oxygen along the Bari -Dubrovnik transect in m/l (a) and oxygen saturation (b) computed from the glider compensated oxygen data collected during the Convex18 glider mission.

The oxygen saturation of the glider data was evaluated (Fig. 15b) and a saturation of 85% was observed at the surface. This value is lower than the one observed by different authors (Zavatarelli

et al., 1998; Manca et al., 2004), therefore, also the qualitative comparison of the oxygen saturation values of different sources confirms the underestimation of the oxygen glider data.

All the performed comparisons and analysis suggested that the oxygen values recorded by the gliders need a careful study to be “calibrated”.

The basic idea is to use all the good available in-situ oxygen observations which are very close in time and space to the glider data to obtain robust calibration coefficients.

For the sake of clarity, we included the term calibration in double quote. Indeed, although the procedure can provide calibration coefficients for the oxygen sensor, we will not change the coefficients inside the instrument and therefore we will apply a correction rather than a calibration.

Glider and float oxygen data comparison

Among all the available data (Fig. 13 and Table 3), we considered the glider missions and only the validated Winkler samples and/or the quality-controlled oxygen float data which were previously Winkler-calibrated in the South Adriatic Sea (Gerin et al., 2020 and Gerin and Martellucci, 2020). The strategy of “calibrating” the glider oxygen data with Winkler-calibrated data from other instruments is not new and was already used with good results by Quest et al. (2015). In particular, we selected the oxygen data within varying time and space thresholds from the glider measurements (1 day and 50 km; 2 days and 35 Km; 3 days and 20 Km; Table 4). The profiles collected in particular geographical areas of the SAP (i.e. the slope) characterized by very strong variability were excluded. Unfortunately, the chosen thresholds discard all the Winkler samples and only the Winkler-calibrated oxygen float data were considered. Additionally, for some glider missions it was not possible to find useful oxygen data to compared with (PreConvex18 performed by Slocum glider 402, Convex17 and Convex18 by Slocum glider 403; Table 3).

Float						Glider						Distance	
WMO	Cycle	Date	Time	Latitude	Longitude	Mission	id	Date	Time	Latitude	Longitude	(km)	(hours)
6901865	8	26/02/2014	11:39	41.8780	17.5760	Convex 14	554	26/02/2014	09:54	41.8942	17.6089	4	1.5
6901865	9	27/02/2014	11:33	41.8950	17.5850	Convex 14	554	27/02/2014	02:57	41.8047	17.7198	15	8.5
6903178	9	27/11/2015	02:22	42.0680	17.6580	Preconvex 16	403	28/11/2015	20:40	41.8413	17.4846	5	42
6903178	59	29/04/2016	05:33	41.8750	17.4980	Convex 16	403	26/04/2016	15:00	42.0660	17.6820	2	60
6903197	7	25/04/2016	10:31	41.6890	17.9840	Convex 16	403	24/04/2016	21:34	41.8362	17.4496	47	13
6903197	73	07/12/2016	10:32	41.7430	17.4740	Preconvex 17	403	08/12/2016	17:40	41.8145	17.3241	15	7
6903250	22	23/11/2019	11:38	41.9210	17.5900	Preconvex 19	661	24/11/2018	14:33	41.7956	17.5567	14	20
6903250	24	03/12/2019	11:40	41.8490	17.5850	Preconvex 19	661	02/12/2018	07:13	41.8412	17.5506	3	52.5
6903250	36	01/02/2019	11:36	41.7090	17.6500	Convex 19	403	31/01/2019	23:30	41.8648	17.6496	17	12
6903250	37	06/02/2019	11:35	41.6210	17.6360	Convex 19	403	07/02/2019	05:30	41.8381	17.4603	28	18
6903250	96	28/11/2019	11:38	41.9210	17.8630	Preconvex 20	554	28/11/2019	08:56	41.9689	17.6827	20	2

Table 4: Float ID, cycle number, date, time and position and glider ID, date, time and position used in the comparison. Time and distance gaps between the selected profiles.

Figures 16 and 17 show the location of the glider surfacings and the float profiles used in the comparison.

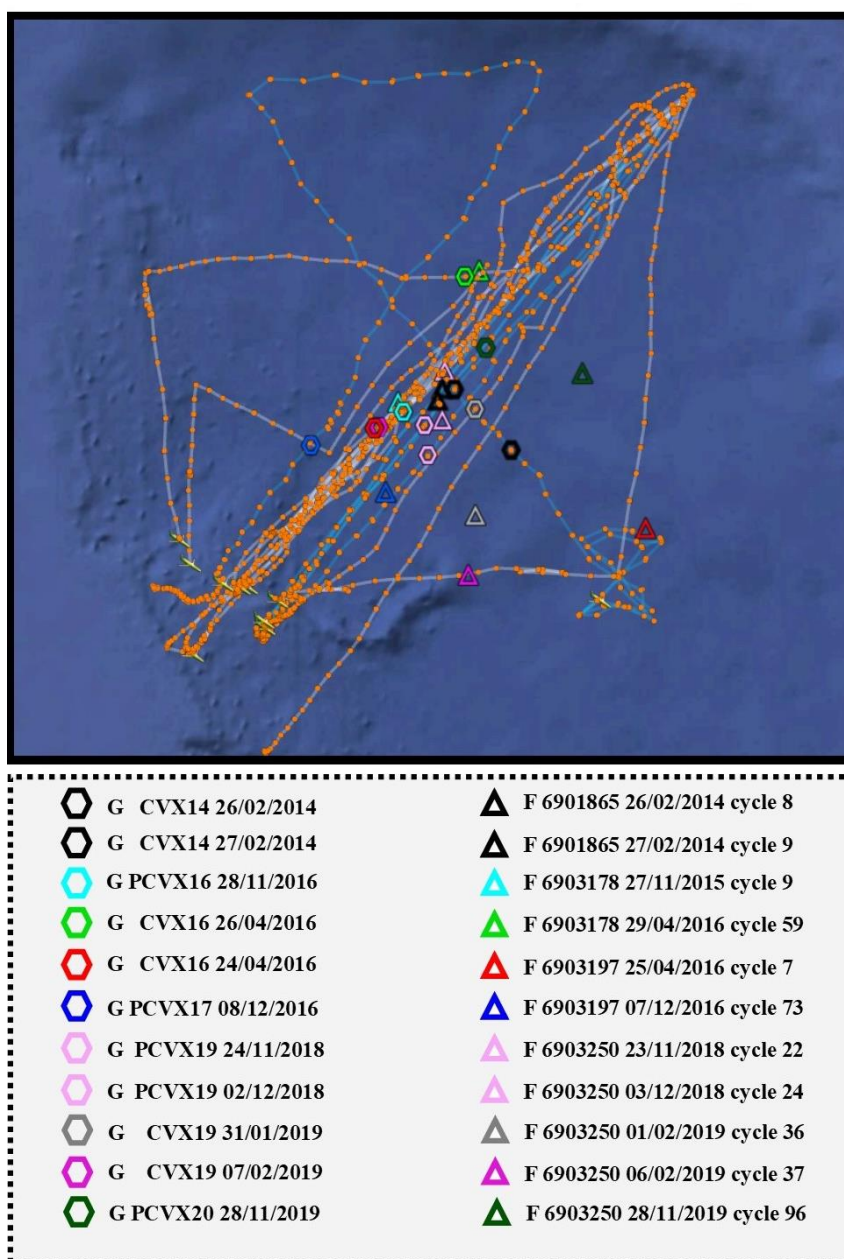


Fig. 16: Location of the glider surfacings and the float profile used in the comparison of all the cases selected in Table 4. Diamonds and triangles represent the glider surfacings and the float profiles, respectively. The symbols are color-coded with respect to time. The legend reports at the side of diamonds the glider mission names (shortened: PCVX16 stays for Preconvex16) and the time, at the side of triangles the float WMO number, the time and the float cycle number.

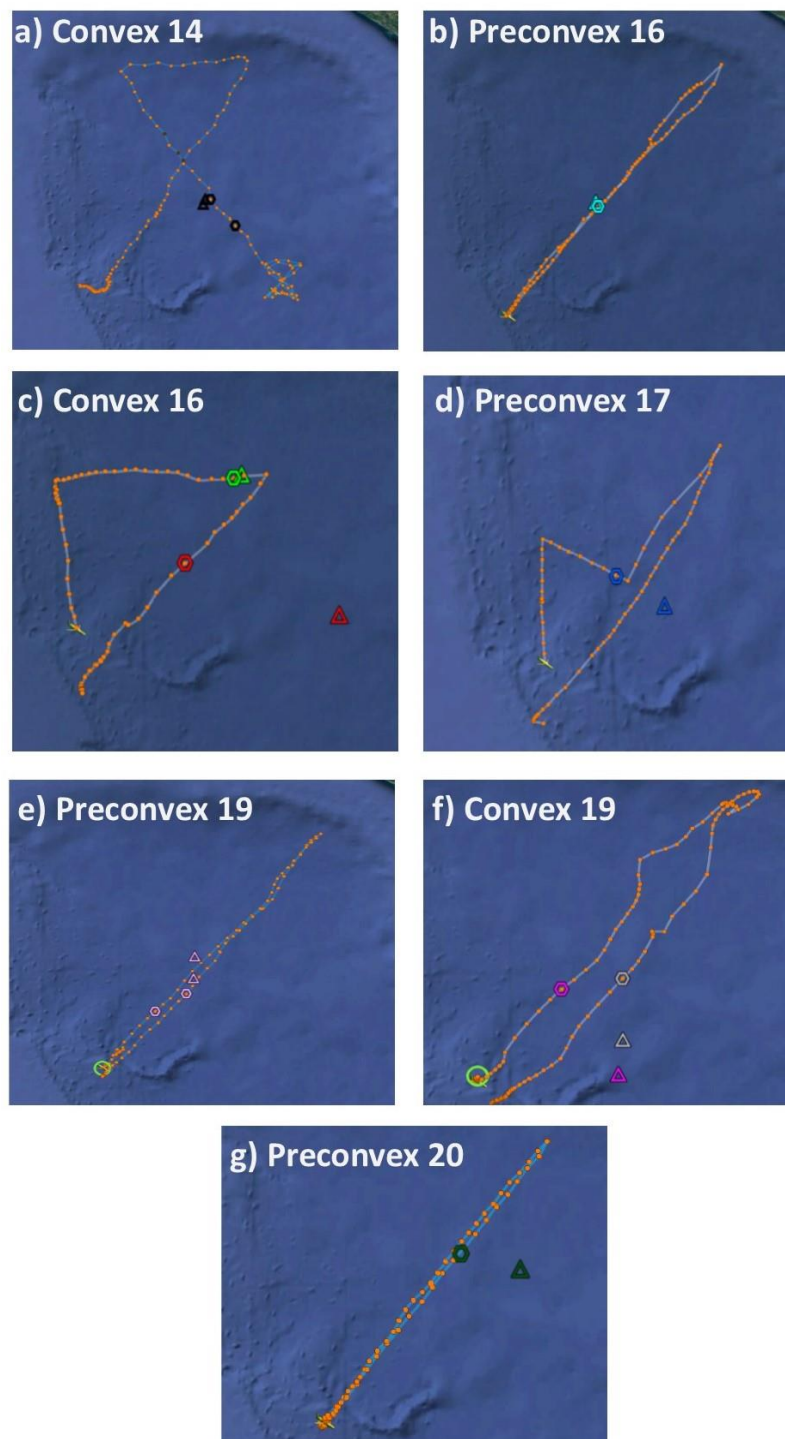


Fig. 17: Same as Fig. 16 but separated by missions: Convex14 (a); Preconvex16 (b); Convex 16 (c); Preconvex17 (d); Preconvex19 (e); Convex 19 (f); Preconvex20 (g).

A qualitative comparison of the glider compensated oxygen data with the selected in-situ reference float profiles (Winkler-calibrated data; Fig. 18) evidenced a good agreement of the profile shapes. The gaps between the glider-float profiles is not constant and it varies between 0.5 and 1.1 ml/l.

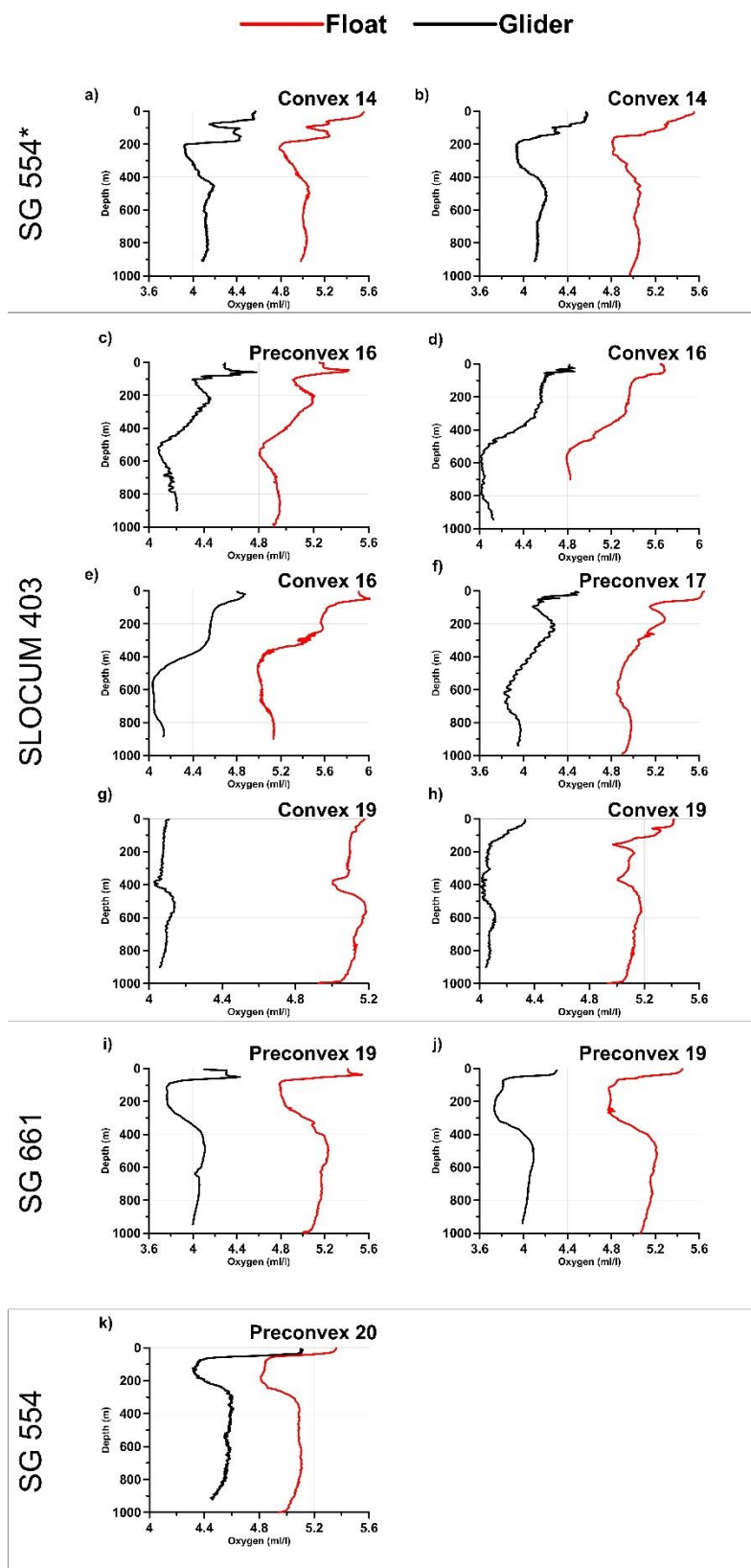


Fig.18: Comparison between glider (black line) and float (red line) oxygen profiles for the selected profiles (see Table 4 and Fig. 17). SG554* represents the SeaGlider 554 data before the last factory calibration.

Best fit line using least square minimization of the glider oxygen data

The compensated oxygen values obtained from the glider data were then “calibrated” using the least square minimization (model $Y=X+A$, where A has to be optimized) as already done in Gerin et al. (2020) and Gerin and Martellucci (2020) for the float data (Fig. 19 and Table 5).

The coefficients of determination of the least square minimization are always quite high (6 out of 11 are higher than 0.8; 0.73 is the lowest value).

During the Convex 14 glider mission, performed by the SeaGlider 554 the oxygen data was “calibrated” using two float profiles. In the first comparison (Fig. 19a) the coefficient of determination is 0.81 and the A coefficient is equal to 0.87 ml/l, while in the second comparison the coefficient of determination is 0.79 and the A coefficient increases a little bit to 0.90 ml/l (Fig. 19b). Using both data together, the coefficient of determination is 0.80 and the A coefficient 0.89 ml/l (Table 5).

The Slocum glider 403 was used in several missions. The least square minimization always evidences an underestimation of the glider oxygen concentration and, generally, a very high coefficient of determination (R^2) between 0.65 and 0.97 and an A coefficient increasing with the time of usage from 0.74 ml/l to 1.05 ml/l (Figs. from 19c to 19h and Table 5).

The SeaGlider 661 dissolved oxygen sensor was “calibrated” using two float profiles recorded during the early December 2019 (Figs. 19i and 19j and Table 5).

The oxygen data minimization with the earliest float profile and the glider gives a coefficient of determination of 0.95 and a A coefficient equal to 1.1 ml/l, while the second occurrence presents a coefficient of determination of 0.94 and a coefficient A equal to 1.09 ml/l. The use of these data together displays a coefficient of determination of 0.95 and a coefficient A equal to 1.09 ml/l.

The SeaGlider 554 was used also during the Preconvex 20 glider mission after being factory calibrated (therefore it was considered as a different unit). The minimization displays a coefficient of determination of 0.74 and A coefficient equal to 0.50 ml/l (Fig. 19k and Table 5).

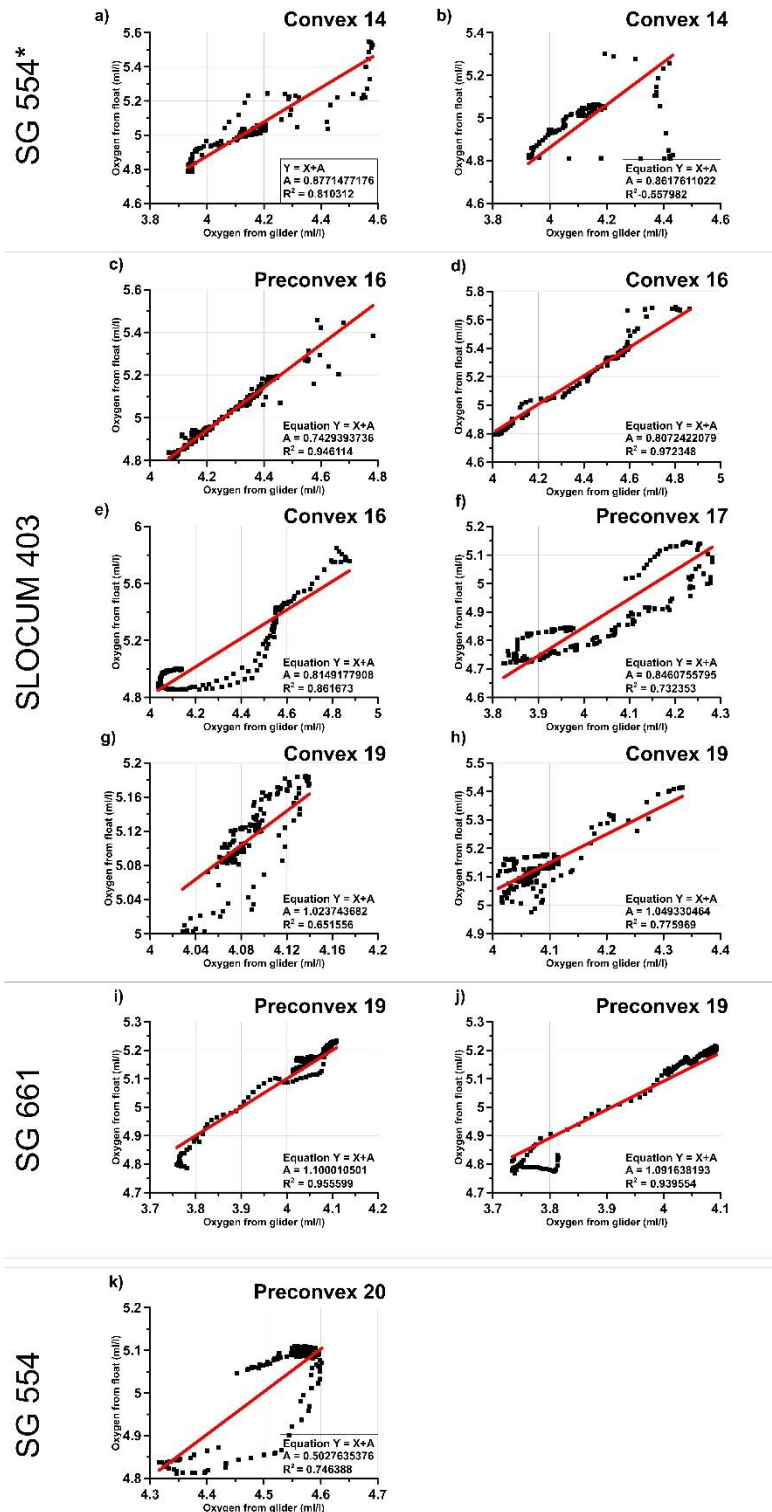


Fig.19: Least square minimization between the compensated oxygen glider data and the float data. In the legend the A coefficient and the coefficient of determination are reported. SG554* is the SeaGlider 554 before the last factory calibration.

Mission	id	R ²	A	R ²	A
Convex 14	SG 554*	0.8103	0.8771	0.8002	0.8898
Convex 14	SG 554*	0.7902	0.9024		
Preconvex 16	SL 403	0.9461	0.7429	0.9170	0.8111
Convex 16	SL 403	0.9723	0.8072		
Convex 16	SL 403	0.8617	0.8149		
Preconvex 17	SL 403	0.7324	0.8461		
Convex 19	SL 403	0.6516	1.0237	0.7137	1.0365
Convex 19	SL 403	0.7759	1.0493		
Preconvex 19	SG 661	0.9556	1.1000	0.9476	1.0958
Preconvex 19	SG 661	0.9396	1.0916		
Preconvex 20	SG 554	0.7464	0.5028		

Table 5: Results of the least square minimization between the compensated oxygen glider data and the float data. The coefficient of determination (R²) and the A coefficient are reported. The last two columns are referred to the campaign. SG554* is the SeaGlider 554 before the last factory calibration.

Drift of the oxygen sensor with time (Slocum 403 case)

The results of the least fit minimization for the Slocum glider 403 evidence an increase of the A coefficient over the time (Table 5). The reason for the increase can be attributed to the degradation of the Optode sensor mounted on the gliders or to a sensor drift. This drift may also affect the float according to Bushinsky et al., 2016 that reports a $\pm 0.1\%$ per year, undermining our method, in which the float data are used as a reference for the “calibration” of the glider oxygen data. The oxygen float drift is amplified especially when the glider-float minimization is done a long time after the float “calibration”.

The Slocum 403 was used longer than the other gliders allowing a better analysis of the glider oxygen drift over time. The A coefficient computed by mission using a set of float oxygen data provided by sensors with different aging (Table 5), plotted versus time shows a regular increase over time of +0.1 ml/l per year (Fig. 20). The high regression coefficient of R²=0.99 of the four “calibration” versus time suggests that the possible drift of the float oxygen sensor is negligible with respect to the one mounted on the glider. Indeed, the drift observed is 1 order higher than the one declared by the Aanderaa.

The fact that gliders are operated in the water only for limited periods and then stored for a long time might be the reason of the higher observed drift. Despite the standard maintenance of the Optode sensor after every mission following the Aanderaa TD269 Oxygen Optode operating manual, (2017) is performed, its membrane tends to dry out and consequently is affected by an important degeneration.

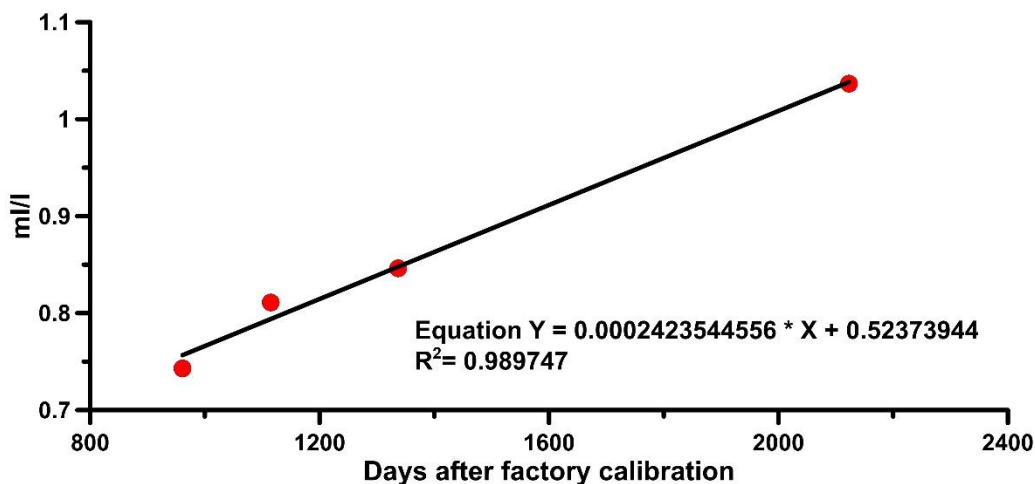


Fig.20: Regression of the A coefficient for the Slocum glider 403 over time. Red dots are the A coefficient as in Table 5; the x axis represents the days after the factory calibration (11 April 2013).

Oxygen drift due to foil: Aanderaa factory indications

The Aanderaa support center notified that in some cases the foil can have a drift of 3 - 8% offset prior to deployment, and after that stabilized with a drift of about 0.2% per year.

This evidences the importance of our “calibration”, which is about one order higher than Aanderaa's notification.

Possible correction for the oxygen glider data without a reference

As discussed in the report (e.g.: Fig. 13), it was not possible to “calibrate” the collected glider oxygen data using the above method during the PreConvex18 (Slocum glider 402), the Convex17 and Convex18 (Slocum glider 403) missions, due to the lack of validated Winkler samples and/or quality-controlled and Winkler-calibrated oxygen float data close in space and time.

We propose an alternative way to correct the compensated oxygen glider data of the Convex17 and Convex18 using the computed regression (Fig. 20). The estimated coefficients are summarized in Table 6.

The correction of the PreConvex18 glider data requires an assumption: the membrane (sensing foil) of the two sensors mounted on 402 and 403 units degraded over time at the same rate. This assumption is comforted by the calibration certificate that reports the calibration on the same day (11 April 2013). We can therefore speculate that the regression obtained for the Slocum glider 403 (Fig. 20) can be applied on the glider 402.

Mission	id	A
Convex 17	SL 403	0.88461
Convex 18	SL 403	0.95150
Preconvex 18	SL 402	0.93938

Table 6: Estimated coefficients for the oxygen calibration for the Convex17, Convex18 and Preconvex18 missions.

Final results

All the oxygen glider data were corrected applying the coefficient of Tables 5 and 6. The final glider dataset (Fig. 21) was compared with the data collected at P-1200 L-term station (Fig. 14) and at the E2M3A station (not shown) obtaining a very good qualitative agreement.

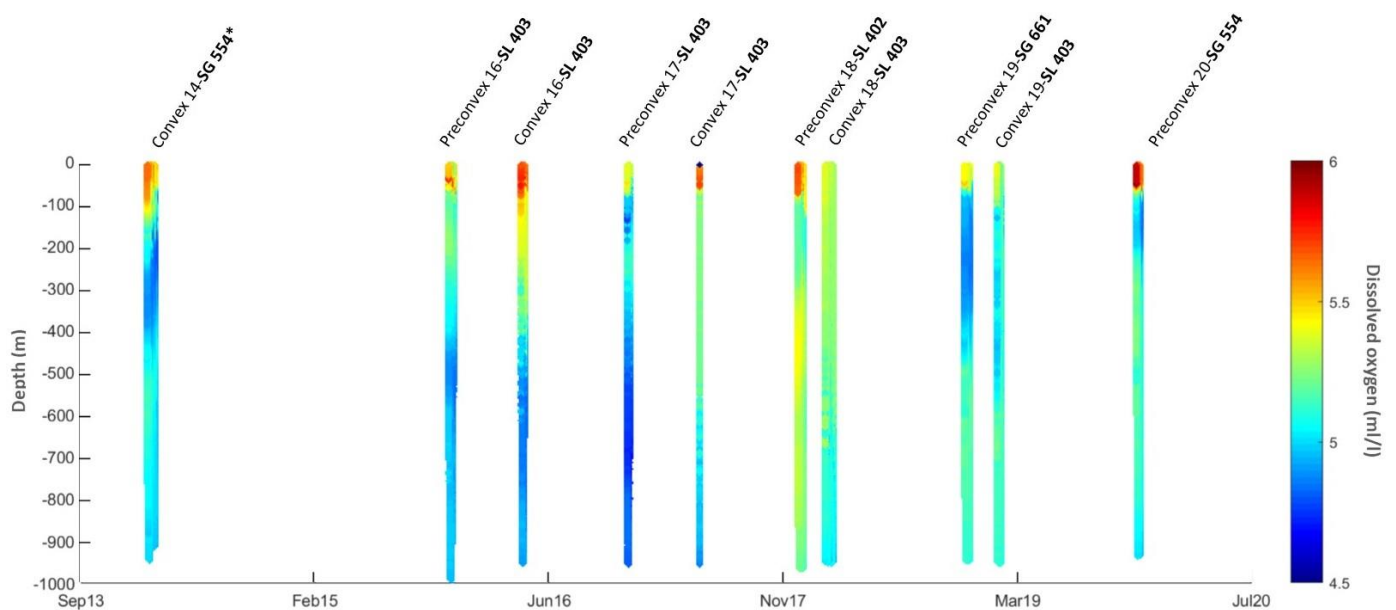


Fig. 21: Time series of the “calibrated” and compensated oxygen data of the different glider missions. SG554* is the SeaGlider 554 before the last factory calibration.

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