Float oxygen data calibration with discrete Winkler samples in the South Adriatic Sea.

Gerin R., Martellucci R., Notarstefano G. and Mauri E.

SUMMARY:

1. Introduction

Argo float is a sub-surface profiling instrument that collects high-quality temperature salinity profiles from the upper 2000m of the ocean. It can autonomously operate for 3-4 years and can be equipped with sophisticated probes to measure biogeochemical properties in the seawater. Most of them are tracked by Argos or GPS positioning systems when they are on surface, and the data are transmitted first to the satellites and then to the ground receiving stations. National Centres prepare the data for dissemination using a basic set of quality control tests (Wong et al., 2020 and Thierry et al., 2018). They also relay the data to the appropriate PI for delayed mode qualification. Two GDACs (Global Data Assembly Center) provide an FTP and a WWW access to the Argo data.

A method to assess the quality of the oxygen data as derived from Argo floats and to calibrate them consists of comparing the data measured by Argo platforms with in-situ Winkler samples close in time and space. This work focuses on the Adriatic Sea that is considered one of the main sources of the dense water for the Mediterranean Sea. Since a decade, the Southern area was highly sampled with autonomous instruments (float and glider) and oceanographic cruises to understand the thermohaline variability of the area.

2. Float selection for the comparison

Several floats explored the South Adriatic Pit (SAP). Some of them were deployed there to sample the main dominant cyclonic feature, other platforms entered the Adriatic Sea and remained entrapped in the cyclone (Table 1 and Fig. 1).

FLOAT WMO	DEPLOY DATE	DEPLOY LAT	DEPLOY LON	LAST DATE	LAST LAT	LAST LON	MISSION DAYS
6901040	29/03/2012 15:51	42.22	17.72	12/10/2014 06:39	42.26	18.31	926
6901827	11/05/2013 01:04	42	18.6	26/06/2018 01:08	41.7	18.5	1872
6901826	10/05/2013 04:10	42.02	16.18	01/06/2018 04:12	36.66	16.32	1848
6901822	23/03/2013 15:58	41.52	18.08	27/02/2018 16:09	41.11	17.77	1802
6901865	18/02/2014 17:28	41.83	17.76	14/05/2015 10:35	37.22	15.7	449
6901862	26/03/2015 20:25	41.53	18.06	27/06/2019 11:00	37.09	16.94	1553
6903178	30/10/2015 14:08	41.74	17.69	14/02/2018 02:10	41.37	16.98	837
6903197	07/04/2016 21:46	41.57	17.38	10/02/2017 10:37	41.17	18.14	308
6903236	11/03/2018 11:09	37.38	20.33	12/05/2019 06:13	38.03	15.47	426
6903250	08/10/2018 22:31	39.1	18.22	21/04/2020 11:37	42.19	17.51	560

Table 1: Time and location of the deployment and of the last operational day and total days of mission.

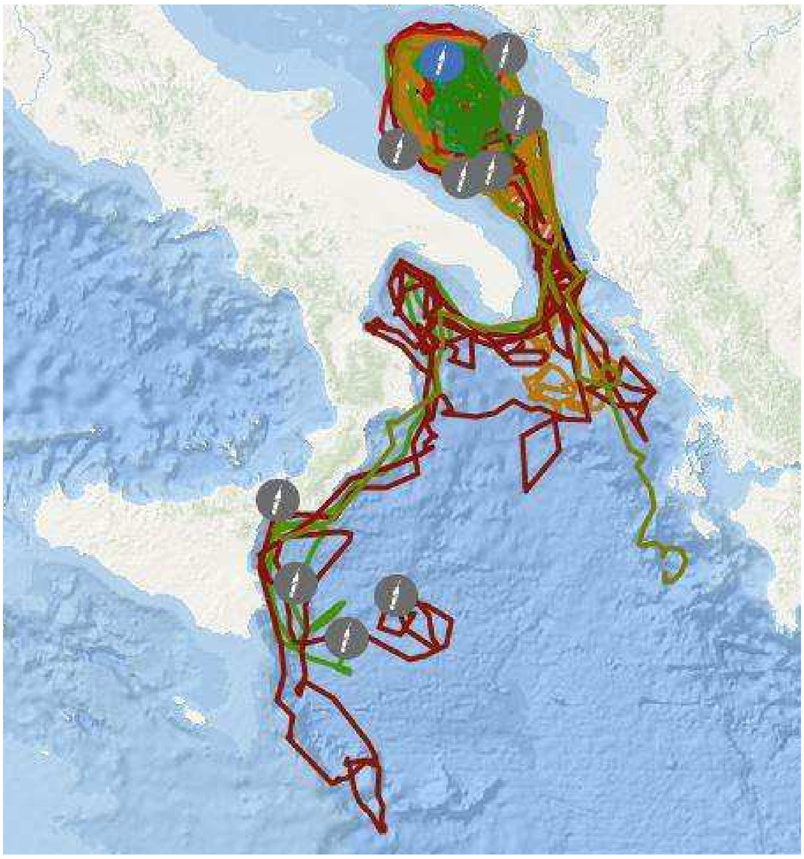

Fig. 1: Trajectories of the floats which covered the South Adriatic Sea. Some of them entered the Adriatic and remain entrapped in the main feature in the SAP, others exit the Adriatic end explored the Ionian Sea.

Three out of ten Argo floats were equipped with the oxygen sensor (WMO 6903178 with a SBE63 and WMOs 6903197 and 6903250 with an Aanderaa Optode). The data of these floats were compared to Winkler data collected along a transect joining Bari to Dubrovnik. The transect was performed in a few days, therefore only a limited number of float profiles can be compared with the cruise data (Fig.2). Anyway, at the time of the cruise, floats equipped with oxygen sensor were located in the center of the pit at a distance between 17 and 38 km with respect to the transect (see Table 2 and Figs. from 3 to 5). As a result, during December 2015 we selected one profile (profile 17) of float 6903178 collected the day before the Winkler sample (at station 9; ESAW-1 cruise) about 35 km apart (Table 2 and Fig. 3). In April 2016, although two floats were near the Winkler samples, one of them (float 6903197) have a temporal gap of about 11 days with respect to the Winkler samples (it was deployed after this cruise ESAW-2) and was not considered for the comparison (Table 2 and Fig. 4). Two consecutive profiles of the float 6903178 were chosen with a time gap of 2 days. In particular, the float profile 48 was associated to the Winkler performed at station 10 of the ESAW-2 cruise (distance 33 km; time gap about 2.5 days) and float profile 49 to the one at station 9 of the ESAW-2 cruise (distance 17 km; time gap about 1 day).
Lastly, in October 2019, profile number 89 of float 6903250 was selected, with a distance of 38 km from the Winkler sample collected almost contemporaneously on the same day (E2M3A Fix-19 in Table 2 and Fig. 5).

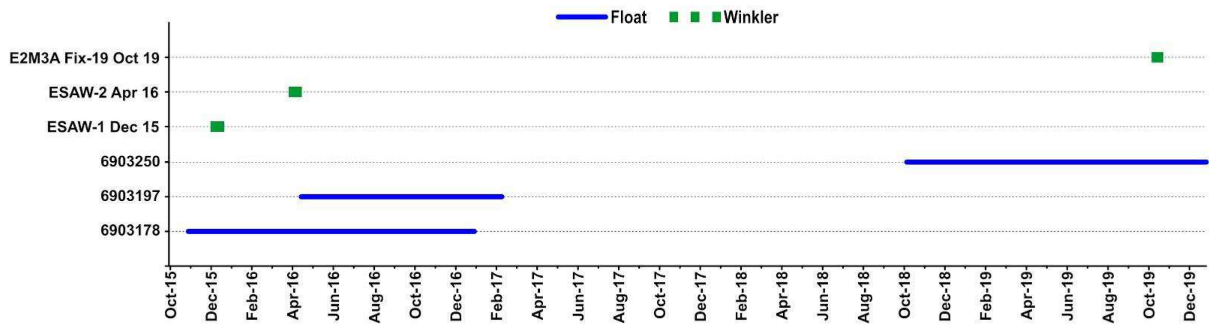

Fig. 2: Float and Winkler samples timing in the South Adriatic Sea.

Floats						Winkler						Distance	
WMO	Cycle	Date	Time	Latitude	Longitude	Cruise	Station	Date	Time	Latitude	Longitude	(km)	(hours)
6903178	17	16/12/2015	02:45	42.199	17.479	ESAW-1	9	14/12/2015	21:43	42.040	17.834	35	29
6903178	48	07/04/2016	06:14	42.225	17.629	ESAW-2	10	09/04/2016	21:05	42.220	18.016	33	63
6903178	49	09/04/2016	06:14	42.151	17.700	ESAW-2	9	08/04/2016	08:51	42.040	17.834	17	21
6903197	1	19/04/2016	10:35	41.662	17.718	ESAW-2	7	08/04/2016	09:01	41.862	17.678	18	265
6903250	89	19/10/2019	11:40	41.866	17.931	E2M3A-Fix19	Buoy	19/10/2019	09:50	41.544	18.059	38	2

Table 2: Float profiles and Winkler samples time and distance gaps of the associated cases. Table reports also the float profiles and Winkler samples time, position and cycle (profile) or station number.

Distribution of Winkler stations and Argo float (6903178) vertical profiles

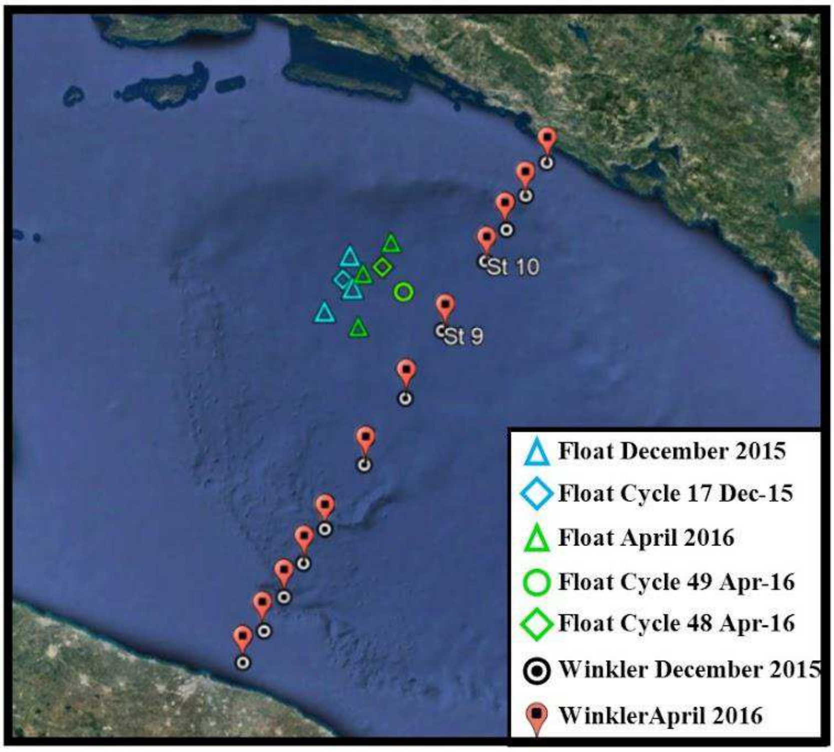

Fig. 3: Cruise ESAW-1 stations in December 2015,cruise ESAW-2 stations April 2016 both with Winkler samples (red marks) and float 6903178 positions cyano for the first period and green for the second.The cyano diamond indicates the chosen float profile for the December 2015 comparison and the green diamond and circle the ones for the April 2016 comparison.

Distribution of Winkler stations and Argo float (6903197) vertical profiles

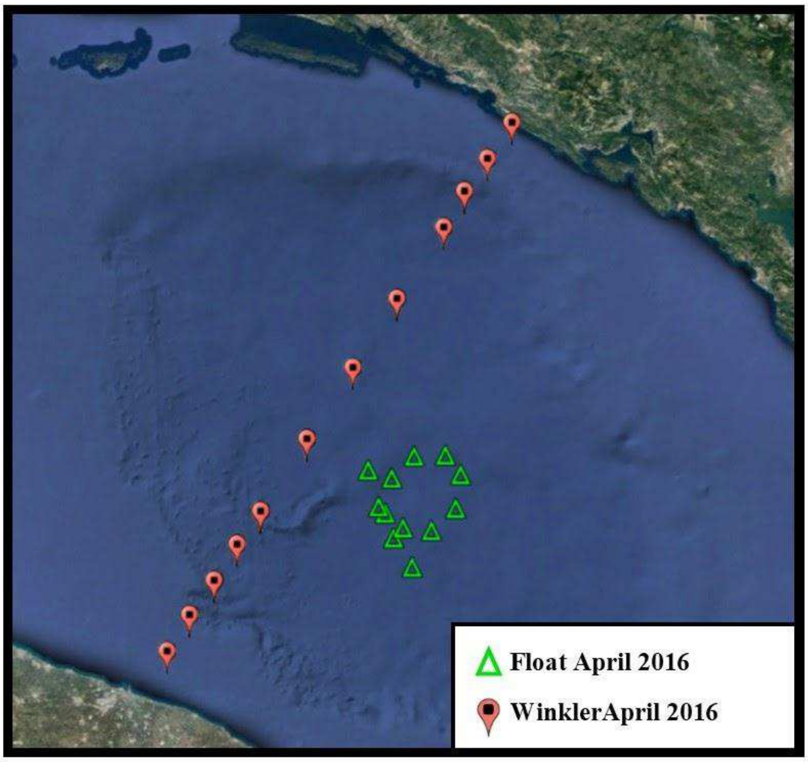

Fig. 4: Cruise (ESAW-2) stations with Winkler samples during Aprile 2016 and float 6903197 positions in the same period (green triangulus).

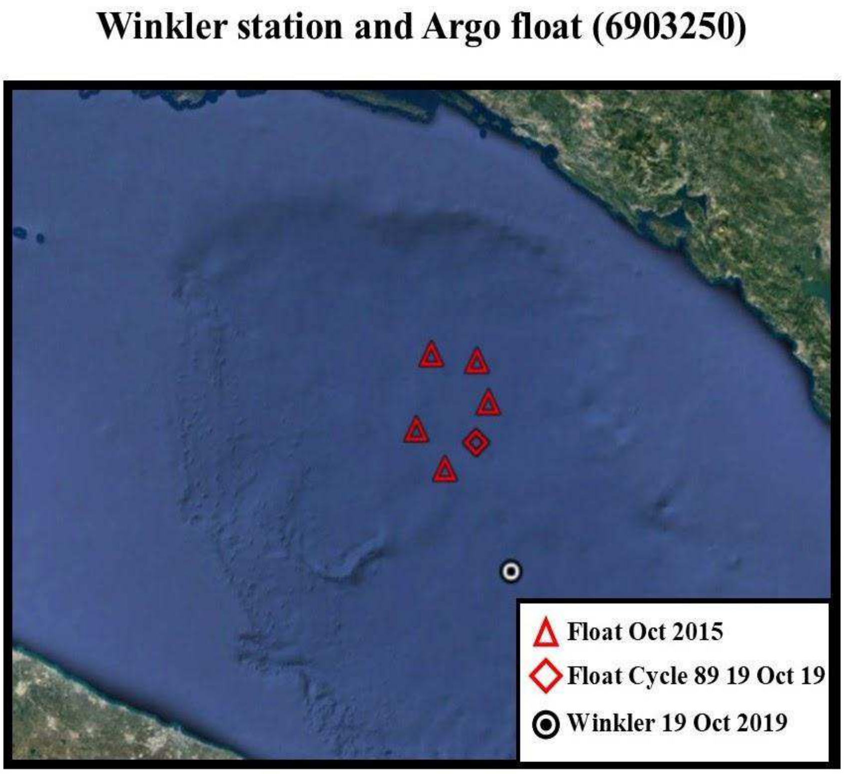

Fig. 5: Winkler sample position in October 2019 (E2M3A Fix-19) and float 6903250 profiles positions in the same period (red and diamond triangulus respectively). The red diamond indicates the chosen float profile for the comparison.

3. Winkler and float oxygen data comparison

The selected float profiles (data from /ifremer/argo/dac/coriolis/6903***/profiles) were then qualitatively compared with the Winkler data obtained from about 12 Niskin bottles along the water column from the surface down to 1000 m depth. Fig.6 shows an anomalous shape of the Winkler profile in April 2016 (box B and C), while the shape of the float and Winkler profiles in December 2015 (box A) and October 2019 (box D) are quite similar. This suggests the possibility to correct the 6903178 and 6903250 float oxygen data by using the Winkler data. Focusing on the April 2016 cases, it is important to note that, while the variability of the oxygen in the two consecutive float profiles (profile 48 and 49; temporal gap 48 hours and distance 10 km) is very small (see Fig. 7), the variability of the Winkler data is higher and the values obtained at some point seem erroneous (see Fig. 7) as also observed by Šantić et al. (2019).

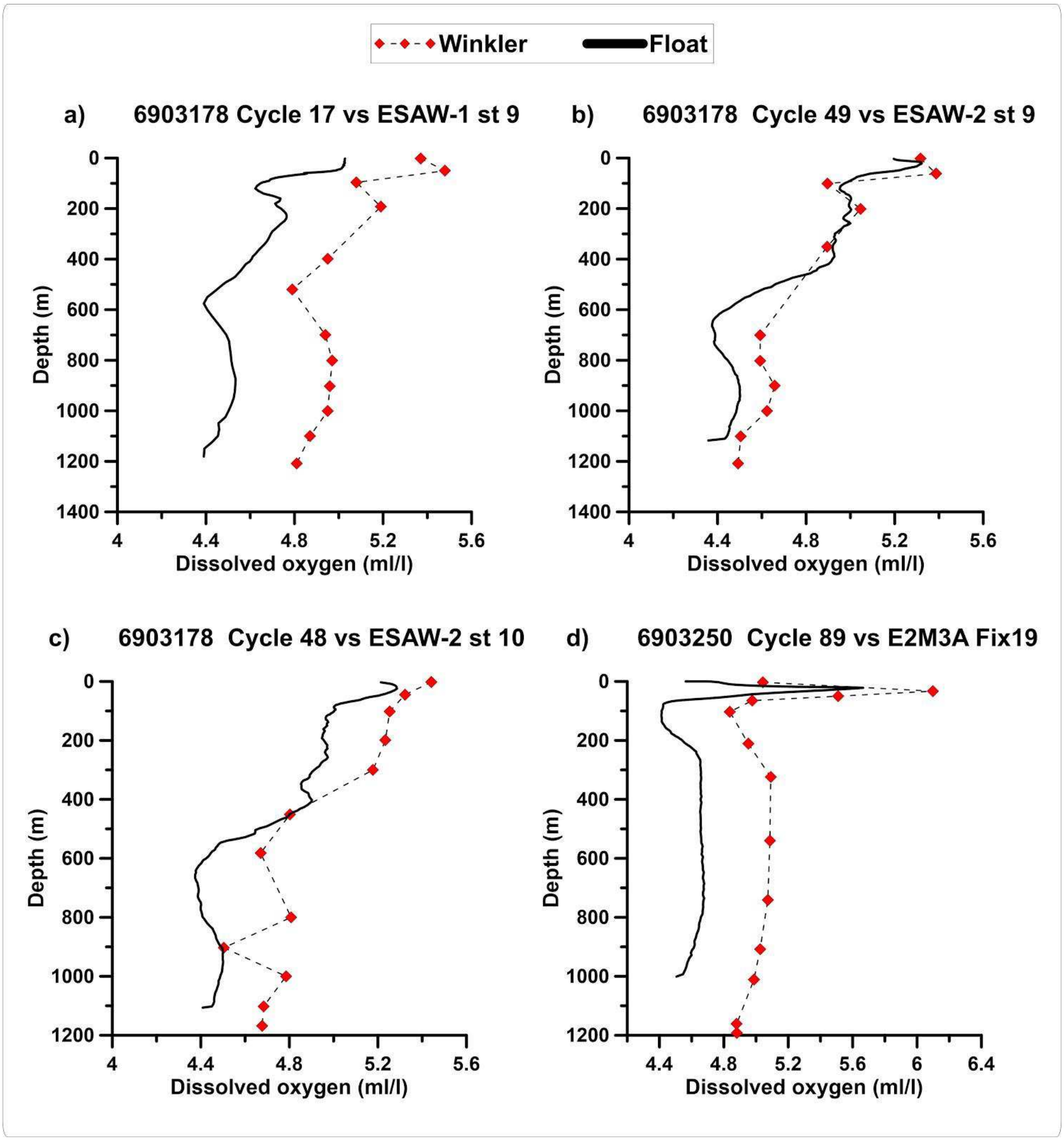

Fig. 6: Comparison between Winkler data and float oxygen measurement for the selected cases (a: December 2015, b and c: April 2016, d: October 2019).

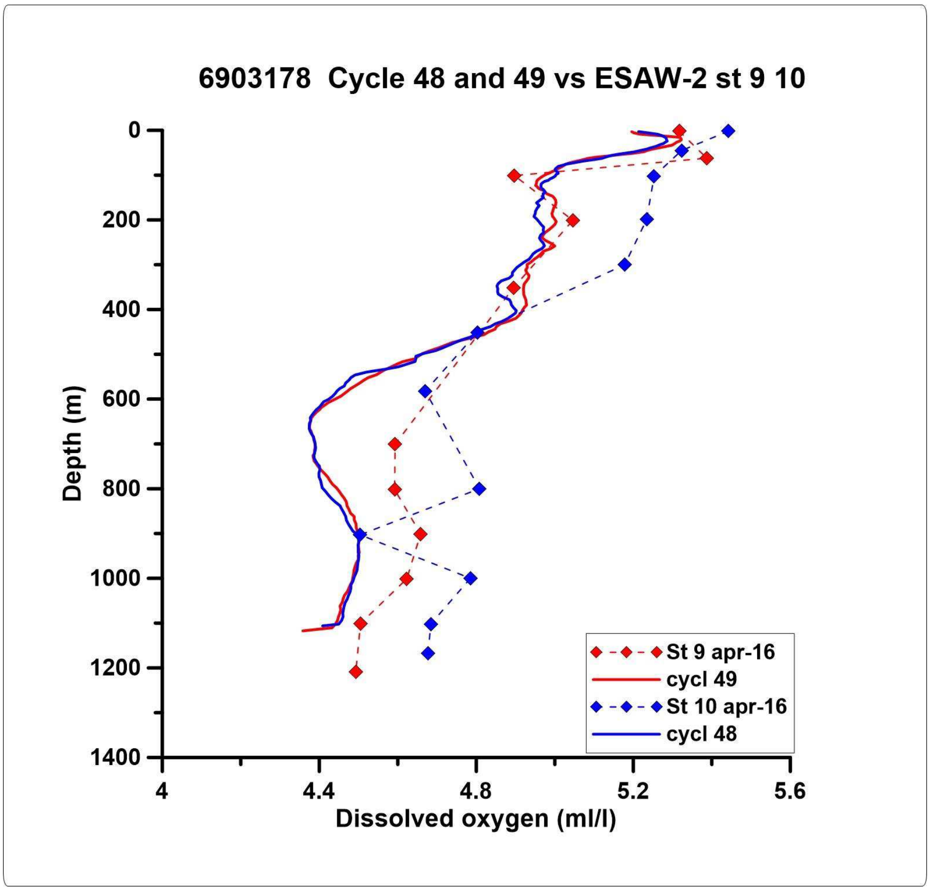

Fig. 7: Float oxygen measurements and Winkler data comparison for the April 2016 case.

From 20 November to 1 December 2015 and from 22 April to 1 May 2016, the SAP area was covered also by two glider missions in which oxygen data were collected along the Bari-Dubrovnik transect (Preconvex16 and Convex16 missions, respectively). Further details on the glider missions are described in Kokkini et al. (2019). The float 6903178 was very close to the glider path in both periods (Fig. 8 upper panels). The sampling points which minimize the distance and the time gap were selected (Table 3) and a qualitative comparison between the float and the glider data was performed (Fig. 8 lower panels). The shape of the oxygen profile as measured by the float and the glider during the Preconvex16 and Convex16 missions are almost identical, confirming that the Winkler data obtained in April 2016 are questionable and can not be used in the analysis.

Float						Glider					Distance	
WMO	Cycle	Date	Time	Latitude	Longitude	Mission	Date	Time	Latitude	Longitude	(km)	(hours)
6903178	9	*27/11/2015*	*02:22*	*42.068*	*17.658*	Preconvex 16	*28/11/2015*	*20:40*	*41.841*	*17.485*	*5*	*42*
6903178	59	*29/04/2016*	*05:33*	*41.875*	*17.498*	Convex 16	*26/04/2016*	*15:00*	*42.066*	*17.682*	*2*	*60*

Table 3:Float time, position, cycle number and glider profiles time, position used in the comparison. Time and distance gaps between the selected profiles.

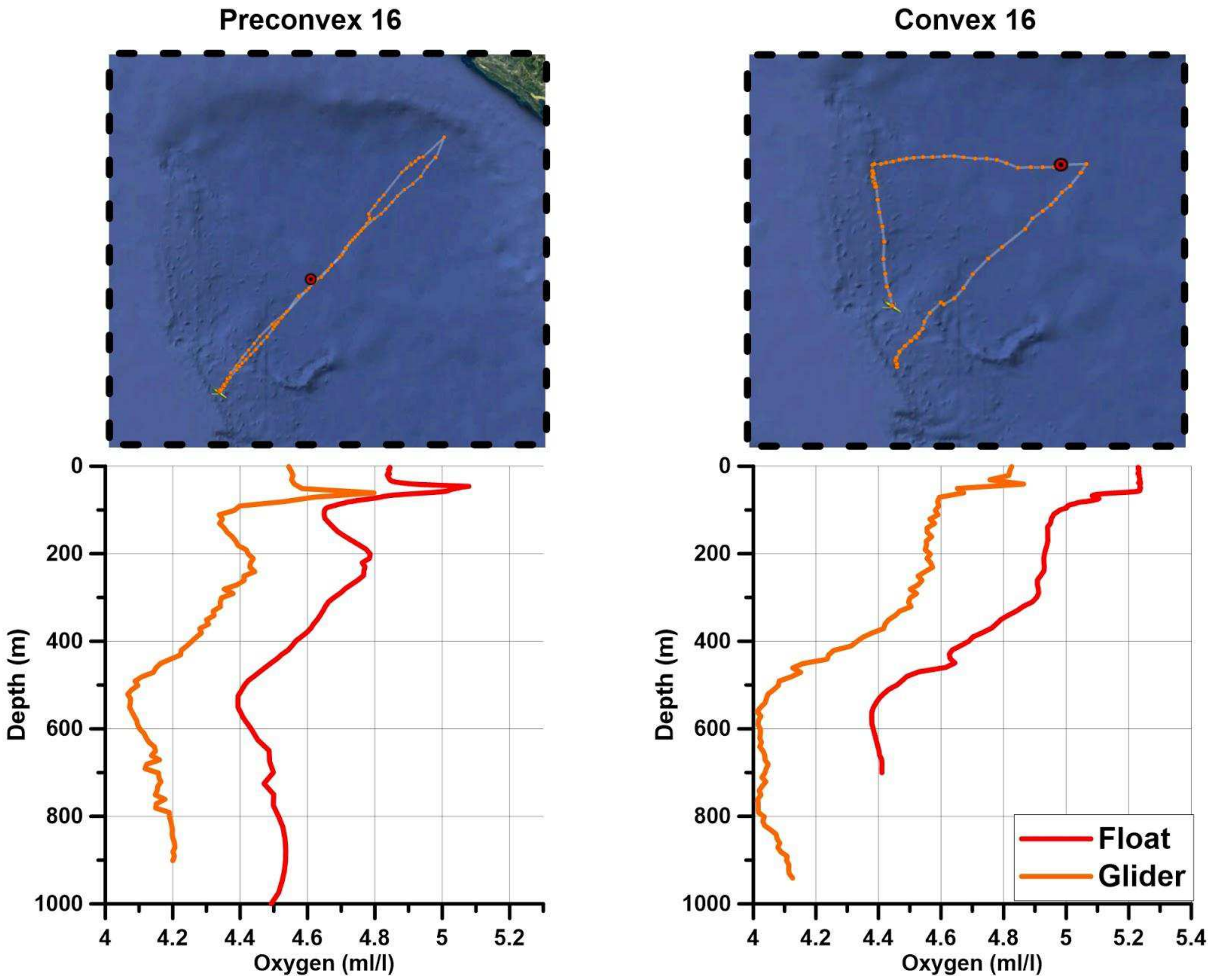

Fig. 8: Glider surfacings and float positions during the Preconvex16 and Convex16 glider missions (upper panel) and comparison between glider and float oxygen data for the above selected profiles.

Hence, Winkler data of April 2016 can not be used to correct the oxygen data of floats 6903178 and 6903197.

4. Float oxygen calibration

A least square minimization between the float and Winkler oxygen data (model Y=X+A, where A has to be optimized) was used to calibrate the oxygen recorded by the float (as done by Körtzinger et al., 2005). The minimization displays an underestimation of the float oxygen data and very high R^2 (coefficient of determination) values between 0.85 and 0.95.

Float 6903178

The minimization defines a coefficient A equal to 0.419 and a R^2 of 0.93 (Fig. 9).

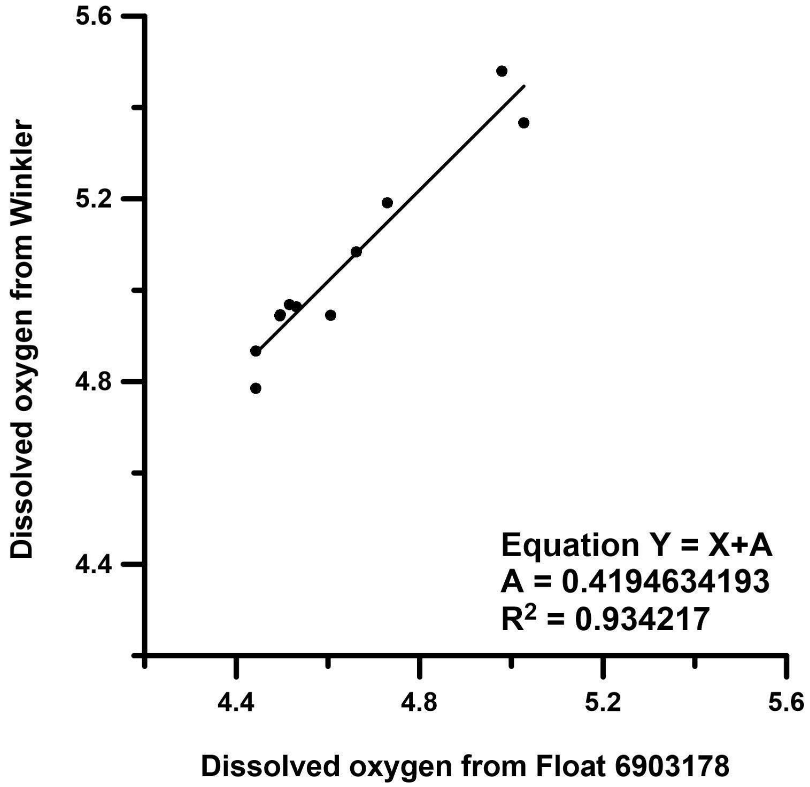

Fig. 9: Least square minimization between the float 6903178 and the Winkler data.

Float 6903197

In order to correct oxygen data measured by the float 6903197 without using the Winkler sample (see chapter 3), we considered the Winkler calibrated oxygen data of float 6903178 as reference. The basic idea is to select the profiles of the two floats which are close in time and space to each other and to correct the oxygen data of the float 6903197 using the Winkler calibrated oxygen data of float 6903178.

Table 4 and Fig. 10 show the location and time of the two floats used in the comparison. The shape of the oxygen profiles measured by the two floats are very similar in all the selected cases (Fig. 11; oxygen data of float 6903178 are calibrated).

	6903197			6903178			Distance	
	Date	Latitude	Longitude	Date	Latitude	Longitude	(km)	(days)
A	04/06/2016	42.14	17.589	30/05/2016	41.811	17.354	40	6
B	03/08/2016	41.569	18.156	24/07/2016	41.615	18.189	5	10
C	24/07/2016	41.534	17.653	09/07/2016	41.371	17.71	17	15
D	28/08/2016	42.273	18.017	28/08/2016	42.358	18.091	11	0
E	23/08/2016	42.213	18.069	23/08/2016	42.251	17.928	11	0
F	18/08/2016	42.072	18.148	18/08/2016	42.223	17.922	27	0
G	02/09/2016	42.293	17.996	02/09/2016	42.398	18.018	11	0
H	13/10/2016	42.015	17.373	12/10/2016	42.447	17.688	56	1
I	13/09/2016	42.349	17.62	02/10/2016	42.449	17.724	13	19

Table 4: Profile details of the floats 6903197 and 6903178 with time and distance differences of the associated cases. Table reports also the float profiles time and position.

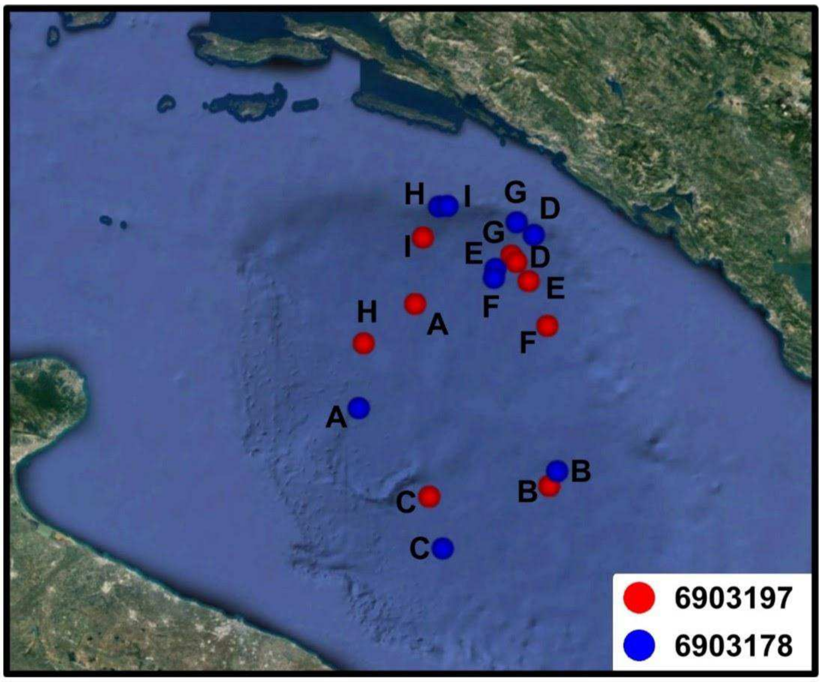

Fig. 10: Selected positions of the floats 6903197 and 6903178 for the oxygen profile comparisons.

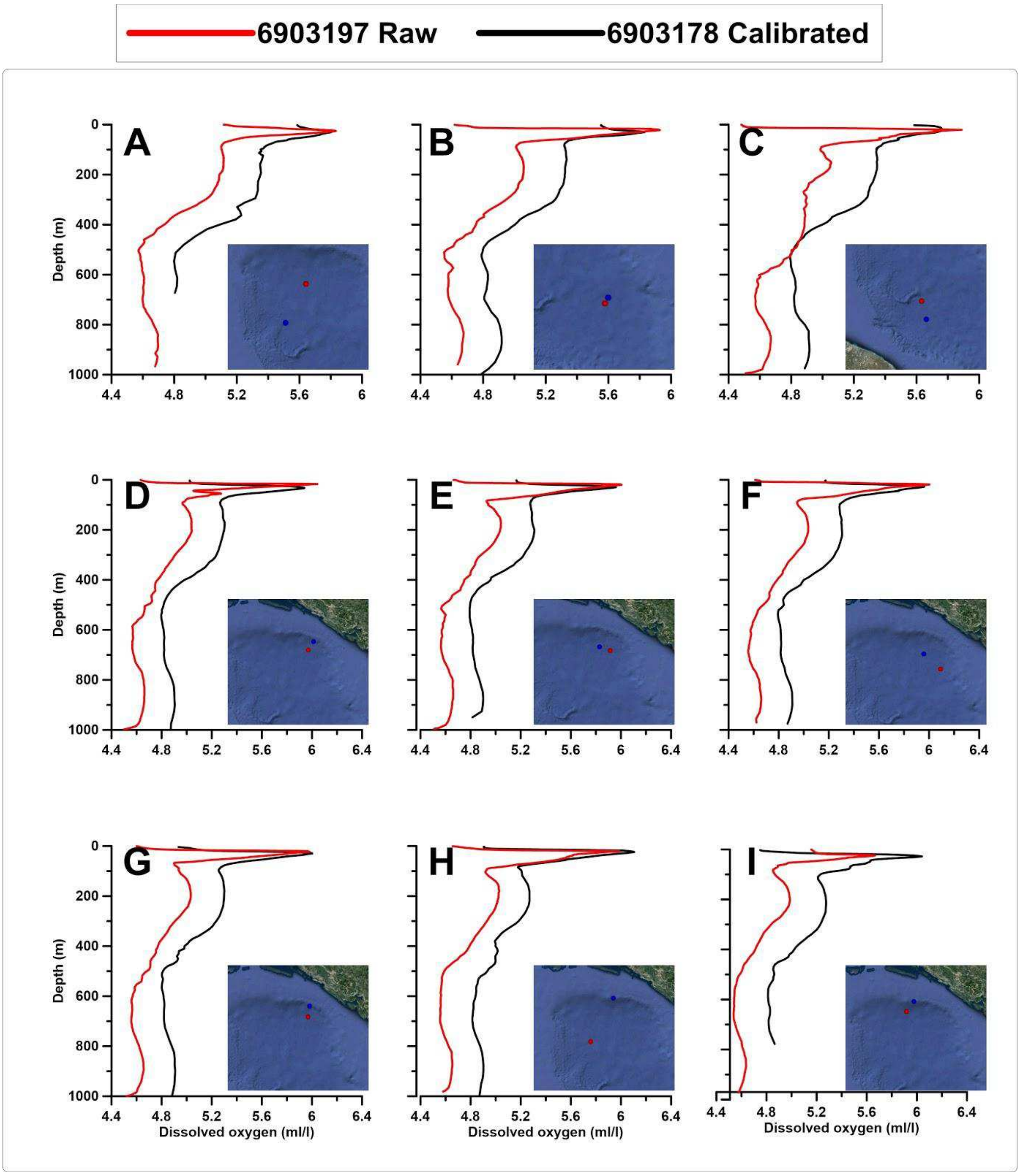

Fig. 11: Oxygen profile comparison between floats 6903197 and 6903178 for the above selected cases.

We chose the cases where time difference is less than 10 days and distance less than 11 km. In this way we selected 4 out of 9 cases: B, D, E and G. We used the 4 cases removing the data over 100 and below 900 m, to exclude the variability of the surface layer and to cut the profiles at the same depth. The Least square minimization displays a coefficient A equal to 0.246 and a R^2 of about 0.95 (Fig. 12).

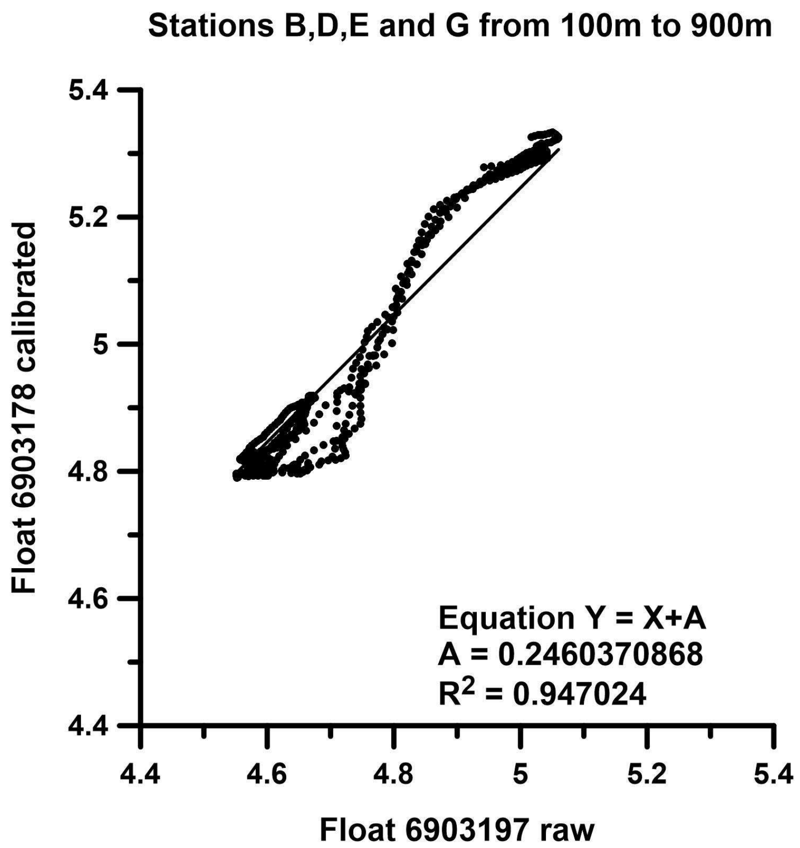

Fig. 12: Least square minimization between the float 6903197 and float 6903178 (calibrated) oxygen data. Only data between 100 and 900 m were considered.

Float 6903250

The minimization defines a coefficient A equal to 0.470 and a R^2 of 0.85 (Fig. 13).

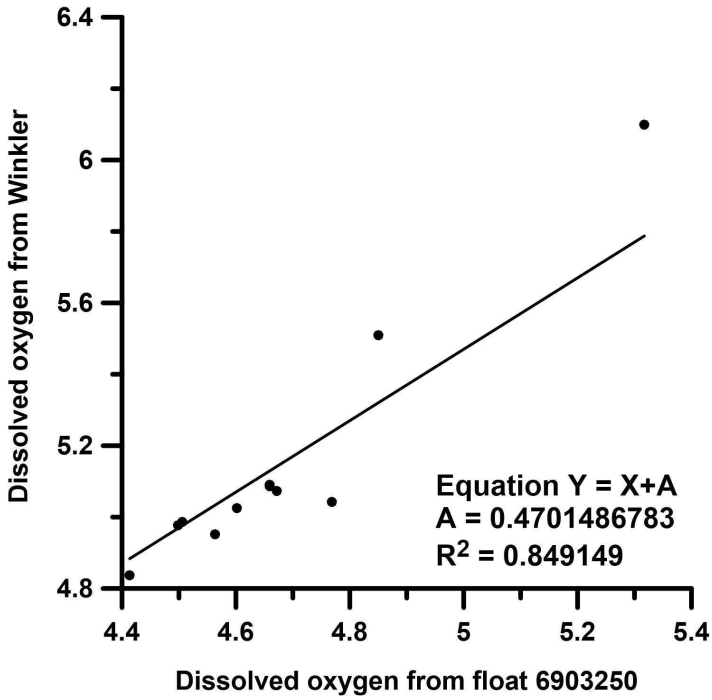

Fig. 13: Least square minimization between the float 6903250 and the Winkler data.

5. Discussions and conclusions

The Winkler samples collected during two cruises (2015 and 2019) were used to calibrate the oxygen data measured by two Argo floats (6903178 and 6903250) in the SAP. This is a recommended procedure (Bittig and Körtzinger, 2015) for the correction of the in-situ oxygen data obtained from oceanographic instrumentation.

We decided to apply a simple offset to the oxygen measured by the float as the float and Winkler oxygen profiles has a very similar shape and (as already done by Körtzinger et al., 2005). We are aware that this correction is valid only in the range of values used for the minimization and that it may give incorrect results in different ranges (Seabird Note 6.2). On the same time, we are supported by the fact that the oxygen values in the SAP remain almost always inside the expected range (Zavatarelli et al. 1998, Manca et al. 2004) with extremes of the uncalibrated float oxygen values between 4 and 6 during the last 5 years.

A third float (6903197) sampled the area close to the transect of another cruise campaign during which Winkler samples were taken. Unfortunately, these Winkler data were found to be questionable. We took the advantage of some profiles of this float which were nearly contemporaneous and close in space with respect to the float 6903178 (which was calibrated using Winkler data) to indirectly obtain its calibration coefficient.

The values of the coefficients of determination of all the least square minimization are high and confirm the robustness of the data and of the method used.

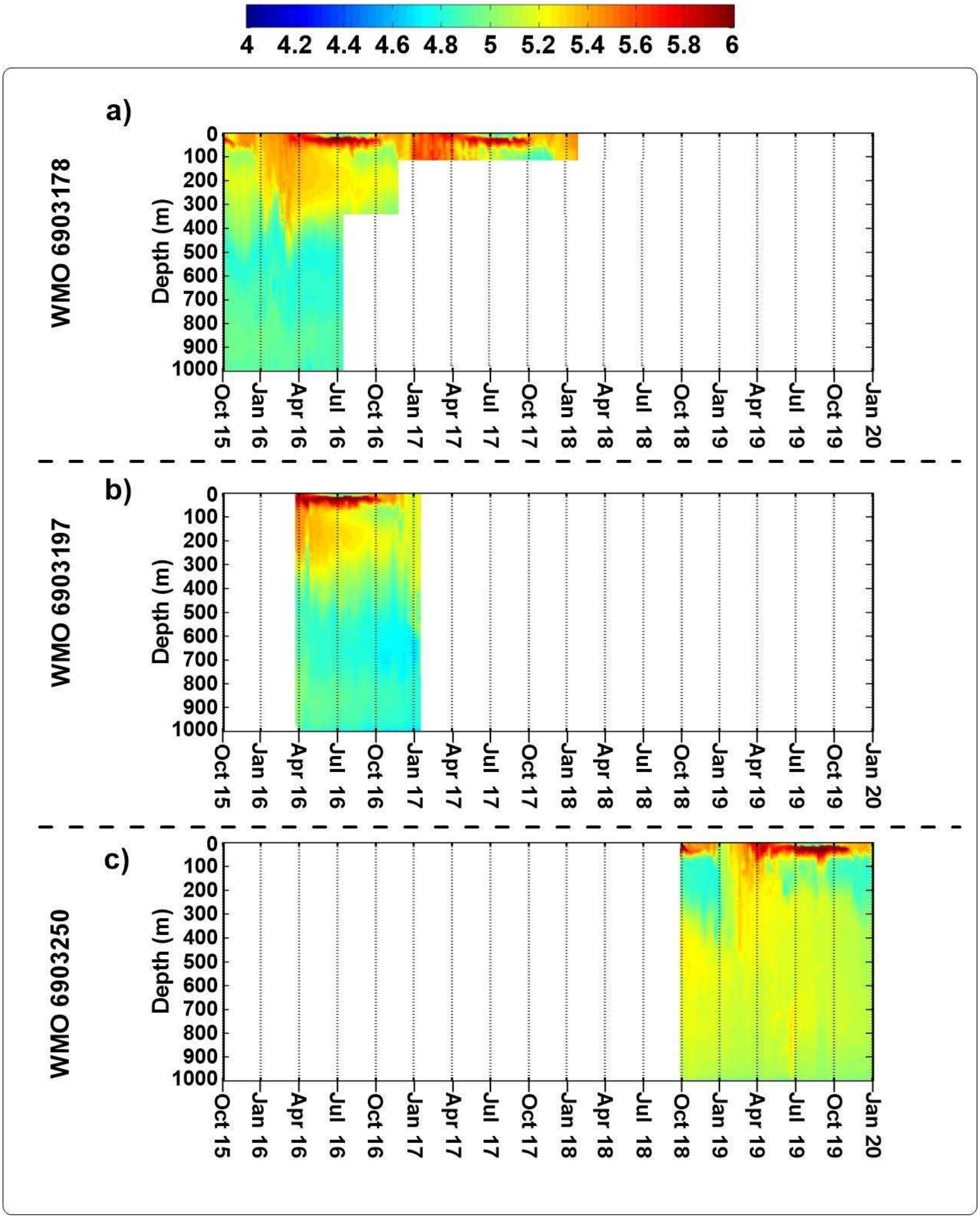

Fig. 14. Calibrated oxygen concentration (ml/l) for float WMO 6903178 (a), WMO 6903197 (b) and WMO 6903250 (c).

Calibrated dissolved oxygen data show similar concentrations (fig. 14) with those observed in other studies conducted in the southern Adriatic sea. As observed by Artegiani et al. (1996), Zavatarelli et al. (1998) and Manca et al. (2004), dissolved oxygen concentrations in the water column vary between 6 ml/l (at surface) and 5 ml/l (at bottom).

In addition, calibrated oxygen concentration obtained from floats (Fig. 14) also fits with the one observed in the P-1200 L-term station site in the SAP (Fig. 15; courtesy of dr. Garić and dr. Batistić). In both datasets the positive increase of the oxygen concentration along the whole water column and especially below 300 m from 2015 to 2019 is striking.

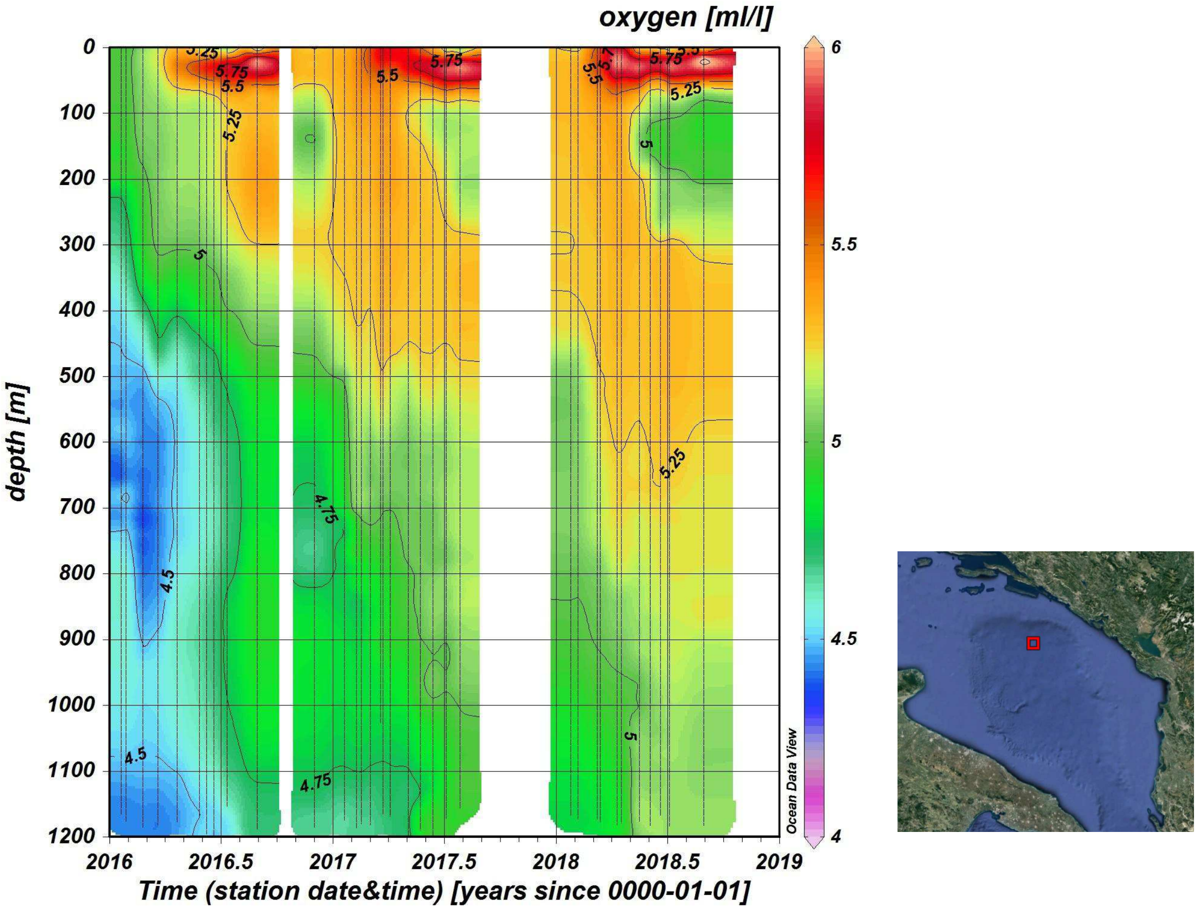

Fig. 15: Dissolved oxygen time series recorded at P-1200 L-term station (left, courtesy of dr. Garić and dr. Batistić) and location of the station in the SAP (right).

To further evaluate the quality of the calibrated oxygen data, the oxygen saturation before and after the calibration was computed and compared (Fig.16). The surface values of the dissolved oxygen saturation clearly indicate that before the calibration the saturation is too low. There are some periods in which these values are well below the 95%.

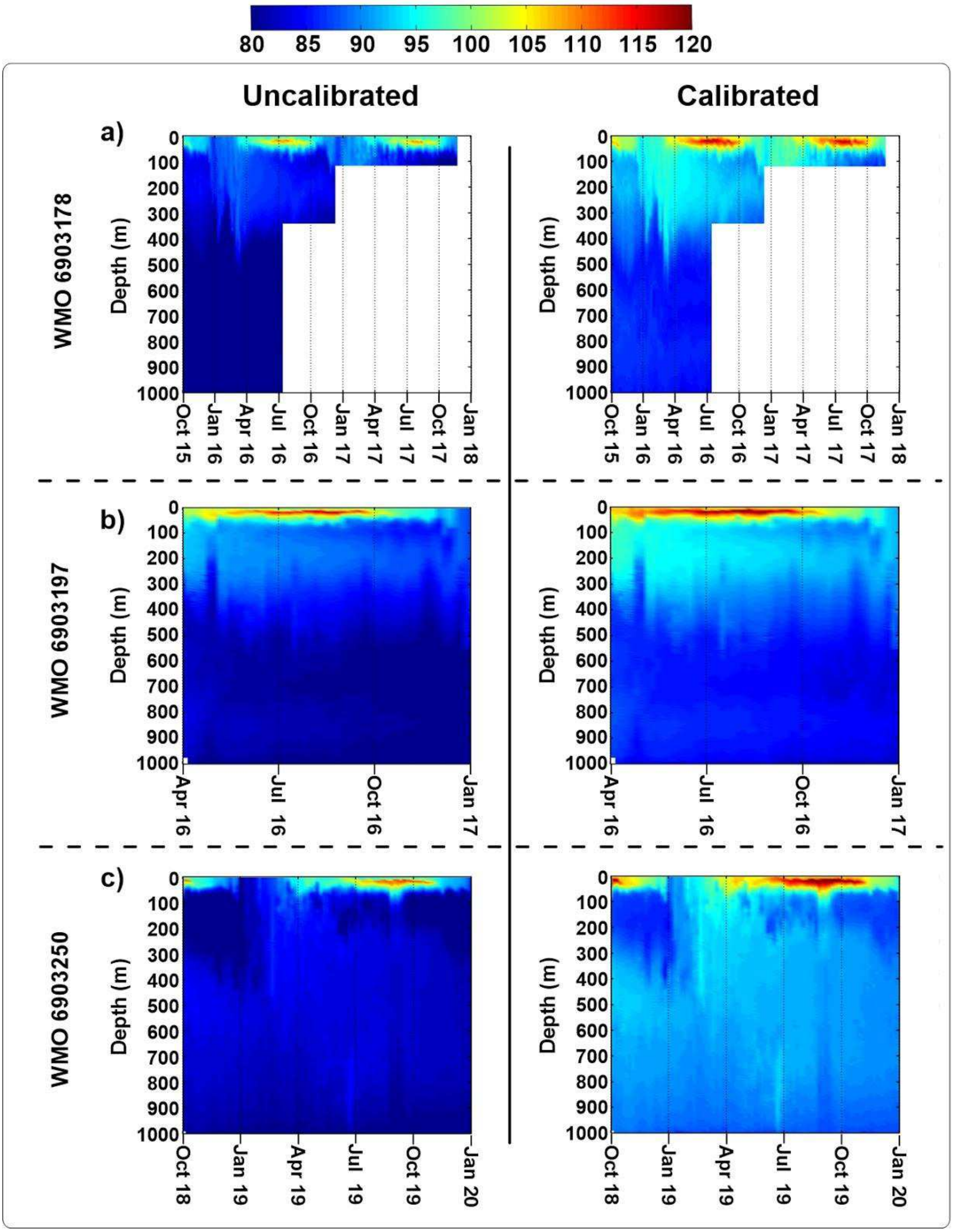

Fig. 16: Hovmöller diagram of dissolved oxygen saturation (%) for uncalibrated (left) and calibrated float (right).Float WMO 6903178 (a), WMO 6903197 (b) and WMO 6903250 (c).

The uncalibrated float data show inconsistent values for the common period of float 6903178 and float 6903197 (cases a and b in Fig. 16, respectively). The percentage indicated by float

6903197 is clearly lower than that of other floats. After calibration, the values are consistent throughout the common period.

Additionally, after the calibration the surface oxygen saturations are always higher than 100%, while the uncalibrated oxygen float data present percentages lower than 90%. This is unlikely especially during the winter period (Fig. 16 a and b), when the southern Adriatic sea is characterized by convection events that produce high oxygenated water masses in the surface waters. Other high oxygen dense water masses, formed in the north Adriatic Sea during winter, are present in deeper layers in the SAP (Kokkini et al 2019).

The oxygen saturation for uncalibrated floats are less than 90% in January 2016 and even less than 85% in January 2019. The calibrated floats have saturation values greater than 100% in the same time range, confirming the strength of the applied calibration.

In addition, observing the oxygen saturations in the deep layer, the uncalibrated floats have values less than 80%, while for calibrated floats the oxygen values range between 95% and 85%, as observed in Batistic et al. 2012, in the SAP.

6. Repository of the calibrated oxygen data

The calibrated float oxygen data were organized in a matrix (time, depth, calibrated oxygen) which includes all the float profiles. Data were saved in matlab format at the OGS Cayman server (storage/sire/dati/float/data/coriolis_profiles/6903***).

7. Acknowledges

The authors would like to thank dr. Garić and dr. Batistić for the plot of the oxygen saturation measured at P-1200 L-term station. It was very useful to confirm the quality of the calibrated float oxygen data. The authors thank also dr. Bensi and dr. Kovačević for sharing the ESAW-1 and ESAW-2 data, dr. Cardin for the E2M3A Winkler data and dr. Coppola for the interesting discussion on the oxygen data correction of the Argo floats.

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