Quality assurance and control on hydrological data off western Sardinia (2000 - 2004), western Mediterranean

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Abstract. Seven oceanographic cruises in five years were organized in the Sardinia Sea with the repeated collection of physical, chemical and biological data. An accurate and sustained quality assurance on physical sensors was acted through prior and post-cruise calibration and verified during *in-situ* acquisitions with the use of redundant sensors and other instruments. Moreover, for dissolved oxygen and conductivity, seawater samples at standard depths were frequently analyzed on-board. Then an accurate quality control was used to verify all hydrological data profiles, that passed a further quality check following standard procedures. Finally all hydrological data have been included in two online public open access datasets in the SEANOE repository (https://doi.org/10.17882/59867 and https://doi.org/10.17882/70340, Ribotti et al., 2019a,b). During and after all cruises also Chlorophyll-*a* and nutrients analyses were carried on but data are not yet open access; the same for water current profiles, both at casts and during vessel moves, and geophysical data. These ocean data are the first covering the whole Sardinia Sea for its whole extension. Here data and assurance/control procedures used are described as they became standards in deep sea acquisitions in the years.

Keywords: Sardinia, CTD, hydrological data, data quality check, sensor calibration

1 Introduction

Between May 2000 and January 2004 the National Research Council (CNR) of Italy collected hydrodynamic, chemical and biological data in the Sardinia Sea during seven multidisciplinary oceanographic cruises, named from medgoos1 to medgoos7. These cruises were the first covering the whole Sardinia Sea, from the shelf to the open sea, with oceanographic measurements. They were realized with the main aim to give a useful contribution on the knowledge of the local upper, intermediate and deep circulation and its interaction with the general Mediterranean circulation.

The study area is limited between 38°N and 42°N in latitude and between 7°E and the western Sardinian coast in longitude, with an offshore bottom reaching a depth of 2950m in the abyssal plain. The shelf extends from 5.5km at north to 37km in its center with a shelf break at about 200m depth (Conforti et al., 2016; Brambilla et al., 2019). It is an area of passage of re-

circulating waters between the two Mediterranean sub-basins and the Atlantic Ocean (Astraldi et al., 1999; Millot, 2005;

30   Millot and Taupier-Letage, 2005; Schroeder et al., 2013) and is strongly influenced by the Algerian large scale dynamics (Bouzinac and Millot, 1999; Puillat et al., 2002; Pessini et al., 2018). Very energetic surface fronts, cyclonic and anticyclonic vortices, up and downwelling events play an important role in variability and transport of physical, biological and chemical characteristics of the water masses (Puillat et al., 2003, 2006; Santinelli et al. ,2008; Olita et al., 2013, 2014). Here, thanks to the data acquired during the first medgoos cruises, Puillat et al. (2003) and Ribotti et al. (2004) identified the main water

35   masses usually observed in the rest of the western Mediterranean sea, like the Atlantic Water (AW) in the upper 150 m, the Winter Intermediate Water and its modified version known as the Temperature Minimum Layer (Benzohra and Millot, 1995; Sorgente et al., 2003; Allen et al., 2008) at about 100-120 m depth in the AW, the Intermediate Waters below to 800 m depth and the Western Mediterranean Deep Waters (WMDW) to the bottom. Here, since 2005 the old WMDW has been undermined by the warmest and saltier new WMDWs that diffused all over the Western Mediterranean sub-basin due to the

40   transfer of the Eastern Mediterranean Transient signal inside. This water is characterized by high heat and salt contents from the advected LIW, originating the new WMDW in the north-western Mediterranean sub-basin (Gasparini et al., 2005; Schroeder et al., 2006; Zunino et al., 2012; Ribotti et al., 2016).

Due to such an oceanographic importance, since the '50s French or Italian unsystematic cruises have been organized in the area whose data are available in the PANGAEA (https://www.pangaea.de) and SEANOE repositories (Dumas et al., 2018).

45   In 2014, the Science and Technology Organisation - Centre for Maritime Research and Experimentation of the North Atlantic Treatment Organization (NATO STO-CMRE), based in La Spezia, organized a 2-week experiment with a large use of ocean instruments and two research vessels in a limited area (110x110km^2). Its aim was to improve local ocean numerical simulations and forecasts and study the local ocean variability and structures (Onken, 2017a,b; Knoll et al., 2017; Hemming et al., 2017; Onken et al., 2018; Hernandez-Lasheras and Mourre, 2018).

50   Then recent experiments with drifters and deep sea gliders were realized in the Sardinia Sea and between Sardinia and Balears, partially described by Olita et al. (2014).

In 2000-2004, instruments, sensors and data passed severe controls following internationally accepted oceanographic processes, necessary to obtain high-quality data. These practices included quality assurance, control and assessment, standards and best practices refined till nowadays (Hood et al., 2010; Bushnell et al., 2019; Pearlman et al., 2019). In this

55   paper we describe all the procedures or best practices followed to assure and control the quality of the acquired data during the medgoos cruises, the sensors used, their calibrations and intercomparisons.

Acquired hydrological data are in two datasets stored in an open access repository, called SEA scieNtific Open data Edition (SEANOE) (Ribotti et al., 2019a,b), linked with the EMODnet Data Network of marine centers and European thematic data portals like SeaDataNet and EurOBIS.

60   In the following two paragraphs (2 and 3) vessel, instruments and sensors used in the seven cruises are described, with a distinction between data in repositories (par. 2) and not part of any repository (par. 3). The calibration of temperature and

conductivity sensors are part of the paragraph 4 while in paragraph 5 the on board control of CTD sensors stability is detailed. Discussion and conclusions close the paper.

2 Instrumentation technology

65   During the seven cruises profiles of physical/chemical parameters were acquired at planned stations whose number varied due to the length and the strategy adopted at each cruise, the wideness of the covered area, and the sea conditions. So the activities range from the 38 stations realized during the 6-days-long medgoos1 in 2000 and the 92 during the 21-days-long medgoos6 in 2003. In September 2001, only the southern part of the Sardinia Sea with 41 stations was covered due to bad weather conditions.

70   The 61,30 meters long R/V Urania of CNR was used in all cruises. This was a modern multidisciplinary research vessel equipped with instruments to study physical and chemical water quality parameters, and laboratories for biological and geological analyses. For its dynamic positioning the vessel was equipped with an integrated navigation system constituted by two DGPS antennas and one Loran C that ensured an optimal use of the scientific equipment during the cruises. Such a system was managed through a software by Andrews Hydrographics installed on PC HP386, 33 MHz that permitted to

75   download navigation and meteorological data in ASCII format with geographic and kilometric coordinates at frequency till 10 minutes.

On board, a SBE911 plus CTD probe (by Sea-Bird Inc.), mounted on a 24 10-liters Niskin bottles rosette for water column sampling, was used to acquire hydrological data during all the seven cruises (figure 1).

In specific, the sensors installed on the probe had the following characteristics (table 1):

80   • pressure [db]: a Digiquarz 4000 pressure transducer was used. The transducer had a resolution of 0.01ppm, oscillator frequency 34KHz - 38KHz and temperature range 0°C - 125°C;

• water temperature [deg C]: a SBE-3/F thermometer with response time of 70 ms, temperature range -5°C - + 35°C, accuracy about 0.004°C per year, resolution 0.0003°C. The international practical temperature scale known as IPTS-68 was applied on data from medgoos1, 2 and 6 while the international temperature scale of 1990, known as ITS-90, on data from

85   medgoos4 and from medgoos3, 5, 7 on secondary sensors;

• conductivity [mS/cm]: a SBE-4 sensor with a range of 0.0S/m - 7S/m, resolution 0.00004S/m, accuracy about 0.0003S/m per month and response time of 0.085sec with pump or 0.17sec without pump;

• dissolved oxygen: a SBE-13 Beckman/YSI sensor with a range of 0.0ml/l - 15ml/l, accuracy of 0.1ml/l, resolution 0.01ml/l and response time 2 sec at a temperature of 25°C during cruises medgoos1, 2, 3, 4. During cruises medgoos5, 6, 7 a SBE-43

90   polarographic membrane sensor for pumped CTD applications with titanium (7000m) housing was used with a range of 120% of surface saturation in all natural waters, accuracy of ±2% of saturation;

• fluorescence: a Sea Tech Inc. fluorometer with energy emitted by the flash lamp of 0.25J for flash, temperature range 0°C - 25°C, resolution 0.15µg/l.

Redundant or secondary sensors were always used for a data quality assessment (as defined in Bushnell et al., 2019) of both temperature and salinity measurements, except during the cruise medgoos1 in May-June 2000 (see table 1). A secondary SBE-43 sensor for dissolved oxygen was also added just in the last three cruises, from medgoos5 to 7. These redundant sensors were a useful method of comparison to evaluate the stability of primaries both during the acquisition and at a following visual quality check of profiles.

For the same reason, digital deep sea reversing thermometers RTM 4002 by Sensoren Instrumente Systeme GmbH (SiS) were mounted on Niskin bottles during medgoos4 (3 thermometers) and 5 (4 thermometers). These instruments acquired sea temperature at depths, defined by the closing of the Niskin bottle where they were mounted on, usually sampling near the bottom where temperature is more stable. Reversing thermometers had a depth range of up to 10000 meters and a temperature range between -2°C and +40°C. They had a resolution of ±0.001°C between -2.000°C and 19.999°C, of ±0.01°C between 20.00°C and 40.00°C and a stability of 0.00025°C per month. Its pressure housing was made of a glass tube closed at its ends by metal stoppers, one containing the platinum sensor and the other the battery. Its internal mercury switch was activated by inverting the instrument at defined depths.

3 Other acquisitions

In some cruises (see table 1) currentmeters data were acquired on both at a station (Lowered Acoustic Doppler Current Profiler or LADCP) and in route (Shipborne Acoustic Data Current Profiler or SADCP) while geophysical sub-bottom profiler data just during the cruise medgoos2. At casts, the real time display of CTD data made it possible to identify a certain number of stations where to take water samples for the estimation of nutrients (nitrites, nitrates and phosphates), Chlorophyll-*a*, chromophoric dissolved organic matter (CDOM) and dissolved organic carbon (DOC). As all these data are not in the two datasets in the SEANOE repository mentioned above (Ribotti et al., 2019a,b), they will be shortly described here as part of the amount of cruises data. All measures were carried out trying to reconcile the different procedures.

The Sub-Bottom Profiler was a GeoPulse Transmitter Model 5430A at frequencies ranging between 2kHz and 15kHz with a maximum emitted power of 10KW. It was used on a small portion of the western Sardinian shelf north of Oristano just in April 2001 during the cruise medgoos2.

Starting from the cruise medgoos2, profiles of current speed were acquired during CTD casts by two synchronized 300 kHz RDI Workhorse ADCPs, by RD Instruments Inc. in USA (now Teledyne), configured in modality Lowered and installed on the rosette one looking up (named slave) and the second down (named master). They acquired horizontal current data in 20 cells 10m width each from the instrument with an impulse per second. Then under the keel of the vessel, a 38kHz ADCP profiled currents in 8m wide cells over 1000m depth through an impulse per second during transfers between stations. Another impulse was used to correct the water speed and obtain its real speed as regards to the sea bottom (bottom tracking). Configuration of ADCPs used in the two modes, Lowered and Shipborne, in 2001-2004 are in agreement with the more recent internationally recognized GO-SHIP protocols described by Hood et al. (2010).

For Chlorophyll-*a (*Chl-*a*), CDOM and DOC all the water samples were filtered on 0.42µm Whatmann GF/F glass microfiber filters for Chl-*a* and 0.22µm membrane filter (Sartorius, Minisart, SM 16534 K) for DOC and CDOM; this to remove the particulate fraction immediately after collection. Then filters were frozen at +4°C to be analyzed at labs following standard procedures described by Lazzara et al. (1990) for Chl-*a*, and by Vignudelli et al. (2004) and Santinelli et al. (2008) for CDOM and DOC. For nutrients, during the first three medgoos cruises water samples were partially analyzed on-board by a Systea µCHEM Auto-analyzer, while remaining samples frozen at -20°C following Strickland and Parsons (1972). In the following cruises all water samples were frozen and then analyzed once back.

4 Pre- and post cruise calibration procedures

The pre- and a post-cruise calibration of the sensors of temperature and conductivity was performed at the oceanographic instrument (CTD) calibration facilities of the SACLANT Undersea Research Center (SACLANTCEN, now STO-CMRE) in La Spezia, Italy. The Centre was funded in 1959 initially for submarine warfare but it developed and maintained unique, in Italy and for years, an oceanographic instruments test and calibration facility that enabled the acquisition of high-quality ocean data. Two calibration seawater tanks were equipped with two very high precision Neil Brown ATB-1250 Platinum Resistance Thermometer Bridge for temperature and two very high precision Neil Brown CSA-1250 conductivity/salinity adaptor for conductivity. Seawater samples were analyzed for conductivity by highly précised 8400B Autosal Laboratory Salinometer, from Guildline Instruments Ltd[™], standardized with IAPSO Standard Seawater and an accuracy of <0.002psu on a range of salinity between 2psu and 42psu.

Before SBE sensors calibration, the two temperature sensors in the bath were adjusted to a triple-point-of-water cell (TPW) at the temperature of 0.01°C and a thermometric standard Gallium-melting-point cell for the highest value of 29.7646°C. So at SACLANTCEN a calibration of these sensors was realized exceeding WOCE standards (Millard and Yang, 1993). These two calibrations permitted to substantially generate a slope correction, used in the configuration file of the SBE Seasoft[™] suite of programs, for data acquired during each cruise then improving their quality.

5 On board control of CTD sensors stability

Despite the calibration of temperature and conductivity sensors before and after each cruise, all sensors can significantly drift over the course of a cruise. This can dramatically reduce the quality of the data. As high quality conductivity and oxygen data enable the definition of local water masses with high precision, particularly in the deep, then the use of international standards is mandatory in oceanography. The stability of conductivity and dissolved oxygen sensors must be verified on-board through the comparison with data from water samples. During the cruise all involved personnel and all acquired data are usually together so it is easier to check and correct repetitive problems before they can further degrade the data.

155 Conductivity data were checked against the on-board analyses by a Guildline™ 8400B Autosal Laboratory Salinometer, similar to that described above, while dissolved oxygen data against Winkler titration method with a measured precision in triplicate analyzed sample of 0.01ml/l (expressed in standard deviation). The sampling was at defined depths at surface, 25, 50, 100, 200, 300, 400, 500, 750, 1000, 1250, 1500, 1750, 2000, 2500, 3000 metres, and bottom.

The Autosal salinometer was operated in a small temperature-regulated room part of the on board wet laboratory and its bath

160 temperature was held at 24±2°C. The salinometer was daily standardized with the use of IAPSO Standard Seawater provided by 200 ml clear sealed glass bottles, before starting the analyses. Seawater for conductivity was taken after that for dissolved oxygen and collected in 250ml clear bottles with screw cap. Each bottle and its cap were rinsed three times with the sampled water, and filled to its shoulder. Then they were stored no longer than 24 hours in the conditioned room before their analyses. Niskin bottles collected water at the deepest casts of the cruise and at least once a day.

165 The oxygen sensors used during the cruises were not calibrated, so during each cruise different verifications were realized to verify possible sensors shifts through the Winkler titration method (Winkler, 1888). This method, used for *in-situ* dissolved oxygen analyses, consists of reacting oxygen in the samples with two reagents (I and II) and with a final titration. The reagent I is a solution of $MnSO_4$ and NaOH while the reagent II is a solution of NaI and H_2SO_4. The utmost attention is paid to draw the oxygen samples first from Niskins and into dark glass bottles. This avoids the formation of air bubbles during the

170 sampling itself or the execution of the analysis. The sampling was realized as for conductivity considering frequency and methodology. The water sampled at 100m of depth was used to obtain three blank solutions in dark glass bottles and one standard solution in a larger plastic bottle. So blanks and standards were run often. Then different quantities of reagents were added: 0.5ml (the usual for all samples) of reagent I and reagent II in the first blank, its double in the second blank and the triple in the third. No reagents were initially added in the standard solution. All samples and the three blank solutions, not the

175 standard, were left in the dark for at least 2 hours and then analysed within 24 hours from their collection. During the analysis of the standard solution, reagents I and II, 0.5ml of H_2SO_4 and then of KIO_3 were added. The samples have been analysed through the programme TIAMO 2.0™, that stands for *TItration And MOre*, by Metrohm. Thanks to the data from the water samples, the possible estimations of changes of slope (Soc) and offset (Voffset), in the linear relationship between oxygen concentration and voltage output that indicate a loss of sensitivity of the sensors, were realized performing a linear

180 regression line of the data calculated from the following Eq. (1) (Owens and Millard Jr., 1985; Millard and Yang, 1993; SBE, 2008a):

$$\varphi = Oxsol(T,S) * (1.0 + A * T + B * T^2 + C * T^3) * e^{\left(\frac{E*P}{K}\right)} \tag{1}$$

where Oxsol(T,S) is the oxygen solubility (ml/l) at a defined temperature and salinity, T and K are the CTD temperatures in °C and in °K, P is the CTD pressure (dbars) and A, B, C, E are calibration coefficients.

185 At a defined deep station, the regression is calculated by using the measured Winkler oxygen concentration divided by φ as dependent variable and the oxygen sensor output voltage as independent variable.

In figure 2 an example of linear regression applied on a deep CTD station with the calculation of the new Soc (0.3936) and the new Voffset = -0.2094/SOC = -0.2094/0.3936 = -0.53201

During cruises from medgoos4 to medgoos7 temperature data were checked at defined depths against reverse thermometers
190 installed in correspondence of the bottles number 1, 3, 5, 7 of the rosette sampler.

Furthermore CTD and oxygen data were compared with those analyzed on board from samples or acquired with other instruments in order to determine or visually check possible shifts. Acquired CTD data were processed through the standardized procedures of the SBE Data Processing™ software. After comparisons and in case of malfunction, the use of the secondary sensor instead of the primary was evaluated (in figure 3 a plot for conductivity and dissolved oxygen).

195 After the post-cruise calibration, if the shift was constant or systematic then an average of all data (primary, secondary, samples, etc) was used to correct data. If the shift was random, Soc and Voffset for dissolved oxygen, slope and offset for conductivity/temperature were recalculated and the data corrected following the procedures described in the application notes number 64-2 (SBE, 2008b, 2012) and 31 (SBE, 2016), respectively.

Chl-*a* fluorescence was calibrated following the instructions given by SBE (2008a) where the SEASOFT™ coefficients for
200 the Sea Tech fluorometer are calculated. No validation of the data has been applied after the cruises. It is reported as Relative Fluorescence Unit (R.F.U.) in the datasets. Also pressure sensors were not calibrated as usually stable but, if problems occurred, it was sent to SBE Inc. in USA for its calibration.

6 Data availability

The two datasets described in this study are publicly available and free of charge from the SEANOE data repository (Ribotti
205 et al., 2019a, https://doi.org/10.17882/59867 and Ribotti et al., 2019b, https://doi.org/10.17882/70340). The presented datasets are composed of CTD data in Ocean Data View (ODV) TXT Spreadsheet and Collection files formats divided per cruise. Metadata are available in TXT, RIS, XLS, RTF, BIBTEX formats. Data and metadata from all cruises, apart medgoos1, are also stored and available under request in the Mediterranean Marine Data at http://www.mediterranean-marinedata.eu/, a CNR - ENEA collaborative initiative with the aim to archive and distribute oceanographic data and
210 information.

The rescue and reprocessing of hydrodynamic data is ongoing in order to reorganize them, quality controlled, in a database. The same will be for the biological parameters. A first dataset is of nutrients data from more recent cruises (late 2014 - 2017) is available at https://doi.org/10.5194/essd-2019-136 (Belgacem et al., 2019).

7 Discussion and conclusion

215 Several processes to obtain high-quality ocean data were followed during the 2000-2004 medgoos cruises in the Sardinia Sea, western Mediterranean. Quality assurance, control, assessment, standard and best practices, defined at international

level (see Bushnell et al., 2019) and after decades of practices in ocean data acquisition, were considered during all cruises and are in agreement with recent standardized procedures for all sensors (Hood et al., 2010). Sensors pre and post-calibration, use of redundant ones, comparisons with on-board analyzed water samples showed their efforts resulted in

220 achieving the required accuracy standard for that period, due to sensors accuracies, and for today. Uncertainty of measurements, defined as "the quantification of the doubt that exists about results of any measurements", exists in these data but reduced by the skill of the same operators or analysts following all the processes at any time for all the years and cruises. Now oceanographic data from seven cruises are collected in two open access datasets available online, including ocean parameters like conductivity, temperature, dissolved oxygen and Chlorophyll-*a* fluorescence. These ocean data are the first

225 available for the Sardinia Sea, important to characterize the general circulation and the dynamics in the western Mediterranean.

Author contribution

AR led some cruises, organized the two datasets and led the writing of the paper. MB led some cruises, finalized QA and QC procedures described in the paper and collaborated to the paper writing. RS collaborated to the paper writing.

230 **Competing interests**

The authors declare that they have no conflict of interests.

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Figure Captions

Figure 1. All the CTD casts during the seven cruises in the Sardinia Sea (western Mediterranean)

Figure 2. Linear regression line calculated for the dissolved oxygen data of a CTD station

365   **Figure 3. The salinity (up) and dissolved oxygen (down) errors between what measured by the sensor on the probe and what measured on board from water samples for the two conductivity/oxygen sensors, 1 and 2, along a vertical profile in a deep station.**

Table Captions

Table 1. The list of sensors used and activities realized during the seven medgoos cruises. Numbers in brackets for reversed thermometers are the numbers of the Niskin bottles where installed. L and SADCP stand for Lowered and Shipborne Acoustic
370   **Current Profile, respectively**

Figure 1

375

Figure 2

380

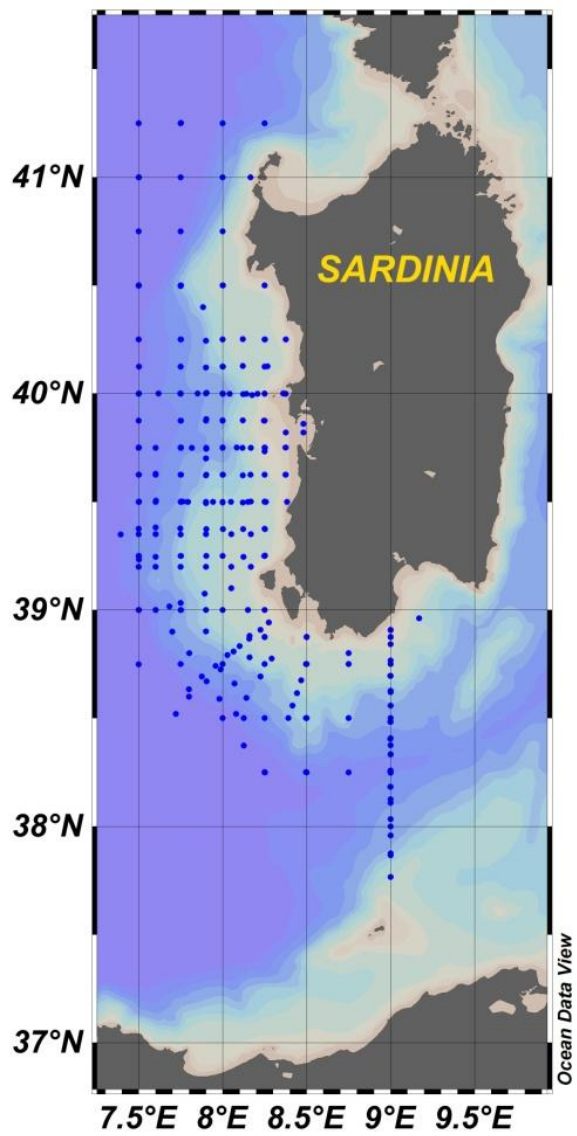
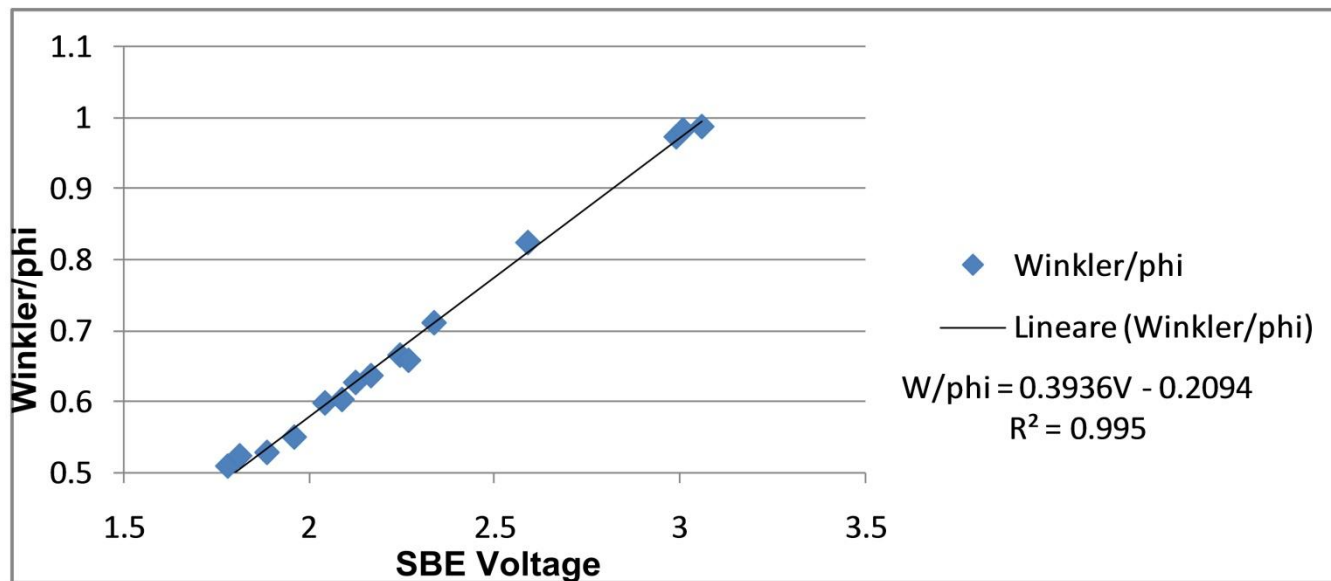
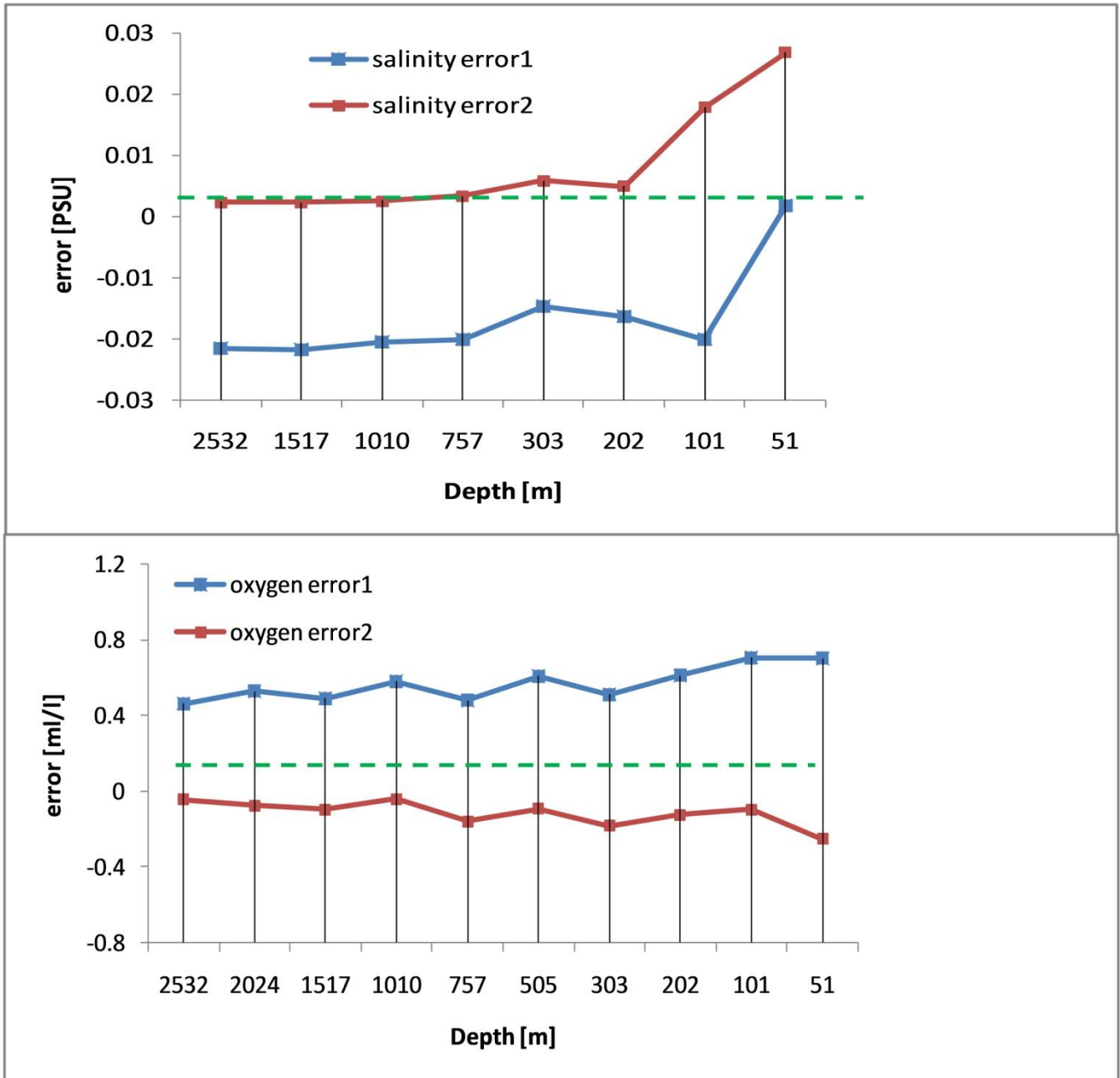



Figure 3

385 **Table 1**

	medgoos1	medgoos2	medgoos3	medgoos4	medgoos5	medgoos6	medgoos7
Date	2000/05/28-2000/06/02	2001/03/23-2001/04/03	2001/09/ 10-20	2002/05/4-23	2002/10/31-2002/11/18	2003/03/28-2003/04/17	2004/01/07-26
# days	6	12	11	20	20	21	20
R/V	Urania	Urania	Urania	Urania	Urania	Urania	Urania
# CTDs	38	67	41	68	42	92	87
Reverse Thermometer (bottle #)				3 (1, 3, 5)	4 (1, 3, 5, 7)		
SBE-13 O2 Sensor	X	X	X	X			
SBE-43 O2 Sensor					X	X	X
Fluorescence	X	X	X	X	X	X	X
LADCP	X	X	X	X	X		
SADCP	X						
CTD secondary sensors							
Secondary Temperature		X	X	X	X	X	X
Secondary Conductivity		X	X	X	X	X	X
SBE-43 O2					X	X	X
Water samples for following analyses of							
DOC	23	66	39		55		
Nutrients	23	66	39		55		
Phytoplancton		X	X	X	X		
Chl-*a*		66	39	X	55		
On-board analyses							
O2	X		X	X	X	X	X
Conductivity	X		X	X	X	X	X