Calculation of Oxygen Concentration in the Black Sea using data from Argo Automatic Profiling Floats

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Abstract.
In the last years in connection with climate change on Earth more relevant and discussed is the question of the characteristics of the World Ocean. Measurements there are labor-intensive and expensive, so there is no comprehensive information, especially in the deep layers. Therefore a number of programs to monitor of ocean are recently funded. The purpose of the Argo program is to investigate the sea water to a depth of 2000 m using automatic profiling floats equipped with sensors for temperature, salinity, depth and others. The data is distributed freely on the Internet. Examination of the oxygen content is very important for studying marine ecosystems, especially in the Black Sea, which is one of the largest oxygen-free pool in planet.

The purpose of this study is to calculate the concentration of dissolved oxygen in seawater by using data from Argo float for pressure, temperature, salinity and attenuation of blue light. The oxygen content is very difficult to determine in a laboratory or in conditions of sea expedition, so the more common way is to calculate it from the above-mentioned parameters.

The raw data from Argo float 6900804 for 25 profiles in 2011 are downloaded and interpolated on standard horizons. By an algorithm, provided by the manufacturer of the optical sensor Aandera Optode 3830, the concentration of dissolved oxygen (micromoles) in the programming environment MATLAB is calculated.

Keywords: oxygen concentration, Argo floats, Aandera Optode, Black Sea
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1. INTRODUCTION

In the last years in connection with climate change on Earth more relevant and discussed is the question of the characteristics of the World Ocean. Measurements there are labor-intensive and expensive, so there is no comprehensive information, especially in the deep layers. The satellite observations are one of the best for data collection, but the disadvantage is that they do not provide information about the deeper layers of the ocean. Therefore a number of programs to monitor ocean are recently funded. Cheap and efficient method to collect profiles continuous information over the whole water column is Argo program. It aims is to study the ocean to 2000 m depth using automatic profiling floats which are equipped with sensors for temperature, salinity, depth, dissolved oxygen, etc.. Examination of oxygen content is very important in the study of marine ecosystems, particularly in the Black Sea, which is one of the largest oxygen-free pools on the planet.

The Argo floats were introduced in 2000 and in November 2007 a 100 percent of initially scheduled network is full. Now days Argo network has 3560 floats, but in order to maintain this level should be produced and placed in service in 800 probes per year [1].

Argo data for the Black Sea are needed because the data collection so far is related to the organization of costly expeditions in different territorial waters. The aim is to establish a new national maritime infrastructure for observations in the Black Sea, which is based on autonomous profiling floats. The main priority of Bulargo program is monitoring the status of the Black Sea from the surface to deep stagnant layers. The Black Sea region is extremely important because of their specific sensitivity to climatic and anthropogenic influences, therefore is so important monitoring in depth of the sea basin. There are a large number of coastal meteorological and oceanographic observations, but the observations at sea are still insufficient. This deficiency can be compensated by the observations from floating buoys, which will measure the concentration of dissolved oxygen, physical processes and optical characteristics of seawater.

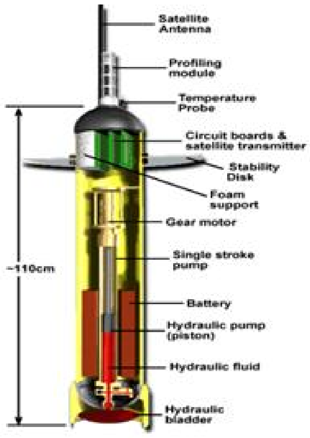

FIGURE 1. Construction of Argo float.

2. STRUCTURE OF AUTOMATIC MEASURING FLOATS ARGO

The measuring float is designed to collect high quality profiles of temperature and salinity from the upper 2000 m of the ice-free part of the global ocean and the currents from intermediate depths. They operate from battery power and spend most of their time of life, floating on the depths in which they are stable. With the aid of the hydraulic device buoyancy equal to the surrounding environment is achieved. This allows the passage of a float on isobaric surface. Isobaric surface can be changed, which leads to floating or sinking of the float. The most commonly used profiling floats are three types. They work in a similar way, differing in the characteristics of their design. The floats pumped fluid in the outer bladder, and come to the surface for about 6 hours at a given interval, which is programmed in advance. During this time the floats measure salinity, temperature and other characteristics, if they are equipped with appropriate sensors. Through satellite communication the position of the probe is determined after its ascent to the surface and the data transmission is performed. Then the bladder was emptied, the float returns to its normal buoyancy and sinking into the parking depth, where it navigate until the cycle is repeated. The floats are designed to make about 150 such cycles, after that their batteries are exhausted. The construction of the Argo float includes four main parts (Fig. 1)

- Hydraulics: it controls the buoyancy of the probe by an external inflatable rubber bladder so that the probe can emerge and dive
- Microprocessors: to control the functions and interval of data collection;
- System for data transfer: control the link with the satellite;
- Power system: 7.2 V and 14.4 V, lithium or alkaline batteries

The lifetime of the float is about 3 years, but the data quality is not always good. Often there are missing data, there are also errors arising from unrealistic measured values for pressure, temperature and salinity [2].

3. MODE OF OPERATION OF OXYGEN SENSOR AANDERA OPTODE 3830

The principle of operation of the optical sensor for oxygen determination is based on the phenomenon of dynamic fluorescent quenching and the ability of certain molecules, such as oxygen, to appear as a fluorescent quenchers [3], [4].

Optical part of the oxygen electrode includes the following elements: sensing foil, indicator layer, support layer, optical window, blue LED, red LED and photodiode (see Fig. 2). The sensing foil is exposed into the water. The indicator layer is a platinum porphyrine complex. There are a two LED diodes and a photo diode placed on the inner part of the optical window. The blue light (505 nm) from the blue LED is used for excitation of the sensing folio. The sensing foil will return the red light thanks to its fluorescent properties. In the presence of oxygen the fluorescent will

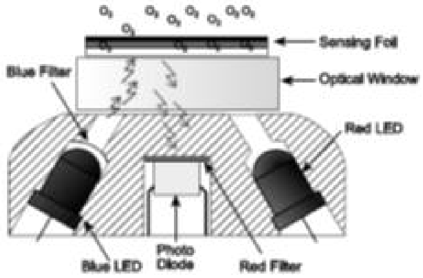

FIGURE 2. Optical part of the oxygen sensor, source [5]

be quenched. Therefore, the concentration of dissolved oxygen depends on the change in the intensity of the reflected light.

4. EXPERIMENTAL PART

To calculate of the oxygen concentration an algorithm represented by the manufacturer of the sensor Aanderaa Optode 3830 is used. The phase difference (DPhase) is calculated as a polynomial of third degree of the difference between the measured phase with excitation with blue light and excitation with red light [5]. The oxygen concentration is calculated in micromols (microM):

$$[O_2] = C_0 + C_1 P + C_2 P^2 + C_3 P^3 + C_4 P^4 \tag{1}$$

where P is calibrated phase of measurement (DPhase), C_0 ... C_4 are dependent temperature coefficients which is calculated using the formula:

$$C_X = C_{x0} + C_{x1} t + C_{x2} t^2 + C_{x3} t^3 \tag{2}$$

C_x0 ... C_x3 - constants, provided by the manufacturer of the sensor, t - ambient temperature. Uncalibrated phase (UPhase) is the difference between the phase obtained with blue light (BPhase) and phase obtained with red light (RPhase):

$$UPhase = BPhase - RPhase \tag{3}$$

Typically RPhase is not used and it is taken equal to zero (RPhase = 0). Here you have to calculate also DPhase, necessary for calculating the oxygen in the form:

$$C_x = A_0 + A_1 UPhase + A_2 UPhase^2 + A_3 UPhase^3 \tag{4}$$

A_0 ... A_3 - constants, provided by the manufacturer of the sensor

For the calculation of the oxygen concentration in the Black Sea data obtained from autonomous profiling float APEX 6900804 are used. This float is used to monitor sea currents, to measure profiles of temperature, salinity, depth, and dissolved oxygen. For the purposes of the study the data for 25 profiles from 2011 for temperature, depth and Bphasedoxy are downloaded in its original from [6] and interpolated of standard horizons.

By suggestions from the manufacturer of oxygen sensor Aandera Optode 3830 algorithm the concentration of dissolved oxygen is calculated in the programming environment MATLAB. As turned out that APEX 6900804 has two temperature sensors - T-sensor for profiling temperature and built-in thermistor in the oxygen sensor, oxygen concentration is calculated twice. First, using the temperature data from T - sensor of APEX float and the data for BPhasedoxy from the oxygen sensor (O2dtemp), in the second calculation of the oxygen temperature data obtained from the thermistor in the oxygen sensor (O2dtempdoxy) is used. In Fig. 3, Fig. 4, Fig. 5, and Fig. 6, the resulting profiles for oxygen content are shows. Data for four randomly selected profiles are shown: 20.04.2011, 23.05.2011, 07.07.2011, 11.08.2011. The obtained values for the oxygen in both temperature sensors are almost identical, but there is a slight difference. This difference is more pronounced in the profiles of 07.07.2011 and 11.08.2011.

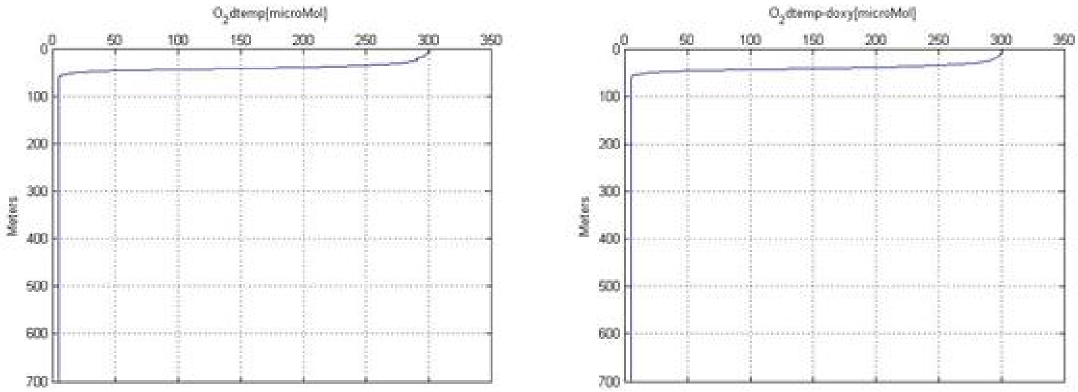

FIGURE 3. Oxygen profiles for 20.04.2011; a) with temperature data from T-sensor of the float; b) with temperature data from thermistor in DO-sensor of the float

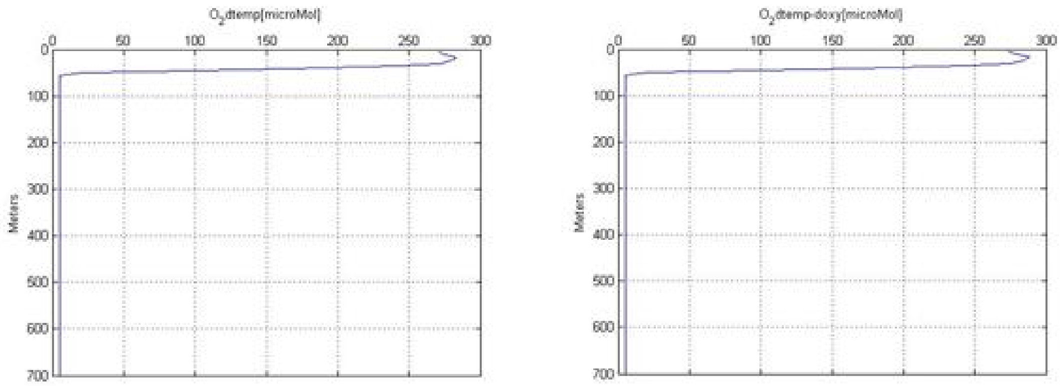

FIGURE 4. Oxygen profiles for 23.05.2011; a) with temperature data from T-sensor of the float and b) with temperature data from thermistor in DO-sensor of the float

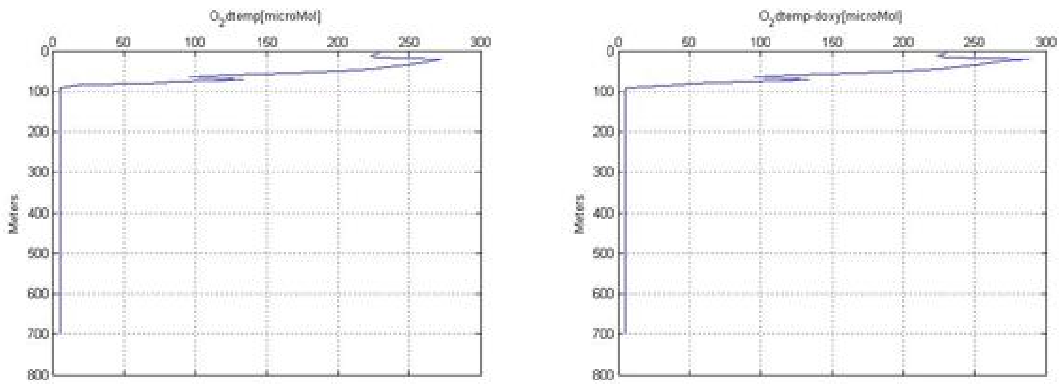

FIGURE 5. Oxygen profiles for 07.07.2011; a) with temperature data from T-sensor of the float and b) with temperature data from thermistor in DO-sensor of the float

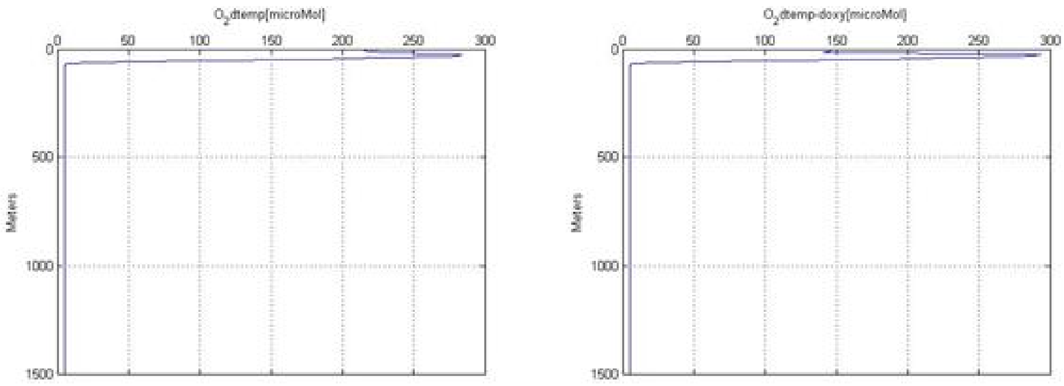

FIGURE 6. Oxygen profiles for 11.08.2011; a) with temperature data from T-sensor of the float and b) with temperature data from thermistor in DO-sensor of the float

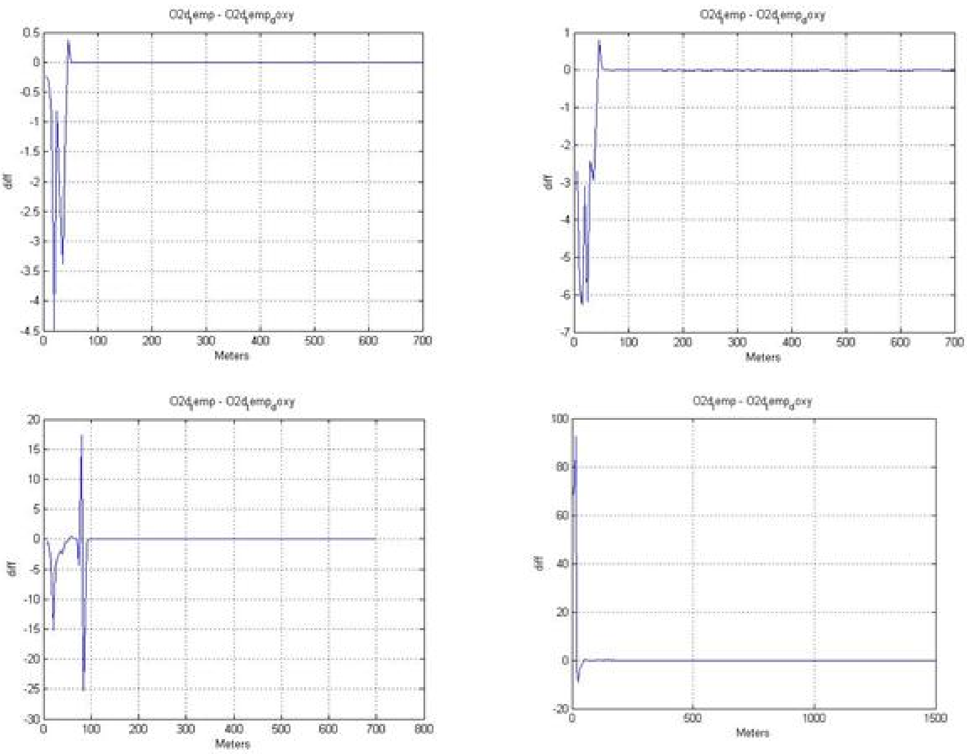

FIGURE 7. Difference in concentration of DO at both temperatures for different dates a) 20.04.2011 b) 23.05.2011 c) 07.07.2011 d) 11.08.2011

A comparison between the values obtained for the concentration of dissolved oxygen at two temperatures is made. In graphical form are shown the results obtained for the difference in the concentration of dissolved oxygen in the temperature of the T-sensor and a thermistor (delta DO = O2dtemp-O2dtempdoxy) depending from the depth (see Fig. 7). It was found that a large difference in concentration of dissolved oxygen was observed in the profiles for 07.07.2011 and 11.08.2011.

5. CONCLUSIONS.

For the first time in the programming environment MATLAB algorithm to calculate the concentration of dissolved oxygen in seawater was developed. The data for pressure, temperature, salinity and decay of blue light from Argo APEX float 6900804 Black Sea are used. As it turned out that the float has a temperature data from two temperature sensor dissolved oxygen concentration is calculated twice. The difference in oxygen content using temperature data from T-sensor of float and built-in thermistor in DO-sensor of float is shown. It was found that the concentration of dissolved oxygen depends on the temperature and depth. The different seasons also affect of the oxygen content. After the hundredth meter there is no difference in the reading of the two temperature sensors and there is no difference in the oxygen concentration.

6. ACKNOWLEDGEMENTS.

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