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Processing Bio-Argo chlorophyll-a concentration at the DAC level Version 1.0 September 30Th 2015





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Table of contents

<u>1</u>	INTRODUCTION	<u>6</u>
<u>2</u> <u>CC</u>	RECOMMENDATIONS FOR ADDRESSING THE CHLOROPHYLL-A ONCENTRATION DATA PROCESSING	7
<u>3</u>	ECO SENSOR	<u>7</u>
3.1	MEASUREMENTS AND DATA PROCESSING	7
3.2	SENSOR METADATA AND CONFIGURATION PARAMETERS	9
3.2	2.1 SENSOR AND PARAMETER METADATA	9
3.2	2.2 CONFIGURATION PARAMETERS	9
3.3	CHLOROPHYLL-A DATA RELATED PARAMETERS 1	0
3.3	CHLOROPHYLL-A RELATED PARAMETERS FOR THE B-FILE	0
3.3	2.2 CHLOROPHYLL-A DATA FOR THE B-FILE AND THE MERGED FILE 1	1
4	REFERENCES	2

History of the document

Version	Date	Authors	Modification
1.0	September 2015	C. Schmechtig	Initial version

Preamble:

This document does NOT address the issue of chlorophyll-a quality control (either real-time or delayed mode). As a preliminary step towards that goal, this document seeks to ensure that all countries deploying floats equipped with chlorophyll-a sensors document the data and metadata related to these floats properly. We produced this document in response to action item 3 from the first Bio-Argo Data Management meeting in Hyderabad (November 12-13, 2012).

If the recommendations contained herein are followed, we will end up with a more uniform set of chlorophyll-a data within the Bio-Argo data system, allowing users to begin analyzing not only their own chlorophyll-a data, but also those of others, in the true spirit of Argo data sharing.

1 Introduction

Presently, two types of sensors can be implemented on profiling floats to estimate chlorophyll-a concentration: radiometers and fluorometers. Radiometric measurements can be inverted into chlorophyll-a concentration on the basis of bio-optical models and fluorescence measurements are converted to chlorophyll-a concentrations thanks to laboratory or in-situ fluorimeter calibrations. This second method is the more widely used for shipboard measurement (mainly through fluorometer mounted on CTD rosette) so that fluorescence of the chlorophyll-a is (with oxygen) the most measured biological property in the open ocean. It is also the one used routinely "on board" floats. Hereafter we briefly describe the principle of this method.

Part of the photons absorbed by a chlorophyll-a molecule in the blue part of the spectrum is re-emitted as less energetic photons in the red part. This rapid (~ns) process is known as fluorescence and actually corresponds to the relaxation of the excited chlorophyll-a molecule to its ground state. The light emitted through chlorophyll-a fluorescence, F (mole quanta $m^{-3} s^{-1}$), can be roughly expressed through:

$$F = E$$
 [Chla] $a^* \Phi f$

Where E is the excitation irradiance (mole photons $m^{-2}s^{-1}$) provided by a light source. [Chla] corresponds to the concentration in chlorophyll-a (mg/m³), a* is the chlorophyll-a specific absorption coefficient (m² mg Chla⁻¹) and Φf , the fluorescence quantum yield (number of emitted photons per number of absorbed photons). The retrieval of [Chla] from the measurement of F depends, then, on the excitation irradiance, which is relevant to the instrumentation, and on an absorption term (a*) and an efficiency term (Φf), both of which depend on phytoplankton photo-physiology. Practically, while F and E are measurable physical quantities, the retrieval of [Chla] thus also depends on physiological terms. Therefore, to account for this "biological" dependence, calibration curves relating fluorescence reading to known amount of chlorophyll-a from phytoplankton culture (laboratory) or natural populations (in-situ) are established prior to or at the deployment site.

At the moment all fluorescence sensors implemented on floats are developed by the WET labs Company and are of the ECO serie. These Chla fluorometers are not standalone sensors and combine the Chlorophyll-a measurements together with a turbidity/scattering measurement (ECO FLNTU/FLBB) or with two measurements (ECO triplet) which generally are CDOM fluorescence and backscattering at 700 nm. The present document is focused on the management of the Chlorophyll-a fluorescence data flow acquired by those sensors (section 3). Similar sensors begin to be proposed by other companies (e.g. the Cyclops integrator Submersible Fluorometer from Turner). As soon as these sensors are implemented and successfully tested on floats, the present document would be accordingly updated.

2 Recommendations for addressing the chlorophyll-A concentration data processing

The official Bio-Argo unit for chlorophyll-a concentration is mg/m^3 . Presently the fluorometers implemented on floats provide counts for chlorophyll-a fluorescence. Here are the recommendations to address the chlorophyll-a processing:

- Store any data transmitted by the chlorophyll-a fluorometer with meaningful names. It is important to store those data, if changes occur in the calibration/conversion equations used to convert the sensor output in chlorophyll-a concentration. The name for the counts transmitted by the fluorometer is "FLUORESCENCE_CHLA".
- Store in "CHLA" the chlorophyll-a concentration in mg/m³, estimated from the "FLUORESCENCE_CHLA" counts.
- Fill properly the metadata to document the calibration, the conversions equations and the fields to identify a sensor.

As for the other sensors, the model number and serial number of the chlorophyll-a sensor must be provided. This tracking way is essential if a specific failure concerns all the sensors from the same batch for instance, or if the manufacturing process changes after a certain serial number.

Indications provided in the two following sections and the examples on how to fill metadata are valid as of the date of writing this document. It is very likely that changes in calibrations and conversions equations will occur in the future. Metadata will then have to be filled accordingly with the new procedures.

3 ECO sensor

3.1 Measurements and Data processing

Raw data from the ECO chlorophyll-a fluorometer (FLUORESCENCE_CHLA) are transmitted as counts, ranging from 0 to 4120 with an uncertainty of +/- 5 counts.

The basic equation allowing the retrieval of Chlorophyll-a concentration from raw transmitted measurement is:

CHLA = (FLUORESCENCE_CHLA – DARK_CHLA) * SCALE_CHLA

Or

CHLA = (FLUORESCENCE_CHLA – DARK_CHLA_O) * SCALE_CHLA

where

CHLA = concentration of chlorophyll-a of a sample of interest (mg/m³)

FLUORESCENCE_CHLA = raw counts output when measuring a sample of interest

7

- DARK_CHLA = dark counts, the measured signal output of the fluorometer in clean water with black tape over the detector from the manufacturer calibration sheets
- DARK_CHLA_O = dark counts, the measured signal output of the fluorometer in clean water with black tape over the detector performed by an operator before the deployment (If present it should replace DARK_CHLA in the PREDEPLOYMENT_CALIB_EQUATION)

SCALE_CHLA = multiplier in mg/m³/counts

The scale factor is factory-calculated by obtaining a consistent output of a solution with a known chlorophyll-a concentration, then subtracting the sensor's dark counts. The scale factor (SCALE_CHLA), dark counts (DARK_CHLA) are on the instrument's characterization sheet, supplied by WET Labs and will be stored in the "**PREDEPLOYMENT_CALIB_EQUATION**" and in the "**PREDEPLOYMENT_CALIB_COEFFICIENT**".

Examples :

First case, a DARK_CHLA_O, is provided

PREDEPLOYMENT_CALIB_EQUATION=" CHLA = (FLUORESCENCE_CHLA – DARK_CHLA_O) * SCALE_CHLA"

PREDEPLOYMENT_CALIB_COEFFICIENT="SCALE_CHLA=0.007, DARK_CHLA=50, DARK_CHLA_0=51"

Second case, a DARK_CHLA_O is not provided:

PREDEPLOYMENT_CALIB_EQUATION=" CHLA = (FLUORESCENCE_CHLA – DARK_CHLA) * SCALE_CHLA"

PREDEPLOYMENT_CALIB_COEFFICIENT="SCALE_CHLA=0.007, DARK_CHLA=50"

PREDEPLOYMENT_CALIB_COMMENT="No DARK_CHLA_O provided"

Argo data management

3.2 Sensor METADATA and Configuration parameters

3.2.1 Sensor and parameter metadata

This section contains information about the sensors of the profiler and the parameters measured by the profiler or derived from profiler measurements that need to be filled. All the reference tables can be found in the Argo user's manual.

Sensor metadata		
SENSOR	FLUOROMETER_CHLA	
SENSOR MAKER	WETLABS	
SENSOR_MODEL	ECO_PUCK	
SENSOR_SERIAL_NO	To be filled	

Parameter metadata				
PARAMETER	FLUORESCENCE_CHLA			
PARAMETER_SENSOR	FLUOROMETER_CHLA			
PARAMETER_UNITS	Counts			
PARAMETER_ACCURACY				
PARAMETER_RESOLUTION				
PARAMETER	CHLA			
PARAMETER_SENSOR	FLUOROMETER_CHLA			
PARAMETER_UNITS	mg/m ³			
PARAMETER_ACCURACY	0.08 mg/m ³ *			
PARAMETER_RESOLUTION	0.025 mg/m ³			

*The relationship between fluorescence output (i.e. signal, FLUORESCENCE_CHLA) and chlorophyll concentration for WET Labs chlorophyll fluorometers, is determined using a dilution series of a phytoplankton monoculture (either *Thalassiosira weissflogii* or *Thalassiosira pseudonana*) that is in exponential growth phase, and grown in nutrient replete conditions and under high irradiance (see Proctor and Roesler, 2010 for a description of the culture conditions and dilution methods). Chlorophyll concentrations were determined using benchtop fluorometric extraction techniques. Under these conditions, the precision as determined through calibrations of several in situ chlorophyll sensors is 0.08 mg/m³ over the 0 to 70 mg/m³ range.

3.2.2 Configuration parameters

CONFIG_EcoChlaFluorescenceExcitationWavelength_nm Wavelength of ECO sensor for excitation of chlorophyll-a fluorescence measurements (in nanometer)

 $CONFIG_EcoChlaFluorescenceEmissionWavelength_nm$

Wavelength of ECO sensor for emission of chlorophyll-a fluorescence measurements (in nanometer)

 $CONFIG_EcoChlaFluorescenceExcitationBandwidth_nm$

9

Bandwidth of ECO sensor for excitation of chlorophyll-a fluorescence measurements (in nanometer)

$CONFIG_EcoChlaFluorescenceEmissionBandwidth_nm$

Bandwidth of ECO sensor for emission of chlorophyll-a fluorescence measurements (in nanometer)

Fluorescence sensors do not collect data at the same pressure as the CTD sensors. We define a configuration parameter to illustrate the offset in pressure due to the difference of the vertical alignment between the Eco and the CTD. As the Eco is about 10 cm below the CTD:

CONFIG_EcoVerticalPressureOffset_dbar Vertical pressure offset due to the fact that the sensor is not exactly at the CTD pressure

As an example :

$CONFIG_EcoChlaFluorescenceExcitationWavelength_nm=470$

CONFIG_EcoChlaFluorescenceEmissionWavelength_nm=695

```
CONFIG_EcoVerticalPressureOffset_dbar=0.1
```

3.3 Chlorophyll-a data related parameters

During the ADMT13, the decision to separate data files for floats with biogeochemical sensors was taken. Then for biogeochemical floats, there are three files: one (c-file) for P,T,S, one (b-file) containing P, intermediate parameters and ocean state variables and one merged file (m-file) containing P, T, S and ocean state variables.

3.3.1 Chlorophyll-a related parameters for the b-file

Raw data from the ECO sensor is output in counts (FLUORESCENCE_CHLA) from the sensor.

PARAMETER="FLUORESCENCE_CHLA"

PREDEPLOYMENT_CALIB_EQUATION="none"

PREDEPLOYMENT_CALIB_COEFFICIENT="none"

PREDEPLOYMENT_CALIB_COMMENT="Uncalibrated chlorophyll-a fluorescence measurement"

10

3.3.2 Chlorophyll-a data for the b-file and the merged file

This FLUORESCENCE_CHLA is converted in chlorophyll-a concentration (CHLA)

PARAMETER="CHLA"

PREDEPLOYMENT_CALIB_EQUATION="CHLA=(FLUORESCENCE_CHLA DARK_CHLA)*SCALE_CHLA"

PREDEPLOYMENT_CALIB_COEFFICIENT=" SCALE_CHLA=0.007, DARK_CHLA=51"

PREDEPLOYMENT_CALIB_COMMENT="No DARK_CHLA_O provided"

Argo data management

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