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1. Acknowledgement

This work is largely based on the work carried out in MyOcean WP15, the DATA-MEQ group and most recently in the Copernicus Marine Environmental Monitoring Service (CMEMS) In Situ TAC, where especially NIVA, SYKE and ACRI have contributed largely; work dealing with recommendations for an automatically quality control for both physical and biogeochemical (BGC) parameters, the latter with special focus on the chlorophyll parameter.

2. Executive Summary

2.1. Sensor based observations of biogeochemical data

The number of biogeochemical, BGC, sensors in marine research and monitoring has increased during the last decade. These sensors collect a large amount of data and the importance of metadata and quality control is invaluable when scientist want to use the data from different platforms for research, development or modelling.

2.2. The need of harmonization in parameters, units etc. for biogeochemical data

To be able to compare biogeochemical parameters measured at different stations and platforms, with different sensor brands and parameter names and units, the metadata has to be harmonized. Parameter names must be comparable for the same parameter and the same units have to be used in order to avoid misunderstandings. The metadata must be added to the data set in order to be able to correlate and analyze the data in the most accurate way. Because of the importance of the metadata, it is therefore suggested that analysis method, latest calibration date and/or inter calibration and sensor brand are included in the meta data.

2.3. Standard quality controls

The work with producing recommendations for quality control of the BGC parameters has not been adopted in the same way as for physical marine parameters. During previous years joint projects such as MyOcean and CMEMS have introduced a best practice for the quality control of salinity and temperature. CMEMS In Situ Tac are to introduced a best practice and quality controls for BGC parameters that could act as the foundation for the community. In order to harmonize the BGC measuring community the participants in JERICO-NEXT are recommended to adopt the best practice and quality controls, which is in detailed described in the CMEMS In Situ TAC working document Quality Control of Biogeochemical Measurements V3.2(see annexes).

At the same time, the data providers who have more metadata, and/or where data has undergone further quality control, must be able to add this information to the data set in the same way as for the standard controls, which will simplify a future adoption for all active and potential data providers to extend their recent quality procedure with more tests and to include more detailed metadata when gained.

3. Introduction

3.1. Observations and harmonisation of biogeochemical data

Physical parameters have been monitored in a rather straight forward way historically, including quality controls that make the observations comparable. Later, sensors for physical parameter (e.g. temperature and salinity) were developed and automatic quality control adapted in what seems a relatively easy way.

The number of biogeochemical sensors in marine research and monitoring has increased during the last decade, but it is not as straight forward as for the physical parameters when it comes to analyses and comparison of the BGC parameters and results. As an example the parameter Chlorophyll-a is sensitive for different sensor brands and if the sensors have been calibrated on different algae cultivations. Further there are other BGC parameters e.g. oxygen, inorganic nutrients, fluorescence of colored dissolved organic matter, turbidity, other photosynthetic pigments that have to be handled, sometimes with more specific metadata or quality controls. The BGC data is highly desirable to develop indicators of the marine environmental status. These sensors measure a large amount of data and the importance of metadata and quality control is therefore invaluable when scientist want to use the data from different platforms for research, development and modelling. Without quality control there is no long term value of data.

4. Main report

4.1. Quality Controls

As for the physical parameters the biogeochemical parameter must undergo a quality control to make it possible to compare data sets from different platforms.

4.1.1. ***Previous work done by MyOcean WP15 and CMEMS In Situ TAC- Linking with JERICO Next activities***

A great effort has been made to obtain and develop quality control for near real time data in different joint projects. Best practice and quality control for salinity and temperature were developed in MyOcean and later on in Copernicus (CMEMS In Situ TAC).

Data distributed by the Copernicus webpage benefits largely from the mainstreamed use of best practice and quality controls implemented by the institutes and dissemination units providing data from all regions covering Europe organized by the In Situ TAC. Both near real time data and historical data are given in the same format and have undergone the same quality controls which facilitate further use of data for the scientific community and other end users. Due to the success of the implementation of the best practice and quality control for salinity and temperature, CMEMS in situ TAC moved on to the biogeochemical parameters, which are a far more complicated task to master.

Recently the CMEMS In Situ TAC has provided a working document (CMEMS In Situ TAC Quality Control of Biogeochemical Measurements V3.2) lead by NIVA, SYKE and ACRI. The document focuses in detail on the Chlorophyll parameter, but which would be possible to extend to a larger range of BGC parameters, while the standard quality controls are the same and the importance of well documented metadata is vital for the further analyses. It is worth remembering that in the beginning all the metadata about sensor calibrations dates etc. can't be mandatory but desirable, while some data providers will find it difficult to provide all metadata wanted. Instead, implementing it into the standard meta fields, the data provider has the possibility to fill it in and later it will be possible to make more and more of the standard fields mandatory.

For other platforms than profilers and buoys, additional quality test will be added, e.g. for the ferrybox the quality control needs to contain a check of pump or flow-meter test and speed range test.

Due to the benefit of using the same best practice and quality controls in the oceanographic community, JERICO-NEXT needs to adapt the recommendations done by MyOcean and further developed by the CMEMS In Situ TAC. Harmonization of parameter names, units and quality flags are of great importance for the scientific community and end users. It would be preferable if JERICO-NEXT participants provide data with parameter names and units according to the most recent CMEMS INSTAC parameter list (present version V3.0 http://archimer.ifremer.fr/doc/00297/40846/49097.xlsx).

4.1.2. *Recommended QC flags*

To harmonize the data provided within the JERICO-NEXT project, participants should use the below system of quality controls and flags. The codes 0, 1, 4 and 9 are mandatory to apply after the near real time quality control procedure.

Code	Meaning	Comment
0	No QC performed	-
1	Good Data	All real-time QC test passed
2	Probably good data	-
3	Bad data that are potentially correctable	These data are not to be used without scientific correction.

4	Bad data	Data have failed one or more of the tests.
5	Value changed	Data may be recovered after transmission error.
6	Not used	-
7	Nominal value	Data were not observed but reported. Example: an instrument target depth.
8	Interpolated value	Missing data may be interpolated from neighboring data in space or time.
9	Missing value	The value is missing

4.2. Biogeochemical parameters measured

The results from a fluorescence sensor will largely differ between sensors with respect to sensor brand, equation of choice and calibration routine. For a fluorescence sensor that measure chlorophyll-a concentration, the result can only act as proxy for the real chlorophyll-a concentration due to the dependence on light conditions and the algae culture used during the calibration procedure. There is also a difference in measurement techniques when analyzing bottled data for chlorophyll-a. The chemicals for extraction can vary between methanol, ethanol and acetone whereas the instrumentation can be HPLC or fluorometric determination. Due to this huge variability in measurement techniques, sensors and calibrations it is of great importance that metadata is included in the data delivery.

4.2.1. *Recommend quality control test and metadata fields*

Work done within the JERICO-NEXT is recommended to use the most recent CMEMS In Situ TAC working document *Quality Control of Biogeochemical Measurements v.3.2* in addition with MyOcean 1.2 (see annexes). JERICO-NEXT recommend the following QC test, divided into general standard tests and more specific test due to platform or measurement dimension:

Quality controls available for most platforms	**Additional quality controls especially for profilers**	**Additional quality controls especially for time series**	**Additional quality controls especially for underway monitoring as timeseries (ferryboxes)**
Impossible data test	Frozen Profile Test	Gradient test	Pump or flow-meter test
Impossible location test			Speed range test
Frozen Value Test			
Global/Local/climatological Range Test			

Spike Test			
Biofouling Test			

Table1. Quality tests suggested for different platforms.

The metadata suggested to be provided, with the possibility of filling in an "Unknown", at least in the beginning, would be for BGC parameters:

Name	**Description**
sensor_type	Brand of the sensor use
last_calibration_date	The date in the format YYYY-MM-DD when the specific sensor was calibrated
calibration_method	A description or link to the method used to calibrate the sensor
sensing_method	dependent on parameter: "HPLC", "spectrophotometry", "fluorometry_analysis", "fluorescence"

Table.2.

4.2.2. *Recommend quality control in delayed mode*

BGC data have to be quality controlled also in delayed mode to be able to validate data with reference samples such as water samples (manually or automatically) and/or CTD casts. There is a risk of degradation of water samples due to biological activity, which makes storage and preservation a problem. Further, there is also a need to determine the detection limit in similar conditions to where the data will be collected and the repeatability when analysing the reference data. Calibrations need to be carried out carefully to get a standard curve and factory calibration may be problematic.

Within the JERICO-NEXT project, deliverable 5.12 "Software for QC of biochemical data from FerryBox and fixed platforms", SMHI will deliver a developed free and open source based software to enhance and simplify quality control of BGC data in delayed mode. In Fig.1 and Fig. 2 a brief overview captures how the graphical interface will look. One main feature is the ability to compare water sample data with sensor data, but also standard functionalities as plotting, filter data and flag data will be included.

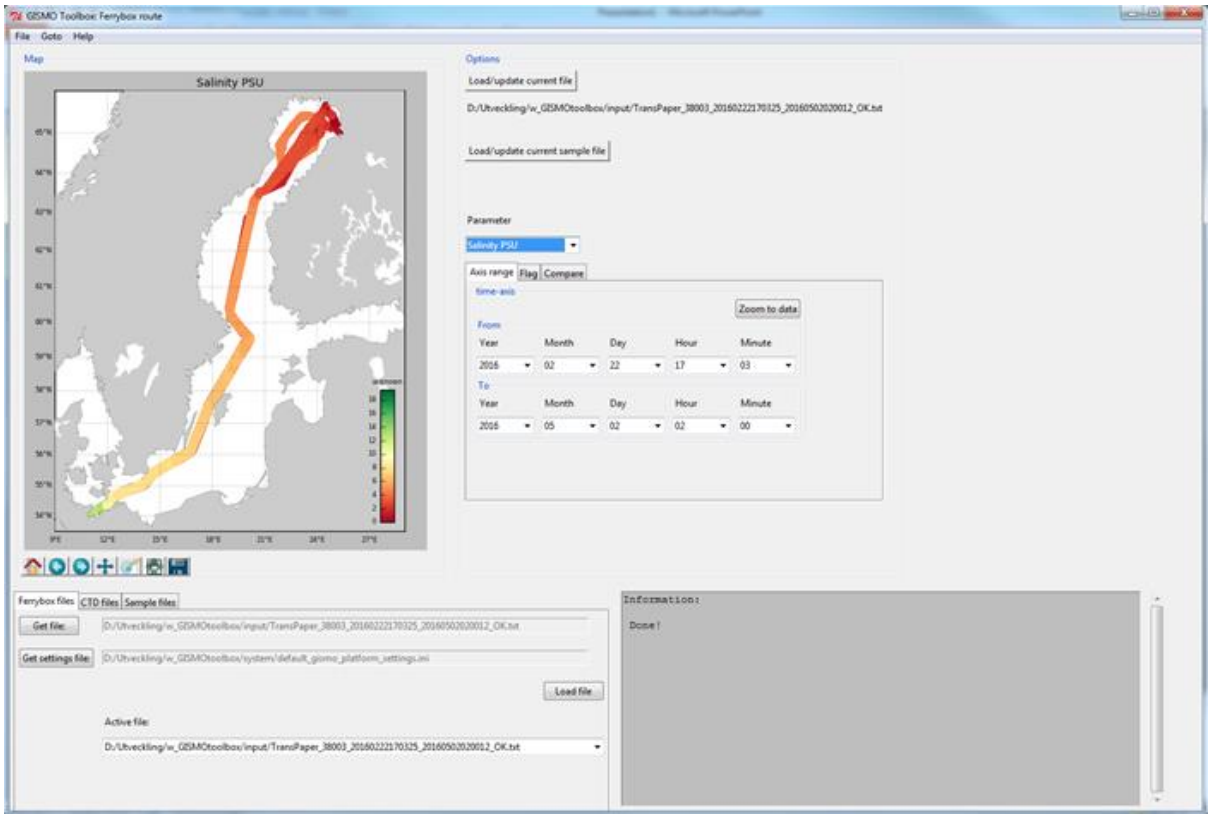

Figure 1. View of the graphical interface of the software to be delivered by SMHI for quality control of BGC sensor data in delayed mode.

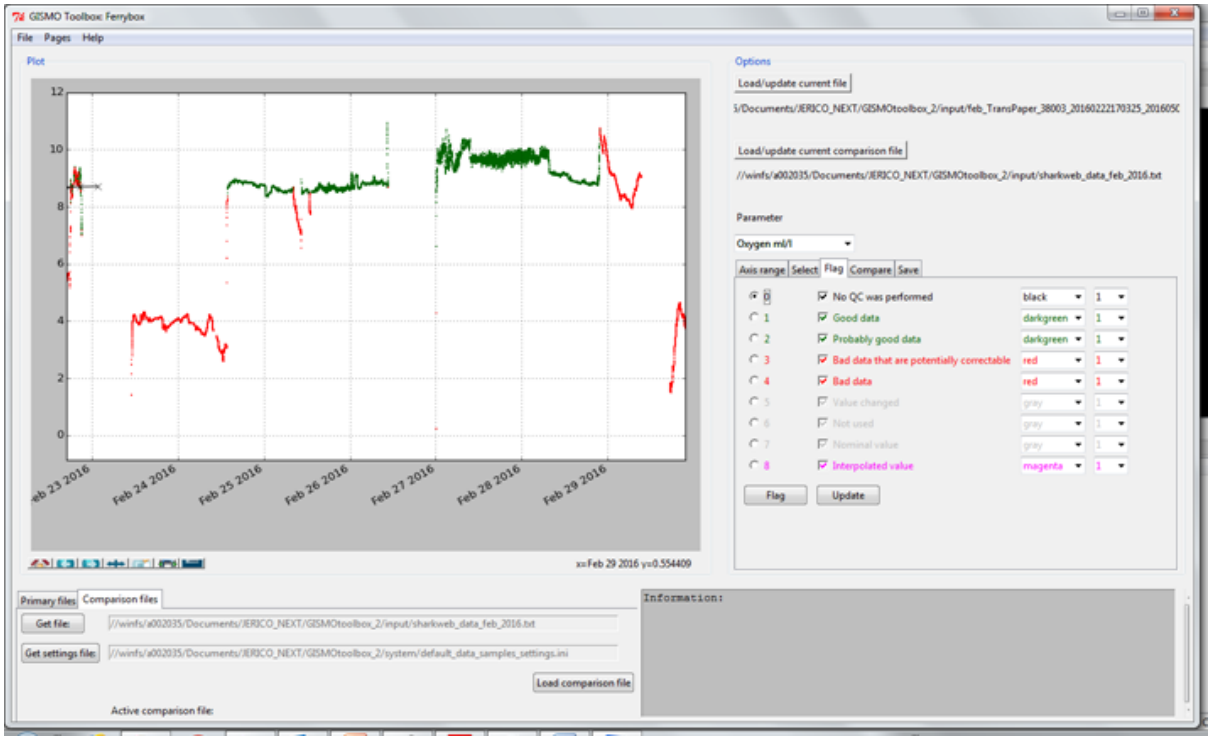

Figure 2. View of the graphical interface of the software to be delivered by SMHI for quality control of BGC sensor data in delayed mode. Visualisation and manually flagging data not captured by the automatic quality controls.

5. Conclusions

The work with the recommendations for quality control of the BGC parameters has not been adopted in the same way as for marine physical parameters. Recommendations have been worked out by projects such as MyOcean and further within the EuroGOOS DATAMEQ working group. Now a maturity level to start implementing these ideas has been reached. It is suggested to implement some standard quality controls, e. g. minimum requirements and at the same time make it possible for those who have more meta data, and/or where data has undergone further quality controls, to add this information to the data set in the same way as for the standard controls and in this way simplify a future adoption for all active and potential data providers to extend their recent quality procedure with more tests and to include more detailed meta data when gained.

CMEMS In Situ TAC has continued the work done by MyOcean and has provided a working document (*Quality Control of Biogeochemical Measurements v.3.2*) which introduce a best practice for the quality control of BGC parameters (with focus on Chlorophyll but will be extended to more BGC parameters) that should act as the foundation for the community.

6. Annexes and references

6.1. Working document: CMEMS Insitu TAC: Quality Control of Biogeochemical Measurements v3.2

IN SITU TAC
CMEMS ELEMENT

Quality Control of Biogeochemical Measurements

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Glossary and abbreviations
Additional terms:

BGC	Bio Geo Chemical
QC	Quality Control
CMEMS	Copernicus Marine and Environmental Monitoring Service

HISTORY

Previous versions of this document and up to version 2.5 were generated during MyOcean, MyOcean2 and MyOceanFO EU-projects. Starting in CMEMS, several updates have been performed but not officially released.
Version 3.1 is the first official release within CMEMS with focus on chlorophyll-a fluorescence.
Although not complete yet, it includes much of the conclusions obtained from the last years' work.

Foreword

Introduction

An important step within CMEMS is to harmonize existing quality control and quality assurance procedures of the different areas involved. As the Copernicus service is thought to be available at any time and open to anyone, an agreement in good QC methods and procedures is vital to guarantee high data quality distributed to users via international exchange. The agreement on the implementation of uniform QC procedures has the potential to overcome the non- consistency within the existing datasets actually provided by the international community.
The detection of anomalous values of BGC parameters is challenging due to their inherent high spatial and temporal variability, e.g., Diel Chl a fluorescence can vary by an order of magnitude or more due to changes in incident irradiance, self-shading, physiological states, community composition with as much as a factor 4, and can change as a result of cloud cover (Huot and Babin, 2010). It is therefore a challenge to define regional tests to check data quality in sea regions having different characteristics. Historically, the amount of data available for building regional climatology of BGC parameters is very limited. The lack of a common reference database for these parameters makes it difficult to identify anomalies at regional level.

Table 1 File occurrences with selected BGC parameters in the history repository on a total of 71068 files. Status from January 9, 2017.

Chlorophyll	2460
Oxygen	2635
Turbidity	1121
Nitrate	1044
Alkalinity	693
Phosphate	418
Silicate	398
Ammonium	311
CDOM	140
Carbon	1

The main focal point of this document is to describe quality tests recommended to be commonly applied for biogeochemical (BGC) data from the various observational platforms available in the service. Table 1 lists how many files from the history repository are expected to contain selected BGC parameters. While oxygen has the largest number of files, it is intentionally placed as second because this parameter is frequently reported in different units which are not always easy to convert. Therefore, this document will focus on Chl *a* measurements to provide examples of good practice in data handling Hence, chlorophyll shows the largest occurrences and this is the reason why this parameter has retained most of the focus for now. The proposals for RTQC given within this document are built on the heritage from previous efforts, e.g. PABIM White Book (D'Ortenzio et al., 2010), Coriolis (Coatanoan and Petit de la Villéon, 2005), SeaDataNet (SeaDataNet, 2007) ECOOP (Tamm and Soetje, 2009), GOSUD (GOSUD, 2006), M3A (Basana et al., 2000), Argo (Argo, 2009), MyOcean T/S QC procedures (Schuckmann et al., 2010), MyOcean Real Time Quality Control of biogeochemical measurements (Jaccard et al., 2015) as well as in-house expertise from contributors to this report.

Moreover, the goal of this document is to present quality assessment tools for the *latest*, *monthly* and *history* CMEMS repositories. Some tests can be applied to all of them, but other need a certain amount of data in order to build the test itself. In the latter case, *monthly* or *history* repositories are more adequate. Another set of tools developed are dedicated for the evaluation of the tests themselves and likely to be applied on monthly and history repositories only. These evaluation tools are not expected to be implemented at DU level. It is the responsibility of the partners in task 3.2 to use and assess them.

About this document

This document is divided in the following parts

- **Scientific Background:** This part summarizes challenges observed when measuring specific BGC parameters. Its aim is to inform users about common known errors and uncertainties arising from measurements.
- **Quality Control Flags:** provides a description of the flags used.
- **Parameter Naming Convention**: defines how the different BGC parameters are supposed to be defined in the netCDF files.
- **Quality Control Tests:** This section the algorithms and tools to be applied, as well as a short summary of the underlying scientific background for these methods.

Scientific background

1. Chlorophyll

As described below, conditions affecting in vivo or *in situ* Chl a fluorescence emission are:

- Light regime (t/day, day length)
- Self-shading and dense blooms
- Different species and groups
- Regional variability
- Nutrient status

When eukaryotic algae absorb light (Photosynthetically Active Radiation (PAR, 400-700 nm)), 1-5 % of this light will be re-emitted as fluorescence. Many pigments (light absorbing molecules) are involved in the light harvesting (Figure 1), but the fluorescence is mainly (95 %) emitted from the pigment Chl a in the reaction center II (RC II) of the photosynthesis light reactions in photosystem II (PSII).

Pigments in the phytoplankton cells form antenna like structures for an effective harvesting of the spectral light. The absorption happens when an electron of the pigment is excited into a higher energy state. This energy is sent down the antennae of pigments to the reaction center (RC) Chl a (Figure 1). When the RC Chl a is excited, the excitation energy can be released mainly by three competing de-excitation pathways; heat, photochemistry and fluorescence. The amount of fluorescence from the absorbed light is the yield of fluorescence (ΦF), which increases from 0 in total darkness to 3-5% in saturating light intensities. If the cells are extracted, e.g. in methanol, the connection from RC to photosynthesis is broken and fluorescence can reach 30 % (Krause and Weis, 1991, Owens, 1991, Govindje, 1995, Falkowski and Raven, 1997, Huot and Babin, 2010, Johnsen et al., 2011).

The ratio of in vivo Chl *a* fluorescence against extracted Chl a concentration may vary remarkably (Figure 2). This is a result of physiological processes in algae such as photosystem regulation, acclimation to environmental conditions (e.g. low light, nutrient stress etc.), or adaptation to different environmental pressures conditions in order to optimize their evolutionary

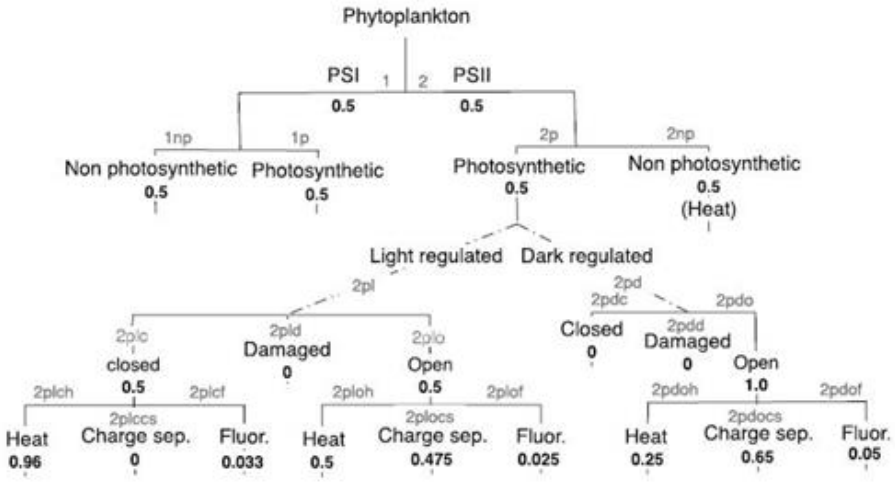

Figure 1 Fates of absorbed photons in phytoplankton as originally shown in Huot and Babin, 2010. RC's can either be closed (excited) or open (not exited) and is dependent on light acclimation status.

fitness (Raven and Geider, 2003). One example from the Ferrybox system in Norway (Figure 2) shows that the Chl a fluorescence often appears too high at low Chl *a* concentrations and too low at high Chl *a* concentrations, using a calibration of the sensor based on cultures (Figure 1). This figure does not leave out any outliers, which i.e. could be caused by patchiness in the distribution of algae, leading to inconsistency between sensor and sampling, and thus it also shows how a validation and calibration procedure can be biased by inaccurate sampling (Johnsen et al., 2011).

This high variation in fluorescence is a result of varying light conditions (irradiance, spectral composition and day length) and different algae groups and species (described below). In low light conditions, light harvesting pigments (LHP's) efficiently transfer the light energy to the reaction centers (RC) of photosynthesis, and chloroplasts are distributed to give maximum light harvesting. The efficiency is reduced in high light conditions, because photo-protecting carotenoids (PPC's) increase in amount and thereby reduce the flux of photons to the reaction centers. In addition, high light conditions can cause a reduction in the amount of Chl a within each cell as well as the number, size and distribution of the chloroplasts (Johnsen et al., 2011, Brunet et al., 2011).

Different groups/species of phytoplankton contain different additional pigments (LHC's and PPC's), and different xanthophyll cycles, i.e in diatoms (diadinoxanthin to diatoxanthin) or green algae (violaxanthin to zeaxanthin) which are processes related to light stress (Brunet et al., 2011). Some algae (green and phycobiliprotein-containing) have state transitions between light harvesting complexes related to RCII and RCI.

The processes described above all reflect in in vivo fluorescence measurements, because, as mentioned before, the absorbed light energy (photons) can be released mainly by three competing de-excitation pathways; heat, photochemistry and fluorescence as was schematically shown in Huot and Babin, 2010 (Figure 1).

In some regions cyanobacteria can dominate the phytoplankton biomass. Cyanobacteria are considered to be the most primitive organisms and they have prokaryotic cell structure. They have a different allocation of energy regarding the photosystems. In cyanobacteria the most of Chl a is located in the non-fluorescing photosystem I. However this Chl a is

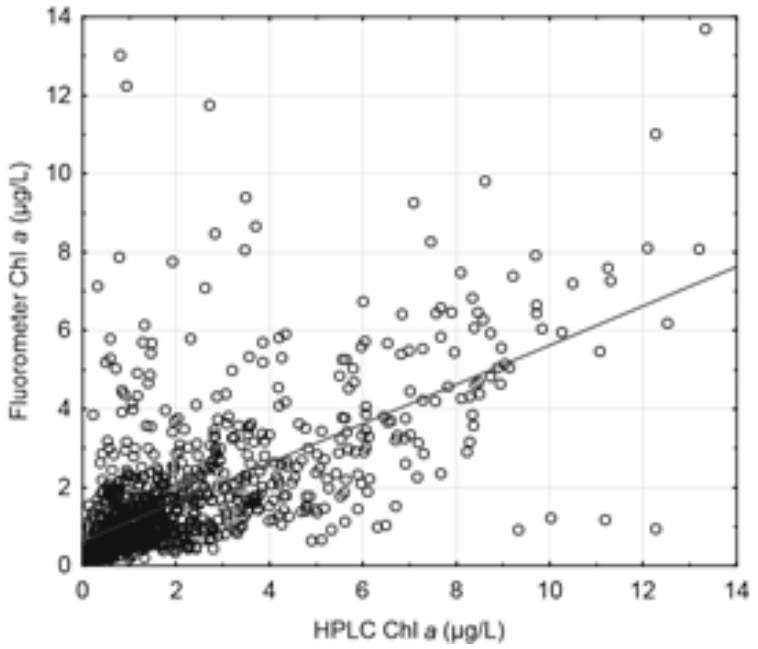

Figure 2 Regression plot between Fluorometer Chl a and HPLC Chl a concentration (from Ferrybox data during the years 2003-2008), r2= 0.3909.

included in the extracted Chl a yield. On the other hand, phycobilin pigments such as phycocyanin (specific for filamentous cyanobacteria) provide strong in vivo fluorescence. Consequently during abundant cyanobacteria blooms occurring annually in the Baltic Sea, the phycocyanin fluorescence should be used as auxiliary parameter to correct the ratio of in vivo Chl a fluorescence against extracted Chl a concentration (Seppälä et al., 2007).Moreover, the ratio between in vivo Chl a fluorescence measurements and in vitro HPLC or spectrophotometric Chl a concentration is not constant and may vary significantly with a factor 3-4 depending on various conditions. Thus, when using real-time measurements of Chl a fluorescence as a proxy for Chl a concentration, the users should be aware of the natural variation in Chl a fluorescence relative to Chl a concentration. Subsequently, there is a need to make clearly distinctions between bad Chl a fluorescence data caused by sensor failure, or a bad calibration, and "uncertain" estimates of Chl a concentration caused by inherent natural variations in the Chl a fluorescence.

This is clearly observed in Figure 3where one year of Chl a measurements using both fluorescence sensor from a Ferrybox and HPLC analysis from water samples are compared. The signal from fluorescence is higher during the night. The difference between day and night is even higher during blooming periods. This difference is also depending on whether the HPLC analysis is using samples taken during day or night.

Similarly, Figure 4 shows the difference one will measure with the same fluorescence sensor in water masses containing different algae species. This introduces typically uncertainties on measurements from moving platforms travelling through different water masses.

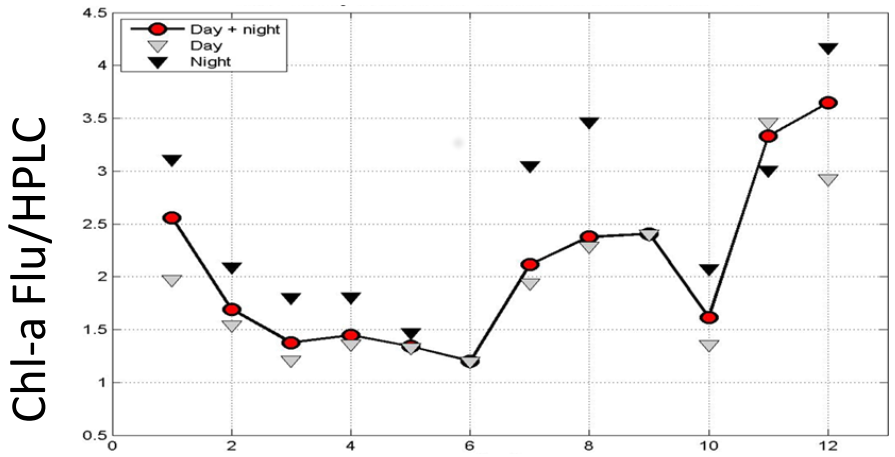

Figure 3 Study of measurements for Chl a from fluorescence sensor and HPLC analysis during one year of Ferrybox data.

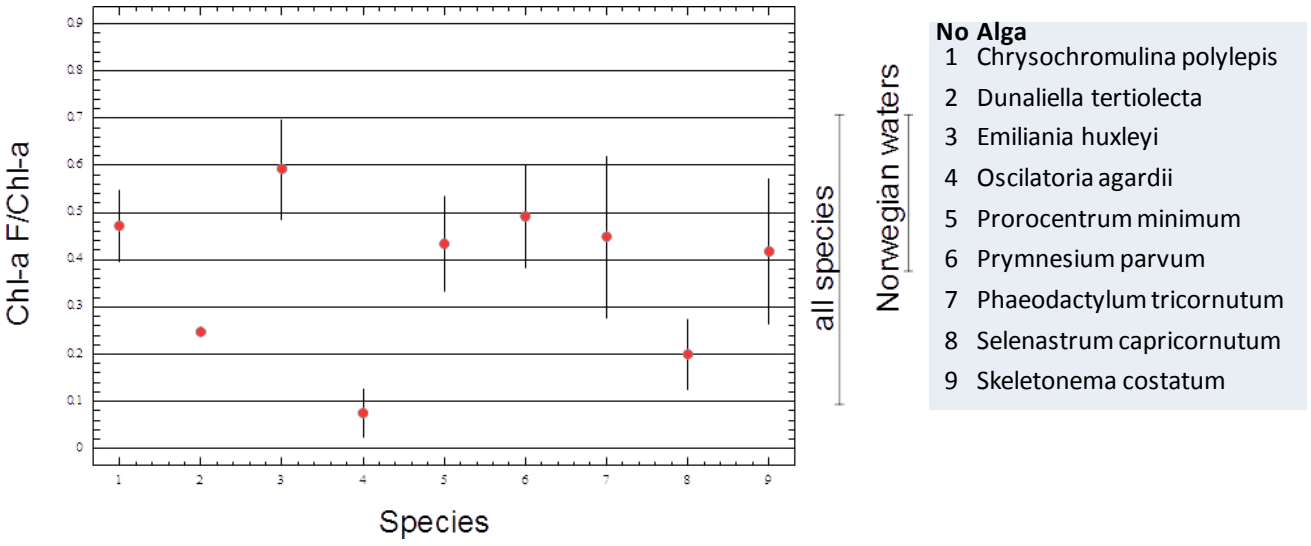

Figure 4 Study of measurements for Chl *a* from fluorescence sensor and HPLC analysis for different algae species. The list of algae species on the x-axis is on the right side of the figure.

Phytoplankton growth, chlorophyll content and fluorescence response are strongly related with nutrient status (Kruskopf & Flynn 2006). Nutrient stress cause increased chlorophyll a fluorescence. Consequently, when the phytoplankton spring bloom collapses after the dissolved nitrogen is exhausted, the increased chlorophyll fluorescence in comparison to chlorophyll a content is observed.

1.1 Concluding remarks

Using a fluorescence sensor to measure Chl a concentration can only provide a proxy for the real chlorophyll -a concentration. Results will depend on incident irradiance, self-shading, physiological states, community composition etc. light conditions and algae species the sensor was used during calibration. The sensor will provide a measurement close to reality for the conditions closest to those applied during calibration. For measurements performed in the field, different light conditions and water masses should lead to a relative uncertainty of anything up to 50% or more.

2. Quality control flags

The in-situ data provided by the CMEMS In-situ Thematic Assembly Centre (In Situ-TAC) is thought to be used by different users, with different requirements. Thus, one of the goals of the RTQC procedure is the provision of known quality flags, which characterize the data.
These flags should always be part of data delivery, in order to maintain standards and to ensure data consistency and reliability. The QC flags for BGC data within CMEMS are oriented on the existing standards defined for other observational data sets. Table 2 indicates the flags and their specific meanings.
To avoid unnecessary failure in using the data sets, a clear guidance to the user of CMEMS in Situ-TAC data is necessary:

Table 2 Quality flag scale. Codes marked in red are mandatory following the RTQC procedure

Code	Meaning	Comment
0	No QC was performed	-
1	Good data	All real-time QC tests passed.
2	Probably good data	-
3	Bad data that are potentially correctable	These data are not to be used without scientific correction.
4	Bad data	Data have failed one or more of the tests.
5	Value changed	Data may be recovered after transmission error.
6	Not used	-
7	Nominal value	Data were not observed but reported. Example: an instrument target depth.
8	Interpolated value	Missing data may be interpolated from neighbouring data in space or time.
9	Missing value	The value is missing

A data with QC flag = 0 indicates no QC has taken place, i.e. the data are not recommended to be used without a quality control carried out by the user.
A data with QC flag ≠ 1 for either position or date should tell the user to proceed with caution. The data should not be used without additional controls and checks carried out by the user.
Otherwise

- only measurements with a data QC flag = 1 can be used safely without further analyses
- if the data QC flag = 2 the data may be good for some applications but the user should verify this and document results accordingly.
- if the data QC flag = 3 the data are not usable as they are, but the data center see potential for correcting the data in the delayed mode
- if the data QC flag = 4 measurements should be rejected.

Quality control flag application policy (i.e. Argo, 2009): The QC flag value assigned by a test (see section 3) cannot override a higher value from a previous test.

3. Parameters naming conversion

Agreement on how to name the different BGC parameters and the units to use has been established and is presented in Table 3. This has been a first important step in the development of standardized tools for the quality control of such measurements.

Table 3 Naming conventions to use for the different BGC parameters

Name	Long Name	Unit	CF Standard Name
FLU2	Chlorophyll-a fluorescence	mg m^{-3}	mass_concentration_of_chlorophyll_a_fluorescence_in_sea_water
CPHL	Chlorophyll-a	mg m^{-3}	mass_concentration_of_chlorophyll_a_in_sea_water
DPAR	downwelling photosynthetic active radiation	µmole m^{-2} s^{-1}	downwelling_photosynthetic_photon_flux_in_sea_water

3.1 Common Attributes

For all netCDF variables containing BGC data, the following set of attributes should be provided, if possible (Table 4). These come in addition to the standard required attributes. They are not present yet in the products, but it would be a good practice to provide them as this information is very relevant in the development, evaluation and improvement cycle of quality control tools.

Table 4 Parameter independent additional attributes to netCDF BGC variables.

Name	Description
last_calibration_date	The date in the format YYYY-MM-DD when the specific sensor was calibrated
calibration_method	A description or link to the method used to calibrate the sensor

The next sections specify in more details the parameter specific information to be included in the netCDF files.

3.2 Chl-A Fluorescence

Measurements of Chl-a fluorescence are saved in variable FLU2. For historical reasons, using CPHL is also allowed for BioArgo platforms *only*, and in this case the netCDF variable must have attribute *sensing_method* set to **fluorescence.** If the latter is not provided or wrong, it will be considered as a Chl-a concentration, as those obtained from laboratory analysis from HPLC or spectrophotometry. Note that this exception is only accepted for data from BioArgo. All other must use FLU2.

Attributes

Name	Description
proxy_method	A description or a link to the method used to relate the fluorescence measurements to Chl-a concentration
last_proxy_method_date	The date in the format YYYY-MM-DD when the proxy relation to Chl-a concentration was generated.

Downwelling photosynthetic active radiation (DPAR) if provided could be used in the future to improve quality control procedures.

3.2 Chl-A Concentration

Chl-a concentration is described with CPHL. If possible, the variable attribute *sensing_method* should be set to the laboratory analysis method used, such as *HPLC*, *spectrophotometry, fluorometry analysis*.

Attributes

Name	Description
Laboratory_technique	"HPLC", "spectrophotometry", "fluorometry_analysis"…
Laboratory_method	e.g. if fluorometry, acidification or not; e.g. if HPLC, using Van Heukelem & Thomas (2001) ? e.g. if total Chl *a* (does it include phaeopigments etc.)
sensing_method	"fluorescence" (required if using CPHL instead of FLU2, BioArgo only).

4. QC tests

4.1 Introduction

This section enumerates the tests to be implemented. It is mostly designed to be used for programmers. Any additional information about the tests should be found in the previous sections of this document.

Tests have been tagged in the following categories

LATEST [L]	The test can be applied as soon as the measurement is received, for example on the real time netCDF files
MONTHLY [M]	The test requires a certain amount of data. Normally the monthly directory should be a good candidate, unless the measurement frequency is too low, in which case the specific test has to be moved to the next category.
HISTORY [H]	The test requires most available data.

Note that tests applicable for data from the *latest* repository can also be applied on data found in the *monthly* and *history* repositories. Similarly, tests defined for data in the *monthly* repository can be applied on the data found in the *history* repository.
The first revision of these tests has been developed on the basis of existing data in the CMEMS repository in winter 2017. As a consequence, only measurements in the upper 10m were used since this layer contains by far the majority of all observations (Figure 5).

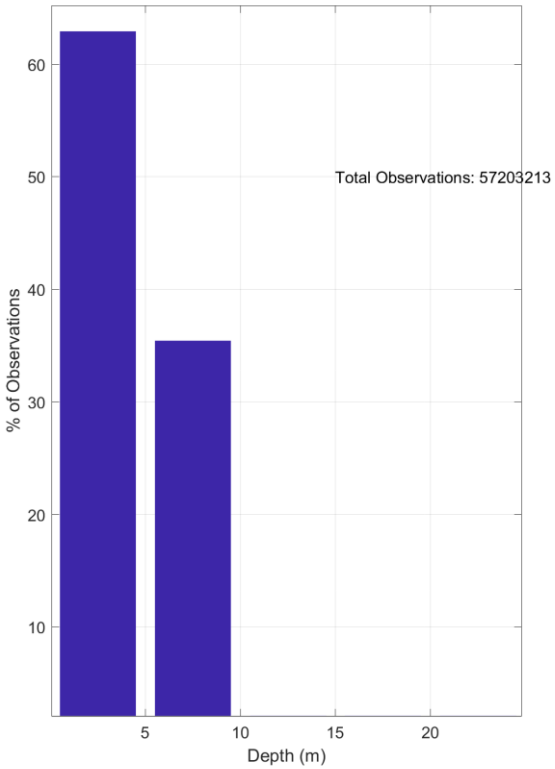

Figure 5 Depth occurrences of BGC parameters in January 2017 accounted for approximately 97% of the total observations within the top 10m.

4.2 Naming Convention Test [L,M,H]

The purpose of this test is to verify the correctness of variable semantics. Data failing this test must be ignored in further quality assessment as they may introduce bias in other quality control tests. Moreover, users should avoid using these variables in order to avoid confusion and erroneous analysis.

- Check variable name
- Check variable attributes
- Check unit

Any mismatch should result in a bad value flag QC=3.

FLU2

The variable name is either

1. FLU2 or
2. CPHL with the attribute `sensing_method` set to `fluorescence`

In addition, the unit for the variable, in either case is `mg m-3` or an equivalent.
If true, the data from this variable is considered as a Chlorophyll-a fluorescence **FLU2** parameter. All remaining tests specific to it and parameter unspecific tests can be applied.
If false, try to identify another BGC parameter.

4.3 Missing Value Test [L,M,H]

This tests checks for missing values, usually called *Fill Values* in netCDF file. Any data matching this test should result in a bad value flag QC=9

4.4 Frozen Value Test [L,M,H]

This test checks whether the values of subsequent measurements are identically the same. If so, all of these should be marked as bad, QC=4.The effect is to comment out periods of sensor malfunctions.

4.5 Global Range Tests [L,M,H]

The purpose of this test is to comment out data that are far from values one can expect. For this test, one need minimal and maximal threshold values that can be applied on a global scale. Consequently, it is a very coarse control, but will in most circumstances detect sensor calibration errors or other malfunctions.
Thresholds must be obtained using statistical method on all available measurements. Any data not within the specified range should result in a bad value flag QC=4.

The high variability of BGC data can be caused by both high natural variations as well as sensor problems (e.g., biofouling, calibration). From the study of the data itself with no extra information, it is hard to separate natural variation from suspicious values.
This test checks whether the measured value is within a specified interval. Any value failing the test should be marked as bad, QC=4.

$$v_{min} \leq v \leq v_{max}$$

FLU2

In order to get an overview of "typical high" values, the dominating data sources of FLU2 have been subdivided by platform, month and area. Then, for each of these subsets, a maximum and selected percentiles were calculated. As shown by the upper 97.5 % of the data (Figure 6), there is a tendency for higher measurements in spring (February-May). This pattern is supported by ecological knowledge, and in addition it occurs in all areas with most data, the North Sea and the Baltic Sea. In contrast, there is no clear evidence for differences among these areas.
Small negative values of Chl a can also occur, and explained mainly by instrumental and electronic "noise" or a small drift in the calibration.
Based on this, global limits for FLU2 are defined in Table 5.

Table 5 Global thresholds for FLU2

FLU2 (mg m^{-3})	Min	Max
February-May	-0.1	60
January, June-December	-0.1	35

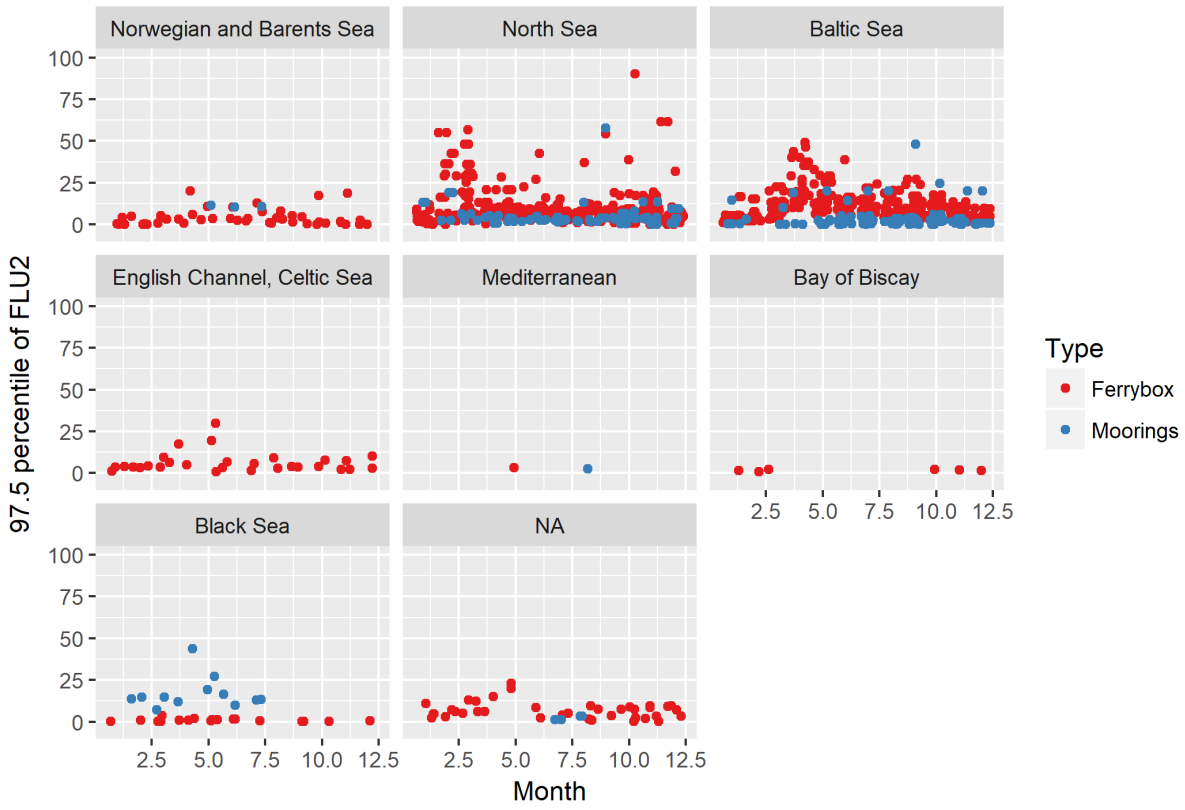

Figure 6 97.5 percentiles of the FLU2 parameter, divided per month, platform and area. Only data with and depth <= 10 m has been selected. Also, a number of values >100 are not shown in the graph.

4.6 Local Range Tests [L,M,H]

This test is similar to the Global Range test, but with more specific thresholds based on regional and temporal scales. Any value failing the test should be marked as bad, QC=4.

$v_{min} \leq v \leq v_{max}$ Value for threshold limits rely on further analysis and expert knowledge from the selected areas.

FLU2

Limits for FLU2 are listed in Table 6.

Table 6 Local thresholds for FLU2

FLU2 (mg m^{-3})			Min	Max	Time period
Arctic			0	10	Jan-Dec
IBI -Cantabria Sea			0.01	5	Jan-Dec
Baltic/Western Gulf of Finland	59.45N, 23.22E	60.3N, 30.2E	0.5	25	Oct-Feb
			1.5	77.6	Mar-May
			0.5	36.8	Jun-Sep
Northern Baltic Proper	58.36N, 19.88E	59.62N, 23.21E	0.5	6	Oct-Feb
			1.5	31	Mar-May
			0.5	13	Jun-Sep
Southern Baltic Proper	54.52N, 12.27E	56.2N, 17.09E	0.5	7.6	Oct-Feb
			1.5	27.3	Mar-May
			0.5	20.5	Jun-Sep

4.7 Spike Test [M,H]

As mentioned earlier, biogeochemical parameters may vary very much on all scales. Tests built on threshold limits would require very large threshold values and loose some effect. Moreover, BGC sensors based on optics often generate non-negligible noise. For example this can be due to the presence of solid or gaseous particles in water affecting the optical properties of the water masses in the vicinity of the measured volume and hereby providing unwanted spikes. These oscillations depend on sensor technology but also local water masses and must be taken into account.
Therefore, the suggested procedure for spike detection is performed in 3 steps

1. Estimate inherent noise in measurements
2. Identify potential outliers
3. Cross check outliers

Step 1: Estimation of noise in measurements

Data must be filtered through a high pass filter in order to keep only the high frequency variations. Because the resulting signal will be used to identify potential outliers in step 2, one has to apply the filter in both directions in order to avoid the introduction of a delay in measurements. Then the mean signal peak value related to the filtered signal energy is estimated with

Where ρ=2 is for a pure sine and ρ<16 is a good approximation for white noise signals. (QUIROGA et al.) suggest a value of 2.198. However, this is very dependent on the nature of the signals analyzed. They also suggest the use median instead of mean values in order to avoid influence of high amplitude outliers.

Step 2: Identify potential outliers

Potential outliers are values in the filtered signal whose amplitudes are larger than a certain threshold above the estimated energy level.

Step 3: Cross check outliers

In this last step we use a simplified form of the Akaike information criterion to confirm whether suspicious measurements found in step 2 are outliers or if they are part of a natural variation. The AIC is based on the approximation of UEDA (2009), and yields

$$U_t = \frac{1}{2} AIC = n_g \log(\sigma) - n_b \frac{\log(n!)}{n} \sqrt{2}$$

Where σ the uncorrected standard deviation based on the z-score values z

$$\sigma = \sqrt{\frac{\sum \left(x_i - \bar{x} \right)^2}{n_g}} \quad i = 1 \ldots n_g$$

from good measurements, n_g the number of good measurements and n_b the number of potential outliers. This formula provides an estimate of the statistical entropy for the n points considered. Apply this formula for at least 2 additional point on each side of the potential outlier (1) with all points, then (2) omitting the potential outlier. If the AIC value is less in the second case, it could be an outlier.

General Comments

As presented here, at least 5 consecutive measurements are required to perform this test. If filtering in step 1 is of order N, the outer 5*N points on each side of the interval should not be used.

This test can also be useful for other parameters such as temperature and salinity, especially in coastal waters where the ARGO spike test based on constant thresholds will often fail due to frontal activity. has failed. Spikes are likely not to be drastically present in oxygen optode measurements. This is expected because optodes have a typical response time of 20s. As a consequence, it implies that if other parameters are seen to vary faster than that, then oxygen measurements are likely to be wrong and should be flagged as bad data.

Implementation

Step 1: Filter Signal

Select a range of N measurements to be analyzed and add 30 points on each side of the range. These extra points are required in order to stabilize the filter. N should be sufficiently larger than then 30. Apply the following classic filter as follow:
$y(t_j) = b_0 x(t_j) + b_1 x(t_{j-1}) + \ldots + b_n x(t_{j-n}) - a_1 y(t_{j-1}) - \ldots a_n y(t_{j-n}) \quad j = -30 \ldots N + 30$ Where x(t_i) is the i^{th} previous data. For the first n points, only part of the formula can be applied since there are not enough data. This formula has to be applied for all points from t_{-30} to t_{N+30}. Then apply the same formula in reverse order, from t_{N+30} to t_{-30},
$z(t_j) = b_0 x(t_j) + b_1 x(t_{j+1}) + \ldots + b_n x(t_{j+n}) - a_1 y(t_{j+1}) - \ldots a_n y(t_{j+n}) \quad j = N + 30 \ldots -30$ The coefficients are given in Table 7.

Table 7 Coefficients for filtering signal

index	a	b
0		3.40537653E-04
1	3.57943480E+00	-2.04322592E-03
2	5.65866717E+00	5.10806479E-03
3	4.96541523E+00	-6.81075305E-03
4	2.52949491E+00	5.10806479E-03
5	7.05274115E-01	-2.04322592E-03
6	8.37564796E-02	3.40537653E-04

Step 2: Identify Potential Outliers

Using the resulting filtered signal. Keep only the selected N points and calculate the following threshold
$\lambda = \rho \langle z^2 \rangle$,where ρ=5 and identify the times for where $x \geq \lambda$.

Cross Check Outliers

For each potential outlier, calculate the outlier detection statistic U_t, using extra 2 points on each side of the outlier

$$U_t = \frac{1}{2} AIC = n_g \log(\sigma) - n_b \frac{\log(n_b!)}{n_b} \sqrt{2}$$

Do this twice

$$\sigma = \sqrt{\frac{\sum \left(x_i - \bar{x} \right)^2}{n_g}} \quad i = 1 \ldots n_g$$

1. Once considering all 5 points as good, ie. n_g=5 and n_b=0. This will yield U_{tx}
2. The second time by considering the outlier point as bad, ie. n_g=4 and n_b=1, yielding U_{t0}.

Step 4: Final Test

The final test is: if $U_{tx} < U_{t0}$, then the central point is an outlier and should be marked as bad, QC=4.

4.8 Frozen Profile Test [L,M,H]

This test can detect an instrument that reproduces the same profile (with very small deviations) over and over again. It has been introduced for temperature and salinity data (e.g. Schuckmann et al 2010) and should be equally applicable to BGC data.

Step 1: Average Profiles

For each parameter derive an averaged profile by taking the median in 50 dbar slabs. This is necessary because the instruments do not sample at the same level for each profile. It is also preferable to use the median in order to reduce the effect of localized variation of BGC measurements. This yields the two new profiles

$\overline{P_{prev}}$ $\overline{P_{next}}$

Step 2: Compare Averaged profiles

Subtract the subsequent resulting profiles and compute the average, minimum and maximum values

$$\overline{\Delta P} = \left\langle \overline{P_{next}} - \overline{P_{prev}} \right\rangle$$
$$\overline{\Delta P}_{\min} = \min\left(\overline{\Delta P}\right)$$
$$\overline{\Delta P}_{\max} = \max\left(\overline{\Delta P}\right)$$

The test itself consist in checking these values against minimal thresholds. If all computed averages are less, the data must be flagged with flag QC=4.

FLU2

The thresholds to be used for data from variable FLU2 are

$$\overline{\Delta P} < 0.02 \mu g / l$$
$$\overline{\Delta P}_{\min} < 0.001 \mu g / l$$
$$\overline{\Delta P}_{\max} < 0.3 \mu g / l$$

4.9 Biofouling Test [M,H]

Biofouling accumulates on the sensors, typically on a time scale of a few days. Often, this can be observed with steady increase of drifting values from the sensor. This bias is removed once the sensor is cleaned or replaced. Because the different platforms are maintained differently, a general rule is not obvious. In this chapter we suggest experimental methods that were derived from the CMEMS dataset. An evaluation will be required for improving results.

FLU2

For chlorophyll-a fluorescence, biofouling leads to a steady increase of measured values. However, variations may still be superimposed. When the sensor is cleaned, values drop quickly to a much lower level. In a natural bloom, data variance will tend to increase less. Moreover, the lower 5th percentile is expected to increase slower than the median value.
Statistical parameters are first calculated over a data subset of 6 hours. These include the lower and upper 5th percentiles as well as the median value reducing hereby a day of data to 12 values. These are then analysed over a period of several days during which one assumes a biofouling event could happen. The analysis itself consists of normalizing the percentiles and median in the considered time interval and then estimating a rate of increase for the median. A coefficient of biofouling probability $P_{biofoul}$ is defined with help of logistic regression. This procedure is then repeated with overlap for the next group of days.
Figure 7shows an example of values for the biofouling probability. Because this coefficient indicates whether a biofouling or cleaning event has occurred during the previous days, higher values are expected after cleaning has taken place. As such, measurements before such events should be potentially flagged as potentially correctable, QC=3.

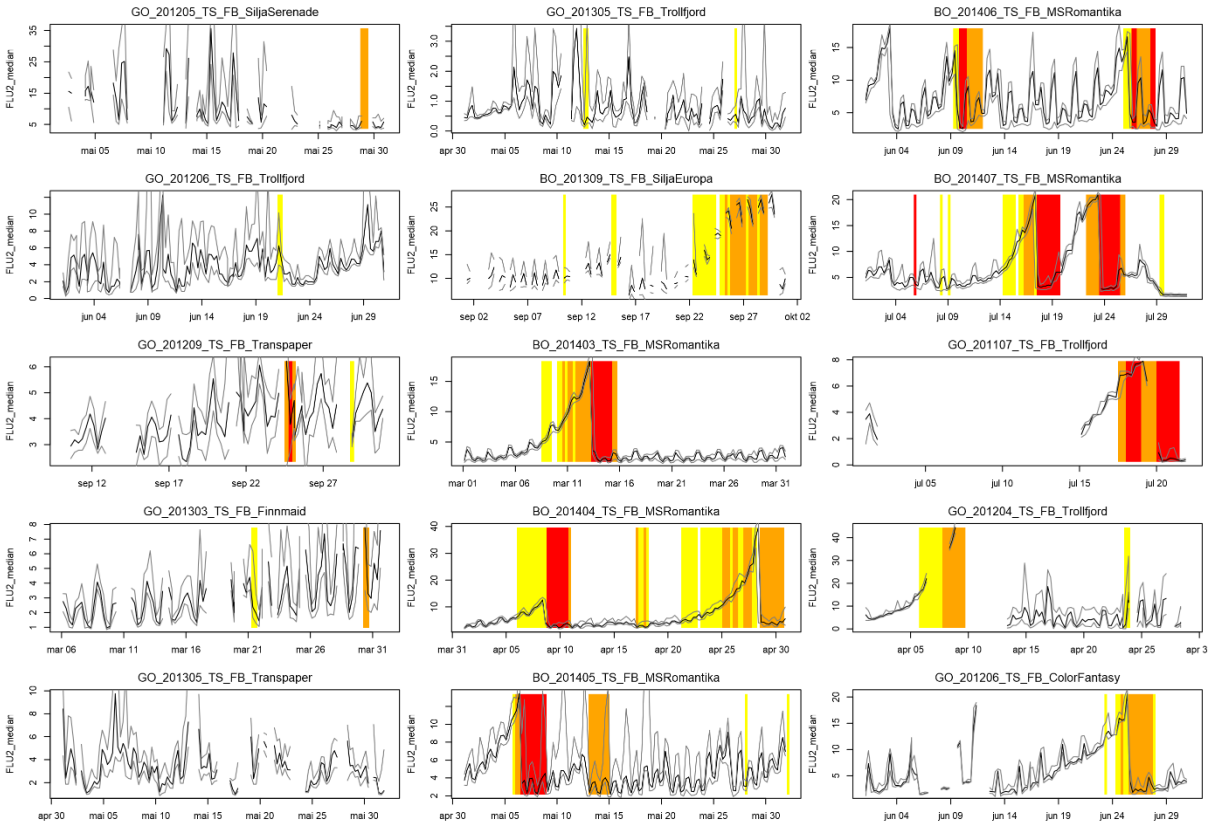

Figure 7 Values of $P_{biofoul}$. The colours indicate 0.3 < $P_{biofoul}$ < 0.5 (yellow), 0.5 < $P_{biofoul}$ < 0.8 (orange), and $P_{biofoul}$ < 0.8 (red). The color code indicates whether a biofouling/cleaning event has occurred during the last 5 days, and therefore tends to give red color <u>after</u> cleaning has taken place.

Implementation

Step 1: Generate 6 hour statistics

Extract slabs of 6-hour duration and calculate the following parameters on these

- $Q_{5,i}$ $Q_{5,i}$ 5th percentile
- $Q_{95,i}$ $Q_{95,i}$ 95th percentile
- M_i M_i median

The dataset is now described by 4 such parameters a day. They are indexed by *i=1…N* where N is then *4* times the number of days.

Step 2: Normalize over a 5-day period

Group these parameters over a 5-day period (*i=1…20*) and normalize them so that $Q_{5,i}$ and $Q_{95,i}$ fill the range 0 to 100 inclusive

$$Q_{\min} = \min(Q_{5,i}, Q_{95,i})$$
$$Q_{\max} = \max(Q_{5,i}, Q_{95,i})$$
$$q_{j,i} = \frac{Q_{j,i} - Q_{\min}}{Q_{\max} - Q_{\min}} \quad j = 5,95$$

And the same is performed for the median values

$$M_{\min} = \min(M_i)$$
$$M_{\max} = \max(M_i)$$
$$m_i = \frac{M_i - M_{\min}}{M_{\max} - M_{\min}}$$

Now consider the interval from the beginning of this group to the index i_{max} where the median *M* is at its highest level. Within this interval, perform a linear regression on the normalized median (*m*) yielding both the slope estimates α and the standard error (*SE*). We define the following coefficients

- α_m estimate of the normalized median slope *m*
- ε_m lower confidence interval of the estimated normalized median $\alpha_m - 2SE$

Repeat the same for the interval ending where the lower 5th percentiles (Q_5) is at its maximum level and similarly, define the following coefficients

- α_{q5} estimate of the normalized 5th percentile slope q_5
- ε_{q5} lower confidence interval of the estimated normalized 5th percentile $\alpha_{q5} - 2SE$

Finally, an additional coefficient is defined $i_{m,\min}$ the index at which the median is at its minimum.

Step 3: Compute the biofouling probability coefficient

The probability biofouling coefficient is defined a s follow

$$P_{biofoul} = e^{A}$$
$$A = 0.126 + 2.291\mathrm{E}^{-2} \cdot \mathrm{i}_{\mathrm{m,min}} - 9.173\mathrm{E}^{-3} \cdot \alpha_{\mathrm{m}} + 7.673\mathrm{E}^{3} \cdot \varepsilon_{\mathrm{m}} + 7.930\mathrm{E}^{3} \cdot \alpha_{q5} - 3.812\mathrm{E}^{3} \cdot \varepsilon_{\mathrm{q5}}$$

Where the coefficients of *A* were estimated from logistic regression.

Within the 5-day period considered, find the first occurrence where $P_{biofoul} > 0.8$.If so, identify the first previous point for which $P_{biofoul} < 0.3$. In the original dataset, flag all data between these 2 points (exclusive) as potentially correctable, QC=3.

Move out the range where $P_{biofoul} > 0.8$ and repeat this operation on the remaining points.

Finally, repeat from the second step, by moving the 5-day window by one 6-hour slab, i.e. i=2…21. Do this for the whole dataset.

4.10 Summary

Table 8 Summary of the QC tests for the different data types

	Repository	Profiles	Time Series
Naming Convention	L,M,H	x	x
Missing Value	L,M,H	x	x
Frozen Value	L,M,H	x	x
Global Range	L,M,H	x	x
Local Range	M,H	x	x
Spike	M,H	x[1]	x
Frozen Profile	M,H	x	
Biofouling	M,H		x

A summary of the tests and which type of data they should be applied to as summarized in Table 8.

References

ARGO 2009. Argo quality control management, Version 2.4, Argo data management

BASANA, R., CARDIN, V., R., C. & L., P. 2000. Data quality control level 0. *Mediterranean Forecasting System Pilot Project.* OGS, Tecnomare S.p.A. .

BRUNET, C., JOHNSEN, G., LAVAUD, J. & ROY, S. 2011. Pigments and photoacclimation processes. *Phytoplankton Pigments, Characterization, Chemotaxonomy and Application in Oceanography*, 445-471.

COATANOAN, C. & PETIT DE LA VILLÉON, L. 2005. Coriolis data centre, In-situ data quality control. *Coriolis Ifremer*

D'ORTENZIO, F., THIERRY, V., ELDIN, G., CLAUSTRE, H., TESTOR, P., COATANOAN, C., TEDETTI, M., GUINET, C., POTEAU, A., PRIEUR, L., LEFEVRE, D., BOURRIN, F., CARVAL, T., GOUTX, M., GARÇON, V., THOURON, D., LACOMBE, M., LHERMINIER, P., LOISIEL, H., MORTIER, L. & ANTOINE, D. 2010. White Book on Oceanic Autonomous Platforms for Biogeochemical Studies: Instrumentation and Measure (PABIM, Version 1.3.

FALKOWSKI, P. & RAVEN, J. (eds.) 1997. *Aquatic photosynthesis,* Massachusetts: Blackwell science.

GOSUD 2006. REAL-TIME QC, Version 1.0.

GOVINDJE, E. 1995. Sixty-Three Years Since Kautsky: Chlorophyll <I>a</I> Fluorescence. *Functional Plant Biology,* 22, 131-160.

HUOT, Y. & BABIN, M. 2010. Overview of fluorescence protocols: theory, basic concepts, and practice. *Chlorophyll a Fluorescence in Aquatic Sciences: Methods and Applications.* Springer.

JOHNSEN, G., BRICAUD, A., NELSON, N., PRÉZELIN, B. & BIDIGARE, R. 2011. In vivo bio-optical properties of phytoplankton pigments. *Roy S., Llewellyn C., Egeland ES, Johnsen G. Phytoplankton Pigments: Characterization, Chemotaxonomy and Applications in Oceanography. Cambridge University Press, Cambridge, United Kingdom. ISBN-10,* 1107000661.

KRAUSE, G. & WEIS, E. 1991. Chlorophyll Fluorescence and Photosynthesis: The Basics. *Annual Review of Plant Physiology and Plant Molecular Biology,* 42, 313-349.

KRUSKOPF M,, FLYNN KJ 2006. Chlorophyll content and fluores-cence responses cannot be used to gauge reliably phyto-plankton biomass, nutrient status or growth rate. NewPhytologist 169:525–536.

OWENS, T. 1991. Energy transformation and fluorescence in photosynthesis *Particle Analysis in Oceanography, edited by S. Demers (Springer-Verlag),* 27, 101-137.

QUIROGA, R. Q., NADASDY, Z. & BEN-SHAUL, Y. 2004. Unsupervised Spike Detection and Sorting with Wavelets and Superparamagnetic Clustering. *Neural Computation*, 1661–1687.

RAVEN, J. & GEIDER, R. 2003. Adaptation, Acclimation and Regulation in Algal Photosynthesis. *In:* LARKUM, A. D., DOUGLAS, S. & RAVEN, J. (eds.) *Photosynthesis in Algae.* Springer Netherlands.

SCHUCKMANN, K., GARAU, B., WEHDE, H., GIES, T., DURAND, D. & F., R. 2010. MyOcean: Real Time Quality Control of temperature and salinity measurements, 1st release. .

SEADATANET 2007. Data quality control procedures, Version 0.1. *6th Framework of EC DG Research.*

SEPPÄLÄ, J., YLÖSTALO, P., KAITALA, S., HÄLLFORS, S., RAATEOJA, M. & MAUNULA, P. 2007. Ship-of-opportunity based phycocyanin fluorescence monitoring of the filamentous cyanobacteria bloom dynamics in the Baltic Sea. *Estuarine, Coastal and Shelf Science,* 73, 489-500.

TAMM, S. & SOETJE, K. 2009. ECOOP IP, Report on the common QA-protocols to be used in the ECOOP DMS.

UEDA, T. 2009. A simple method for the detection of outliers. *Electronic Journal of Applied Statistical Analysis*, 67-76.

6.2. MyOcean document: Real Time Quality Control of Biogeochemical Measurements

Project: WP15

Real Time Quality Control of biogeochemical measurements

Version 2.5

First release: November 2012

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History

Version 1.0: The first version of this document, issued in January 2011. Constructive feedback on the initial version has been received from the MyOcean insitu-TAC and taken into account when providing the current update.
Version 1.2: The main issues of biological sensors have been explained and an effort to unify units included. The document was sent for review and feedback to the work package partners and the In Situ-TAC on November 17, 2012.
Version 1.5: Includes further unification work as well as additional information about oxygen sensors. It was sent for review and feedback to the work package partners and the In Situ-Tac on April 15, 2013.
Version 2.0: A new outline. Tests which are not specific to BGC sensors have been removed. Information about oxygen optodes has been completed. Spikes and gradient tests have been reformulated.
Version 2.1: Biofouling correction has been removed because of its delayed mode aspect.
Version 2.2 and version 2.3: Comments from partners have been included. Version 2.4 and 2.5: Includes a simplified spike test and some cleanup.

Foreword

The present version includes a more detailed description of challenges and difficulties related to real-time data quality control (RTQC) from biogeochemical (BGC) sensors as opposed to data from physical sensors has been added to this document (Section 2).
The main goal of adding this information is to help the reader to understand the possibilities and limitations regarding RTQC of BGC data.
For instance, there is a need to clearly distinct between bad Chlorophyll a (Chl a) data caused by sensor failure and uncertain data caused by inherent natural variations in the Chl a fluorescence:Chl a concentration ratio. An extra paragraph addressing this issue has also been included in Section 1.
Further progress of the current document will include a refined and extended set of real- time quality tests that can realistically be established to work on BGC data from various in situ platforms. Additions are under development and will be provided in Section 4. The following tests are under consideration for revision:

- Gradient/ spike test
- Range test (global + regional)
- Inter-sensor comparison
- Vertical range test
- Biofouling detection test

- Parameter relationship test
- Oxygen vs Chl a fluorescence
- T/S vs fluorescence
- Day/night; sun height

The revised tests should be applied on a selected dataset in order to assess their validity. These revisions provide also a better roadmap for delayed mode quality control procedures.

1. Introduction

MyOcean is the implementation project of the GMES Marine Core Service, aiming at deploying the first concerted and integrated pan-European capacity for Ocean Monitoring and Forecasting (http://www.myocean.eu.org). The project objective is to analyze, forecast and observe the oceans at global and regional (European Seas) scales in order to provide a monitoring service for marine environment and security.
Based on the approach on combining space and in-situ observations and their assimilation into 3-D simulation models, the MyOcean Service aims to provide the best information available on the global and regional ocean. Observations included in the MyOcean Service are temperature, salinity, currents, ice extent, sea level and primary ecosystems. Its target applications are marine safety, marine resources, climate and seasonal forecasting as well as marine and coastal environment in addition to the large value in situ data has in itself.
An important step within the MyOcean project is to harmonize existing Real Time Quality Control (RTQC) and quality assurance procedures of the different areas involved. As the MyOcean service is thought to be available at any time and open to anyone, an agreement in good RTQC methods and procedures is vital to guarantee high data quality distributed to users via international exchange. The agreement on the implementation of uniform RTQC procedures has the potential to overcome the non- consistency within the existing datasets actually provided by the international community.
One of the various tasks of the MyOcean project - the Work Package (WP) 15 - deals with the scientific and technical validation of In Situ-TAC (Technical Assembly Centres) products and forms the frame of this document. WP15 aims to perform operational quality control (QC) of global and regional products as well as to lead scientific assessment validation activities with regional responsibilities. Beside global scale products, regional specifications are performed in the Arctic, the Black Sea, the North- western Shelves, the Baltic Sea, the South-western Shelves and the Mediterranean Sea. It follows therewith the EuroGOOS regional approach, with establishing regional alliances.
The main focal point of this document is to describe quality tests recommended to be commonly applied for biogeochemical (BGC) data from the various observational platforms. At present the use of nutrient sensors on autonomous platforms is very limited (d'Ortenzio et al 2010). The amount of nutrient data delivered to MyOcean in real time was very low. The quality tests in this document are therefore defined for Chlorophyll a (Chl a) fluorescence and oxygen measurements only.

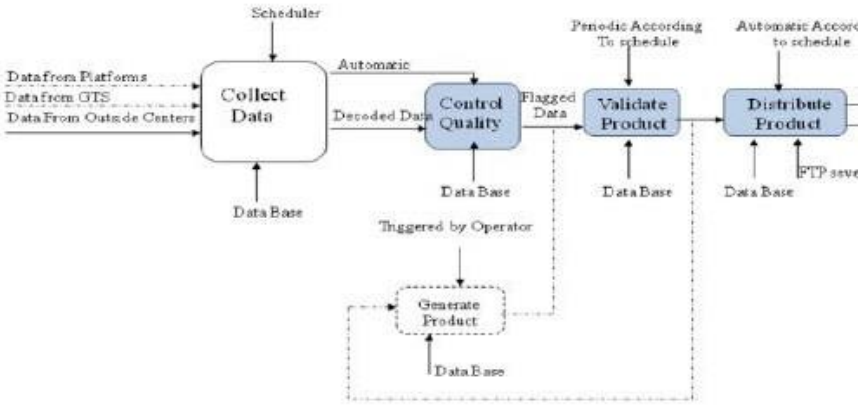


Figure 1: Functions to be implemented by an in-situ TAC component (Meeting report MYO-INS-MR-2009-03-30)

The different functions to be implemented by the global and regional components of the In-Situ Tac are summarized in Figure 1. This document describes the RTQC to be performed on BGC in-situ data in the MyOcean project. In MyOcean the quality controlled biogeochemical data will be mainly used for model validation and for satellite ocean color data assessment. Data will also be made available to users of the marine core service under special agreements.

As recommended at OceanObs09 (i.e Claustre et al., 2009), the BGC data compiled within MyOcean are confined to:

- Chl a fluorescence
- Oxygen (concentration and saturation)
- Nutrients (e.g NH4, NO3/NO2, PO4, Si(OH4))

The proposals for RTQC given within this document are built on the heritage from previous efforts, e.g. PABIM White Book (D'Ortenzio et al., 2010), Coriolis (Coatanoan and Petit de la Villéon, 2005), SeaDataNet (SeaDataNet, 2007) ECOOP (Tamm and Soetje, 2009), GOSUD (GOSUD, 2006), M3A (Basana et al., 2000), Argo (Argo, 2009)

and MyOcean T/S QC procedures (Schuckmann et al., 2010), as well as in-house expertise from contributors to this report.

Moreover, the ratio between in vivo Chl a fluorescence measurements and in vitro HPLC or spectrophotometric Chl a concentration is not constant and may vary with a factor 3-4 depending on various conditions. Thus, when using real-time measurements of Chl a fluorescence as a proxy for Chl a concentration, the users should be aware of the natural variation in Chl a fluorescence relative to Chl a concentration. Thus, there is a need to

clearly distinct between bad Chl a fluorescence data caused by sensor failure or bad calibration and "uncertain" estimates of Chl a concentration caused by inherent natural variations in the Chl a fluorescence.

The detection of anomalous values of BGC parameters is challenging due to their inherent high spatial and temporal variability, e.g., Diel Chl a fluorescence can vary with as much as a factor 4, and can change as a result of cloud cover (Huot and Babin, 2010). It is therefore a challenge to define regional tests to check data quality in sea regions having different characteristics. Historically, the amount of data available for building regional climatologies of BGC parameters is very limited. The lack of a common reference database for these parameters makes it difficult to identify anomalies at regional level.

SeaDataNet and EmodNet are ongoing initiatives contributing in the collection and compiling, respectively, of historical biogeochemical data as well as new data in near real time within the European Seas, but with a number of gaps in the comprehensiveness of the datasets. Taking these initiatives as a framework, an effort should therefore be made to extend compiled climatologies, based on additional existing historical datasets. There is also an increasing amount of autonomous platforms collecting BGC data that should be exploited in order to produce the required climatologies. Given the present situation, most quality tests at regional level must be based on expert knowledge, until reliable climatologies are available.

The data qualification tests proposed within this document is threefold:

- Tests that are related to physical sensors artefacts as adopted from Argo (2009) and Schuckmann et al (2010). (Argo, 2009, Schuckmann et al., 2010).
- Tests for quality Control of Chl a data as adopted from the PABIM white book (D'Ortenzio et al., 2010)
- Tests needed for BGC data due to calibration and biofouling.

The actual document is organized as follows. The introduction given in this section (1) is followed by an introduction to the theory behind the advantages and limitations in autonomously sensing BGC variables (Section 2). Section 3 will specify Quality control flags. In section 4, automatic RTQC procedures are detailed for different types of measurements.

The validation procedure (Figure 1) includes the delayed mode quality control of the data and will be specified in another guideline, which will be a task for following projects.

2. Deliverables for BGC sensor data

The life and function of animals and plants in the ocean are important to understand in order to increase the sustainability of our use of the ocean. Autonomous measurements from different platforms (i.e. Ferrybox or

underwater vehicles (AUV's), buoys) increase the amount of data that can be interpreted to illustrate parts of the ecosystem structure and functioning and is therefore an important tool for researchers. The available sensors are detecting Chl a fluorescence and oxygen concentration and saturation. These sensors can for example detect phytoplankton blooms or hypoxic/anoxic waters or give additional information on ocean currents and water types.

An important task when distributing BGC data is to commit to a high degree of transparency of the measurements; The experienced user will then be able to interpret data more correctly, and the less experienced user should be alarmed that these data should be used with caution.

2.1 Real-time Chl a fluorescence measurements

2.1.1 Theoretical background for Chl a fluorescence

As described below, conditions affecting in vivo or in situ Chl a fluorescence emission:

- Light regime (nigh/day, day length)
- Self-shading and dense blooms
- Different species and groups
- Regional variability
- Nutrient status

When eukaryotic algae absorb light (Photosynthetically Active Radiation (PAR, 400-700 nm)), 1-5 % of this light will be re-emitted as fluorescence. Many pigments (light absorbing molecules) are involved in the light harvesting, but the fluorescence is mainly (95 %) emitted from the pigment Chl a in the reaction center II (RC II) of the photosynthesis light reactions in photosystem II (PSII).

Pigments in the phytoplankton cells form antenna like structures for an effective harvesting of the spectral light. The absorption happens when an electron of the pigment is excited into a higher energy state. This energy is sent down the antennae of pigments to the reaction center (RC) Chl a. When the RC Chl a is excited, the excitation energy can be released mainly by three competing de-excitation pathways; heat, photochemistry and fluorescence. The amount of fluorescence from the absorbed light is the yield of fluorescence (ϕF), which increases from 0 in total darkness to 3-5% in saturating light intensities. If the cells are extracted, e.g in methanol, the connection from

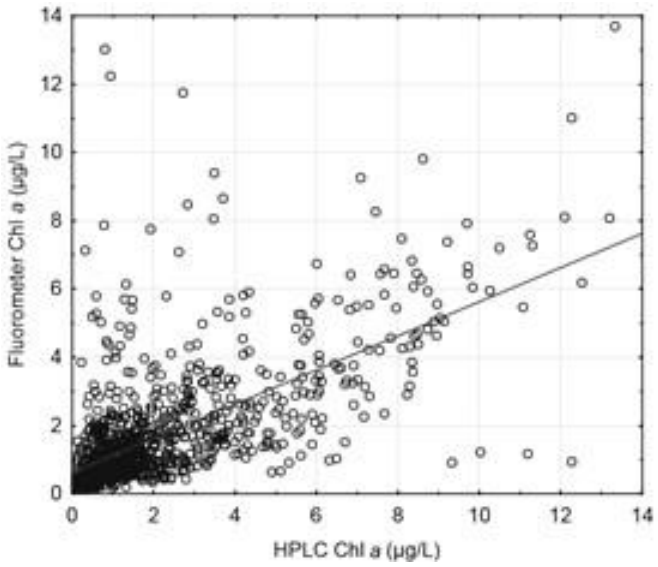


Figure 2 Regression plot between Fluorometer Chl a and HPLC Chl a concentration (from Ferrybox data during the years 2003-2008).r2= 0.3909.

RC to photosynthesis is broken and fluorescence can reach 30 % (Krause and Weis, 1991, Owens, 1991, Govindje, 1995, Falkowski and Raven, 1997, Huot and Babin, 2010, Johnsen et al., 2011).

The ratio of in vivo fluorescence against extracted Chl a may vary remarkably. This is a result of certain processes in algae such as regulation, acclimation or adaptation to different environmental conditions in order to optimize their evolutionary fitness (Raven and Geider, 2003). One example from the Ferrybox system in Norway shows that the Chl a fluorescence often appear too high at low concentrations and too small at high concentrations using a calibration of the sensor based on cultures (Figure 2). This figure does not leave out any outliers, which i.e could be caused by patchiness in the distribution of algae, leading to inconsistency between sensor and sampling, and thus it also show how a validation and calibration procedure can be biased by inaccurate sampling. (Johnsen et al., 2011)

This high variation in fluorescence is a result of varying light conditions (irradiance, spectral composition and day length) and different algae groups and species (described below). In low light conditions, light harvesting pigments (LHP's) efficiently transfer the light energy to the reaction centers (RC) of photosynthesis, and chloroplasts are distributed to give maximum light harvesting. The efficiency is reduced in high light conditions, because photoprotecting carotenoids (PPC's) increase in amount and thereby reduce the flux of photons to the reaction centers. In addition, high light conditions can cause a reduction in the amount of Chl a within each cell as well as the number, size and distribution of the chloroplasts (Johnsen et al., 2011, Brunet et al., 2011).

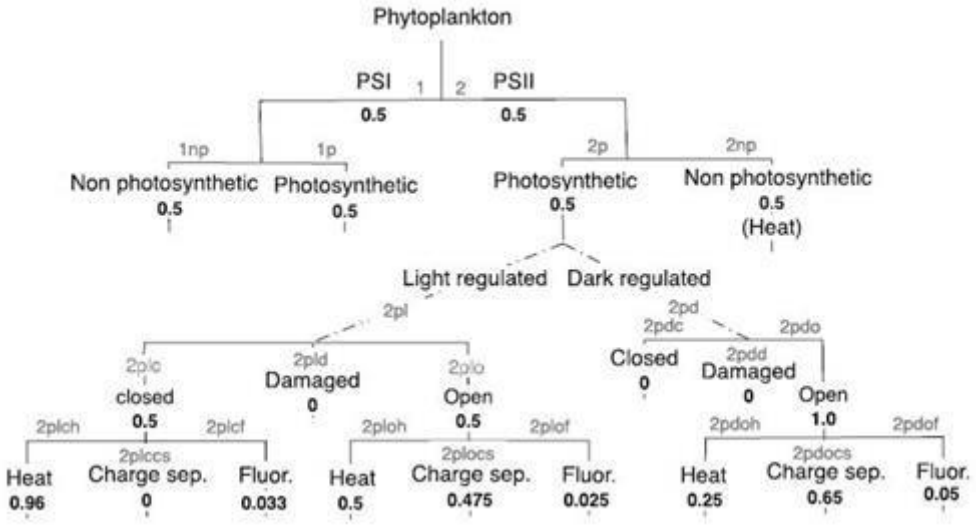


Figure 3 Fates of absorbed photons in phytoplankton as originally shown in Hout and Babin, 2010. rc's can either be closed (excited) or open (not exited) and is dependent on light acclimation status.

Different groups/species of phytoplankton contain different additional pigments (LHC's and PPC's), and different xanthophyll cycles, i.e in diatoms (diadino-xanthin to diatoxanthin) or green algae (violaxanthin to zeaxanthin) which are processes related to light stress (Brunet et al., 2011). Some algae (green and phycobiliprotein-containing) have state transitions between light harvesting complexes related to RCII and RCI.
The processes described above all reflect in in vivo fluorescence measurements, because, as mentioned before, the absorbed light energy (photons) can be released mainly by three competing de-excitation pathways; heat, photochemistry and fluorescence as was schematically shown in Hout and Babin, 2010 (Fig. 3).
In some regions cyanobacteria can dominate the phytoplankton biomass. They have a different allocation of energy regarding the photosystems. In cyanobacteria the most of Chl a is located in the non-fluorescing photosystem I. However this Chl a is included in the extracted Chl a yield. On the other hand phycobilin pigments such as phycocyanin (specific for filamentous cyanobacteria) provide strong in vivo fluorescence.
Consequently during abundant cyanobacteria blooms occurring annually in the Baltic Sea, the phycocyanin fluorescence should be used as auxiliary parameter to correct the ratio of in vivo Chl a fluorescence against extracted Chl a (Seppälä et al., 2007).

2.1.2 Deliverables when providing Chl a fluorescence

The natural situations affecting the fluorescence yield which result in a suggested list of deliverables for each data provider in order to clarify the quality and control of the provided data for the user. Suggestions for deliverables from each data provider:

0.	**Type of fluorometer.** There are many manufacturers providing fluorometers, and information on this is relevant for some users, Example: `TriOS microFlu-chl.`
1.	**Calibration procedure** What calibration procedure is being used (e.g. lab methods, algal culture, which algae species has been used). Example: `2013, NIVABAC 1, Skeletonema costatum, HPLC, 3 p. reg., R2=0.95` MyOcean will include data from different types of fluorescence sensors on a wide range of platforms, and it is necessary for the different regions to calibrate their instrument for the typical species in the area. We here suggest reporting the method because it will be will be helpful for users when interpreting the data.
3.	**Validation procedure**. Whether validation using HPLC or other in vitro methods is performed. Example: `2013, Natural samples, HPLC, monthly validation, 12 p. reg., R2=0.60` We here suggest delivering last known validation results with the data. One method currently in use by NIVA is to monitor the Chl a concentration by HPLC from water samples taken at different conditions throughout the year. An overall relationship between Chl a fluorescence and extracted Chl a was calculated for each year by linear regression. This relationship was studied and reported in the EC-Ferrybox project (Sørensen et.al EC-FerryBox D-5-2).

2.1.3 Future directions for RTQC of Chl a fluorescence

Several new instruments have proven to give good estimates of fluorescence yield, and should be implemented in monitoring platforms. Future directions should involve development of methods for in situ discrimination between algae groups and their light acclimation status.

2.2 Real-time Oxygen measurements

2.2.1 Theoretical background for Oxygen measurements

Most biological and chemical processes are influenced by dissolved oxygen concentrations. The standard measurement of oxygen includes fixation and precipitation followed by titration and is known as the Winkler titration (Winkler, 1888).
For high temporal and spatial resolution data this method is not suitable. For direct measurements of oxygen, optodes may be more suitable (Tengberg et al., 2006). Optodes are based on excitation of ruthenium-complexes and measurements of the red luminescence. Oxygen measurement is made by phase shift detection of the returning, oxygen quenched red luminescence. This phase shift is a function of the O2 partial pressure and hereby dissolved oxygen concentration.

2.2.2 Deliverables when providing Oxygen measurements

2.2.2.1 Calibration

Calibration of optodes is usually performed using water solution with 0% and 100% saturation. Temperature and salinity are used to calculate the concentration. For the AADI optode, the first parameter is provided by an internal sensor while salinity is a constant with a factory default set to zero psu.

2.2.2.2 Cleaning

The optode should be cleaned with wet paper towel as often as needed as biofouling will affect the oxygen measurements. In order to check the sensor, validation routines should be developed for the different ships and needs. For validation, we suggest to take in-situ samples in order to measure drift in the sensor. These samples should be carefully sampled in glass bottles, fixated with Winkler solutions and titrated using the Winkler technique (Winkler 1888).
In order to ensure both a consistent data quality control and adequate use of data, it is suggested that providers should send concentration of oxygen in µM (µmol/l) together with the correct water temperature and salinity. If available, air pressure should also be provided. Oxygen saturation can be derived from these measurements and calculated by users.
A delayed mode calibration has to be performed on a yearly basis.

Procedures to get new corrected values for oxygen concentrations are obtained by using the linear correlation between Winkler Oxygen and Optode Oxygen (w:w) (Hydes et al., 2007).
For accurate real-time data, cleaning and calibration are mandatory.

3 Quality Control Flags

The in-situ data provided by the MyOcean In-situ Thematic Assembly Centre (In Situ- TAC) is thought to be used by different users, with different requirements. Thus, one of the goals of the RTQC procedure is the provision of known quality flags, which characterise the data.
These flags should always be part of data delivery, in order to maintain standards and to ensure data consistency and reliability. The QC flags for BGC data within MyOcean are oriented on the existing standards defined for other observational data sets. Table 1 indicates the flags and their specific meanings. It is important to note that the codes 0, 1, 4 and 9 are mandatory to apply after the RTQC procedure (marked in red). Theminimum requirements for flagging, as defined by MyOcean, are based on a four-level coding, marked red in Table 1.

To avoid unnecessary failure in using the data sets, a clear guidance to the user of MyOcean In Situ-TAC data is necessary:
Data with QC flag = 0 are recommended not to be used without a quality control made by the user.
Data with QC flag ≠ 1 on either position or date should not be used without additional control from the user.
If data and position QC flag = 1

- only measurements with QC flag = 1 can be used safely without further analyses
- if QC flag = 2 the data may be good for some applications but the user should verify this eventually by contacting the service manager for more information.
- if QC flag = 3 the data are not usable but the data centre see potential for correcting the data in the delayed mode
- if QC flag = 4 measurements should be rejected.

Code	Meaning
0	No QC was performed
1	Good data
2	Probably good data
3	Bad data that are potentially correctable
4	Bad data
5	Value changed
6	Below detection limit
7	In excess of quoted value
8	Interpolated value
9	Missing value
A	Incomplete information

Table 1 Quality flag scale. Codes marked in red are mandatory following the RTQC procedure

Quality control flag application policy (i.e. Argo, 2009): The QC flag value assigned by a test (see section 3) cannot override a higher value from a previous test.

4. Real Time Quality Control: Automatic Checks

One central part of the functions to be implemented by the In-Situ TAC is the control of incoming decoded measurements (Figure 1). Since at this step data should be available in real time, the QC during that process is limited and automated. An agreement on the RTQC procedure recommendations need to be achieved in order to guarantee good quality data as well as data consistency throughout the MyOcean in-situ RT database.
This is a vital step to be taken before data exchange and scientific analysis can be initiated.
In the following, automated RTQC will be listed for measurements of BGC parameters originating from different platforms, i.e. vertical profiles as well as time series and

Ferrybox. Some of the automated QC procedures described here have been derived from those developed for the QC of Argo data management (Argo, 2009).
Formulations for the QC tests on Chl a data have also been adopted from the PABIM white book (D'Ortenzio et al., 2010). To improve the efficiency of some tests, specifications are incorporated into the validation process of regional measurements, depending on local water mass structures, statistics of data anomalies, as well as using regional enhanced bathymetry.
It should be stressed out that some BGC parameters cannot be thoroughly quality controlled without knowledge of the sensor, the way it was calibrated and even when it was used. This particularity is not (or to several orders of magnitude less) present in the measurements of physical parameters like temperature or conductivity. MyOcean does only cover data management but it is out of the scope of the project to establish best practice. There have been several initiatives in the past, and there are still ongoing projects trying to address such standards. However, the way is still long. Some limitations are due to technology. BGC real-time sensors are relatively new and the lack of knowledge still plays a non-negligible role. The improvement that can be achieved here is to provide recommendations to data providers.
As a consequence, in a real-time automated quality control system some data marked good may be bad and vice versa. What makes may be BGC measurement special is that the contrast between good and bad is not always as clear as it usually is for measurements from physical sensors. As such, flags are to be considered as a hint and not as the truth, and it is to the end users to take the responsibility to accept these.

4.1 Required Metadata

Detailed metadata are needed to guideline those involved in the collection, processing, QC and exchange of data. The quality controlled data set requires any data type (profiles, time series, trajectories, etc.) to be accompanied by key background information. A detailed metadata guideline for specific types of data can be found in the document of Eaton et al., 2009 (Eaton et al., 2009). By referring to Eaton et al., 2009, only a short summary of required information is given below:

1. Position of the measurement (latitude, longitude, depth).
2. Date of the measurement (data and time in UTC or clearly specified local time zone).

3. Method of the measurement (instrument type should be specified)
4. Specification of the measurement (platform code should be specified, in addition to e.g. station numbers, cast numbers, name of the data distribution center).

5. PI of the measurement (name and institution of the data originator for traceability reasons).
6. Processing of the measurement (date of last sensor calibration should be given, in addition to e.g. details of processing and calibration already applied, algorithms used to compute derived parameters).
7. Calibration method used (especially important for fluorescence measurements).
8. Comments on measurement (e.g. problems encountered, comments on data quality, references to applied protocols).

4.2 Required Data

Data for Chl a fluorescence and oxygen are not delivered in the same way by the different providers. There are differences in the parameters delivered and the units used. In some situations, parameter and units are not compliant. In order to avoid downstream dependence on providers, standard parameters and units must be required in order to include these measurements into the MyOcean processing. For fluorescence and oxygen, these are

1. Chl a fluorescence in µg/l
2. Oxygen concentration in µM (µmol/l)
3. Oxygen saturation

Temperature and salinity used in the determination of the oxygen concentration In addition, there is a need to monitor at regular interval the state and calibration procedures if these sensors. This step requires an active follow up of providers and their sensors as well as some management to process the information gathered. It is suggested to ask data providers to fill a special form at regular interval in order to keep the scientific content of distributed data up to date. Such an activity should be developed on the base of related work from initiatives specifically focused on best practice.

4.3 Quality Control Tests

Most of the ARGO QC RT tests are performed to identify problems related to bad geolocalization, erroneous timing, wrong platform identification, pressure errors etc. For these tests, the ARGO procedure is strictly adopted also for the RTQC on BGC data, although not explicitly specified here since these tests are not relevant or applicable to the measured BGC data.
Some tests defined in the MyOcean Temperature and Salinity RTQC (Schuckmann et al 2010) are also strictly adopted here. Other tests have been redefined in order to apply to BGC sensors. These are

- global range test,
- regional range test,

- spike test,

- gradient test and
- frozen profile test.

Finally, new tests are introduced here

- instrument comparison test,
- parameter relationship test and
- calibration status test.

Some BGC sensors are combined with auxiliary sensors such as temperature and salinity for optodes. These auxiliary parameters are required in order to fully address the data measured, and they must be quality controlled following the respective procedures. Data providers must also inform which of the parameters are related to the specific BGC measurements and this information must be copied into the MyOcean netCDF distribution files.
As an example, auxiliary temperature measurements for dissolved oxygen could be distributed in the netCDF file as variable DOXY_TEMP and refer to it in specific attribute TEMP of netCDF variable DOXY. For the constant salinity value, it would be enough to specify attribute PSAL to netCDF variable DOXY, and set it to the constant value. There is no unified way yet on how to specify this at the moment. In addition to stress out the necessity of auxiliary information in MyOcean distributed data, these recommendations suggest a protocol that would uniquely provide users full assessment of the provided data.
As a general rule, any quality control failing on auxiliary parameters associated to a BGC measure should imply the same failure on that measure.
The following tests refer to the MyOcean Temperature and Salinity RTQC (Schuckmann et al., 2010)

1. Platform identification
2. Impossible date test
3. Impossible location test
4. Position on land test
5. Impossible speed test
6. Pressure increasing test
7. Stuck value test
8. Grey list
9. Deepest pressure test

In addition, the following tests are defined

4.3.1 Global Range Test

This test applies a gross filter on observed values for Chl a and dissolved oxygen. It needs to accommodate all of the expected extremes encountered in the oceans.
Partners within MyOcean have reported on observed ranges of values in their respective regions (Appendix A), representing the best expert knowledge. Based on this information we propose to use the following global ranges:

- Chl a fluorescence in the range -0.1 to 100 µg/L

- Dissolved oxygen in the range 0 to 900 µM

Small negative values of Chl a could also occur, ascribed mainly to instrumental and electronic "noise" of the fluorescence sensors, e.g. a small drift in calibration can cause retrieval of small negative values (-0.1 to 0 g/L) when the real Chl a concentration is close to zero.
Maximum value for Chl a fluorescence will depend on how the sensor was calibrated. Hence there might be situations for which other threshold values should apply.
Action: If a value falls outside the ranges above, it should be flagged as bad data, with the exception that if the Chl a fluorescence is in the range -0.1 to 0.0 g/l it should be flagged as potentially correctable (flag 3).

4.3.2 Regional Range Test

Biogeochemical parameters are much more variable than temperature and salinity. This variability is observed on the vertical, on the horizontal and on the temporal scales. It can spawn between 2-3 orders of magnitude. In addition, there is a general lack of extensive climatology for the BGC parameters. A regional test, which should check the quality of data in sea regions having specific (and identified) characteristics, is therefore challenging.
Any regional range tests on BGC data should therefore be based on expert knowledge,
e.g. through careful examination of available historical data (e.g. a Ferrybox that has operated in the same waters for several years) that has been thoroughly quality controlled. The expected min/max values may vary throughout the year. For each parameter (especially Chl a fluorescence) several time periods could be specified, thus taking into account expected timing of separate blooming periods. Moreover, the method and instrumentation (such as HPLC or spectrophotometry) used to calibrate the sensors can lead to different values.

As a first step towards establishing a set of regional ranges of the BGC parameters, relevant ranges for selected regions have been collected within the MyOcean partners.
Threshold values are presented in Appendix A. The regions are split into Arctic, Northwest Shelf, Baltic, IBI, Mediterranean, and the Black Sea.
Because of the difficulties mentioned above, regional range test should be combined with instrument comparison and parameter relationship tests. This will reduce the risk of removing good data.
Test: Check if the measured value is within the expected range for the relevant region (see Appendix A for a list of values for each region).
Action: Values that fail the regional range test AND the instrument comparison test AND the parameter relationship test should be flagged as bad. If any of these three tests cannot be performed, this test should not be applied.

4.3.3 Spike Test

As mentioned earlier, biogeochemical parameters may vary very much on all scales. Tests defined for temperature and salinity are not applicable here. Moreover, the latter have been defined without taking into account the relevant sampling frequency.

Usually, BGC measurements are also subject to oscillations around the average measurement. This feature is also much more present than for physical sensors like temperature and salinity. These oscillations must be taken into account and should not trigger the flagging of outliers.
The suggested procedure for spike detection tries to estimate these oscillations before analysis for outliers.

4.3.3.1 Step 1: Estimation of measurement noise

As a first step, data must be filtered through a high filter in order to remove slow variations and keep only high frequencies. This step must be performed in both directions in order to avoid introduction of a delay in measurements.
Estimation of a mean signal peak value is related to the signal energy by
$U2 = \rho\langle u2\rangle$ $\rho = 2 \ldots 16$
Where ρ=2 is for a pure sine and ρ<16 is a good approximation for white noise signals.
Quiroga et al. suggest a value close to 2.198. They also suggest the use median instead of mean values in order to avoid influence of high amplitude outliers.

4.3.3.2 Step 2: Identify potential outliers

Potential outliers are values in the filtered signal whose amplitudes are larger than a certain threshold above the estimated energy level. Correct threshold depend on the geographic area and sensor technology.

$U_{\text{thres}} = kU$
However, the purpose of this step being to focus on doubtful measurements in real-time
quality control, a value of k=5 should be a good starting point.

4.3.3.3 Step 3: Cross check outliers

In this last step we use a simplified form of the Akaike information criterion to confirm whether suspicious measurements found in step 2 are outliers or if they are part of a natural variation. The AIC is based on the approximation of Ueda 1996/2009 and yields

$$\frac{1}{2}AIC = \alpha 2\sigma_g \log(n_g) + \beta 4n_b \; (5 \le n \le 9)$$

$$z = \frac{x - \bar{x}}{\sigma}$$

Where σ is the corrected standard deviation calculated from measurements, σg the
uncorrected standard deviation based on the z-scores values z from good measurements, ng the number of good measurements and nb the number of potential outliers.
In order to check whether a measurement is an outlier, consider 2 to 4 additional measurements on each side the outlier and calculate the AIC value twice: (1) with all points considered as good and (2) with the doubtful value assumed to be bad. If the AIC value is less in the second case, it should be an outlier.

Parameters α and β are normally set to one, but they can be used to fine tune the detection sensitivity of outliers with respect to natural variations. Larger values will allow shorter and larger variations.

4.3.3.4 General Comments

It should be noted that steps 1 and 2 can be ignored and step 3 applied to all points. This will not only increase processing time, but step 1 provides also a good parameter for checking sensor health.

As presented here, at least 5 consecutive measurements are required to perform this test. If filtering in step 1 is applied, the outer 5*N points, where N is the filter order, on each side of the interval considered should not be used.

This test does not apply to bio-geochemical sensors only. It can also be used for Temperature and salinity, especially in coastal waters where the ARGO spike test has failed. Spikes are likely not to be drastically present in oxygen optode measurements. This is expected because optodes have a typical response time of 20s. As a consequence, it implies that if other parameters are seen to vary faster than that, then oxygen measurements are likely to be wrong and should be flagged as bad data.

4.3.4 Gradient Test

Because it would be very unfortunate to mask out localized variations, it is suggested not to perform a gradient test on bio-geochemical data in order to keep transitions in measurements. Bad data related to high gradients should already be commented out from the range and spike tests.

Please note that the vertical distribution of chl a fluorescence is complicated: (1) it does not increase or decrease uniformly with depth, (2) sub surface maxima can be extremely sharp, (values may vary by one or two orders of magnitude within a few meters), and (3) the distribution can be highly noisy, especially at depth, where measured values are close to zero.

4.3.5 Frozen Profile Test

This test can detect an instrument that reproduces the same profile (with very small deviations) over and over again. This test has been introduced for temperature and salinity data (e.g. Schuckmann et al 2010). However, it should be equally applicable to BGC data.

A. For each parameter derive profiles by averaging the original profiles to get mean values for each profile in 50 dbar slabs (CHLprof, CHL_previous_prof and OXYprof, OXY_previous_prof). This is necessary because the instruments do not sample at the same level for each profile.

B. Subtract the two resulting profiles for Chl a (CHL) and oxygen (OXY) to get absolute difference profiles:

- deltaCHL = abs(CH prof CH _previous_prof)
- deltaOXY = abs(OXYprof OXY_previous_prof)

C. Derive the maximum, minimum and mean of the absolute differences for Chl a and oxygen:

- mean(deltaCHL), max(deltaCHL), min(deltaCHL)
- mean(deltaOXY), max(deltaOXY), min(deltaOXY)

D. To fail the test, require that:

- max(deltaCHL) < 0.3 µg/l

- min(deltaCHL) < 0.001 µg/l
- mean(deltaCHL) < 0.02 µg/l
- max(deltaOXY) < 9 µM
- min(deltaOXY) < 0.03 µM
- mean(deltaOXY) < 0.6 µM

Note: Threshold values above are selected as a first approach. They should be investigated and new values may be proposed in the future.
Action: if a profile fails this test, all measurements for this profile are flagged as bad data (flag '4'). If the float fails the test on 5 consecutive cycles, it is inserted in the grey-list.

4.3.6 Instrument Comparison Test

This test applies if the same platform is hosting two or more sensors for the same parameter. If two different sensors measure the same parameter, the difference between two simultaneous measurements should not be greater than a fixed limit.
test_value = |Vs1 - Vs2|

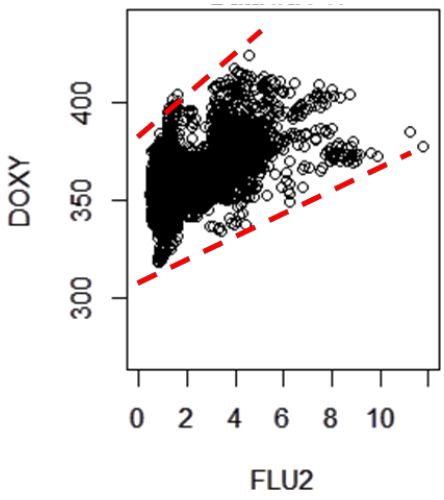
where s1= sensor1 and s2 = sensor2.

The application of this test is not straightforward since measurements of BGC data depend strongly on the type of sensors and the calibration method used. Therefore, it should only be applicable when there is no doubt about comparison of measurements from both sensors.
We propose to set the following fixed threshold values: Threshold_value (CHL): 1 g/L Threshold_value (DO): 10µM
Note: Threshold values above are selected as a first approach. The values should be
investigated and new values may be proposed in the future.

We propose to combine the regional range test (test 7), the instrument comparison test (test 15, if applied) and the parameter relationship test (test 16, if applied). This will reduce the risk of removing good data.
Action: Values that fail the regional range test AND the instrument comparison test AND the parameter relationship test should be flagged as bad. If any of these three tests cannot be performed, this test should not be applied.

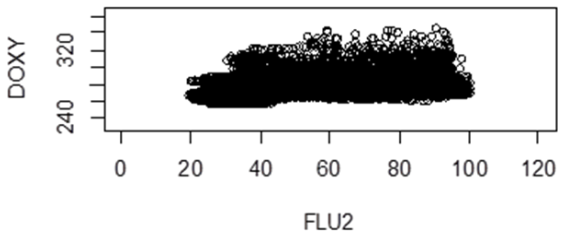
4.3.7 Parameter Relationship Test

The value of different BGC parameters has often a causal relationship. An example of that is the decreased oxygen saturation in the existence of a phytoplankton bloom that is indicated by increased Chl a values. However, such relationship cannot be expected at all times. Moreover, measurements of BGC parameters are strongly dependent on the calibration method which can be different from one platform to another one.

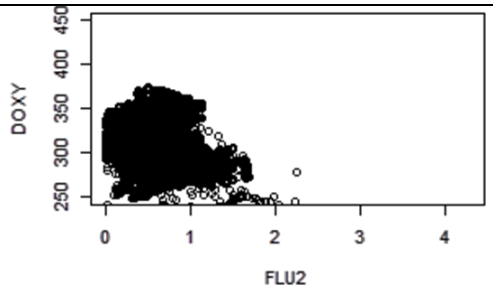


Trollfjord (March 2012)

On the left, the figure shows that for some areas and time periods, there is a positive relationship between dissolved oxygen and Chl a fluorescence. Below, the figures show similar measurements for two different platforms and periods. It is clear that the relationship is at best very weak and has not seen pursued as a basis for quality control.



Pont Aven (June 2012)



Trollfjord (August 2012)

Figure 4 Dissolved oxygen and Chl-a fluorescence from Trollfjord (March 2012), Pont Aven (June 2012) and Trollfjord (August 2012)

Figure 4 illustrates these issues. A deeper scientific research is therefore required.

It is therefore recommended to implement a test taking into account such relationships. If high Chl a and low oxygen saturation is observed during daytime, both parameters should be flagged. The test is failed if

VCHL > Threshold_CHL AND VOXY< Threshold_OXY,

The thresholds should ideally be selected at a regional level. However, as a first approach we propose to apply the

Threshold_CHL = 5 g/L, and Threshold_OXY = 90%.

Note that for this test the oxygen saturation (not concentration) is used. The saturation must be calculated correctly.

Action: Values that fail the regional range test AND the instrument comparison test AND the parameter relationship test should be flagged as bad. If any of these three tests cannot be performed, this test should not be applied.

4.3.8 Calibration Status Check

This test will check the status of the calibration compared to the recommended maximum interval tcal_interval for calibration of the sensor. Recommended values of tcal_interval for different sensors have been collected within MyOcean partners and are summarized in a lookup table (Appendix C). The approach requires the time of the last performed calibration being given in the metadata for each sensor. Furthermore the recommended maximum time interval is platform dependent. For example, in the case of ARGO floats, there are no calibration after deployment and the instruments spen most of their time at depth that are much more stable then on platforms that are always in the upper part of the water column.

The test fails if

tV - tC > tcal_interval

where tv is the time of measurement, tc is the time of last performed calibration and tcal_interval is the recommended maximum time interval for calibration of the sensor (Appendix C).

Action: Flag data as 2 (probably good).

4.4 RTQC for vertical profiles

In addition to the relevant tests described RTQC of Argo data and the MyOcean. Temperature and Salinity RTQC (Schuckmann et al 2010), the following tests defned in this document should be applied to the BGC data.

1. Global Range Test
2. Regional Range Test
3. Spike Test
4. Gradient Test
5. Frozen Profile Test

6. Instrument Comparison Test Parameter 7. Relationship Test
7. Calibration Status Test

4.5 RTQC for vertical profiles: Gliders and AUVs

See vertical profiles.

4.6 RTQC for time series (Argo, moorings)

See vertical profiles.

4.7 RTQC for Ferryboxes

See vertical profiles. In addition the Subsequent Trip Test applies to type of platform

Appendix A Regional Ranges of BGC parameters

Note that only Chl a and Oxygen data ranges are applied for the regional range tests defined in this document

Table 2 Regional ranges of BGC parameters as reported by MyOcean partners.

Chlorophyll-a (µg/L)	Min	Max	Time period
Arctic	0	10	Jan-Dec
NWS	0.01	95	Jan-Dec
Bay of Biscay	0	100	Jan-Dec
IBI -Cantabric Sea	0.01	5	Jan-Dec
Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	0.5	25	Oct-Feb
Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	1.5	77.6	Mar-May
Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	0.5	36.8	Jun-Sep
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	0.5	6	Oct-Feb
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	1.5	31	Mar-May
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	0.5	13	Jun-Sep
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	0.5	7.6	Oct-Feb
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	1.5	27.3	Mar-May
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	0.5	20.5	Jun-Sep

Oxygen (mmol/m^3)	Min	Max	
Arctic	130	425	
NWS2	0.3	720	
IBI-Cantabric Sea1	220	300	
IBI-Iberia1	0	310	
Bay of Biscay1	0	625	
Nitrate (NO-3, µmol/L)	Min	Max	
Arctic	0	14	
NWS	0	450	
IBI-Cantabric Sea	0.01	5	
BayofBiscay	0	1000	
Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	0	33.5	
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	0	8.7	
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	0	17.1	
Phosphate (µmol/L)	Min	Max	
Arctic	0	1	
NWS	0	30	
IBI-Cantabric Sea	0.01	0.6	
BayofBiscay	0	100	

Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	0	5	
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	0	1.1	
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	0	1.4	
Silicate (µmol/L)	Min	Max	
Arctic	0	8	
NWS	0	210	
IBI-Cantabric Sea	0.01	6	
BayofBiscay	0	1000	
Baltic/Western Gulf of Finland (59.45-60.3N, 23.22- 30.2E)	0.3	41	
Northern Baltic Proper (58.36-59.62N, 19.88- 23.21E)	2.3	16.6	
Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)	1.7	56.2	
NH4 (µmol/L)	Min	Max	
BayofBiscay	0	1000	
NO2 (µmol/L)	Min	Max	
BayofBiscay	0	100	

Appendix B User Guide Measurements and Maintenance

Automatic Chl a sensors use the fluorescence properties of the Chl a pigment as a proxy for the Chl a concentration. The Chl a fluorescence sensor must therefore be calibrated against Chl a concentration accurately measured in the laboratory, e.g. by using a standard algae cell culture that is representative for a given water mass and/or by using water samples that are collected in-situ and coinciding with the operation of the sensor. The relationship between in-situ Chl a fluorescence and concentration may vary between night and daytime (due to light adaptation of the phytoplankton), between different growth stages of the phytoplankton population, and with the phytoplankton species assemblage. Therefore, the conversion rate between fluorescence values measured by the sensors and the determined Chl a concentration cannot be assumed to be fixed for all conditions.

The sensors which are exposed to sea water for several days or weeks without manual maintenance (e.g. ferryboxes) are subject to accumulation of microorganisms, algae and/or animals, also called biofouling. Biofouling may affect significantly the accuracy of measurement sensors and especially optical sensors (e.g. Chl a, oxygen). Thus the systems have to be cleaned regularly. Automatic chemical or mechanical (pressure air, wipers or brushing) cleaning or washing is recommended. The EC supported project BRIMOM has undertaken large efforts to develop antifouling methods, in order to enlarge the period between necessary maintenance/cleaning intervals. Since that is still an open issue and the antifouling methods are still under development, the degree of biofouling on the sensors has to be checked frequently and optical systems have to be manually cleaned when necessary. A recommendation for the frequency of maintenance/cleaning intervals for a number of popular sensors is given in Appendix C. In contrast to the physical parameters like temperature and salinity, the biofouling more often lead to decreased quality of BGC data.

The cleaning procedures and methods for subsequent assessment of the magnitude of biofouling and correction or flagging of data will differ between sensors. Taking fluorometers as an example, the cuvette should be filled with distilled water for recording the contaminated blank record. Then the cuvette is removed and the optical lens is cleaned with cleaning tissue for optics using appropriate detergent. After cleaning, the cuvette is filled with distilled water and blank value is recorded. The records before and after cleaning are used to audit the biofouling. The difference between the blank values from previous cleaning procedure (after cleaning) with the current blank value before cleaning should be used to correct the drift of blank values for the record period.

However, this method for detection of sensor drift caused by biofouling cannot be applied in real-time due to the requirement for manual operation. Alternative methods should therefore be sought to detect biofouling in real-time and to perform subsequent flagging of suspicious data.

Appendix C Recommended maintenance/cleaning intervals

The sensor type should be given in the metadata of the in situ data delivered to MyOcean. The list of sensors can therefore be updated and completed when the exact list of applied sensors within MyOcean is known.

Table 3 Recommended maintenance/cleaning intervals for sensors applied within MyOcean InSituTAC.

Parameter	Measurement principle	Sensor	Manufacturer	Unit	Detection range	Accuracy	Resolution	Typical obs. range (min. - max.)	Maintenance procedure	Maintenance interval	Calibration frequencyQuality assessment and other remarks
Chl a	Chl a Fluorescence	Scufa II	Turner design (USA)	µg/l	0 – 200		0.01	0.5 – 55	cleaning, calibration check	weekly	Validation against laboratory measurements of water samples stored by the FerryBox system; analysis done within 24h, if stored

											longer storage below –18 oC; comparison with laboratory analyses..
automatic water sampler	phytoplankton nutrients Chl a analysis		ISCO (USA)						cleaning	Weekly or when samples taken	Temperature volume control.
Chl a	Fluorescence	Chl a fluoro-meter	SeaPoint Sensor Inc	µg/l	0 – 25	< 2%	0.02	0 – 25	cleaning	weekly	
dissolved oxygen	Clark electrode	COS4-2		mg/l	0 – 20	0.2% F.S.	0.2 % F.S.	8 – 15	cleaning, calibration check	monthly	Calibration outside of the flow through system.
nitrate	UV detection	UV-NO3 Analyse	Trios (Germany)	µmol/l	0.5	50	0.1		cleaning, calibration check	monthly	Comparison with filtrated samples;

		r									first tests.
nitrate	Photometric	automatic pump photometer (APP)	ME (Germany)	µmol/l	0.5 – 300	15%	0.01	0 – 250	cleaning, change of chemicals, calibration check	fortnightly	Inter-calibration with monthly taken samples.
ammonia	Fluorometric	automatic pump photometer (APP modified)	ME (Germany)	µmol/l	0.1 – 20	15%	0.01	0 – 7	cleaning, change of chemicals, calibration check	fortnightly	Instrument modified for fluorescence measurements (OPA reagent).
o-phosphate	Photometric	automatic pump photometer (APP)	ME (Germany)	µmol/l	0.05 – 10	15%	0.05	0 – 3	cleaning, change of chemicals, calibration check	fortnightly	
silicate	Photometric	automatic pump photom	ME (Germany)	µmol/l	0.2 – 100	15%	0.01	0 – 70	cleaning, change of	fortnightly	

		eter (APP)							chemicals, calibration check		
fluorescence (flow-through)	Fluorescence		Seapoint	10-6 g/l	00 – 150	10%	0.02	0 – 50	cleaning, calibration check	monthly	Inter-calibration with laboratory measurements; flow-through system.
Chl a	Fluorescence blue LED (470 ± 30 nm)	CTG Mini-Trackall	Chelsea Instruments	V / µg/l	0.03 – 100 µg/l		0.01 µg/l	not yet established		Fortnightly	
Chl a	fluorescence excitation	CTG MiniPack	CTG	µg/l	0.03 – 100		0.01	0 – 20	weekly cleaning, Weekly calibration 2004 weekly drift	Yearly	Inter-calibration with acetone extracted chlorophyll-a

									check		Solid block state test
oxygen	dynamic luminescence quenching	Oxygen Optode 3830	Aandera a	micro-Moles/l	0 -500	<8uM or 5%	<1% or 0.4 %	200-400	weekly cleaning monthly calibration check	Yearly	New 2005 Better than specification . Little drift
Algae groups (chlorophyll-a)	fluorescence (excitation at different wavelengths)	Chl a sensor	bbe-moldaenke (Germany)		1 – 200 0.1	0.5	depends on algae group			.	Inter-calibration with HPLC measurements and cell counting (2-monthly); test phase

Appendix D References

ARGO 2009. Argo quality control management, Version 2.4, Argo data management BASANA, R., CARDIN, V., R., C. & L., P. 2000. Data quality control level 0.
Mediterranean Forecasting System Pilot Project. OGS, Tecnomare S.p.A. .

BRUNET, C., JOHNSEN, G., LAVAUD, J. & ROY, S. 2011. Pigments and
photoacclimation processes. Phytoplankton Pigments, Characterization, Chemotaxonomy and Application in Oceanography, 445-471.
CLAUSTRE, H., ANTOINE, D., BOEHME, L., BOSS, E., DORTENZIO, F., DANDON, O. F., GUINET, C., GRUBER, N., HANDEGARD, N. O. & HOOD, M. 2009. Guidelines
towards an integrated ocean observation system for ecosystems and biogeochemical cycles.
COATANOAN, C. & PETIT DE LA VILLÉON, L. 2005. Coriolis data centre, In-situ data quality control. Coriolis Ifremer.
D'ORTENZIO, F., THIERRY, V., ELDIN, G., CLAUSTRE, H., TESTOR, P., COATANOAN, C., TEDETTI, M., GUINET, C., POTEAU, A., PRIEUR, L., LEFEVRE, D., BOURRIN, F., CARVAL, T., GOUTX, M., GARÇON, V., THOURON, D., LACOMBE, M., LHERMINIER, P., LOISIEL, H., MORTIER, L. & ANTOINE, D. 2010. White Book on
Oceanic Autonomous Platforms for Biogeochemical Studies: Instrumentation and Measure (PABIM, Version 1.3.
EATON, B., GREGORY, J., DRACH, B., TAYLOR, K., HANKIN, S., CARON, J. &
SIGNELL, R. 2009. NetCdf Climate and Forecast (CF) Metadata Conventions, Version 1.4, h ttp. cf-pcmdi. llnl. gov/documents/cf-conventions/1.4/cfconventions. pdf.
FALKOWSKI, P. & RAVEN, J. (eds.) 1997. Aquatic photosynthesis, Massachusetts: Blackwell science.
GOSUD 2006. REAL-TIME QC, Version 1.0.

GOVINDJE, E. 1995. Sixty-Three Years Since Kautsky: Chlorophyll <I>a</I> Fluorescence. Functional Plant Biology, 22, 131-160.
HUOT, Y. & BABIN, M. 2010. Overview of fluorescence protocols: theory, basic concepts, and practice. Chlorophyll a Fluorescence in Aquatic Sciences: Methods and Applications. Springer.

HYDES, D., HARTMAN, M., HARTMAN, S. & BARGERON, C. 2007. Evaluation of the
Aanderaa Oxygen Optode in continuous use in the NOC Portsmouth Bilbao FerryBox system 2005, 2006, with an assessment of the likely errors in the estimation of oxygen concentration anomalies.
JOHNSEN, G., BRICAUD, A., NELSON, N., PRÉZELIN, B. & BIDIGARE, R. 2011. In
vivo bio-optical properties of phytoplankton pigments. Roy S., Llewellyn C., Egeland ES, Johnsen G. Phytoplankton Pigments: Characterization, Chemotaxonomy and Applications in Oceanography. Cambridge University Press, Cambridge, United Kingdom. ISBN-10, 1107000661.
KRAUSE, G. & WEIS, E. 1991. Chlorophyll Fluorescence and Photosynthesis: The Basics. Annual Review of Plant Physiology and Plant Molecular Biology, 42, 313-349.
OWENS, T. 1991. Energy transformation and fluorescence in photosynthesis Particle Analysis in Oceanography, edited by S. Demers (Springer-Verlag), 27, 101-137.
QUIROGA, R. QUIAN, NADASDY, Z., & BEN-SHAUL, Y., Unsupervised Spike
Detection and Sorting with Wavelets and Superparamagnetic Clustering, Neural Computation 16, 1661–1687 (2004), Massachusetts Institute of Technology
RAVEN, J. & GEIDER, R. 2003. Adaptation, Acclimation and Regulation in Algal Photosynthesis. In: LARKUM, A. D., DOUGLAS, S. & RAVEN, J. (eds.) Photosynthesis in Algae. Springer Netherlands.
SCHUCKMANN, K., GARAU, B., WEHDE, H., GIES, T., DURAND, D. & F., R. 2010.
MyOcean: Real Time Quality Control of temperature and salinity measurements, 1st release. .
SEADATANET 2007. Data quality control procedures, Version 0.1. 6th Framework of EC DG Research.
SEPPÄLÄ, J., YLÖSTALO, P., KAITALA, S., HÄLLFORS, S., RAATEOJA, M. &

MAUNULA, P. 2007. Ship-of-opportunity based phycocyanin fluorescence monitoring of the filamentous cyanobacteria bloom dynamics in the Baltic Sea. Estuarine, Coastal and Shelf Science, 73, 489-500.
TAMM, S. & SOETJE, K. 2009. ECOOP IP, Report on the common QA-protocols to be used in the ECOOP DMS.
TENGBERG, A., HOVDENES, J., ANDERSSON, H., BROCANDEL, O., DIAZ, R., HEBERT, D., ARNERICH, T., HUBER, C., KORTZINGER, A. & KHRIPOUNOFF, A.

2006. Evaluation of a lifetime-based optode to measure oxygen in aquatic systems. Limnology and Oceanography methods (depuis 2003), 4, 7-17.
UEDA, T. (2009). A simple method for the detection of outliers. Electronic Journal of Applied Statistical Analysis, 1 (2009), 67-76. (F. Marmolejo-Ramos & S. Kinoshita, Trans.) (Original work published in 1996)
WINKLER, L. W. 1888. Die Bestimmung des im Wasser gelösten Sauerstoffes. Berichte der deutschen chemischen Gesellschaft, 21, 2843-2854.