Project: WP15

Real Time Quality Control of biogeochemical measurements

Version 2.5

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1 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.

2 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.
Contents
1 History ........................................................................................................................................... 2
2 Foreword ......................................................................................................................................... 2
Contents .............................................................................................................................................. 4
1 Introduction ..................................................................................................................................... 6
2 Deliverables for BGC sensor data ................................................................................................. 9
  2.1 Real-time Chl a fluorescence measurements .......................................................................... 9
    2.1.1 Theoretical background for Chl a fluorescence ................................................................. 9
    2.1.2 Deliverables when providing Chl a fluorescence ........................................................... 11
    2.1.3 Future directions for RTQC of Chl a fluorescence ......................................................... 12
  2.2 Real-time Oxygen measurements ............................................................................................ 12
    2.2.1 Theoretical background for Oxygen measurements ....................................................... 13
    2.2.2 Deliverables when providing Oxygen measurements .................................................. 13
3 Quality Control Flags .................................................................................................................... 14
4 Real Time Quality Control: Automatic Checks ........................................................................... 15
  4.1 Required Metadata ................................................................................................................... 16
  4.2 Required Data ........................................................................................................................... 17
  4.3 Quality Control Tests ............................................................................................................... 17
    4.3.1 Global Range Test .............................................................................................................. 19
    4.3.2 Regional Range Test ......................................................................................................... 19
    4.3.3 Spike Test ......................................................................................................................... 20
    4.3.4 Gradient Test .................................................................................................................... 22
    4.3.5 Frozen Profile Test ........................................................................................................... 22
    4.3.6 Instrument Comparison Test ............................................................................................ 23
    4.3.7 Parameter Relationship Test ............................................................................................ 23
4.3.8 Calibration Status Check ................................................................. 26
4.4 RTQC for vertical profiles ........................................................................... 26
4.5 RTQC for vertical profiles: Gliders and AUVs ............................................. 27
4.6 RTQC for time series (Argo, moorings) .......................................................... 27
4.7 RTQC for Ferryboxes ...................................................................................... 27
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.
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 (\( \phi F \)), 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

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
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:

<table>
<thead>
<tr>
<th>0. Type of fluorometer.</th>
</tr>
</thead>
<tbody>
<tr>
<td>There are many manufacturers providing fluorometers, and information on this is relevant for some users, Example:</td>
</tr>
<tr>
<td>TriOS microFlu-chl.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1. Calibration procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>What calibration procedure is being used (e.g. lab methods, algal culture, which algae species has been used). Example:</td>
</tr>
<tr>
<td>2013, NIVABAC 1, Skeletonema costatum, HPLC, 3 p. reg., R2=0.95</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>3. Validation procedure.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whether validation using HPLC or other in vitro methods is performed. Example:</td>
</tr>
<tr>
<td>2013, Natural samples, HPLC, monthly validation, 12 p. reg., R2=0.60</td>
</tr>
</tbody>
</table>

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). The minimum 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.
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

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

\[ \bar{U}^2 = \rho \langle u^2 \rangle \rho = 2 \ldots 16 \]

Where \( \rho = 2 \) is for a pure sine and \( \rho < 16 \) 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.

\[ U_{thres} = k\bar{U} \]

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

\[
\frac{1}{2}AIC = \alpha 2\sigma_g \log(n_g) + \beta 4n_b \quad (5 \leq n \leq 9)
\]

\[
z = \frac{x - \bar{x}}{\sigma}
\]

Where \( \sigma \) is the corrected standard deviation calculated from measurements, \( \sigma_g \) the uncorrected standard deviation based on the z-scores values \( z \) from good measurements, \( n_g \) the number of good measurements and \( n_b \) 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 \( \alpha \) and \( \beta \) 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:

- $\delta \text{CHL} = |\text{CH prof} - \text{CH} _\text{previous prof}|$
- $\delta \text{OXY} = |\text{OXYprof} - \text{OXY} _\text{previous prof}|$

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

- $\text{mean}(\delta \text{CHL}), \text{max}(\delta \text{CHL}), \text{min}(\delta \text{CHL})$
- $\text{mean}(\delta \text{OXY}), \text{max}(\delta \text{OXY}), \text{min}(\delta \text{OXY})$

D. To fail the test, require that:

- $\text{max}(\delta \text{CHL}) < 0.3 \mu g/l$
• $\min(delta\text{CHL}) < 0.001 \mu g/l$
• $\text{mean}(delta\text{CHL}) < 0.02 \mu g/l$
• $\max(delta\text{OXY}) < 9 \mu M$
• $\min(delta\text{OXY}) < 0.03 \mu M$
• $\text{mean}(delta\text{OXY}) < 0.6 \mu M$

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.

$$\text{test\_value} = |Vs1 - Vs2|$$

where $s1 = \text{sensor}1$ and $s2 = \text{sensor}2$.

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 $\mu g/L$ Threshold_value (DO): 10 $\mu M$

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.

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.

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

\[ \text{VCHL} > \text{Threshold\_CHL AND VOXY< Threshold\_OXY}, \]

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 been pursued as a basis for quality control.

\[\text{Trollfjord (March 2012)}\]

\[\text{Pont Aven (June 2012)}\]

\[\text{Trollfjord (August 2012)}\]

\[\text{Figure 4 Dissolved oxygen and Chl-a fluorescence from Trollfjord (March 2012), Pont Aven (June 2012) and Trollfjord (August 2012)}\]
The thresholds should ideally be selected at a regional level. However, as a first approach we propose to apply the

\[
\text{Threshold}_{\text{CHL}} = 5 \mu g/L, \text{ and} \\
\text{Threshold}_{\text{OXY}} = 90\%.
\]

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 \(t_{\text{cal} \_ \text{interval}}\) for calibration of the sensor. Recommended values of \(t_{\text{cal} \_ \text{interval}}\) 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 spend 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

\[
t_V - t_C > t_{\text{cal} \_ \text{interval}}
\]

where \(t_V\) is the time of measurement, \(t_C\) is the time of last performed calibration and \(t_{\text{cal} \_ \text{interval}}\) 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 defined 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 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.*

<table>
<thead>
<tr>
<th>Chlorophyll-a (µg/L)</th>
<th>Min</th>
<th>Max</th>
<th>Time period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arctic</td>
<td>0</td>
<td>10</td>
<td>Jan-Dec</td>
</tr>
<tr>
<td>NWS</td>
<td>0.01</td>
<td>95</td>
<td>Jan-Dec</td>
</tr>
<tr>
<td>Bay of Biscay</td>
<td>0</td>
<td>100</td>
<td>Jan-Dec</td>
</tr>
<tr>
<td>IBI - Cantabric Sea</td>
<td>0.01</td>
<td>5</td>
<td>Jan-Dec</td>
</tr>
<tr>
<td>Baltic/Western Gulf of Finland (59.45-60.3N, 23.22-30.2E)</td>
<td>0.5</td>
<td>25</td>
<td>Oct-Feb</td>
</tr>
<tr>
<td>Baltic/Western Gulf of Finland (59.45-60.3N, 23.22-30.2E)</td>
<td>1.5</td>
<td>77.6</td>
<td>Mar-May</td>
</tr>
<tr>
<td>Baltic/Western Gulf of Finland (59.45-60.3N, 23.22-30.2E)</td>
<td>0.5</td>
<td>36.8</td>
<td>Jun-Sep</td>
</tr>
<tr>
<td>Northern Baltic Proper (58.36-59.62N, 19.88-23.21E)</td>
<td>0.5</td>
<td>6</td>
<td>Oct-Feb</td>
</tr>
<tr>
<td>Northern Baltic Proper (58.36-59.62N, 19.88-23.21E)</td>
<td>1.5</td>
<td>31</td>
<td>Mar-May</td>
</tr>
<tr>
<td>Northern Baltic Proper (58.36-59.62N, 19.88-23.21E)</td>
<td>0.5</td>
<td>13</td>
<td>Jun-Sep</td>
</tr>
<tr>
<td>Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)</td>
<td>0.5</td>
<td>7.6</td>
<td>Oct-Feb</td>
</tr>
<tr>
<td>Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)</td>
<td>1.5</td>
<td>27.3</td>
<td>Mar-May</td>
</tr>
<tr>
<td>Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)</td>
<td>0.5</td>
<td>20.5</td>
<td>Jun-Sep</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td><strong>Oxygen (mmol/m^3)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arctic</td>
<td>130</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>NWS2</td>
<td>0.3</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>IBI-Cantabric Sea1</td>
<td>220</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>IBI-Iberia1</td>
<td>0</td>
<td>310</td>
<td></td>
</tr>
<tr>
<td>Bay of Biscay1</td>
<td>0</td>
<td>625</td>
<td></td>
</tr>
<tr>
<td><strong>Nitrate (NO-3, µmol/L)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arctic</td>
<td>0</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>NWS</td>
<td>0</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>IBI-Cantabric Sea</td>
<td>0.01</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Bay of Biscay</td>
<td>0</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td><strong>Baltic/Western Gulf of Finland (59.45-60.3N, 23.22-30.2E)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td><strong>Northern Baltic Proper (58.36-59.62N, 19.88-23.21E)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td><strong>Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td><strong>Phosphate (µmol/L)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arctic</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>NWS</td>
<td>0</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>IBI-Cantabric Sea</td>
<td>0.01</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Bay of Biscay</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Silicate (µmol/L)</td>
<td>NH4 (µmol/L)</td>
<td>NO2 (µmol/L)</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>-------------------</td>
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<td>--------------</td>
</tr>
<tr>
<td>Baltic/Western Gulf of Finland (59.45-60.3N, 23.22-30.2E)</td>
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<td></td>
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<tr>
<td>Northern Baltic Proper (58.36-59.62N, 19.88-23.21E)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Southern Baltic Proper (54.52-56.2N, 12.27-17.09E)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Values converted from originally reported units in mg/L

2 Values converted from originally reported units 0.01-16ml/L
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.*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measurement principle</th>
<th>Sensor</th>
<th>Manufacturer</th>
<th>Unit</th>
<th>Detection range</th>
<th>Accuracy</th>
<th>Resolution</th>
<th>Typical obs. range (min. - max.)</th>
<th>Maintenance procedure</th>
<th>Maintenance interval</th>
<th>Calibration frequency</th>
<th>Quality assessment and other remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl a</td>
<td>Chl a Fluorescence</td>
<td>Scufa II Turner design (USA)</td>
<td>µg/l</td>
<td>0 – 200</td>
<td>0.01</td>
<td>0.5 – 55</td>
<td>cleaning, calibration check</td>
<td>weekly</td>
<td>Validation against laboratory measurements of water samples stored by the FerryBox system; analysis done within 24h, if stored</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameter</td>
<td>Instrument</td>
<td>Measurement Unit</td>
<td>Lower Limit</td>
<td>Upper Limit</td>
<td>Frequency</td>
<td>Notes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Automatic water sampler</td>
<td>phytoplankton</td>
<td>µg/l</td>
<td>0 – 25</td>
<td>&lt; 2%</td>
<td>weekly</td>
<td>Cleaning weekly or when samples taken</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>nutrients</td>
<td></td>
<td></td>
<td>0.02</td>
<td></td>
<td>Cleaning temperature volume control.</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Chl a analysis</td>
<td></td>
<td></td>
<td>0 – 25</td>
<td></td>
<td>Cleaning weekly or when samples taken</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chl a fluorescence</td>
<td>chlorophyll a</td>
<td>µg/l</td>
<td>0 – 25</td>
<td>&lt; 2%</td>
<td>weekly</td>
<td>Cleaning weekly or when samples taken</td>
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</tr>
<tr>
<td></td>
<td>fluorometer</td>
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<td>0.02</td>
<td></td>
<td>Cleaning temperature volume control.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SeaPoint Sensor</td>
<td></td>
<td></td>
<td>0 – 25</td>
<td></td>
<td>Cleaning temperature volume control.</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolved oxygen</td>
<td>Clark electrode</td>
<td>mg/l</td>
<td>0 – 20</td>
<td>0.2% F.S.</td>
<td>monthly</td>
<td>Cleaning, calibration check, monthly Calibration outside of the flow through system.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>COS4-2</td>
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<td></td>
<td>0.2% F.S.</td>
<td></td>
<td>Cleaning, calibration check</td>
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<td>8 – 15</td>
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<td>Cleaning, calibration check</td>
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<tr>
<td>nitrate</td>
<td>UV detection</td>
<td>µmol/l</td>
<td>0.5</td>
<td>50</td>
<td>monthly</td>
<td>Cleaning, calibration check, monthly Comparison with filtrated samples;</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>UV-NO3 Analyse</td>
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<td></td>
<td>0.1</td>
<td></td>
<td>Cleaning, calibration check</td>
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</tr>
<tr>
<td>Parameter</td>
<td>Methodology</td>
<td>Instrument Model</td>
<td>Unit</td>
<td>Lower Limit</td>
<td>Upper Limit</td>
<td>Cleaning, Calibration, Check Frequency</td>
<td>Calibration Interval</td>
<td></td>
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<tr>
<td>Nitrate</td>
<td>Photometric automatic pump photometer (APP)</td>
<td>ME (Germany)</td>
<td>µmol/l</td>
<td>0.5 – 300</td>
<td>0.01</td>
<td>0 – 250</td>
<td>fortnightly</td>
<td>Inter-calibration with monthly taken samples.</td>
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<tr>
<td>Ammonia</td>
<td>Fluorometric automatic pump photometer (APP modified)</td>
<td>ME (Germany)</td>
<td>µmol/l</td>
<td>0.1 – 20</td>
<td>0.01</td>
<td>0 – 7</td>
<td>fortnightly</td>
<td>Instrument modified for fluorescence measurements (OPA reagent).</td>
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<tr>
<td>Orthophosphate</td>
<td>Photometric automatic pump photometer (APP)</td>
<td>ME (Germany)</td>
<td>µmol/l</td>
<td>0.05 – 10</td>
<td>0.05</td>
<td>0 – 3</td>
<td>fortnightly</td>
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<tr>
<td>Silicate</td>
<td>Photometric automatic pump photometer (APP)</td>
<td>ME (Germany)</td>
<td>µmol/l</td>
<td>0.2 – 100</td>
<td>0.01</td>
<td>0 – 70</td>
<td>fortnightly</td>
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</table>

*First tests.*
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fluorochrome (flow-through)</th>
<th>Seapoint Fluorometer</th>
<th>Detection Range</th>
<th>Calibration Range</th>
<th>Weekly Calibration Check</th>
<th>Monthly Inter-calibration with laboratory measurements; flow-through system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll a</td>
<td>Fluorescence blue LED (470 ± 30 nm)</td>
<td>CTG Mini-Track II</td>
<td>V / µg/l</td>
<td>0.03 – 100 µg/l</td>
<td>0.01 µg/l</td>
<td>not yet established</td>
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<tr>
<td>Chlorophyll a</td>
<td>Fluorescence excitation</td>
<td>CTG MiniPack</td>
<td>µg/l</td>
<td>0.03 – 100 µg/l</td>
<td>0.01 µg/l</td>
<td>weekly cleaning, Weekly calibration 2004 weekly drift</td>
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chemicals, calibration check
<table>
<thead>
<tr>
<th>Oxygen</th>
<th>Dynamic luminescence quenching</th>
<th>Oxygen Optode 3830</th>
<th>Aanderaa</th>
<th>Micro-Moles/l</th>
<th>0 -500</th>
<th>&lt;8uM or 5%</th>
<th>&lt;1% or 0.4%</th>
<th>200-400</th>
<th>Weekly cleaning</th>
<th>Monthly calibration check</th>
<th>Yearly</th>
<th>New 2005</th>
<th>Better than specification.</th>
<th>Little drift</th>
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</thead>
<tbody>
<tr>
<td>Algae groups (chlorophyll-a)</td>
<td>Fluorescence (excitation at different wavelengths)</td>
<td>Chl a sensor bbe-moldaenke (Germany)</td>
<td>1 - 200 0.1</td>
<td>0.5</td>
<td>depend on algae group</td>
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<td>Inter-calibration with HPLC measurements and cell counting (2-monthly); test phase</td>
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