



# ICOS OCEAN STATION LABELLING STEP 2

Version 6

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## **ICOS OTC 2020**

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## Additional comments

Pr. July 2018, it is discussed, based on statistical uncertainty analyses, whether the recommended accuracy for SOOP lines intake and equilibrator temperature and equilibrator pressure should be strengthened to 0.03 °C and 0.5 mbar, respectively. This is not changed in the current document.

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## Section 1: Document Overview

The intent of this document is to provide an overview of step 2 of the labelling process of ICOS ocean stations. Section 2 of this document summarises the core variables for each of the station categories: Ship of Opportunity Program (SOOP lines), Repeat Ocean Sections (ROS), Fixed Ocean Stations (FOS), and Marine Flux Towers (MFT). This station type distinction will be maintained throughout the document. Section 3 of this document summarises the required documents to be submitted to the ICOS Ocean Thematic Centre (OTC) by each station's Principal Investigator (PI) in order to be evaluated for step 2 labelling. Unless otherwise directed by the OTC, only stations that have successfully completed step 1 labelling should provide this information. Furthermore, in section 3, links to excel spreadsheets for metadata information are included, and these must also be completed in order to proceed through step 2 labelling. Section 4 summarises the general processing by the OTC of the 4 to 6 months of raw field data required from the PIs for step 2 labelling.

## Section 2: ICOS Ocean Station Labelling step 2

### 2.1 Introduction

The aim of ICOS ocean stations is to provide harmonized and high quality scientific carbon data to be used to quantify the exchange of carbon between the surface ocean and the atmosphere, ocean acidification, and interior ocean carbon transport and storage. ICOS ocean data should also contribute to assessment of the observed carbon variability and its drivers.

The station labelling is performed to ensure high quality data, and the labelling process consists of three steps:

- 1<sup>st</sup> step: station construction and formal application via the national ICOS representative to the OTC. The applicant needs to confirm a long-term commitment of the necessary station resources (manpower, equipment, consumables, ICOS contributions). The station also needs to be approved by the national stakeholder.
- 2<sup>nd</sup> step: evaluation in relation to OTC data protocols, quality control, and data flow routines. The current document is one of those that describe the methods of this evaluation, and will be subject to revision every 2-3 years.
- 3<sup>rd</sup> step: a formal decision to include the station into the ICOS Monitoring Station Assembly (ICOS MSA) will be made by the General Assembly based on recommendation from the OTC and a proposal to approve the station put forward by the Director General of ICOS.

The ocean network consists of a variety of ships and fixed station installations covering the open ocean and coastal areas, and for this purpose the network is divided into the following categories;

1. Ship of Opportunity Program - SOOP lines (previously Carbon-VOS, open ocean and coastal areas)
2. Repeat Ocean Sections - ROS (open ocean)<sup>not yet accepted by the ICOS structure, see section 2.3</sup>
3. Fixed Ocean Stations - FOS (open ocean and coastal areas)
4. Marine Flux Towers - MFT (coastal areas)

For each category, ICOS defines two classes of ocean stations according to the set of variables measured. A station qualifies as a Class 2 station when it measures a **minimum** set of variables to an accuracy required to meet the ICOS goal. Class 1 label is achieved when the station measures **extra** variables that allow ICOS to pursue further scientific questions. The requirements for data quality are

the same for ICOS Class 1 and Class 2 stations. Please note that, as for GO-SHIP ([Global Ocean Ship-based Hydrographic Investigation Program](#)), if no absolute standards are available for a measurement then accuracy should be understood as the reproducibility present obtained in the better laboratories.

## 2.2 Ship of Opportunity Program (SOOP lines)

On stations categorized as SOOP lines (Ship of Opportunity Program, previously named Carbon-VOS), quasi-continuous measurements are performed of  $x\text{CO}_2$  in the surface ocean (4-10 meters of water depth) and often, but not always, in the lower atmosphere (5-40 m above sea level), giving final surface ocean  $f\text{CO}_2$  data at a frequency of at least once per hour. Besides measuring  $x\text{CO}_2$ , simultaneous observations of water temperature and air pressure are essential (see Table 1). Highest quality measurements are obtained with a set-up that follows *Dickson et al. (2007)* standard operating procedure 5 (SOP5): instrumentation (defined as being bench-top measuring systems) analysing  $\text{CO}_2$  in the headspace of a flow-through equilibrator, equipped with at least two non-zero gas standards traceable to World Meteorological Organisation (WMO) standards, and an infrared absorption detector (including NDIR spectrophotometers, CRDS and TDLA) or a gas chromatograph. In order to maintain accuracy of  $f\text{CO}_2$  of  $\pm 2 \mu\text{atm}$ , alternative flow-through sensors, which do not use a headspace gas, are not currently acceptable for either Class 1 or Class 2 SOOP lines. This may change with changes in technology and the OTC will update this document accordingly. Additional variables are dissolved oxygen and one of the two: total alkalinity (TA) and dissolved inorganic carbon (DIC). OTC acknowledges that environmental variability is higher in coastal waters than in the open ocean, and we will evaluate these stations on individual basis related to what is achievable by the analytical instrument.

### 2.2.1 Requirements for ICOS SOOP lines

#### **For Class 2:**

- Following approved method and SOP criteria (*Dickson et al., 2007*), including measuring quasi-continuous  $x\text{CO}_2$  and calculating  $f\text{CO}_2$  based on this, and not from other carbon variables.
- Utilising a flow-through headspace equilibrator system measuring  $x\text{CO}_2$  in headspace gas.
- Proving calibration by regularly measuring at least two non-zero gas standards ( $\text{CO}_2$  in synthetic air) traceable to WMO standards bracketing the actual measurements.
- Metadata (see Section 3), including description of core variable calibration, are complete.

#### **For Class 1:**

- Following approved methods and SOP criteria (*Dickson et al., 2007*) when measuring one out of the two carbonate variables TA or DIC.
- Following the recommendations by *Bittig et al. (2018)* for the oxygen measurements using sensors.

**Table 1.** Required variables, frequency and criteria for ICOS SOOP lines. The stated uncertainties, see *Steinhoff* (2019) for details, are needed to fulfill the ICOS goals.

Variables	Frequency	Accuracy	Class
Sea surface $f\text{CO}_2$	Quasi-continuous	$\pm 2 \mu\text{atm}$	2
Intake temperature (SST)	Continuous	$\pm 0.05 \text{ }^\circ\text{C}$	2
Equilibrator temperature	Continuous	$\pm 0.05 \text{ }^\circ\text{C}$	2
Delta-T (difference between equilibrator and intake temperature)	Continuous	< 1.5 $^\circ\text{C}$ (normal) <3 $^\circ\text{C}$ (ice-edge)	2
Water vapour pressure <sup>1</sup>	Continuous	$\pm 0.5 \text{ mbar}$	2
Equilibrator pressure <sup>2</sup>	Continuous	$\pm 2.0 \text{ mbar}$	2
Atmospheric pressure/sea level pressure	Continuous	$\pm 1.0 \text{ mbar}$	2
Sea surface salinity (SSS)	Continuous	$\pm 0.1 \text{ PSU}$	2
Dissolved oxygen	Continuous	$\pm 2\%$	1
One out of two: - Total alkalinity (TA) - Dissolved inorganic carbon (DIC)	Discrete <sup>3</sup> Discrete <sup>3</sup>	$\pm 10 \mu\text{mol kg}^{-1}$ $\pm 5 \mu\text{mol kg}^{-1}$	1 1

The stated uncertainties are needed to fulfill the ICOS goals, see *Steinhoff* (2019) for details.

<sup>1</sup> If the analysed headspace gas is not dried completely prior to measurement.

<sup>2</sup> This should be the absolute pressure.

<sup>3</sup> The frequency of these additional variables will be decided on during the labelling process based on the area where the station is operating.

In addition, the following variables are desirable for SOOP lines, but will, at the time being, not be processed by the OTC:

*Atmosphere:*  $x\text{CO}_2$ , pressure, temperature, flask samples of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , wind speed, and wind direction.

*Ocean:* chlorophyll-fluorescence, dissolved inorganic nutrients (nitrate,  $\text{NO}_3$ ; phosphate,  $\text{PO}_4$ ; silicate,  $\text{Si}(\text{OH})_4$ ),  $\delta^{13}\text{C}$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ .

## 2.3 Repeat Ocean Sections (ROS)

**Currently, Repeat Ocean Sections (ROS) as a station type have not been accepted by the ICOS structure. Discussions are currently underway to incorporate this invaluable data into ICOS.**

Repeat Ocean Sections (ROS) are performed at least once per decade using research ships equipped with advanced high precision systems and standard carbon instrumentation following *Dickson et al.* (2007). Analyses are typically done on-board the ships on water samples collected with a rosette, and the sampling covers the full depth of the area. This allows accurate measurements of carbon and transient tracers required to estimate carbon storage and transport. Calibration of the carbon variables is performed using reference material as described by *Dickson et al.* (2007). The measurement criteria follow the GO-SHIP manuals and GLODAPv2 routines (*Hood, 2010; Olsen et al., 2016*).

### 2.3.1 Requirements for ICOS ROS

*For both Class 2:*

- Following approved methods and SOP criteria (*Dickson et al., 2007*) when measuring two out of four carbon variables (DIC, TA,  $\text{pH}_T$ ,  $\text{pCO}_2$ ).
- Following approved methods when measuring nutrients (*Becker et al., 2019*) and sensor oxygen (*Bittig et al., 2018*).
- Metadata (see Section 3), including description of core variables calibration, are complete.

- Proving regular calibration of the instruments.
- Covering full depth of the water column.

**For Class 1:**

- Following approved methods according to, e.g., *Bullister and Tanhua (2010)* when measuring CFC-11, CFC-12, and SF<sub>6</sub>.
- Following Winkler method (*Carpenter, 1965*) when measuring dissolved oxygen.

**Table 2.** Required variables, frequency and criteria for ICOS ROS.

Variables	Frequency	Accuracy <sup>4</sup>	Class
Two out of four: - Dissolved inorganic carbon (DIC) - Total alkalinity (TA) - pCO <sub>2</sub> - pH <sub>T</sub>	> 1 decade <sup>-1</sup> > 1 decade <sup>-1</sup> > 1 decade <sup>-1</sup> > 1 decade <sup>-1</sup>	± 1.5 (< 4) μmol kg <sup>-1</sup> ± 3 (< 6) μmol kg <sup>-1</sup> ± 1 (<3) μatm ± 0.005 (<0.005)	2 2 2 2
Sea temperature	> 1 decade <sup>-1</sup>	± 0.002 °C	2
Sea salinity	> 1 decade <sup>-1</sup>	± 0.001 PSU (<0.005 PSU)	2
Two out of three: - Nitrate (NO <sub>3</sub> ) - Phosphate (PO <sub>4</sub> ) - Silicate (Si(OH) <sub>4</sub> )	> 1 decade <sup>-1</sup> > 1 decade <sup>-1</sup> > 1 decade <sup>-1</sup>	<sup>5</sup> ± 1 (<2)% ± 1-2 (<2 <sup>6</sup> )% ± 1-3 (<2)%	2 2 2
Dissolved oxygen - Sensor	> 1 decade <sup>-1</sup>	± 2%	2
Pressure (depth)	> 1 decade <sup>-1</sup>	± 3 dbar	2
CFC-11/ CFC-12	> 1 decade <sup>-1</sup>	± 1-2 (<5)%	1
SF <sub>6</sub>	> 1 decade <sup>-1</sup>	± 3 (<5)%	1
Dissolved oxygen - Winkler	> 1 decade <sup>-1</sup>	± 0.5 (<1)%	1

Abbreviations: CFC=chlorofluorocarbon.

<sup>4</sup> The two numbers refers to accuracy achieved on the cruise and, in parenthesis, between-cruises bias. The numbers within parentheses are the maximum acceptable bias following the 2nd level QC in GLODAP and represents the uncertainty after recommended adjustments in the GLODAP routines.

<sup>5</sup> The accuracy refers to samples without conservation. If conservation is used (freezing is the most commonly used method) the accuracy might increase (*Becker et al., 2019*).

<sup>6</sup> Note that in the Atlantic the between-cruise precision is relaxed to <4% for phosphate according to GLODAP routines.

In addition, the following variables are desirable for ROS: δ<sup>13</sup>C, Δ<sup>14</sup>C, CH<sub>4</sub>, and N<sub>2</sub>O.

## 2.4 Fixed Ocean Stations (FOS)

Fixed Ocean Stations (FOS) usually consist of a surface buoy with attached instruments or sensors performing continuous carbon measurements in the ocean and in the lower atmosphere, and/or a sub-surface mooring with instruments/sensors measuring continuously at one or several depths of the water column. FOS can also be ship based where discrete measurements are collected from a fixed position. The stations are situated in the open ocean or in coastal waters. Distinction between coastal and open ocean are, in addition to distance from land, connected to habitats, light penetration, nutrient availability, processes (e.g. dense water formation at the shelf and deep open ocean), tidal fronts, and river runoff in coastal waters (*Wollast, 1998*). It is for the station PI to define whether the station is coastal or open ocean.

For FOS, primarily inorganic carbon variables and hydrography are measured, but a wide range of measurements can be performed either using discrete sampling with post analyses or by use of autonomous sensors (see brief description in *Wanninkhof et al. (2013)*, *Coppola et al. (2016)*, or at the IOCCP web page, <http://www.ioccp.org/instruments-and-sensors>). Requirements are split into discrete data (based on GO-SHIP; *Hood, 2010*) and sensor-based data (*Lorenzoni and Benway, 2013*; *Wanninkhof et al., 2013*, *Coppola et al., 2016*).

## 2.4.1 Requirements for ICOS FOS, discrete measurements

### For Class 2:

- Following approved methods and SOP criteria (*Dickson et al., 2007*) when measuring pH, and one out of the two carbon variables DIC or TA.
- Following *Langdon (2010)* and the GO-SHIP criteria when measuring dissolved oxygen.
- Metadata (see Section 3), including description of core variable calibration, are complete.
- Proving regular calibration of the instruments.

### For Class 1:

- Following approved methods (*Becker et al., 2019*) when measuring nutrients.

**Table 3a.** Required variables, frequency and criteria for ICOS FOS - discrete samples - in open ocean and coastal waters.

Variables	Frequency open /coastal	Accuracy open / coastal	Class open / coastal
pH	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.005	2
One out of two: - Total alkalinity (TA) - Dissolved inorganic carbon (DIC)	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup> > 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 3 µmol kg <sup>-1</sup> ± 1.5 µmol kg <sup>-1</sup>	2 2
Sea temperature	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.002 °C	2
Sea salinity - CTD - Bottle samples	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.002 PSU ± 0.001 PSU	2
Dissolved oxygen - Winkler - Sensor	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.5% ± 2%	2
Pressure (depth)	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 3 dbar	2
Two out of three: - Nitrate (NO <sub>3</sub> ) - Phosphate (PO <sub>4</sub> ) - Silicate (Si(OH) <sub>4</sub> )	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	<sup>7</sup> ± 1% ± 1-2% ± 1-3%	1 1 1

<sup>7</sup> The accuracy refers to samples without conservation. If conservation is used (freezing is the most commonly used method) the accuracy might increase (*Becker et al., 2019*).

In addition, the following variables are desirable for a FOS - discrete samples station, but will, at the time being, not be processed by the OTC: chlorophyll, DOC (dissolved organic carbon), CFC-11, CFC-12, SF<sub>6</sub>, CH<sub>4</sub>, N<sub>2</sub>O, δ<sup>13</sup>C, Δ<sup>14</sup>C, CDOM (chromophoric dissolved organic matter).



## 2.4.2 Requirements for ICOS FOS, continuous/ quasi-continuous measurements

### For Class 2:

- Following CO<sub>2</sub> sensor methods evaluated in *Wanninkhof et al. (2013)*, *Coppola et al. (2016)*, and *Lorenzoni and Benway (2013)* for the pCO<sub>2</sub> measurements.
- Following approved methods and SOP criteria (*Dickson et al., 2007*) when measuring pH, and one out of the two carbonate variables DIC or TA.
- Following the recommendations by *Bittig et al. (2018)* for the oxygen measurements.
- Metadata (see Section 3), including description of core variable calibration, are complete.
- Proving *in situ* calibration of pCO<sub>2</sub> by measuring at least one non-zero gas standard traceable to WMO standards, or monthly discrete samples of the pair TA-pH or DIC-pH (duplicates, or preferable triplicates) from the position and depth of the pCO<sub>2</sub> sensor, or, at a minimum, discrete samples (duplicates, or preferable triplicates) at the start and end of deployment.
- Collect and analyse discrete oxygen samples (duplicates, or preferable triplicates) for validation purposes (frequency as for carbon).
- Pre- and post-visit calibration of vital sensors.

### For Class 1:

- Using available sensor technology for measuring inorganic nutrients (nitrate, NO<sub>3</sub>; phosphate, PO<sub>4</sub>; silicate, Si(OH)<sub>4</sub>).
- Collect and analyse discrete nutrient samples (duplicates, or preferable triplicates) for validation purposes (*Becker et al., 2019*).

**Table 3b.** Required variables, frequency and criteria for ICOS FOS – continuous/quasi-continuous samples in open ocean and coastal waters.

Variables	Frequency open / coastal	Accuracy open / coastal	Class open / coastal
Sea surface pCO <sub>2</sub>	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 10 µatm <sup>8</sup>	2
One out of two: - Total alkalinity (TA) - Dissolved inorganic carbon (DIC)	<sup>9</sup> discrete discrete	<sup>10</sup> ± 4 µmol kg <sup>-1</sup> ± 2 µmol kg <sup>-1</sup>	2 2
pH <sup>11</sup>	discrete <sup>9</sup>	± 0.003	2
Sea temperature	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.02 °C	2
Sea salinity	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.1 PSU	2
Dissolved oxygen	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 2%	2
Pressure (depth)	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 3 dbar	2
Two out of three: - Nitrate (NO <sub>3</sub> ) - Phosphate (PO <sub>4</sub> ) - Silicate (Si(OH) <sub>4</sub> )	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	<sup>12</sup> ± 1% ± 1-2% ± 1-3%	1

<sup>8</sup> According to the “weather goal” (*Newton et al., 2014*), results described in *Steinhoff (2019)* ([Uncertainty analysis for the marine carbonate system](#)), and *Wanninkhof et al. (2013)*.

<sup>9</sup> The frequency of these additional variables will be decided on during the labelling process based on the area where the station is operating.

<sup>10</sup> According to the results described in *Steinhoff (2019)* ([Uncertainty analysis for the marine carbonate system](#)).

<sup>11</sup> pH (together with TA or DIC) is required for validation of the pCO<sub>2</sub> data. pH should not be used together with pCO<sub>2</sub> to calculate the full carbonate system due to high resulting uncertainty ([Uncertainty analysis for the marine carbonate system](#)).

<sup>12</sup> The accuracy refers to samples without conservation. If conservation is used (freezing is the most commonly used method) the accuracy might increase (*Becker et al., 2019*).

In addition, the following variables are desirable for a FOS - continuous/quasi-continuous station, but will, at the time being, not be processed by the OTC: *Atmosphere*: xCO<sub>2</sub>, pressure, temperature, wind speed, wind direction.

*Ocean*: continuous pH, chlorophyll, CH<sub>4</sub>, N<sub>2</sub>O, CDOM (chromophoric dissolved organic matter), irradiance, and PAR (Photosynthetically Active Radiation).

## 2.5 Marine Flux Towers (MFT)

The station category Marine Flux Towers (MFT) consist of a flux tower with a variety of meteorological and ecosystem measurements and an ocean mooring which monitors sea surface pCO<sub>2</sub>. The flux tower is described below, while the ocean measurements are described in chapter 2.4.2. Requirements for ICOS FOS, continuous/ quasi-continuous measurements.

Micrometeorological measurements using Eddy Covariance (EC) data are direct measurements of vertical fluxes, but the stations and data need careful quality control for reliable estimates. EC data can be taken on a ship or on a fixed tower system and give a direct estimate of the flux for the representative footprint area. The prerequisites for EC measurements in marine environments are somewhat different from terrestrial requirements and thus special labelling is required. The fluxes are generally smaller, marine environments also include high humidity and salinity thus sea spray deposition on instrumentation is a concern. Flux towers are predominantly situated on shores or in near-shore regions, with varying degrees of terrestrial influence. It is suggested to differentiate the data according to the expected level of terrestrial influence (see table 4a). Group 1: Flux footprint represents open sea conditions, land influence is limited to circulation systems (e.g. upwelling, sea-breeze circulation); group 2: flux footprint represents "coastal zone" with heterogeneous properties; group 3: flux footprint represents shore area and is highly active in terms of the carbon cycle, see also Rutgersson et al. (2020). Flux measurements can also be performed on ships, which requires additional analyses of motion correction and flow distortion. If EC data taken from moving ships are to be introduced in ICOS a common methodology for motion correction should be developed.

**Table 4a.** Suggested groups for measurements collected from MFT (Rutgersson et al., 2020).

Group	Footprint	Wave-field
Group 1	Homogeneous	Undisturbed
Group 2	Heterogeneous	Disturbed
Group 3	Shore area	Land/sea

### 2.5.1 Requirements for ICOS MFT

**For Class 2:**

- Following approved methods (e.g. (e.g. Baldocchi, 2003; Aubinet et al., 2012; Rutgersson et al., 2020) when measuring CO<sub>2</sub> flux and friction velocity.
- Metadata (see Section 3), including description of flux system calibration, are complete. Details on data processing, required corrections and quality control should be included. Flux systems should be calibrated at least bi-annually.
- Stations should be visited on a regular basis (monthly) and instrumentation cleaned.
- For stations with high salinity and large amounts of sea spray, CO<sub>2</sub> flux-system signals should be dried. For a non-dried system, station PIs should provide data showing this is not necessary.

**For Class 1:**

- Following approved methods (e.g. Baldocchi, 2003; Aubinet et al., 2012; Rutgersson et al., 2020) when measuring H<sub>2</sub>O flux and sensible heat flux.

**Table 4b.** Required variables, frequency and criteria for ICOS MFT.

Variable	Frequency	Accuracy	Class
Atmospheric CO <sub>2</sub>	1h	± 1.5%	2
CO <sub>2</sub> flux	1h	± 5%	2
Atmospheric pressure	1h	± 0.1%	2
Wind speed	1h	± 0.5 m s <sup>-1</sup>	2
Wind direction	1h	± 6 °	2
Atmospheric temperature	1h	± 0.2 ° ventilated <sup>13</sup>	2
Atmospheric humidity	1h	± 1%	2
Friction velocity	1h	± 5%	2
H <sub>2</sub> O flux	1h	± 5%	1
Sensible heat flux	1h	± 5%	1

<sup>13</sup> A flow through system of air, to prevent radiation problems to the temperature signal. Necessary for high quality measurements of atmospheric temperature.

In addition, the following variables are desirable for a MFT:

*Atmosphere:* precipitation, incoming shortwave and longwave radiation, photosynthetically active radiation (PAR), photosynthetic photon flux density (PPFD), atmospheric mixed-layer depth.

## Section 3: Metadata

### 3.1 Introduction

In addition to data submission, OTC requires metadata information in order to check the status of stations and to provide transparency to those who use ICOS data. Below, a checklist has been provided to help ensure that all required documents are received by OTC.

### 3.2 Checklist

- Appropriate metadata spreadsheet completed (either SOOP lines, ROS, FOS, or MFT). The spreadsheets can be found on the OTC website (<https://otc.icos-cp.eu/documents>).
- All calibration certificates (from manufacturers or calibration facilities) are provided.
- All in house calibration procedure documents are provided (see in house calibration procedure section in the step 2 labelling document for example).
- At minimum, all core variables for the appropriate station type are provided in the data file submitted to QuinCe, as specified in section 3.5.
- Sensitivity (see definition of terms) of data files submitted to QuinCe meets minimum requirements for the appropriate station type, as specified in section 3.5.
- 4 to 6 months of raw field data is provided to QuinCe. If an adequate amount of data is unavailable, then the station will need to provide more data in the coming months to fulfill this requirement before proceeding through step 2 labelling.

### 3.3 Metadata Spreadsheets

In addition to data submission, each ICOS station should also submit metadata. There is an excel spreadsheet at the OTC web page (<https://otc.icos-cp.eu/documents>) corresponding to each type of station which should be filled out by each ICOS station during step 2 labelling.

### 3.4 Definition of Terms

This section defines some of the terms used in the metadata spreadsheets.

- Sensitivity: The minimum resolvable unit a sensor/instrument/system is capable of reporting. For example, if a temperature sensor reads 21.605 °C, then its sensitivity is 0.001. Please note, the minimum resolvable unit of a probe (the part of the sensor physically measuring the temperature) is not necessarily the same as that shown by the instrument reader.
- Precision: Repeatability of a sensor/instrument/system. Please report one standard deviation.
- Accuracy: A measure of how close a measurement is to the true value.
- Depths of samples: At what depths are discrete samples taken, or at what depths are in situ instruments placed in the water column?
- Poisoning correction description: How is the addition of poison (e.g. mercuric chloride) corrected for in your samples?
- Standardization method: Method description: Which CRM is used, how often is it used, and what (if any) correction is applied to the data?
- Alkalinity: Method description-What type of method is used (e.g. Gran titration)?

- pCO<sub>2</sub> data: Method description-What type of method is used (e.g. headspace equilibration, membrane, dye, etc.)?
- pCO<sub>2</sub> description: Equilibrator type-What type of equilibrator is used (e.g. shower head, percolating packed, etc.)?
- pH data: Cell type- Is the system a flow through or discrete sample system, what is the path length of the cell?
- pH data: Calibration information- Are the samples calibrated for an offset (e.g. by using a tris buffer) and/or is the pH dye calibrated, if so, how?
- Unit conversion: Constant conversion: If, when converting to gravimetric units from volumetric units (i.e. conversion using density), a constant coefficient is used, what is the value of the coefficient?
- Unit conversion: Conversion equation-If, when converting to gravimetric units from volumetric units (i.e. conversion using density), an equation is used to determine the conversion, what is the equation or from which publication is the equation drawn?
- Other metadata: Describe how you achieved this number-What calculations were made to achieve this value or from what publication was this value drawn?
- Variables: Variable names and units should correspond with how they are formatted in the data file sent to QuinCe. Preferably, the variables should be in the same order in the metadata spreadsheet as provided in the data file sent to QuinCe.

### 3.5 Preferred Reported Units and Resolution

In the tables below are the list of variables previously described in Section 2 with the preferred unit and the minimum resolution requirements for each variable to be reported to OTC. The preferred units are not mandatory, however, the minimum resolutions are based on either what is required to ascertain the accuracy of equipment in regards to OTC requirements or by the standards within the field. Note that there are some additional variables under the core variables, which must be reported in addition to the core variables.

**Table 5.** SOOP lines

Metadata Variables	Suggested Unit	Minimum Resolution
Date	dd.mm.yyyy or decimal year	
Time	hh.mm.ss	
Latitude	Decimal Units (N positive)	
Longitude	Decimal Units (E positive)	
Atmospheric xCO <sub>2</sub>	ppm	0.01
Sea surface fCO <sub>2</sub>	µatm	0.01
Intake temperature (SST)	°C	0.01
Equilibrator temperature	°C	0.01
Licor Pressure	mbar	0.1
Water vapour pressure	mbar	0.1
Equilibrator pressure	mbar	0.1
Absolute pressure	mbar	0.1
Differential pressure	mbar	0.1
Sea surface salinity (SSS)	PSU	0.1

Water flow rate lower bound	L min <sup>-1</sup>	0.1
Dissolved oxygen (DO) <sup>18</sup>	μmol kg <sup>-1</sup>	0.1
Total alkalinity (TA)*	μmol kg <sup>-1</sup>	0.1
pH <sub>T</sub>		0.01
Dissolved inorganic carbon (DIC) <sup>14</sup>	μmol kg <sup>-1</sup>	0.1
Sea level pressure	mbar	0.1

<sup>14</sup> Equations to determine units should be included in metadata (ex. density equations, etc.)

**Table 6.** Repeat Ocean Sections

Metadata Variables	Unit	Minimum Resolution
Date	dd.mm.yyyy or decimal year	
Time	hh.mm.ss	
Latitude	Decimal Units (N positive)	
Longitude	Decimal Units (E positive)	
Total alkalinity (TA) <sup>19</sup>	μmol kg <sup>-1</sup>	0.1
pH <sub>T</sub>		0.01
Dissolved inorganic carbon (DIC) <sup>19</sup>	μmol kg <sup>-1</sup>	0.1
Seawater pCO <sub>2</sub>	ppm	0.01
Sea temperature	°C	0.001
Pressure (Depth)	dbar	0.1
Sea salinity	PSU	0.001
Dissolved inorganic nutrients (DIN) <sup>19</sup>		
- Nitrate (NO <sub>3</sub> -)	μmol kg <sup>-1</sup>	0.01
- Phosphate (H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> )	μmol kg <sup>-1</sup>	0.01
- Silicate (Si(OH) <sub>4</sub> , SiO <sub>4</sub> <sup>4-</sup> , etc.)	μmol kg <sup>-1</sup>	0.01
Dissolved oxygen (DO) <sup>19</sup>	μmol kg <sup>-1</sup>	0.1
CFC-11 <sup>15</sup>	pmol kg <sup>-1</sup>	0.01
CFC-12 <sup>15</sup>	pmol kg <sup>-1</sup>	0.01
SF <sub>6</sub> <sup>15</sup>	fmol kg <sup>-1</sup>	0.01

<sup>15</sup> Equations to determine units should be included in metadata (ex. density equations, etc.)

**Table 7.** Fixed Ocean Stations

Metadata Variables	Units	Minimum resolution
Date	dd.mm.yyyy or decimal year	
Time	hh:mm:ss	
Latitude	Decimal Units (N positive)	
Longitude	Decimal Units (E positive)	
Total alkalinity (TA) <sup>16</sup>	μmol kg <sup>-1</sup>	0.1
pH <sub>T</sub>		0.01
Dissolved inorganic carbon (DIC) <sup>16</sup>	μmol kg <sup>-1</sup>	0.1
Seawater fCO <sub>2</sub>	ppm	0.1
Sea temperature	°C	0.001/0.01 <sup>17</sup>

Pressure (Depth)	dbar	0.1
Sea salinity	PSU	0.001/0.01 <sup>18</sup>
Dissolved inorganic nutrients (DIN) <sup>16</sup>		
- Nitrate (NO <sub>3</sub> -)	μmol kg <sup>-1</sup>	0.01
- Phosphate (H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> )	μmol kg <sup>-1</sup>	0.01
- Silicate (Si(OH) <sub>4</sub> , SiO <sub>4</sub> <sup>4-</sup> , etc.)	μmol kg <sup>-1</sup>	0.01
Dissolved oxygen (DO) <sup>16</sup>	μmol kg <sup>-1</sup>	0.1

<sup>16</sup> Equations to determine units should be included in metadata (ex. density equations, etc.)

<sup>17</sup> Resolution of 0.001 °C is required for ship board measurements and 0.01 °C for buoys/moorings.

<sup>18</sup> Resolution of 0.001 PSU is required for ship board measurements and 0.01 PSU for buoys/moorings.

### 3.6 Sensor Calibration

For all sensors, instruments, or systems calibrated at a calibration facility, copies of the certification documentation must be provided to OTC. Preferably, these documents will be bundled together into one document, otherwise, the files should be named for easy identification. On the calibration documentation list page of each of the station metadata spreadsheets is a table where each instrument name and associated file should be listed. For each sensor not calibrated at a certified calibrated facility, but instead calibrated in house using a reference instrument that has been calibrated, we would like a description of the in house calibration method, including the values of each point used to produce the calibration curve.

An example is provided below:

**Temperature Sensors**

Fluke 5626 PRT Temperature Probe combined with a Fluke 1524 Reference Thermometer for read out.

Last manufacturer calibration: 17 Nov. 2017

5610-9 Reference Thermistor combined with Fluke 1524 Reference Thermometer for read out.

Last in house calibration: 01 Apr. 2018

**Calibration Curve Temperatures:**

- 5.0
- 10.0
- 20.0
- 25.0
- 27.5
- 30.0
- 32.5
- 35.0
- 40.0
- 50.0

**In house Calibration Procedure:**

For each calibration curve point, we use a temperature bath (Fluke 6330 Compact Temperature Calibration Bath). The bath is set to the specific temperature and the water allowed to equilibrate for 1 hour before the temperature is measured using the calibration sensor (5626 probe and 1524 readout combination) and the temperature sensor to be calibrated (5610-9 probe and 1524 readout combination). The probes are placed in a submerged rack with a distance of 5 mm between each probe. The probes are left in the bath for 20 minutes to equilibrate. The

temperature readings for each 1524 readout is then recorded. This is repeated for each of the temperature settings. We perform a linear regression of the calibration curve and determine the RMS of the data. We then adjust the correlation coefficients of the 5610-9 probe and 1524 readout combination according to the manual. The 5626 PTR probe and 1524 reference thermometer combination is calibrated at Thermal Care Inc, annually, which is traceable to the NIST temperature standard (most recent certificate included in report).

## Section 4: Data Checks for Labelling

### 4.1 Introduction

The station labelling process for new members of the OTC requires that the station data be monitored for a period of at least 4 to 6 months. This section describes the tasks involved in performing the data checks for the labelling, and a list of the checks that will be performed by the automatic system.

OTC accepts that there will be periods where a particular station does not perform to its highest potential due to system failure, adverse environmental conditions, etc. The purpose of these checks is not to examine every such failure, and nor is it to produce fully quality-controlled data output. The aim of this exercise is to gain an insight into the overall performance of the instrument over time, and whether any changes need to be made in order to increase the quality of that station's data to meet ICOS' goals, both in terms of operation and accuracy. The range of required raw field data (4 to 6 months) is dependent on the quality of the data. If a station provides 4 months of data and the OTC finds it necessary to evaluate more data, the OTC will request more data.

### 4.2 Data Acquisition

Each station PI must provide complete Level 0 (raw) data from their instrument covering at least the most recent 4 to 6 months of the station's operation. Along with the data, the PI must provide the following information:

- Complete details of the format of their data files so they can be processed.
- Details regarding the start/end times of individual crossings.
- Concentrations for the gas standards used to calibrate the instrument must be supplied.
- If sensor calibrations have to be performed during data reduction, the calibration coefficients must also be provided.

### 4.3 Station Analysis and Decision

After a station's data has been processed using the above tools, it must be assessed by an expert to determine whether it meets the quality requirements of the OTC.

This will be a dialogue with the PIs in the context of other station information received by the OTC, and can cover such topics as the station's location, the instrument's characteristics, data output requirements and other factors that can affect the data quality. Possible improvements can be discussed with the PI, which may or may not influence the decision for a station's inclusion in ICOS.



Following the analysis and discussion with the PI, the OTC will decide whether or not the station can be accepted as an ICOS station, or whether the instrument or some of the routines must be improved first. This decision will be passed to the General Assembly for final approval. (The exact process is described in the main Station Labelling documentation.)

## 4.4 Data Checks

### 4.4.1 Automatic Data Checks (in QuinCe)

The automatic data checks will be performed on the data after the data reduction calculations are complete. These checks will be based on the Sanity Checks used by SOCAT’s automated data upload system, which are also being implemented in QuinCe. These provide range checks, outlier detection and spike detection.

**Table 8.** Variable ranges and flagging

Variable (units)	Range	Outlier <sup>19</sup>	Spike <sup>20</sup>
Intake (sea surface) temperature (°C)	-5 : 40	2	3
Salinity (PSU)	0 : 50	2	3
Atmospheric pressure (mbar)	750 : 1200	2	3
Equilibrator temperature (°C)	-5 : 40	2	3
$\Delta T^{21}$ (°C)	0 : 1.5	2	0.005 <sup>22</sup>
Equilibrator pressure (mbar)	750 : 1200	2	30
xCO <sub>2</sub> (µatm)	300 : 600 (review)	2	20
Water flow (l min <sup>-1</sup> , if reported)	Lower bound defined for instrument	N/A	N/A

<sup>19</sup> Outliers are defined as any value outside  $n$  standard deviations from the mean value within a single data set from the station.

<sup>20</sup> Spikes are measured as the delta between two consecutive measurements. The delta is defined as  $n$  units per minute.

<sup>21</sup> The absolute difference between the Inlet (sea surface) temperature and Equilibrator temperature.

<sup>22</sup> Equates to 0.3°C hr<sup>-1</sup>.

In addition to these, no value must be constant for more than 2 hours.

The timestamps of measurements will be checked to ensure that there are no significant dropouts. Within a data set (that typically constitutes a single crossing), having no measurements reported for more than an hour will trigger a notice. If there are too many such notices, it is indicative of operational issues with the instrument.

The ship tracks from the location data will be checked to ensure that there are no jumps in location etc. This will be measured in terms of the calculated ship speed from the time and distance between measurements. Ship speed greater than 150k/h will be triggered (this threshold has to

be set high to account for GPS uncertainty that can be significant if measurements are taken at very short intervals).

#### 4.4.2 Manual Checks

This section lists a few checks that should be performed by the experts after the automatic checks. This is by no means an exhaustive list - it is a reminder of certain things that must be checked in addition to the checker's own assessment of the data quality.

- Ensure that gas standards (and zero/span, where appropriate) are run regularly. The frequency should be specified in the station metadata - ensure that the data reflects this<sup>23</sup>.
- Ensure that the gas standard concentrations are appropriate for the range of CO<sub>2</sub> measured by the station.
- Ensure that the measured standards do not drift too far from the true calibration gas concentrations. Also check for variability, drift etc.<sup>23</sup>.
- The difference between the measured xCO<sub>2</sub> and calculated fCO<sub>2</sub> should be consistent.
- Ensure that data is reported regularly, with no significant drop-outs.
- Compare  $\Delta T$  and Intake temperature over time - the relationship should be consistent.

#### 4.4.3 Comparison to External Data

Comparing measured values against external data sets is a good way to check sensor readings. While this will eventually be added to QuinCe, it cannot happen at this stage. Instead, after the data has been processed by QuinCe, it will be exported to another program that will add the co-located external data to the station's data. These can then be compared during the manual checks by plotting them against each other.

The external data that will be added to the data files will be taken from a time period close to the measured data (or climatologies if these are not available), co-located to the closest grid cell and time step. The variables to be included are:

- SST
- Atmospheric pressure
- Salinity
- Atmospheric CO<sub>2</sub>

#### 4.4.4 Secondary QC

OTC will aim to perform secondary QC on the received datasets to ensure the highest possible quality.

For SOOP lines this includes use of routines similar to those of SOCAT. The SOOP line quality control is deemed acceptable when SOCAT quality control flags are A or B, including cross-over analysis where possible (Pfeil *et al.*, 2013; Wanninkhof *et al.*, 2013).

For ROS, the secondary QC includes checks equivalent to 2<sup>nd</sup> QC routines in GLODAPv2 (Olsen *et al.*, 2016).

For FOS, the secondary QC includes checks using routines from GLODAPv2 (Olsen *et al.*, 2016) or SOCAT (Pfeil *et al.*, 2013), alkalinity-salinity relationships, or Multi Linear Regression (MLR).

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<sup>23</sup> Ideally, these would be automatic checks within QuinCe, but the functionality is not yet available, and is not likely to be within the timescale required for the Station Labelling.

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