



## ICOS MARINE STATION LABELLING STEP 2

Version 5

**ICOS OTC 2018**

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## Document history

Version	Date	Actions
0	February 2016	Creation after OTC & MSA meeting in Bergen, January 2015
1	March 2016	Revised after OTC & MSA meeting in Bergen, February 2016
2	February 2017	Revised after OTC & MSA meeting in Bergen, February 2017
3	November 2017	Compilation with metadata and QC information
4	May 2018	Structural changes
5	July 2018	Revised based on decisions made at OTC & MSA meeting in Trieste, May 2018. Included are results from an uncertainty calculation of pCO <sub>2</sub> based on discrete samples of TA, DIC and pH. For Carbon-VOS, the or

## Additional comments

Pr. July 2018, it is discussed, based on statistical uncertainty analyses, whether the recommended accuracy for Carbon-VOS 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: Introduction

The intent of this document is to provide an overview of the ICOS marine station labelling, step 2. Section 2 of this document summarises the core and desirable parameters for each of the four station types: carbon-VOS, fixed stations, repeat sections, and flux towers. This station type distinction will be maintained throughout the document. Section 3 of this document summarises the required documents to be submitted to ICOS 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, several excel spreadsheets with metadata information are mentioned, which also must 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 Marine Station Labelling step 2

### 2.1 Introduction

The aim of ICOS marine 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. 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 Ocean Thematic Centre (OTC). The applicant need 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 ICOS 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 statement from the Research Infrastructure Committee (ICOS-RI).

The marine network consist 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 4 categories;

1. Carbon-VOS (Carbon Voluntary Observing Ships)
2. Repeat Sections (open ocean)<sup>\*see Section 2.3</sup>
3. Fixed Stations (open ocean and coastal areas)
4. Flux Towers (coastal areas)

For each category, ICOS defines two classes of marine stations according to the set of parameters measured. While Class 1 marine station manages a list of 4-13 mandatory core measurements (number depending of station category), Class 2 marine station operates only a subset of these. The requirements for data quality, however, are the same for ICOS Class 1 and Class 2 stations. In addition, each category also includes a ranked list of desirable parameters. See below for more information. Please note that, as for GO-SHIP, if no absolute standards are available for a measurement then accuracy should be taken to mean the reproducibility present obtained in the better laboratories.

## 2.2 Carbon-VOS

On Carbon-VOS, quasi-continuous measurements are performed of CO<sub>2</sub> 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 fCO<sub>2</sub> data at a frequency of at least once per hour. Besides measuring CO<sub>2</sub>, simultaneous observations of temperature and 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 CO<sub>2</sub> 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  $\pm 2 \mu\text{atm}$ , alternative flow-thru sensors, which do not use a headspace gas, are not currently acceptable for either Class 1 or Class 2 Carbon-VOS stations. This may change with changes in technology and the OTC will update this document accordingly. ICOS OTC acknowledge that the environmental variability is higher in coastal waters than in 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 marine Carbon-VOS Stations

**For both Class 1 and Class 2:**

- Following approved method and SOP criteria (Dickson et al., 2007), including measuring xCO<sub>2</sub> and calculate fCO<sub>2</sub> based on this, and not from other carbon parameters.
- Making quasi-continuous CO<sub>2</sub> measurements, not analyses of discrete samples.
- Utilising a flow-through headspace equilibrator system measuring xCO<sub>2</sub> in headspace gas.
- Proving calibration by regularly measuring at least two non-zero gas standards traceable to WMO standards.
- Metadata<sup>1</sup>, including description of core parameter calibration, are complete.
- Quality control deemed acceptable, equivalent to SOCAT quality control flags A or B, including cross-over analysis where possible (Pfeil et al., 2013; Wanninkhof et al., 2013).

**Additionally,**

The difference between Class 1 and 2 is the inclusion of atmospheric CO<sub>2</sub> and atmospheric pressure to Class 1, above the core parameters required by Class 2 (see Table 1).

**Table 1.** Required parameters, frequency and criteria for Carbon-VOS ICOS MSA.

Type	Parameters	Frequency	Criteria <sup>2</sup>	Class
Core	Sea surface fCO <sub>2</sub>	Nearly continuous	$\pm 2 \mu\text{atm}$	1&2
Core	Intake temperature <sup>3</sup>	Continuous	$\pm 0.05^\circ\text{C}$	1&2
Core	Equilibrator temperature <sup>3</sup>	Continuous	$\pm 0.05^\circ\text{C}$	1&2
Core	Water vapour pressure <sup>4</sup>	Continuous	$\pm 0.5 \text{ mbar}$	1&2
Core	Equilibrator pressure <sup>5</sup>	Continuous	$\pm 2.0 \text{ mbar}$	1&2
Core	Atmospheric xCO <sub>2</sub>	Quasi-continuous	$\pm 1 \text{ ppm}$	1
Core	Atmospheric pressure/sea level pressure	Continuous	$\pm 1.0 \text{ mbar}$	1
Desirable	Sea surface salinity	Continuous	$\pm 0.03 \text{ PSU}$	
Desirable	Dissolved oxygen	Continuous	$\pm 1\%$	
Desirable	TA	Discrete	$\pm 3 \mu\text{mol kg}^{-1}$	
Desirable	pH <sub>T</sub>	Continuous	$\pm 0.01$	
Desirable	DIC	Discrete	$\pm 1.5 \mu\text{mol kg}^{-1}$	

Desirable	Atmospheric flask samples for CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	Discrete	As determined by the ICOS FCL	
Desirable	Chlorophyll-fluorescence	Continuous	2%	
Desirable	Wind speed/wind direction	Continuous or discrete		
Desirable	Atmosphere temperature	Continuous or discrete		
Desirable	Dissolved inorganic nutrients (nitrate, NO <sub>3</sub> ; phosphate, PO <sub>4</sub> ; silicate, Si(OH) <sub>4</sub> )	Discrete	see Table 2	
Desirable	$\delta^{13}\text{C}$	Discrete	$\pm 0.1\text{\%}$	
Desirable	CH <sub>4</sub>	Discrete/continuous	$\pm 1\text{\% of atm. saturation}$	
Desirable	N <sub>2</sub> O	Discrete/continuous	$\pm 1\text{\% of atm. saturation}$	

Abbreviations: DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; FCL=Flask and Calibration Laboratory.

<sup>1</sup> Metadata description document, reference under development.

<sup>2</sup> The numbers refers to accuracy of measurements.

<sup>3</sup> Difference between intake and equilibrator temperature should not exceed 1.5°C.

<sup>4</sup> If the headspace gas analysed is not dried completely prior to measurement.

<sup>5</sup> This should be the absolute pressure.

## 2.3 Repeat Sections

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

Repeat Sections 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 parameters 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 marine Repeat Sections

#### For both Class 1 and Class 2:

- Following approved methods and SOP criteria (Dickson et al., 2007) when measuring two out of four carbonate parameters (DIC, TA, pH<sub>T</sub>, pCO<sub>2</sub>).
- Metadata<sup>6</sup>, including description of core parameter calibration, are complete.
- Proving regular calibration of the instruments.
- Covering full depth of the water column.
- Quality control performed, equivalent to 2<sup>nd</sup> QC routines in GLODAPv2 (Olsen et al., 2016).

#### Additionally,

The difference between Class 1 and 2 is the inclusion of transient tracers and discrete dissolved oxygen to Class 1, above the core parameters required by Class 2 (see Table 2).

**Table 2.** Required parameters, frequency and criteria for ICOS Repeat Sections.

Type	Parameters	Frequency	Criteria <sup>7</sup>	Class
Core	Two out of four:			

	- DIC - TA - pCO <sub>2</sub> - pH <sub>T</sub>	> 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)	1&2 1&2 1&2 1&2
Core	Sea temperature	> 1 decade <sup>-1</sup>	± 0.002 °C	1&2
Core	Sea salinity	> 1 decade <sup>-1</sup>	± 0.001 PSU (<0.005 PSU)	1&2
Core	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 (<2)% ± 1-2 (<2 <sup>8</sup> )% ± 1-3 (<2)%	1&2 1&2 1&2
Core	CFC-11/ CFC-12 SF <sub>6</sub>	> 1 decade <sup>-1</sup>	± 1-2 (<5)% ± 3 (<5)%	1 1
Core	Dissolved oxygen - Winkler - sensor	> 1 decade <sup>-1</sup>	± 0.5 (<1)% ± 1%	1 1 & 2
Core	Pressure (depth)	> 1 decade <sup>-1</sup>	± 3 dbar	1 & 2
Desirable	δ <sup>13</sup> C	> 1 decade <sup>-1</sup>	± 0.04‰	
Desirable	Δ <sup>14</sup> C	> 1 decade <sup>-1</sup>	± 5‰	
Desirable	CH <sub>4</sub>	> 1 decade <sup>-1</sup>	± 1% of atm. saturation	
Desirable	N <sub>2</sub> O	> 1 decade <sup>-1</sup>	± 1% of atm. saturation	

Abbreviations: DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; CFC=chlorofluorocarbon.

<sup>6</sup> Metadata description document, reference under development.

<sup>7</sup> The two numbers refers to accuracy achieved on the cruise and, in parenthesis, between-cruises bias.

The numbers within parenthesis are the maximum acceptable bias following the 2nd level QC in GLODAP and represents the uncertainty after recommended adjustments in the GLODAP routines.

<sup>8</sup> Note that in the Atlantic the between-cruise precision is relaxed to <4% for phosphate according to GLODAP routines.

## 2.4 Fixed Stations

Fixed Stations usually consist of a surface buoy with attached instruments or sensors performing continuous carbon measurements in the ocean and in lower atmosphere, and/or a sub-surface mooring with instruments/sensors measuring continuously at one or several depths of the water column. Fixed Stations 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 fixed stations, primarily inorganic carbon parameters 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), in FixO3 handbook (<http://www.fixo3.eu/2016/07/07/best-practices-for-operations-at-fixed-point-observatories/>, at <http://www.ioccp.org/instruments-and-sensors>, or, in the future, at the OTC web page). Requirements are split into discrete data (based on GO-SHIP; Hood, 2010) and sensor-based data (Lorenzoni and Benway, 2013; Wanninkhof et al., 2013).

## 2.4.1 Requirements for ICOS marine Fixed Stations, discrete samples

**For both Class 1 and Class 2:**

- Following approved methods and SOP criteria (Dickson et al., 2007) when measuring two out of four carbonate parameters (DIC, TA, pH<sub>T</sub>, pCO<sub>2</sub>).
- Metadata<sup>9</sup>, including description of core parameter calibration, are complete.
- Proving regular calibration of the instruments.
- Perform an appropriate secondary QC (for example, GLODAPv2, SOCAT, alkalinity-salinity relationships, Multi Linear Regression (MLR)).

**Additionally,**

The difference between Class 1 and 2 is the inclusion of dissolved inorganic nutrients and discrete dissolved oxygen to Class 1, above the core parameters required by Class 2 (see Table 3a).

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

Type	Parameters	Frequency open /coastal	Criteria <sup>10</sup> open / coastal	Class open / coastal
Core	Two out of four: - DIC - TA - pCO <sub>2</sub> - pH <sub>T</sub>	> 1 yr <sup>-1</sup> /1 month <sup>-1</sup>	± 1.5 µmol kg <sup>-1</sup> ± 3 µmol kg <sup>-1</sup> ± 1µatm ± 0.005	1&2 1&2 1&2 1&2
Core	Sea temperature	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.002 °C	1&2
Core	Sea salinity - CTD - bottle samples	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.002 PSU ± 0.001 PSU	1&2
Core	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>11</sup> ± 1% ± 1-2% ± 1-3%	1 1 1
Core	Dissolved oxygen - Winkler - sensor	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.5% ± 2%	1 1 & 2
Core	Pressure (depth)	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 3 dbar	1 & 2
Desirable	Chlorophyll	- / 1 month <sup>-1</sup>	± 1%	
Desirable	DOC	- / 1 month <sup>-1</sup>	± 2%	
Desirable	CFC-11/ CFC-12 SF <sub>6</sub>	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 1 (<5)% ± 1.5 (<5)%	
Desirable	CH <sub>4</sub>	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 1% of atm. saturation	
Desirable	N <sub>2</sub> O	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 1% of atm. saturation	
Desirable	δ <sup>13</sup> C	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 0.04‰	
Desirable	Δ <sup>14</sup> C	> 1 yr <sup>-1</sup> / 1 month <sup>-1</sup>	± 5‰	
Desirable	CDOM (~300 nm)	- / 1 month <sup>-1</sup>	± 0.01 m <sup>-1</sup>	

Abbreviations: DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; CDOM=Chromophoric Dissolved Organic Matter; DOC=Dissolved Organic Carbon.

<sup>9</sup> Metadata description document, reference under development.

<sup>10</sup> The numbers refers to accuracy of measurements.

<sup>11</sup> The accuracy refer to samples without conservation. If conservation is used (chloroform is the preferred method) the accuracy is doubled.

## 2.4.2 Requirements for ICOS marine Fixed Stations, continuous/quasi-continuous measurements

**For both Class 1 and Class 2:**

- Following CO<sub>2</sub> sensor methods evaluated in Wanninkhof et al. (2013), recommendations in FixO3 handbook (<http://www.fixo3.eu/2016/07/07/best-practices-for-operations-at-fixed-point-observatories/>), and Lorenzoni and Benway (2013) for the core parameters.
- Metadata<sup>12</sup>, including description of core parameter 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, at minimum, discrete samples at the start and end of deployment.
- Pre- and post-visit calibration.
- Perform an appropriate secondary QC (for example, GLODAPv2, SOCAT, alkalinity-salinity relationships, Multi Linear Regression (MLR)).

**Additionally,**

The difference between Class 1 and 2 is the inclusion of dissolved oxygen and pH<sub>T</sub> to Class 1, above the core parameters required by Class 2 (see Table 3b).

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

Type	Parameters	Frequency open / coastal	Criteria <sup>13</sup> open / coastal	Class open / coastal
Core	pCO <sub>2</sub>	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 10 µatm <sup>14</sup>	1&2
Core	Sea temperature	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.02 °C	1&2
Core	Sea salinity	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.03	1&2
Core	Dissolved oxygen	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 2%	1
Core	pH <sub>T</sub>	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.01	1
Core	Pressure (depth)	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 3 dbar	1 & 2
Desirable	Atmospheric xCO <sub>2</sub>	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 1 µatm	
Desirable	Atmospheric pressure	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 1 µatm	
Desirable	Wind speed	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.01 m s <sup>-1</sup>	
Desirable	Chlorophyll	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 0.5 µg L <sup>-1</sup>	
Desirable	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>	± 10%	
Desirable	Atmospheric temperature	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>		
Desirable	CH <sub>4</sub>	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 1% of atm. saturation	
Desirable	N <sub>2</sub> O	> 1 day <sup>-1</sup> / > 3 day <sup>-1</sup>	± 1% of atm. saturation	
Desirable	CDOM	- / > 3 day <sup>-1</sup>	± 0.01 m <sup>-1</sup>	
Desirable	Irradiance	- / > 3 day <sup>-1</sup>		
Desirable	PAR	- / > 3 day <sup>-1</sup>		

Abbreviations: CDOM=Chromophoric Dissolved Organic Matter; PAR=Photosynthetically Active Radiation.

<sup>12</sup> Metadata description document, reference under development.

<sup>13</sup> The numbers refers to accuracy of measurements.

<sup>14</sup> According to results described in the note [calculation uncertainty of pCO2 from discrete samples of TA, DIC, and pH](#), and Wanninkhof et al. (2013).

## 2.5 Flux Towers

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 than 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. 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 flux towers.

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

### 2.5.1 Requirements for ICOS marine Flux Towers

#### For both Class 1 and Class 2:

- Metadata, including description of flux system calibration<sup>15</sup>, are complete. Details on data processing, required corrections and quality control should be included. Flux system 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 signal should be dried. For a non-dried system, station Pls should provide data showing this is not necessary.

#### Additionally,

- The difference between Class 1 and 2 is the inclusion of H<sub>2</sub>O flux, sensible heat flux, sea surface pCO<sub>2</sub>, sea temperature, and sea surface salinity to Class 1, above the core parameters required by Class 2 (see Table 4b).

**Table 4b.** Required parameters, frequency and criteria for ICOS flux towers.

Type	Parameter	Frequency	Criteria <sup>16</sup>	Class
Core	Atmospheric CO <sub>2</sub>	1h	± 1.5%	1&2
Core	CO <sub>2</sub> flux	1h	± 5%	1&2
Core	Atmospheric pressure	1h	± 0.1%	1&2
Core	Wind speed	1h	± 0.5 m s <sup>-1</sup>	1&2
Core	Wind direction	1h	± 6 °	1&2

Core	Atmospheric temperature	1h	$\pm 0.2^\circ$ ventilated <sup>17</sup>	1&2
Core	Atmospheric humidity	1h	$\pm 1\%$	1&2
Core	Friction velocity	1h	$\pm 5\%$	1&2
Core	H <sub>2</sub> O flux	1h	$\pm 5\%$	1
Core	Sensible heat flux	1h	$\pm 5\%$	1
Core	Sea surface pCO <sub>2</sub>	> 3 day <sup>-1</sup>	$\pm 5 \mu\text{atm}$	1
Core	Sea temperature	> 3 day <sup>-1</sup>	$\pm 0.02^\circ\text{C}$	1
Core	Sea salinity	> 3 day <sup>-1</sup>	$\pm 0.03 \text{ PSU}$	1
Desirable	Precipitation	1h	WMO guidelines	
Desirable	SW_in, LW_in	1h		
Desirable	PAR/PPFD	1h		
Desirable	Water-side mixed layer depth	> 1 day <sup>-1</sup>		
Desirable	Atmospheric mixed layer height	> 1 day <sup>-1</sup>		
Desirable	Significant wave height	1h		

Abbreviations: SW\_in=incoming short wave radiation; LW\_in=incoming long-wave radiation; PAR=Photosynthetically Active Radiation; PPFD= photosynthetic photon flux density.

<sup>15</sup> Metadata description document, reference under development.

<sup>16</sup> The numbers refers to accuracy of measurements.

<sup>17</sup> A flow thru system of air, to prevent radiation problems to the temperature signal. Necessary for high quality measurements of atmospheric temperature.

## Section 3: Metadata

### 3.1 Introduction

In addition to data submission, ICOS 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 ICOS OTC.

### 3.2 Checklist

- Appropriate Metadata Spreadsheet completed (either Carbon-VOS, Fixed Station, Repeat Section, or Flux Tower). The spreadsheet should either be provided to you or can be found on the ICOS OTC website.
- 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 parameters for the appropriate station type are provided in the data file submitted to QuinCe, as specified in 5.0 of Section 3: Metadata.
- Sensitivity (see definition of terms) of data file submitted to QuinCe meets minimum requirements for the appropriate station type, as specified in 5.0 of Section 3: Metadata.
- 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, there is a metadata sheet for each type of ICOS OTC station. The figures below depict the metadata sheets, however there is an excel spreadsheet corresponding to each type of station which should be filled out by each ICOS station during step 2 labelling.

			Physical Location	Date
Personal	First Name	First Name		
	Last Name	Last Name		
	Gender	Gender		
	Sex	Sex		
	Role	Role		
Vessel Information	Sticker Number	Sticker Number		
	Vessel Name	Vessel Name		
	Vessel IMO number	Vessel IMO number		
	Call Sign	Call Sign	Yes No Not App	
	IMO	IMO	Yes No Not App	
	Registration Number	Registration Number		
	Port	Port		
	Vessel Length	Vessel Length		
	Headbox Type	Headbox Type		
	Headbox Volume	Headbox Volume		
Underway pCO2 system Description	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
	Measurement Volume (m³)	Measurement Volume (m³)		
Other Sensors (ex. SG, G2 Optode, Conduct. (A-sic))	SG1	SG1		
	SG2	SG2		
	SG3	SG3		
	SG4	SG4		
	SG5	SG5		
	SG6	SG6		
	SG7	SG7		
	SG8	SG8		
	SG9	SG9		
	SG10	SG10		
Variable Information	Variable 1	Variable 1		
	Variable 2	Variable 2		
	Variable 3	Variable 3		
	Variable 4	Variable 4		
	Variable 5	Variable 5		
	Variable 6	Variable 6		
	Variable 7	Variable 7		
	Variable 8	Variable 8		
	Variable 9	Variable 9		
	Variable 10	Variable 10		
Other Info Fields	Deployment Water Date	Deployment Water Date		
	Deployment Water Time	Deployment Water Time		
	Deployment Water Depth	Deployment Water Depth		
	Deployment Water Latitude	Deployment Water Latitude		

Figure 1. Carbon-VOS Metadata sheet.

**Figure 2.** Repeat section metadata sheet.

**Figure 3.** Fixed Station metadata sheet.

## 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 (ex. 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 (ex. Gran titration)?
- pCO<sub>2</sub> data: Method description-What type of method is used (ex. Head space equilibration, membrane, dye, etc.)?
- pCO<sub>2</sub> description: Equilibrator Type-What type of equilibrator is used (ex. 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 (ex. 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. converting 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. converting 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 parameters previously described in Section 1: ICOS Marine Station Labelling step 2 with the preferred unit and the minimum resolution requirements for each parameter to be reported to ICOS 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 ICOS OTC requirements or by the standards within the field. Note that there are some additional parameters under the core parameters, which must be reported in addition to the core parameters.

**Table 5.** Carbon-VOS

Metadata Parameters	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	°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>18</sup>	μmol kg <sup>-1</sup>	0.1
Atmospheric Flask Samples:		
CO <sub>2</sub>	ppm	0.01
CH <sub>4</sub>	ppm	0.01
N <sub>2</sub> O	ppm	0.01
Chlorophyll fluorescence <sup>18</sup>	μg kg <sup>-1</sup>	0.01
Wind Speed (relative or absolute?)	m s <sup>-1</sup>	0.01
Wind Direction	Degrees	0.01
Atmospheric Temperature	°C	0.01
Sea Level Pressure	mbar	0.1
Dissolved Inorganic Nutrients (DIN) <sup>18</sup>		
Nitrate (NO <sub>3</sub> <sup>-</sup> )	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
δ <sup>13</sup> C	‰	0.01
CH <sub>4</sub>	ppb	0.1
N <sub>2</sub> O <sup>1</sup>	nmol kg <sup>-1</sup>	0.01

Abbreviations: DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; CDOM=Chromophoric Dissolved Organic Matter; DOC=Dissolved Organic Carbon.

<sup>18</sup> Equations to determine units should be included in metadata (ex. Density equations, etc.)

**Table 6.** Repeat Sections

Metadata Parameters	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>	$\mu\text{mol kg}^{-1}$	0.1
pH <sub>T</sub>		0.01
Dissolved Inorganic Carbon (DIC) <sup>19</sup>	$\mu\text{mol kg}^{-1}$	0.1
Seawater pCO <sub>2</sub>	ppm	0.01
Sea temperature	°C	0.001
Pressure (Depth)	dbar	0.1
Sea salinity (SSS)	PSU	0.001
Dissolved Inorganic Nutrients (DIN) <sup>19</sup>		
Nitrate (NO <sub>3</sub> -)	$\mu\text{mol kg}^{-1}$	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> )	$\mu\text{mol kg}^{-1}$	0.01
Silicate (Si(OH) <sub>4</sub> ), SiO <sub>4</sub> <sup>4-</sup> , etc.)	$\mu\text{mol kg}^{-1}$	0.01
Dissolved Oxygen (DO) <sup>19</sup>	$\mu\text{mol kg}^{-1}$	0.1
$\delta^{13}\text{C}$	‰	0.01
$\Delta^{14}\text{C}$	‰	0.01
CH <sub>4</sub>	$\text{mmol kg}^{-1}$	0.1
N <sub>2</sub> O*	$\text{nmol kg}^{-1}$	0.01
CFC-11 <sup>19</sup>	$\text{pmol kg}^{-1}$	0.01
CFC-12 <sup>19</sup>	$\text{pmol kg}^{-1}$	0.01
SF <sub>6</sub> <sup>19</sup>	$\text{fmol kg}^{-1}$	0.01

<sup>19</sup> Equations to determine units should be included in metadata (ex. Density equations, etc.)

**Table 7.** Fixed Stations

Metadata Parameters	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>20</sup>	$\mu\text{mol kg}^{-1}$	0.1
pH <sub>T</sub>		0.01
Dissolved Inorganic Carbon (DIC) <sup>20</sup>	$\mu\text{mol kg}^{-1}$	0.1
Seawater fCO <sub>2</sub>	ppm	0.1
Sea Temperature	°C	0.001/0.01 <sup>21</sup>
Pressure (Depth)	dbar	0.1
Sea Salinity (SSS)	PSU	0.001/0.01 <sup>22</sup>
Dissolved Inorganic Nutrients (DIN) <sup>20</sup>		
Nitrate (NO <sub>3</sub> -)	$\mu\text{mol kg}^{-1}$	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> )	$\mu\text{mol kg}^{-1}$	0.01
Silicate (Si(OH) <sub>4</sub> ), SiO <sub>4</sub> <sup>4-</sup> , etc.)	$\mu\text{mol kg}^{-1}$	0.01

CFC-11	$\text{pmol kg}^{-1}$	0.1
CFC-12	ppt	0.1
SF <sub>6</sub>	ppt	0.1
Dissolved Oxygen (DO) <sup>20</sup>	$\mu\text{mol kg}^{-1}$	0.1
DOC	$\mu\text{mol kg}^{-1}$	
CDOM		
$\delta^{13}\text{C}$	$\text{\textperthousand}$	0.01
$\Delta^{14}\text{C}$	$\text{\textperthousand}$	0.01
CH <sub>4</sub>	$\text{mmol kg}^{-1}$	0.1
N <sub>2</sub> O <sup>20</sup>	$\text{nmol kg}^{-1}$	0.01
Atmospheric Temperature	$^{\circ}\text{C}$	0.01
Irradiance		
Photosynthetically Active Radiation (PAR)	Einstein $\text{m}^{-2} \text{ day}^{-1}$	

Abbreviations: DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; CDOM=Chromophoric Dissolved Organic Matter; DOC=Dissolved Organic Carbon.

<sup>20</sup> Equations to determine units should be included in metadata (ex. Density equations, etc.)

<sup>21</sup> Resolution of 0.001 C is required for ship board measurements and 0.01 C for buoys/moorings.

<sup>22</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 ICOS 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

### 4.1 Introduction

The station labelling process for new members of the ICOS 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.

ICOS 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 ICOS 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 ICOS 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 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>23</sup>	Spike <sup>24</sup>
Intake 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
Δ T <sup>25</sup> (°C)	0 : 1.5	2	0.005 <sup>26</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>23</sup> Outliers are defined as any value outside *n* standard deviations from the mean value within a single data set from the station.

<sup>24</sup> Spikes are measured as the delta between two consecutive measurements. The delta is defined as *n* units per minute.

<sup>25</sup> The absolute difference between the Intake Temperature and Equilibrator Temperature.

<sup>26</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>127</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>27</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 ΔT 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 2016 or 2015 data fields (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>

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<sup>127</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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