ICOS MARINE STATION LABELLING STEP 2

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ICOS Marine Station Labelling step 2

Introduction

The aim of ICOS marine stations is to provide harmonized and high precision scientific carbon data to be used to quantify carbon exchange 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:

1st step: station construction and formal application via the national ICOS representative to Ocean Thematic Centre (OTC). The applicant need to confirm long term commitment of the necessary station resources (man power, equipment, consumables, ICOS contributions). The station also needs to be approved by the national stakeholder.

2nd step: evaluation in relation to ICOS data protocols, quality control, and data flow routines. The current document is one of these and will be subject for revision every 2-3 years.

3rd step: a formal decision to include the station into the ICOS Monitoring System Assembly (ICOS MSA) will be made by the General Assembly based on recommendation from the OTC and 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 area)
3. Fixed Stations (open 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 measurements (number depending of station category), Class 2 marine station operates only a subset of these (see Table 0 for an overview). The requirements for data quality, however, are the same for ICOS Class 1 and Class 2 stations. More information about required parameters, frequency of measurements, and criteria to become a Class 1 and Class 2 stations are included below.

Table 0. Overview of variables collected from different marine ICOS categories (Class 1 and Class 2) CHECK WOCE.

Parameters /Name	Carbon-VOS (sea surface)	Repeat Sections (water column)	Fixed Stations, discrete (water column)	Fixed Stations, continuous (water column)	Flux Towers (atmospheric / sea interface)
Sea fCO_2	1&2	1&2	1&2	1&2	1
Atmospheric xCO_2	1	NR	NR	Desirable	1&2
Sea temperature	1&2	1&2	1&2	1&2	1
Water vapour pressure	1&2	NR	NR	NR	1&2
Equilibrator pressure	1&2	NR	NR	NR	NR
Equilibrator temperature	1&2	NR	NR	NR	NR
T difference (equil-sea)	1&2	NR	NR	NR	NR
Salinity	1	1&2	1&2	1&2	1
Dissolved oxygen	Desirable	Desirable	Desirable	1	NR
Atmospheric flask samples for CO_2, CH_4, N_2O	Desirable	NR	NR	NR	NR
Chlorophyll-fluorescence	Desirable	Desirable	Desirable	Desirable	NR
Wind speed/Air temp/Sea level pressure	Desirable	NR	NR	Desirable	1&2
Dissolved inorganic nutrients	Desirable	1	1	Desirable	NR
pH	Desirable	1&2	1&2	Desirable	NR

DIC	Desirable	1&2	1&2	Desirable (calibration)	NR
TA	Desirable	1&2	1&2	Desirable (calibration)	NR
$\delta\ ^{13}C$	Desirable	Desirable	Desirable	NR	NR
$\Delta\ ^{14}C$	NR	Desirable	Desirable	NR	NR
CH_4	Desirable	Desirable	Desirable	Desirable	NR
N_2O	Desirable	Desirable	Desirable	Desirable	NR
CFC-11, CFC-12	NR	1&2	1&2	NR	NR
SF_6	NR	1&2	1&2	NR	NR
CDOM	NR	NR	Desirable	Desirable	NR
DOC	NR	NR	Desirable	NR	NR
Irradiance	NR	NR	NR	Desirable	NR
PAR	NR	NR	NR	Desirable	Desirable
CO_2 flux	Calculated	NR	NR	NR	1&2
Wind direction	NR	NR	NR	NR	1&2
Sensible heat flux	NR	NR	NR	NR	1&2
H2O flux	NR	NR	NR	NR	1&2
Friction velocity	NR	NR	NR	NR	1&2
SW_in, LW_in	NR	NR	NR	NR	Desirable
PPFD	NR	NR	NR	NR	Desirable
Precipitation	NR	NR	NR	NR	Desirable

NR=not relevant

1. Carbon-VOS

On Carbon-VOS, quasi-continuous measurements are performed of CO_2 in the surface ocean (4-10 meters of water depth) and often, but not always, in the lower atmosphere (approx. 10 m above sea level), giving final surface ocean fCO_2 data at a frequency of at least once per hour. Besides measuring CO_2, simultaneous observations of temperature, pressure, and salinity 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_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 or a gas chromatograph. Measurements can also be obtained by alternative flow-thru sensors (defined as being deployable sub-surface; Wanninkhof et al., 2013), yet installed on-board a Carbon-VOS.

Requirements for ICOS marine Carbon-VOS MSA are:

For both Class 1 and Class 2:

Following approved method and SOP criteria (Dickson et al., 2007), including:

- measuring xCO_2 or fCO_2 and not calculating fCO_2,
- making quasi-continuous CO_2 measurements, not analyses of discrete samples,
- utilising a flow-through headspace equilibrator system measuring xCO_2 in headspace gas,
- proving calibration by regularly measuring at least two non-zero gas standards traceable to WMO standards,
- metadata, including description of core parameter calibration and secondary quality control, are complete, and
- second-level 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 are that for Class 1 sea surface salinity and atmospheric CO_2 are added to 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	Class
Core	Sea surface fCO_2	Quasi-continuous[1]	± 2 μatm	1&2
Core	Intake temperature	Continuous	± 0.05 °C	1&2
Core	Water vapour pressure[2]	Continuous	± 0.5 hPa	1&2
Core	Equilibrator pressure[3]	Continuous	± 2.0 hPa	1&2
Core	Equilibrator temperature[3]	Continuous	± 0.05 °C	1&2
Core	Delta-T[4] (difference between intake and equilibrator temperature or sensor)	Continuous	< 1.5 °C < 3 °C	1&2 1&2
Core	Sea surface salinity	Continuous	± 0.02	1
Core	Atmospheric xCO_2	Quasi-continuous	± 1 μatm	1
Desirable	Dissolved oxygen	Continuous	± 1%	
Desirable	Atmospheric flask samples for CO_2, CH_4, N_2O	Discrete	As determined by the ICOS FCL	
Desirable	Chlorophyll-fluorescence	Continuous	2%	
Desirable	Wind speed/Air temp/Sea level pressure	Continuous or discrete		
Desirable	Dissolved inorganic nutrients[5]	Discrete	± 1%	
Desirable	pH	Continuous	± 0.01	
Desirable	DIC	Discrete	± 1.5 μmol kg^{-1}	
Desirable	TA	Discrete	± 3 μmol kg^{-1}	
Desirable	$\delta\ ^{13}C$	Discrete	± 0.1‰	
Desirable	CH_4	Discrete/ continuous	± 1% of atm. saturation	
Desirable	N_2O	Discrete/ continuous	± 1% of atm. saturation	

DIC=Dissolved Inorganic Carbon; AT=Total Alkalinity; FCL=Flask and Calibration Laboratory.

[1] No Carbon-VOS measuring system can truly be continuous, as regular gas standards need to be measured; hence the term quasi-continuous is used here for atmospheric and sea surface fCO_2.

[2] If the headspace gas analysed is not dried completely prior to measurement.

[3] If a continuous flow-through equilibrator system is used.

[4] Delta-T criteria are < 1 °C for measurements at low and mid- latitudes; when a Carbon-VOS is close to the ice-edge, this is relaxed to < 3 °C.

[5] Dissolved inorganic nutrients=NO_3, PO_4, SiO_2.

2. Repeat Sections

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 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).

Requirements for ICOS marine Repeat Sections are:

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, pCO_2).
- Metadata, including description of core parameter calibration and secondary quality control, are complete.

- Proving calibration by regular use of reference material for carbon analysis (Dickson et al., 2007).
- Covering full depth of the water column.
- Second-level quality control deemed acceptable, equivalent to 2nd QC routines in GLODAPv2 (Olsen et al., 2016).

Additionally,
The difference between Class 1 and 2 are the addition of transient tracers to 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[6]	Class
Core	Two out of four: DIC TA pCO_2 pH	> 1 decade^{-1}	 ± 1.5 (< 4) μmol kg^{-1} ± 3 (< 6) μmol kg^{-1} ± 1 (<3) μatm ± 0.005 (<0.005)	 1&2 1&2 1&2 1&2
Core	Sea temperature	> 1 decade^{-1}	± 0.002 °C	1&2
Core	Sea salinity	> 1 decade^{-1}	± 0.003 (<0.005)	1&2
Core	Dissolved inorganic nutrients[7]	> 1 decade^{-1}	± 1 (<2)%	1&2
Core	CFC-11/ CFC-12 SF_6	> 1 decade^{-1}	± 1 (<5)% ± 1.5 (<5)%	1 1
Desirable	Dissolved oxygen - Winkler - CTD sensor	> 1 decade^{-1}	 ± 0.5 (<1)% ± 1%	
Desirable	CH_4	> 1 decade^{-1}	± 1% of atm. saturation	
Desirable	N_2O	> 1 decade^{-1}	± 1% of atm. saturation	
Desirable	$\delta\ ^{13}C$	> 1 decade^{-1}	± 0.04‰	
Desirable	$\Delta\ ^{14}C$	> 1 decade^{-1}	± 5‰	

DIC=Dissolved Inorganic Carbon; AT=Total Alkalinity; CFC=chlorofluorocarbon; SF_6=sulphur hexafluoride.
[6] The two numbers refers to within cruise precision and, in parenthesis, between cruises bias. The numbers within parenthesis are the maximum acceptable bias following the 2nd level QC in GLODAP; this includes the bias after recommended adjustments in the GLODAP routines.
[7] Dissolved inorganic nutrients=NO_3, PO_4, SiO_2.

3. Fixed stations

Fixed Stations usually consist of a surface buoy performing carbon measurements in the surface ocean and in lower atmosphere and/or a sub-surface mooring covering parts of or full water depth. Fixed Stations can also be ship based. The stations are situated in open ocean or in coastal waters. Distinction between coastal and open ocean are connected to habitats, light penetration, nutrient availability, processes, e.g. dense water formation (shelf and deep open ocean), tidal fronts and river runoff in coastal waters (Wollast, 1998) and it is for the station PI to define if the station is coastal or open ocean. It is acknowledged that the environmental variability is higher in coastal waters than in open ocean, however, the criteria is related to what is achieved by the analytical method.

For fixed stations, primarily, inorganic carbon parameters and hydrography are measured, but a wide range of measurements are 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 (reference will be included), or at 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).

Requirements for ICOS marine Fixed Stations, discrete samples, are:

For both Class 1 and Class 2:

- Following approved methods and SOP criteria (Dickson et al., 2007) with coulometric or IR detection when measuring two out of four carbonate parameters (DIC, TA, pH, pCO_2).
- Metadata, including description of core parameter calibration and secondary quality control, are complete.
- Proving calibration by regular use of reference material for carbon analysis (Dickson et al., 2007).
- Perform an appropriate secondary QC (GLODAPv2, SOCAT, alkalinity-salinity relationships, Multi Linear Regression (MLR), etc.).

Additionally,

The difference between Class 1 and 2 are the addition of dissolved inorganic nutrients to 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. Note that some of the desired parameters are more relevant for open ocean, while others are more relevant for coastal waters.

Type	**Parameters**	**Frequency** open /coastal	**Criteria**[8] open / coastal	**Class** open / coastal
Core	Two out of four: DIC TA pCO_2 pH	> 1 yr^{-1}/monthly	 ± 1.5 / ± 1.5 μmol kg^{-1} ± 3 / ± 3 μmol kg^{-1} ± 1 / ± 1μatm ± 0.005 / ± 0.005	 1&2 / 1&2 1&2 / 1&2 1&2 / 1&2 1&1 / 1&2
Core	Sea temperature	> 1 yr^{-1}/monthly	± 0.02 / ± 0.02 °C	1&2 / 1&2
Core	Sea salinity	> 1 yr^{-1}/monthly	± 0.03/ ± 0.03	1&2 / 1&2
Core	Dissolved inorganic nutrients[9]	> 1 yr^{-1}/monthly	± 1 / ± 1%	1 /1
Desirable	Dissolved oxygen	> 1 yr^{-1}/monthly	± 1 / ± 1%	
Desirable	CFC-11/ CFC-12 SF_6	> 1 $decade^{-1}$	± 1 (<5)% ± 1.5 (<5)%	
Desirable	CH_4	> 1 yr^{-1}/monthly	± 1 / ± 1% of atm. saturation	
Desirable	N_2O	> 1 yr^{-1}/monthly	± 1 / ± 1% of atm. saturation	
Desirable	$\delta^{13}C$	> 1 yr^{-1}/monthly	± 0.04 / ± 0.04‰	
Desirable	$\Delta^{14}C$	> 1 yr^{-1}/monthly	± 5‰	
Desirable	CDOM (~300 nm)	- /monthly	± 0.01 m^{-1}	
Desirable	Chlorophyll	- /monthly		
Desirable	DOC	- /monthly		

DIC=Dissolved Inorganic Carbon; AT=Total Alkalinity; CDOM=Chromophoric Dissolved Organic Matter; DOC=Dissolved Organic Carbon.

[8] The numbers refers to precision of measurements.

[9] Dissolved inorganic nutrients=NO_3, PO_4, SiO_2.

Requirements for ICOS marine Fixed Stations, continuous/quasi-continuous measurements, are:

For both Class 1 and Class 2:

- Following CO_2 sensor methods evaluated in Wanninkhof et al. (2013) and recommendations in FixO3 handbook (reference will be included) and Lorenzoni and Benway (2013) for the core parameters.

- Metadata, including description of core parameter calibration procedure and secondary quality control, are complete.
- Perform an appropriate secondary QC (GLODAPv2, SOCAT, alkalinity-salinity relationships, Multi Linear Regression (MLR), etc.).
- Proving in situ calibration of pCO_2 by regularly measuring at least one non-zero gas standard traceable to WMO standards, or frequently validation of alternative calibration (e.g., pre- and post-visit calibration).

Additionally,
The difference between Class 1 and 2 are the addition of dissolved oxygen to 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. Note that some of the desired parameters are more relevant for open ocean, while others are more relevant for coastal waters.

Type	**Parameters**	**Frequency** open / coastal	**Criteria** open / coastal	**Class** open / coastal
Core	pCO_2	> 1 day^{-1}/ > 3 day^{-1}	± 5 μatm	1&2 / 1&2
Core	Sea temperature	> 1 day^{-1}/ > 3 day^{-1}	± 0.02 °C	1&2 / 1&2
Core	Sea salinity	> 1 day^{-1}/ > 3 day^{-1}	± 0.03	1&2 / 1&2
Core	Dissolved oxygen[10]	> 1 day^{-1}/ > 3 day^{-1}	± 1%	1 / 1
Desirable	pH	> 1 day^{-1}/ > 3 day^{-1}	± 0.01	
Desirable	Dissolved inorganic nutrients[11]	> 1 day^{-1}/ > 3 day^{-1}	± 1%	
Desirable	Atmospheric pCO_2	> 1 day^{-1}/ > 3 day^{-1}	± 1 μatm	
Desirable	Wind speed/Air temp/Atm pressure	Continuously/ continuously		
Desirable	CH_4	> 1 day^{-1}/ > 3 day^{-1}	± 1% of atm. saturation	
Desirable	N_2O	> 1 day^{-1}/ > 3 day^{-1}	± 1% of atm. saturation	
Desirable	Chlorophyll	> 1 day^{-1}/ > 3 day^{-1}		
Desirable	CDOM	- / > 3 day^{-1}	± 0.01 m^{-1}	
Desirable	Irradiance	- / > 3 day^{-1}		
Desirable	PAR	- / > 3 day^{-1}		

CDOM=Chromophoric Dissolved Organic Matter; PAR=Photosynthetically Active Radiation.
[10] Dissolved oxygen is set to 'core' due to few available nutrient sensors.
[11] Dissolved inorganic nutrients=NO_3, PO_4, SiO_2.

4. Flux towers

Micrometeorological measurements using Eddy Covariance (EC) data are the most direct measurements of vertical fluxes, however the stations and data need careful quality control for reliable estimates. EC data gives direct estimate of the flux for the representative footprint area, but can also be used to develop/validate the mechanisms controlling the exchange and the transfer velocity. The prerequisites for EC measurements in marine environments are somewhat different compared to terrestrial conditions and thus the labelling need to be done specifically for marine environments. As the fluxes are generally smaller in marine conditions higher requirements are needed for instrument accuracy and quality control of the data. Marine environments also include high humidity, salinity and concern needs to be taken for sea spray on instrumentation. Flux towers are dominantly situated on shores or near-shore regions, with a more or less dominating land influence. It is suggested to differentiate the data concerning what level of land influence one can expect (see table 4a). Group 1: Flux footprint represent open sea condition, land influence 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, highly active in terms of carbon cycle. Flux measurements can also be performed on ships, and careful analysis is then required concerning motion correction and flow distortion.

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

Requirements for ICOS Flux tower stations:

For both Class 1 and Class 2:

- Stations should be visited on a regular basis (monthly) and instrumentation cleaned.
- For stations with high salinity and large amounts of sea spray, CO_2 flux-system should be dried.

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

Type	Parameter	Frequency	Criteria	Class
Core	Atmospheric CO_2	1h	± 1.5%	1&2
Core	CO_2 flux	1h	± 5%	1&2
Core	Atmospheric pressure	1h	± 0.1%	1&2
Core	Wind speed	1h	± 0.5 m/s	1&2
Core	Wind direction	1h	± 6 °	1&2
Core	Atmospheric temperature	1h	± 0.2 ° ventilated	1&2
Core	Atmospheric humidity	1h	± 1%	1&2
Core	Friction velocity	1h	± 5%	1&2
Core	H_2O flux	1h	± 5%	1
Core	Sensible heat flux	1h	± 5%	1
Core	Sea surface pCO_2	> 3 day^{-1}	± 5 μatm	1
Core	Sea temperature	> 3 day^{-1}	± 0.02 °C	1
Core	Sea salinity	> 3 day^{-1}	± 0.03	1
Desirable	SW_in, LW_in	1h		
Desirable	PAR/PPFD	1h		
Desirable	Precipitation	1h	WMO guidelines	
Desirable	Water-side mixed layer depth	> 1 day^{-1}		
Desirable	Atmospheric mixed layer depth	> 1 day^{-1}		
Desirable	Significant wave height	1h		

SW_in incoming short wave radiation; LW_in=incoming long-wave radiation; PAR= Photosynthetically Active Radiation; PPFD= photosynthetic photon flux density.

Documents/references:

Dickson, A.G., C.L. Sabine, and J.R. Christian (Eds.), 2007, Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp. (*Recommended standard operating procedures, incl. quality assurance, accuracy).*

FixO3 handbook of best practise (full reference will be inserted when it is released to the public).

Hood, M., 2010, Introduction to the collection of expert reports and guidelines. In: The GO-SHIP Repeat Hydrography Manual, IOCCP Report No. 14, ICPO Publication Series No. 134, Version 1.

Lorenzoni, L., Benway, H. M. (Editors), 2013, Report of *Global intercomparability in a changing ocean: An international time-series methods workshop*, Bermuda, Nov. 28-30, 2012, Ocean Carbon and Biogeochemistry (OCB) Program and International Ocean Carbon Coordination Project (IOCCP), 60 pp. (*Recommendations of shipboard sampling order, methodological protocols, best practice of discrete and in-line measurements, methods evaluation, precision).*

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