# 2018 ICOS OTC Workshop

7-9 March 2018

General Oceanics-KM Contros-ICOS OTC

# General Oceanics Underway pCO<sub>2</sub> Uncertainty and Offset Analyses

**Charles Roman Battisti** 

Chief Engineer, ICOS OTC

Geophysical Institute, UiB, Norway

ICOS Ocean Thematic Centre Be

Bergen, Norway | otc.icos-cp.eu/

#### Equations

#### From Pierrot et al. 2009 $(pCO_2)_{equT}^{wet} = (xCO_2)_{equT}^{dry} [P_{equ} - pH_2O(CO_2, equT)]$ (1) $(fCO_2)_{equT}^{wet} = (pCO_2)_{equT}^{wet} * exp\left\{\frac{\left|B(CO_2, equT) + 2\left(1 - (xCO_2)_{equT}^{dry}\right)^2 \delta(CO_2, equT)\right| P_{atm}}{R * equT}\right\}$ (2) $(fCO_2)_{SST}^{wet} = (fCO_2)_{equT}^{wet} * exp\{0.0423(\underline{SST} - equT)\}$ (3) $B(CO_2, equT) = -1636.75 + 12.0408 * equT - 3.27957 * 10^{-2} * equT^2 + 3.16528 * 10^{-5} * equT^3$ (4) $\delta(CO_2, equT) = 57.7 - 0.118 * equT$ (5) $pH_2O(CO_2, equT) = exp\left\{24.4543 - 67.4509\left(\frac{100}{equT}\right) - 4.8489ln\left(\frac{equT}{100}\right) - 6.8489ln\left(\frac{equT}{100}\right)\right\}$

#### Parameters

Parameter	Range	
P <sub>equ</sub> and P <sub>atm</sub>	1 atm	
equT	0 to 40 °C	
ΔΤ	0 to -2 °C	
xCO <sub>2</sub>	200 to 800 ppm	
S	35 PSU	
Standard Gases	250, 450, 600, 800 ppm	

Parameter	High Uncertainty	Low Uncertainty		
$\Delta P_{equ}$ and $\Delta P_{atm}$	2*10 <sup>-3</sup> atm	5*10 <sup>-4</sup> atm		
$\Delta equT$ and $\Delta SST$	0.05 °C	0.02 °C		
$\Delta xCO_2 = \Delta LI - COR$	0.2 ppm	-		
ΔS	0.5 PSU	-		
∆Standard Gases	0.27 ppm	0.15 ppm		

#### Equations

$$(pCO_{2})_{equT}^{wet} = ((xCO_{2})_{equT}^{dry} \pm \Delta xCO_{2}) [(P_{equ} \pm \Delta P_{equ}) - pH_{2}O(CO_{2}, equT)]$$

$$(fCO_{2})_{equT}^{wet} = (pCO_{2})_{equT}^{wet} * exp \left\{ \frac{\left[ B(CO_{2}, equT) + 2\left(1 - \left((xCO_{2})_{equT}^{dry} \pm \Delta xCO_{2}\right)\right)^{2}\delta(CO_{2}, equT) \right] (P_{atm} \pm \Delta P_{atm})}{R*(equT \pm \Delta equT)} \right\}$$

$$(fCO_{2})_{SST}^{wet} = (fCO_{2})_{equT}^{wet} * exp\{0.0423((SST \pm \Delta SST) - (equT \pm \Delta equT))\}$$

$$(3)$$

$$B(CO_{2}, equT) = -1636.75 + 12.0408 * (equT \pm \Delta equT) - 3.27957 * 10^{-2} * (equT \pm \Delta equT)^{2} + 3.16528 * 10^{-5} * (equT \pm \Delta equT)^{3}$$
(4)  

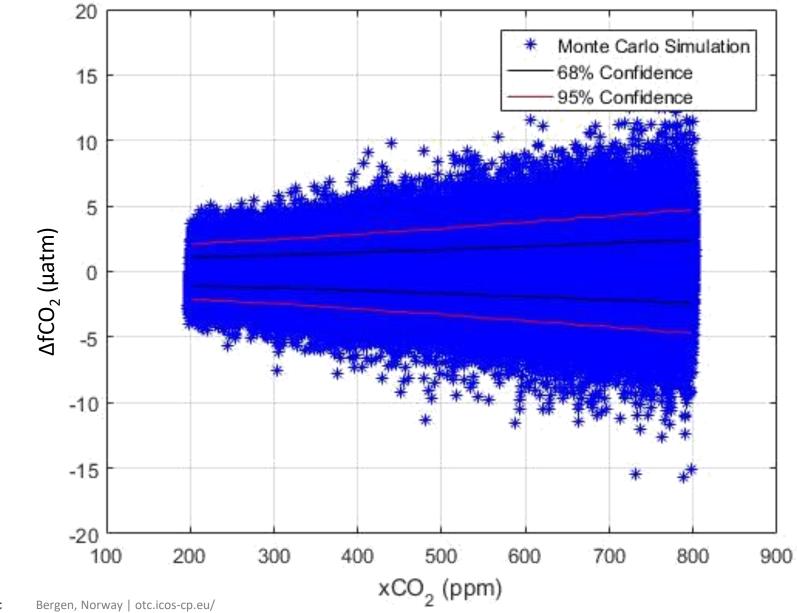
$$\delta(CO_{2}, equT) = 57.7 - 0.118 * (equT \pm \Delta equT)$$
(5)  

$$pH_{2}O(CO_{2}, equT) = exp \left\{ 24.4543 - 67.4509 \left( \frac{100}{equT \pm \Delta equT} \right) - 4.8489 ln \left( \frac{equT \pm \Delta equT}{100} \right) - 0.000544 * (S \pm \Delta S) \right\}$$
(6)

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#### Method

- Monte Carlo
  - Randomly selected uncertainty using a Gaussian Distribution
  - Compute  $(fCO_2)_{SST}^{wet}$  with and without uncertainty
    - $\Delta(fCO_2)_{SST}^{wet} = ((fCO_2)_{SST}^{wet})_{with \ Uncertainty} ((fCO_2)_{SST}^{wet})_{without \ Uncertainty}$
  - Repeat 500000 times
    - $\Delta(fCO_2)_{SST}^{wet} = Standard Deviation of \{((fCO_2)_{SST}^{wet})_{with Uncertainty}$

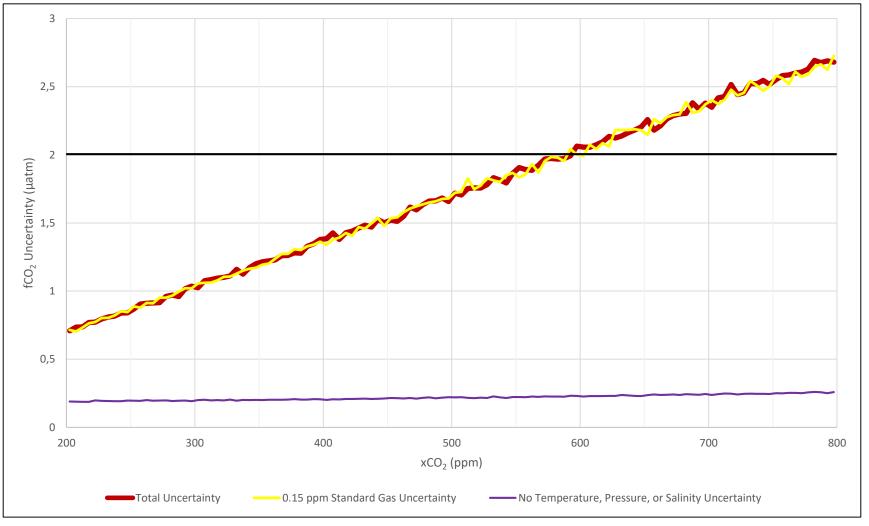




••• Ocean Thematic Centre

ICOS

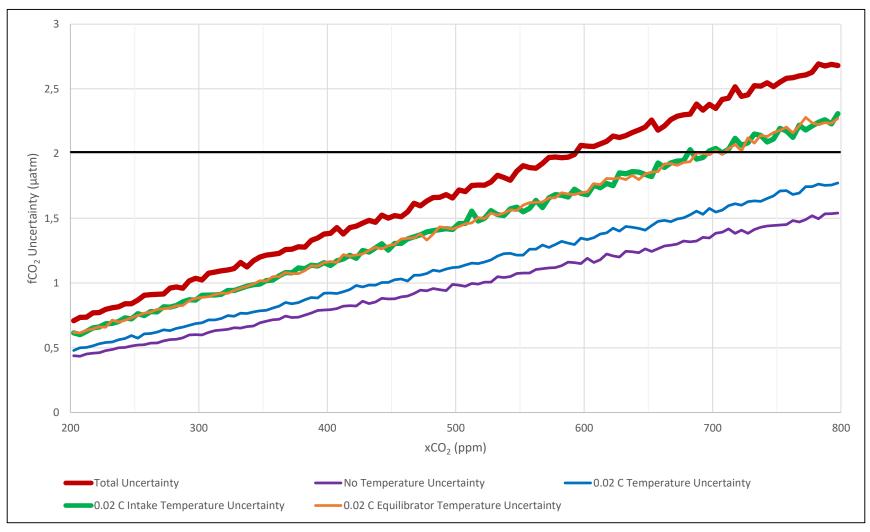
#### Results



ICOS Ocean Thematic Centre

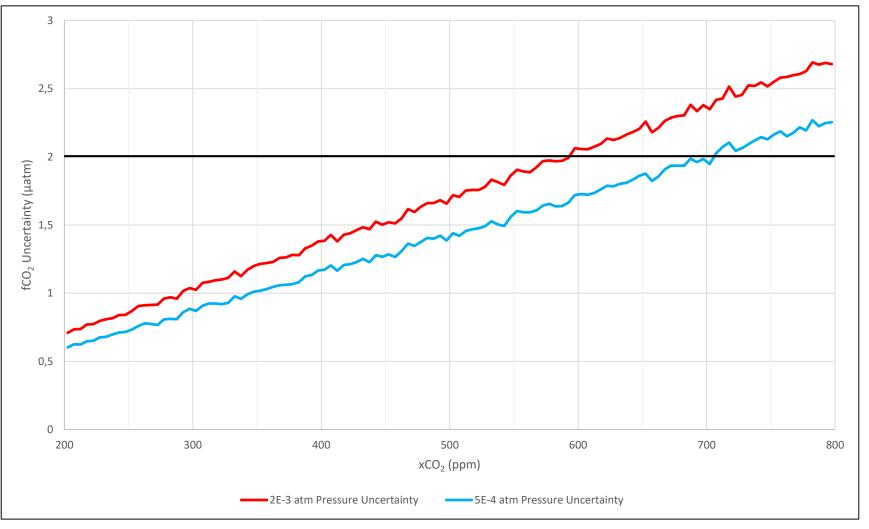
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#### Results



ICOS Ocean Thematic Centre

#### Results



ICOS Ocean Thematic Centre

#### Continued Work

$$(pCO_{2})_{equT}^{wet} = (xCO_{2})_{equT}^{dry} [P_{equ} - pH_{2}O(CO_{2}, equT)]$$

$$(fCO_{2})_{equT}^{wet} = (pCO_{2})_{equT}^{wet} * exp \left\{ \frac{\left[ B(CO_{2}, equT) + 2(1 - (xCO_{2})_{equT}^{dry})^{2}\delta(CO_{2}, equT) \right] P_{atm}}{R * equT} \right\}$$

 $(fCO_2)_{SST}^{wet} = (fCO_2)_{equT}^{wet} * exp\{(0.0423 \pm 0.0002)(SST - equT)\}$ 

(SD, Takahashi et al 1993)

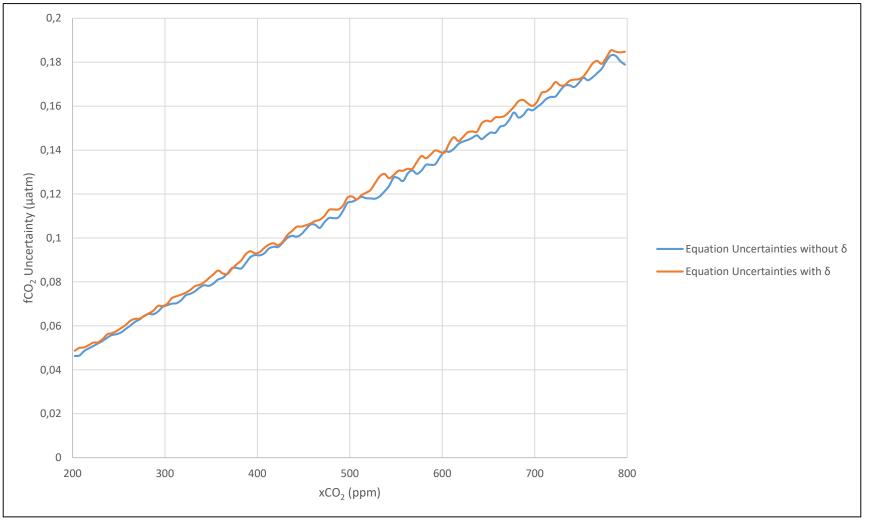
$$B(CO_{2}, equT) = -1636.75 + 12.0408 * equT - 3.27957 * 10^{-2} * equT^{2} + 3.16528 * 10^{-5} * equT^{3} \pm 2.314$$
 (SD, Sengers et al 1971)  

$$\delta(CO_{2}, equT) = 57.7 - 0.118 * equT \pm 3\%$$
 (Estimate)  

$$pH_{2}O(CO_{2}, equT) = exp\left\{24.4543 - 67.4509\left(\frac{100}{equT}\right) - 4.8489ln\left(\frac{equT}{100}\right) - 0.000544 * S\right\} \pm 0.015\%$$
 (SE, Weiss and Price 1980)

 
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#### Preliminary Results



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## Standard Gas and Pressure Offset Analysis

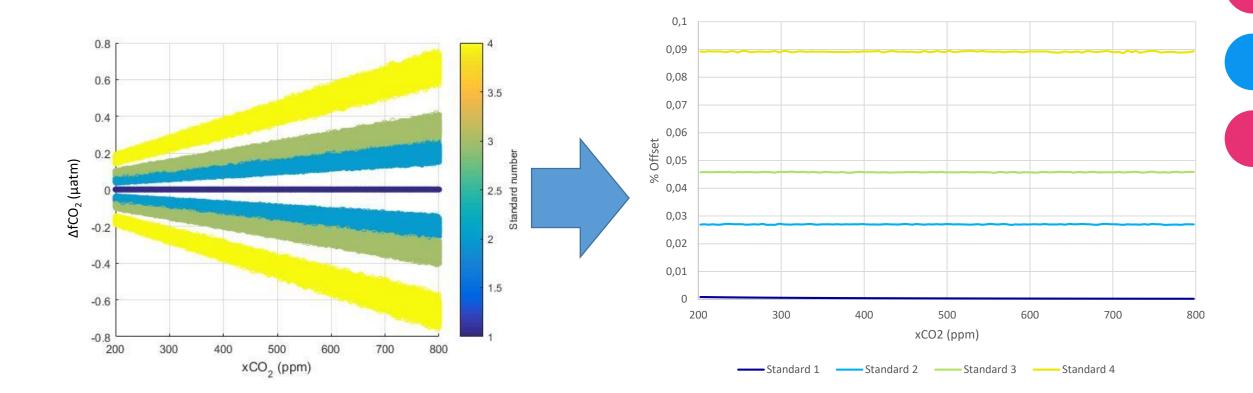
#### **Equations and Method**

- Same equations as previous
- Offset one Standard Gas or Pressure measurement by specified amount
- Compute  $(fCO_2)_{SST}^{wet}$  with and without offset
  - $Offset = ((fCO_2)_{SST}^{wet})_{with Offset} ((fCO_2)_{SST}^{wet})_{without Offset}$
- Repeat over 500000 cycles

#### **Data Ranges**

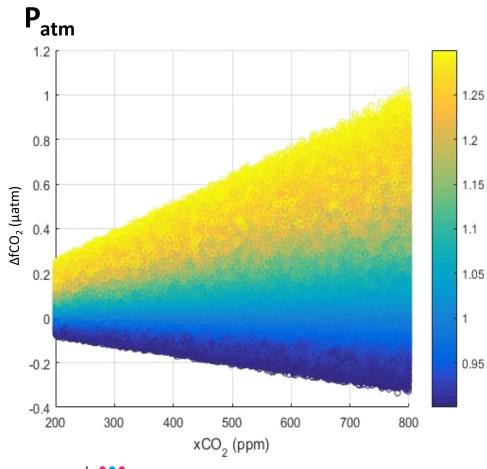
	Parameter		Range		
	P <sub>equ</sub> and P <sub>atm</sub>		1 atm		
	equT		0 to 40 °C		
	ΔΤ		0 to -2 °C		
	xCO <sub>2</sub>		200 to 800 ppm		
	S		35 PSU		
	Standard Gas 1 Standard Gas 2 Standard Gas 3 Standard Gas 4		0 ppm		
			200 to 300 ppm		
			350 to 500 ppm		
			800 to 850 ppm		
Ра	rameter	Lo	w Offset	High Of	fset
	P <sub>atm</sub>	0.9 atm		1.3 atm	
	P <sub>equ</sub>	0.99 atm		1.01 atm	
Stan	dard Gas 1	0 ppm		1 ppr	n
Stan	dard Gases	-1 ppm		1 ppm	

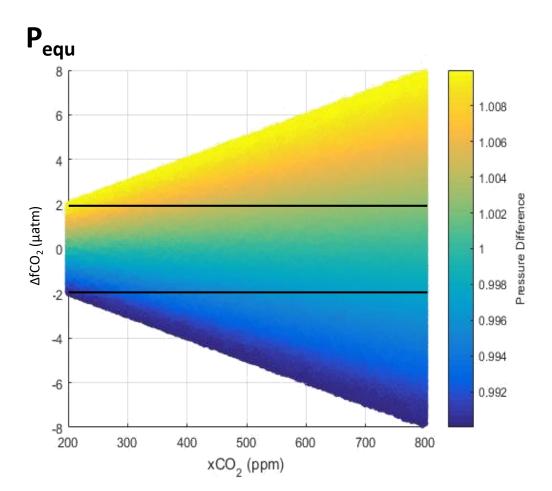
#### Standard Gases



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#### Pressure Offset





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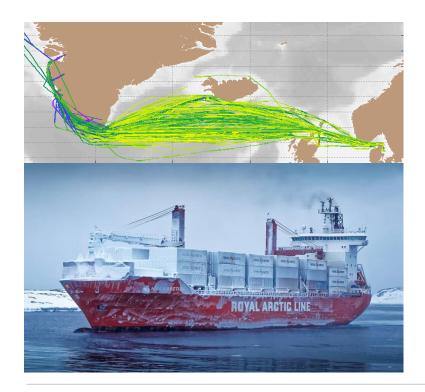
Bergen, Norway | otc.icos-cp.eu/

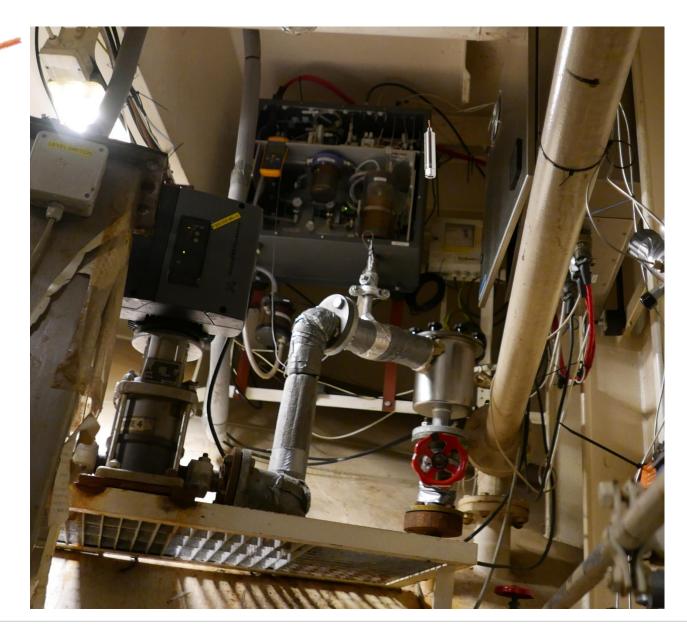


> Nuka Arctica



> Licor 6262





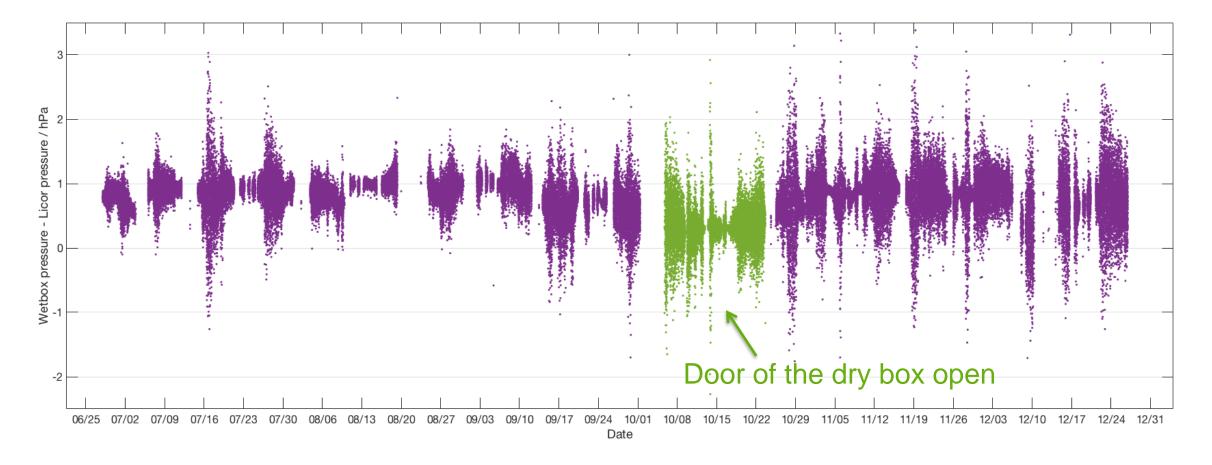






#### Installing a pressure sensor in the WetBox

#### Mean difference: 0.81 hPa Mean difference (October): 0.33 hPa





# Trans Carrier

Sea-Cargo

110

20

TRANS CARRIER

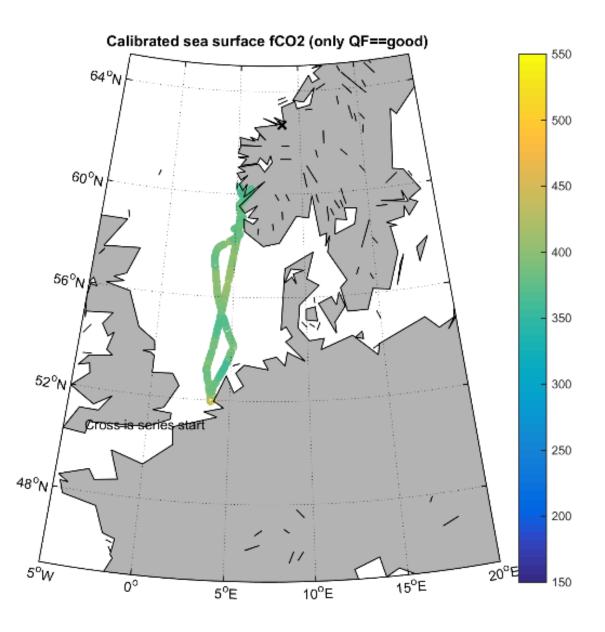
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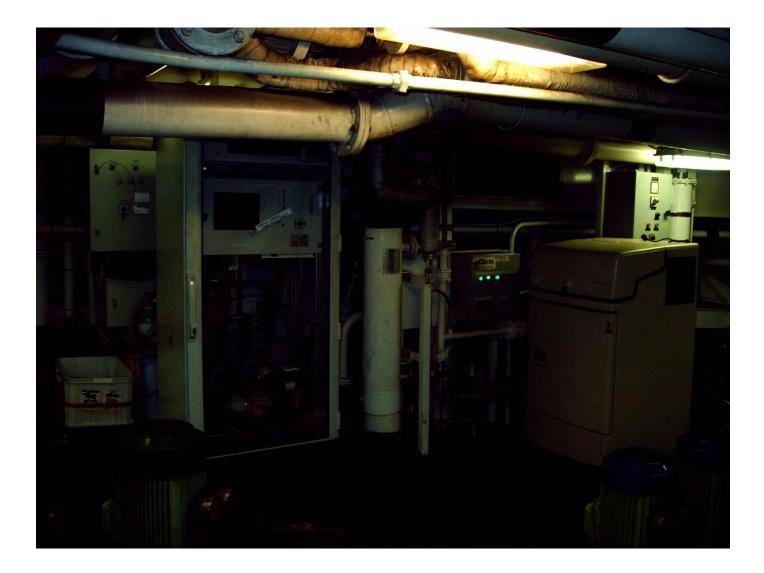
## **Trans Carrier**

- Commercial ro-ro cargo vessel.
- Sailing between Bergen and Rotterdam.
- Costal/fjords in Norway, then crossing the North sea.
- 1 week round trip.



## Removing old installation



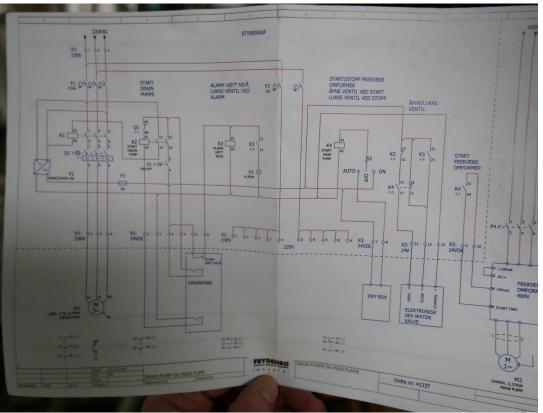


## Making and installing brackets



### **Electrical distribution**





## Water supply and drain



#### Box installation



# The problems

## Schedule

• Port call in Bergen Monday - Tuesday/Wednesday every week.

## Schedule

- Port call in Bergen Monday Tuesday/Wednesday every week.
- Planned port call in Bergen every Sunday evening.
- Sometimes the port call in Bergen is cancelled.
- Notification about changes in schedule Friday afternoon or Saturday.

## **PPM-values**

- Known standards were way off after zero-span.
- Spending much zero gas (STD1).

## **PPM-values**

- Known standards were way off after zero-span.
- Spending much zero gas (STD1).

- Valco MPV had an internal problem with the TX-line. Causing the valve to receive commands, but failing to report its position back to the computer.
- This caused the MPV to move to position 1 (STD1) instead of stopping the flow (even position).

### Water restriction

- Low water flow in system
- High flows when the water line was disconnected to locate the problem.

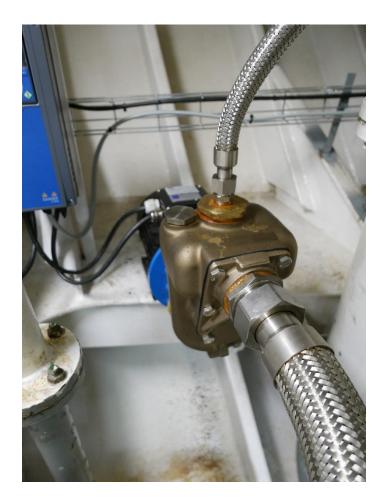
### Water restriction

- Low water flow in system
- High flows when the water line was disconnected to locate the problem.

- Flow regulator in wet box did not open properly.
- Regulator was removed, and water flow is now controlled using the frequency converter and an external flow regulator.

## Water pump

- Scraping sound when running on high speed.
- Several gaskets between motor and pump housing trying to prevent scraping.
- Could only run on low speed, not delivering enough water
- This occurred at the same time as the water restriction problem.



## Tubing and pipes

• Flag state did not like flexible tubing



## Water leak

- The flexible tubing was not made for sea water, so it started leaking.
- The supplier of the tubing could not come up with a solution, or supply adequate tubing or pipes.

• At the same time the water pump started leaking, probably due to the need of several gaskets.

### Water leak

- Crew made a solid pipe to replace the leaking flexible tube.
- Water pump was replaced on warranty.

# Just in: Drain tank flooding

- Drain pump running continuously
- Drain tank flooding
- System stopped by ship crew

• We hope the ship will come to Bergen this Sunday.



Katharina Seelmann, PhD student

# Test and evaluation of the Contros HydroFIA® TA system in field





## Who am I?



PhD student in the chemical oceanography department at the GEOMAR Helmholtz-Centre for Ocean Research Kiel

- Working group:
  - Observational Chemical Oceanography (PI: Prof. Arne Körtzinger)





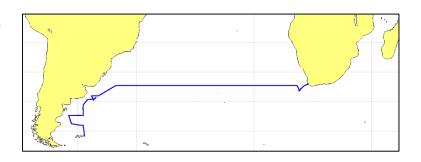


- Production of valid and comparable results with the Contros HydroFIA<sup>®</sup> TA system during an autonomous long-term installation on a North Atlantic VOS (voluntary observing ship) line
- Before:
  - Comprehensive testing of the analyser regarding to the behaviour under semi-continuous measurement condition





- Research cruise on RV Meteor (M133)
- 15.12.2016 13.01.2017
- From Cape Town, South Africa to Stanley, Falkland Islands
- Measurement conditions:
  - Installed in bypass to a continuous underway seawater stream (filtered with a 50 µm flowthrough filter)
  - Calibration only at the start of the cruise with CRM
  - Measurement interval: 7 minutes









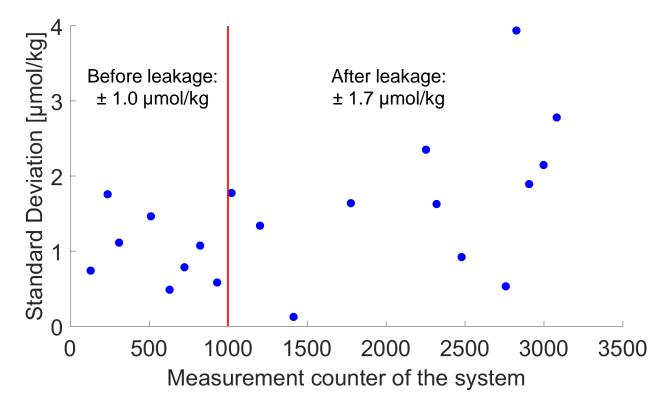


- Overall 3358 measurements
  - > 2702 underway measurements
- Daily substandard measurements for precision monitoring
- Regular CRM measurements and collecting of discrete samples for accuracy monitoring
- Problem:
  - $\blacktriangleright$  Around1000 measurements  $\rightarrow$  leakage in the degasser unit





Precision evaluation: Averaged standard deviation = ± 1.5 µmol/kg

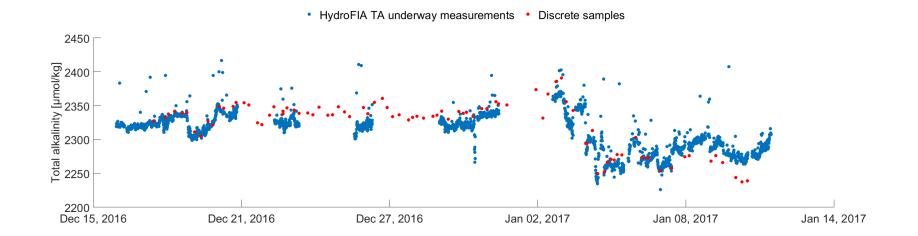


• Standard Deviation of substandard measurements

### HELMHOLTZ RESEARCH FOR GRAND CHALLENGES



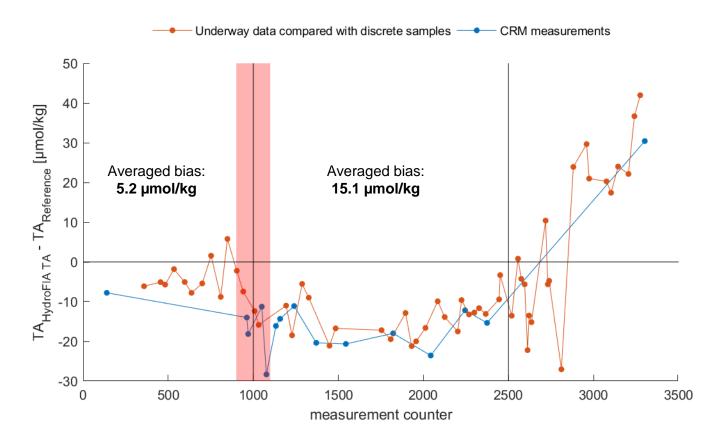
• Accuracy evaluation:







• Accuracy evaluation:







Main finding from M133:

- Daily quality insurance measurements are mandatory
- Second evaluation cruise without leakage was necessary





- MSM68/2 on RV Maria S. Merian (From Emden, Germany to Mindelo, Cape Verde)
- 03.11. 14.11.2017
- Final evaluation of the data still in progress









- With the findings of the two evaluation cruises
  - Install the system on board of the container vessel for autonomous longterm measurements





 Developing of a preparative and analytical HPLC method similar to a existing method for meta-cresol purple<sup>(1)</sup>

> Is there a possible improvement for the TA measurements?

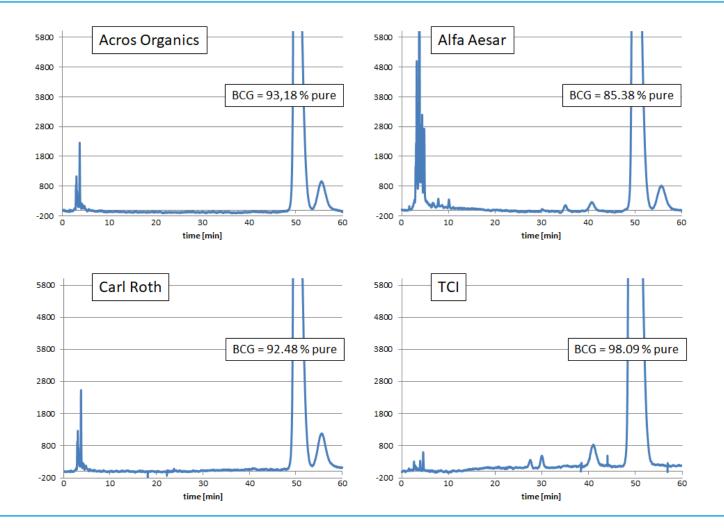
- Analyse BCG from different vendors with this method
- First purification of BCG

(1) Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements, Xuewu Liu, Mark C. Patsavas, and Robert H. Byrne, *Environmental Science & Technology* **2011** 45 (11), 4862-4868





## **Bromocresol green purification**





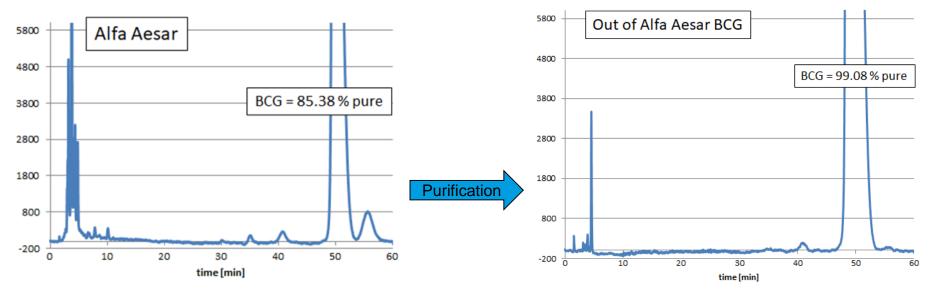
Katharina Seelmann | Monday, 30 April 2018



RESEARCH FOR GRAND CHALLENGES

HELMHOLTZ

### **Bromocresol green purification**



- Purity improvement of 14%
- Next steps:
  - ➢Purification of TCI BCG
  - >Spectrophotometric measurements
  - ➤ Measurements with the HydroFIA<sup>®</sup> TA system



# ICOS

INTEGRATED CARBON OBSERVATION SYSTEM

# ICOS Data Management – the way towards operational oceanography

Benjamin Pfeil, Steve Jones, Camilla Stegen Landa, Jonas Fagnastøl Henriksen, Rocio Castano Primo ICOS Ocean Thematic Centre / Bjerknes Climate Data Centre



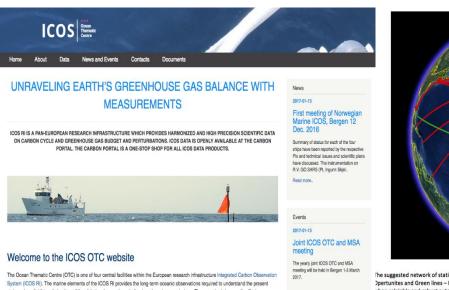
Bjerknes Centre for Climate Research BCDC Bjerknes Climate Data Cent





# The Ocean Thematic Centre ICOS

#### Marine observation routes and stations



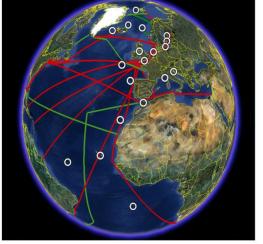
The Ocean Thematic Centre (OTC) is one of four central facilities within the European research infrastructure Integrated Carbon Observation System (ICOS RI). The marine elements of the ICOS RI provides the long-term oceanic observations required to understand the present state and predict future behaviour of the global carbon cycle and climate- relevant gas emissions. The oceanic sink currently offsets approximately 25% OCG, emissions from human activities. Oceanic net air-sea CCg. fluxes of the Atlantic are a large proportion of the net global marine flux, together with CH4 and NgO fluxes.

OTC coordinate and support the European network of Monitoring Stations Assembly (MSA) in the North Atlantic, Nordic Seas, Baltic and the Mediferenaen (Fig. 1). DTC cooperates with the International Ocean Cachon Coordination Project (IOCCP) to cover the global cosan observing systems, such as Voluntary Observing Ships (VOS), Fixed Ocean Stations (FOS), Repeat Ocean Sections (ROS), Marine Flux Twees (MFT) and new technologies.

#### OTC builds on expertise and results

gained during previous and current ELF-hinded science projects (CMASSOQ), CAREOCEAN, CAR

#### https://otc.icos-cp.eu/



The suggested network of stations for the ocean-network: Cicles - Fixed Ocean Stations, Red lines – Ships of Opertunities and Green lines - Repeat Section. In addition, new technologies like floats and gliders will be implement when reliable and robust autonomious sensors for the ouroos to developed.



- The goal in 2013
- > About 35
  - stations
- Future
   Vision
   about 50
   stations

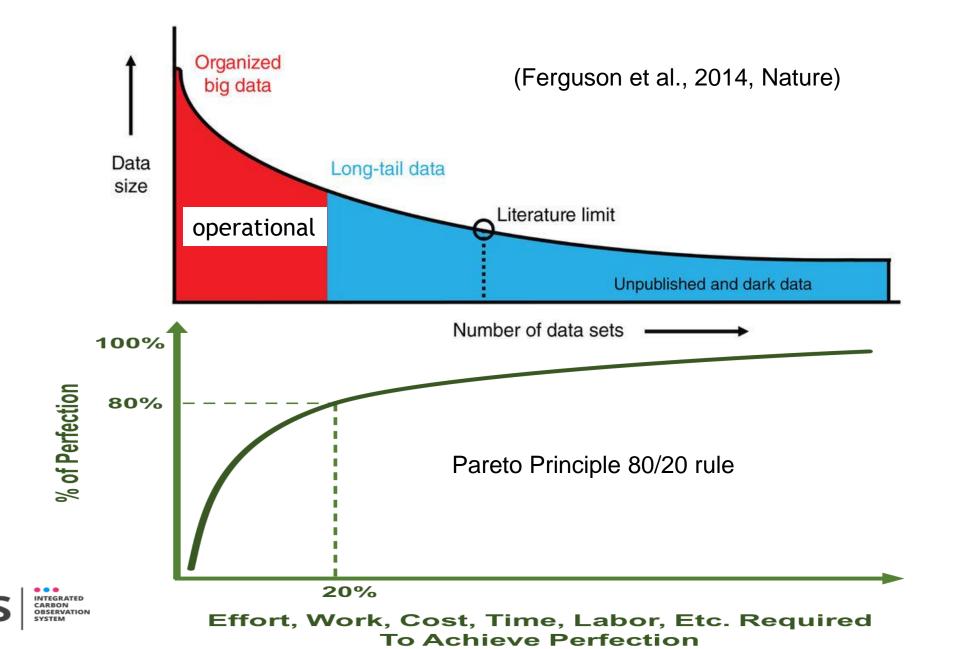
- The reality in 2017
- 21 station ready to be labelled
- 21 passed step 1 and ready for step 2



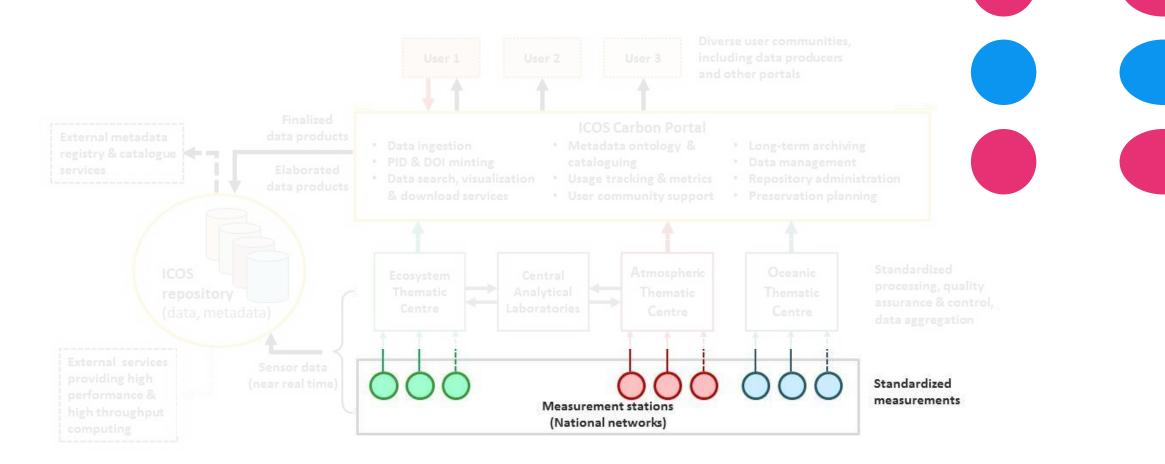
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### Challenges

ICO



# **General Overview**

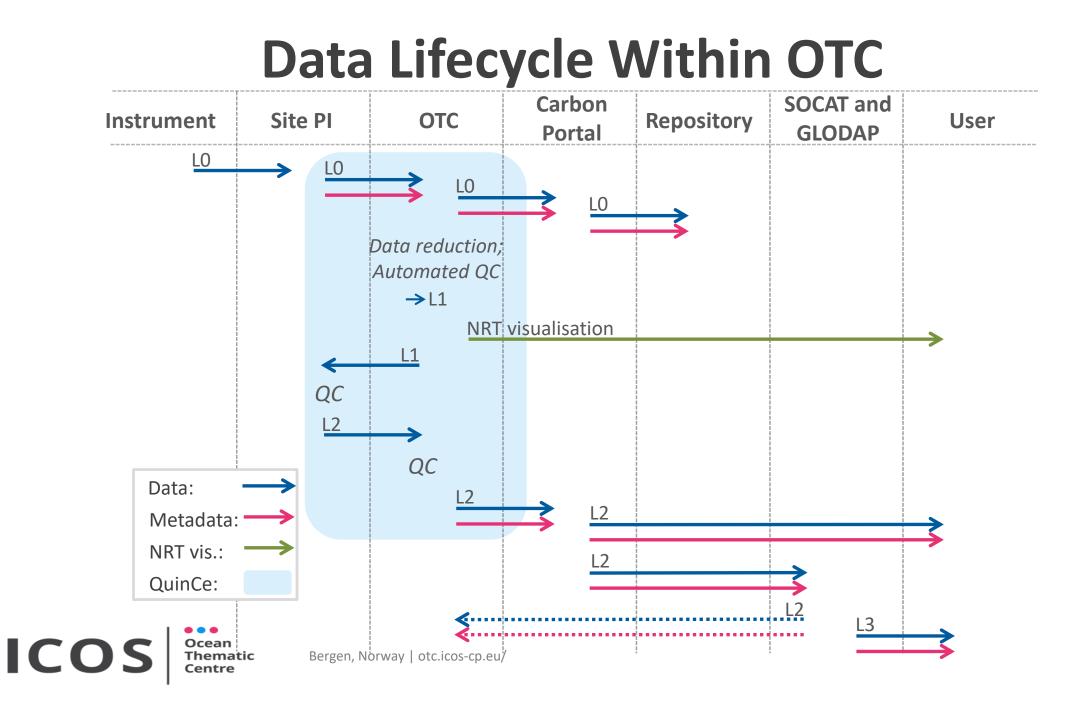


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# **Data Levels**

- Level 0: raw sensor output
- Level 1: gone through data reduction and automatic QC
- Level 2: final data set, QCed by PI
- Level 3: external data products using ICOS data



# **Data Policy**

... takes into account the overall European legal framework related to access, sharing, protection and re-use of environmental data, information and databases



https://otc.icos-cp.eu/node/16

### All ICOS data, metadata and ICOS data products are

- public = open to all users
- made available with minimum time delay
- made available with minimum and whenever possible no cost

# **Data License**



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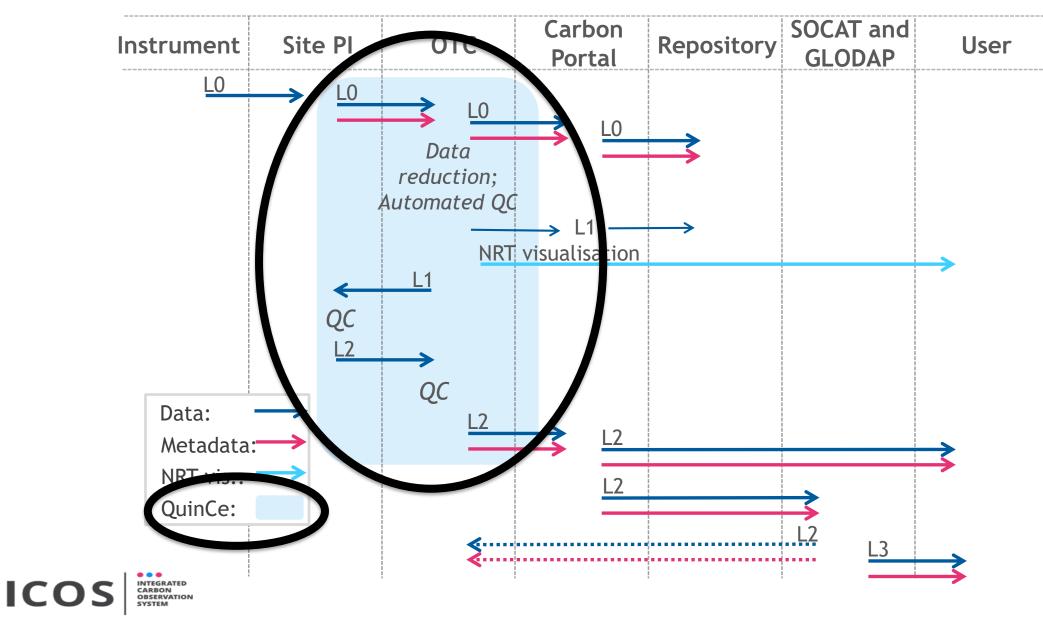


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# Data Lifecycle Within OTC





# Data reduction and quality control software QuinCe: Features

- Web applications (runs through the browser = no Matlab or R expertise needed)
- Ingests raw data (streaming and delayed mode)
- Follows SoPs and approved routines (Pierrot el al.)
- Automatic data reduction with calibration, gas standards and automated initial QC
- Offers manual QC tools for visualising and flagging
- Standardised tools for data processing (consistency and documentation) -> become operational
- Currently underway pCO2 but will be extended to pH





# Data reduction and quality control software QuinCe

- about longitudinal studies of drift
- long-term performance (feedback to producers)
- Archives data and calibration information

Opens up for:

- Online training
- Standardized data treatment outside ICOS
- Collaboration outside the ICOS network (strong interest e.g. EuroGOOS, CMEMS, SDC)







Benjamin Pfeil

IOCCP SSC member responsible for data and information management

Bjerknes Climate Data Centre @ University of Bergen

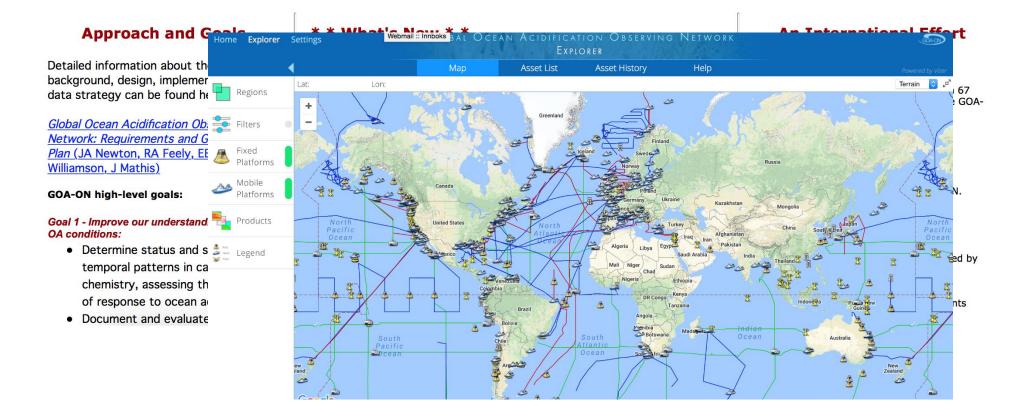




The Global Ocean Acidification Observing Network (GOA-ON) is a collaborative international approach to document the status and progress of ocean acidification in open-ocean, coastal, and estuarine environments, to understand the drivers and impacts of ocean acidification on marine ecosystems, and to provide spatially and temporally resolved biogeochemical data necessary to optimize modeling for ocean acidification.



Home References/Reports GOA-ON Activities Interactive Map Network Members Governance/Contact Pier2Peer





### Framework for Ocean Observing Approved governance structure

## **GOOS Steering Committee**



The Global Ocean Observing System

#### **GOOS Panels**

#### Essential Ocean Variables Panels

are advisory bodies which supply the GSC with scientific studies and expertise underpinning the strategic goals of GOOS. The Ocean Observations Panel for Climate (OOPC) continues its role advising GOOS and GCOS on global ocean physics essential ocean variables. The Biogeochemistry Panel will naturally be organized by the International Ocean Carbon Coordination Panel (IOCCP). The Biology & Ecology panel is a new creation, which has received support for a new Secretariat hosted by Australia. Biology & Ecosystem and Biogeochemistry Panels had their first formative meetings in Nov. 2013.

Links to the Three different Panels:

GOOS Biology and Ecosystems Panel (Bio-Eco)
 GOOS Biogeochemistry Panel (IOCCP)
 GOOS Physics Panel (OOPC)

GOOS Physics Parler (OOPC)

(Observing technologies and networks, Variable focus: data and products, synthesis, link to models)

#### **IOCCP SSG**

Chair Toste Tanhua (Germany)

Underway pCO<sub>2</sub>: Rik Wanninkhof (USA)

Surface CO<sub>2</sub> Data: Kim Currie (New Zealand)

Repeat Hydrography: Masao Ishii (Japan)

**Ocean Interior Data:** Are Olsen (Norway)

Time Series Networks: Laura Lorenzoni (US)

Instruments and Sensors: Todd Martz (US)

**Data Management:** Benjamin Pfeil (Norway)

Nutrients Michio Aoyama (Japan)

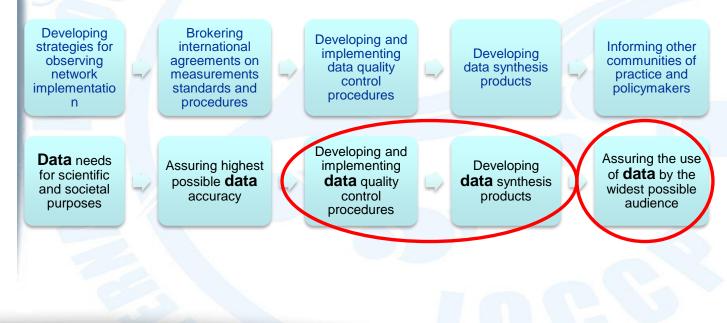
Ocean Acidification Richard Feely (USA)

SOLAS/IMBER: Andrew Lenton (Australia) Niki Gruber (Switzerland)

Project Director: Maciej Telszewski (Poland)

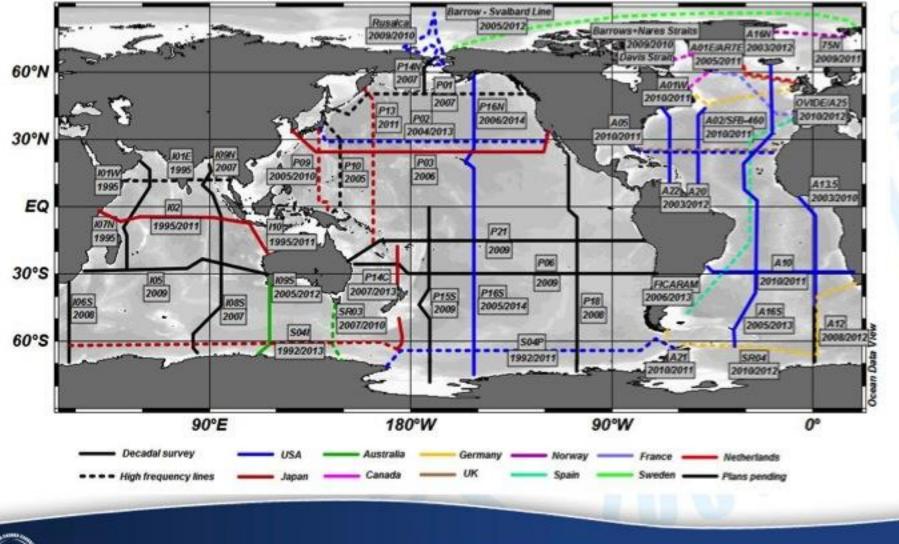
### **IOCCP Mission and Field of Expertize**

The IOCCP promotes the development of a global network of observations for marine biogeochemistry through technical coordination and communication services, international agreements on standards and methods, and advocacy and links to the global ocean observing system. In each of the fields of our interest (left) IOCCP follows the following scheme:

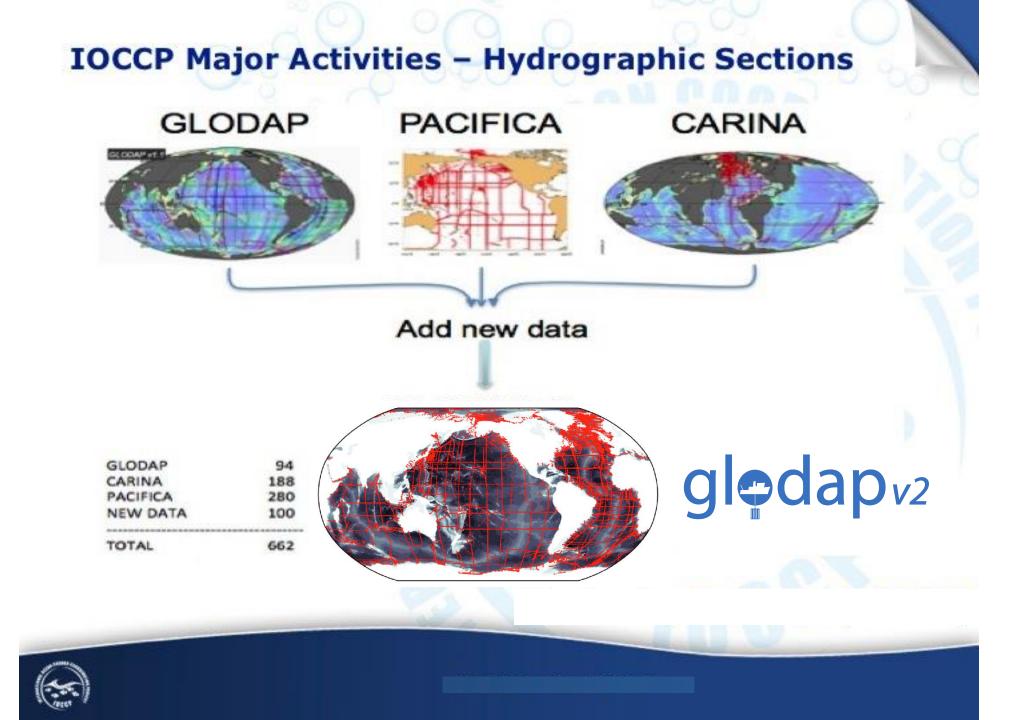




### **IOCCP Major Activities – Hydrographic Sections**

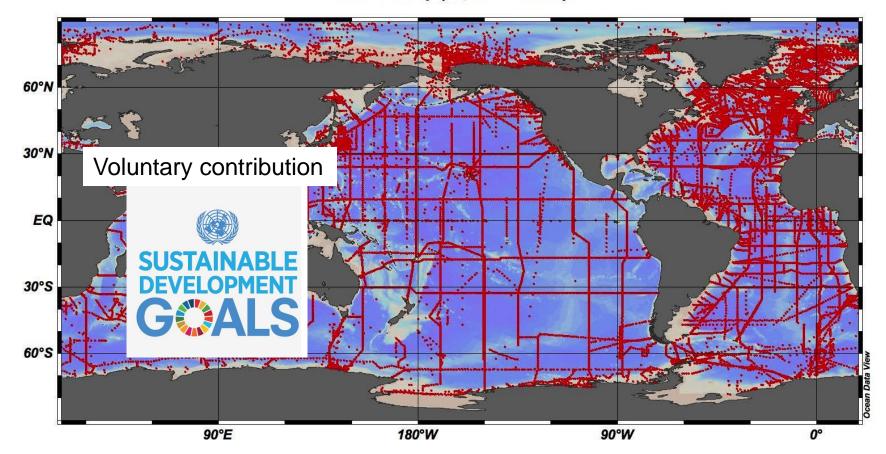


Source: CDIAC

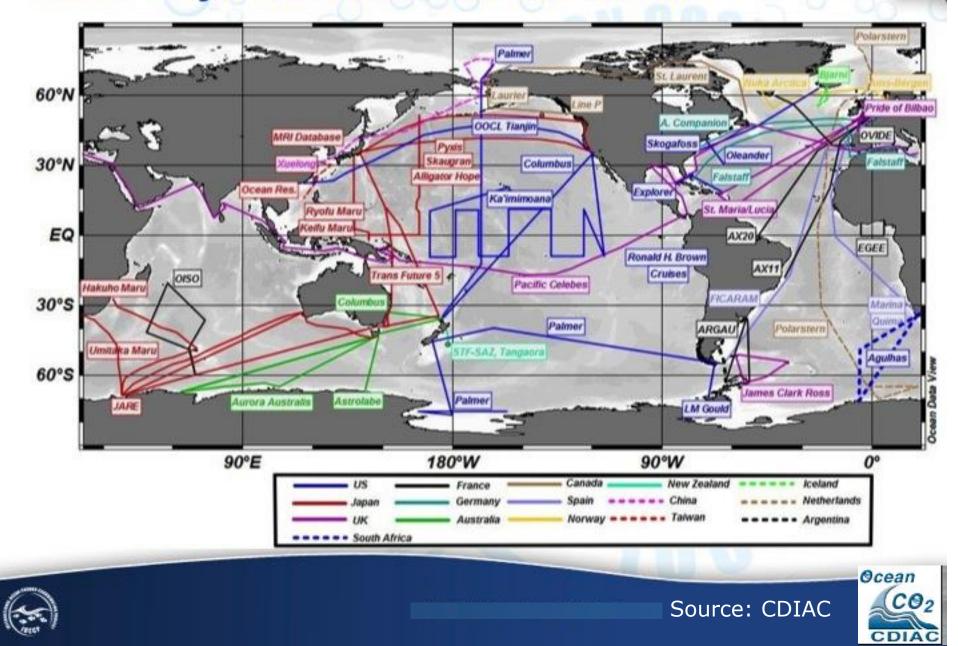




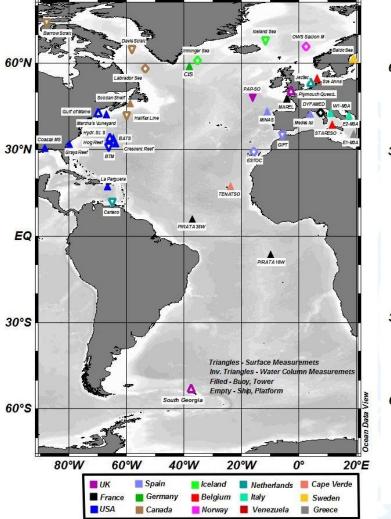
GLODAPv2 Map (45,475 stations)

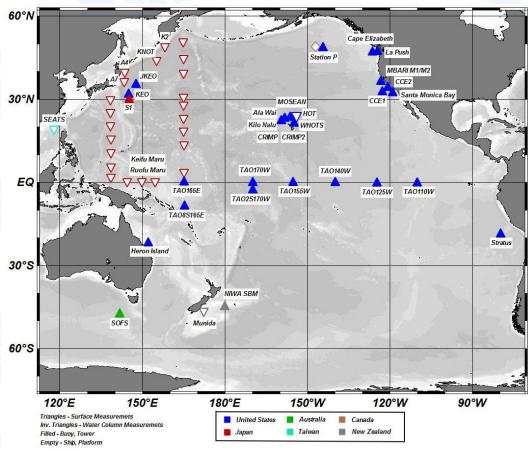


#### **IOCCP Major Activities – Surface Ocean**



#### **IOCCP** Major Activities – Time Series stations



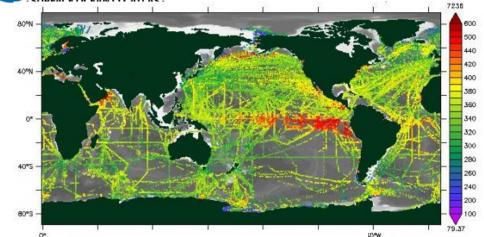




Source: CDIAC



# Surface Ocean CO2 Atlas

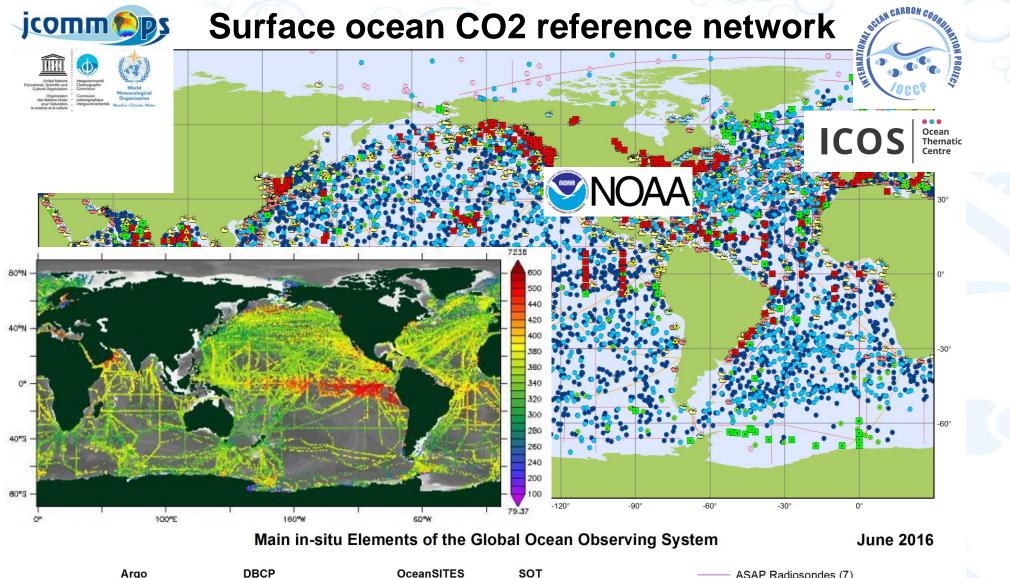


Voluntary contribution



- SOCATv5 released in 2017
- Consists of 20 million fCO<sub>2</sub> data on > 4800 cruises covering the years 1957-2016
- Data from SOOP/VOS, RVs, fixed ocean timeseries, buoys,
- Prominent users: Global Carbon Project (GCP) and Intergovernmental Panel on Climate Change (IPCC)
- DM infrastructure supported by NOAA and ICOS OTC (RINGO)





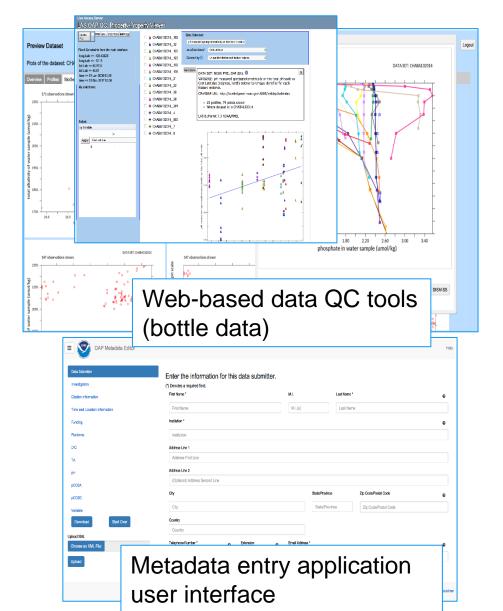




INTEGRATED CARBON OBSERVATION SYSTEM

### **US-European collaboration**

- close collaboration NOAA PMEL Data Integration Group and ICOS OTC
- develop processes to provide homogeneous bgc data management and QC capabilities
- OAP and ICOS efforts are complementary, with overlap where required to better serve regional groups
- ICOS will adopt the OA metadata entry application as developed by NCEI and NOAA/PMEL



### **Societal Challenges**





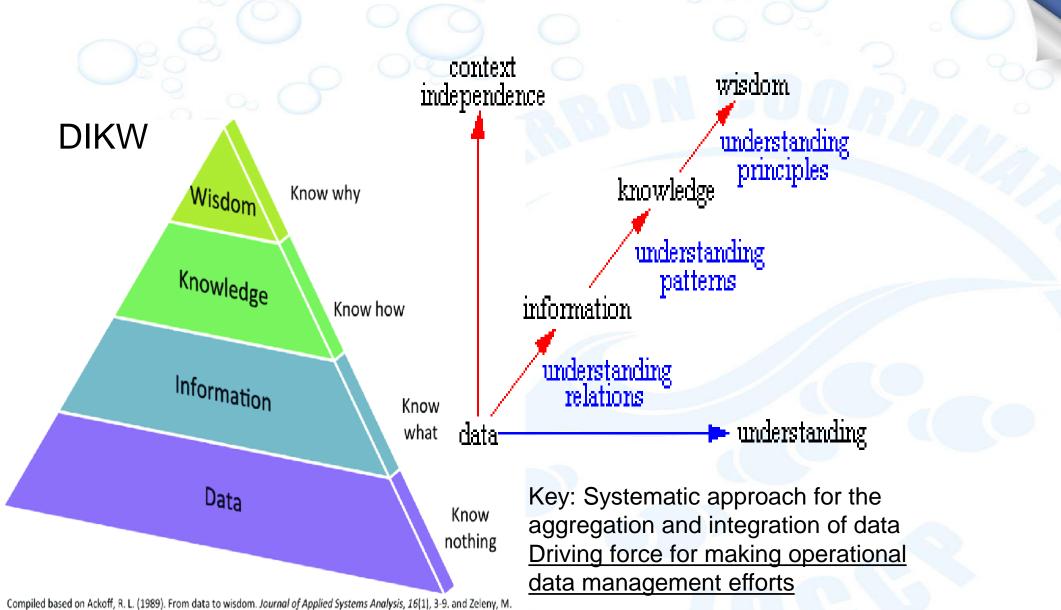
14.1 14.2 14.3 14.4 14.5 14.6 14.7 14.a 14.
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ced scientific cooperation at all levels.

HOME         SDG 14         ABOUT THE CONFERENCE         CALL FOR ACTION         VOLUNTARY COMMITMENTS         COMMUNITIES OF OCEAN ACTION           REGISTRY         COMMUNITIES OF OCEAN ACTION         REGISTER COMMITMENT         SHARE UPDATE         ABOUT & RESOURCES	TION PREP PROCESS DOCUMENTATION EVENTS NEWS & MEDIA	
Updates of GLODAP data product by GLODAP - the Global Ocean Data Analysis Project (Scientific community)	Annual, public releases of the Surface Ocean CO2 Atlas (SOCAT) by SOCAT scientific community (Scientific community)	#OceanAction20464
DESCRIPTION SDG 14 TARGETS COVERED DELIVERABLES RESOURCES MOBILIZED	DESCRIPTION SDG 14 TARGETS COVERED DELIVERABLES RESOURCES MOBILIZED	f y in P < <



(1987). Management support systems: towards integrated knowledge management. Human Systems Management, 7(1), 59-70.



#### CO<sub>2</sub> in air measurements: Integrating with the Atmospheric Thematic Centre

Gregor Rehder and the IOW ICOS team

ICOS OTC Workshop, March 2018, Bergen

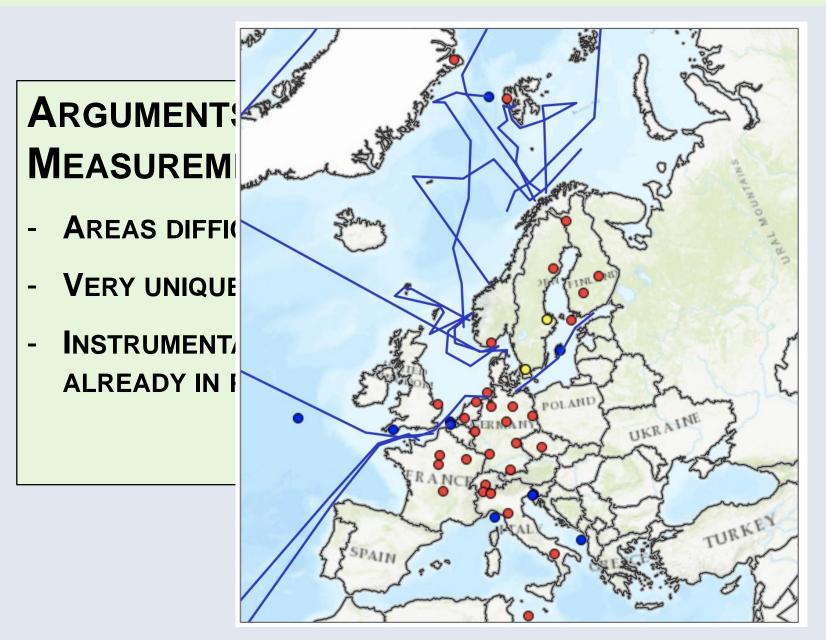




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### THE PROBLEMS

- HISTORICALLY, ATMOSPHERIC MEASUREMENTS ON RV AND VOS DRIVEN BY WISH FOR PERFORMANCE CONTROL OR LOCAL  $\Delta PCO_2$
- NOT TUNED FOR BEST ATM. MEASUREMENT
- USUALLY NO ASSESSMENT OF ACCURACY AND PRECISION (QC)
- **REQUIRES INSTALLATION OF AIR LINE**
- AT THE COST OF WATER MEASUREMENT FREQUENCY
- NOWHERE CONFORM TO ICOS ATC STANDARDS





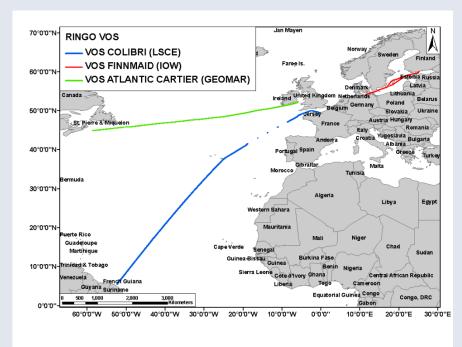
Readiness of ICOS for Necessities of Integrated Global Observations



### TASK 3.2.

Improving atmospheric measurements on Voluntary Observing Ships (VOS) **Rationale:** 

- Spatial vs. temporal coverage
- Not covered by atm. station grid
- Potential value for improved inverse modeling



#### THREE COMLEMENTARY TEST LINES VOS Finnmaid (IOW)

Baltic (Lübeck – Helsinki)

- easy to access,
- surrounded by ICOS atm. station network
- aim for "easy to move"-unit

#### **VOS COLIBRI (LSCE)**

France – French Guiana

- undersampled equatorial Atlantic
- extreme range of external conditions

#### VOS ATLANTIC SAIL (GEOMAR)

English Channel – Westwards

- Attempt to use instrumentation also used for water measurements
- Cost optimization

#### (MPI JENA, CAL. and ATC)

Consulting during construction phase, assembly of flask sampler, provision of calibration gases, assessment of added value through inverse modelling runs



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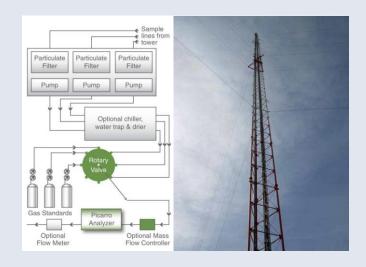
Gregor Rehder and the IOW ICOS team

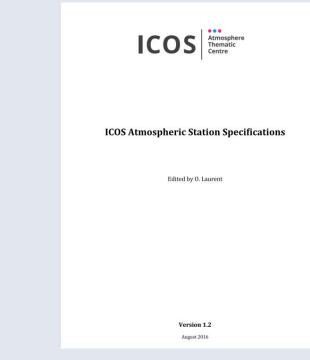
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# Technological requirements for atmospheric measurements.

#### **Atmospheric Station:**

- typically consists of a set of integrated analyzers
- that reside in a shelter with an
- air intake system in ideal position
- that collects air on a mast.





#### ATC approach:

to achive a homogeneous dataset:

- standardization of equipment,
- measurement protocol & data

processing of

- associated Atmospheric Stations (AS).



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### Continuous measurements - recommendations

Component	Guaranteed	Precision <sup>1</sup>	<b>Repeatability</b> <sup>2</sup> Std. dev. (1-σ);	
	Specification Range	<i>Std. dev.</i> (1-σ);		
		1' / 60' average raw data	10' average raw data	
CO <sub>2</sub>	350 - 500 ppm	< 50 ppb / 25 ppb	< 50 ppb	
$CH_4$	1700 - 2900 ppb	< 1 ppb / 0.5 ppb	< 0.5 ppb	
N20	300 - 400 ppb	< 0.1 ppb / 0.05 ppb	< 0.1 ppb	
СО	30 - 1000 ppb	< 2 ppb / 1 ppb	< 1 ppb	

Test conditions : dry air; room temperature : 20 °C ± 2°C; room pressure: atmospheric pressure with a natural variation.

<sup>1</sup> Measuring a gas cylinder (filled with dry natural air) over 25 hours; first hour rejected (stabilization time).

<sup>2</sup> Measuring alternately a gas cylinder (filled with dry natural air) during 30 minutes and ambient air (not dried) during 270 minutes over 72 hours. Statistics based on the last 10 minute average data of each 30 minute cylinder gas injection (first 20 minutes rejected as stabilization time).

Table 3 : Gas analyzer performance required by ICOS (as of August 2016)

Brand	Model	Species	ICOS	ICOS Compliance		Eligibility Conditions
			<b>CO</b> <sub>2</sub>	CH4	со	
PICARRO	G1301	CO <sub>2</sub> /CH <sub>4</sub> /H <sub>2</sub> O	•	•	-	
PICARRO	G2301	CO <sub>2</sub> /CH <sub>4</sub> /H <sub>2</sub> O	•	•	-	
PICARRO	G2401	CO <sub>2</sub> /CH <sub>4</sub> /CO/H <sub>2</sub> O	•	•	•	With ICOS specifications
LGR	907-0015	CO/N <sub>2</sub> 0/H <sub>2</sub> O	-	-	•	Precaution with
LGR	913-0015 (EP)	CO/N <sub>2</sub> 0/H <sub>2</sub> O	-	-	•	Δ temperature

ΡΙΟΔ R R Ο

G2401 Analyzer for CO<sub>2</sub>/CO/CH<sub>4</sub>/H<sub>2</sub>O

**User's Guide** 



• : ICOS Compliant - : Not applicable

Table 4: list of continuous gas analyzers meeting the ICOS specifications (as of August 2016)



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### Calibration and target gas requirements

#### Set of 3 Calibration and 2 Target Gases

- all by CAL
- VERY unusual range for the atm community
- recommended to be stored horizontally
- Cylinder: 6061 Aluminum cylinder manufactured by Luxfer UK
- Cylinder valve: Rotarex membrane valve (D200 type with PCTFE seat).
- Pressure regulator fitting: DIN 14 by preference, CGA 590 also possible

2	2015	C	02	CH <sub>4</sub>		CO		$N_2O$	
	Trend ≈ +2.5 ppm/yr		≈ +5 ppb/yr		≈ 0 ppb/yr		≈ +1 ppb/yr		
Site		Bckgnd	Peri- urban	Bckgnd	Peri- urban	Bckgnd	Peri- urban	Bckgnd	Peri- urban
set	CAL 3	450	470	2100	2200	250	400	340	345
CALS	CAL 2	415	420	1950	1970	150	200	330	333
30	CAL 1	380	380	1800	1800	60	60	320	320
L.	CAL 4	450	470	2100	2200	250	400	340	345
4 CAL set	CAL 3	420	430	2000	2060	175	200	335	337
4 CA	CAL 2	400	410	1900	1930	100	100	330	330
	CAL 1	380	380	1800	1800	60	60	320	320
	LTT	450	470	2100	2200	250	400	340	345
	<b>STT</b> 400		1900		100		330		
	STWS	40	00	1900		100		330	

Table 12: Values of the mole fractions recommended for the gas cylinders.



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### Continuous measurements - recommendations

- <u>Shelter</u> enclosed mounting rack, air-conditioned (+/- 2° C, adapted to on-site conditions, beware of overheating / condensation effects!)
- <u>Air-sampling & -distribution system</u> for different inlet lines / cylinders recommended: VICI Valco model EMT2SD\*\*
- <u>Time server</u> helps with time stamp to identify origin of gas analyzed
- <u>Pressure regulators</u> two models <u>accepted</u>:
- <u>SCOTT MODEL 14 M-1</u>4C (or -14B) Nickel-plated brass.
- <u>TESCOM Serie 64-3400</u> stainless steel electropolished, PCTFE valve seat & stainless steel high purity gas pressure gauge.
- <u>Tubing</u> Synflex 1300 (EATON), alternatively: stainless steel tubing Attention: outdoor/indoor delta T → risk of water condensing! Diameter & flushing flow rate → residence time ideally < 1 minute, e.g. ¼" Synflex tubing (<40m), flushing flow rate around 5-10 SLPM.</li>
- \*\* Alternatives possible after proving its suitability (dead volume, material compatibility, absence of leakages), best to contact ATC for guidance.













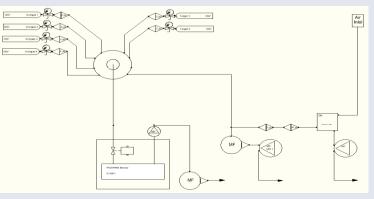
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### Continuous measurements - recommendations

- Plumbing recommendations no standardized Architecture imposed, but station PI may best contact ATC for guidance, station designs can be provided if requested.
- <u>Sampling line</u> required to continuously flush the line, with pump) for each line or a shared pump or blower. Lines at best in **one single piece!**



Example of station design by ATC, one sample height

At least the following additional sampling lines are required:

- one dedicated sampling line at highest sampling height for the travelling instrument
- a spare sampling line at each sampling height for quality control purpose
- $\rightarrow$ allows swapping lines when one is obstructed.
- rain guard for each sampling air inlet, additional filters recommended.
- Dryer (peltier, fridge etc.) in the sampling line recommended.
- <u>Station ancillary data</u> automated monitoring of mandatory station ancillary data:
  - flushing flow rate each tubing
  - *instrument flow rate*
  - room temperature





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...however, the data will always be processed by ATC !





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### The weather station

In order to characterize the weather conditions at the ambient air sampling site, ICOS requires monitoring of the following meteorological parameters:

- barometric pressure
- relative humidity
- air temperature
- wind direction
- wind speed



Variable	Range <sup>1</sup>	<i>Resolution</i> <sup>2</sup>	Mode of measurement <sup>3</sup>	Required measurement uncertainty <sup>4</sup>	Sensor time constant <sup>5</sup>	Output average time <sup>6</sup>	Achievable uncertainty <sup>7</sup>
Wind speed	0 to 75m/s	0.5m/s	Averaging	0.5m/s [0m/s; 5m/s] 10% [5m/s; 75m/s]	Distance Constant	2 and 10min	0.5m/s [0m/s 5m/s] 10% [5m/s;
Wind direction	0 to 360°	1°	Averaging	5°	1s	2 and 10min	75m/s] 5°
Temperature (Air)	-80 to +60°C	0.1°C	Instantaneous	0.3K [-80°C; -40°C] 0.1K ]-40°C; +40°C] 0.3K ]+40°C; +60°C]	20s	1min	0.2 K
Relative humidity	0 to 100%	1%	Instantaneous	1% 40:		1min	3%
Barometric pressure	500 to 1080hPa	0.1hPa	Instantaneous	0.1hPa	20s	1min	0.3 hPa

Table 5: WMO operational measurement uncertainty requirements and instrument performance (Annex 1.B of WMO-N. 8 -Guide to Meteorological Instruments and Methods of Observation, 7<sup>th</sup> Ed.)



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### TAKE AWAYS AND POINTS FOR DISCUSSION

- CLEAR DOCUMENTATION AND REQUIREMENTS FOR ATC-CONFORM MEASUREMENTS
- DIGESTING DATA FROM DIFFERENT SOURCE WOULD NEED A PARADIGM SHIFT AT ATC
- MAKE UP YOUR MIND WHY ATM. MEASUREMENTS ON THE SHIP ARE TAKEN, AND WHO WILL USE IT
- THERE IS A MISMATCH IN THE APPRECIATION OF ATM. MEASURMENTS BETWEEN OTC (CLASS 1 CRITERION) AND ATC
- MORE AFTER RINGO TP3.2 IMPLEMENTATION
- ??? PERIPHERAL PACKAGE (CLOSE TO GO-DRY BOX)



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#### The Team

Gregor Rehder



Oliver Schmale

Jens Müller

#### Acknowledgements



Thanks to our collegues from SYKE

Petri Maunula Seppo Kaitala

and FINNLINES

Bernd Schneider



Bernd Sadkowiak

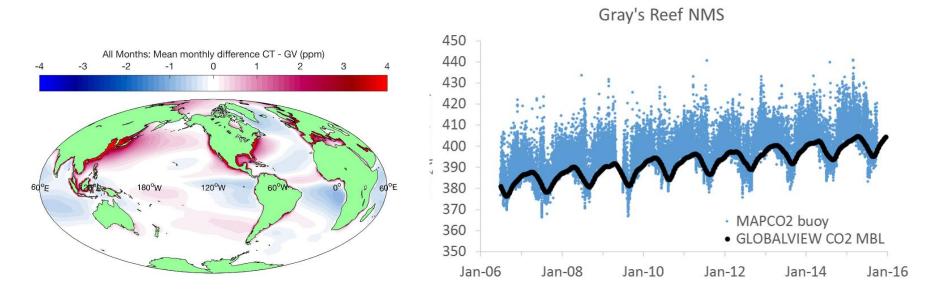


Michael Glockzin

#### Improving the $\Delta pCO_2$ estimates

Impacts of regional patterns of atmospheric CO<sub>2</sub> on ocean uptake

For  $\Delta pCO_2$  we use zonal averaged (y,t) atmospheric  $CO_2$  values

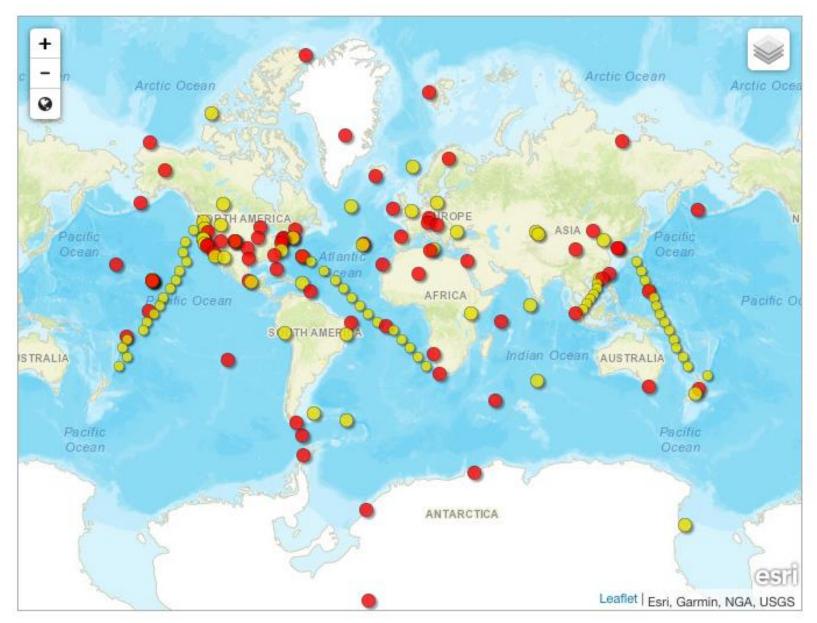


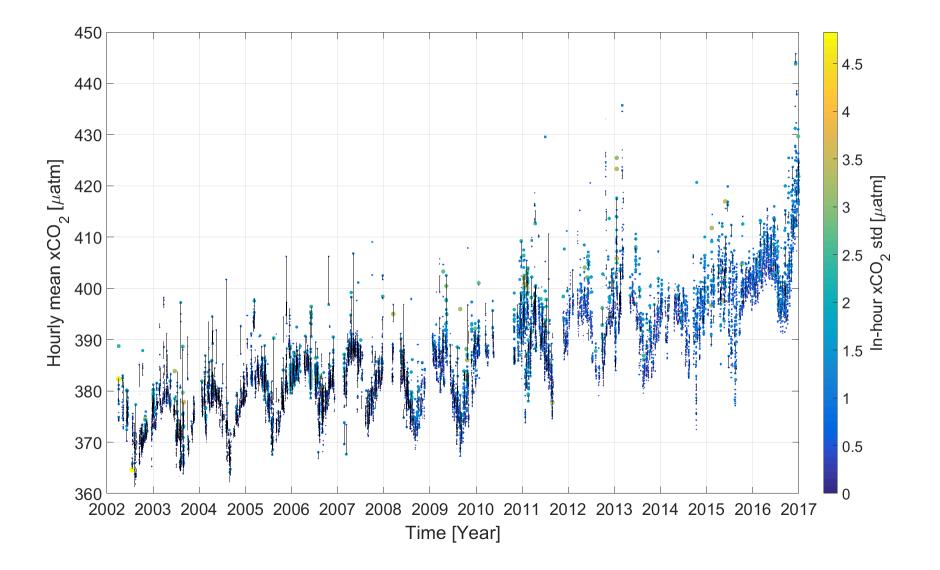
Carbon Tracker (3D)- Globalview-CO<sub>2</sub>(2D)

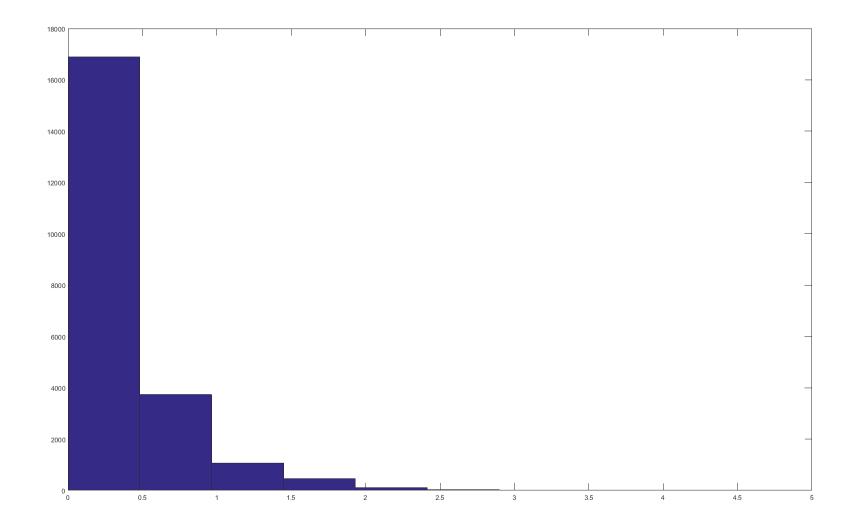
Ships and Mooring instruments provide precise CO<sub>2</sub> estimates. Need to validate these for:

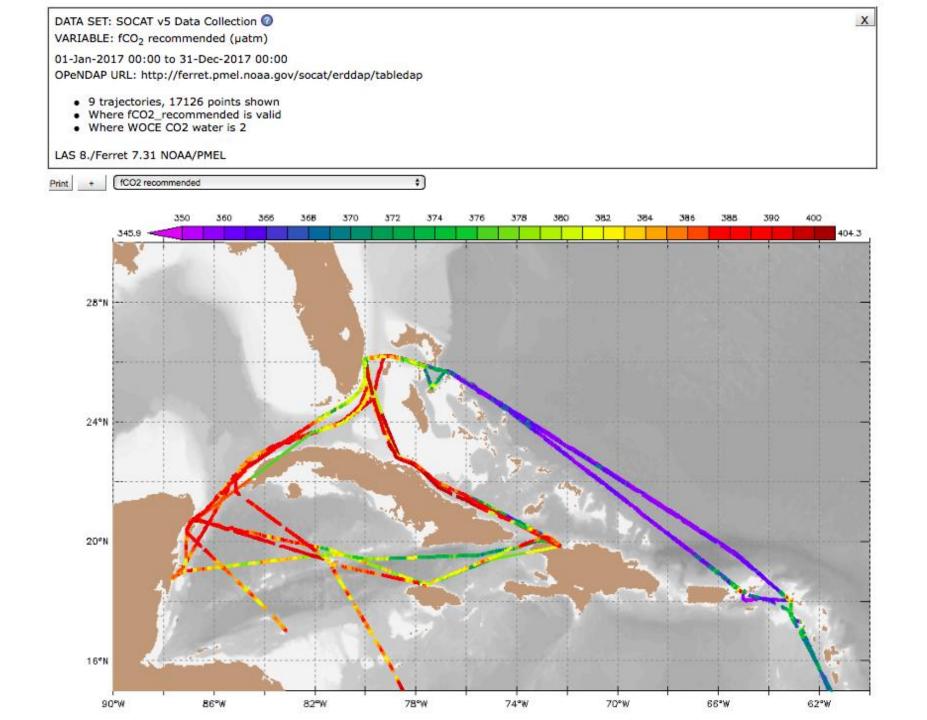
- Better air-sea CO<sub>2</sub> flux estimates
- Validation atmospheric transport models
- Validation of satellite sensors (OCO)

#### Cooperative flask sampling stations ESRL/GMD



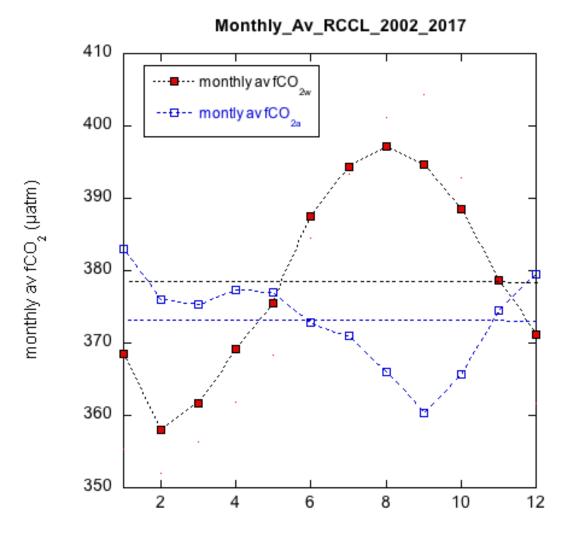




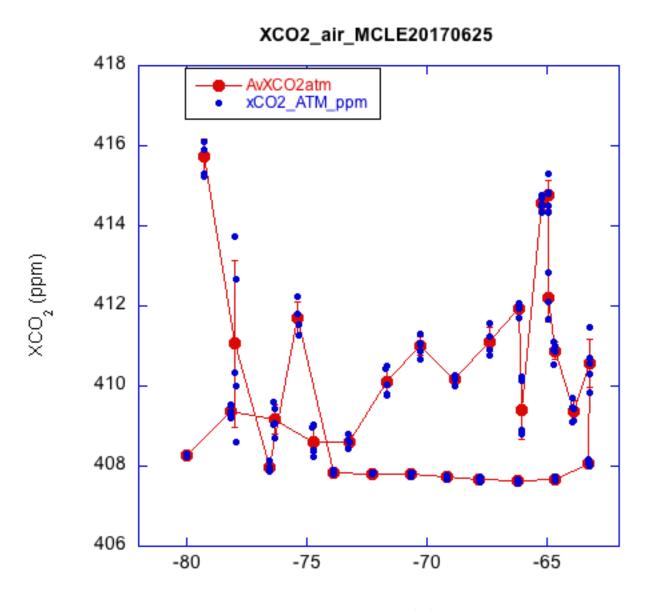


#### ΔpCO<sub>2</sub> Caribbean Sea

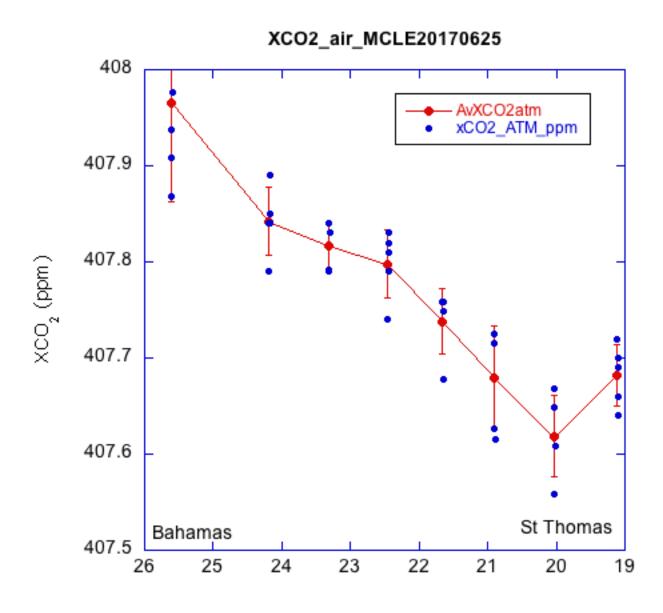
Seasonal cycle of  $pCO_{2w}$  in opposite phase and greater than seasonal cycle  $pCO_{2air}$ 



month

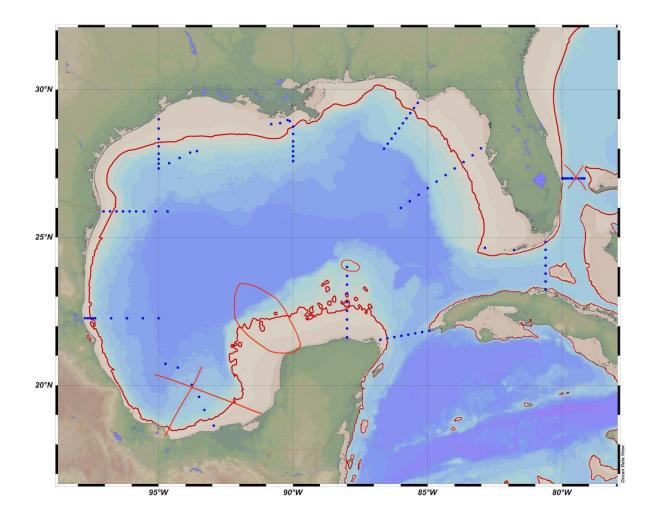


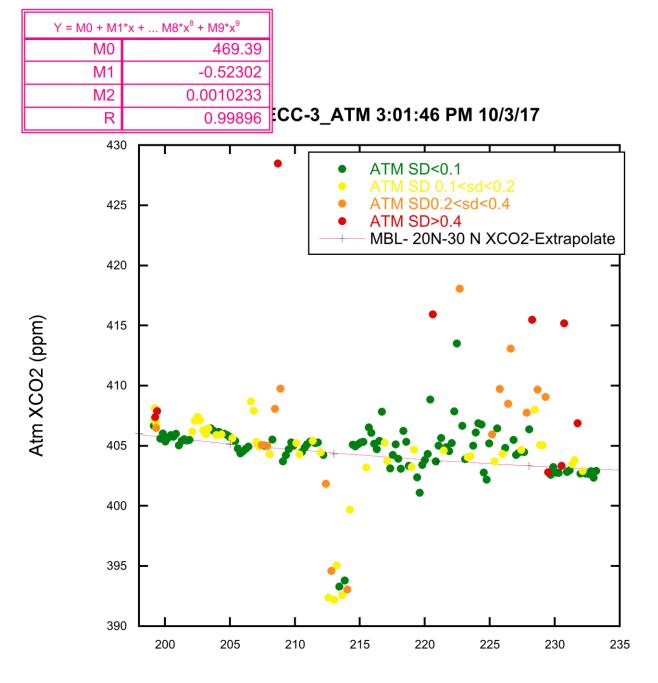
Longitude (E)



Latitude

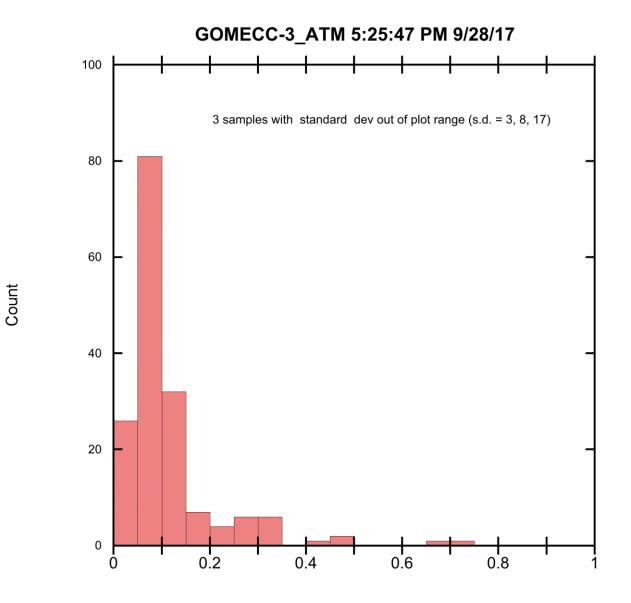
GOMECC-3 July 2017



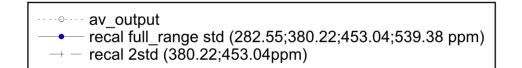


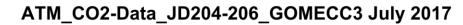
YearDay-utc

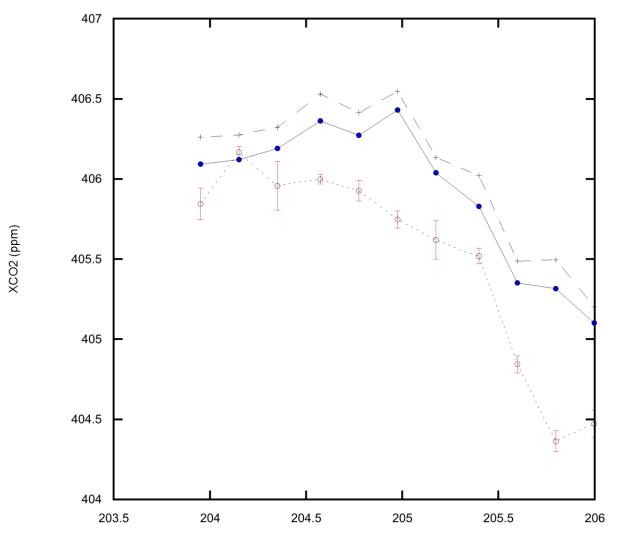




standard deviation XCOa









#### Transportable System (ESRL/GMD) on NOAA SHIP BROWN





## CONSIDERATIONS OF THE RESPONSE TIME OF EQUILIBRATION SYSTEMS

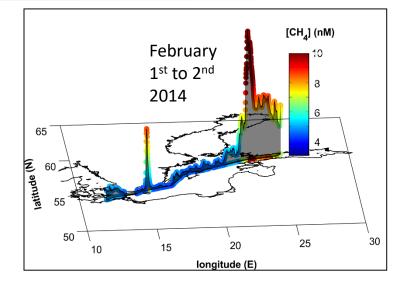
A: GENERAL



### REMEMBER ....

•Sparingly soluble gases equilibrate slower

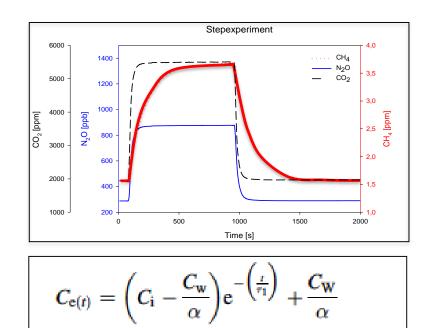
•In particular methane distribution can be patchy with small small scale differences



- Response time: systemdependent
- For τCH<sub>4</sub> / τCO<sub>2</sub> : ~ 25 to 3 (Webb et al., 2016)

# •Equilibrator always in disequilibrium

(Johnson et al., 1999)



### So what is a correct value?

•Implications for "Quality Goals", i.e. SOCAT, ICOS (remember talks by Truls and Dorothee)

IBNIZ INSTITUTE FOR ALTIC SEA RESEARCH

