# MODUSS

# Marine Observatory Development with autonomous Silicon Sensor


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Isblue theme 5, 10 Jan 2024

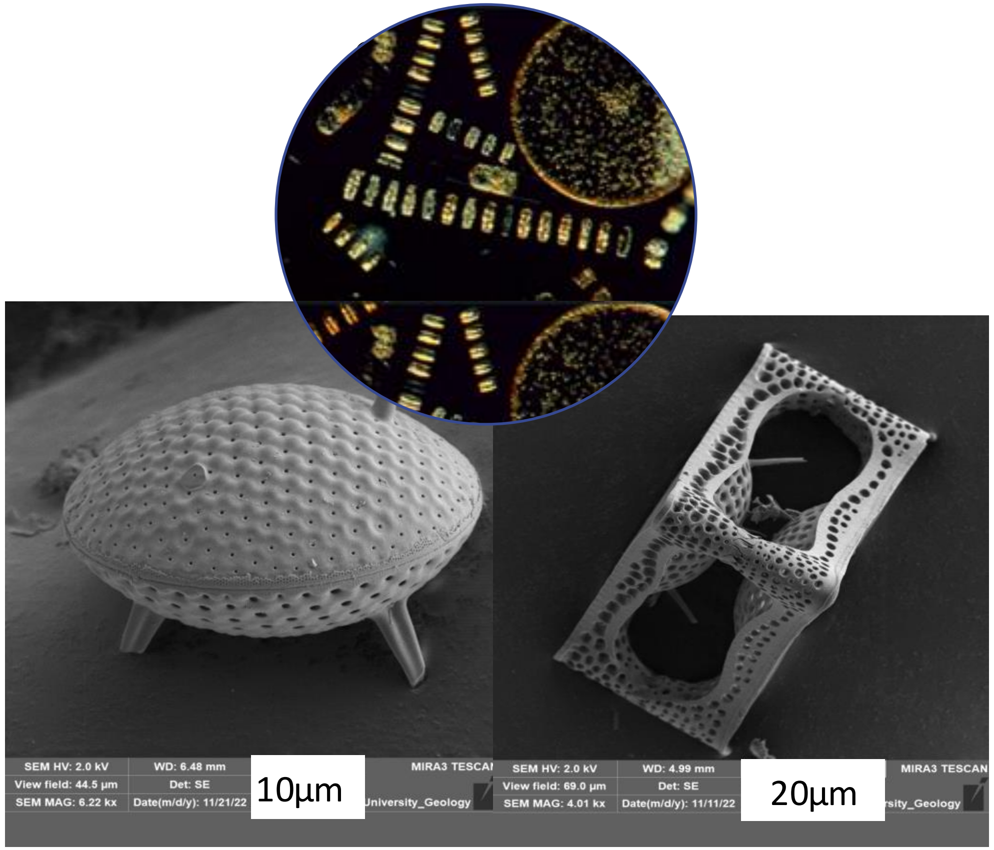
# Silicon in the ocean

**Si = 2nd most abundant element on Earth.**

**Essential for marine siliceous organism.**

## Diatoms

Unicellular photosynthetic




## Siliceous sponges

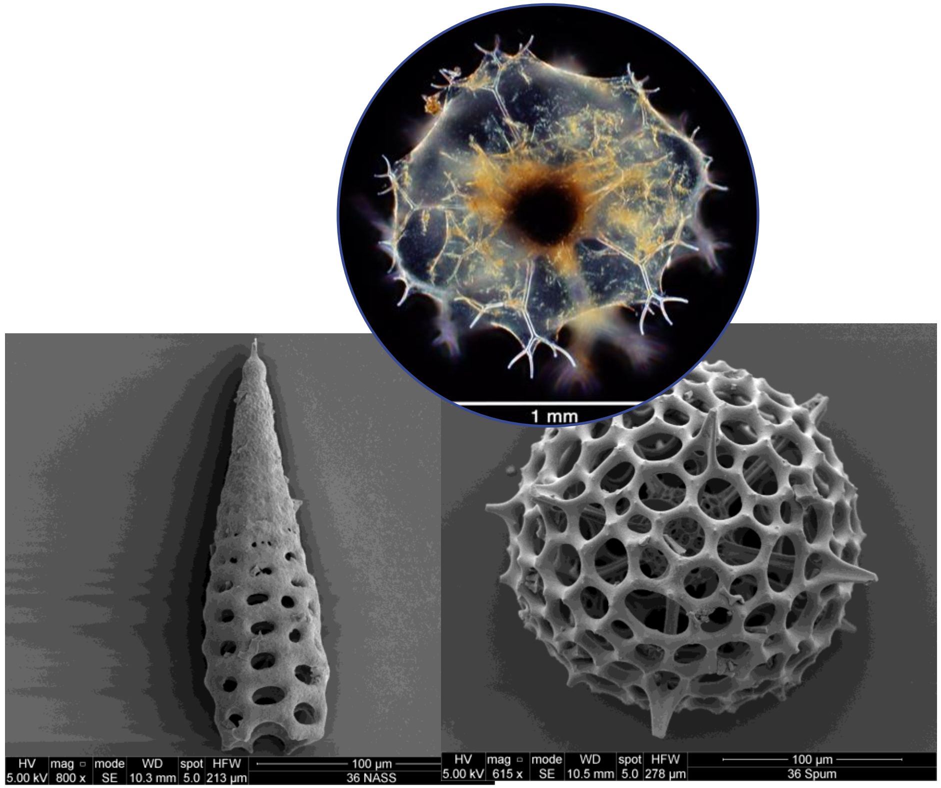
Eukaryote

Hexactinellida, *Euplectella aspergillum*

Demospongiae, *Suberites carnosus*

## Rhizaria

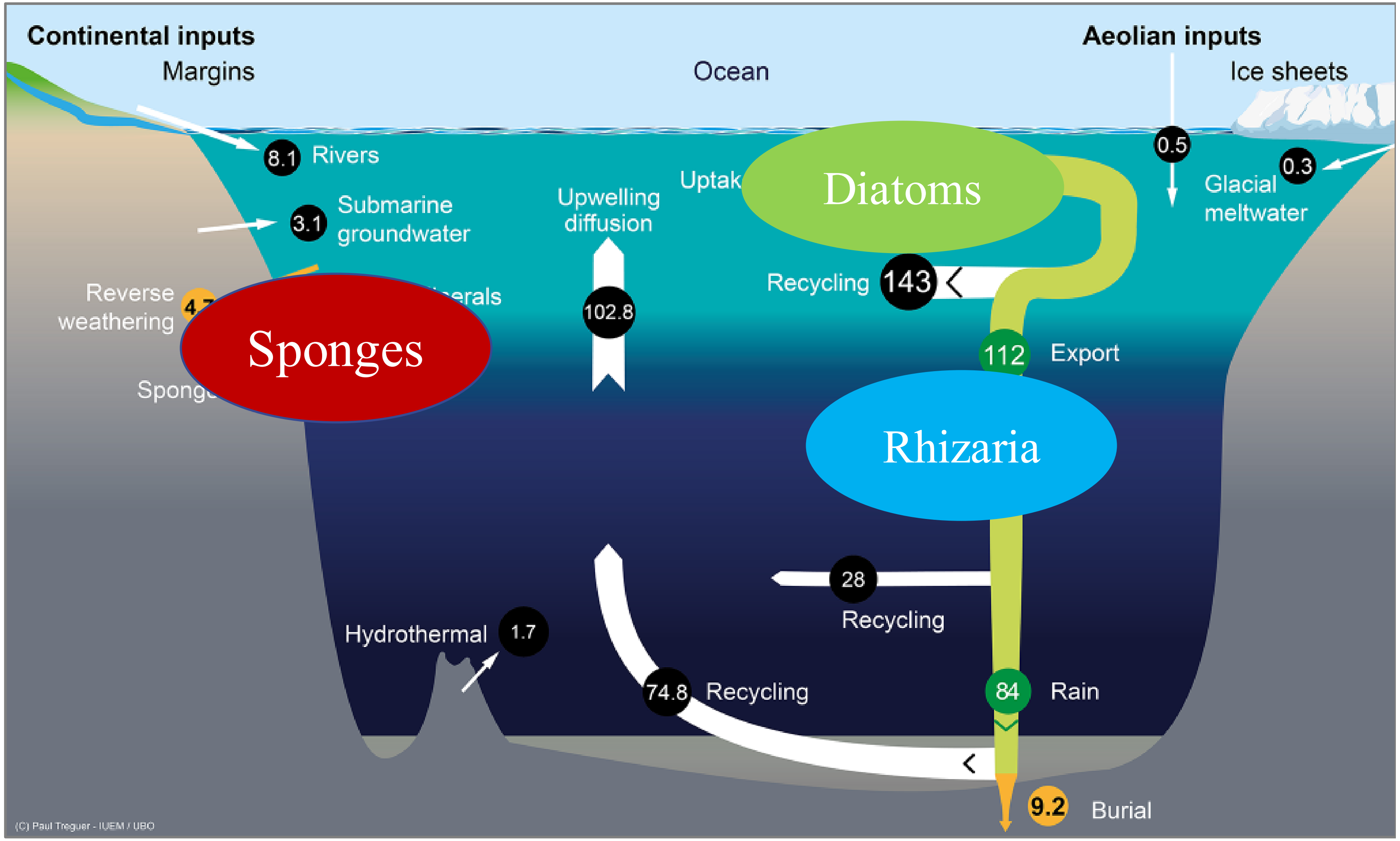
Zooplankton




Nassellaria

*Spumellaria*

# The Marine Si cycle




*(Tréguer et al., 2021)*

**Diatoms**

**40 to 75%** of the NPP in ocean *(Nelson et al., 1995)*

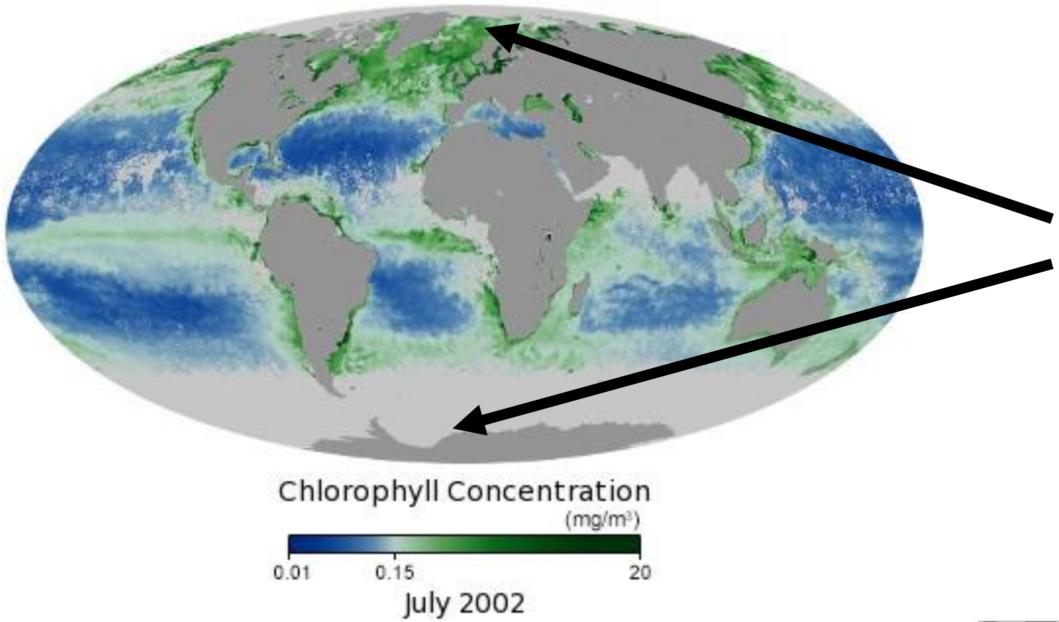
**Siliceous sponges**

A silicon sink added in the budget *(Tréguer and De La Rocha, 2013)*

**Rhizaria**

In progress

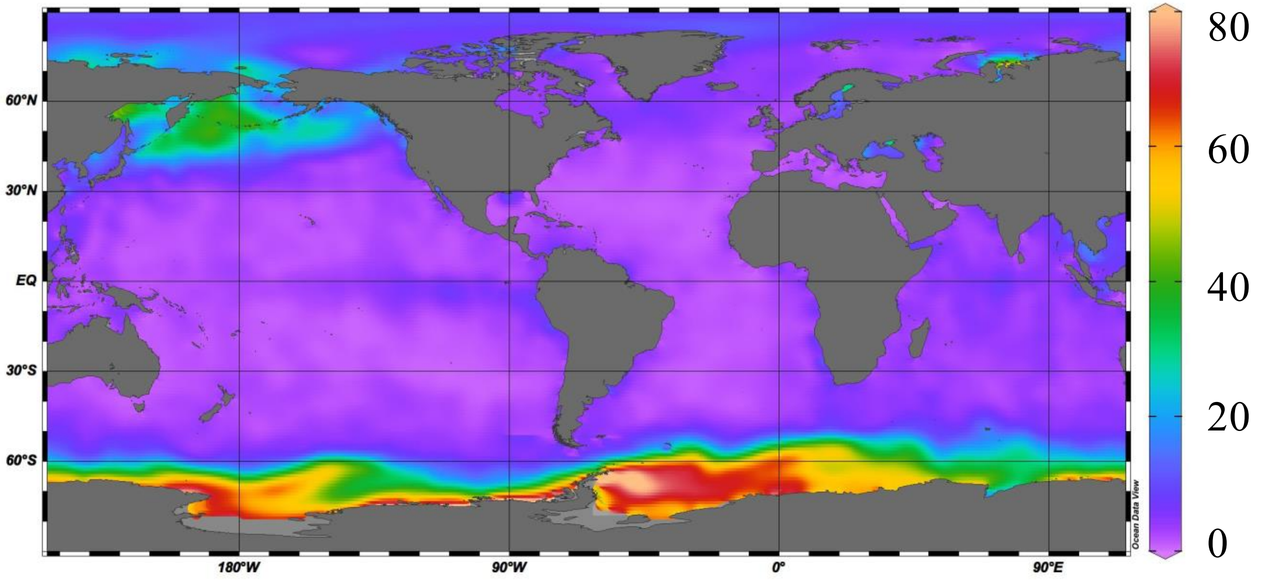
# Diatoms and dSi in the Ocean




Dominated by diatoms

*earthobservatory.nasa.gov*

dSi concentration in surface water (µM)

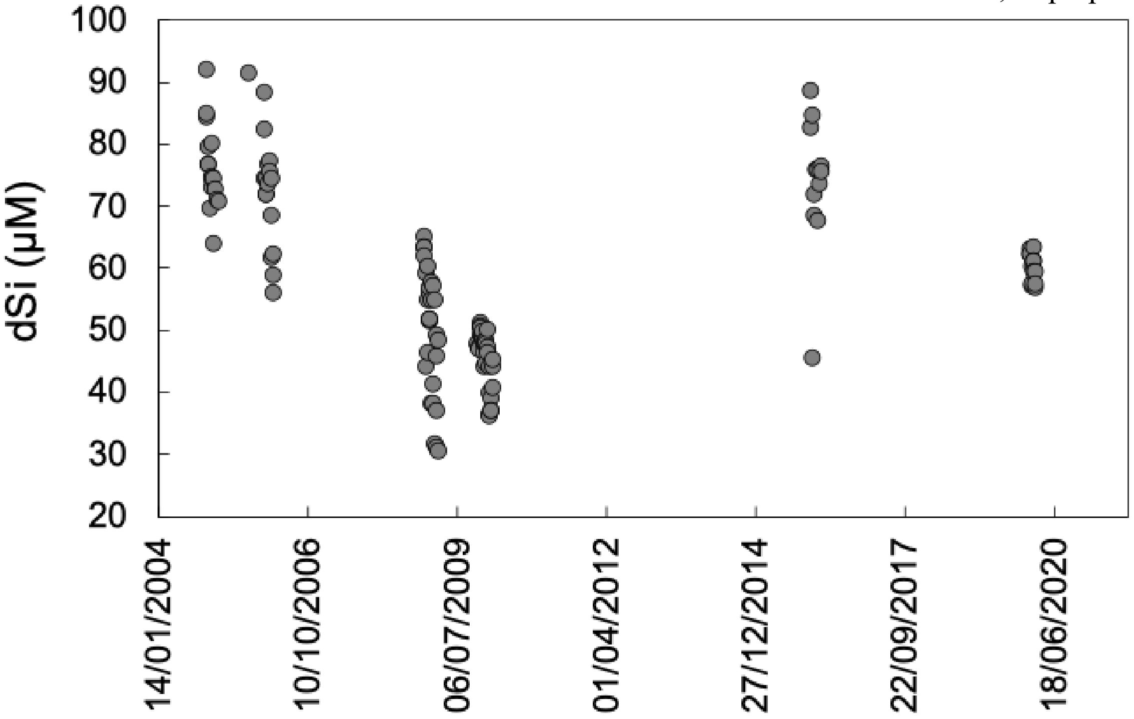



**Change in nutrient ➔ Impact on PP ➔ Impact on the entire food chain and carbon sequestration**

# Diatoms and dSi through time

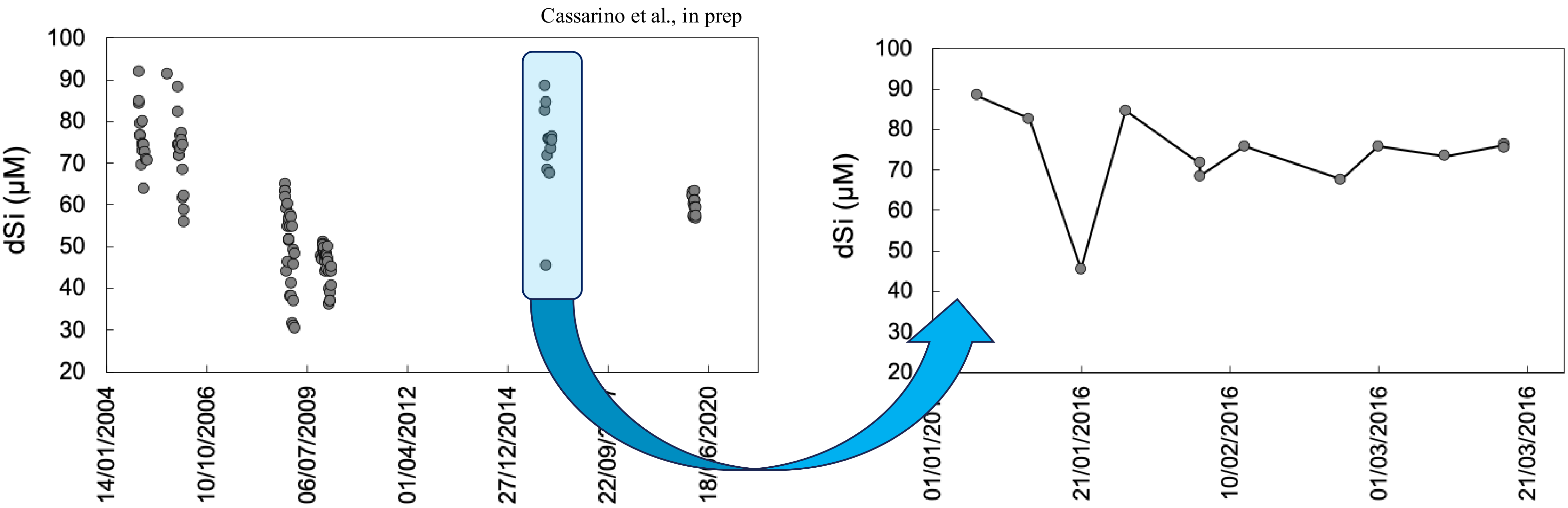
## RaTS – Rothera Time Series, West Antarctic Peninsula

Cassarino et al., in prep



# Diatoms and dSi through time

**RaTS – Rothera Time Series, West Antarctic Peninsula**




→ Large variations in dSi explained by stratification and biological uptake

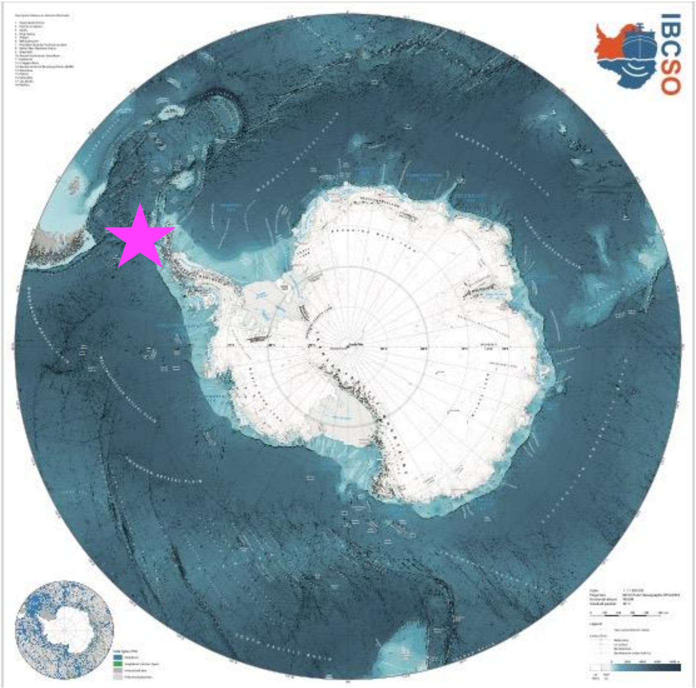
# MODUSS’ Motivations

**Lack of time-series with nutrients specifically on silicon data and polar environments to better characterize nutrients distributions and their impacts on productivity**

SOMLIT

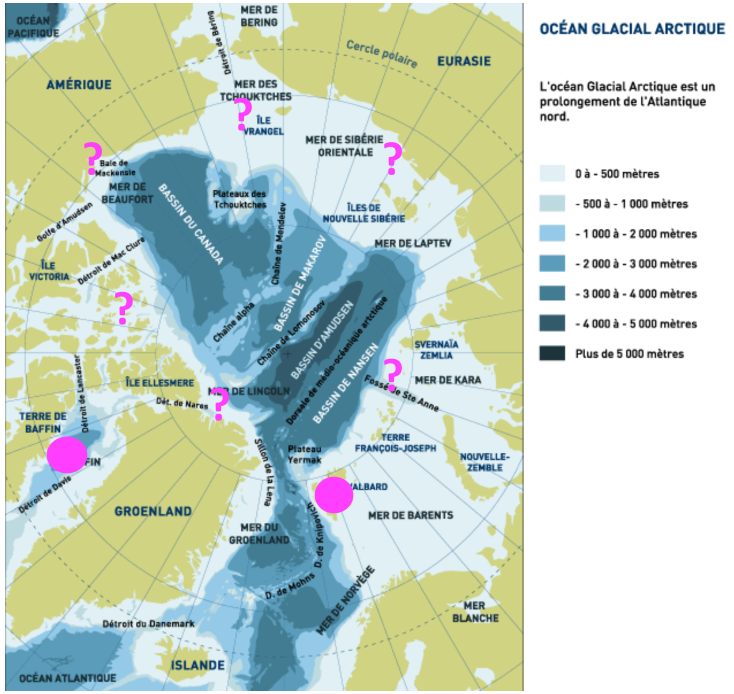

France

Palmer, RaTS




Antarctica

BBOS*, and more?




Arctic

*Baffin Bay Observing System

# MODUSS' Motivations

Rothera station (Antarctica) © Lucie Cassarino

**Why *in-situ* sensor deployment?**

- Accessibility to difficult zone (e.g. under-ice)
- Reduce volume requirement
- Time and human constrain for high frequency measurements.
- Reduce environmental perturbation

Green Edge, Qikiqtarjuaq, Nunavut, Canada

© Chawarski and de la Torre (-29°C)

# MODUSS


- Silicate sensor (CWSi - Microfluidic)
- Nitrate sensor (SUNA deep - Optique)
- CTD (RBR concerto[3])
- Fluorimeter (Seapoint)
- PAR (RBRcoda[3])
- Batteries (Li-SOCl2, **LEMAR-DC&I** Design)
- EdLogger (**LEMAR-DC&I** Design)

Ajustable

45 < weight < 65kg

40 x 40 x 110 cm

# MODUSS' Objectives

High frequency data

Catch occasional and unforeseen events

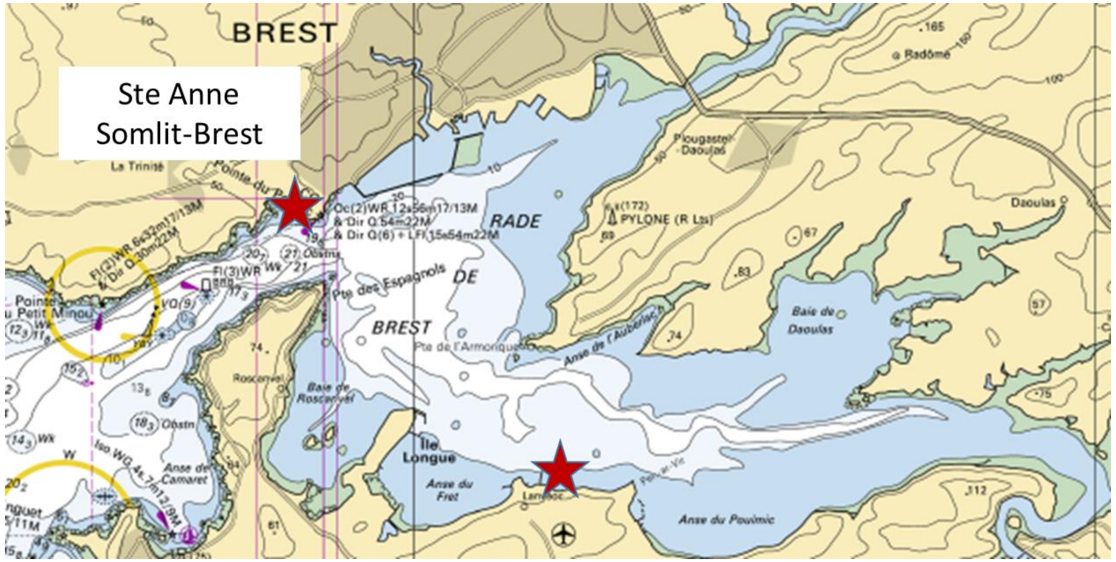
Investigate the dynamic of dSi (and other nutrients) and diatoms

Examine winter season (no data so far)

Avoiding discontinuity in time series studies

# MODUSS' METHODS

1) **Lab experiments (1µM < [dSi] < 100µM):** certified standard vs CWSi
2) **Control environments (-1.8°C < temperature < 25°C)**
3) **In-situ deployment (seasonnal variations):** SOMLIT Lanveoc and St Anne site (spring), summer and automn 2024.



# CWSi: characteristics

- **High performance** - Sensitive wet-chemical methods
- **High-resolution data** - Up to every 5 minutes
- **User friendly** - Easily swappable reagents
- **Long endurance** - Thousands of readings per cartridge
- **High stability** - Onboard calibration and standardisation
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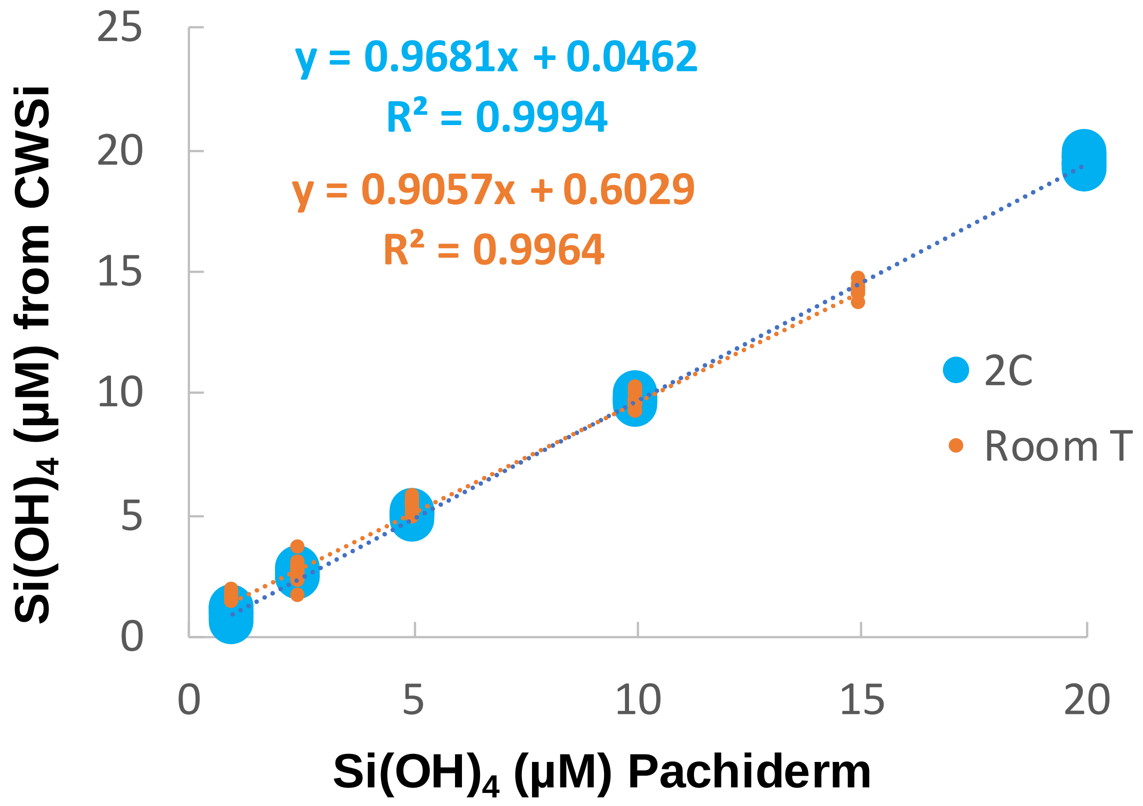
# MODUSS' Results

## CWSi: Positive temperature

**Mode** = Time Series, **Internal Standard** = 20µM, **Reagent** = positive temperature reagent




➔ **Good correlation between CWSi and Standards at both temperatures**

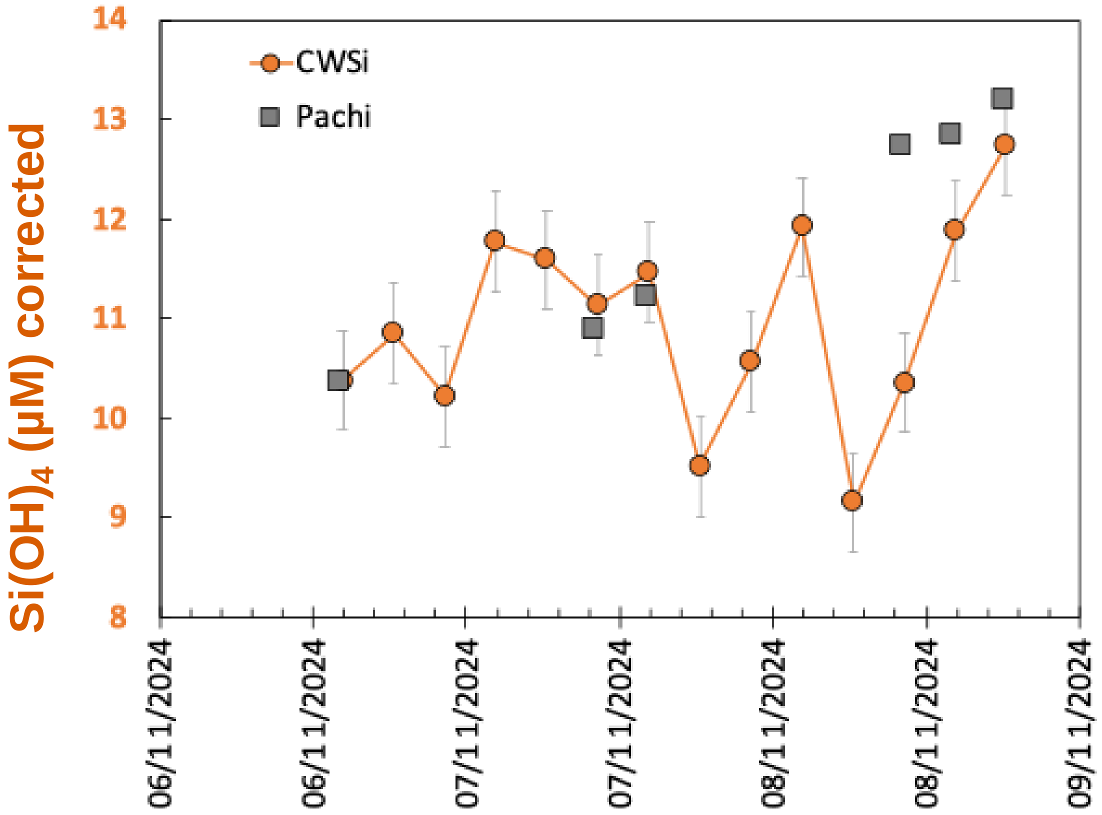
| Value | 2°C | Room T |
|---|---|---|
| 1 | 0.93 ± 0.19 | 1.56 ± 0.28 |
| 2.5 | 2.57 ± 0.12 | 2.70 ± 0.29 |
| 5 | 4.93 ± 0.10 | 5.48 ± 0.84 |
| 10 | 9.97 ± 0.14 | 9.95 ± 0.90 |
| 15 | / | 16.44 ± 1.15 |
| 20 | 19.41 ± 0.22 | / |

Pachiderm: Plateau d'analyses des sels nutritifs du LEMAR

# MODUSS' Results

## CWSi: Under ice conditions Preliminary tests

**Mode** = Time Series, **Internal Standard** = 20µM, **Reagent** = Specific cold water reagent




➔ **Battery and CWSi electronic and microfluidic operate at negative temperature**

- dSi increase due to ice formation
- Water temperature ~ -1.5°C

➔ Correction of 1.89µM (standard measurement and Pachiderm subsampling)

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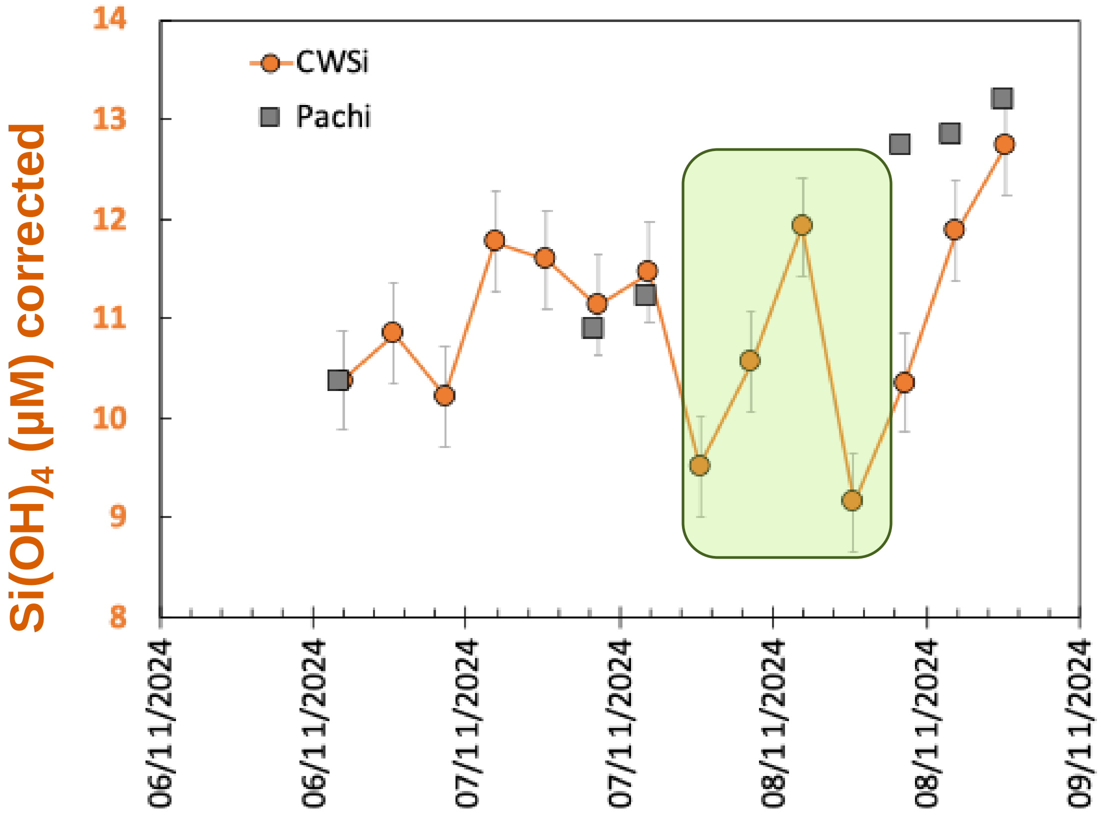



➔ **Battery and CWSi electronic and microfluidic operate at negative temperature**

- dSi increase due to ice formation
- Water temperature ~ -1.5°C
- Variability likely due to refill of water and sampling

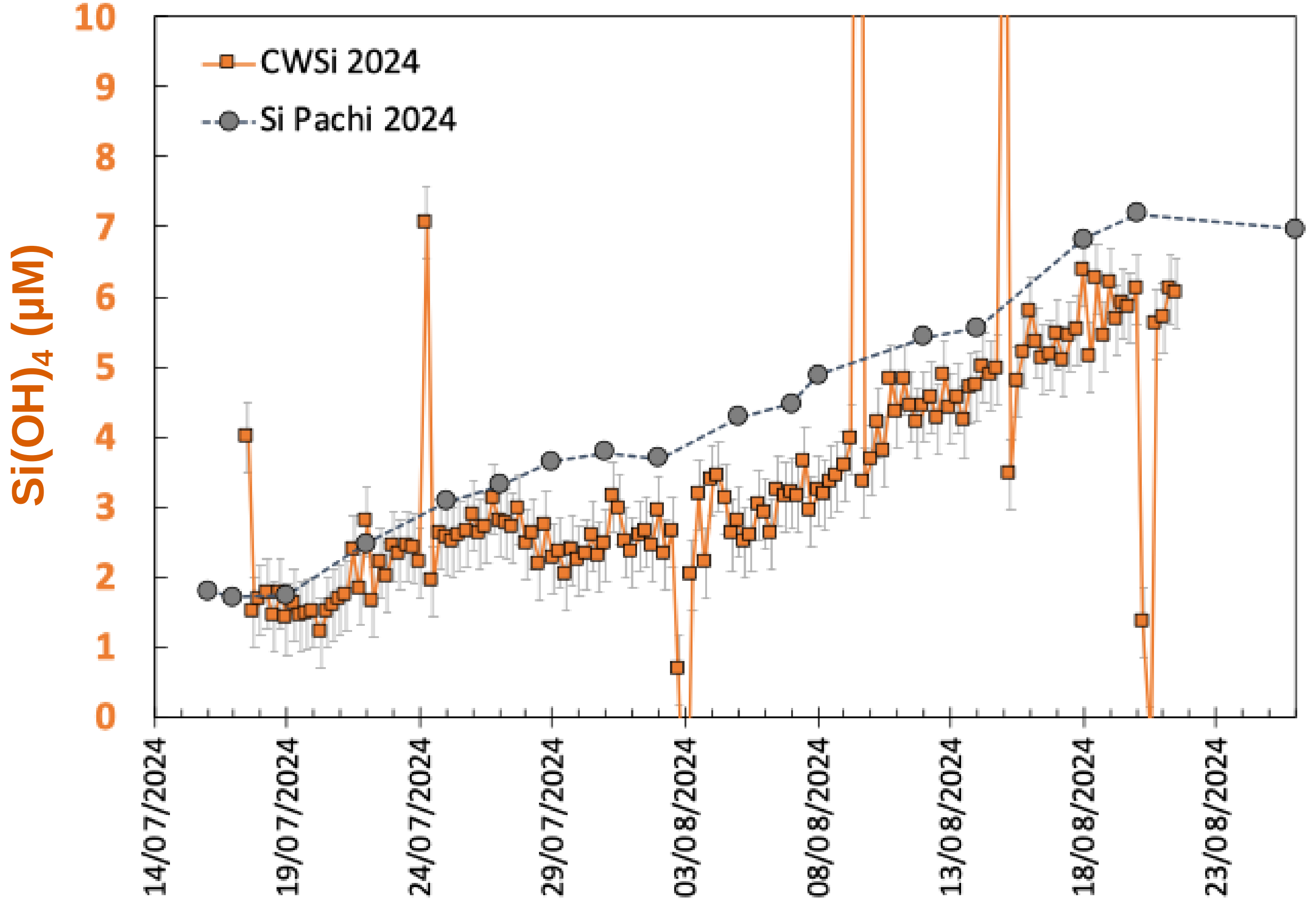
➔ Correction of 1.89µM (standard measurement and Pachiderm subsampling)

## MODUSS: In-situ deployment summer 2024

# MODUSS' Results

**Mode** = Time Series, **Internal Standard** = 20µM, **Reagent** = positive temperature reagent

Monitoring without anti-fouling, water temperature = ~16˚C




➔ **Similar trend for CWSi and SOMLIT sampling results**

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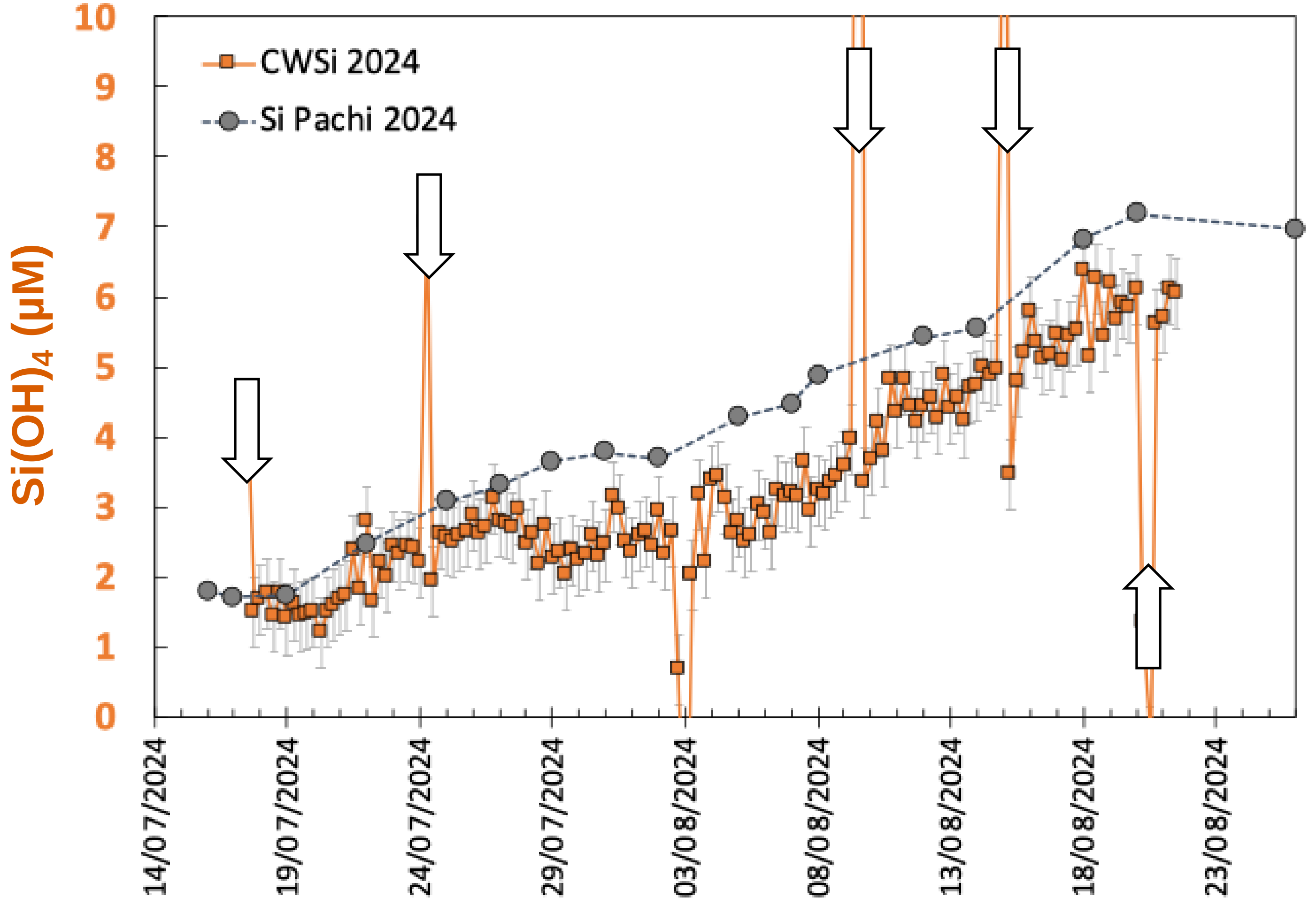


- **Similar trend for CWSi and SOMLIT results**
- Data recovery = 96.5%

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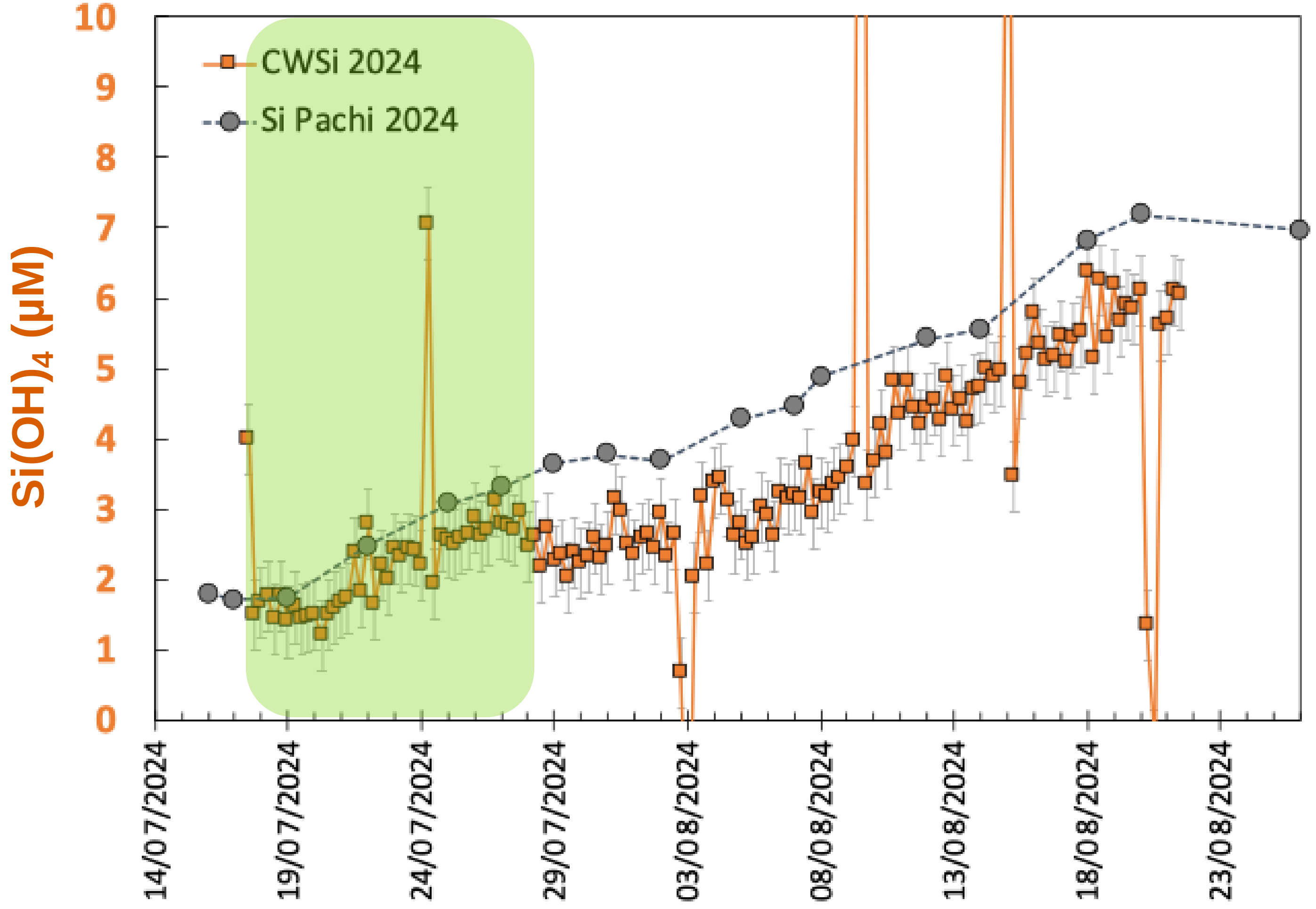


➔ **Good accuracy the first 12 days**

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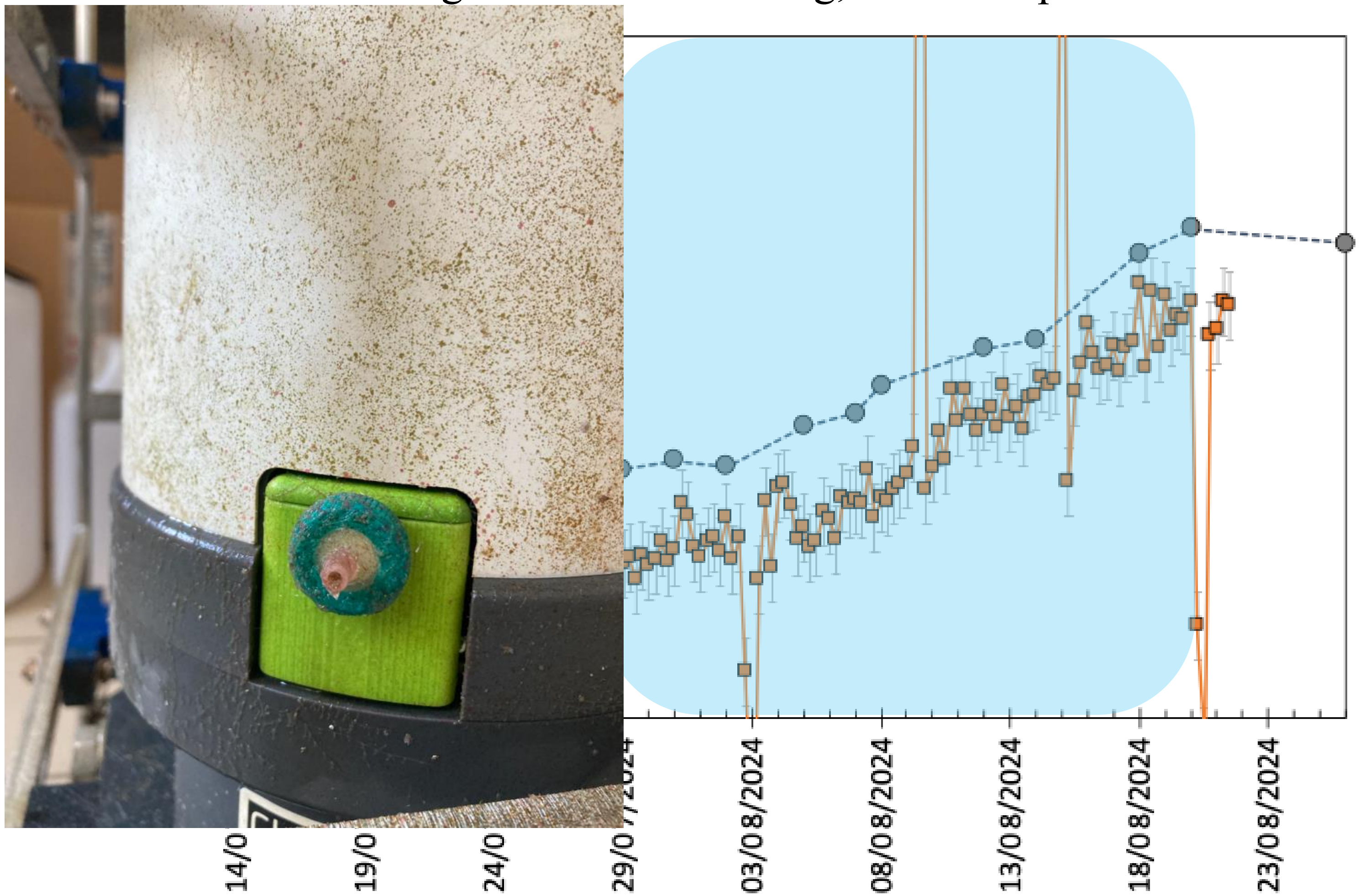


➔ Good accuracy the first 12 days

➔ After 12 days, constant bias of -1.12 ± 0.77µM

Is the fouling action increasing the bias?

Does it change the volume sampled by sensor?

# MODUSS' on going work

**Freezer Test:** under ice conditions

**Data Communication test:** IUEM – Argenton (IFREMER)

# MODUSS' Conclusions

Detection Limit = 0.85µM

error up to 20% for 1µM solution

Error up to 2% for higher dSi

## Constructor characteristics tested

- **High performance** - Sensitive wet-chemical methods
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High performance →
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User friendly → Yes

Long endurance → Yes, but reagent are aging

# MODUSS' Conclusions

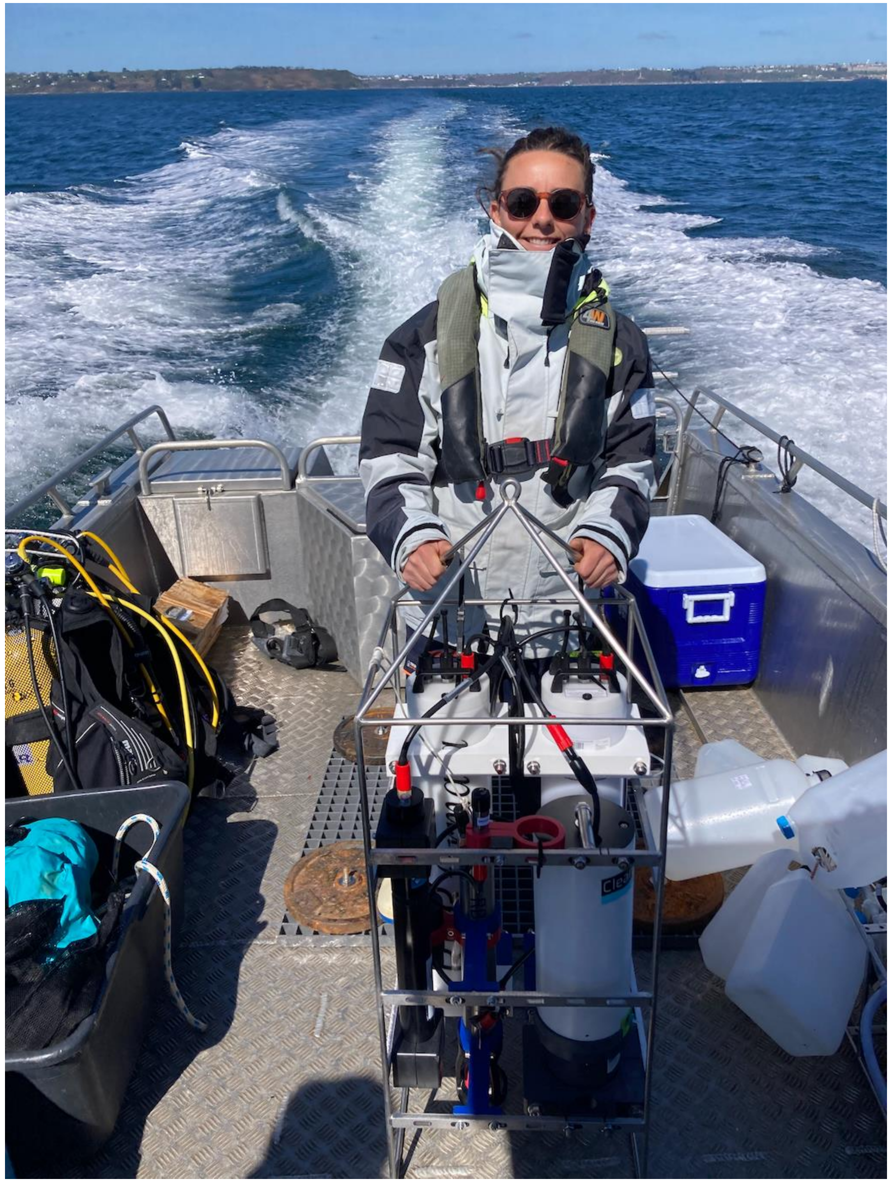
## Constructor characteristics tested

| Characteristic | Result |
| --- | --- |
| **High performance** - Sensitive wet-chemical methods | Detection Limit = 0.85µM<br>error up to 20% for 1µM solution<br>Error up to 2% for higher dSi |
| **High-resolution data** - Up to every 5 minutes | 12min (profiling) or 38min (Time Series) |
| **User friendly** - Easily swappable reagents | Yes |
| **Long endurance** - Thousands of readings per cartridge | Yes, but reagent are aging |
| **High stability** - Onboard calibration and standardisation | **2.5µM** STD over 4 months<br>= **2.6 ± 0.7** (n = 51)<br>**5µM** STD over 1 year<br>= **4.9 ± 1.5** (n = 54) |

**Environmentally friendly** - Self-contained onboard waste storage

**Deep sea operation** - Deployable to 6000 m

# MODUSS' Conclusions



- CWSi: the only dSi sensor on the market
- Operates at $-1.8^{\circ}C < T < 20^{\circ}C$
- Each new cartridge need standard test
- Better protect against fouling
- Find origin of long term bias

# Acknowledgements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- ISblue project, Interdisciplinary graduate school for the blue planet (ANR-17-EURE-0015) and co-funded by a grant from the French government under the program "Investissements d'Avenir" embedded in France 2030

(ISblue – Research at sea and ISblue – Animation of Isblue research themes)

- Brittany area
- Finistere council
- LEMAR Laboratory
- P2i
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# Acknowledgements


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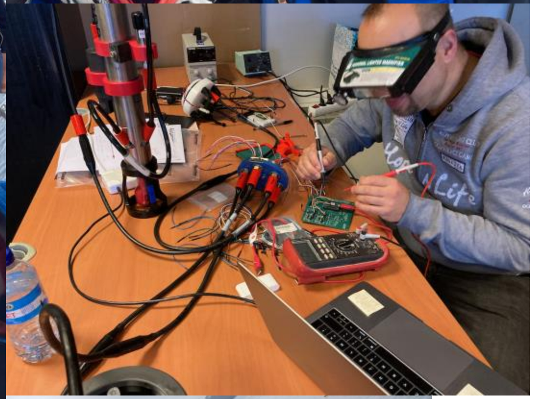
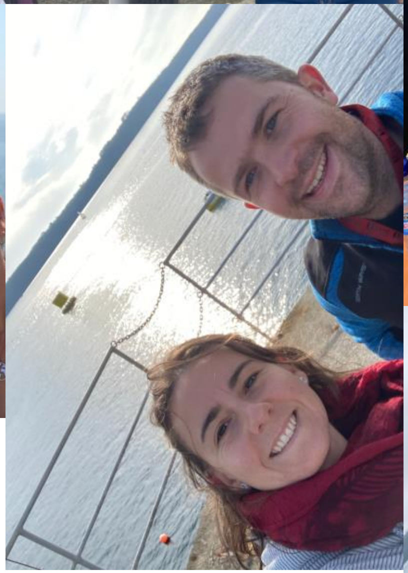
- **Jill Sutton** (LEMAR – IUEM – UBO)
- **Albert Lucas crew** (Moyen à la mer – IUEM)
- **Séverine Enet** (SHOM)
- **Erwan Le Gall** (IFREMER Plouzané)
- **Michel Repecaud** (IFREMER Plouzané)
- **Didier Clech** (RBR company)



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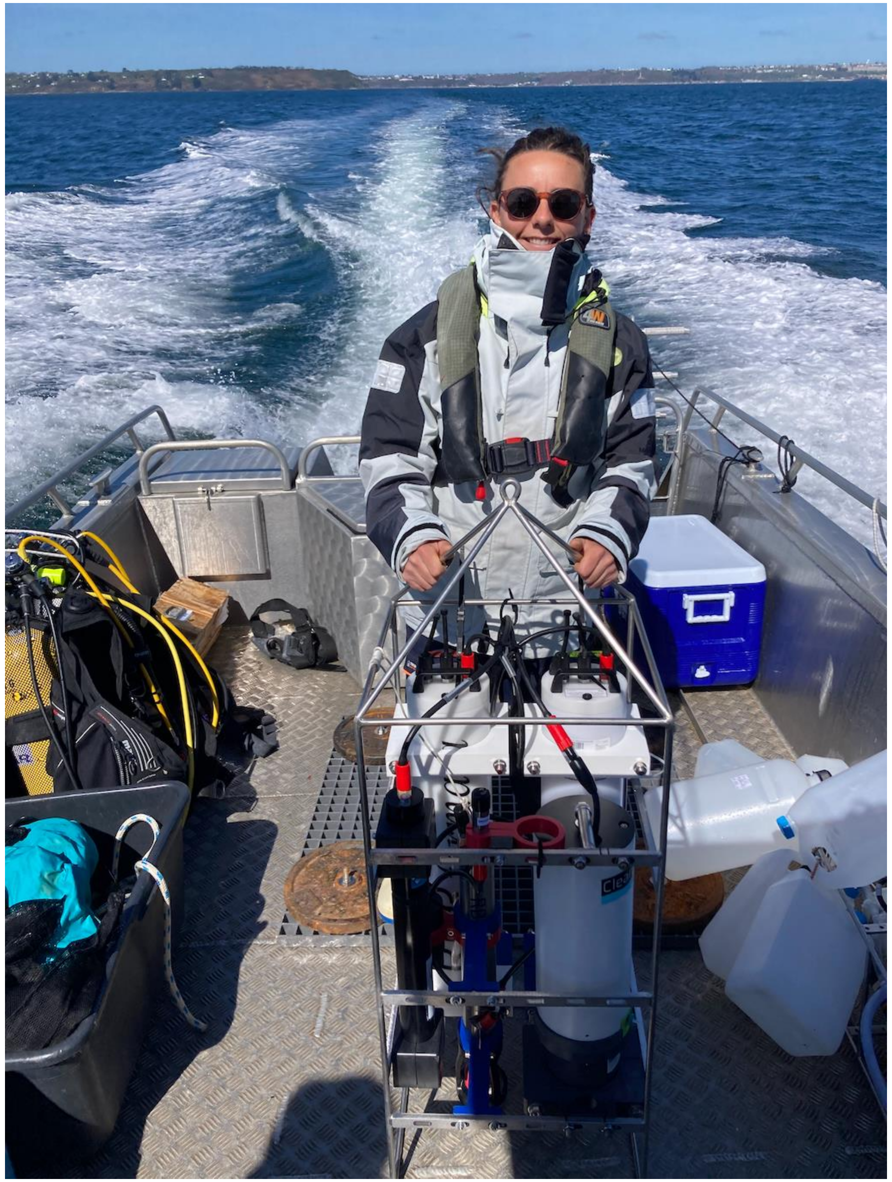
COAST-HF
COASTAL OCEAN OBSERVING SYSTEM – HIGH FREQUENCY

# Thanks for your attention



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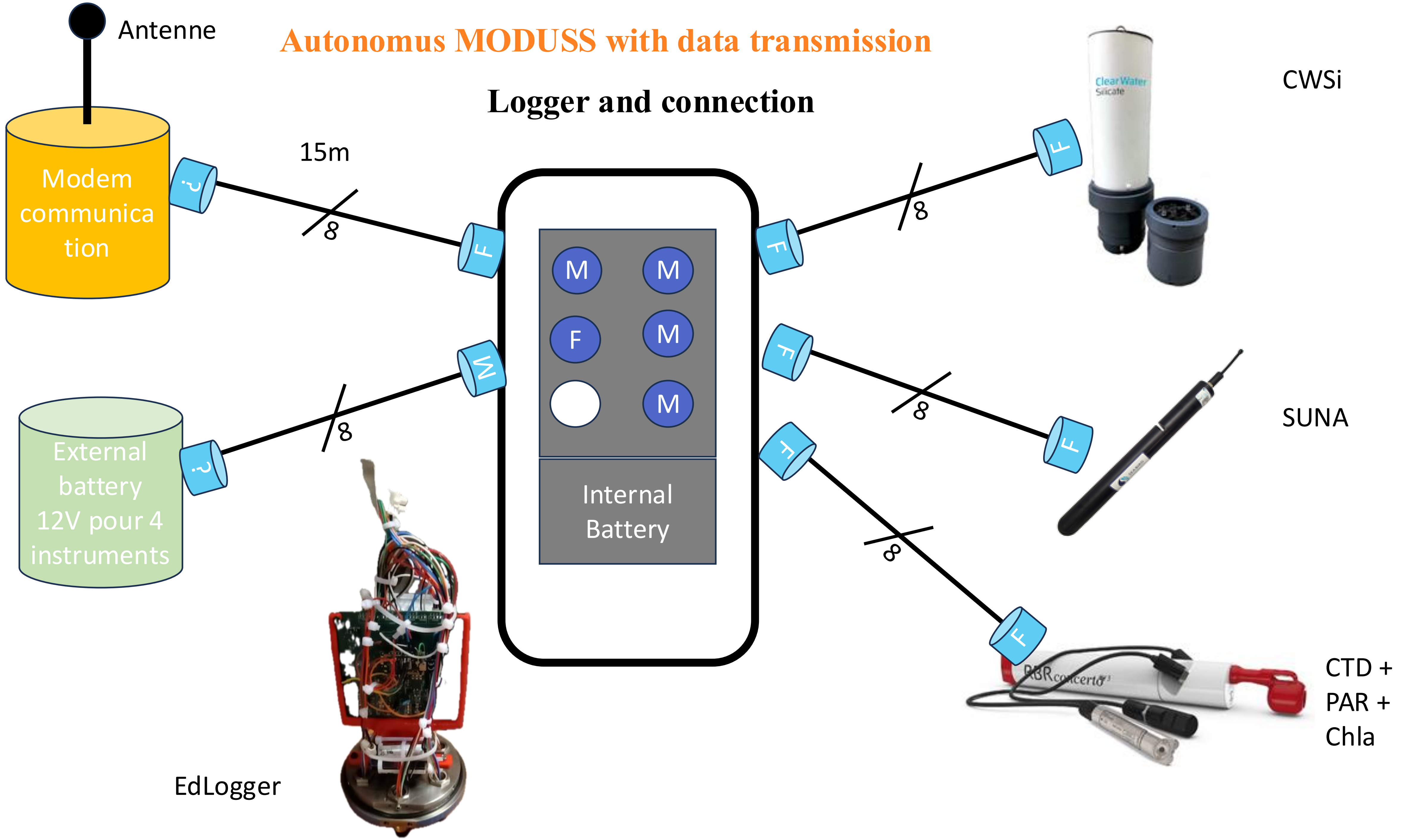
**Contact: lucie.cassarino@univ-brest.fr**


Autonomus MODUSS with data transmission
Logger and connection
Antenne
Modem communica tion
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External battery 12V pour 4 instruments
Internal Battery
EdLogger
CWSi
ClearWater Silicate
SUNA
CTD + PAR + Chla
RBRconcerto

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**Detection Limit** = 0.85μM

- **Reagents:**
  - → >0˚C
  - → <0˚C

- **Bags:**

**Moly** – Sulfuric acid, amonium molybdate tetrahydrate

**R1** – Oxalic acid

**R2** – Ascorbic acid and glycerol

**STD** – NaCl, Sodium hexafluorosilicate

**Blk** – Fluoride

**Rinse** – NaOH

**Waste**

- **Status:**
  - → Time Series (Blk – Sample – STD)
  - → Profiling (Blk – STD - 10x Sample)

- **Time for analysis:**

38min for Time Series

25min and 10min for Profiling