# *In situ* monitoring of nutrients in marine waters


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# Long term monitoring of nutrients concentrations

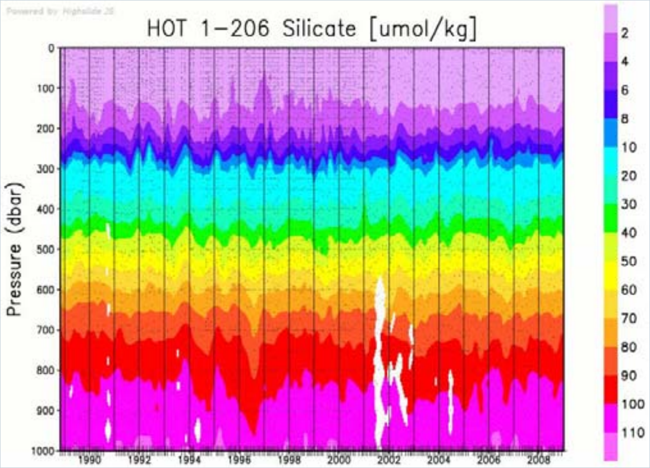
• to deconvolute natural signal from anthropogenic perturbation

in order to understand and to predict effects on global climate change

HOT : Hawaii Ocean Time Series

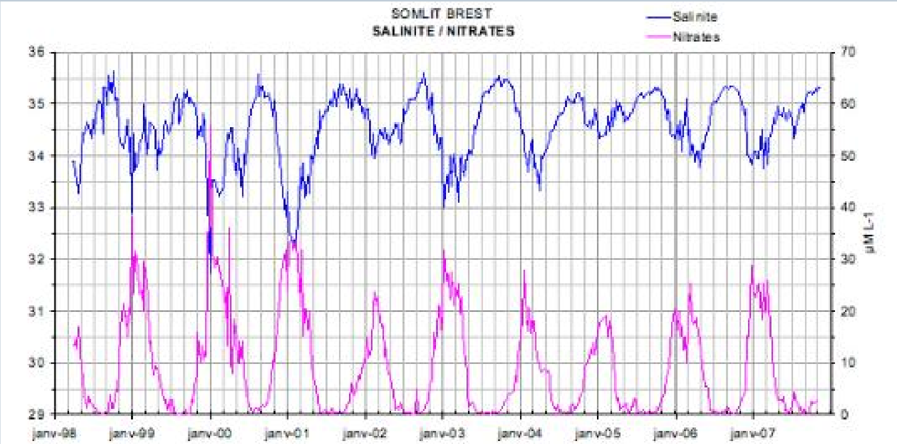
BATS : Bermuda Atlantic Time Series

JGOFS




© HOT

• to contribute to the Marine Strategy Framework Directive (MSFD)

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SOMLIT (CNRS/INSU)

ROCCH, RNC (Ifremer)

# Marine Strategy Framework Directive (MSFD)

Determination of a Good Environmental Status, based on 11 qualitative descriptors


Green algae / Brittany - 2010

## Eutrophication

Ecosystem response to an over enrichment of waters by nutrients such as nitrogen or phosphorus

(Ferreira et al. 2011 ECSS)

excessive algal growth

harmful algal blooms

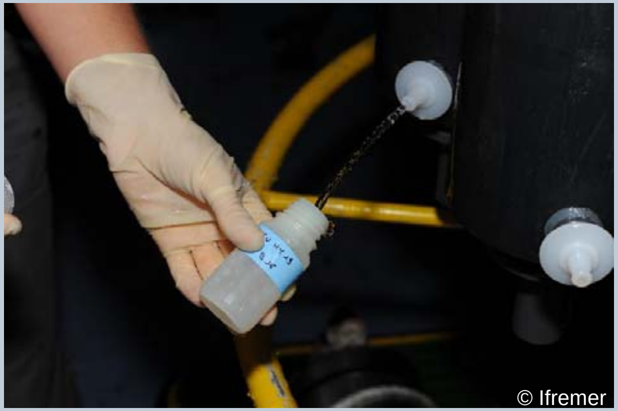

Phaeocystis bloom

# Usual sampling strategy

Every month from November to February and twice a month from March to October

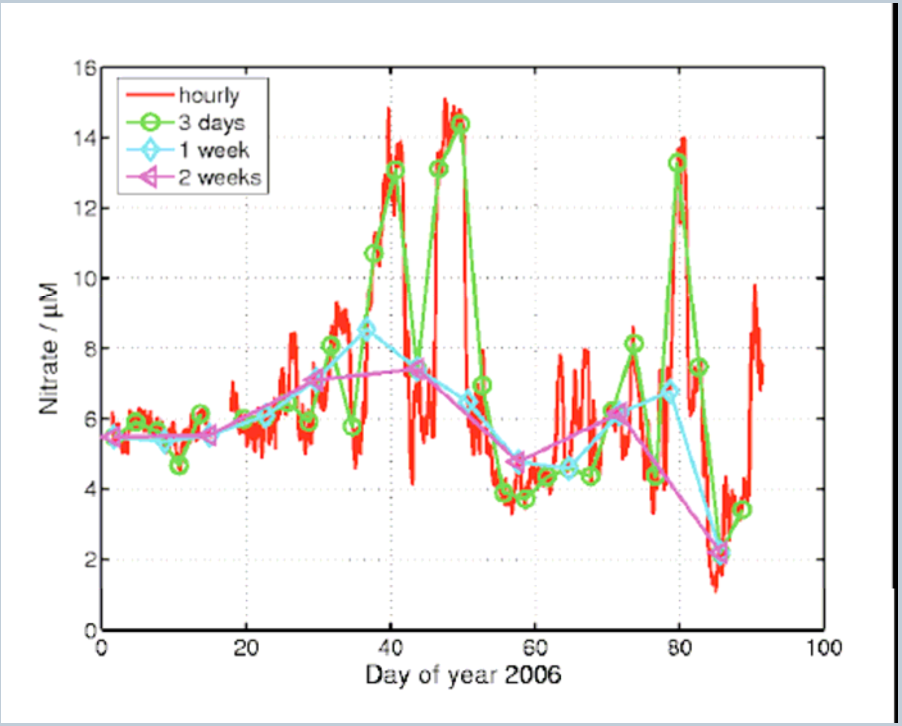
Ammonia, nitrate, nitrite, particulate nitrogen, total nitrogen, phosphate, total phosphorus, particulate phosphorus and silicate

Sampling is realized at sub-surface (0 - 1 m)


# Nutrients distribution vary widely in marine ecosystems

## episodic and transient events missed



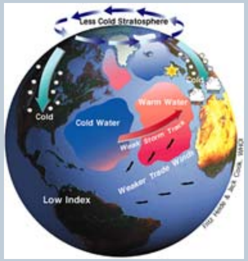

Johnson and Coletti (2002)

increase temporal and spatial resolution of sampling and analysis (Prien et al. 2007)

given the spatial extent of the MSFD and the sampling frequency, innovative approaches are required to allow meaningful monitoring (Ferreira et al. 2011 ECSS) from years, weeks, days, hours to seconds …

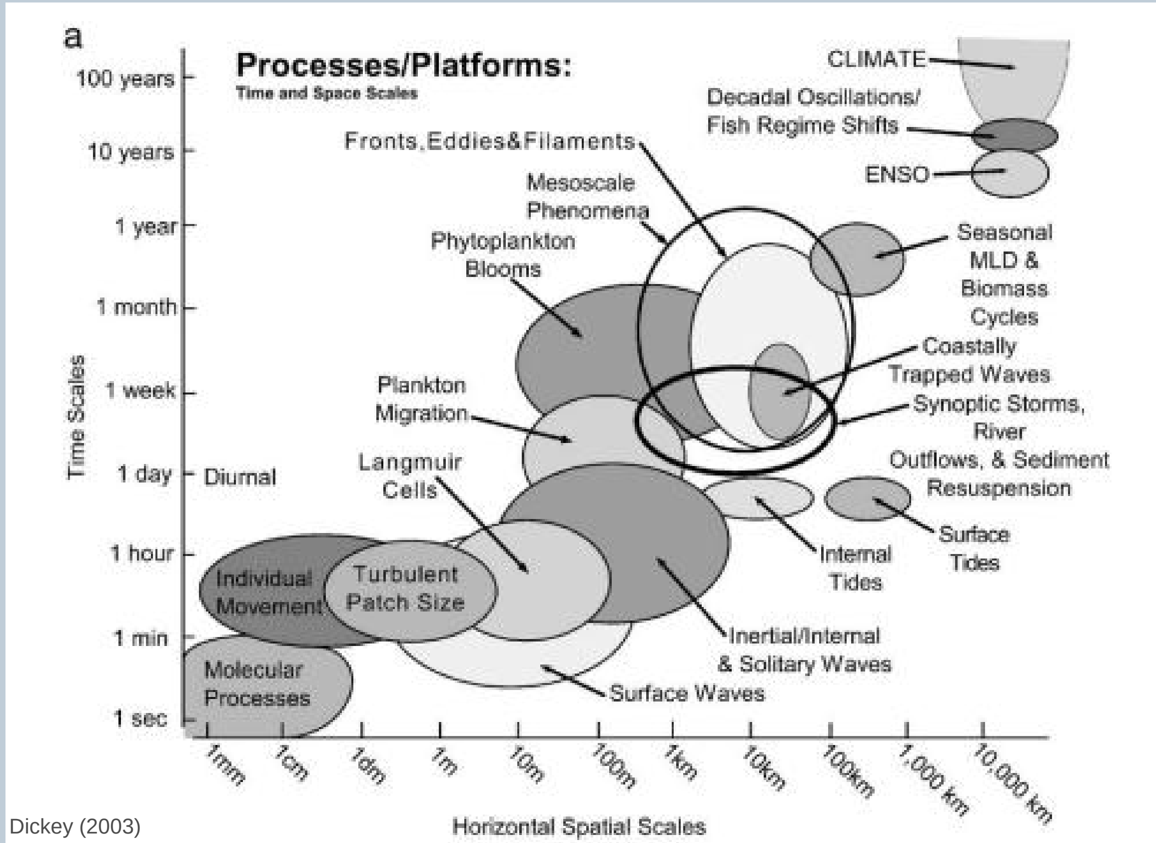
from piers, buoys, profilers to AUVs …

from one dimension to 3D …

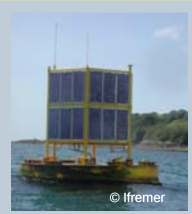








Dickey (2003)



# Essential to develop *in situ* instrumentation for nutrient analysis

robust

miniaturised

small energy consumption

few maintenance

High frequency of analysis

precise, accurate, high level of detection

not influenced by biofouling

If it’s cheap, it’s even better !

# Various types of *in situ* instruments for nutrient analysis

| | Product | Brand/ Research Institute | Reference | Detection technique | Chemical species | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Nitrate | Nitrite | Ammonium | Phosphate | Silicate |
| Europe | ANAIS | Prototype/ LEGOS | Vuillemin 1999/Thouron et al 2003 | wet chemistry | X | X | | X | X |
| | ANESIS | Prototype/ LEGOS | Thesis Lacombe, Lacombe et al 2007 | electrochemical | | | | X | X |
| | CHEMINI | Ifremer | Vuillemin et al. 2009 | wet chemistry | X | X | X | X | X |
| | DPA Pro | SYSTEA S. p. A. | Gunatilaka et al. 2009 | wet chemistry | X | X | X | X | |
| | Props UV | TriOS | Zielinski et al. 2011 | optical | X | | | | |
| | Prototype | University of Hull/ UK | A. Webster 2010 | ion Chromatography | X | X | X | X | |
| | Prototype | University of Hull/ UK | Al-Gailani et al. 2007 | wet chemistry | | | X | | |
| | Prototype | NOC/ Nano research group | Beaton et al. 2011 | wet chemistry | | X | | | |
| | Prototype | NOC/ Nano research group | Legiret 2010 | wet chemistry | | | | X | |
| | Prototype | NCSR, Dublin | Bowden et al. 2003 | wet chemistry/ microfluidic | | | | X | |
| | Prototype | GKSS, Germany | Franck et al. 2006 | wet chemistry | | | X | X | |
| | SIA analyser | Helmholtz-Zentrum Geesthacht | Petersen | wet chemistry | | | X | X | |
| | WIZ | SYSTEA S. p. A. | Vuillemin et al. 2009b | wet chemistry | X | X | | X | X |
| International | APNA | SubChem Systems | Egli et al. 2009 | wet chemistry | X | X | X | X | |
| | AutoLAB 4 | EnviroTech | | wet chemistry | X | | X | X | X |
| | CYCLE | Wet Labs | Barnard et al. 2009 | wet chemistry | | | | X | |
| | Digiscan NH4 | Mbari | Plant et al. 2009 | wet chemistry | | | X | | |
| | EcoLAB 2 | EnviroTech | | wet chemistry | X | X | X | | X |
| | ISUS V3 | Saltantic | Jonhson 2002/ Sakamoto et al. 2009 | optical | X | | | | |
| | NAS-3X | EnviroTech | | wet chemistry | X | | X | X | X |
| | NITRATAX | HACH | | optical | | | | | |
| | Nutrient ISES | YSI | | ion selective electrodes | X | | X | | |
| | Nutrient ISES | HACH Environmental | | ion selective electrodes | X | | X | | |
| | SCANNER | Mbari | Johnson et al. 1994 | wet chemistry | | | | | X |
| | SEAS | University of South Florida | Adornato et al. 2007/ Steimle 2002 | wet chemistry | X | X | | X | |
| | SubChemPak | SubChem Systems | | wet chemistry | X | X | X | X | X |
| | SUNA | Satlantic | | optical | X | | | | |
| | TROLL 9500 | In-situ Inc. | | ion selective electrodes | X | | X | | |
| | Ysi 9600 (Digiscan) | Ysi | Weeks and Johnson 1996 Mbari | wet chemistry | X | | | | |

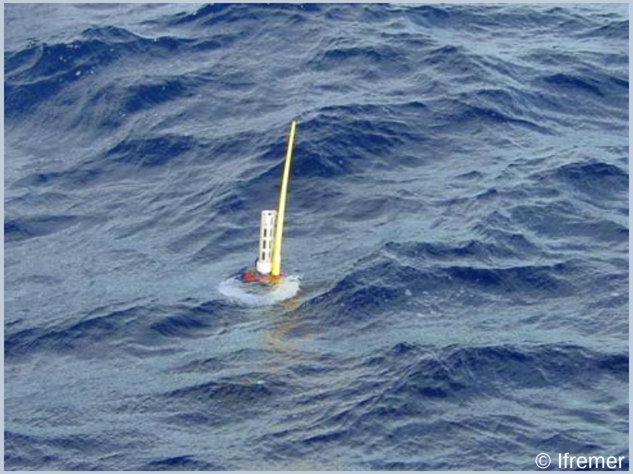
**Huge disparity** in terms of detection, analytical performances

# What we have done so far at the Ifremer Brest …

- Wet chemistry on a buoy : temporal case study



- Optical Sensor on a profiler : spatial and temporal case study

- CHEMINI
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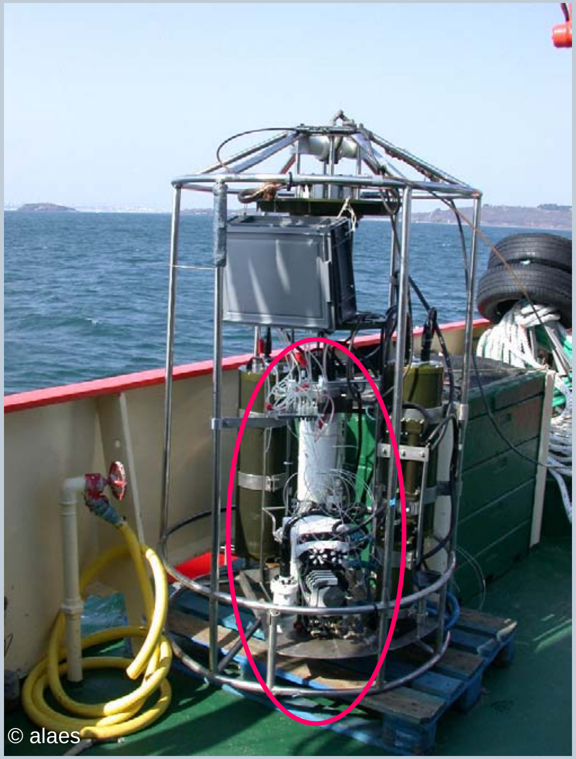
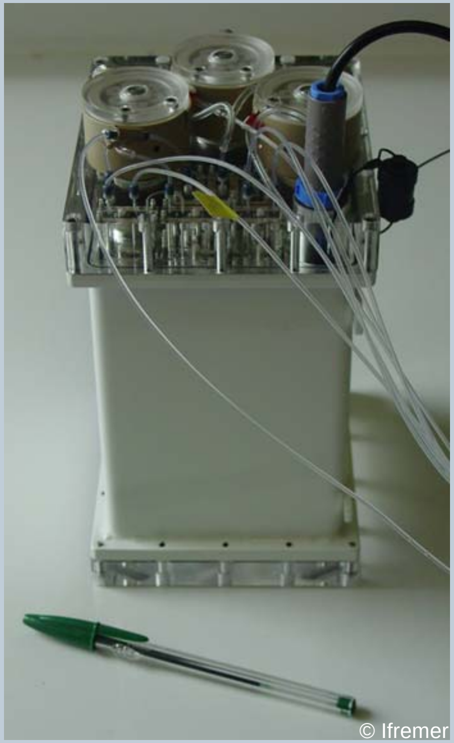
# CHEMINI




• First generation of chemical analysers in the 90's

ALCHIMIST

Daniel *et al.* 1995, Floch *et al.* 1998, Le Bris *et al.* 2000, Laës *et al.* 2005, Sarradin *et al.* 2005

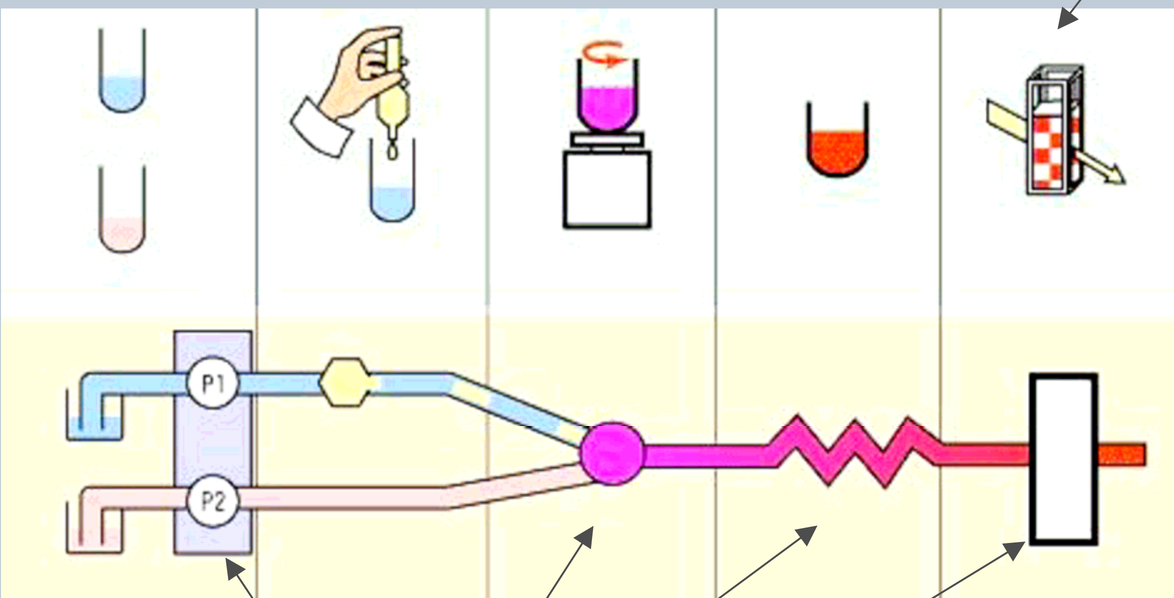



• New generation of chemical analysers in 2004

CHEMINI: CHEmical MINIaturised analyser

Vuillemin *et al.* 2009



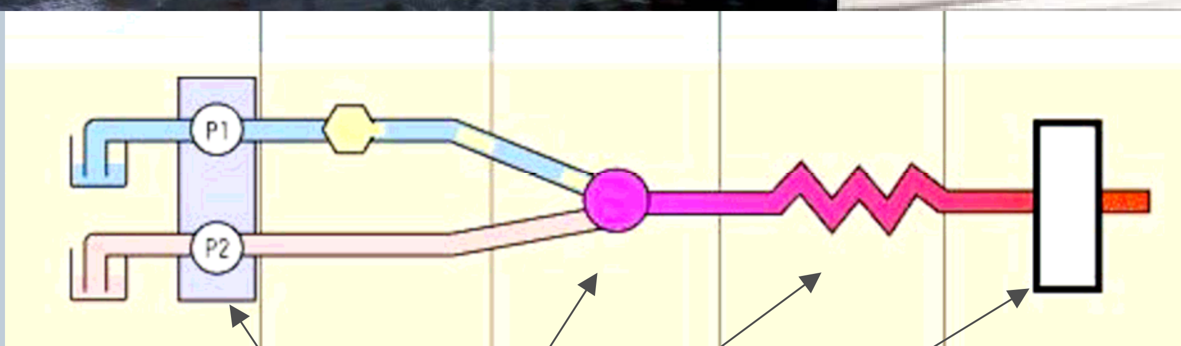




Traditional sampling and analysis

*In situ* flow injection analyser

- Automated (less contamination)
- No sampling cruise
- High frequency of measurement
- In situ calibration






High quality and high frequency data even when harsh and hostile conditions are encountered

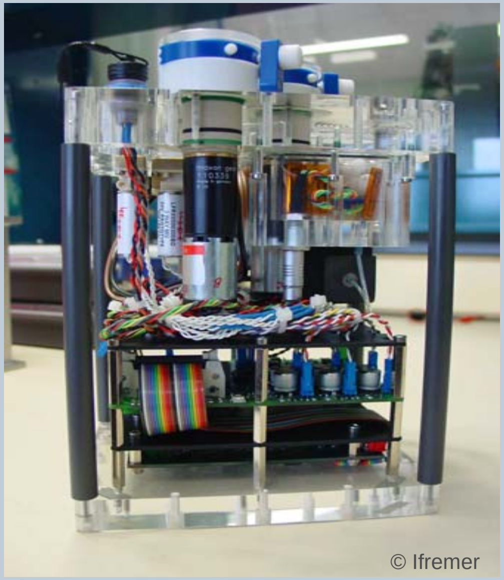
# Flow injection analysis (FIA) with spectroscopic detection

weight : 5 kg (without reagents)

Dimensions : 233mm h x 148mm l x 121mm L

Power supply : 12 V, Consumption : 0,5A - 12V

Remotely controlled by automate

- Ammonia (4)
- Nitrate (2)
- Silicate (1)
- Phosphate (1)

## Figures of merit for nitrate determination

Detection limit : 0,017 µmol.l$^{-1}$ $NO_3$

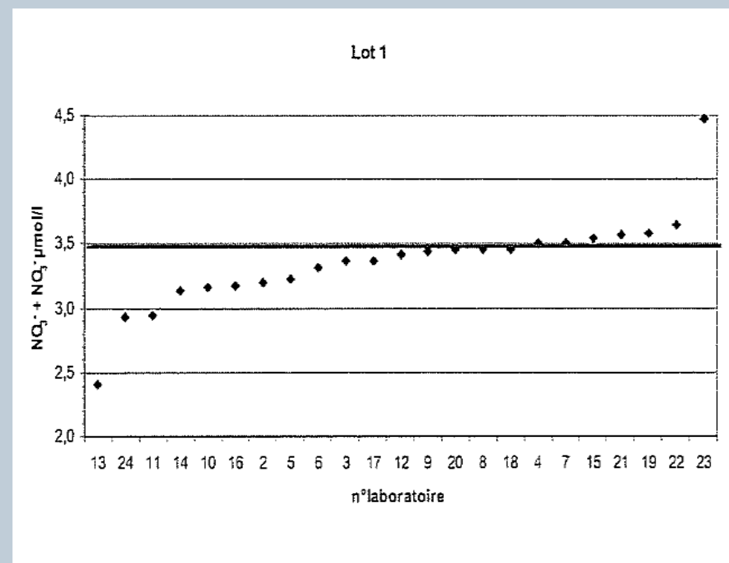
Linearity : 0 -100 µmol.l$^{-1}$ $NO_3$

Precision : 3,1% $NO_3$ (1,5 µmol.l$^{-1}$ , n = 5)

Measure frequency : 13 minutes $NO_3$

## Interlaboratory comparison (EILs)

Verify the accuracy of the method



Protection box


Reagent bags


Multiconnectors


Vibration tests

Verify the robustness of the instrumentation

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PRECODD

PRogramme de recherche
ECOtechnologies et Développement Durable

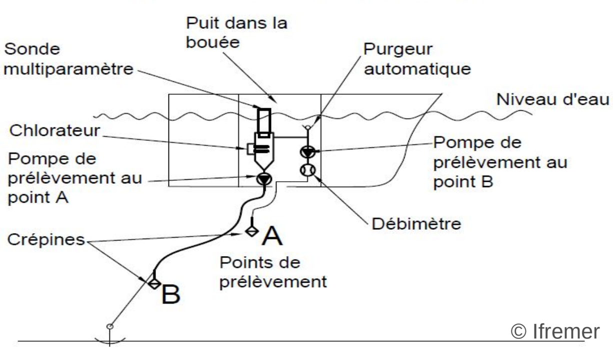
# Sampling and analysis simultaneously to the other parameters (S, T°C, Dissolved $O_2$, Turbidity)

## Marel technology

| Temps (H) | 0 | 30 | 60 | 90 | 120 |
|---|---|---|---|---|---|
| MOLIT | Prélèvement surface | Prélèvement fond | Prélèvement surface | Prélèvement fond | |
| | C 2, R 4, M 2, Cl 17, Rp 5 | C 2, R 4, M 2, Cl 17, Rp 5 | C 2, R 4, M 2, Cl 17, Rp 5 | C 2, R 4, M 2, Cl 17, Rp 5 | |
| CHEMINI | Prélèvement surface | Std 1 | Std 2 | Prélèvement fond | |
| | A, A, M, M, Rp | A, A, M, M, Rp | A, A, M, M, Rp | A, A, M, M, Rp | |

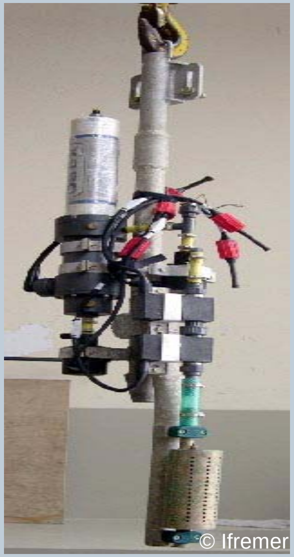
| | |
|---|---|
| C | Chasse |
| R | Rincage |
| M | Prélèvement et Mesure |
| Cl | Chloration |
| Rp | Repos |
| A | Attente |

SCHEMA CIRCUIT HYDRAULIQUE MOLIT





4 surface and bottom measurements per day
nitrate and silicate



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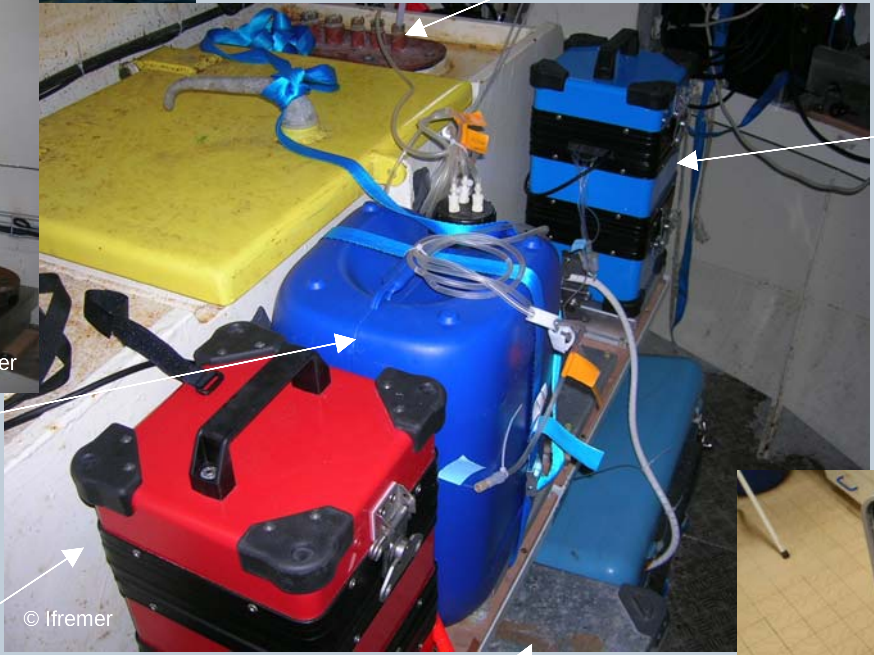



Communication module GSM

Sampling tube with prefilter

Nitrate Chemini

Reagent trash

Silicate Chemini

Reagent containers

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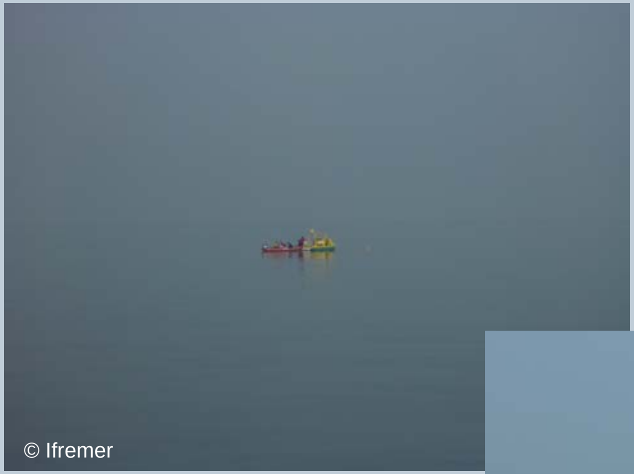
# Vilaine Bay

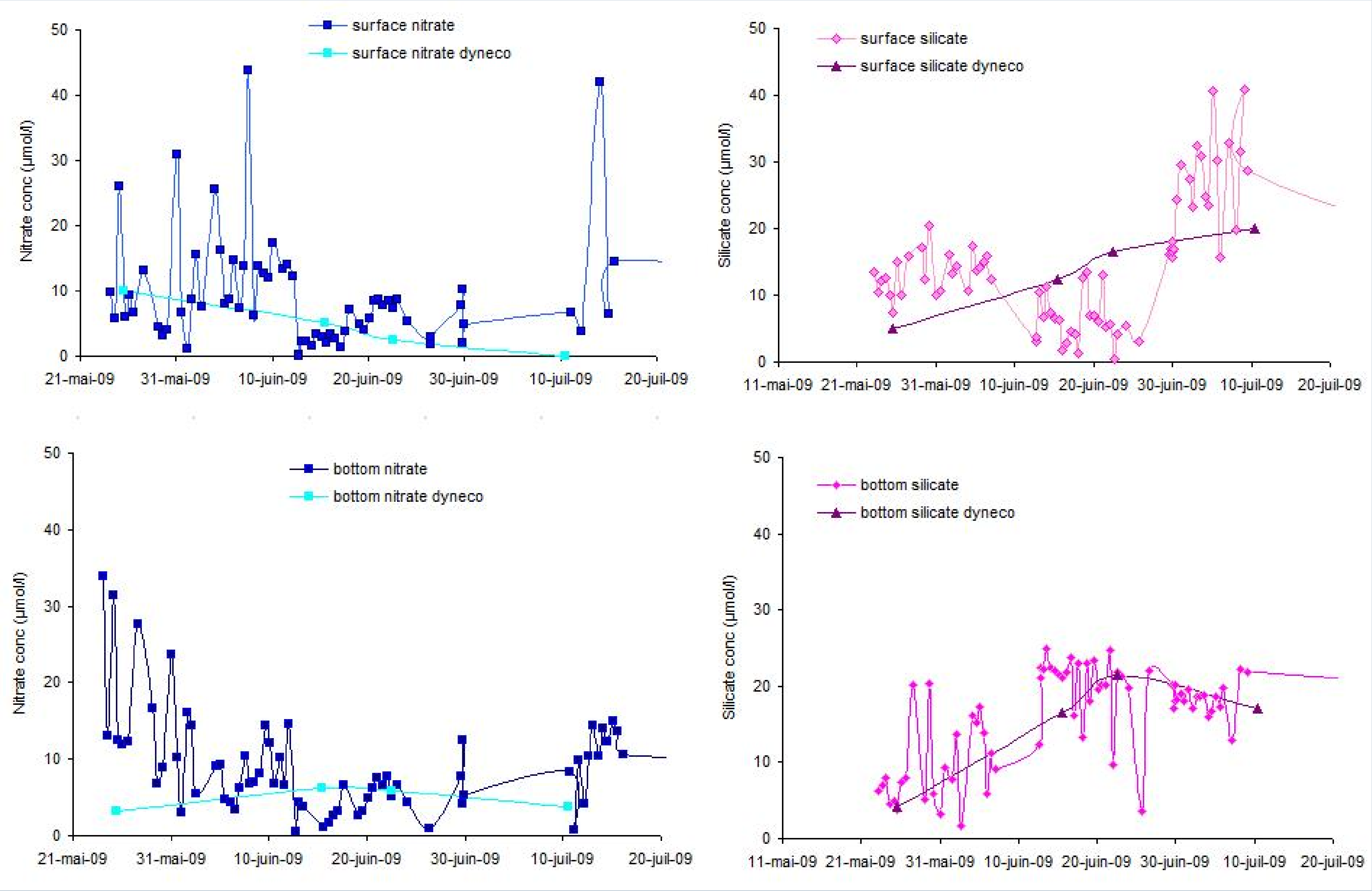





• To understand and to simulate the apparition of Pseudo-nitzschia in the Vilaine Bay

• To contribute to the Marine Strategy Framework directive and compared it to high frequency measurements

# 2009 : 7 months of deployment



2009 : 7 months of deployment

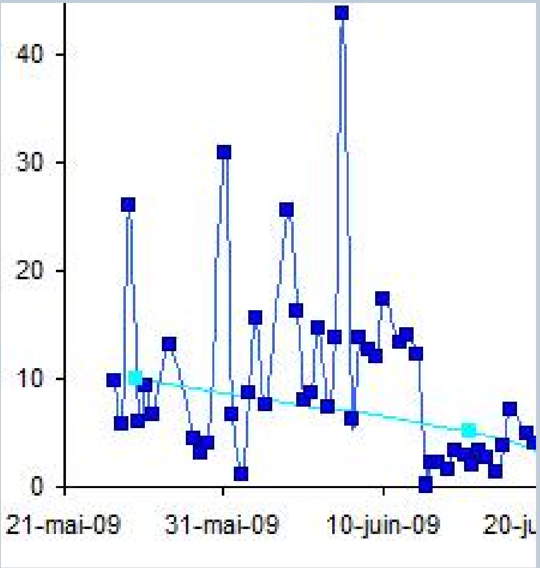
- Comparison with discrete samples :

prefiltration, time gap between both analysis (2h), sampling at the same depth ?

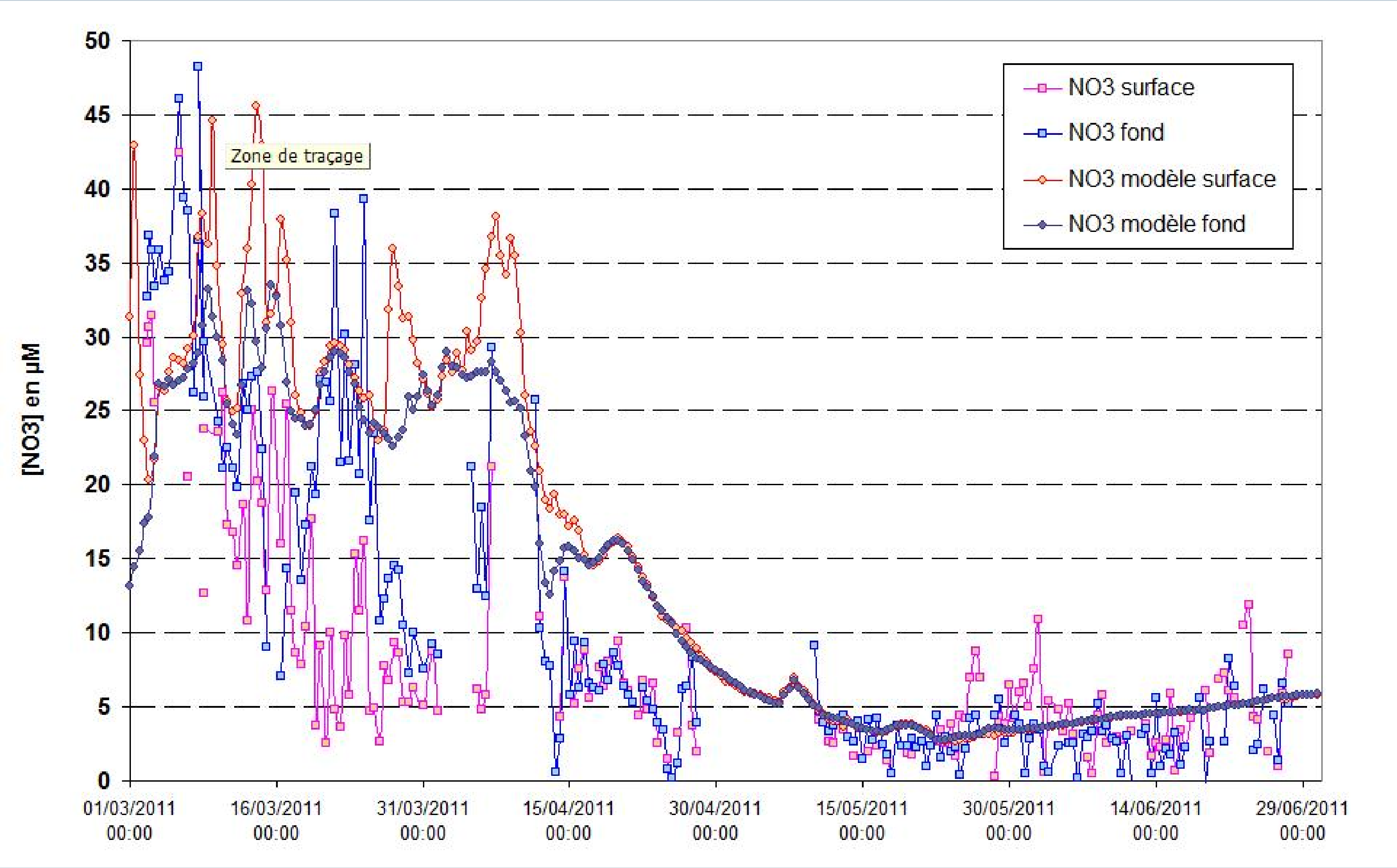
- Comparison with traditional strategy :

underestimation for nitrate : difference of 2,96 µmol/l for surface nitrate concentrations, and 1,73 µmol/l for bottom nitrate concentrations

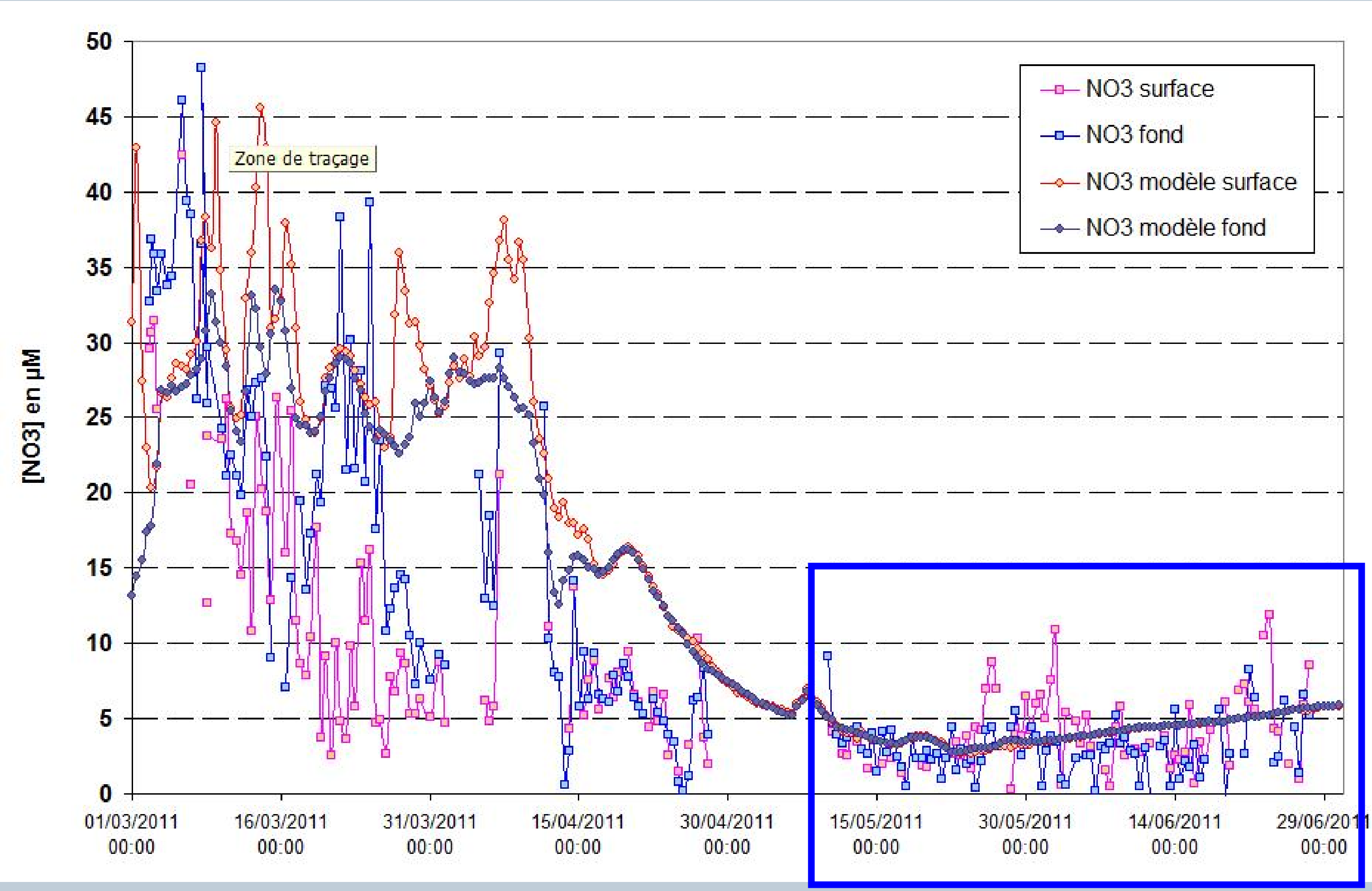
missing extreme concentrations



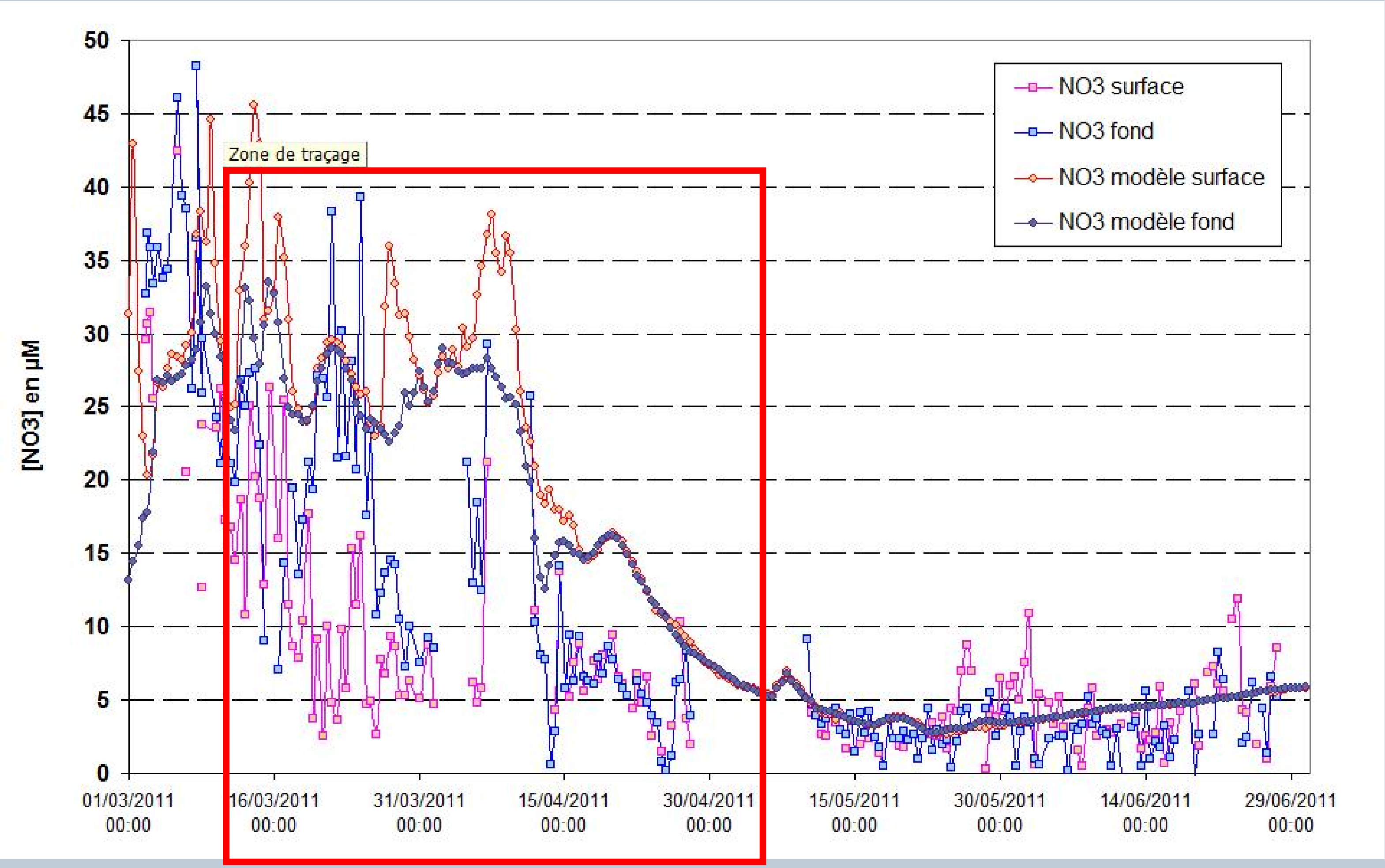
2011 : 4 months of deployment




Input in biogeochemical model




- Beginning of May, mid June to July : good estimation




- Mid March to end of May :

  much more difficult to simulate

# CHEMINI

Cheminis gave data analytically pertinent

better characterization of the nutrient distribution as a function of time

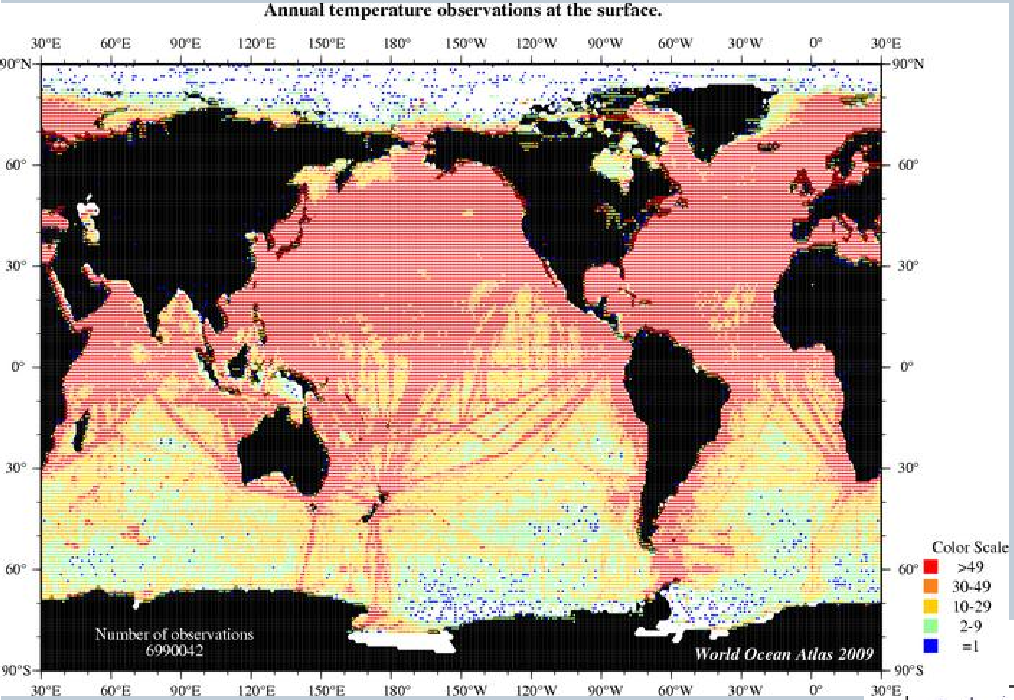
but still not enough data to simulate correctly this marine ecosystem

Need of more deployments

Relevant temporal frequency for nitrate and silicate concentrations ?

Nutrients, what about spatial coverage ?

# Spatial observation of temperature versus nitrate concentrations

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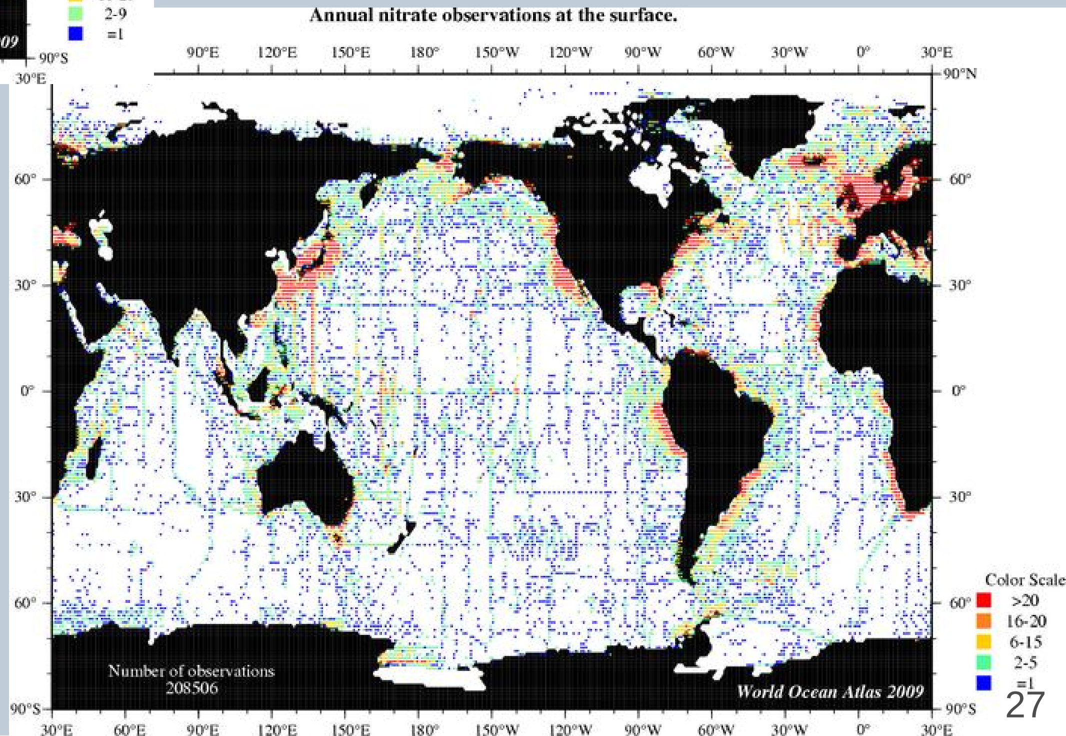
Temperature

Nitrate

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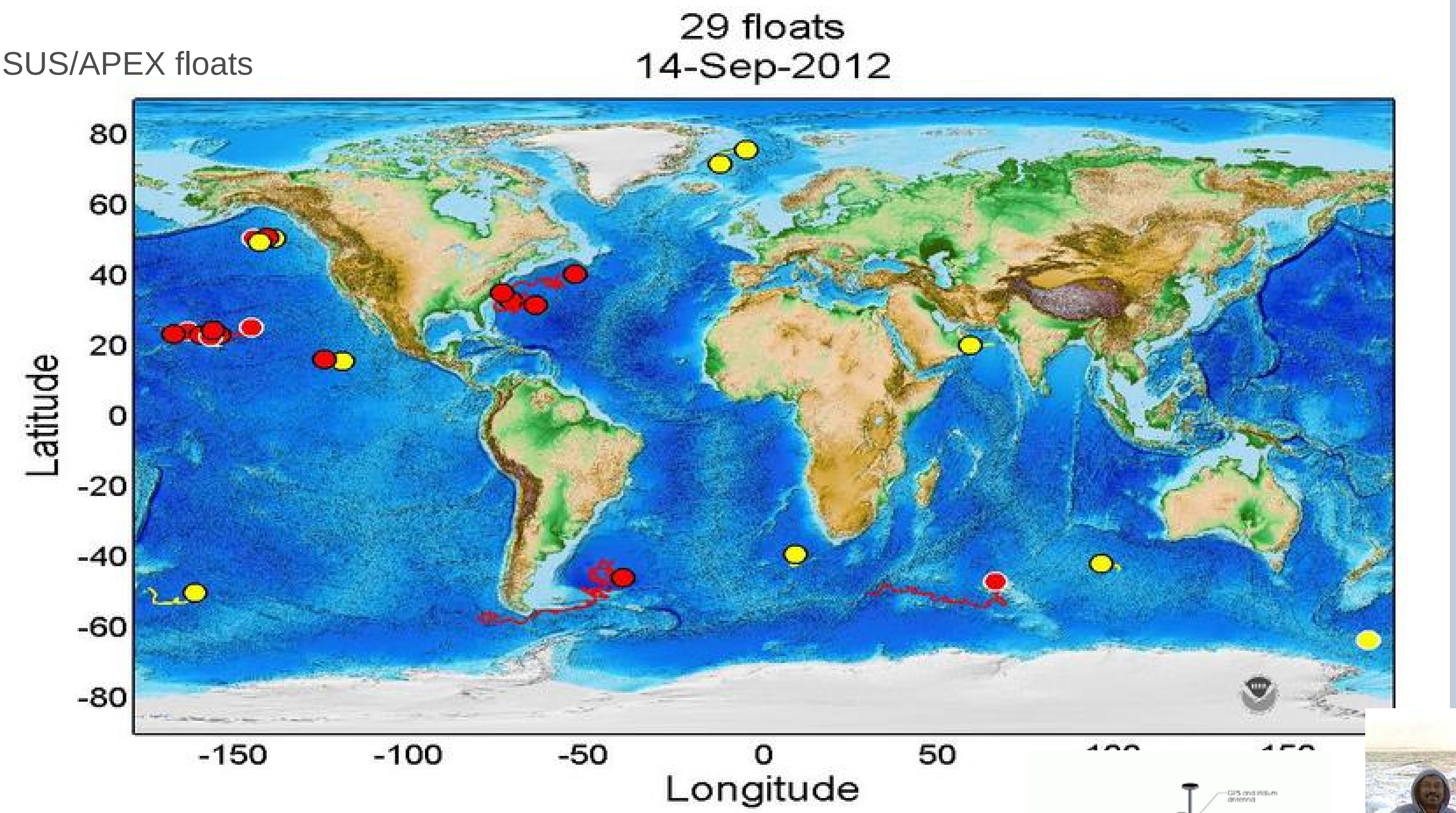
# In situ determination of salinity and temperature in open ocean

About 3000 floats operating at sea, profiling from surface to 2000m every 10 days, measuring temperature and salinity


*http://www.argo.ucsd.edu,  http://argo.jcommops.org*

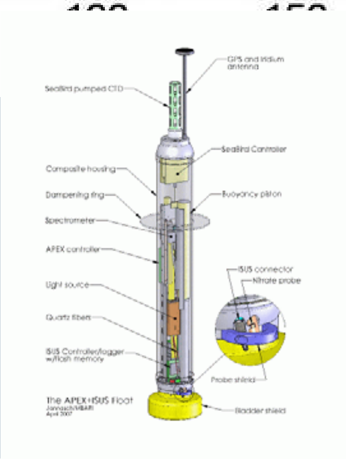
# *In situ* determination of nitrate in open ocean ?

ISUS/APEX floats




Data Sources and Analysis. NOAA Technical Memorandum NESDIS NGDC-24, 19 pp, March 2009

*What about phosphate, silicate, ammonia ?*




*Hans Jannasch © 2007 MBARI*

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# ISUS integrated into a Provor profiling float



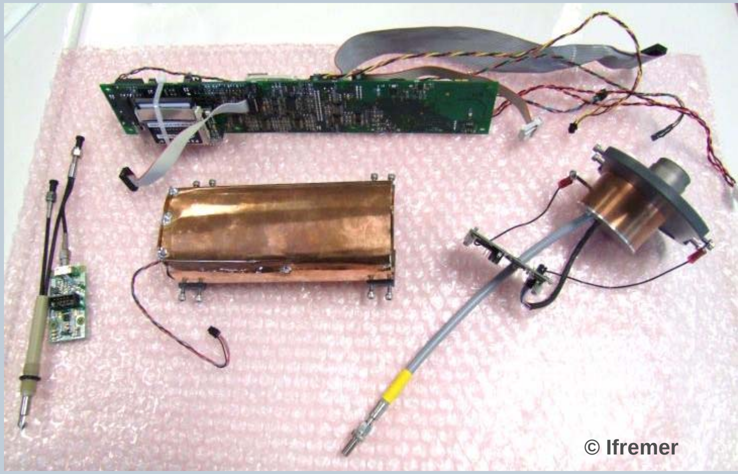
**ISUS Satlantic**

In situ ultraviolet spectrometer for nitrate concentrations measurement

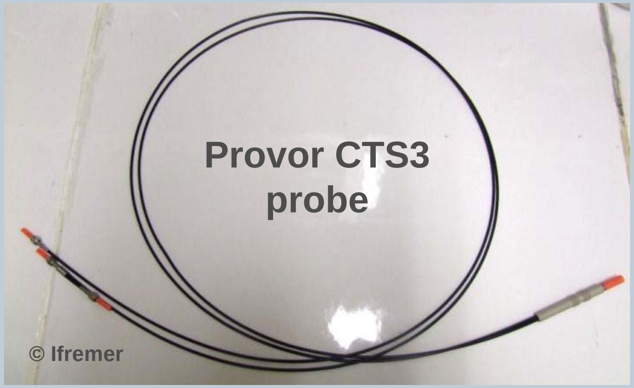
**Provor CTS3 float**

- Postdoctoral research of Damien Malardé , ENSTA-Bretagne, LOV
- PRONUTS project (Group Mission Mercator Coriolis (GMMC) and by the PACA region)

- Identify the optical constraints
- Dimension the various electronic and optical elements
- Modify of the optical probe
- Adapt the hardware of the two systems
- Integrate the optical probe inside the CTD device to avoid biofouling







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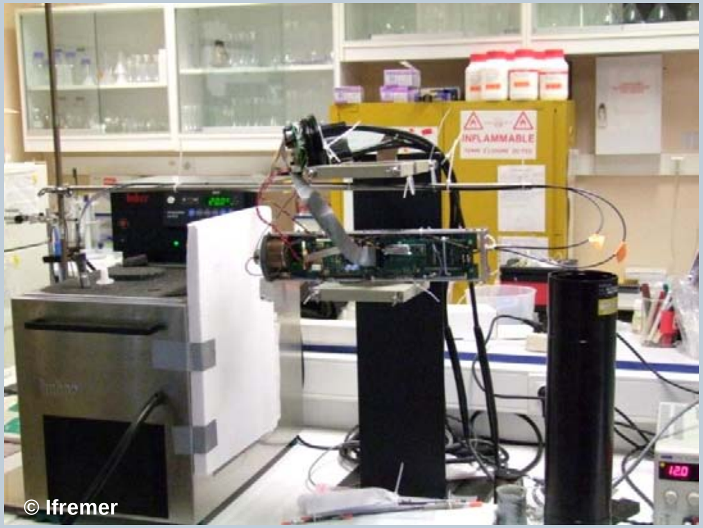


• Calibration performed using Aquil and « Provor » ISUS

• Variation of the ISUS response as a function of temperature, salinity, turbidity

• Integration of the optical probe inside the CTD device to avoid biofouling

No influence of tributyltin on the measurement of nitrate concentration

Malardé *et al.* (submitted Journal of atmospheric and Oceanic Technology )

# Technical assays in the Bay of Brest, May 2011

The SOMLIT network (Blain et al. 2004) gave similar values for temperature and salinity.

nitrate concentrations obtained using the ISUS stronger (4.96 µmol/l) than those obtained by the SOMLIT network (1.02 µmol/l 2m depth).

influence of the Aulne River at the origin of the enhancement, observed at the east of Roscanvel compared to the SOMLIT

Malardé *et al.* (submitted Journal of atmospheric and Oceanic Technology )

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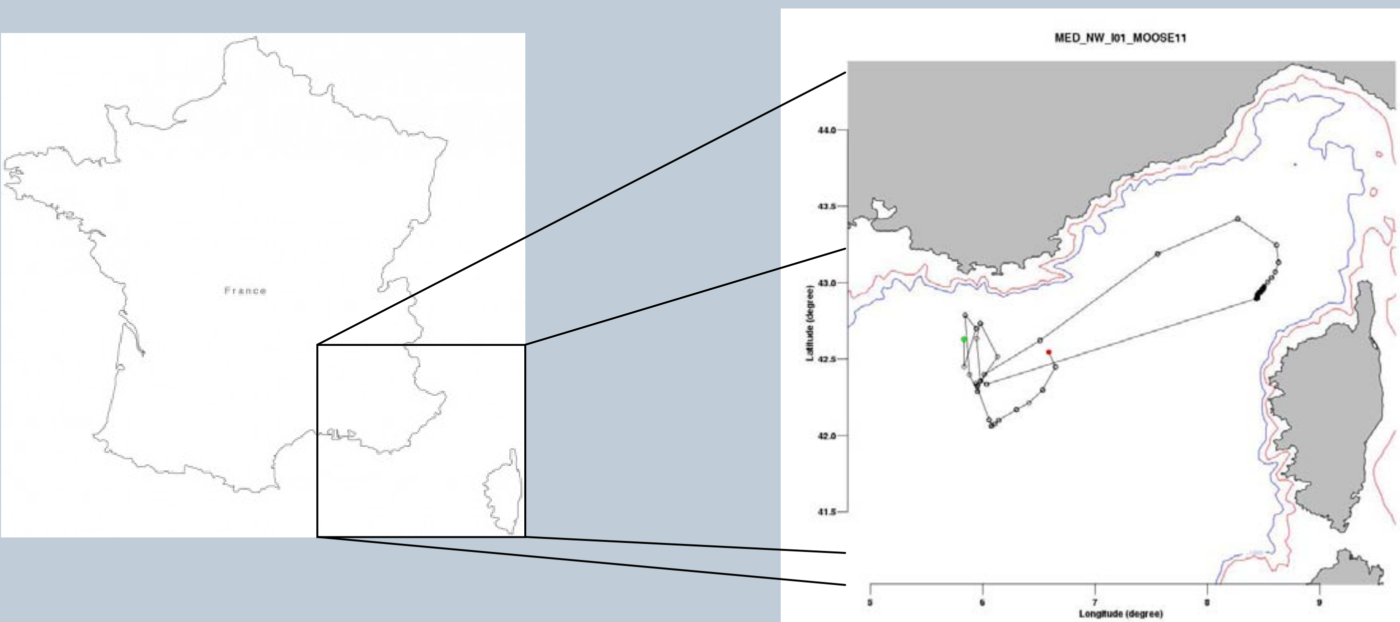
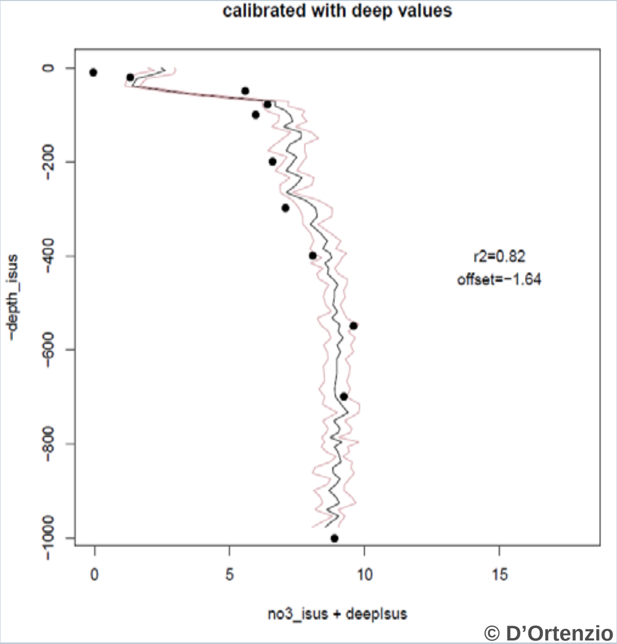
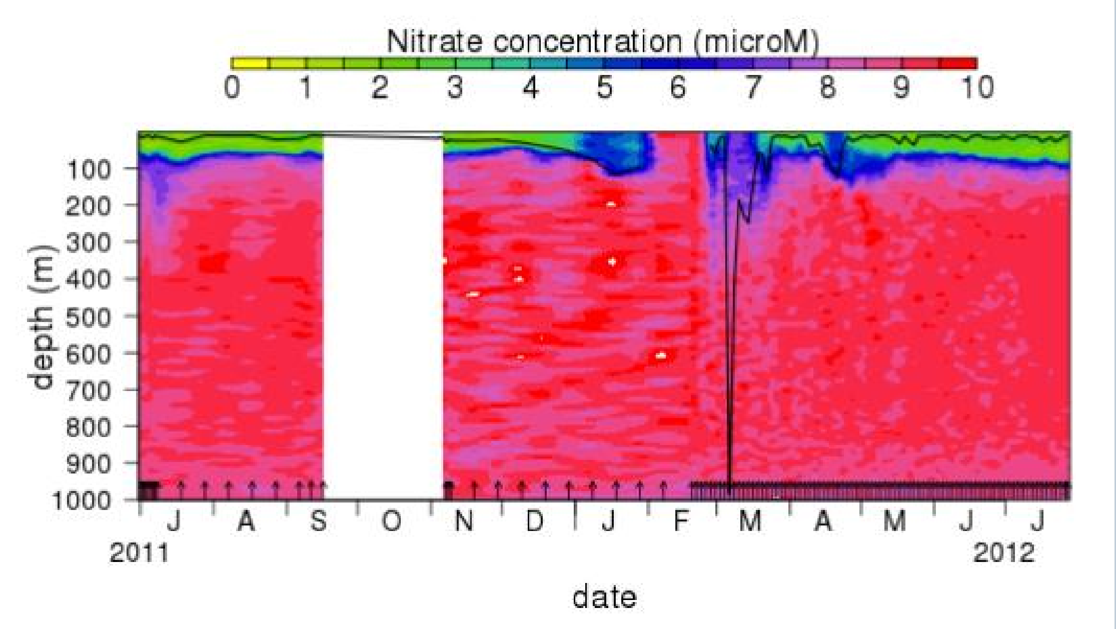
- MOOSE program (Mediterranean Ocean Observing System on Environment)
- Pronuts ISUS deployed from 15 June 2011 - 27 July 2012
- seven measurements were acquired from 0 to 1000m depth
- 162 profiles of the Pronuts ISUS were collected

• surface values during the oligotrophic period are close to zero

• complete homogenization of the $NO_3$ concentrations probably due to mixed layer deepening




© D'Ortenzio

Courtesy Fabrizio d' Ortenzio

(http://www.obs-vlfr.fr/OAO/provbio/Lavigne/PRONUTS.htm)

# ISUS integrated into a Provor profiling float

Provor good vector for optical sensors

drift in the ISUS response ( ~ 2 µmol/l)

but significant increase in the spatial distribution of nitrate concentrations in 3D

Recovery of the Pronuts ISUS



Biofouling ?

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# Conclusions

- Wet chemistry on a buoy : temporal case study

Good analytical performances
In situ calibration
No biofouling
Ideal for coastal monitoring (MSFD)

Maintenance every month
Frequency of analysis 13 mins

- Optical Sensor on a profiler : spatial and temporal case study

Provor good vector for optical sensors
High frequency of measurement
significant increase in the spatial distribution of nitrate in 3D
Ideal for open ocean monitoring

Drift in the ISUS response ( ~ 2 µmol/l)
Poorer accuracy
No *in situ* calibration
Biofouling …

**And which one is the cheapest ???**

# Conclusions

Need to consider each method as complementary

High temporal and spatial frequency and *in situ* instrument can better characterise the nutrient evolution

- data to store, validate
- valorisation
- human implication

# MERCI !!

Karenn Bucas
Virginie Antoine
Florian Caradec
Michel Repecaud
Loic Quemener
David Le Piver
Laurent Gautier
Stéphane Barbot
Patrick Rousseaux
Michael Retho
Jean - Pierre Allenou
Raoul Gabellec …

Damien Malardé
Vincent Dutreuil
Serge Le Reste
Fabrizio D’Ortenzio
Antoine Poteau
Dominique Le Roux …

All the persons involved in the development and deployment of the cheminis since the last 8 years,

the Pronuts team, ANR PRECODD (Trophimatique), Previmer, GMMC, PACA region, LOV, Europole Mer and Ifremer