High frequency automated ammonia analysis for coastal water monitoring and FerryBox applications

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User requirements for an on-line nutrient analyzers in Ferrybox systems

- Long term unattended autonomy
- Compactness
- High sensitivity
- Low reagents and sample consumption
- Low life-cycle cost
- Excellent reliability
- Easy interface with data-loggers
- Low maintenance by non expert users

Ferrybox applications with Micromac nutrient analyzers

AWI – BAH
(Biologische Anstalt Helgoland)
2005

Marine Institute Tallinn
2007

MUMM (Belgica)
2011

NLWKN (Burchana)
2016

Micromac-1000 features and limitations in Ferrybox systems

Features:

- Unattended long term use
- High sensitivity for sea water measurements
- Compactness and portability
- Modularity
- Multiparametric capability
- 12 Vdc power supply.

Limitations:

- Silicone based not sealed hydraulics
- Electronics not separated from hydraulics
- Limited internal space for reagents
- No cooling for reagents
- High concentration requires dilution, with longer measurement time.

Trans National Action, Jerico project (2014)
NH_3 and PO_4 µLFR units field test in Cuxhaven station and Lysbris Ferrybox

Data validation:

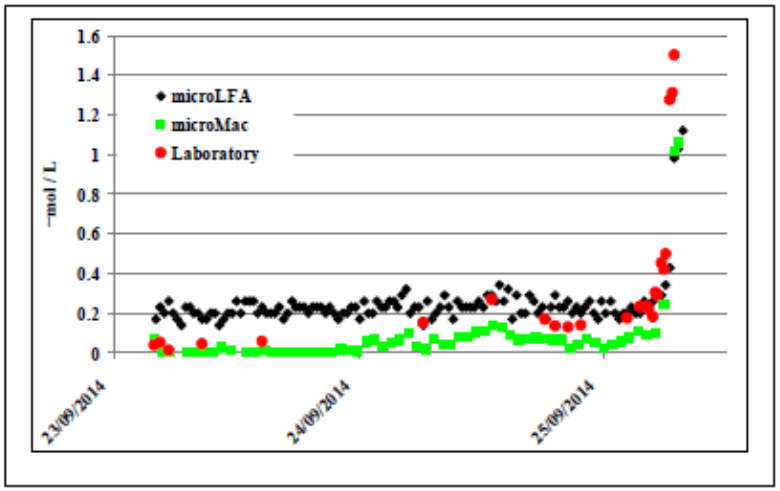


Fig. 9. Ferrybox PO_4 measurements performed with µLFA module (black diamonds), Micromac-1000 (green squares) and with a CFA instrument in laboratory (red dots).

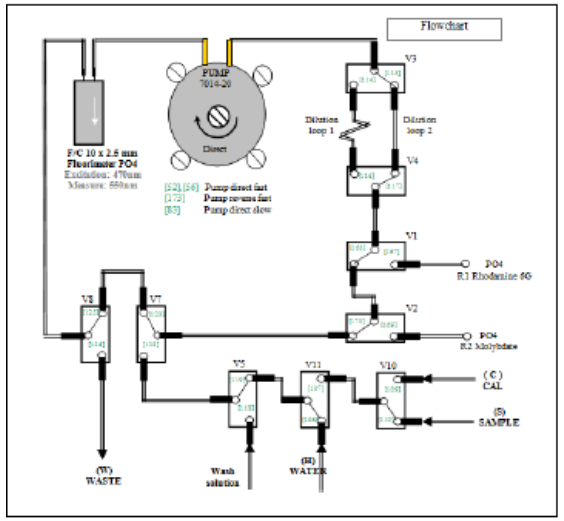


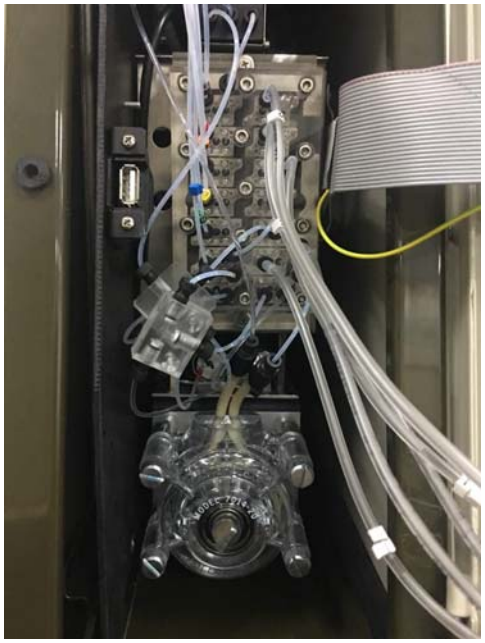
Fig. 4. The µLFA hydraulic circuit for fluorimetric phosphate analysis.

NH_3 and PO_4 by fluorimetry. New instrumental layout, with sealed electronics and frontal hydraulics, to allow an easier maintenance

Field tests supported by:

Helmholtz-Zentrum Geesthacht

Micromac-1000 Total P & NH_3 with µLFR hydraulics (2017)



New features:

- Teflon sealed hydraulics
- Lower reagents consumption enables longer unattended operation
- Smaller reagents volume -> easier cooling for longer unattended operation

Last proposed Micromac-1000 Nutrient instrumental configuration for Ferrybox systems

Micromac-1000 MP2 NO_x&NO_2:

- **NO_x by UV-DTPA reduction and NED-SAA colorimetric method, cal. range 0-300** µg/L as N, MDL < 5 µg/L
- **NO_2 by NED-SAA colorimetric method, range 0-50** µg/L as N, MDL < 2 µg/L

Micromac-1000 MP2 PO_4&SiO_2:

- **PO_4 by Molibdenum blue colorimetric method, cal. range 0-200** µg/L as P, MDL < 3 µg/L
- **SiO_2 by Molibdenum blue colorimetric method, cal. range 0-1.500** µg/L as **SiO_2**, MDL < 20 µg/L

Micromac-1000 NH_3:

- **NH_3 by OPA fluorimetric method, cal. range 0-300** µg/L as P, MDL < 3 µg/L**.**

Max. measurement frequency: 20 minutes

Micromac Fast prototype, 2002 (NH_3, NO_3+NO_2, PO_4)

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Automatic colorimetric analyzer prototype for high frequency measurement of nutrients in seawater

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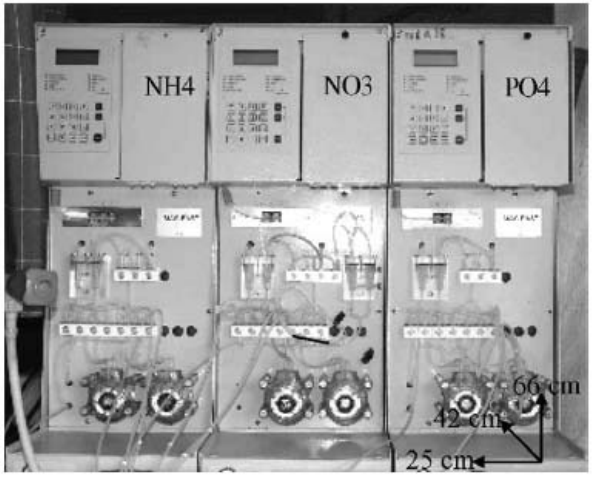


Fig. 1. MicroMac Fast MP3; module ammonia, nitrate and orthophosphate.

On-line nutrients monitoring on board of a boat.

For each module, n.2 detectors with sample heaters were integrated in the same hydraulics, working alternatively to speed-up the measurement.

Micromac Fast prototype, 2002 (NH_3, NO_3+NO_2, PO_4)

Table 2
Accuracy and precision for each method

Nutrient species		Known concentration (ppb)				
		15	10	7.5	5	2.5
Ammonia	Mean concentrat.	15.01	9.64	7.30	4.68	2.10
	Stand. deviation	0.13	0.16	0.10	0.20	0.10
	% RSD	0.84	1.68	1.37	4.13	4.55
Nitrate	Mean concentrat.	15.07	10.01	7.46	5.01	2.47
	Stand. deviation	0.37	0.32	0.18	0.29	0.15
	% RSD	2.36	3.18	2.45	5.85	6.23
Phosphate	Mean concentrat.	15.00	10.00	7.52	4.97	2.46
	Stand. deviation	0.11	0.23	0.15	0.18	0.13
	% RSD	0.74	2.35	2.01	3.54	5.11

Very high accuracy

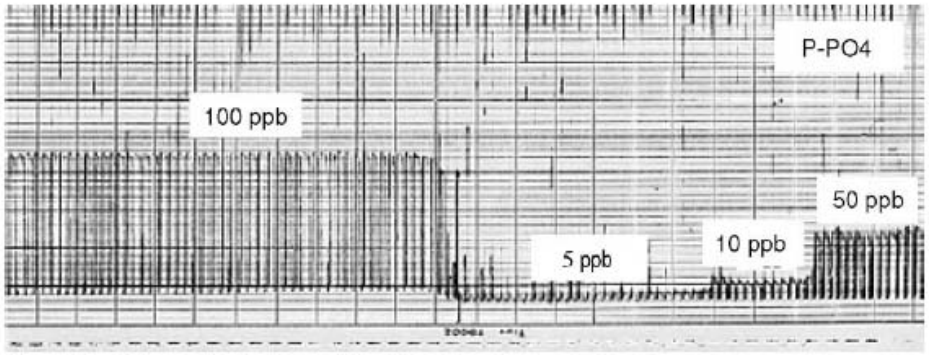
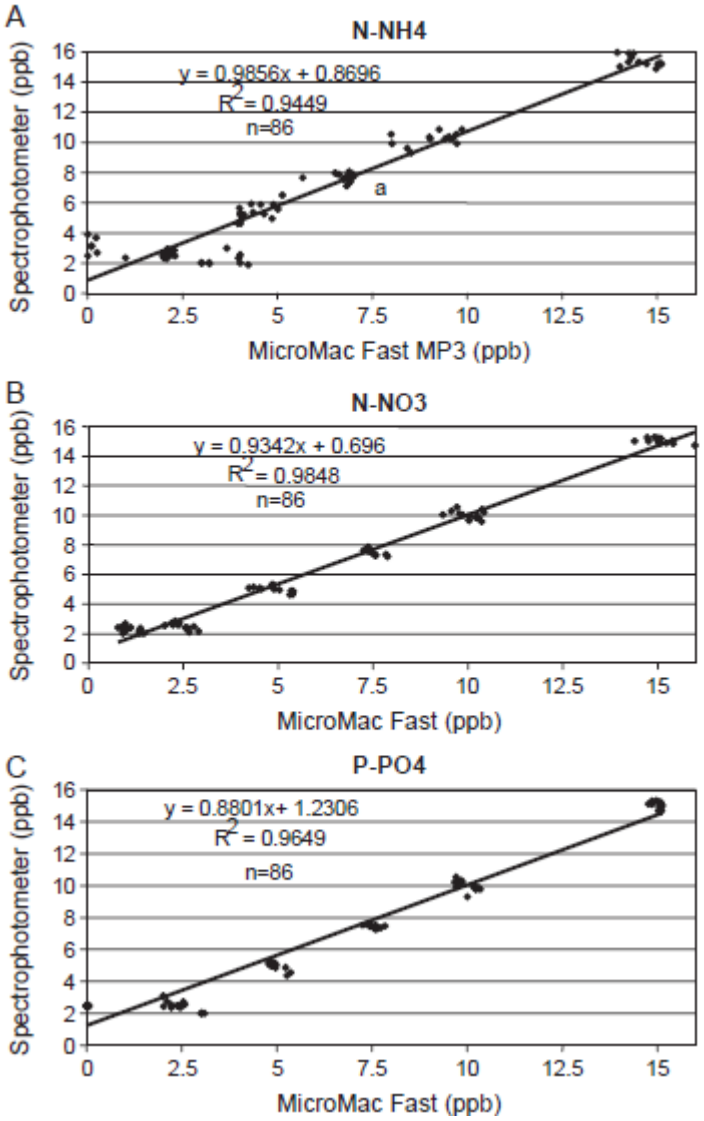
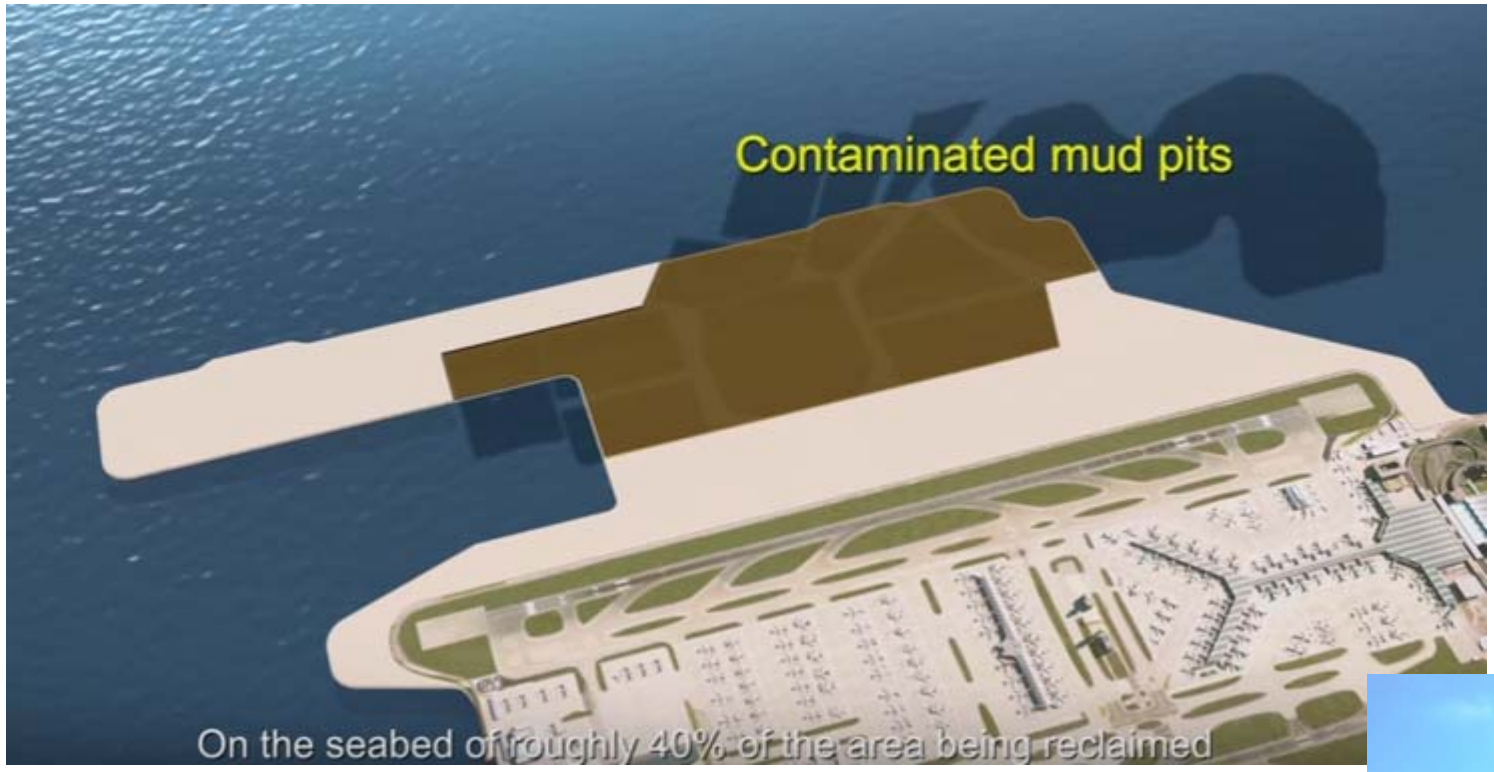


Fig. 3. Recorder traces-orthophosphate product of reaction in 300 s, frequency samples each 150 s.

Measurement frequency: 150 seconds !



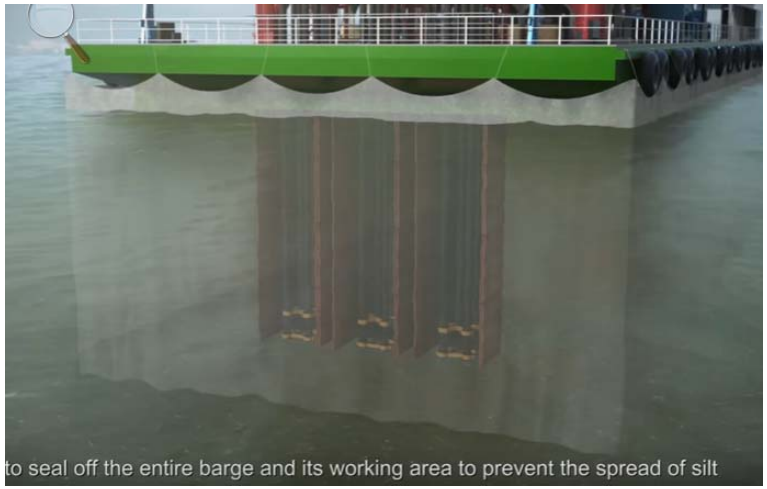
NH_3 on-line monitoring for land reclamation project 3rd Hong Kong airport runaway (2016)

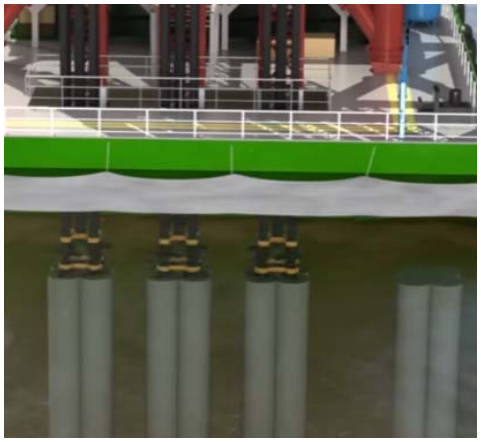


Land formation of around 650 hectares requires more than 40 barges in continuous operation day&night

NH_3 on-line monitoring for land reclamation project 3rd Hong Kong airport runaway (2016)

Deep Cement Mixing





NH_3 on-line monitoring for land reclamation project 3rd Hong Kong airport runaway (2016)

Each barge includes n.4 points of water quality monitoring of standard physical-chemical parameters and ammonia at the corners of the platform.

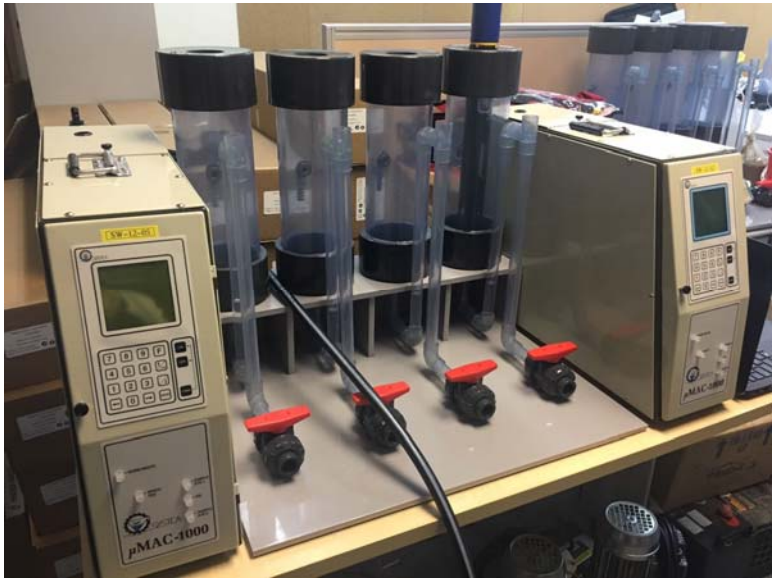
More than 40 barges are actually in operation, including more than 130 Micromac-1000, working as:

- Single stream analyzers, allowing 5 minutes monitoring frequency
- Double stream analyzers, allowing 6 minutes monitoring frequency on both streams.

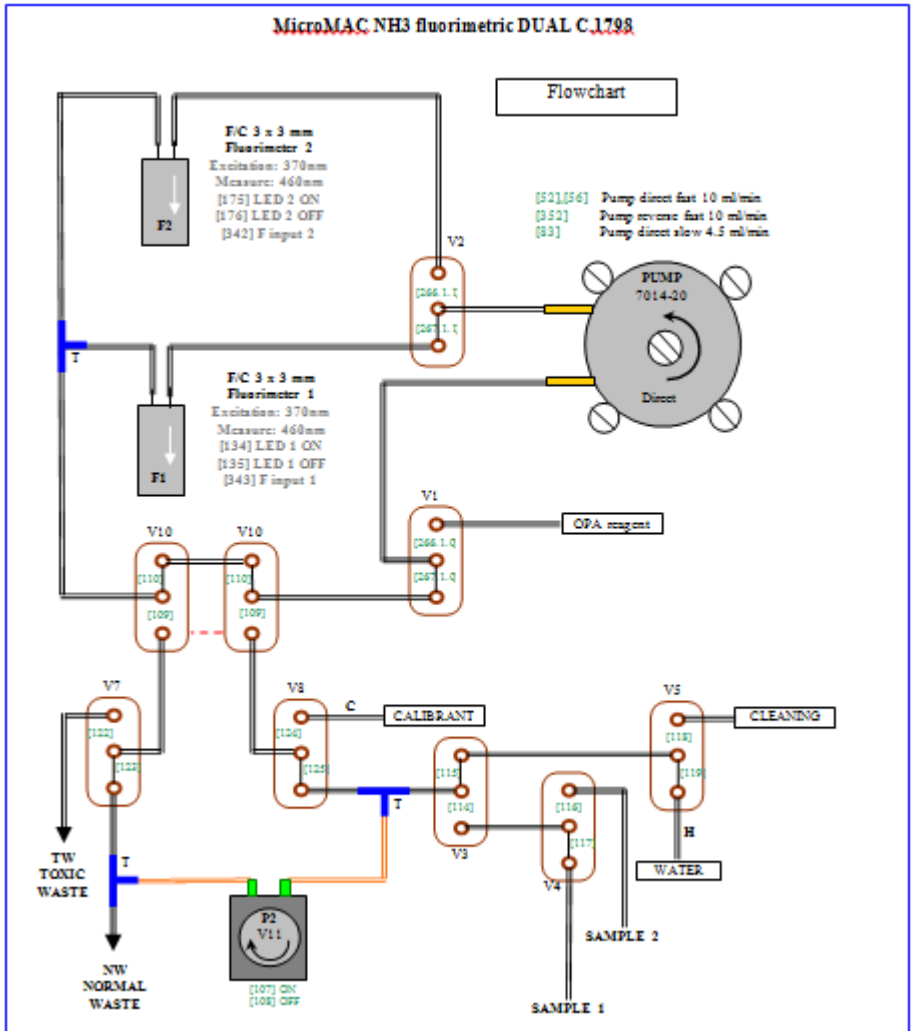
Measurement range:
0-1 mg/L as N, up to 20 mg/L in dilution

µLFR hydraulic schema
Micromac-1000 NH_3 double stream

OPA fluorimetric
Range: 0-1 mg/L
MDL: 20 µg/L

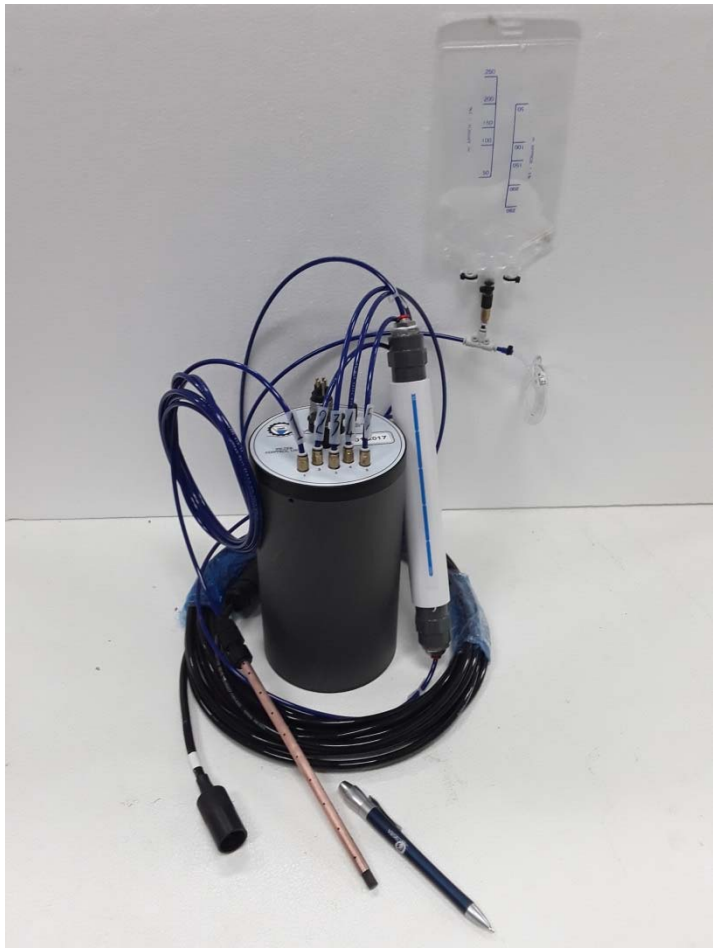


NH_3 on-line monitoring system
on each barge
(4 points of measurement)



0.1 microns cut-off filtration unit with autocleaning capability

- 150 mL of filtered water in 3 minutes
- Automatic backwash using the same filtrate performed after analyzer's sampling
- Easily managed by an external data-logger
- Tested long term unattended operation
- Volume compatible with µLFR units for Ferrybox application.



Nutrient Sensor Challenge by ACT, USA (2016)

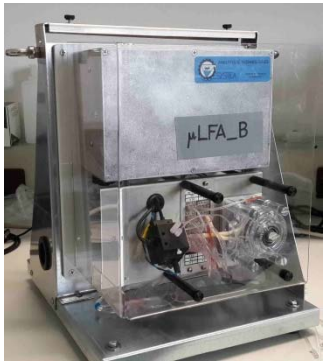
SYSTEA was awarded for both Nitrate and Phosphate WIZ in-situ probes

Open perspectives for the use of µLFR technology for on-line nutrients monitoring in Ferrybox systems

- **Lower reagents consumption -> longer unattended use, lower reagent volumes, easier cooling and lower maintenance frequency**
- **Measurement frequency down to 5 minutes (monoparametric configuration)**
- **Enhanced hydraulics reliability -> lower maintenance**
- **Full compatibility with existing monitoring systems**
- **Two operation modes available:**
  - **5 minutes frequency near the coast -> to measure higher concentrations, without dilution**
  - **10 minutes frequency -> higher sensitivity in open sea**

QUESTIONS TO FERRYBOX USERS

- **Multiparametric configuration:**
  - Lower capital cost, higher complexity of each module
  - 20 minutes minimum measurement frequency
- **Monoparametric configuration:**
  - Higher capital cost. Easier handling and maintenance
  - 5 minutes minimum measurement frequency
- **Available instrumental layouts:**



Waiting your answer and comments, thanks for your attention !