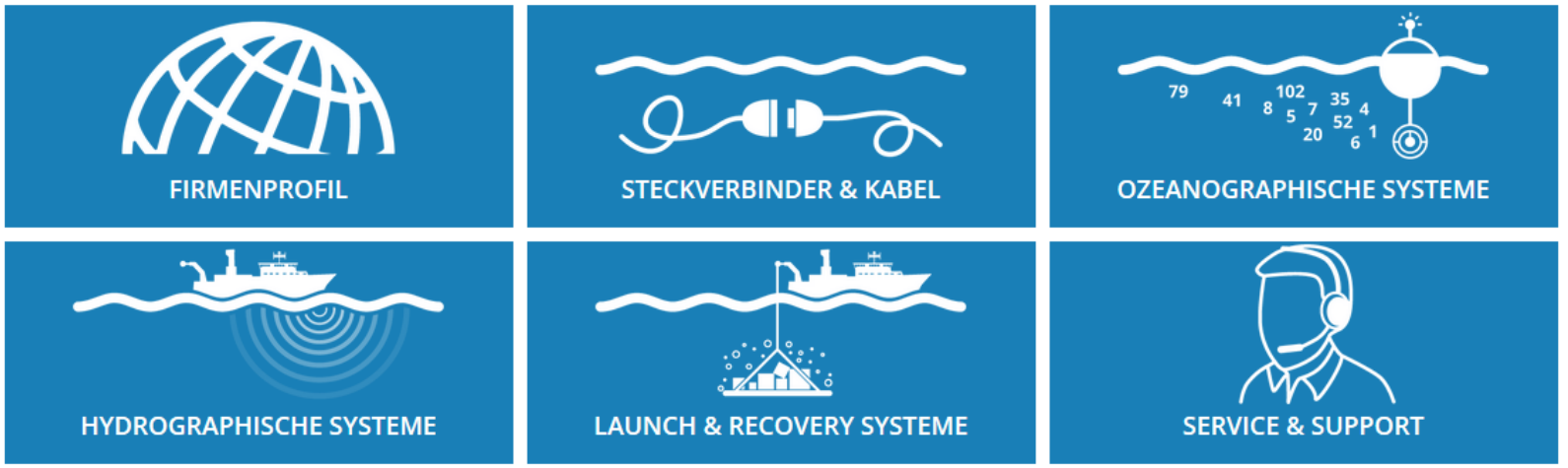
NuLAB wet chemistry nutrient analyser

Verena Dauben[1], Alexander Davidov[1] & Vincent Kelly[2]

[1] MacArtney Germany GmbH, [2] Green Eyes Environmental LLC, MD, USA

In 2018
MBT - Meerestechnisches Büro Turla GmbH
became
MacArtney Germany GmbH, Kiel

www.macartney.com



Key facts:

- located in Kiel
- part of the MacArtney Group – with over 400 employees and offices or partner on all continents

Co-operation with Green Eyes Environmental LLC:

- Since 2001 co-operation, service and support for former EnviroTech and later Green Eyes nutrient analysers
- Since 2016 sales representation of Green Eyes products in Europe
- 2017 – setting up of facilities at MacArtney Germany to test and service Green Eyes nutrient analysers and prepare reagents
- Nutrient analyser training, installations and workshops

Green Eyes Environmental LLC:

- Based in Easton, Maryland, United States
- Founded in 2006 by Vincent Kelly, Chemical Oceanographer
- Further development into state of the art analysers

Three NuLAB versions for various applications

Basic NuLAB

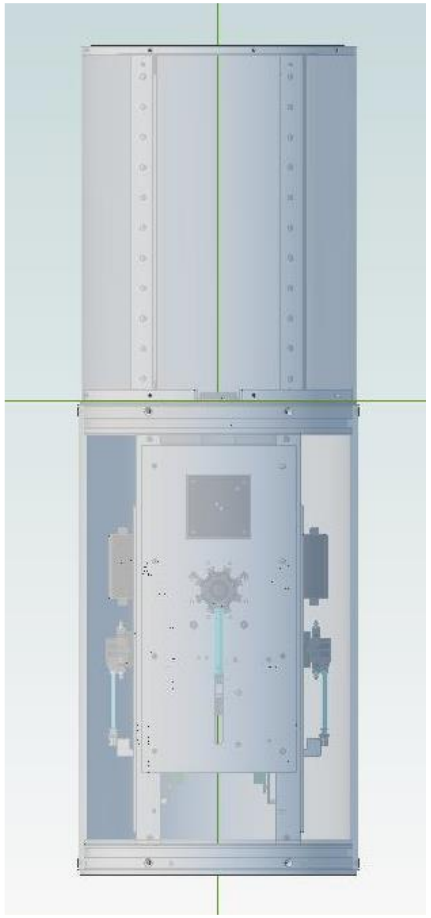
- smaller size (1-2 channels)

NuLAB Plus

- Included touch screen controller, relays for pump and water2web data posting
- Up to 3 channels

NuLAB Submersible (buoy or shallow water monitoring station)

- Up to 10 m water depth
- Up to 4 channels



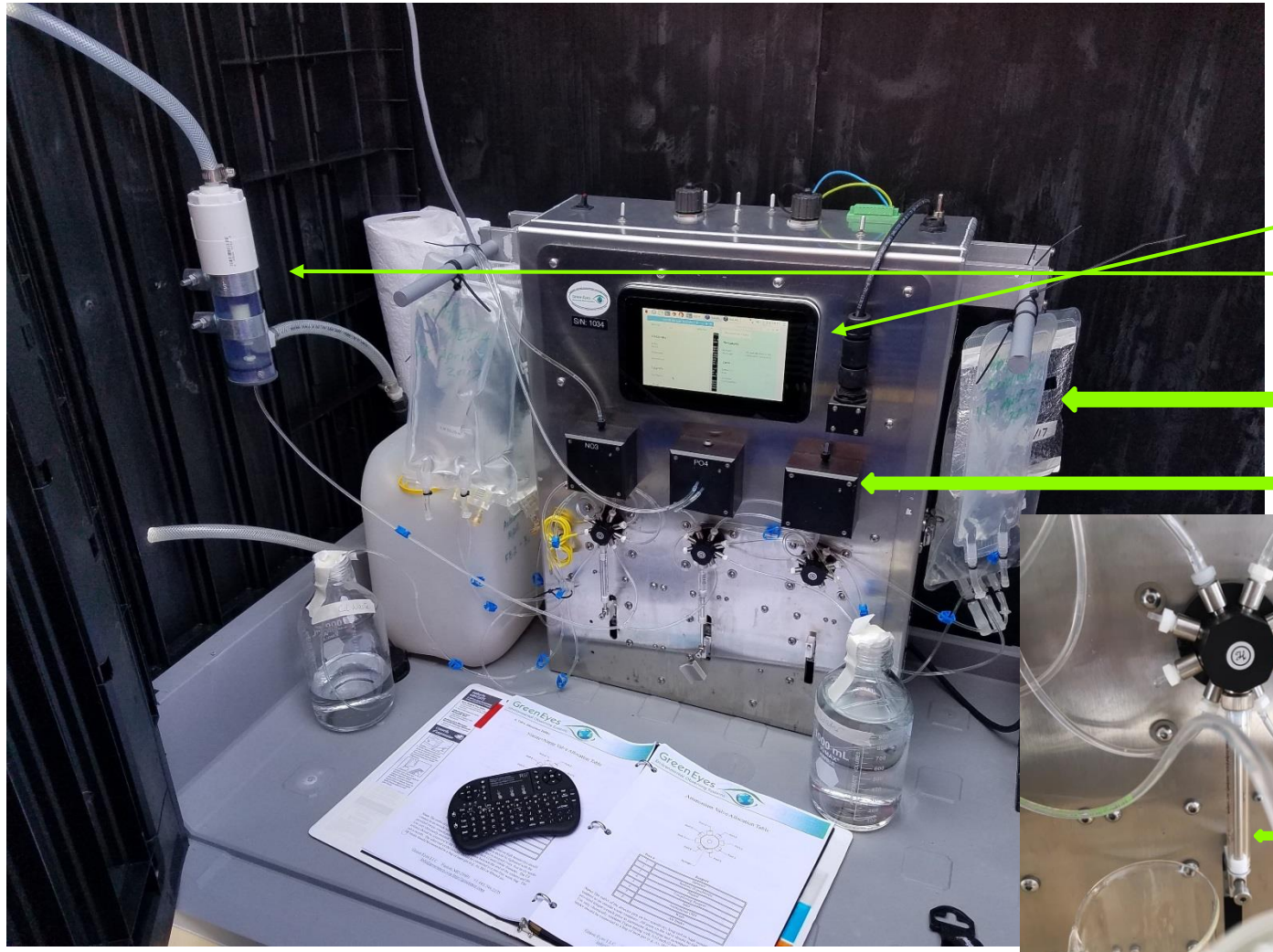
- **What NuLAB does:**

- Application of established wet chemical methods (US EPA) to a field chemical analyser (for Nitrate, Phosphate, Ammonia and Silicate)
- Precise volumes of sample
- Data is calibrated via an On-Board-Standard (OBS)
- Reagents connected to a rotary valve and mixed by a syringe pump
- Analysed in high precision colorimeters.
- Operates with 8 pre-defined macros that determine how analyses are carried out

MacArtney
UNDERWATER TECHNOLOGY

GreenEyes
Environmental Observing Systems

NuLAB Plus Set-up



Controller

Inlet with filter

Reagent bags
(gas tight)

Detector

8-port rotary valve

Syringe

Specification of NuLAB

Standard Ranges (detection limit to linear range, micro M)

mg/L:	N+N	Nitrite	Phosphate	Ammonium	Silicate
High Sensitivity Detectors (2 mm)	0.003 to 0.70	0.002 to 0.5	0.006 to 0.8	0.004 to 0.3	0.008 to 1.7
Low Sensitivity Detectors (10 mm)	0.01 to 2.8	0.008 to 2.1	0.025 to 2.0	0.02 to 1.0	0.04 to 2.8

micro mol/L:	N+N	Nitrite	Phosphate	Ammonium	Silicate
High Sensitivity Detectors	0.2 to 50	0.15 to 35	0.2 to 25	0.3 to 20	0.3 to 60
Low Sensitivity Detectors	0.8 - 200	0.6 - 150	1.0 - 75	1.5 to 75	1.5 to 100

- Precision (one SD @ midrange of scale): Nitrate 3%, Nitrite 2%, Phosphate 3%, Ammonium 3%, Silicate 3%
- Expanded Ranges: Up to 5 mg/l through auto-dilution
- Accuracy: Based on the accuracy of the preserved on-board standard and sample replicate precision
- Analyses: Typically 1000 per channel, per deployment. Controlled by reagent payload and chemistry
- Analysis Time: N+N 13 min, Nitrite 9 min, Phosphate 14 min, Ammonium 17 min, Silicate 16 min
- Consumption: Sample ~ 2 ml, each reagent ~ 0.1 ml and DIW

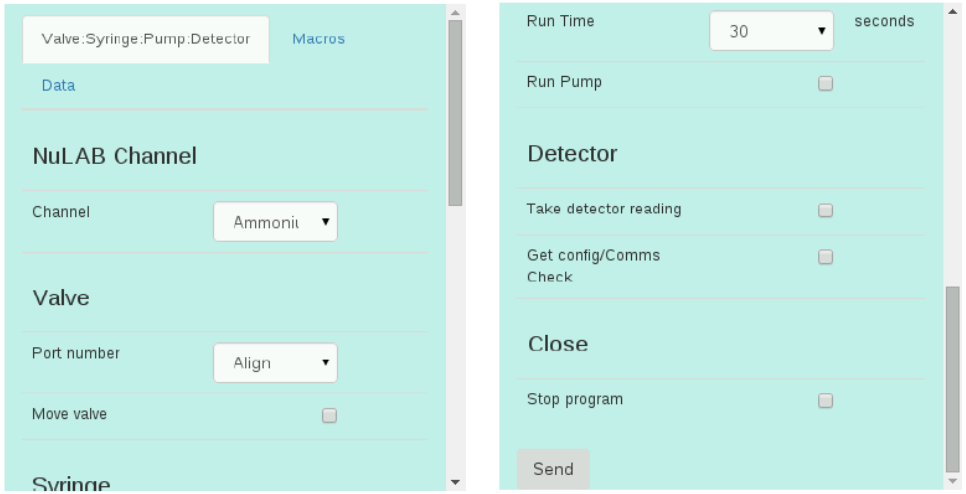
Analysis definition NuLAB

Aim: Turning mass equivalents into colours

- Macros can be customized to specific requirements and to third party analysis protocols i.e.
  - Change of the sample and reagent volumes
  - Change of the mixing times and volumes
  - Change of the flushing
  - Change of temperature and heating duration etc,

```
# ASL NITRATE STANDARD V1
# POWER ON
Y1
D2
# TURN ON HEATERS
H3
# ALIGN
U1
G1
# PORT H (AIR)
U1
P8
# RETRACT 1.0ML
U2
-15080
# PORT A (DETECTOR)
U1
P1
# INSERT 1.0ML
U2
+15080
# PORT F (STANDARD)
U1
P6
# RETRACT 0.25ML
U2
-3770
# PORT A (DETECTOR)
U1
P1
# INSERT 0.25ML
```

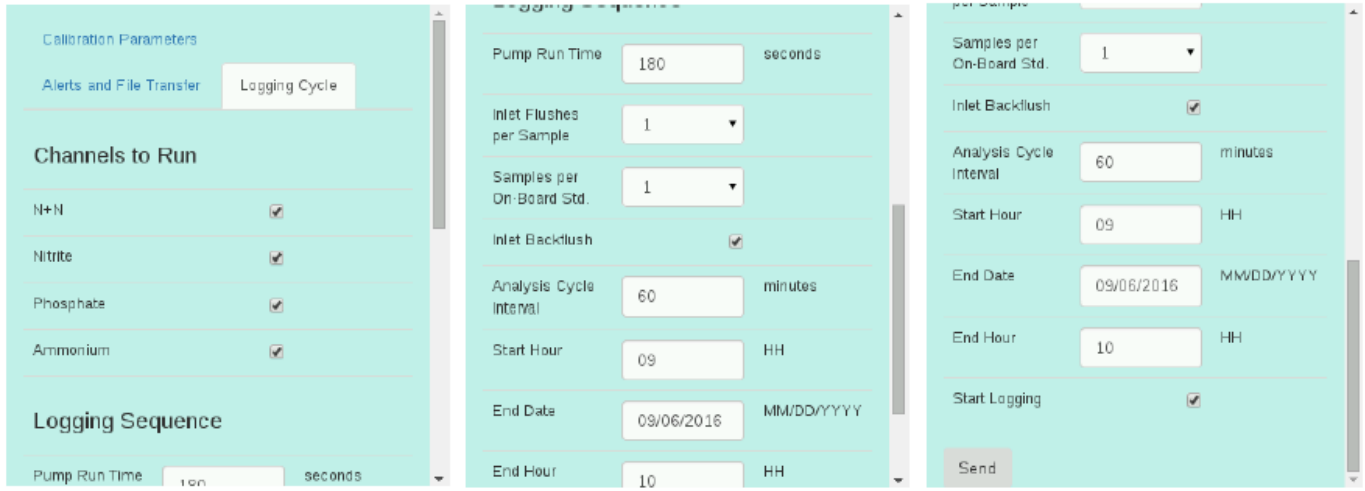
Manual Mode



NuLAB Software

- NuLAB is operated via a software running on the controller
- Software includes two different modes (”Manual” & “Logging”)
- Analyses are executed by macros
- Macros can be selected via the software interface
- Individual channels can be selected
- Deployment mode is defined

Logging Mode



Development of the NuLAB for FerryBox:

- The NuLAB was originally designed for fixed station monitoring with sample intervals of two hours or longer.
- In contrast, FerryBox application often desire higher sample frequencies to resolve sharp spatial gradients

The following adjustments were introduced:

Elevated reaction temperatures:

- By raising reaction temperatures, the influence of ambient and sample water temperature on color development will be minimized.
- This will stabilize the on-board standard (OBS) results used for sample calibration and reduce the necessary OBS analysis frequency.
- This will reduce analysis time
- Elevating reaction temperature required simple hardware and software changes

Maintain detector heaters and LEDs for extended periods:

- To reduce detector warm up times, the heaters and LEDs can be left ON between analyses. This will also improve instrument precision.
- These changes are limited to the analytical macros and an additional "detector warm-up" command from the controller.

Addition of a solenoid switching valve:

- Currently all channels other than nitrate (when also measuring nitrite) have deionized water (DIW) connected to the eight-port rotary valve that is used for flushing and re-agent blanks.
- Users are now able to add an optional solenoid valve to the nitrate channel so that all channels will be equipped with DIW.
- The valve will switch be-tween imidazole buffer and DIW and be controllable via terminal commands, the NuLAB controller and NuLAB macros.
- This option requires an additional solenoid valve and relays

New controller:

- New microprocessor based controller allow one serial port of a computer or datalogger to run and collect data from up to four Nu-LAB channels simultaneously.
- This is better option than present Linux controller for FerryBox or other heavily integrated applications with master computers.

Conclusion: Strenghts of NuLAB

- NuLAB determines a reagent blank before each sample
- An OBS can be measured before each sample and NuLAB uses the most recent OBS for concentration calculation
- NuLAB macros are customizable
- NuLAB is easy to operate and easy to integrate into other systems (e.g. Ferry Box)
- Data can be transmitted via internet to web gateways (like MetOcean Gateway)
- Support, development (improvement), compact, manageable but also affordable

Thank you for your attention!

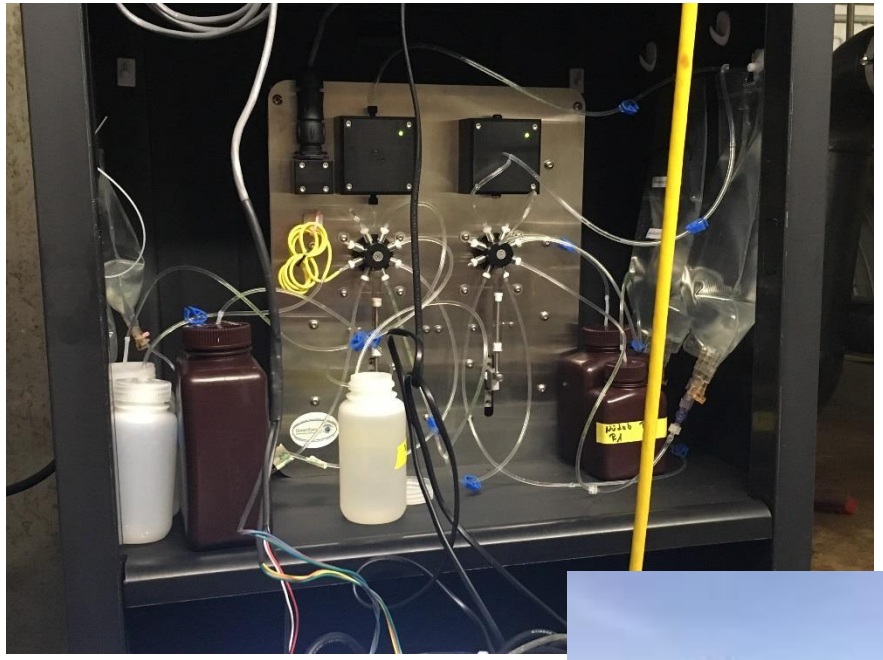
Contacts:

Dr Verena Dauben – MBT GmbH ved@macartney.com

Dr Alexander Davidov – MBT GmbH ad@macartney.com

Chemical Methods used:

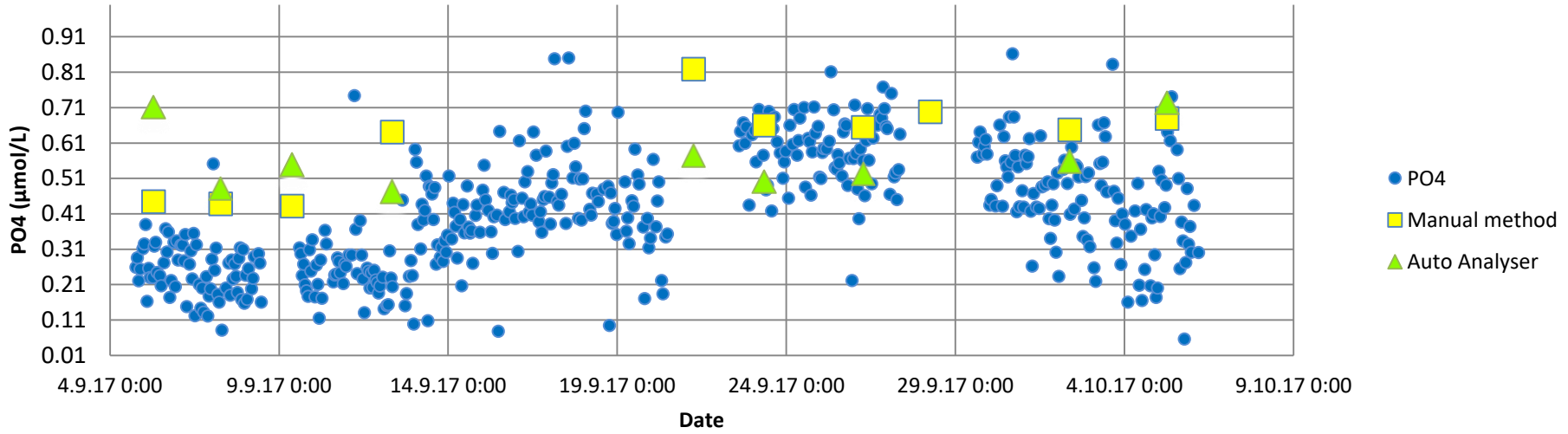
- Ortho-phosphate P-PO4 – Molybdenum reaction
  - L. Drummond and W. Maher: Determination of phosphorus in aqueous solution via formation of the phosphoantimonylmolybdenum blue complex - Rexamination of optimium conditions for the analysis of phosphate. Analytica Chimica Acta 302 (1995) pp. 69 – 74.
  - J. Murphy and J. P. Riley: A modified single solution method for the determination of phosphate in natural waters, Analytical Chimica Acta, 27 (1962) p. 31
- Nitrate (N-NO3) plus Nitrite (N-NO2) Analysis
  - J. D. H. Strickland and T. R. Parsons: A Practical Handbook of Seawater Analysis. Ottawa: Fisheries Research Board of Canada, Bulletin 167, 2nd Ed., 1972. 293 pp.
  - Grasshoff, K: Methods of Seawater Analysis, Verlag Chemie, Weinheim and New York, 1976, pp.149 – 156
- Ammonium (NH4) Analysis
  - J. D. H. Strickland and T. R. Parsons: A Practical Handbook of Seawater Analysis. Ottawa: Fisheries Research Board of Canada, Bulletin 167, 2nd Ed., 1972. 293 pp.
  - L Solorzano: Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceangr. Vol.14(5). 1969. pp. 799-801.
- Silicate (SO4) Analysis
  - Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis
  - Jia-Zhong Zhang, Cooperative Institute for Marine and Atmospheric Studies, Rosenstiel School of Marine and Atmospheric Science.
  - Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, University of Miami, Miami, FL 33149
  - George A. Berberian, National Oceanic and Atmosheric Administration, Atlantic Oceanographic and Meteorological Laboratory, Ocean Chemistry Division, Miami, FL 33149



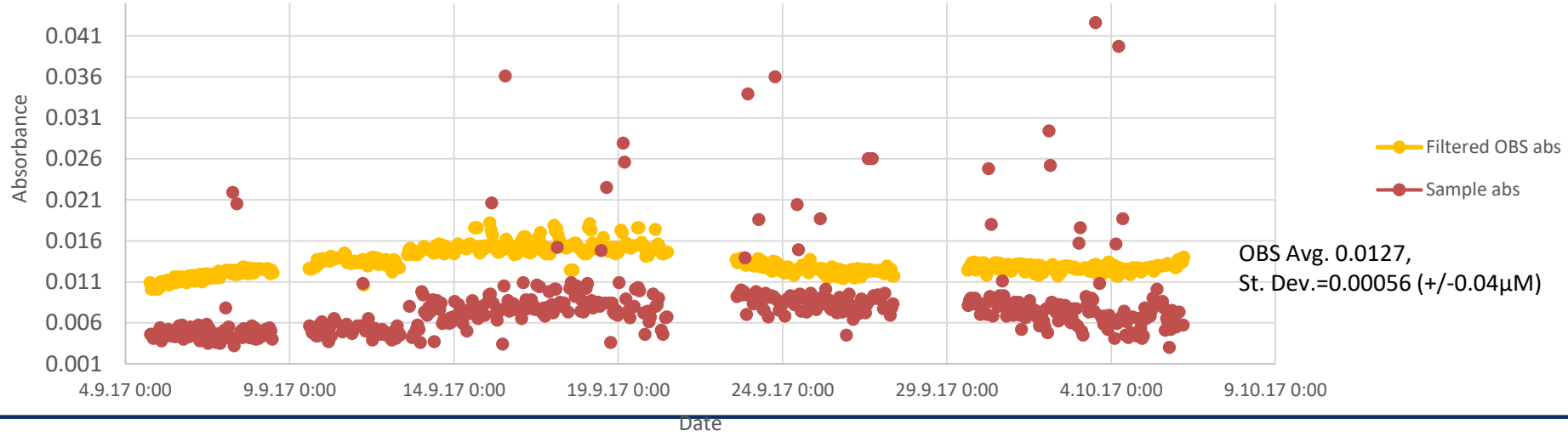
NuLAB installation at Helgoland

- Installation of a 2-channel NuLAB system (Nitrate & Phosphate) next to Ferry Box based at "Helgoland Einlaufbauwerk"
- Continuous test measurements since mid-July 2017
- Hourly samples of NO_3+NO_2 and PO_4 from Ferry Box sampling water

NuLAB Phosphate Concentration (µM)
Helgoland Island

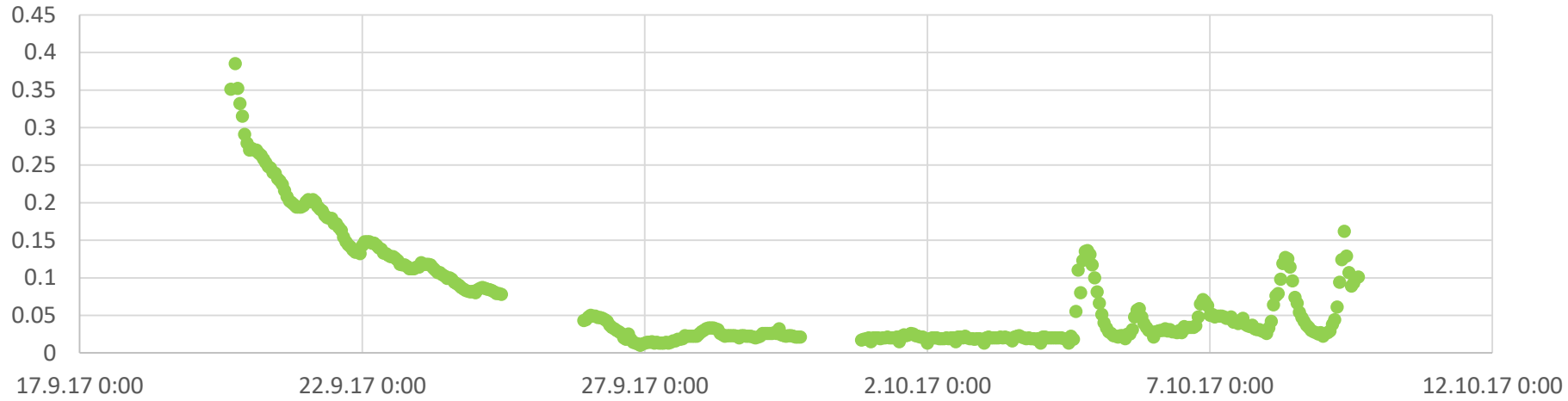


NuLAB PO4 On-board Standard (1.0 µM) and sample Absorbance
Helgoland Island

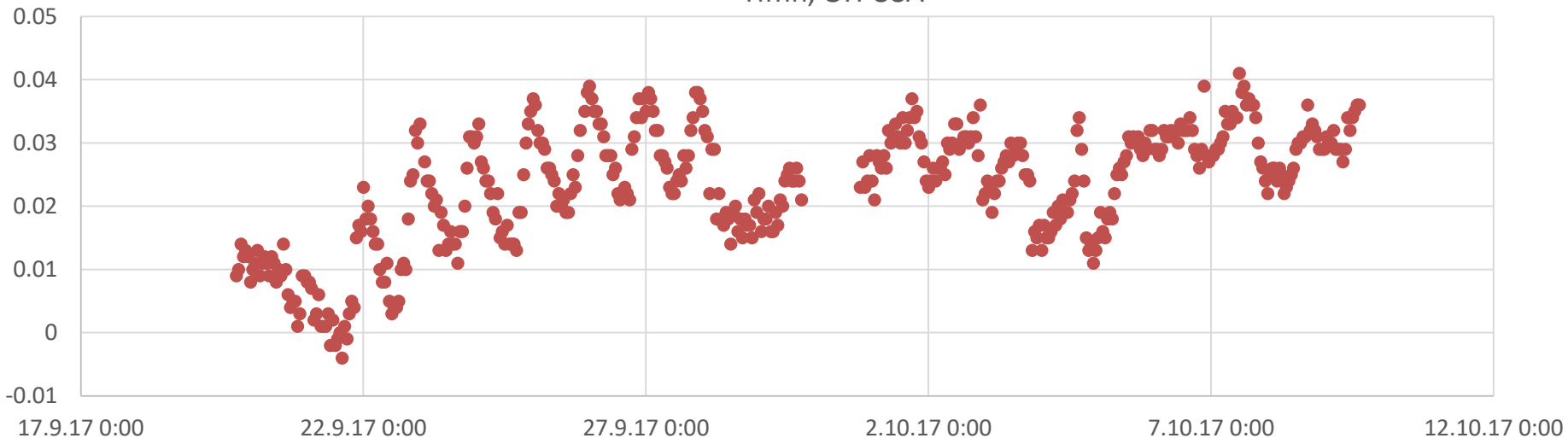


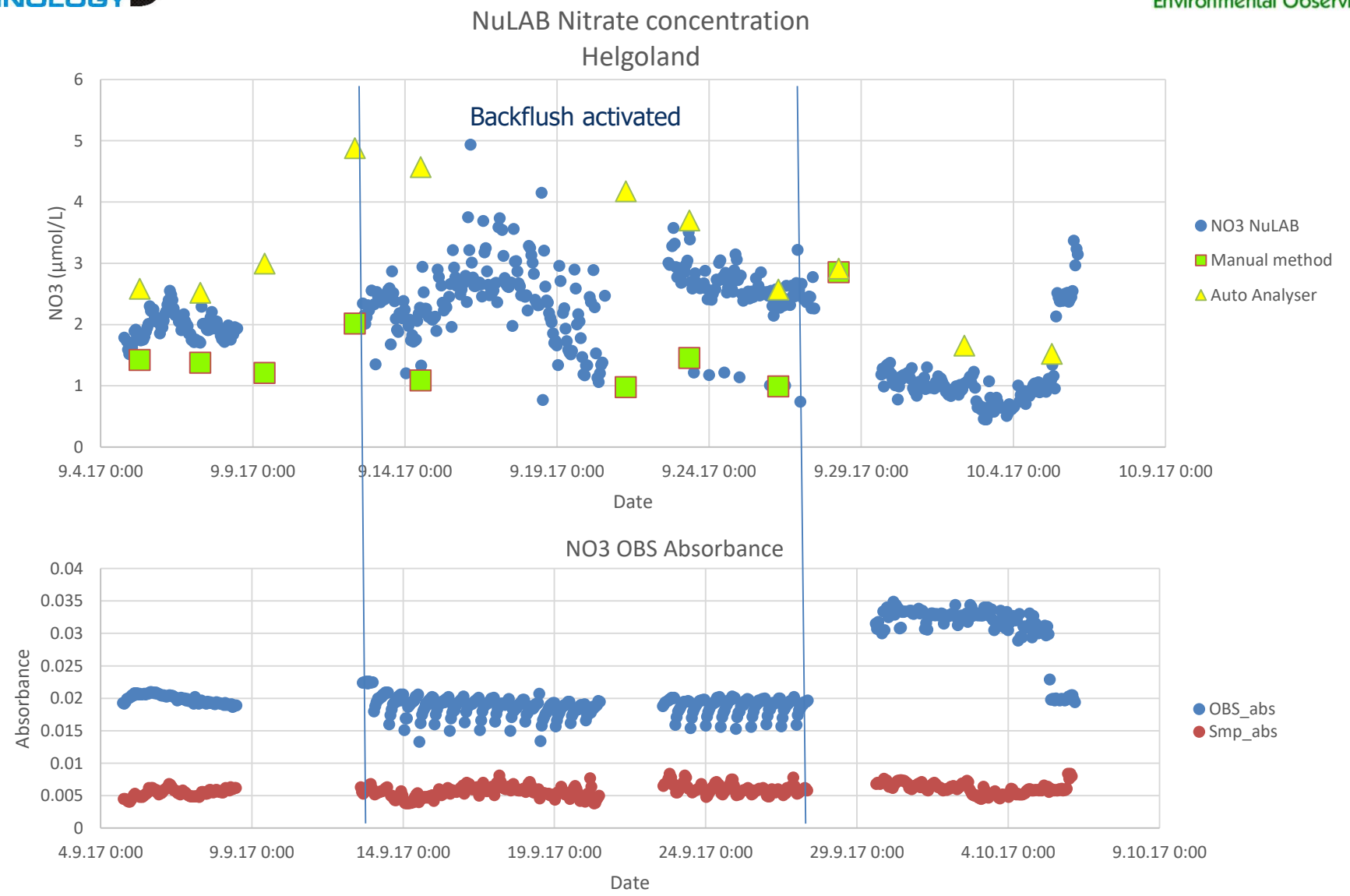
OBS Avg. 0.0127,
St. Dev.=0.00056 (+/-0.04µM)

NuLAB Nitrate+Nitrite (mg/L)
Tiffin, OH USA



NuLAB Reactive Phosphorus (mg-P/L)
Tiffin, OH USA




NuLAB Nitrate concentration
Helgoland
Backflush activated
NO3 (µmol/L)
0
1
2
3
4
5
6
9.4.17 0:00
9.9.17 0:00
9.14.17 0:00
9.19.17 0:00
9.24.17 0:00
9.29.17 0:00
10.4.17 0:00
10.9.17 0:00
Date
NO3 NuLAB
Manual method
Auto Analyser
NO3 OBS Absorbance
Absorbance
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
4.9.17 0:00
9.9.17 0:00
14.9.17 0:00
19.9.17 0:00
24.9.17 0:00
29.9.17 0:00
4.10.17 0:00
9.10.17 0:00
Date
OBS_abs
Smp_abs