

TNA PROJECT REPORT

1. Project Information

Proposal reference number	JN_CALL_3_12
Project Acronym (ID)	Easy On-line microLFA
Title of the project	Field test of a reliable and Easy to use microLFA based nutrient sensor package for Ferrybox On-line monitoring applications
Host Research Infrastructure	NIVA NorFerry/Color Fantasy (FA)
Starting date - End date	12/11/2018 – 30/06/2019
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2. Project objectives

The proposed TNA project aimed to test in operative conditions an updated version of the SYSTEAS Micromac-1000 on-line analyzers in a FerryBox system for unattended nutrients monitoring in sea water, with the scientific, technical and logistic support of the Norwegian Institute for Water Research (NIVA).

The biparametric Micromac-1000 analytical modules to measure:

1. NH₃ and PO₄ by fluorimetric methods
2. NO₃+NO₂ and NO₂ by spectrophotometric methods
3. PO₄ and SiO₂ by spectrophotometric methods

were manufactured, tested in factory and then installed in Color Fantasy Ferrybox system, running periodically go/back along the commercial route Oslo-Kiel and Kiel-Oslo.

The measurement data were acquired from the analyzers by the FerryBox PC, properly programmed at the time of the installation by NIVA's SW specialist, then correlated with GPS data + temperature and salinity and transferred via satellite Internet to FTP server in NIVA HQ.

The on-line analyzers run unattended for 2.5 months, then they had a maintenance by NIVA technicians; a second visit of SYSTEAS specialist was done in the 4th week of May to solve some technical problems.

27 discrete nutrient samples were collected by NIVA on 26-27 February and 8-10 April 2019 for laboratory analysis comparison, using a CFA routine analyzer.

3. Main achievements and difficulties encountered

The main new features of the updated version of the Micromac on-line analyzers follow:





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

The following table summarize the reagents and DI water consumption for each measurement method:

Parameter	Reagent 1/3 (µL)	Reagent 2/4 (µL)	DI water (mL)
NH3	70	70	25
PO4 fluo	140 70	140 70	25
NO2	70	70	10
NOX	140 280	140	10
PO4	70	70	25
SiO2	140 70	140 70	25

The following table summarizes the difficulties encountered and the actions done or suggested to solve each problem:

Issue	Action done
Data storage every minutes didn't allow an easy and direct data interpretation and evaluation	Data filtration by Excel macro was provided by NIVA. NIVA's data-logger was updated in May to store only real measured data
SiO2 missing data after 15 days of operation, due to the use of an alternative reagent generated crystals blocking reagent and sampling line	Use of the right reagent as requested by the standard method. Problem solved in the 4th week of May
PO4 fluorimetric method collected too high concentrations, due to missing DI water generated false ODS values	DI water consumption was minimized by measurement cycle update and internal control check to be improved
Missing correlation between PO4 fluorimetric and PO4 colorimetric data	On board activity in the 4th week of May was done to cross check the issue
NOx too high values over some periods	On board activity in the 4th week of May was done to cross check the issue
Missing automatic positive controls even if on board standards were available	Requested SW improvement in NIVA data-logger, to perform automatic positive controls along the trip
Missing periodic recalibration of the analyzers	Suggested to be done manually in harbour based on results of positive control checks
Missing written procedure to perform on board maintenance	Written procedure was defined and started to be tested on board in June
Difficulty to correlate GPS position of collected water samples with on-line nutrients data, due to continuous sample flow in the Ferrybox	Suggested installation of a storage tank to be updated periodically, where the same sample from Micromac and lab water sample have to be collected
Difficulty of cross comparison between lab and on-line measurements	Suggested to measure again the collected and stored lab samples on the Micromac analyzers, when the Ferrybox is stopped in Oslo using the grab sample function.



4. Dissemination of the results

Two oral presentations of the activity done and results obtained were performed in:

- 9th FerryBox Workshop, 24-26 April 2019 in Genova (Italy)
- JERICO-NEXT final meeting on 4 July 2019 in Brest (France).

5. Technical and Scientific preliminary Outcomes

Scientific preliminary outcomes:

Based on reliable nutrient data that was collected (approximately n=800 during a ~1 month period between 1-28 February 2019), a preliminary assessment includes the observed spring phytoplankton bloom in in mid Feb at ~56-57 deg N and expanded to 55-59 deg N by late February. The reported chl a fluorescence in Fig. 1 are uncorrected values on a ln scale. The phytoplankton bloom was also indicated by increased oxygen saturation in the same time/region (Fig. 1; >100% = photosynthesis). The spatial and temporal pattern of the phytoplankton bloom correspond very well to the time/regions of observed PO₄ and NO₃ drawdown (Fig. 1). By late February, the winter nutrient reserves appear to be fully utilized by the phytoplankton bloom, and chlorophyll a fluorescence declines in region of ~56-57 deg N chl where PO₄ and NO₃ availability are low (<5 µg P/L and <1 µN/L).

One reagent for silicate analysis was not available at NIVA at the time of the startup and it could not be shipped from SYSTEA due to shipment regulations; the decision to substitute it with another substance brought after two weeks a severe hydraulic clogging that disabled its operativity for months. Ammonia fluorescence measurements showed high signal to noise in a relatively low NH₄ environment. This resulted in unreliable data. It should be noted that NH₄ measurements at low concentrations is generally difficult to measure.

The analytical systems became fouled and clogged since a pre-filter was not installed by the User. This corresponded to the time of the spring bloom. Unclogging and restoring flow took several trips and was not initially successful. Later, the main 220 Vac power supply of the installation room inside the ship had an electrical fault that took some time to repair by the User, not allowing any data collection. These delays combined with no systematic calibration of the system resulted in the collection of unreliable data between March and June.

Despite this, the data collected in February caught the spring bloom and it was quite successful and unique.

The experience teaches both User and Provider would have to dedicate more time on the technical training to more than one operator, to ensure a proper backup along the time.

After February the User had some personnel availability weakness due to overlapping field activities, that affected the quick evaluation of the collected data and our related reaction for the required field maintenance operations.

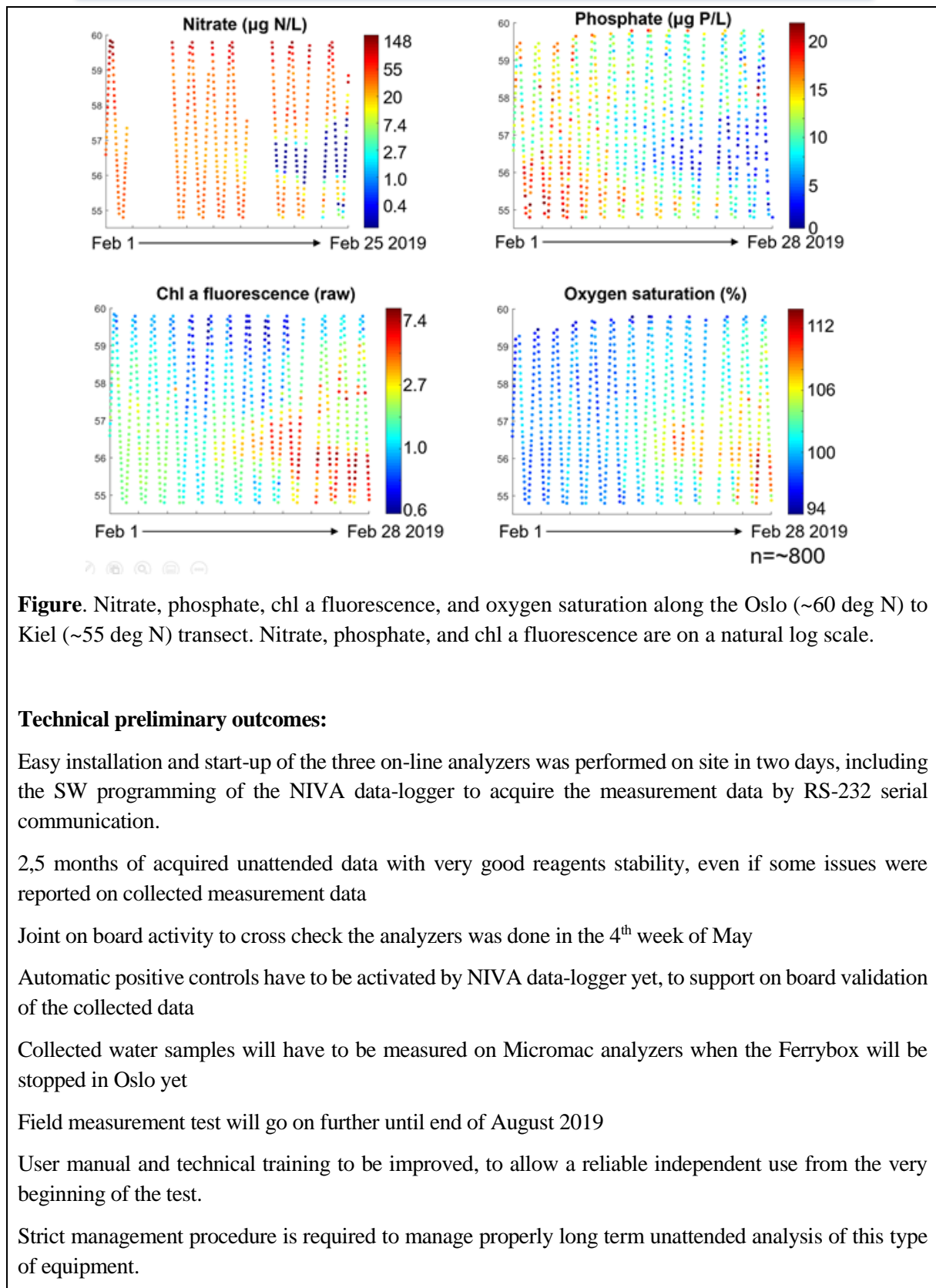


Figure. Nitrate, phosphate, chl a fluorescence, and oxygen saturation along the Oslo (~60 deg N) to Kiel (~55 deg N) transect. Nitrate, phosphate, and chl a fluorescence are on a natural log scale.

Technical preliminary outcomes:

Easy installation and start-up of the three on-line analyzers was performed on site in two days, including the SW programming of the NIVA data-logger to acquire the measurement data by RS-232 serial communication.

2,5 months of acquired unattended data with very good reagents stability, even if some issues were reported on collected measurement data

Joint on board activity to cross check the analyzers was done in the 4th week of May

Automatic positive controls have to be activated by NIVA data-logger yet, to support on board validation of the collected data

Collected water samples will have to be measured on Micromac analyzers when the Ferrybox will be stopped in Oslo yet

Field measurement test will go on further until end of August 2019

User manual and technical training to be improved, to allow a reliable independent use from the very beginning of the test.

Strict management procedure is required to manage properly long term unattended analysis of this type of equipment.

SUBMITTED, 17 JULY 2019; FINAL REVISION, 29 AUGUST 2019