TNA PROJECT REPORT

1. Project Information

Proposal reference number	JN_CALL_3_8
Project Acronym (ID)	NitrateComp
Title of the project	In-situ inter-comparison of nitrate sensors
Host Research Infrastructure	NIVA Research Station (NRS)
Starting date - End date	20/11/2018 – 07/04/2019
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2. Project objectives

The main objective of NitrateComp project was to deploy a commercial Opus UV (TriOS GmbH) nitrate sensor and a recently developed Lab on Chip (National Oceanography Centre Southampton) technology on a FerryBox-like stationary system located at the NIVA Solbergstrand Research Facility in order to evaluate their performances. The two systems use different analytical principles for the determination of nitrate so that simultaneous measurements on a common platform are ideal for providing an in-depth comparison and a solid evaluation of their operational capabilities.
In costal environments, physical and biological processes together with anthropogenic inputs, contribute to generate large temporal and spatial variability in the concentration of nitrate. The objective was to test the sensors suitablility for long-term monitoring of nitrate concentrations in such highly variable environments. As a final objective, this project aimed to develop an improved computational strategy to calculate nitrate concentrations for the in-situ Opus UV sensor and to determine optimal settings for the LOC technology in terms of reagent consumption, precision and long-term stability in order to implement their technological development.

3. Main achievements and difficulties encountered

Within the NitrateComp project the performances of the Opus UV and the LOC nitrate sensors were compared during a field test deployment. Over a period of five months the two sensors were installed at the NIVA Solbergstrand Research Facility and continuously recorded nitrate concentrations of the surface and deep water of the Oslofjord. Both sensors showed great stability over time and only minimal maintenance operations were required. The formation of copper deposits on the Opus UV optical window prevented nitrate measurements to be undertaken for the period between December 16th, 2018 and January 16th, 2019 so that no data during this period could be retrieved. The Opus UV sensor optical lens were therefore cleaned, and new reagents and sampling filter were installed on the

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LOC sensor. Sensor operations were monitored remotely (in Kiel) over the whole period. On several occasions, communication with the sensors was not possible due to failure of the remote connection. Faulty communication did not affect sensor operations or measurements as data were logged internally. Instability and minor gaps in CTD data retrieval during the initial period prevented adequate processing of Opus UV nitrate measurements for these days. In general, for the remaining part of the deployment, following appropriate data processing procedures, results from both sensors were highly comparable, which was vey encouraging.

4. Dissemination of the results

During the recent years the scientific community has increased its interest in nutrient sensors and the stationary Ferrybox deployment at the NIVA Research Station provided a unique opportunity to showcase the potential of the sensors for high quality oceanographic monitoring activities. The NitrateComp project allowed for the first simultaneous oceanographic deployment of UV nitrate and LOC nitrate sensors. The GEOMAR marine biogeochemistry department has excellent links and work collaboration with TriOS GmbH as well as with the National Oceanography Centre in Southampton. Results from this project will contribute to optimize sensor metrologies and to improve technical features of the current sensors.

The OPUS nitrate sensor lacks a solid post data processing method that takes into account in-situ temperature and salinity to calculate the nitrate concentrations. The GEOMAR group has developed algorithms over the last year to treat the data. The UV nitrate and LOC nitrate sensor deployment allowed the testing of the new UV nitrate sensor algorithm. Results from this work will be included in the manuscript as a validation of the new algorithm (Nehir et al., in preparation) computed specifically for the Opus.

5. Technical and Scientific preliminary Outcomes

The NitrateComp project describes the deployment of two nitrate sensors in the Oslofjord. The field deployment can be divided into two parts. During the first part of the work, the sensors were fully immersed into a small sensor test tank (60 L) connected to a water switching system that allowed for a fast replacement of the water inside the container. The sensors were deployed from the 22nd of November 2018 up to the 20th of February 2019. A Seabird SBE45 CTD was set to record water temperature and conductivity at one-minute interval while the measurement frequency of the Opus UV was set to ten minutes and the LOC to one hour.

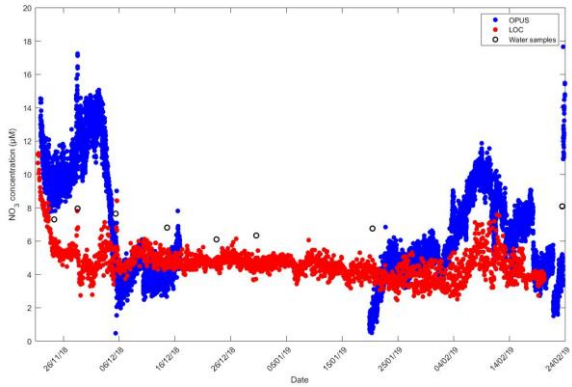
The second deployment was on a stationary FerryBox system from the 16th of March to the 6th of April 2019. The FerryBox was equipped with a de-bubbling unit to remove air bubbles from the water flow and a Seabird SBE45 CTD for water temperature and salinity measurements. The water from the Oslofjord was pumped at a constant rate (1.2 $L \cdot min^{-1}$) into the measuring circuit, where the two sensors (Opus UV and Lab on Chip) were connected in series. The water from the fjord was pumped through a flow cell cuvette installed on the Opus UV sensor allowing for UV nitrate measurements. The same water was also pumped into the LOC sensor. A 0.45 µm PES filter (Fisherbrand® Syringe filter, Fisher Scientific) was installed at the end of the inlet tubing of the LOC sensor in order to avoid particles entering the LOC microfluidic channels. An additional tubing with a clamp was installed at the end of the circuit to allow for manual water sampling. The measurement frequency of the Opus UV was set to two minutes, while LOC measurements were taken every 30 minutes.

A new algorithm (Nehir et al., in preparation) specific for the Opus that takes into account in-situ

temperature and salinity to calculate the nitrate concentrations was computed and applied herein. A sensor specific calibration file consisting of waterbase spectra and extinction coefficients of sea salt (bromide) and nitrate at a range of temperatures was derived experimentally and used for data processing. The raw absorbance at each wavelength from 200 to 260 nm was calculated using the Beer Lambert Law. A new absorption spectrum at each wavelength was then calculated by subtracting the theoretical seawater spectrum (Sakamoto et al., 2009) from the in-situ seawater spectrum both based on external calibration and sample salinity and temperature values. The absorption spectrum of cDOM was estimated from a linear function between absorbance and wavelength from 240 to 260 nm. The final concentrations of nitrate were than calculated in the wavelength range between 217 and 240 nm.

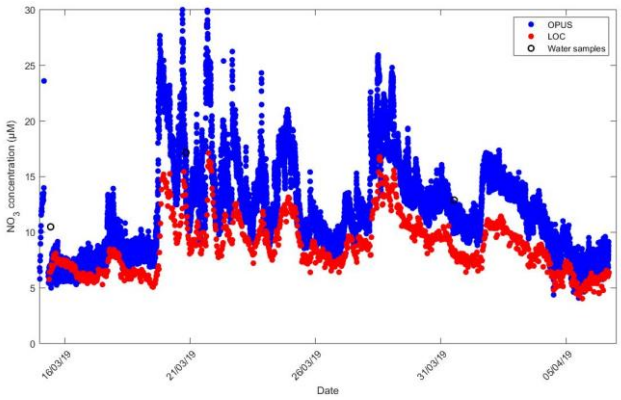
To calculate the nitrate concentration of the water sample, the LOC sensor uses the relative absorption of the sample to the standard solutions of known concentrations. For each sample analysed the sensor performed a measurement of the blank, sample and standard ([NO3] = 12 µM). The photodiodes placed at the end of each measuring channel measured the transmitted light emitted by the LEDs and propagated through the medium. The average photodiode voltages recorded during the last 5 seconds of the stopped flow period were used to compute nitrate concentrations. Monitoring of the photodiodes intensities of the blank and standard/sample were used as scaling factor to correct for thermal drifts while measurements of the photodiode voltages taken prior to the mixing of the blank or sample with the reagents were used to compensate for potential optical refraction effects.

During the first days of the experiment, temperature and salinity data showed high variability as several activities at NIVA station which required water from the water supply system were being undertaken and changes in the normal water flow occurred. From December onwards, the water flowing through the tank was mostly coming from 60 m depth with switching to surface water only on two occasions. Nitrate measurements from both the LOC and Opus sensors for the first deployment period are shown below.



Nitrate values determined by the two sensors exhibit a similar trend, however a large difference in concentrations is observed at the beginning until December 6th. Inhomogeneous mixing of the water inside the container and/or instability of the CTD data used for UV nitrate data processing might have contributed to the large discrepancy found in nitrate measurements during this period. After the initial period, temperature and salinity values were more stable and both sensors gave comparable nitrate concentrations, with values ranging between 5 and 8 µM.

During the deployment on the stationary FerryBox system, the Opus UV and the LOC sensors were connected in series and surface water from the Oslofjord was pumped through. Nitrate concentrations measured by the Opus and LOC sensors during the FerryBox system deployment are shown below.



Concentrations were variable showing several peaks of different height reflecting the natural variability of Oslofjord surface waters. Identical patterns for nitrate concentrations were given by both the sensors. The fast water flow through the system allowed for simultaneous detection of changes in nitrate concentration. The LOC nitrate values varied between 5 and 15 µM, while the Opus measured values up to 30 µM. Comparison with values from discrete water samples agrees with the LOC measurements so that it is possible that further corrections in the Opus data processing calculation is required. However, it not to be excluded the possibility that the faster sampling frequency of the Opus allowed for a better temporal resolution of nitrate concentrations in the Oslofjord waters compared to the LOC.

The simultaneous deployment of the Opus UV and LOC nitrate sensors provided a first positive field based assessment of the potential of the sensors for high quality oceanographic monitoring. Both the Opus UV and LOC sensors demonstrated to be suitable for long-term monitoring of nitrate concentrations in highly variable environments opening the door to potential future use and deployments on FerryBox systems and ships of opportunities.

SUBMITTED, 24 JUNE 2019