

Nitrate observations with autonomous gliders

Gerd Krahmann, Johannes Karstensen, and Marcus Dengler

Start

Sensor

Principle

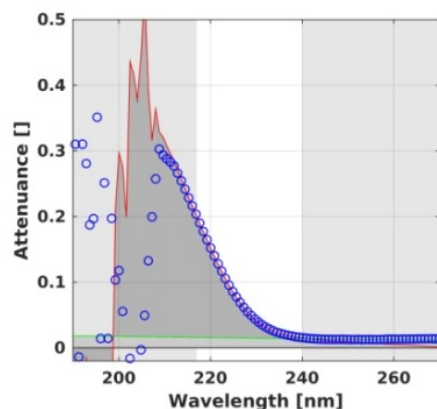
Toolbox

Example 1

Example 2

Setup

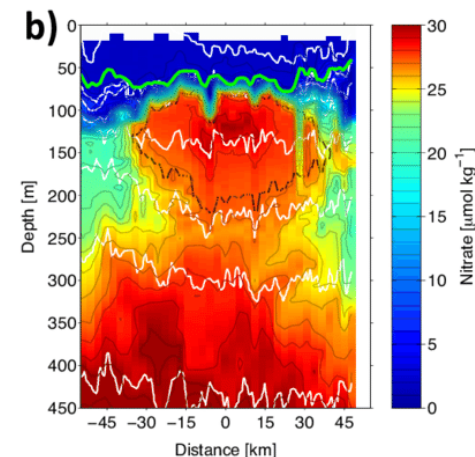
Principle



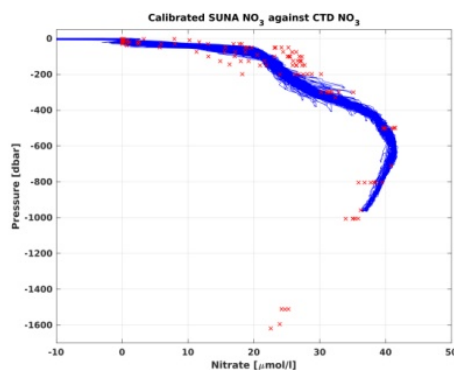
Nitrate Sensors



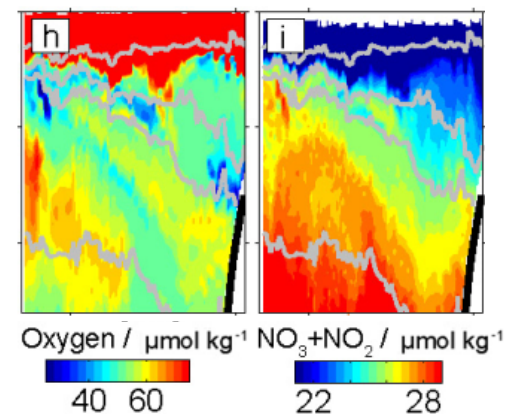
Example 1 (eddy)



Toolbox



Example 2 (coastal section)



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- ‘In Situ Ultraviolet Spectrophotometer’ (ISUS) originally developed by Ken Johnson and Luke Coletti at Monterey Bay Aquarium (MBARI).
- In 2002 they published an article on the successful first deployment of the ISUS.
- ISUS uses absorption spectra of UV light to determine the concentration of Nitrate (and possibly other species) in (sea-)water.
- Commercially available in modified form as Submersible Ultraviolet Nitrate Analyzer (SUNA).
- In 2009 and 2017 Carole Sakamoto and colleagues at MBARI published further improvements to the calculation algorithms greatly improving the quality of the resulting concentrations.

Johnson and Coletti, 2002
Sakamoto et al., 2009
Sakamoto et al., 2017

Image sources: www.mbari.org www.seabird.com

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Sensor(s)



Seabird/Satlantic Deep SUNA

wavelengths: 190 to 370 nm (256 elements)
 lamp type: Deuterium (900 h lifetime)
 accuracy: 2.0 μM (or 10%)
 precision: 0.3 μM
 minimum: 1.0 μM
 min. sample rate: 1 sec
 max. pressure rating: 2000 dbar

Trios OPUS



wavelengths: 200 to 360 nm (256 elements)
 lamp type: Xenon flash ($>10^9$ flash lifetime)
 accuracy: 3.5 μM (or 5%)
 precision: 0.4 μM
 minimum: 1.1 μM
 min. sample rate: 3 sec
 max. pressure rating: 6000 dbar

Image sources: www.seabird.com www.trios.de

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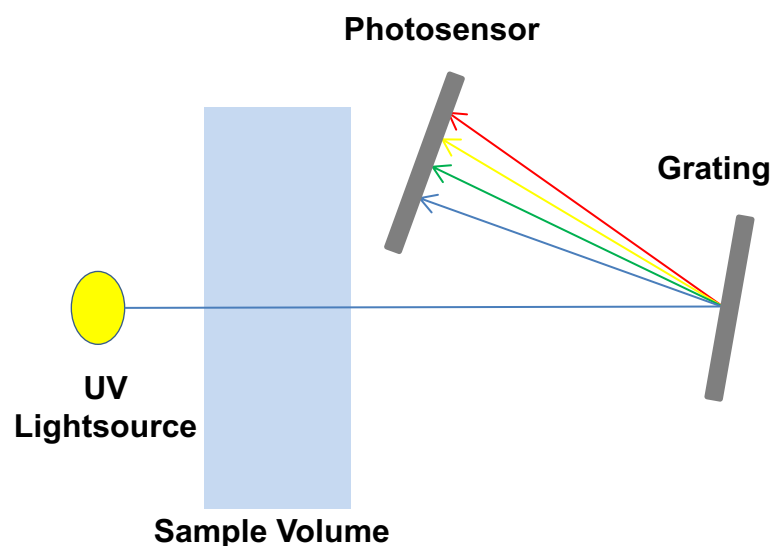
Toolbox

Example 1

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Wide spectrum UV light is emitted by a lamp and collimated to form a beam.

The beam passes through the sample medium where some of the light is absorbed or reflected.

With the help of a grating the light is separated into its different wavelengths.

A photosensor at measures the strength of the light at various wavelengths.

The comparison of the observed light with a reference spectrum of the lamp for clear water gives a measure of the attenuation (absorption & reflection) from which the concentration of NO_x can be determined. Only the range from 217 to 240 nm is used.

NO_x stands for 'mostly' NO_3 . Since the absorption by NO_2 is quite similar to that of NO_3 the presence of NO_2 will influence the determined values.

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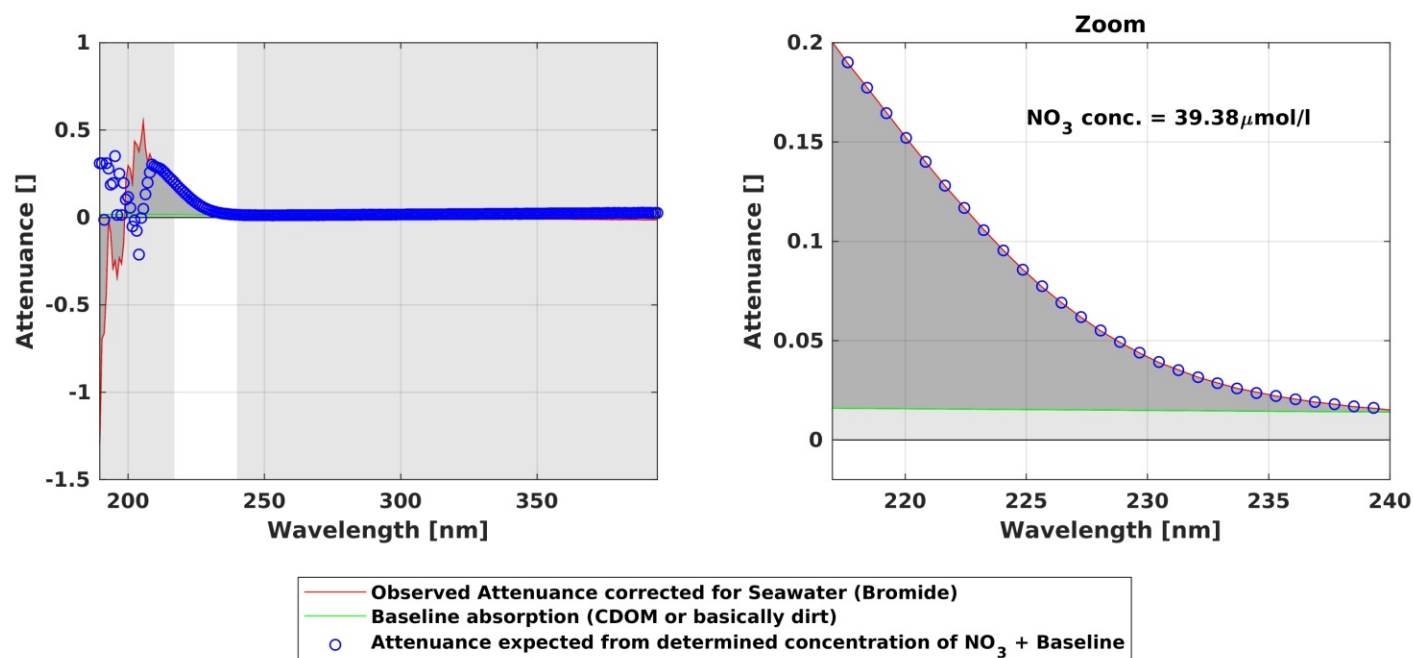
Example 1

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A NO_3 reference spectrum (shape of the blue line) has been determined by the manufacturer and is, together with a linear baseline, fitted to the corrected attenuation spectrum.



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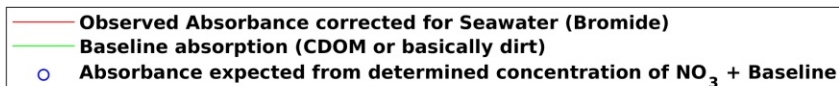
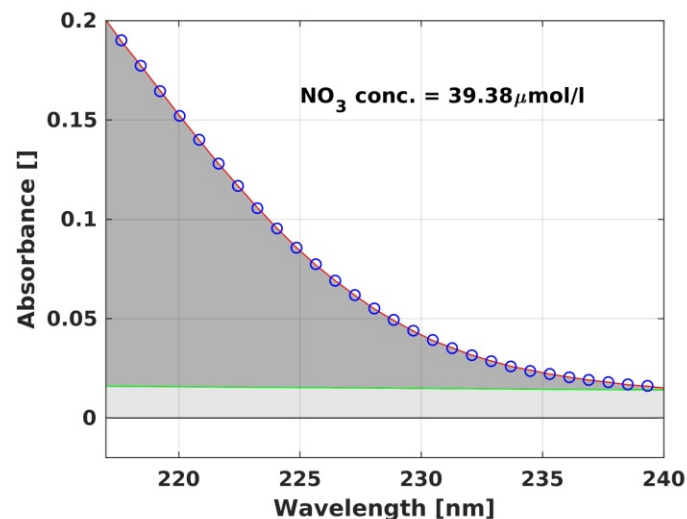
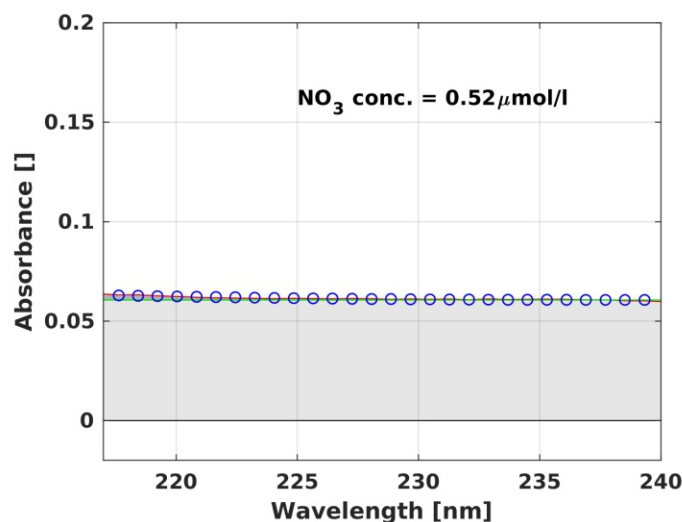
Example 1

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The optimal fit gives an amplitude of the NO_3 component and a height and slope of the baseline. The baseline includes all parts of the attenuation spectrum that cannot be explained by NO_3 . I.e. CDOM, turbidity etc.



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GEOMAR

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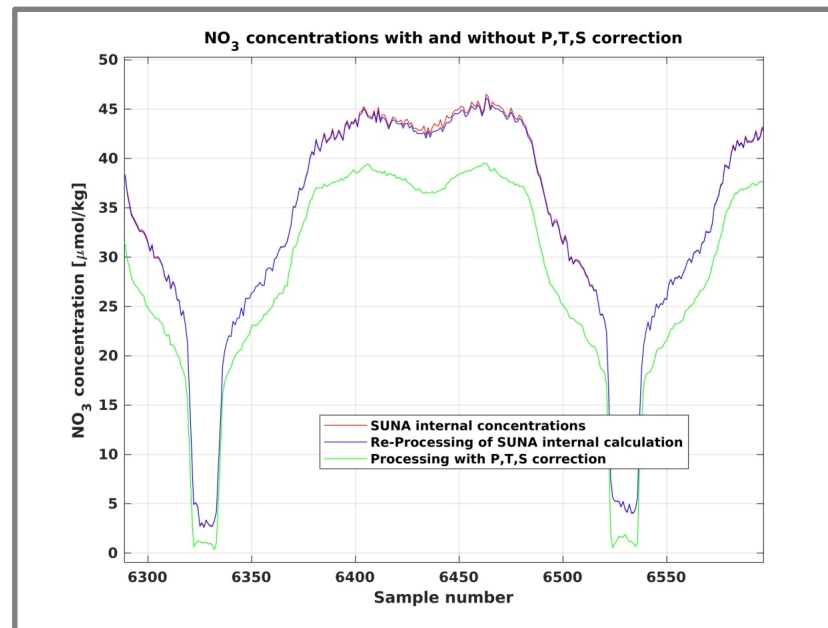
Matlab Toolbox

An important part of SUNA data post-processing is the recalculation of Nitrate values with known pressure, temperature and salinity. This reduces noise levels by a factor of 5. This Also removes some (sensor-) temperature dependence.

A Matlab toolbox has been developed to simplify the processing of SUNA Nitrate data and make the processing steps more transparent.

The original code base was graciously provided by Ken Johnson and Joshua Plant of MBARI.

•Contact gkrahmann@geomar.de if you are interested in the toolbox.



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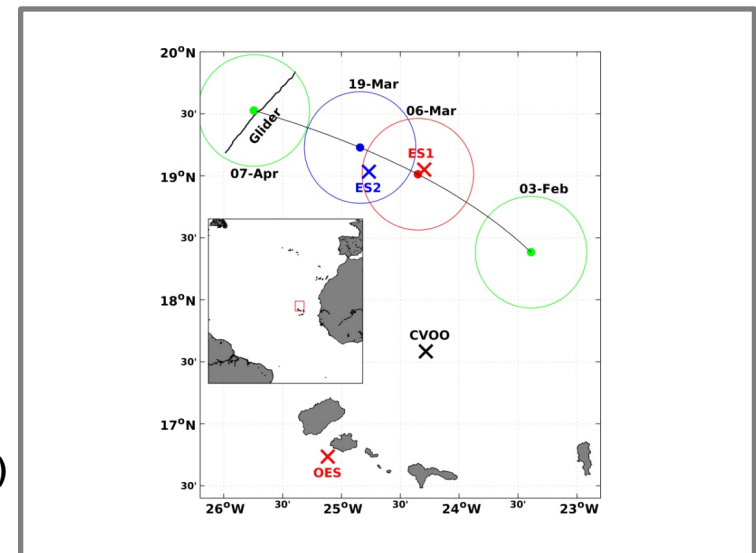
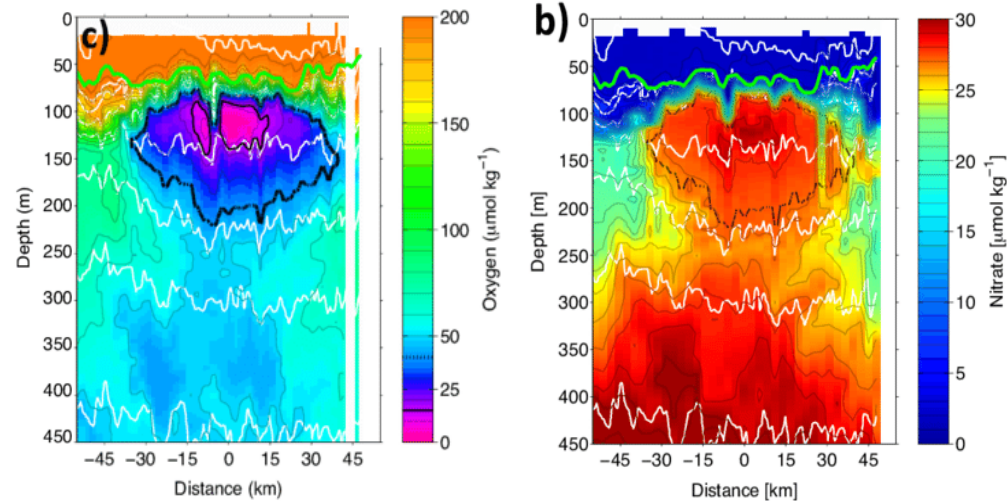
Setup

Example 1:

Our first SUNA deployment:

- In spring 2014 an anti-cyclonic modewater eddy was observed north of the Capeverde archipelago.
- The eddy had a core with oxygen concentrations as low as $<5 \mu\text{mol/kg}$. At the same time the NO_3 concentrations were elevated hinting to a continuing 'import' of NO_3 by remineralization of sinking particles.
- Some of our SUNA settings were not optimal but even so the data quality was very good in particular when during the post-processing the known P,T,S were used (noise level is reduced by a factor 5).

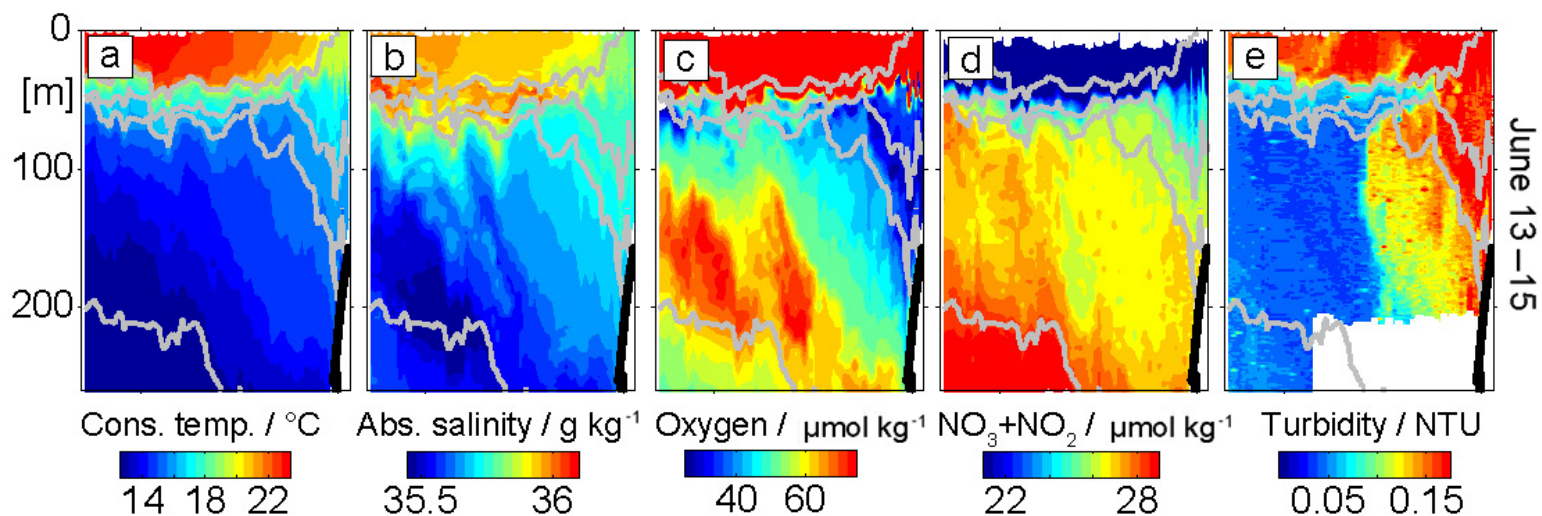
Karstensen et al., 2016 (Biogeosciences Special Issue 213)
Grundle et al., 2017



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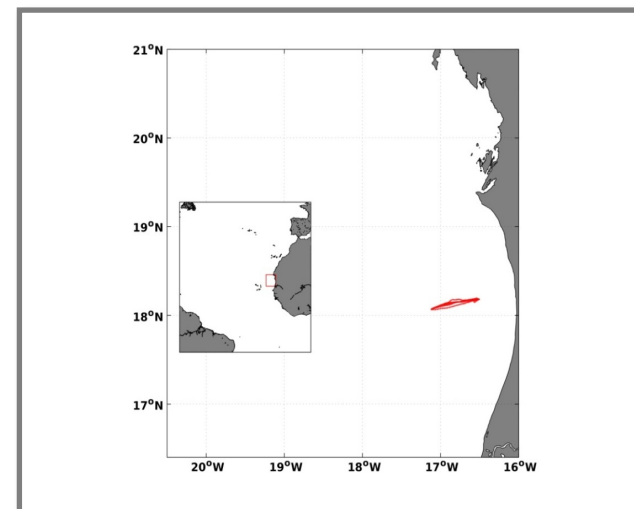
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Example 2



Our second SUNA glider deployment:

- Summer 2014 on a glider off the Mauritanian coast.
- One section was covered repeatedly with a SUNA-equipped glider.
- Pronounced horizontal variability is visible in the sections.
- NO₃ variability goes hand in hand with other watermass properties.



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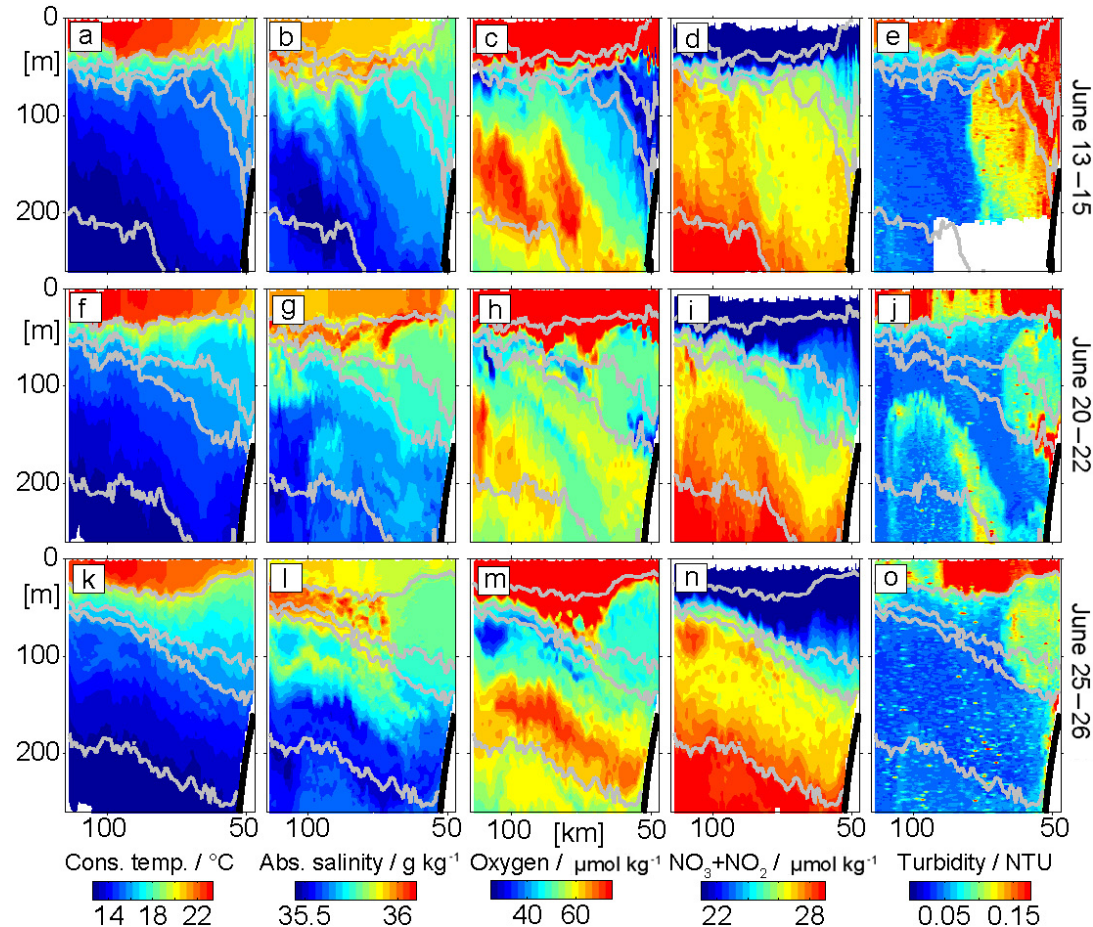
Example 2

Substantial temporal variability can also be seen when the repeat sections are compared.

NO_3 is strongly anti-correlated with oxygen.

Watermass analysis together with current observations suggest a more rapid inflow of waters with South Atlantic origin. The fraction of South Atlantic water does however not change.

Increased flow speed likely leaves less time for oxygen consumption during the northward transport.



Thomsen et al., 2019

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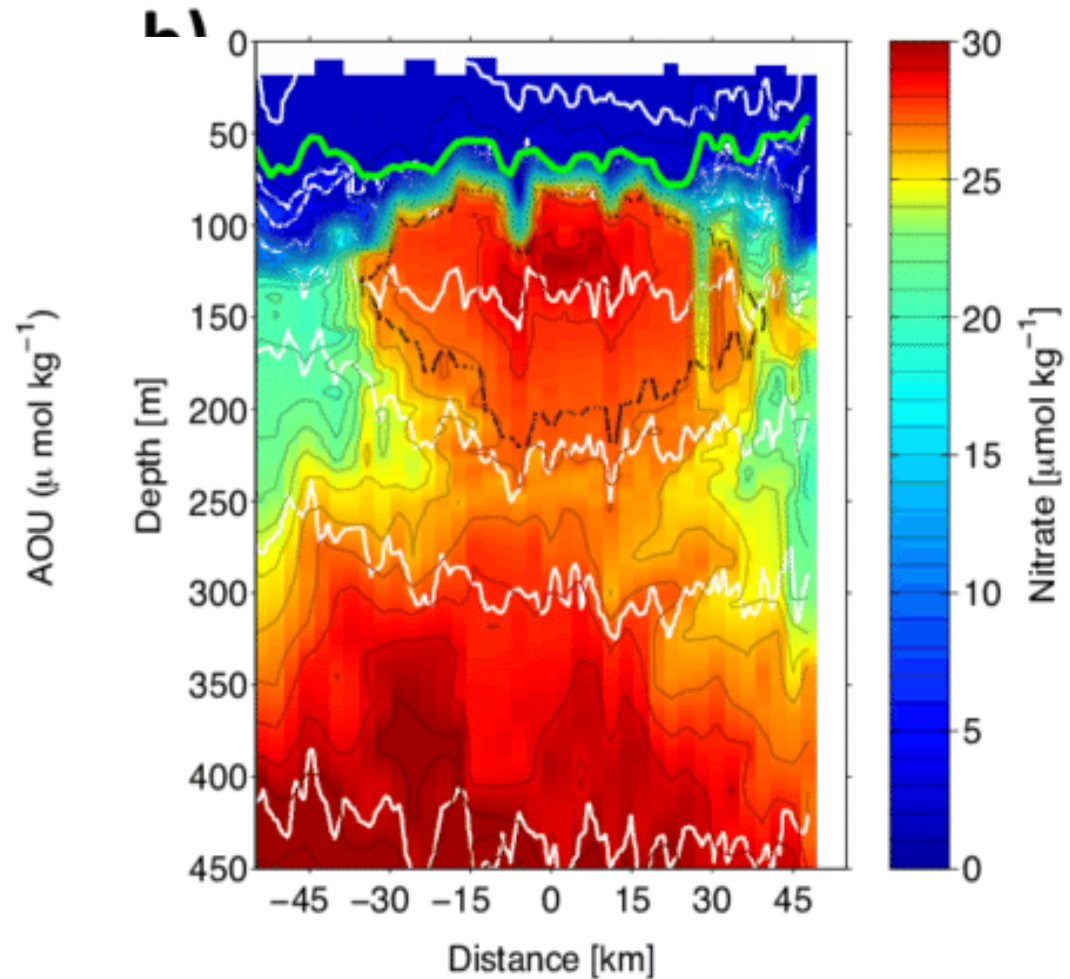
Setup (or lessons learned)

- Our SUNA Nitrate sensors have shown to be a valuable addition to the gliders (and CTDs) giving stable and reproducible values.
- The standard setup of the SUNA on Slocum gliders was (is?) not optimal.
 - Internal recording of the SUNA should be set to 'full binary'
 - Internal recording of the SUNA should store in daily files
- The clock of the SUNA should be set correctly (most important for usage on the CTD).
- The SUNA internal calibration files have to be recorded (xml and cal files, see SUNA manual for the somewhat hidden location of the xml file) before and after the deployment. Some xml files from the manufacturer are wrong for reduced binary data!
- SUNA internal calibrations with de-ionized water should be done before and after the deployment. (The recommended procedure changed recently. You should use a consistent one before and after the deployment.)
- Best (field-) calibration results can be obtained by attaching the SUNA to a CTD and comparing to nutrient concentrations from water samples. (The SUNA needs power from the CTD for that.)

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Thank you !



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Grundle, D., C.R. Loescher, G. Krahmann, M.A. Altabet, H.W. Bange, J. Karstensen and B. Fiedler (2017). Low oxygen eddies in the eastern tropical North Atlantic: Implications for N₂O cycling. *Scientific Reports*, 7: 4806. doi:10.1038/s41598-017-04745-y

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. <https://doi.org/10.1351/goldbook>.

Johnson, K. S., and L. J. Coletti. 2002. In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep-Sea Res. Part I Oceanogr. Res. Pap.* 49: 1291–1305. doi:10.1016/S0967-0637(02)00020-1

Karstensen, Johannes & Schütte, Florian & Pietri, A & Krahmann, Gerd & Fiedler, Bjoern & Grundle, Damian & Hauss, Helena & Arne, Körtzinger & Löscher, Carolin & Testor, Pierre & Vieira, Nuno & Visbeck, Martin. (2016). Upwelling and isolation in oxygen-depleted anticyclonic modewater eddies and implications for nitrate cycling. *Biogeosciences Discussions*. 10.5194/bg-2016-34.

Naqvi, S. W. A., D. Gilbert, T. Treude, and L. Cotrim da Cunha (Eds.) (2015). Hydrography, biogeochemistry, and biology of "dead-zone eddies" in the eastern tropical North Atlantic, *Biogeosciences*, Special Issue 213.

Sakamoto, C. M., K. S. Johnson, and L. J. Coletti. 2009. Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer. *Limnol. Oceanogr.: Methods* 7: 132–143. doi:10.4319/lom.2009.7.132

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Sakamoto, C. M., Johnson, K. S., Coletti, L. J. and Jannasch, H. W. (2017), Pressure correction for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer. *Limnol. Oceanogr. Methods*, 15: 897-902.
doi:10.1002/lom3.10209

Thomsen, S., Karstensen, J., Kiko, R., Krahmman, G., Dengler, M., and Engel, A.: Remote and local drivers of oxygen and nitrate variability in the shallow oxygen minimum zone off Mauritania in June 2014, *Biogeosciences*, 16, 979-998,
<https://doi.org/10.5194/bg-16-979-2019>, 2019.