Nitrate sensors on profiling floats

1) Why measure nitrate
2) Principle of operation
3) Data requirements
4) Sensor performance
5) QC & Reprocessing requirements

Ken Johnson, Luke Coletti, Hans Jannasch
Monterey Bay Aquarium Research Institute

Steve Riser, Dana Swift
University of Washington
MBARI/UW floats with nitrate, oxygen, and some with biooptics (yellow)
• Argo data organized around netCDF files – not for casual user

• Informal user access at MBARI web site (Ascii flat files in Ocean Data View format)
AUTONOMOUSLY PROFILING THE NITRATE CONCENTRATIONS IN THE OCEAN: THE PRONUTS PROJECT.

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Introduction
MBARI Chemical Sensor Lab

Why make these measurements?
Ocean Station Papa, 50°N in the N. Pacific
Float 5143, Ocean Station P, 50°N Pacific Ocean

(a) Temperature [°C]
(b) Nitrate [μM]
(c) Temperature [°C]
(d) Nitrate [μM]

0 to 30 m

1000 m
Why measure nitrate?

- The annual cycle is a direct tracer of Net Community Production (Primary Production – Respiration at all trophic levels)

- NCP estimate not impacted by gas exchange rates, as is $O_2$

- NCP = Carbon export in balanced system

- Seasonal change in concentration more important than long-term change – big signal compared to noise
Float 6391 launched at BATS. Interannual/spatial variability in nitrate entrainment into mixed layer during deep mixing in late spring.
LETTERS

Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre

Kenneth S. Johnson¹, Stephen C. Riser² & David M. Karl³
Denitrification in low oxygen zones regulates ocean stock of nitrate and potential NCP.
Nature of Ultra-violet Absorption of Sea Water

It has already been suggested that ultra-violet absorption of natural water is a useful index of water quality. Armstrong and Bonich showed that the ultra-violet absorption of sea water is about twice that of a solution containing the same concentration of inorganic salts, and they attributed the difference to the presence of organic matter. They also recognized that absorption by nitrate is likely to be important in deep water. The nature of

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Fig. 1. Absorbance of sea water. A, Western North Pacific (28° 00' N, 135° 55' E, 5,050 m); B, Sazami Nada (24° 08' N, 120° 02' E, 5,000 m).
Absorbance$_\lambda = -\log \left( \frac{I}{I_{DW}} \right)_\lambda = \left[ \varepsilon_{NO_3-,\lambda} \ (NO_3^-) + \varepsilon_{Br-,\lambda} \ (Br^-) + c + d* \lambda \right] * b$

$\varepsilon_{NO_3-,\lambda} = \text{molar absorptivity of nitrate at wavelength } \lambda, \text{ a fundamental physical property that can be measured}$

$\varepsilon_{Br-,\lambda} = \text{molar absorptivity of bromide at wavelength } \lambda, \text{ a fundamental physical property of bromide ion that can be measured (T dependent)}$

$b = \text{optical path length}$

$c, d \text{ are coefficients for a linear baseline offset (DOC).}$
Measurement process:

1. Nitrate absorbs light in the deep UV.

2. So does Br\(^{-}\) ion (mean conc. 840 µM in ocean, constant ratio to S)

3. Measure seawater UV absorbance from \(~217 \text{ nm to } ~240 \text{ nm, salinity, temp.}\)

4. Compute Br\(^{-}\) concentration, compute light absorption by Br\(^{-}\) from known \(\varepsilon_{\text{Br}^{-}, \lambda}\) (T dependent), subtract from seawater UV spectrum, compute NO\(_3^{-}\) using known \(\varepsilon_{\text{NO}_3^{-}, \lambda}\) and coefficients c and d of linear baseline
Instruments and Methods

In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean

Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer

Monterey Bay Aquarium Research Institute, Moss Landing, CA, 95039 USA
In situ ultraviolet spectrophotometer (ISUS)

ISUS Block Diagram

Equitech RetroReflection
Probe – 3000 psi

SiC Ref.  UV Fiber

Heraeus Fiber Light
Source

Zeiss/
Cronin
Spec

MBARI
TT8
Instrument

MBARI Chemical
Sensor Lab
MBARI ISUS nitrate sensor integrated into modified Apex profiling float.

- $\text{NO}_3^-$ detected from UV spectra
- 60 $\text{NO}_3^-$ meas./profile to 1000 m
- Precision $\leq \pm 0.2 \mu\text{M (1 SD)}$
- Float endurance 320 profiles to 1000 m. ~4.5 year life at 5 day cycle time
- 44 Joule/meas = 20% of battery

[Diagram of sensor with labels: Optical probe, Electronics and sensor, Pressure hull extended 20 cm (limits max Z to ~1700 m in much of ocean, next version fixes that)]
Oxygen

ISUS Nitrate, built into float

Chlorophyll fluorescence & particle concentration

pH

Salinity, Temperature, Depth

Iridium Comms., GPS

Oxygen

ISUS Nitrate, built into float

Chlorophyll fluorescence & particle concentration
Submersible UV Nitrate Analyzer (SUNA) – similar optical components, but straight-thru optical path. Mounted on outside of float. Easier to adapt to floats, but cables/connectors are the weakest link of all parts.

Data stream and math are the same as for ISUS. Both instruments give similar results.
A .isus file is transmitted on each profile. It contains a 33 line header, one line (see below) for each nitrate measurement, and a 36 line footer. About 21 kbytes of data in each file (60 nitrate obs). Computed nitrate is also returned in the .msg file, but the .isus file allows us to reprocess data with improved algorithms.

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0xC39E,A,02/16/2011 15:13:26,1297869199,901.47,2.9963,34.3537,0,1,0,-1.00,
3.18,27.11,23.81,1.746,1376.00,3.32,1553.71,4.69,34.35,49.15,4.955e-004,36,77,
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RECORD_16BIT_CR,RECORD_DATA_TYPE, ISUS_TIMESTAMP (GMT), CTD_TIMESTAMP (1970 EPOCH SECS), CTD_DEPTH (D BAR), CTD_TEMPERATURE (DEG C), CTD_SALINITY (PSS), SAMPLE_COUNTER, POWER_CYCLE_COUNTER, ERROR_COUNTER, ENDCAP_SEAWATER_TEMPERATURE (DEG C),

HOUSING_TEMP (DEG C),HOUSING_REL_HUMIIDIY (%),ISUS_BATT_VOLTAGE (V), ISUS_CURRENT (A), REF_CH_MEAN, REF_CH_STDEV, DARK_CURRENT_MEAN, DARK_CURRENT_STDEV, ISUS_SALINITY (PSS), ISUS_NITRATE (uM), ISUS_FIT_RESIDUALS (RMS), FIT PIXEL_BEG, FIT PIXEL_END,

PACKED_HEX_DATA, SEAWATER_DARK_CURRENT
We also need a calibration file for each sensor with the arrays for wavelength, $\varepsilon_{\text{NO}_3^{-}, \lambda}$ & $\varepsilon_{\text{Br}^{-}, \lambda}$. File on the float and on shore:

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<th>CalTemp</th>
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<td>H</td>
<td>Wavelength (nm)</td>
<td>$E_{\text{Br}^{-}}$ (but in terms of salinity, not Br-)</td>
<td>$E_{\text{NO}_3^{-}}$ (L mol$^{-1}$ cm$^{-1}$)</td>
<td>Not used or Satlantic proprietary</td>
<td>Pure water intensity – Dark Current (counts)</td>
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<td>E</td>
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Profiling float nitrate measurements versus bottle samples (autoanalyzer NO$_3^-$). Need an initial surface sample to control for offsets in calibration (shipping damage?).

HOT 5145

\[ y = 1.00x + 0.36 \]
\[ R^2 = 1.00 \]

So. Ocean 5146

\[ y = 1.01x + 3.56 \]
\[ R^2 = 0.99 \]
UV spectrum & components

UV Spectrum

Br- Component

Nitrate Component

Baseline (aka DOC)

Residuals - Abs x 20

Wavelength (nm)

Can # 70
Date 01/29/2008
Temp 20.6635

Ref 989.86
Salinity 34.68
Intercept -.02115

Nitrate 1.89
Slope1 .0002973

Absorbance

Start

Pause

Stop

-0.02

0.3
Drift and fouling are nearly linear biases to the spectrum.

But when baseline nears 1.0 Abs, non-linearities accumulate & data are definitely questionable.

Wavelength (nm)

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<td>17.531</td>
<td>1.33</td>
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Float 7564 in the Arctic.
What QC is required? Float 7564 in the Arctic. Nitrate sensor has property that an offset is constant over the whole profile (Johnson et al., in review). QC would apply this offset to all subsequent data.
What QC is required? Float 7564 in the Arctic. Nitrate sensor has property that an offset is constant over the whole profile (Johnson et al., in review). QC would apply this offset to all subsequent data.
Float 5145 near Hawaii. Offsets occur as a constant shift over whole profile.
Allowing negative concentrations is perfectly acceptable. While a real concentration cannot be negative, we are dealing with estimates of concentration. An estimate can be negative. Fixing it will bias your statistics in an unhelpful manner.
Temperature coefficient of Br⁻ absorptivity at salinity 35 is

\[ A_{Br^-} = (a + b \times T) \exp ((c + d \times T) \times (WL - 210)) \] (Sakamoto et al)

\( T = \) Temperature, \( WL = \) wavelength (nm) and \( A_{Br^-} \) is bromide absorbance at \( WL \) and \( T \) and salinity 35.

Float 7663 near Bermuda

WL – 210 nm

WL – 208.7 nm
Why not 210 nm for all floats?

- The spectrometer manufacturer calibrates the wavelengths of the 256 elements of the diode array only at wavelengths above 250 nm. Their specification is a wavelength accuracy of 1 nm.

- The actual wavelength of light striking pixels around 217 nm is a bit uncertain and it’s not unreasonable to treat the parameter 210 as a tuneable parameter within <2 nm (combined uncertainty of new spectrometer and old spectrometers used to determine Br⁻ temperature coefficient).

- The floats all have 210 built in, but by sending the intensity data back, we adjust the algorithm and reprocess nitrate on shore.
Annual nitrate observations at 2000 m. depth.

Number of observations 24873

World Ocean Atlas 2009
Data probably can be corrected to +/- 1 µmol/L using WOA in many areas??????
Raw absorbance data is probably useful for studies of CDOM.
ISUS detects hydrogen sulfide – floats in the Black Sea would be very interesting

MWARI Chemical Sensor Lab
The Center for Southern Ocean Biogeochemical Observations & Modeling (C-SOBOM) is a candidate NSF Science & Technology Center to be housed at Princeton University.

Our goal: to form a Center that will
– enable a transformative shift in our scientific and public understanding of the role of the vast Southern Ocean in climate change and biogeochemistry.
Overarching Facilities Objective

- Build an array of some 200 profiling floats equipped with biogeochemical sensors (nitrate, oxygen, pH, biooptics) in the Southern Ocean.

- Provide high quality data in all seasons and weather for models, analysis, education and outreach.

40 floats/year for 5 years, 2nd 5 years likely.
NO3 = some matrix math

Deep correction

Satellite correction = 1

Compute Satellite correction

RT Tests

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MLD from T&S

Satellite correction = 1

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