The 2008 North Atlantic Bloom Experiment
Calibration Report # 5

Calibration of the ISUS Nitrate Sensor on Float 48

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ABSTRACT

An in-situ ultraviolet spectrophotometer (ISUS) was integrated with a suite of instruments on an autonomous float deployed during the 2008 North Atlantic Bloom Experiment. Post calibration of the ISUS instrument and subsequent processing of the spectrophotometric data acquired by the ISUS incorporating *in-situ* temperature and salinity measurements to correct for the temperature-dependent, ultraviolet absorbance by the bromide ion significantly improved the precision of duplicate nitrate measurements from 0.4 to 0.1μM. These newly derived nitrate concentrations were then calibrated against bottle measurements collected during the R.V. Knorr process cruise (April 17 through May16). A simple linear regression ($NO_3^{cal} = 1.1536 \times NO_3^{ISUS} + 2.6227$; $R^2 = 0.927$; n = 53) was sufficient to make the ISUS nitrate concentrations fit the bottle measurements with a standard deviation of 0.6μM. Comparisons with water samples taken on the R.V. Bjarni Saemundsson deployment cruise are inconclusive due to high spatial variability. No obvious drift of the ISUS response with time or depth was apparent.

1. Float Mission

Float 48 was the primary float in the North Atlantic Bloom (NAB) experiment. It was deployed on April 4, 2008 (yearday 95), stopped sampling on May 25 (yearday 146), and was recovered on June 3 (yearday 155). The float mission included three general operation modes, including vertical profiling to ~250 meters depth, auto-ballasting (settle mode), and mixed layer Lagrangian drift (Fig. 1). During drift mode, the float adjusts its buoyancy to match the density of the surrounding water in the mixed layer and freely drifts with the surrounding currents.

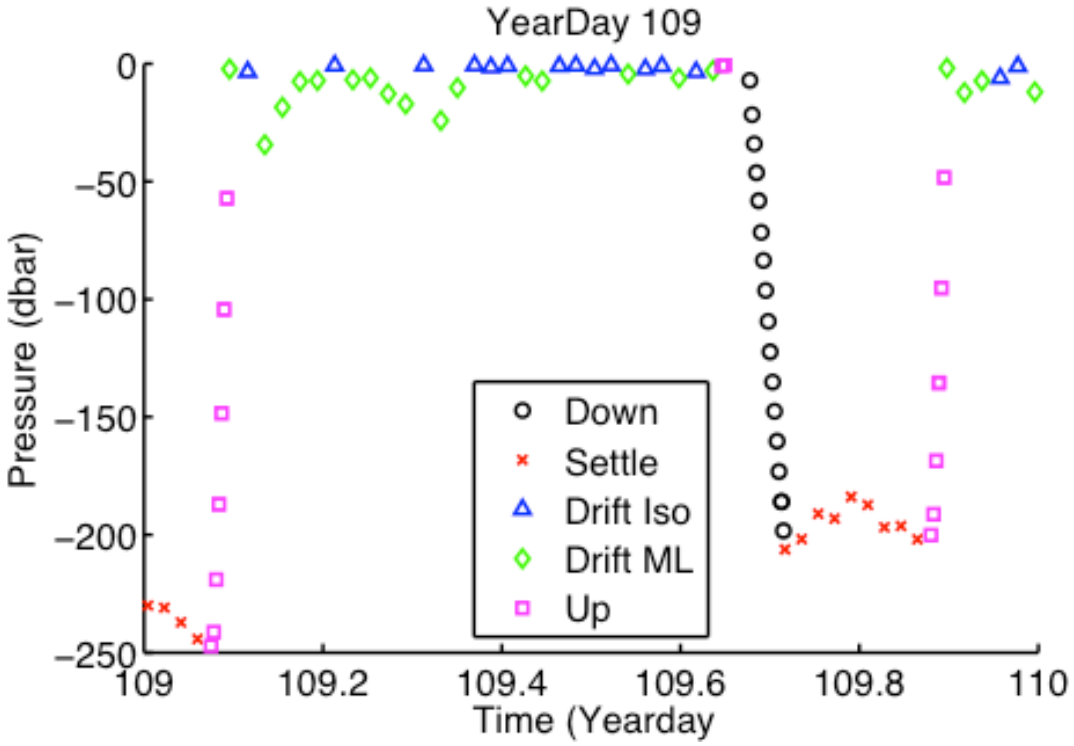


Fig. 1. Example of daily float operation modes including downcast, settle, drift, and upcast movements of float for 2008 yearday 109.

The float was equipped with two Seabird SBE43 conductivity-temperature (CT) sensors located on the top and bottom endcaps, separated vertically by ~1.4 meters. The bottom sensor was also equipped with an in-line an SBE43 oxygen (O_2) sensor. The pumped outflow of the bottom CT-O_2 sensor was directed to an in-situ ultraviolet spectrophotometer (ISUS), which was strapped to the side of the float (Fig. 2). The sensor cap served to ensure both the integrity of the sample stream as measured by all sensors and that the ISUS probe did not experience biofouling during the experiment. The CT sensors were pumped for 2 seconds at 'slow' speed, approximately every 50 seconds (0.02 Hz), to measure temperature and salinity. The bottom sensor was pumped for each oxygen measurement for 17 seconds at 'slow' speed and 15 seconds at 'fast' speed at sampling intervals of ~50 seconds during profiles and 400 seconds during settle and drift modes.

Data streams were synchronized via interpolation of the higher-resolution CT- O_2 records onto the coarser ISUS data using internal timestamps recorded by each instrument. Comparisons between the top and bottom salinity sensors revealed uncertainties with each sensor due to air intake, plankton ingestion, drift, etc. Therefore, the final CT data merged

with the ISUS output represents the most accurate measurement available from either the top or bottom sensors. Details regarding the calibrations of the CT and O_2 sensors can be found in separate calibration reports (http://iop.apl.washington.edu/wiki/index.php/NAB_North_Atlantic_Bloom_collab). The relatively small vertical separation (~1.4 meters) between the two CT sensors, generally weak stratification in the upper layers of the water column during the mission, and reduced sampling rate of the ISUS limits potential bias in merging the two data streams in this manner. Furthermore, the lack of any obvious contamination or errors in both the ISUS and O_2 data indicates the uncertainties observed in the bottom CT sensor did not carry over to the sensors downstream.

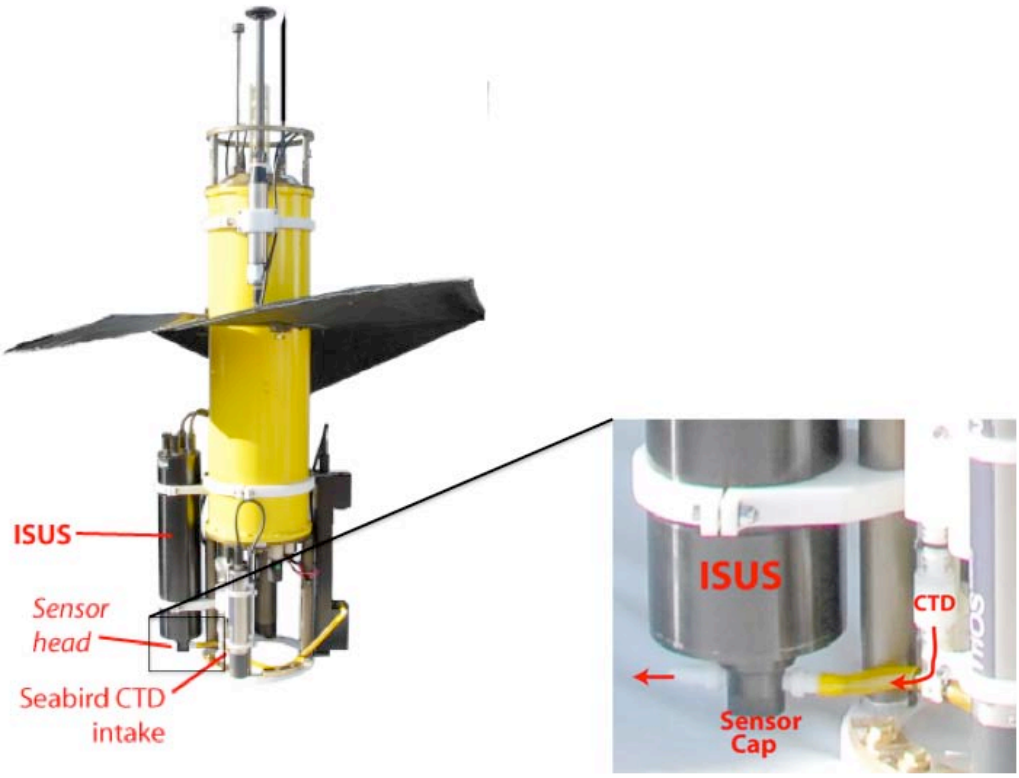


Fig. 2. Diagram of NAB Float 48 showing position of ISUS and Seabird instruments with inset showing close-up of ISUS plumbing.

2. General ISUS Operation & Background

Nitrate concentrations were estimated *in-situ* by the ISUS instrument via measurement of the ultraviolet (217-240nm) absorbance of seawater across the probe's 1 cm path length at sampling rate of ~0.005 Hz (once every 200 seconds). Although the ISUS can be operated at frequencies up to ~1 Hz, this reduced sampling rate was chosen to enhance battery life. Each time the instrument was powered ON, two absorbance readings were recorded, preceded by a dark absorbance reading (shutter closed to light source) to track any drift in instrument background. In essence, every 200 seconds, the ISUS made a duplicate sampling of the surrounding water column ultraviolet absorbance.

Numerous inorganic ions absorb ultraviolet radiation. The ions responsible for the largest absorbance include bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), and bisulfide (HS^-). In most oceanic environments (including the North Atlantic), concentrations of nitrite and sulfide are extremely low, such that absorbance by these constituents can be ignored. Therefore, attention can be restricted to bromide and nitrate as the predominant, inorganic species responsible for ultraviolet absorption. However, color dissolved organic matter (CDOM) also absorbs in the ultraviolet range. Again, in many open ocean environments, the concentration of colored dissolved organic matter is low and thus its absorption should be minimal.

The ultraviolet absorbance (A) at each wavelength (λ) is computed using the equation:

$$A_\lambda = -\log_{10} \{(I_\lambda - I_D) / (I_{\lambda,0} - I_D)\}$$

where I_λ = raw detector intensity counts at wavelength λ
I_D = detector intensity for dark readings (shutter closed)
$I_{\lambda,0}$ = detector intensity for deionized water

Once the absorption spectrum is computed, concentrations of bromide and nitrate can be estimated using the equation:

$$A_\lambda = b (\Sigma_j \varepsilon_{\lambda,j} C_j + e + f\lambda)$$

where b = path length (1 cm)

$\varepsilon_{\lambda,j}$ = molar absorptivity for species J at wavelength λ
C_j = concentration of species J

The remaining terms (e, f) constitute adjustable parameters used to estimate of the baseline absorption by dissolved organic matter. Concentrations are calculated by fitting the above equation to the observed absorbance spectrum using a least-squares minimization procedure (Sakamoto et al., 2009).

Raw data files (.DAT) were logged for each year day sampled and stored internally. These files were extracted and converted to CSV format by Eric Rehm using the SatCon program (available from Satlantic). Note this conversion process does not alter the raw spectral counts in any way but does not export dark readings or auxiliary channels. Separate CSV files containing only the dark readings were also created using SatCon. The converted (CSV) data files were combined and sorted by time (decimal yearday), such that the final data file resembled the original sampling pattern on the ISUS (i.e., dark, light, light).

This final data file was augmented with in-situ temperature and salinity measured by the CT sensor on-board the float. The resulting data file was then processed using a program (ISUSDataProcessor) developed by Ken Johnson (MBARI), which incorporates algorithms correcting the spectral data collected by the ISUS for temperature effects. The ultraviolet absorption by nitrate is not temperature-dependent (Johnson and Coletti, 2002). However, the absorption spectrum of bromide is sensitive to variations in temperature as it results from an interaction with the solvent volume (Sakamoto et al., 2009). Sakamoto et al. (2009) conducted laboratory calibration experiments varying the temperature and salinity of standards and produced an algorithm correcting for this effect. Consequently, optimal results can be achieved if the temperature and salinity of the sampled seawater is known.

The original processing of the data collected by the NAB float using ISUSDataProcessor resulted in unusually low nitrate concentrations ($\leq$ 6μM). Therefore, the ISUS instrument was re-calibrated at the Applied Physics Laboratory via an update of the reference spectrum. Details of this re-calibration and comparison of the resultant nitrate concentrations with those calculated on-board the ISUS (Satlantic algorithms) and the

ISUSDataProcessor results incorporating the original calibration are given in Appendix A.

3. Bottle Calibration

Calibration of the ISUS data was achieved via intercomparison with seven bottle casts taken during the *Knorr* cruise in close proximity with Float 48. Only float data collected within 0.1 decimal days (2.4 hours) and 2 kilometers of corresponding bottle casts were included in the calibration (Fig. 3). Two additional casts (9 and 47) were sufficiently close in time and space to include in the calibration; however, large disagreements between the float and bottle nitrate concentrations were evident. These data were therefore excluded from the calibration. We cannot address the reasoning behind these differences at this time, but plan to investigate this phenomenon further.

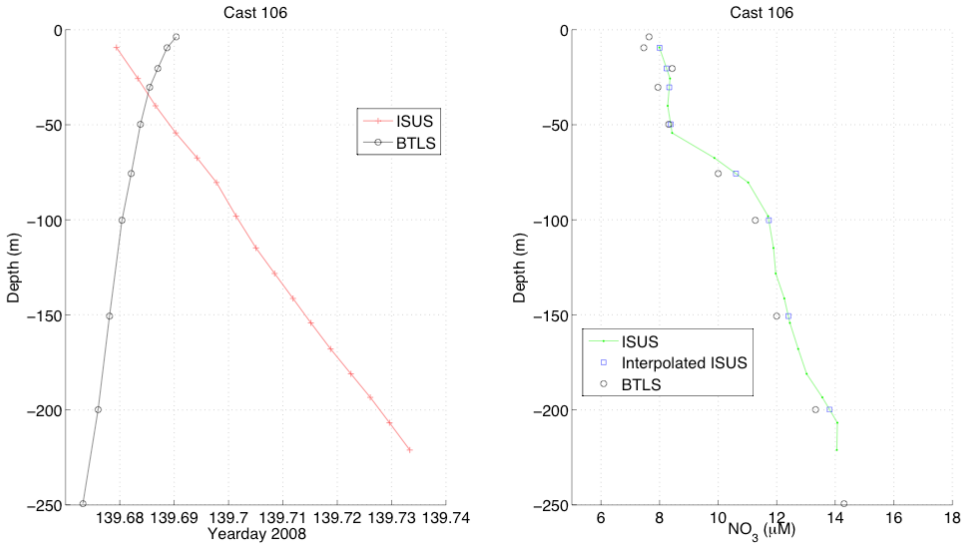


Fig. 3. Sample ISUS calibration cast. Left panel: Time of sampling (in decimal yeardays) versus depth for bottle samples (black circles) and corresponding ISUS measurements (red pluses). Right panel: Vertical profiles of nitrate concentration derived from calibration ISUS data and bottle measurements.

Float data satisfying these spatial and temporal requirements consisted of duplicate nitrate measurements at sampling depths ranging from 0.5 to 230 meters. These duplicates yield some measure of the precision of the ISUS instrument. Histograms of the standard deviation of all duplicate

measurements, calculated using nitrate concentrations taken from the ISUS instrument (utilizing algorithms supplied by Satlantic) versus those derived from ISUSDataProcessor indicate a significant improvement in precision using the latter algorithms to process the data collected by ISUS (Fig. 4). An average of these standard deviations (n = 917) yields 0.4μM for Satantic-processed nitrate versus 0.1μM for those estimated using ISUSDataProcessor.

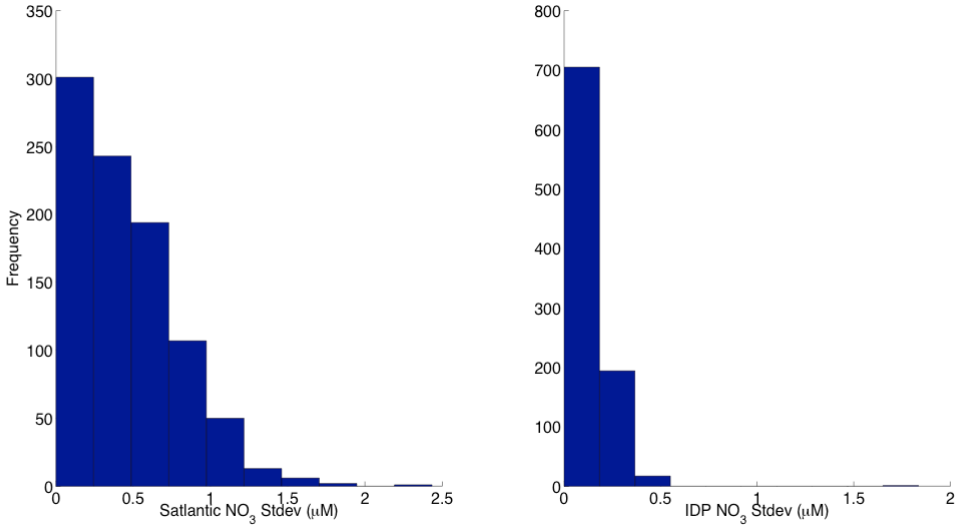


Fig 4. Histograms of the standard deviation of duplicate nitrate measurements where nitrate concentrations were calculated using algorithms supplied by Satlantic (left) or ISUSDataProcessor (right).

The duplicate measurements collected over the period of the *Knorr* cruise were averaged and the resulting depth profile linearly interpolated to match the depths at which the bottle samples were collected. Depth profiles of bottle nitrate concentrations used in the calibration as well as the corresponding, calibrated ISUS measurements are shown in Appendix B. A simple linear regression (Bottle NO_3 = ISUS NO_3 x 1.1536 + 2.6227, Fig 5) between the interpolated, ISUS-derived nitrate concentrations and those measured from the bottle samples comprised the calibration equation for correcting the ISUS data. After correcting ISUS data using this calibration, differences between ISUS and bottle concentrations averaged ($\pm 1\sigma$) 0.0 ± 0.6 μM (Fig. 6).

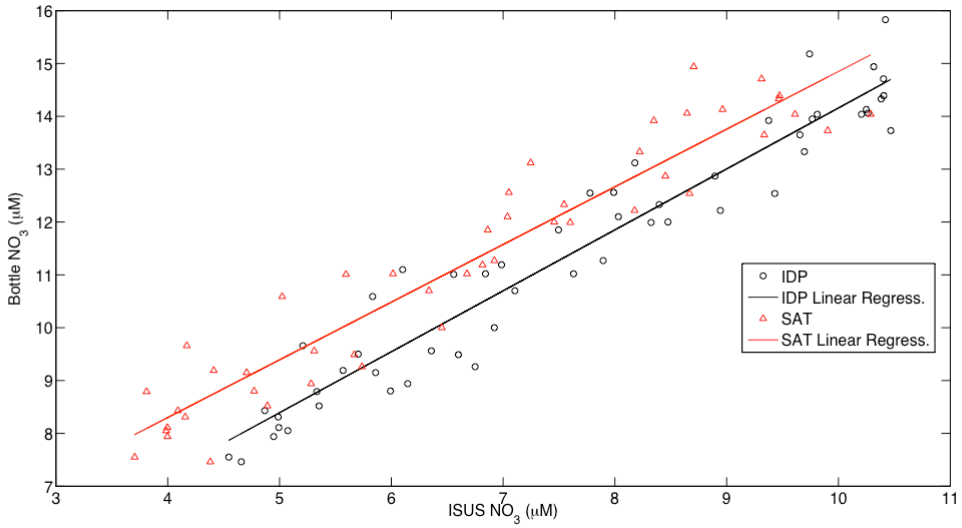


Fig. 5. Simple linear regression of ISUS-derived nitrate concentrations computed using ISUSDataProcessor (IDP) and Satlantic's algorithms (SAT) versus bottle nitrate concentrations from the R.V. Knorr process cruise. Solid lines represent IDP (black) and SAT (red) least-squares linear regressions.

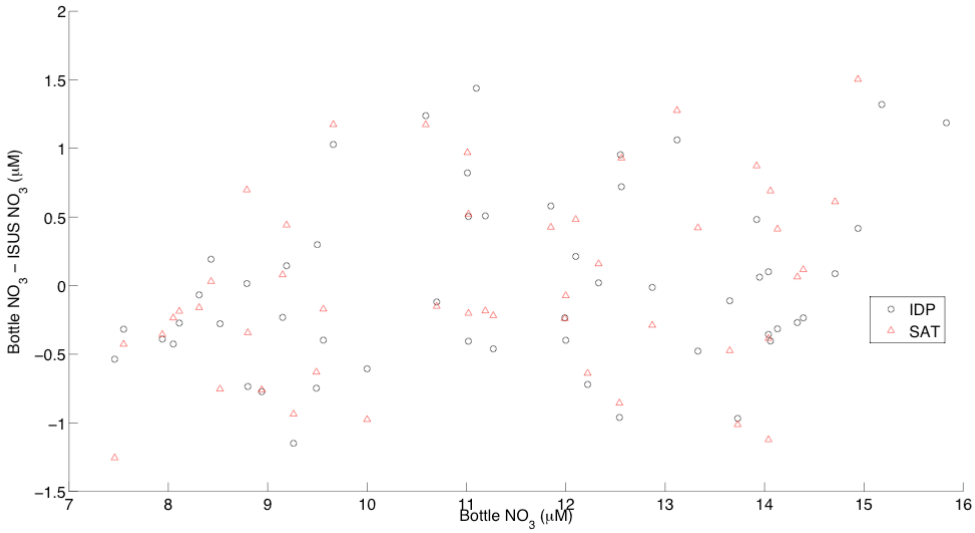


Fig. 6. Differences in nitrate concentrations between bottle measurements and calibrated ISUS measurements for calibration casts.

4. Summary

Re-calibration of the ISUS instrument and processing of the spectrophotometric data collected during the NAB 2008 float deployment resulted in significant improvements in the precision (~0.1μM) of nitrate concentrations measured with no substantial change in accuracy. The improved precision likely results from the incorporation of *in-situ* temperature and salinity data to estimate bromide absorption. A simple linear regression (Bottle NO_3 = ISUS NO_3 x 1.1536 + 2.6227) between the interpolated, ISUS-derived nitrate concentrations and those measured from the bottle samples comprised the calibration equation for correcting the ISUS data. Accuracy of the ISUS-derived nitrate concentrations, limited by comparing *in-situ* float data with bottle measurements collected up to 2km and 2.4 hours apart, was estimated at an average of 0.6μM with maximum uncertainties yielding more conservative estimates (~1μM).

New variables:

IDP_NO3 = nitrate (μmol L^{-1}) computed using ISUSDataProcessor
IDP_NO3_corr = IDP_NO3 corrected using Knorr bottle calibration
Ref_Channel = average shutter dark readings over $217 \leq \lambda \leq 240$ nm
RefStdDev = standard deviation of Ref_Channel
BL_Int = intercept of linear baseline (adjustable parameter)*
BL_Lin_Slope = slope of linear baseline (adjustable parameter)*
fit_error = RMS deviations of linear, least-squares optimization

*Note: A simple linear function of wavelength ($\lambda < 245$ nm) is used to approximate a background spectrum of absorption due to dissolved organic matter (Sakamoto et al., 2009).

5. References

Johnson, K.S., L.J. Coletti (2002), In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean, *DSR I 49*, 1291-1305.

Sakamoto, C.M., K.S Johnson, L.J. Coletti (2009), Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer, *Limn. & Ocean. Methods 7*, 132-143.

Appendix A. Comparison of Satlantic and ISUSDataProcessor Algorithms

The ISUSData Processor (IDP) takes advantange of *in-situ* measurement of temperature and salinity supplied by the user. The post-processing of the data using IDP requires that the calibration files provided by Satlantic be altered somewhat. The approximate calibration temperature must be known to achieve this step. This calibration temperature was confirmed, by two independent sources, to be ~20°C. Furthermore, the data files themselves must be formatted such that the program can read the raw spectra (counts at each wavelength), differentiate between light and dark readings, and utilize in-situ CTD temperature and salinity data to estimate (and subtract) the total ultraviolet absorption due to the bromide ion. These steps are carried out using a simple MATLAB code (Appendix C).

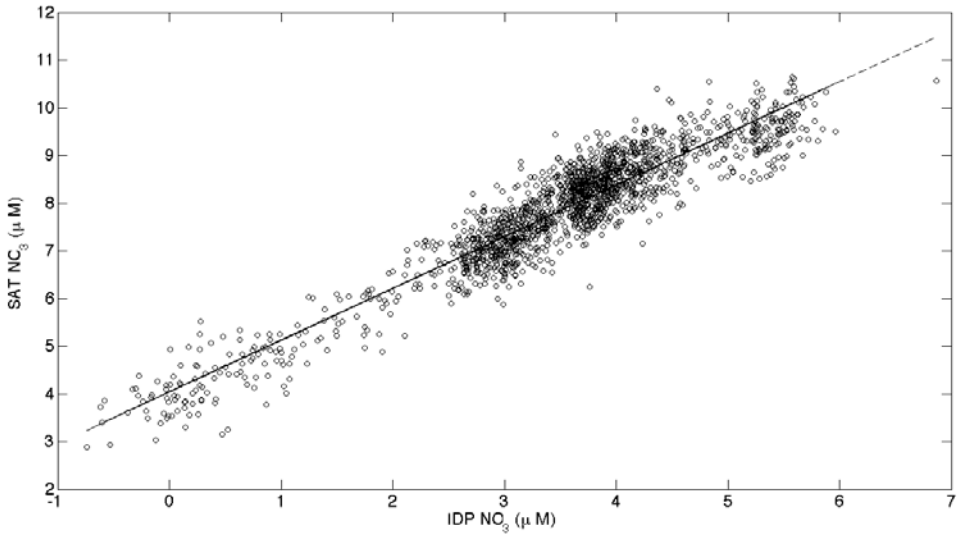


Fig 7. Uncalibrated ISUS nitrate concentrations derived via ISUSDataProcessor (IDP) versus Satlantic (SAT) algorithms, both of which utilized the original calibration (ISUS128d.CAL). The solid black line shows the linear regression: SAT NO_3 = (1.0850 x IDP NO_3) + 4.0434.

A comparison (Fig. 7) of the nitrate concentrations calculated using Satlantic's (SAT) processing versus that obtained from ISUSDataProcessor (IDP), both of which incorporate the original (old) calibration shows much lower concentrations ($\leq$ 6μM) derived from the IDP processing. However, nitrate concentrations derived from SAT algorithms are closer to those measured from bottle samples collected during *Knorr* process cruise (see Fig. 5). These results are contrary to what would be expected given the direct inputs of temperature and salinity data into the IDP algorithms. If the IDP-derived nitrate concentrations are supposed to be more accurate than those obtained using SAT algorithms, what is the origin of the discrepancy?

The most plausible explanation is a problem with the original calibration of the ISUS instrument. A simple linear regression of the IDP and SAT-processed nitrate concentrations shown in Fig. 7 indicates a slope insignificantly different from unity and a positive intercept of ~4μM. The slope $\approx$ 1 suggests the response of the ISUS in terms of gain was not adversely affected during the mission and likely processed at least somewhat similarly by the two different algorithms. However, the positive intercept suggests a difference in the baseline. Assuming the data output by the IDP is correct, the resulting low nitrate concentrations might be explained by an erroneously large baseline, which could be produced by a bad calibration.

Calibration of the ISUS instrument is completed (by Satlantic) via the estimation of molar absorptivities (or extinction coefficients) of sea salt (i.e., bromide) and nitrate by measuring absorption over a range of wavelengths for various standards. The reference spectrum, or the spectral counts measured by the instrument when immersed in deionized water (NO_3^- = 0, salinity = 0), is also measured. A reference spectrum could be incorrectly defined if the procedure was completed using contaminated water (by nitrate and/or salt). An obvious question arises from this possibility: why wasn't the IDP-processed nitrate data affected by this calibration error, since IDP requires the calibration file as an input? The answer may lie in the different means by which the bromide absorption is estimated.

Satlantic algorithms assume a linear correction to the salinity extinction coefficients using an internal temperature reading. In contrast, the IDP algorithms utilize in-situ temperature and salinity data inserted by the user. The bromide absorption is then estimated using the provided temperature and salinity data, together with laboratory calibrations (Sakamoto et al., 2009) and the baseline-corrected absorbances. The

bromide absorption is subtracted from the measured absorption and the nitrate concentration calculated via a least-squares non-linear fit to the resultant spectrum. This series of calculations essentially uses baseline approximations twice and is therefore prone to higher baseline error if the calibrations are incorrect.

A contamination problem during the original calibration would result in a more sensitive (higher) reference spectrum, which when subtracted from the raw counts to estimate absorbance, would result in lower overall nitrate concentrations, which is what we observed from a comparison of the IDP and SAT nitrate concentrations (Fig. 7). Fortunately, all that results is a higher baseline, which is simple to correct.

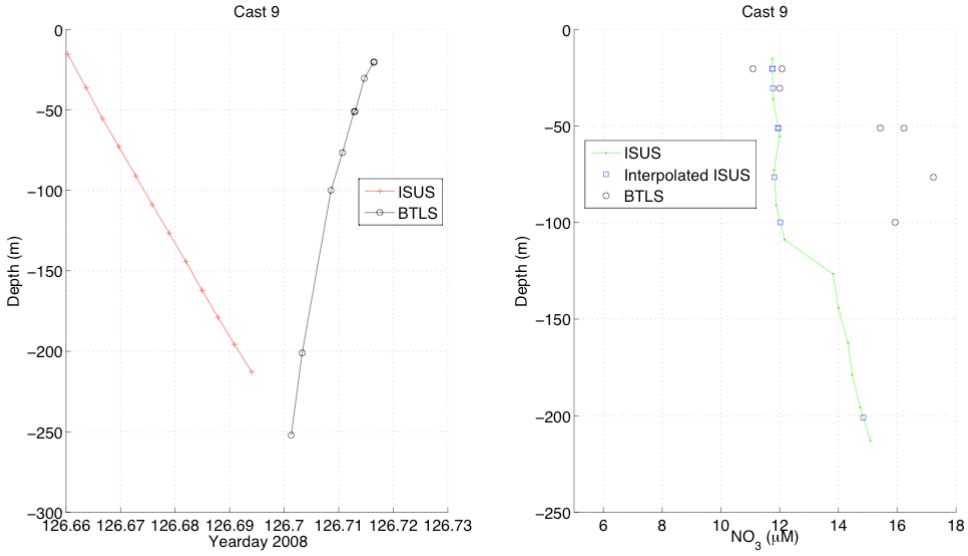
The ISUS128 instrument was re-calibrated at the Applied Physics Laboratory by means of resetting the reference spectrum. This procedure is relatively simple and details can be found in the Operation Manual, available on Satlantic's website (www.satlantic.com). Briefly, after a warm-up period of approximately 10 minutes, the ISUS was operated in continuous mode (sampling rate ~1 Hz and a dark absorbance reading collected once every ten samples) while the probe was submerged in Milli-Q water for a period of ~20 minutes. The resultant data file and original calibration files were run through ISUSCal, a software program also available from Satlantic, to create a new calibration file. The new calibration file was used to post-process the raw ISUS data using the ISUSDataProcessor program and the results reported in the main portion of this calibration report.

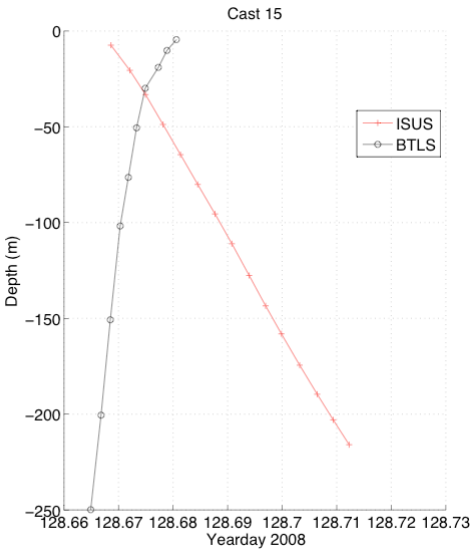
The nitrate concentrations determined using the new calibration file more closely resembled those determined from bottle measurements during the *Knorr* process cruise. Although we cannot be sure of the apparent error in the original ISUS calibration as the instrument was not re-calibrated immediately after recovery, the close correspondence between re-calibrated ISUS nitrate concentrations and bottle measurements are, at least, encouraging. It is also important to note that the fit errors (RMS deviations) reported in the ISUSDataProcessor output average ~0.003 whereas the RMS deviations associated with the Satlantic-derived nitrate concentrations were significantly lower ($1\text{-}2 \times 10^{-6}$). Although some error might have been introduced during the re-calibration of the instrument (or as a consequence of the long shelf time the instrument experienced between calibrations), the resulting fit errors do not render the ISUS data unusable. In fact, fit errors of this magnitude are more likely for longer mooring operations, especially

where the ISUS operates for such short periods of time, in contrast with collecting continuous profiles (Ken Johnson, personal communication).

Appendix B. Inter-comparison casts from *Knorr* & *Bjarni* cruises

Knorr Casts

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ISUS
BTLS
Depth (m)
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−100
−150
−200
−250
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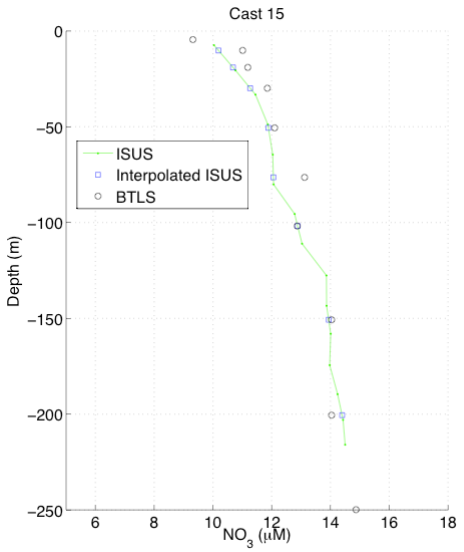
Yearday 2008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ISUS
Interpolated ISUS
BTLS
Depth (m)
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−50
−100
−150
−200
−250
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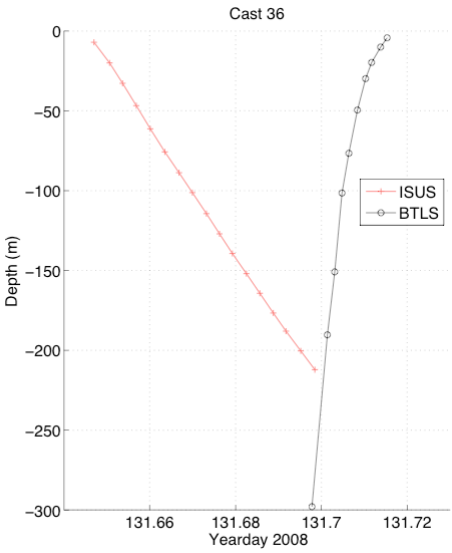
NO3 (μM)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BTLS
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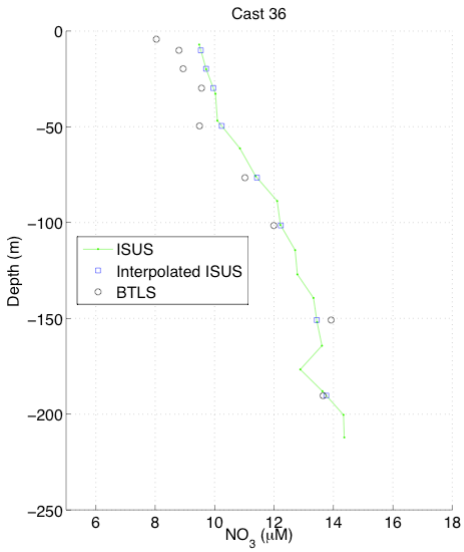
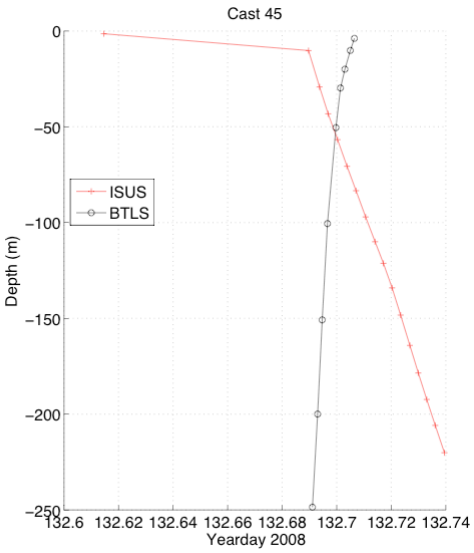
−150
−200
−250
−300
131.66 131.68 131.7 131.72
Yearday 2008


Cast 36
ISUS
Interpolated ISUS
BTLS
Depth (m)
0
−50
−100
−150
−200
−250
6 8 10 12 14 16 18
NO3 (μM)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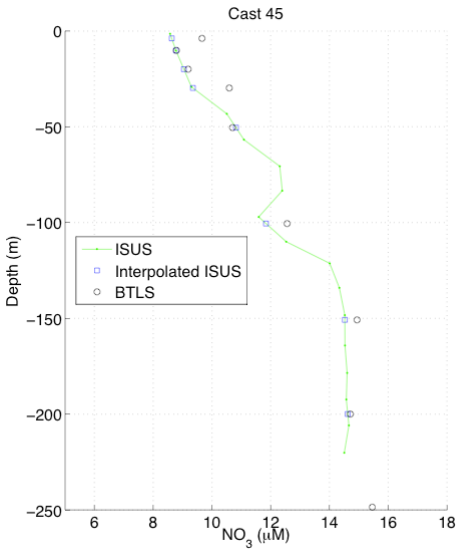
ISUS
BTLS
Depth (m)
Yearday 2008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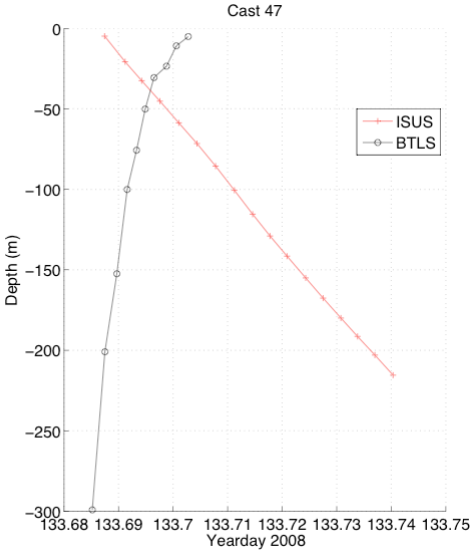
ISUS
Interpolated ISUS
BTLS
Depth (m)
NO3 (μM)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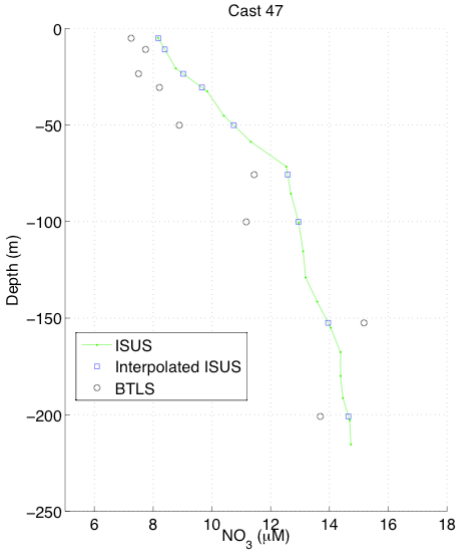
ISUS
BTLS
Depth (m)
Yearday 2008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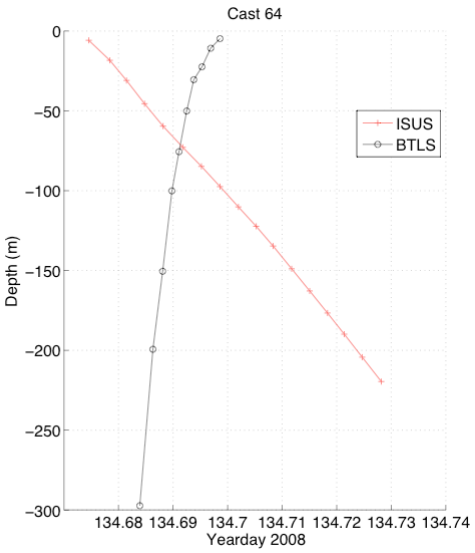
ISUS
Interpolated ISUS
BTLS
Depth (m)
NO3 (μM)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ISUS
BTLS
Depth (m)
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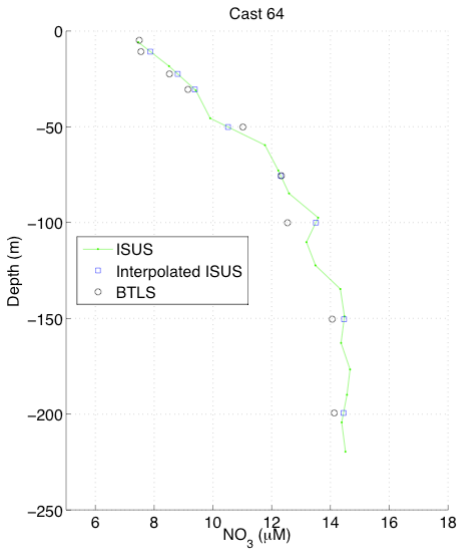
−250
−300
134.68 134.69 134.7 134.71 134.72 134.73 134.74
Yearday 2008


Cast 64
ISUS
Interpolated ISUS
BTLS
Depth (m)
0
−50
−100
−150
−200
−250
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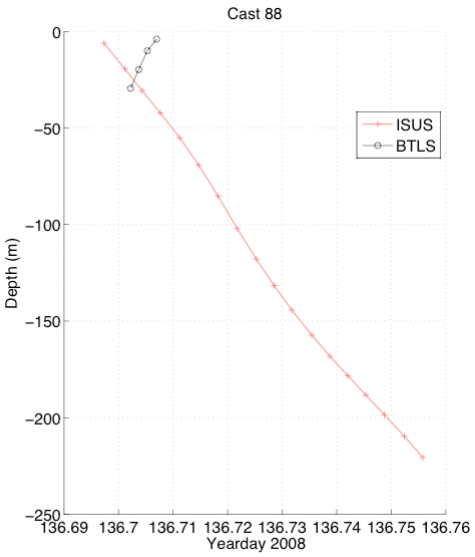
NO3 (μM)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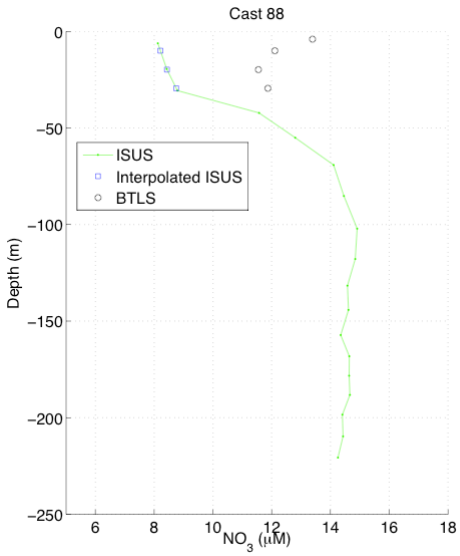
ISUS
BTLS
Depth (m)
0
−50
−100
−150
−200
−250
136.69 136.7 136.71 136.72 136.73 136.74 136.75 136.76
Yearday 2008


Cast 88
ISUS
Interpolated ISUS
BTLS
Depth (m)
0
−50
−100
−150
−200
−250
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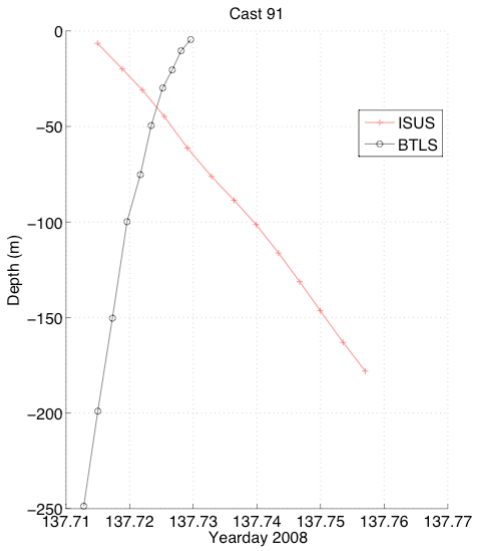
NO3 (μM)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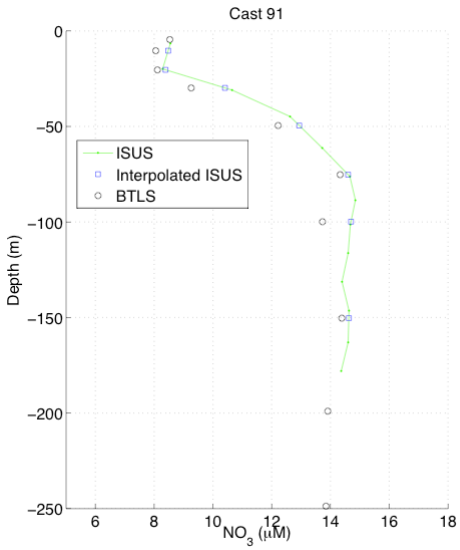
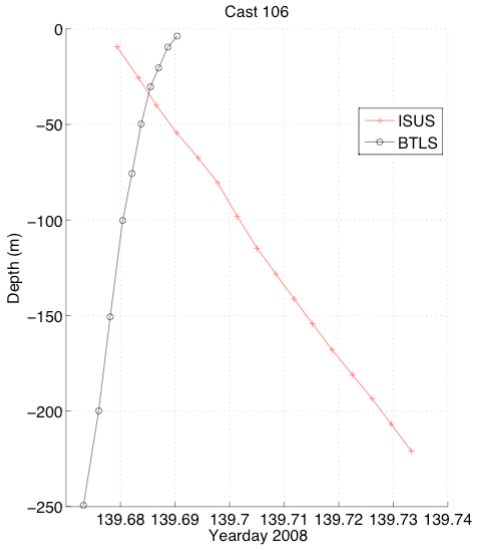
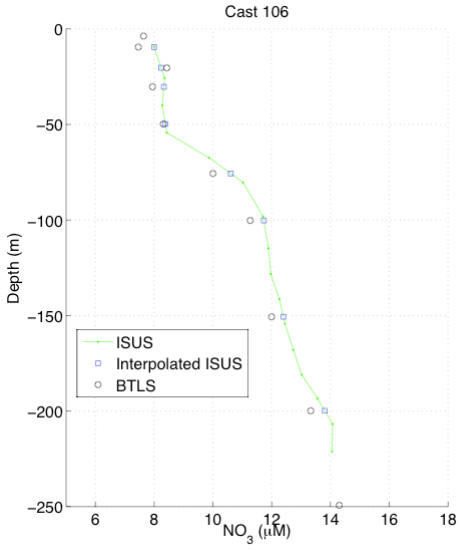
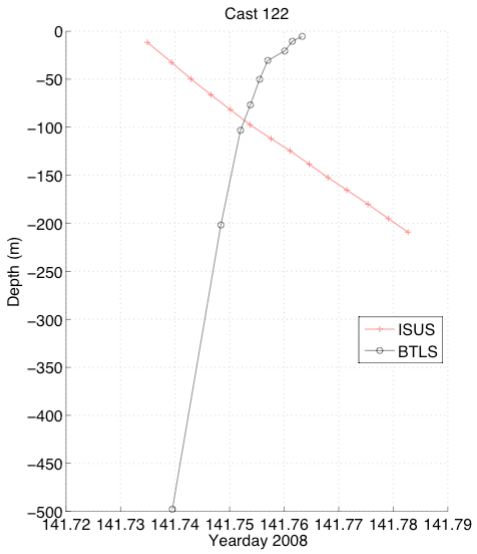
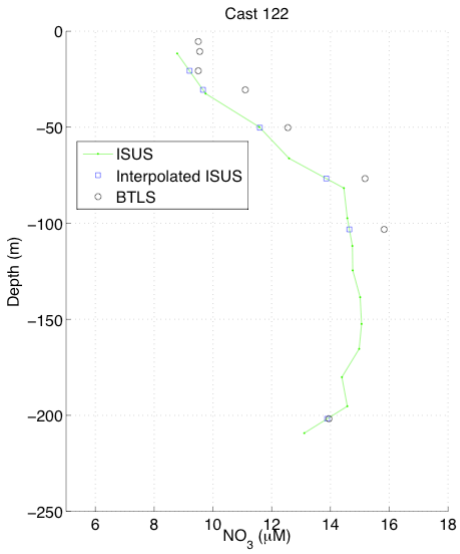
ISUS
BTLS
Depth (m)
Yearday 2008


Cast 91
ISUS
Interpolated ISUS
BTLS
Depth (m)
NO3 (μM)

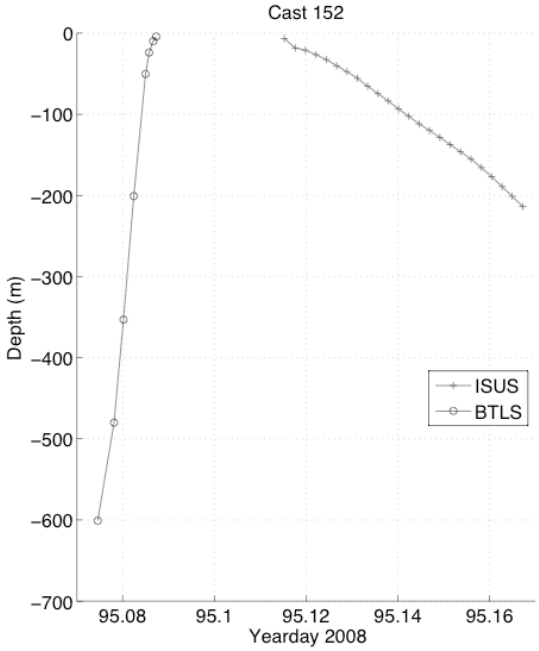

Cast 106
ISUS
BTLS
Depth (m)
Yearday 2008

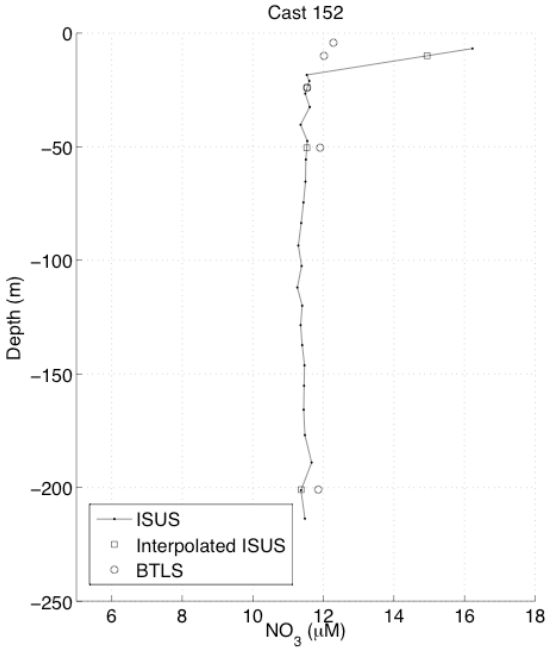

Cast 106
ISUS
Interpolated ISUS
BTLS
Depth (m)
NO3 (μM)

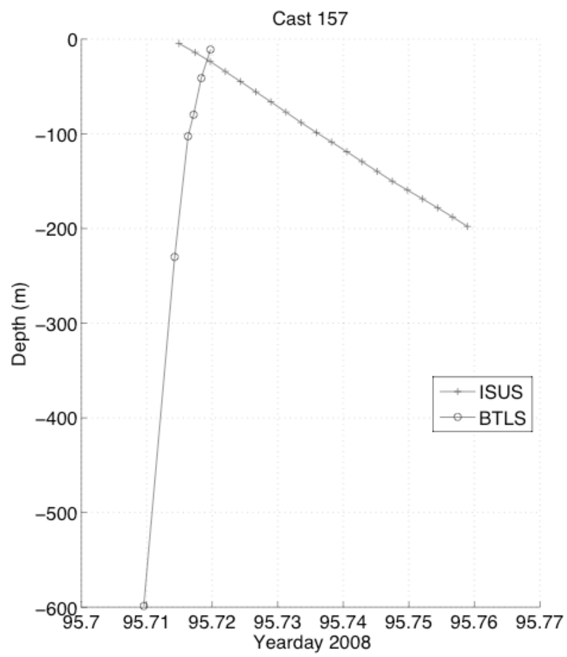


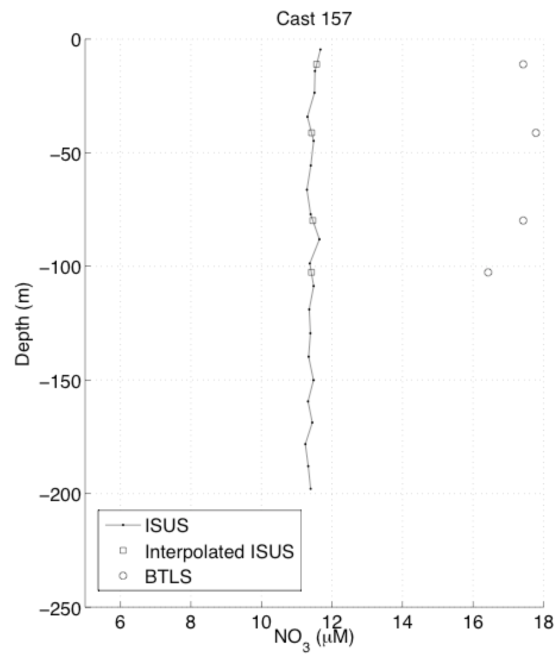


Bjarni Casts









Appendix C. MATLAB Codes

```
% BuildNAB_dat_file.m created by M.B. Alkire on 4/23/10
% This routine loads LIGHT & DARK frames (csv files) output
by SatCon (data
% provided by Eric Rehm), separately and combines them,
along with
% temperature and salinity data associated with the LIGHT
frame data (data
% provided by Eric Rehm).  The code then copies temperature
and salinity
% data from LIGHT frames to associated dark frames after
sorting all data
% by time.  The combined data file is then written into a
separate .DAT
% file (csv format) with a lead column identifying the
frame as "L" = LIGHT
% or "D" = DARK - which is necessary for input into
ISUSDataProcessor
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%

clear all; close all; clc
```

```
% Load data files:
for d = 95:146              % BEGIN MAIN LOOP

    % Load LIGHT FRAME data:
    cd('/Users/malkire/Desktop/isus-nab08-float48/isus-
nab08-float48/isus.processed')
    Filename_LIGHT = ['SCH08',num2str(d,'%03i'),'-
ISUS0128NLF.csv'];
    data = dlmread(Filename_LIGHT,',',1,0);

    % Add identifier (L or D) column of 1's:
    L = ones(size(data,1),1);
    data = [L,data];


    % Load DARK FRAME data:
    cd('/Users/malkire/Desktop/isus-nab08-float48/isus-
nab08-float48/isus.processed.dark')
    Filename_DARK = ['SCH08',num2str(d,'%03i'),'-
ISUS0128NDF.csv'];
    data2 = dlmread(Filename_DARK,',',1,0);

    % Add identifier (L or D) column of 0's:
    D = zeros(size(data2,1),1);
    data2 = [D,data2];

    % Store data into LIGHT & DARK compile matrices:
    if d == 95

        MATRIX_L = data;
        MATRIX_D = data2;
    else MATRIX_L = [MATRIX_L; data];
        MATRIX_D = [MATRIX_D; data2];
    end

    % Clear out workspace variables:
    clear Filename_LIGHT Filename_DARK data data2 L D

end             % END MAIN LOOP
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Load pre-determined temp & salt matches to LIGHT FRAMES:
cd('/Apps/MATLAB/work/NAB 2008/Float 48')
load('Bio48-2010-04-29-v7-sensor.mat')
clear Full TS arc dc floatID licor outfile QL acc cstar
flntu optode seabird
```

```
% Cut off the very end of the data (no T,S, or P -
determined manually):
MATRIX_L(4858:4865,:) = [];
isus.S(4858:4865) = [];
isus.T(4858:4865) = [];
isus.yd(4858:4865) = [];

% Locate NaN's in temp:
i = find(isnan(isus.T) == 1);

% Deal with salinity NaN's individually (only two of them):
isus.S(1:2) = isus.S(3);

% Define needed variables:
T = isus.T; T(i) = [];
t = isus.yd; t(i) = [];


% Use interpolation to replace temp = NaN:
TI = interp1(t,T,isus.yd,'linear');
isus.T(i) = TI(i);

% Replace columns 7 & 8 in LIGHT frame ISUS data matrix
with T & S:
MATRIX_L(:,3) = isus.yd;
MATRIX_L(:,7) = isus.T;
MATRIX_L(:,8) = isus.S;
clear isus T t i
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Format time field to match that of LIGHT frames:
MATRIX_D(:,3) = (MATRIX_D(:,2)-2008000) +
(MATRIX_D(:,3)/24);

% For the DARK files, replace columns with zeros:
MATRIX_D(:,7) = 0;
MATRIX_D(:,8) = 0;

% Combine LIGHT & DARK matrices into a single data matrix:
MATRIXLD = [MATRIX_L; MATRIX_D];

% Sort using time:
[Y, IND] = sort(MATRIXLD(:,3));

for k = 1:size(MATRIXLD,2)

    M2(:,k) = MATRIXLD(IND,k);
```

```
end
clear Y IND MATRIXLD

% Now that we have a data stream ordered according to time,
the DARK
% readings need salinity & temp.  To do this, salt & temp
values will
% simply be copied from the next, subseqent LIGHT value.
This method takes
% advantage of the fact the ISUS turned ON, took a dark
reading, followed,
% by 2 light readings, and then turned OFF.  This code
assumes salinity and
% temperature did not change significantly over that time
period.
DARK = find(M2(:,7) == 0);

for e = 1:length(DARK)-1

    M2(DARK(e),7:8) = M2(DARK(e)+1,7:8);
end
clear e

% A little manual clean-up with missed readings:
M2(7290:7293,7) = 9.4571;
M2(7290:7293,8) = 35.2315;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% I have identified L and D by 1's and 0's respectively, in
the first
% column on the "M2" matrix.  I need to replace these with
the appropriate
% letters during the write process:
% Set up data formats for printing data files (later):
format1 =
['%c,%7.0f,%8.6f,%5.2f,%5.2f,%8.6f,%7.4f,%7.4f,%5.2f,%6.0f,
%5.2f,%5.2f,%5.2f,%5.2f,%8.2f,%6.2f,%7.2f,%6.2f,'];
format2 = repmat('%4.0f,',1,255);
format3 = ['%4.0f'];
dataformat = [format1 format2 format3 '\n'];
clear format1 format2 format3

% Create a separate variable identifying frame as LIGHT or
DARK:
LD = repmat('L',length(M2),1);
LD(DARK) = 'D';
clear DARK
```

```
% Remove first column from M2 (original L/D identifier):
M2(:,1) = [];
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%

% Write data files to new .DAT file:
M2 = M2'; % some odd convention necessary to output data!
LD = LD';

% Run loop to write .DAT file:
cd('/Users/malkire/Desktop/')
fid = fopen('NAB_ISUS128float.DAT','wt');
fprintf(fid,'\n'); % put a space at the beginning of the
file!
for i=1:length(LD)
    fprintf(fid,dataformat,LD(i),M2(:,i));
end
fclose(fid);
```

```
% ISUSCAL_new.m created by M.B. Alkire on 5/21/10
% This routine loads newly-calibrated ISUS nitrate
concentrations for
% comparison and inter-calibration with bottle measurements
obtained during
% the Knorr process cruise.  This m-file serves as an
updated version to
% the original NAB_BottleComparison.m created on 4/27/10
using older ISUS
% instrument calibrations.  Additional updates include the
use of time
% (rather than depth) to find duplicate measurements and
calculated
% averages and the order through which duplicate averaging,
interpolation,
% and bottle-to-ISUS matching take place.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%
clear all; close all; clc

% INPUTS:

% Define threshold values for isolating ISUS data in close
proximity
```

```
% to Knorr stations (in both time & space):
thresh = 2;  % km - most data for calibration within 1 km;
Cast 91 a bit farther 1.5-2.0 km
hr = 0.1;       % time

% Select Knorr casts closest to float:
Kcast = [15; 36; 45; 64; 91; 106; 122];
%Kcast = [9; 47; 88]; % problem casts reported by Eric
D'Asaro
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% LOAD ALL DATA & AVG ISUS DUPLICATES:
% Load Knorr bottle data:
cd('/Users/malkire/Desktop/Bottle Data/Knorr Process')
load('Knorr_bottle_data.mat')
clear data phosphate salt silica temp

% Load data:
cd('/Applications/MATLAB/work/NAB 2008/Float 48')
load('Bio48-2010-04-29-v7-sensor.mat')
clear Full QL TS acc arc cstar dc flntu floatID licor
optode outfile
clear outfileSensor seabird

% Load IDP-processed data:
cd('/Users/malkire/Desktop')
%data = dlmread('NAB_ISUS128float.CNC',',',4,0); % old CAL
files
data = dlmread('NAB_ISUS128float_NewCal.CNC',',',4,0); %
newest CAL file!!!
IDP_NO3 = data(:,7);
fit_error = data(:,12);
bad = find(fit_error > 0.004);
IDP_NO3(bad) = nan;
clear bad fit_error data

% I originally cut the last 8 measurements from the ISUS
data due to a lack
% of both temp & press (BuildNAB_dat_file.m).  Add NaN's to
ensure all
% vectors are the same size (these get cut off again
anyway):
IDP_NO3 = [IDP_NO3; nan; nan; nan; nan; nan; nan; nan;
nan];

% Get rid of upcasts & settle modes, as well as any ISUS
NaN's:
```

```
kill = find(isus.mode == 1 | isus.mode == 2 |
isnan(IDP_NO3) == 1);
%kill = find(isus.mode ~= 0 |isnan(IDP_NO3) == 1); %
restrict to downcasts!
isus.mode(kill) = [];
isus.z(kill) = [];
isus.yd(kill) = [];
IDP_NO3(kill) = [];
isus.lat(kill) = [];
isus.lon(kill) = [];
isus.nitrate0(kill) = [];

% Average ISUS duplicate readings:
n = 1;
for i = 2:2:length(isus.yd)

    dt = abs(isus.yd(i) - isus.yd(i-1));

    if dt < 0.001
        mode(n) = mean([isus.mode(i);isus.mode(i-1)]);
        Idepth(n) = mean([isus.z(i);isus.z(i-1)]);
        time(n) = mean([isus.yd(i);isus.yd(i-1)]);
        NO3(n) = mean([IDP_NO3(i);IDP_NO3(i-1)]);
        SAT(n) = mean([isus.nitrate0(i);isus.nitrate0(i-
1)]);
        Ilat(n) = mean([isus.lat(i);isus.lat(i-1)]);
        Ilon(n) = mean([isus.lon(i);isus.lon(i-1)]);


    else mode(n) = isus.mode(i);
         Idepth(n) = isus.z(i);
         time(n) = isus.yd(i);
         NO3(n) = IDP_NO3(i);
         SAT(n) = isus.nitrate0(i);
         Ilat(n) = isus.lat(i);
         Ilon(n) = isus.lon(i);

    end
    clear dt
    n = n+1;
end
clear n IDP_NO3 isus
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%

% LOCATE ISUS DATA MOST CLOSELY CORRESPONDING TO KNORR
BOTTLES:
```

```
for i = 1:length(Kcast)           % BEGIN MAIN LOOP
%i = 1; % Diagnostic

    % Identify bottle data of interest by cast:
    L = find(cast == Kcast(i));

    % Calculate the difference between ISUS and Knorr
sampling time:
    w = abs(time - mean(yd(L)));

    % Use CSIRO Seawater library to calculate distance (in
kilometers):
    cd('/Applications/MATLAB/work/seawater_ver3_2')
    for m = 1:length(Ilat)
    [dist(m),phase(m)] = sw_dist([lat(L(1));
Ilat(m)],[long(L(1)); Ilon(m)],'km');
    end
    clear phase

    % Find ISUS data corresponding to closest space & time
of the float to
    % the specified bottle casts based on thresholds
defined above:
    keep = find(dist <= thresh & w <= hr);

    % Interpolate ISUS data of interest onto depth grid:
    NIDP_linear = interp1(Idepth(keep), NO3(keep),
depth(L), 'linear');
    NIDP_nearest = interp1(Idepth(keep), NO3(keep),
depth(L), 'nearest');
    SAT_linear = interp1(Idepth(keep), SAT(keep), depth(L),
'linear');


    % Create a data matrix containing bottle NO3 data and
associated,
    % interpolated ISUS data (IDP- and Satlantic-
processed):
    if i == 1              % BEGIN IF STATEMENT

        CalMatrix = [yd(L), nitrate(L), NIDP_linear,
NIDP_nearest, SAT_linear];
    else CalMatrix = [CalMatrix; yd(L), nitrate(L),
NIDP_linear, NIDP_nearest, SAT_linear];
    end                    % END IF STATEMENT
```

```
    % Correct ISUS nitrate using existing/specified
calibrations:
    ISUScorr = (NO3(keep) * 1.1536) + 2.6227;
    ISUScorr_interp = (NIDP_linear * 1.1536) + 2.6227;
    %OldCal = (SAT(keep) * 1.2007) + 3.277;

    % Plot figures to compare with Eric's calibrations:
    figure(i); hold on
    subplot(1,2,2); hold on
    plot(ISUScorr,-Idepth(keep),'g.-')
    plot(ISUScorr_interp,-depth(L),'bs')
    %plot(OldCal,-Idepth(keep),'r.-')
    plot(nitrate(L),-depth(L),'ko')
    axis([5 18  -250 0])
    title(['Cast ',num2str(Kcast(i))])
    xlabel('NO_3 (\muM)')
    ylabel('Depth (m)')
    %legend('IDP','Interp. IDP','SAT','BTLS',0)
    legend('ISUS','Interpolated ISUS','BTLS',0)
    grid on

    subplot(1,2,1); hold on
    plot(time(keep),-Idepth(keep),'r+-')
    plot(yd(L),-depth(L),'ko-')
    title(['Cast ',num2str(Kcast(i))])
    xlabel('Yearday 2008')
    ylabel('Depth (m)')
    legend('ISUS','BTLS',0)
    grid on

    % Clear out variables:
    clear NIDP_linear NIDP_nearest j dist w keep L ISUScorr
    clear ISUScorr_interp OldCal SAT_linear


end                                 % END MAIN LOOP

% Remove NaN's from CalMatrix:
kill = find(isnan(CalMatrix(:,3)) == 1);
CalMatrix(kill,:) = [];
clear kill

--------------------------------------------------------------------------

% Bjarni Bottle Comparison.m created by M.B. Alkire on
```

```
5/24/10
% This routine loads in newly-calibrated ISUS-derived
nitrate data and
% locates the most comparable data in time & space to the
Bjarni deployment
% cruise.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%
clear all; close all; clc

% Define threshold values for isolating ISUS data in close
proximity
% to Knorr stations (in both time & space):
thresh = 2;  % space (kilometers)
hr = 0.1;       % time (decimal days)
Kcast = [152; 157; 159];

% Load bottle data:
cd('/Users/malkire/Desktop/Bottle Data/Bjarni Deployment')
load('B200804Bottle_V3.mat')
kill = find(bottle.NO3 == -999);
bottle.NO3(kill) = [];
bottle.SiO4(kill) = [];  %NOTE: Data were entered WRONG!!!!
: SiO4 = NO3 & vice versa
bottle.z(kill) = [];
bottle.lat(kill) = [];
bottle.lon(kill) = [];
bottle.yd(kill) = [];
bottle.cast(kill) = [];
clear units longnames kill

% Load ISUS data:
cd('/Applications/MATLAB/work/NAB 2008/Float 48')
load('Bio48-2010-04-29-v7-sensor.mat')
clear Full QL TS acc arc cstar dc flntu floatID licor
optode outfile
clear outfileSensor seabird

% Load IDP-processed data:
cd('/Users/malkire/Desktop')
%data = dlmread('NAB_ISUS128float.CNC',',',4,0); % old CAL
files
data = dlmread('NAB_ISUS128float_NewCal.CNC',',',4,0); %
newest CAL file!!!
IDP_NO3 = data(:,7);
fit_error = data(:,12);
bad = find(fit_error > 0.004);
```

```
IDP_NO3(bad) = nan;
clear bad fit_error data

% I originally cut the last 8 measurements from the ISUS
data due to a lack
% of both temp & press (BuildNAB_dat_file.m).  Add NaN's to
ensure all
% vectors are the same size (these get cut off again
anyway):
IDP_NO3 = [IDP_NO3; nan; nan; nan; nan; nan; nan; nan;
nan];

% Get rid of upcasts & settle modes, as well as any ISUS
NaN's:
kill = find(isus.mode == 1 | isus.mode == 2 |
isnan(IDP_NO3) == 1);
%kill = find(isus.mode ~= 0 |isnan(IDP_NO3) == 1); %
restrict to downcasts!
isus.mode(kill) = [];
isus.z(kill) = [];
isus.yd(kill) = [];
IDP_NO3(kill) = [];
isus.lat(kill) = [];
isus.lon(kill) = [];
isus.nitrate0(kill) = [];

% Average ISUS duplicate readings:
n = 1;
for i = 2:2:length(isus.yd)

    dt = abs(isus.yd(i) - isus.yd(i-1));

    if dt < 0.001
        mode(n) = mean([isus.mode(i);isus.mode(i-1)]);
        Idepth(n) = mean([isus.z(i);isus.z(i-1)]);
        time(n) = mean([isus.yd(i);isus.yd(i-1)]);
        NO3(n) = mean([IDP_NO3(i);IDP_NO3(i-1)]);
        SAT(n) = mean([isus.nitrate0(i);isus.nitrate0(i-
1)]);
        Ilat(n) = mean([isus.lat(i);isus.lat(i-1)]);
        Ilon(n) = mean([isus.lon(i);isus.lon(i-1)]);


    else mode(n) = isus.mode(i);
         Idepth(n) = isus.z(i);
         time(n) = isus.yd(i);
         NO3(n) = IDP_NO3(i);
```

```
        SAT(n) = isus.nitrate0(i);
        Ilat(n) = isus.lat(i);
        Ilon(n) = isus.lon(i);

    end
    clear dt
    n = n+1;
end
clear n IDP_NO3 isus
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%

for i = 1:length(Kcast)    % BEGIN MAIN LOOP
%i = 1; % Diagnostic

    % Identify bottle data of interest by cast:
    L = find(bottle.cast == Kcast(i));

    % Calculate the difference between ISUS and Knorr
latitude & sampling
    % time:
    w = abs(time - mean(bottle.yd(L)));
    cd('/Applications/MATLAB/work/seawater_ver3_2')
    for m = 1:length(Ilat)
    [dist(m),phase(m)] = sw_dist([bottle.lat(L(1));
Ilat(m)],[bottle.lon(L(1)); Ilon(m)],'km');
    end
    clear phase

    % Find ISUS data corresponding to closest space & time
of the float to
    % the specified bottle casts based on thresholds
defined above:
    keep = find(dist <= thresh & w <= hr);

    % Interpolate ISUS data of interest onto depth grid:
    NIDP_linear = interp1(Idepth(keep), NO3(keep),
bottle.z(L), 'linear');
    NIDP_nearest = interp1(Idepth(keep), NO3(keep),
bottle.z(L), 'nearest');
    SAT_linear = interp1(Idepth(keep), SAT(keep),
bottle.z(L), 'linear');


    % Create a data matrix containing bottle NO3 data and
associated,
    % interpolated ISUS data (IDP- and Satlantic-
```

```
processed):
    if i == 1              % BEGIN IF STATEMENT

        CalMatrix = [bottle.SiO4(L), NIDP_linear,
SAT_linear];
    else CalMatrix = [CalMatrix; bottle.SiO4(L),
NIDP_linear, SAT_linear];
    end                    % END IF STATEMENT

    % Correct ISUS nitrate using existing/specified
calibrations:
    ISUScorr = (NO3(keep) * 1.1536) + 2.6227;
    ISUScorr_interp = (NIDP_linear * 1.1536) + 2.6227;
    %OldCal = (SAT(keep) * 1.2007) + 3.277;

    % Plot figures to compare with Eric's calibrations:
    figure(i); hold on
    subplot(1,2,2); hold on
    plot(ISUScorr,-Idepth(keep),'g.-')
    plot(ISUScorr_interp,-bottle.z(L),'bs')
    %plot(OldCal,-Idepth(keep),'r.-')
    plot(bottle.SiO4(L),-bottle.z(L),'ko')
    axis([5 18  -250 0])
    title(['Cast ',num2str(Kcast(i))])
    xlabel('NO_3 (\muM)')
    ylabel('Depth (m)')
    %legend('IDP','Interp. IDP','SAT','BTLS',0)
    legend('ISUS','Interpolated ISUS','BTLS',0)
    grid on

    subplot(1,2,1); hold on
    plot(time(keep),-Idepth(keep),'r+-')
    plot(bottle.yd(L),-bottle.z(L),'ko-')
    title(['Cast ',num2str(Kcast(i))])
    xlabel('Yearday 2008')
    ylabel('Depth (m)')
    legend('ISUS','BTLS',0)
    grid on

    % Clear out variables:
    clear NIDP_linear NIDP_nearest j dist w keep L ISUScorr
    clear ISUScorr_interp OldCal SAT_linear


end                              % END MAIN LOOP

% Remove NaN's from CalMatrix:
```

```
kill = find(isnan(CalMatrix(:,3)) == 1);
CalMatrix(kill,:) = [];
clear kill
```