




Introduction to Biogeochemical Data Processing

Sea-Bird Scientific University Module 27




Overview



 **Introduction to Biogeochemical Data Processing**

This module covers the following:

- Oxygen sensors in profiling applications
 - Calibrations and Sensor Drift
 - Field Validations – techniques and best practices
 - Alignment and tau corrections
- Using Sea-Bird Software to process other Biogeochemical Data
 - Using factory calibrations to get scientific


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Dissolved Oxygen Calibration



Oxygen sensors: Calibration

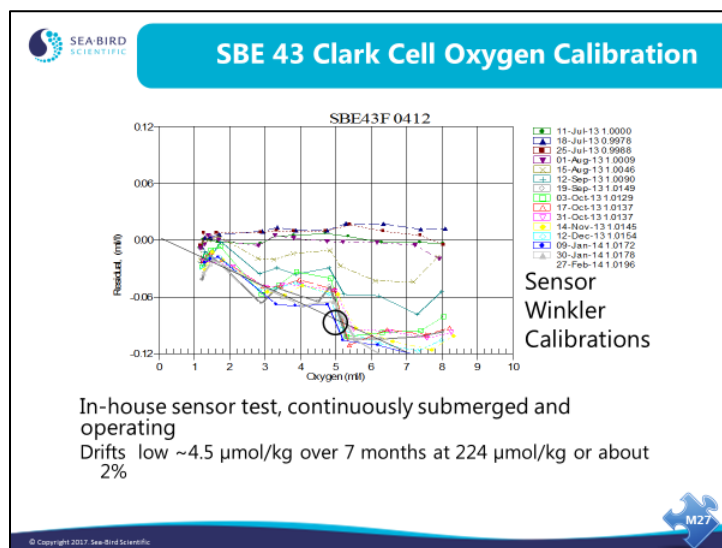
- SBE 43 Electrochemical Dissolved Oxygen
 - 18-point calibration
 - 3 oxygen, 6 temperatures
 - 5 coefficients
- SBE 63 Optical Dissolved Oxygen
 - 24-point calibration
 - 4 oxygen, 6 temperatures
 - 8 coefficients
- Laboratory Dissolved Oxygen Standard
 - Winkler Titrations
- Factory service/calibration interval depends on use and deployment environments
- Annual to biennial factory service advised
 - Longer intervals possible if Best Practices followed and oxygen validation capability exists in your facility



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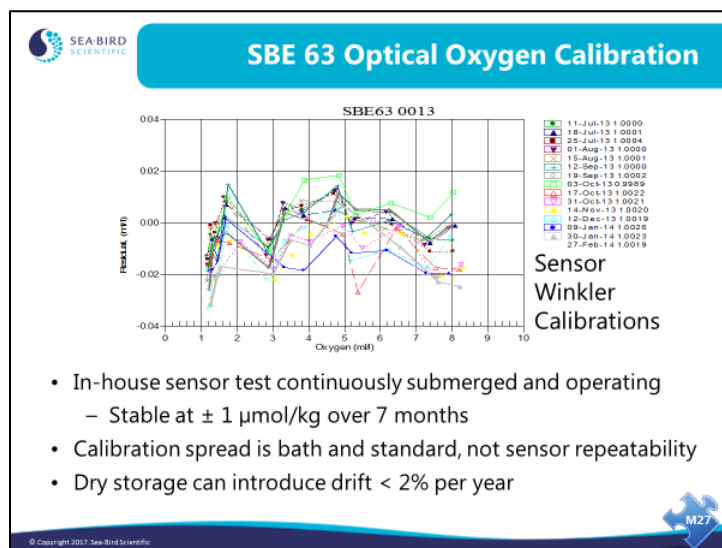
Each SBE 43 and SBE 63 is calibrated individually in a temperature-controlled bath. Bath temperatures are varied at each of 3 to 4 oxygen values, providing a comprehensive 18 to 24-point calibration. Two reference sensors in each bath are standardized against Winkler titrations weekly and monitored with high-quality controlled wet chemistry standards. Response time tests are conducted on each sensor, using gas. Salinity and pressure impacts on sensor response are each checked at two separate points.

Dissolved Oxygen Calibration (*continued*)

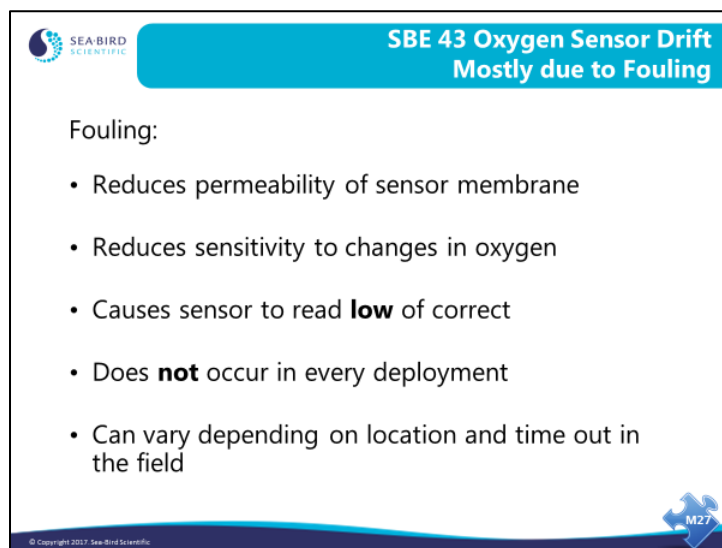


Plot indicates a slope drift of $< 0.1 \text{ mL/L}$ ($\sim 4.5 \text{ } \mu\text{mol/kg}$) over seven months at saturation

Dissolved Oxygen Calibration (*continued*)



SBE 43 Dissolved Oxygen Sensor Drift



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SBE 43 Oxygen Sensor Drift Mostly due to Fouling

Fouling:

- Reduces permeability of sensor membrane
- Reduces sensitivity to changes in oxygen
- Causes sensor to read **low** of correct
- Does **not** occur in every deployment
- Can vary depending on location and time out in the field


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There are two mechanisms at work when it comes to SBE 43 oxygen sensor drift:


1. The primary cause of sensor calibration drift is **fouling** of the sensor membrane. This can be a slow change over time, as the membrane accumulates oils and other materials during cruises and long deployments. Fouling can also occur in an event, such as after passing through an oil slick or impaling a jelly fish. Following recommended cleaning procedures can take care of most fouling problems (see **Application Note 64**).
2. A lesser concern is electrolyte consumption. The SBE 43 is continuously polarized, so will continue to react with oxygen in its plenum housing when not sampling in the water, unless the oxygen supply is choked off. Though this process is reduced by the semi-enclosed housing of the DO sensor, we do recommend that after cleaning the sensor, that it be stored with a closed loop of Tygon tubing. Enclose with a small piece of damp sponge inside the tubing if there is no risk of freezing. We do not recommend storing the SBE 43 in water, as this can lead to *in situ* fouling.

Field Calibrations for Dissolved Oxygen



**Field Calibrations for
Correcting Dissolved Oxygen**


- Dissolved oxygen sensors drift in slope, like conductivity
 - Slope correction of data is usually all that is needed; provides most steady and reliable method for oxygen sensor correction
 - Only 1 good Winkler/CTD sample pair required
- Factory setting for *Voffset* is electronic, and does not change in normal drift
 - Slope and offset corrections only work with a large number of samples for comparison, **and** for a wide range of DO values (for example, 2 – 6 ml/L)
 - Easy to introduce lots of error when correcting for offsets
 - Offset corrections are **not** recommended

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Terms that can be modified by the user to adjust the calibration of the SBE 43:

- *Soc* only (*Soc* can change in time due mostly to fouling)
- *Soc* and *Voffset* together (*Soc* can change in time due mostly to fouling)
- *E* calibration constant
 - The factory value is determined at 0 db and works well for most, but can be adjusted by the user.
 - This is a one-time correction determined using deep pressure sensor and water sample comparison taken at depths > 1000 m.

Dissolved Oxygen Calibration Equation




SBE 43 Calibration Equation

• *Sea-Bird* dissolved oxygen equation (ml/l):

$$\text{Oxygen (ml/l)} = \left\{ \text{Soc} * \left(V + V_{\text{offset}} + \text{tau}(T, P) * \frac{\partial V}{\partial t} \right) \right\} * \text{Oxsol}(T, S) * \left(1.0 + A * T + B * T^2 + C * T^3 \right) * e^{\left(\frac{E * P}{K} \right)}$$

where:


- V = SBE 43 output voltage signal (volts)
- $\partial V / \partial t$ = time derivative of SBE 43 output signal (volts/second)
- $\text{Tau}(T, P)$ = sensor time constant = $\text{tau20} * \exp(D1 * P + D2 * [T - 20])$
- T, P, S = CTD temperature (°C), pressure (dbar), salinity (psu)
- $\text{Oxsol}(T, S)$ = oxygen saturation (ml/l)
- K = absolute temperature (K)
- Soc, Voffset (voltage at zero oxygen signal), A, B, C, E, tau20 are calibration coefficients fit to 18 point calibration at Factory
- D1 and D2 are characteristic of the SBE 43

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What one needs to consider in the Sea-Bird DO calibration equation:


- The basis for calculating dissolved oxygen is a modified version of the algorithm from Owens and Millard (1985), referred to in our software as the *Sea-Bird* algorithm or *Sea-Bird Calibration Equation*.
- **The calibration slope term (Soc), which changes as the sensor sensitivity is modified, typically by fouling, is the coefficient we are most concerned with.**
- An electronic offset term (*Voffset*) related to the voltage output observed at a zero oxygen signal is unique to each sensor and is constant.
- A third-order polynomial component that compensates for changes in the sensor's sensitivity as a function of temperature remains constant.
- An exponential term that compensates for the instantaneous changes in the sensitivity of the sensor with changes in pressure (*E*) can be modified to fine tune deep-ocean oxygen data (covered in more detail later in this module).

Sample Validation Procedure for Dissolved Oxygen Sensor



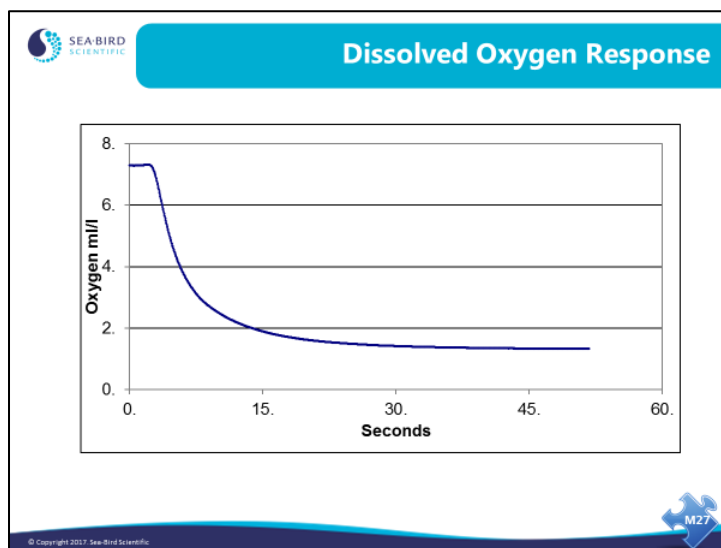
Sample Validation Procedure for Dissolved Oxygen Sensor

- Fouling correction is not a fixed quantity (not an offset)
- SBE 43: Only 1 term in calibration equation needs modification due to fouling, slope scaling term **Soc**
 - All other terms in calibration equation deal with temperature, salinity, and pressure effects on sensor
- SBE 63: Can also use a slope correction to data, but not via the calibration equation



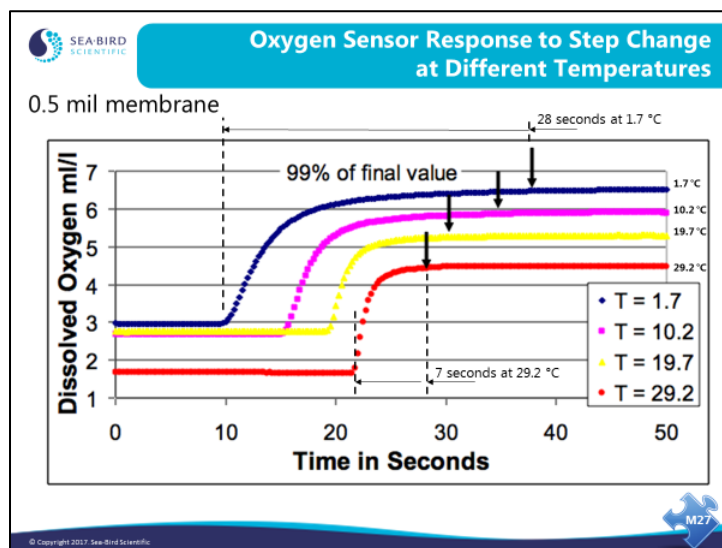
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Dissolved Oxygen Sensor Response



This graph (and the graphs on the following pages) is for an SBE 43 with a 0.5 mil membrane. The 0.5 mil membrane is recommended for profiling applications. Sea-Bird also offers a 1 mil membrane for moored applications

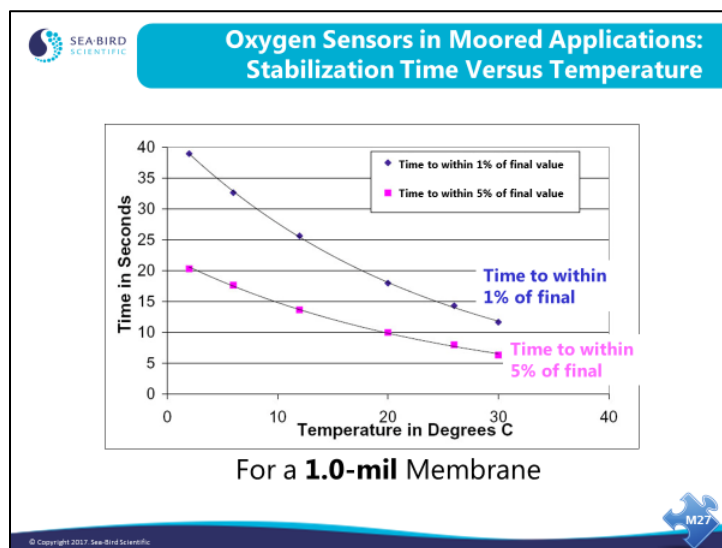
Dissolved Oxygen Sensor Response (*continued*)



The plot above illustrates the effect that temperature has on a dissolved oxygen sensor. The colder the water that the sensor is working in, the longer it requires to come to a final value. In profiling applications this phenomenon is observable as upcast and downcast hysteresis.

Oxygen sensors installed in moorings are always pumped and are typically plumbed between the pump and conductivity sensor of an SBE 16*plus* or 16*plus* V2. Between samples the pump does not run and water ceases to move past the oxygen electrode. As we have discussed, the electrode of the SBE 43 oxygen sensor is powered by an internal battery. When the water becomes still, the electrode depletes it of oxygen; if the CTD were to continue logging data you would observe oxygen concentration inside the sensor plenum approaching a steady state well below the ambient oxygen levels. When the CTD initiates a normal sampling interval by turning on the pump, you would observe a curve similar to the ones shown above. The water flow establishes a normal boundary layer above the oxygen electrode and the sensor equilibrates to the ambient oxygen level. The time required to reach 99% of the final equilibrium value depends on temperature, warmer water allowing faster equilibration. The arrows on the plot show the point at which the sensor has achieved 99% of the final value at each temperature

Dissolved Oxygen Sensor Response (*continued*)




To induce a change in the oxygen sensor reading, oxygen in the environment must diffuse through a water boundary layer to the membrane surface. Next it must diffuse through the Teflon membrane that covers the electrode and into the electrolyte above the electrode. There a chemical reaction takes place at the electrode surface. The rates of these processes are temperature dependent. Thus the response of the sensor to a step change in its environment is temperature dependent. The plot above shows the changes in Tau for a typical sensor. Nominally, Tau at 20° C is 2 seconds, but varies with the age and condition of the sensor and membrane

Prior to 2007, all SBE 43s were sold with a 0.5-mil thick membrane. Beginning in 2007, Sea-Bird began offering two membrane thicknesses – 0.5 mil (faster response, typically for profiling applications and 1.0 mil (slower response but more durable, typically for moored applications). This plot is for a **1.0-mil membrane**.

This plot may be used to determine the time required from power up and pump turn on to the availability of an acceptable dissolved oxygen sample. For example, if you were working in 20° C water and wanted your oxygen data to be better than 1% of actual ambient oxygen concentrations, you would want the sample interval to be longer than 18 seconds. Set the SBE 16*plus* or 16*plus* V2 pump mode to pump during the entire sample time (**MooredPumpMode=2** for 16*plus*; **PumpMode=2** for 16*plus* V2), and set the delay before sampling to 20 seconds (**DelayBeforeSampling=15**). We have allowed 2 extra seconds in our sampling time; this ensures that if the instrument finds itself in colder than expected water, that the sample will still be good. Note that longer pump times reduce battery endurance.


Processing Dissolved Oxygen



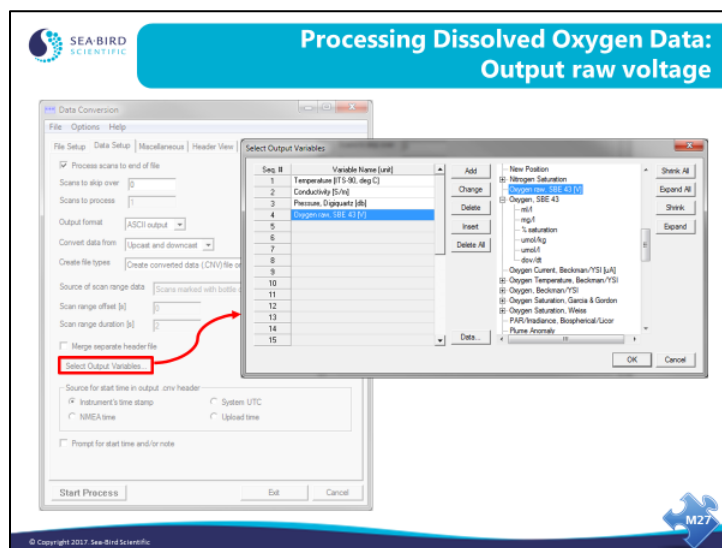
Introduction to processing Dissolved Oxygen Data for Profiling Applications

- Convert to .cnv using *Data Conversion*
 - Output raw voltage
 - Apply hysteresis correction
 - Apply tau correction
- Align oxygen data using *Align*
- Calculate Oxygen concentrations using *Derive*


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Removing Misalignment in Dissolved Oxygen




Removing Misalignment in Dissolved Oxygen (continued)



Dissolved O₂ Alignment

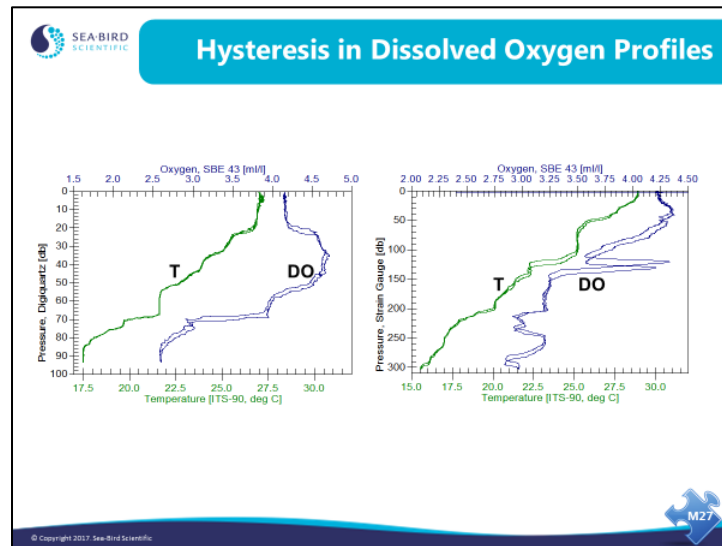
- Sensor time constants ~ 2 - 5 seconds, depending on temperature
- Plumbing delay < 2 seconds, depending on location of sensor in flow path
- Delays add for ~ 4 seconds total
- Hysteresis in DO profiles caused by plumbing delays, temperature mismatch, and sensor response time
 - Recommend corrections for deep ocean pressure > 1000 dbar



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Aligning oxygen current and temperature in relation to pressure can improve hysteresis (mismatch) in dissolved oxygen profiles. The SBE 43 has a faster time constant and shows improvement in hysteresis over the Beckman- or YSI-type of sensor. Deep-ocean hysteresis corrections are advised at depths greater than 1000 dbar

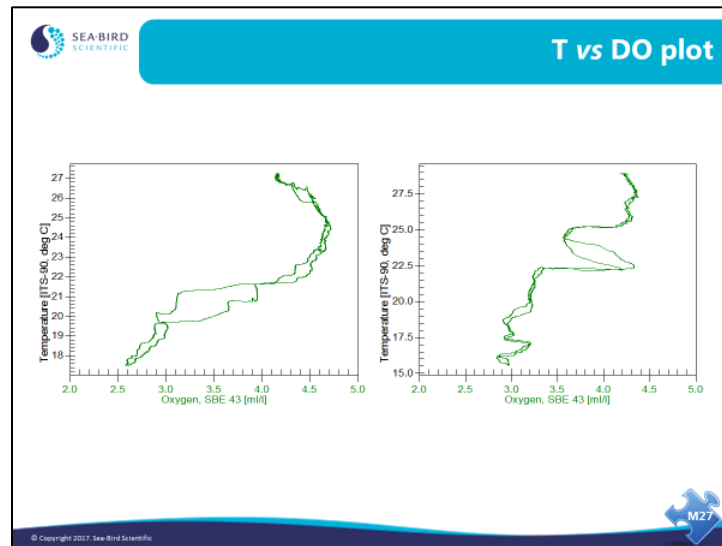
Removing Misalignment in Dissolved Oxygen (continued)



While hysteresis is easily observed in pressure vs. oxygen profiles, it is also easy to confuse hydrographic phenomenon with hysteresis. The plot on the right is a shallow water plot < 1000 dbar, so is not experiencing deep-ocean hysteresis here. However, it does show hysteresis in both temperature and oxygen; the peak in oxygen has a sharp gradient in temperature associated with it. The cast was taken near the Gulf Stream, and it is likely that the ship drifted during the cast. The CTD downcast probably moved through the hydrographic feature at a different depth than the upcast. A hydrographic phenomenon should not be removed with data manipulation.

Pressure-induced hysteresis can explain differences between downcast and upcast oxygen data at depths greater than 1000 meters. For these exercises, we will not worry about deep-ocean hysteresis effects, which will be covered later in this module.

Removing Misalignment in Dissolved Oxygen (continued)



Viewing hysteresis in this manner is an effective way of eliminating the confusion of hysteresis and hydrographic phenomenon.

Removing Misalignment in Dissolved Oxygen (continued)

Processing Dissolved Oxygen Data: Hysteresis correction

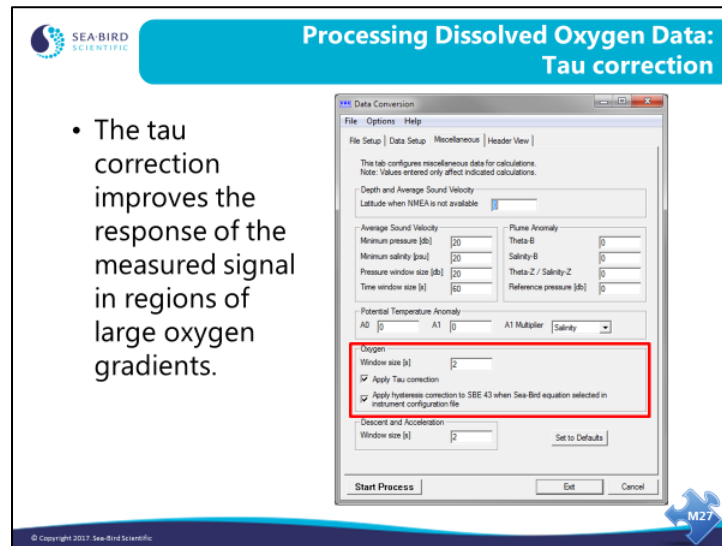
- Can be applied using checkbox in Miscellaneous tab or pop-up window when Oxygen raw is added to Output Variables.

The screenshot displays the SEA-BIRD Scientific software interface. The 'Data Conversion' window is open, showing the 'Miscellaneous' tab. In the 'Oxygen' section, the checkbox 'Apply hysteresis correction to SBE 43 when Sea-Bird equation selected in instrument configuration file' is highlighted with a red box. A red arrow points from this checkbox to the 'Select Output Variables' window, where 'Oxygen raw, SBE 43' is selected. A pop-up window titled 'Oxygen raw, SBE 43' is also shown, with the 'Apply hysteresis correction' checkbox checked. The pop-up window contains the text: 'You can review and change this entry on the Miscellaneous tab after completing variable selection.'

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Tau Correction for Dissolved Oxygen

- The tau correction improves the response of the measured signal in regions of large oxygen gradients.



Activity: Align DO Data and Derive

Explanation: For this activity, we convert the raw data in *Data Conversion*, then align the data with *Align CTD*, trying a few advances. We then use *Derive* to calculate oxygen from the original .cnv file and from each aligned file. You should end up with the following files to plot in *Sea Plot* to see which advance gives the best results:

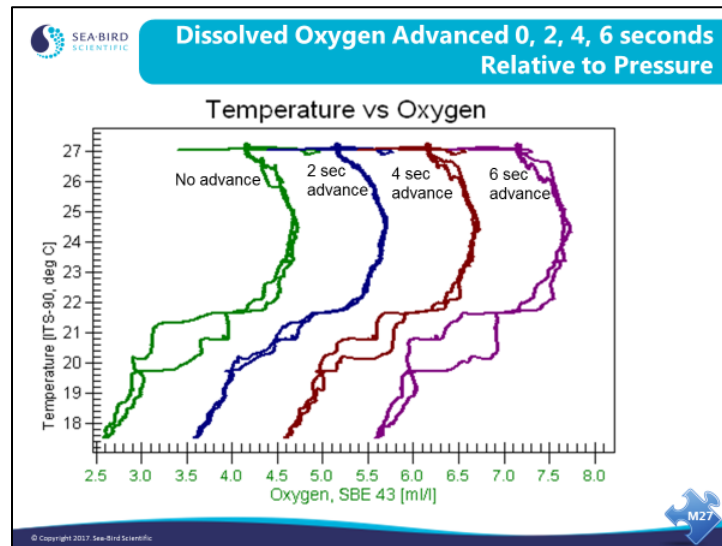
- GulfMexD.cnv original data, not advanced
- GulfMexA2D.cnv dissolved oxygen advanced 2 seconds
- GulfMexA4D.cnv dissolved oxygen advanced 4 seconds
- GulfMexA6D.cnv dissolved oxygen advanced 6 seconds

1. In SBE Data Processing, run *Data Conversion*:
 - Use C:\Data\Module9\AlignDO\GulfMex.dat and GulfMex.con
 - Convert upcast and downcast
 - Output P, T, S, and Oxygen **raw, SBE 43 [V]**
2. In SBE Data Processing, run *Align CTD* **three times**:
 - Advance Oxygen Voltage SBE 43 relative to pressure 2, 4, and 6 seconds
 - Name append A2, A4, and A6
3. In SBE Data Processing, run *Derive* **one time**, on all 4 files:
 - Use GulfMex.cnv, GulfMexA2.cnv, GulfMexA4.cnv, GulfMexA6.cnv
 - Name append D
 - Calculate Oxygen, SBE 43 -> ml/l
 - Accept default 2.0 second window size for oxygen (on Miscellaneous tab)
4. In SBE Data Processing, run *Sea Plot* **one time** to compare results with an Overlay plot:
 - De-select *Sort input files* in Options menu, and then select input files **in order** (GulfMexD.cnv, GulfMexA2D.cnv, GulfMexA4D.cnv, and GulfMexA6D.cnv)
 - Overlay plot of T (17 to 28) vs Oxygen (2.5 to 8.0), with 1.0 offset for oxygen


If you have time, align the data in C:\Data\Module9\AlignDO\SBE19plus\ and derive oxygen, using the same procedure.

- Check your results with Sea Plot (try T from 15 to 30, Oxygen from 2.2 to 5.5, and offset 0.3).

Activity: Align DO Data and Derive

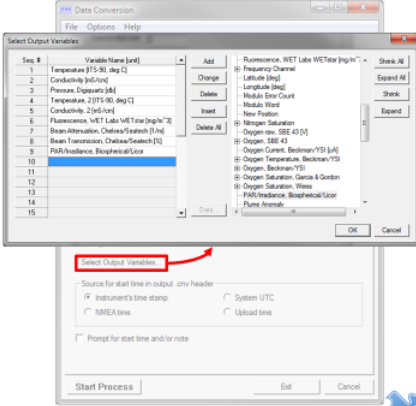


Biogeochemical Data Processing Software



Processing Biogeochemical Data: Profiling Applications

- Data conversion module can be used to process biogeochemical data
- Derives values from analog voltage and calibration coefficients
- Uses calibration coefficients found in .xmlcon or .con file



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Using Factory Calibrations to Process Biogeochemical Data

**Processing Biogeochemical Data:
Editing the .xmlcon file**

- Use most recent factory calibrations

Configuration for the SBE 911plus/917plus CTD

Configuration file opened: GullMex.con

Frequency channels suppressed: 0 Voltage words suppressed (1 word = 2 channels): 0

Deck unit or SEARAM: SBE1plus Firmware Version >= 5.0

Computer interface: RS-232C

Scans to average: 1

☒ NMEA position data added ☐ NMEA depth data added

☒ NMEA device connected to deck unit ☐ NMEA line added

☐ NMEA device connected to PC

☐ Surface PAR voltage added ☐ Scan time added

| Channel | Sensor | New |
|-------------------|----------------------------------|------------|
| 1. Frequency | Temperature | Open... |
| 2. Frequency | Conductivity | Save |
| 3. Frequency | Pressure, Digiquartz with TC | Save As... |
| 4. Frequency | Temperature, 2 | Select |
| 5. Frequency | Conductivity, 2 | Modify... |
| 6. A/D voltage 0 | Oxygen, SBE 43 | |
| 7. A/D voltage 1 | Free | |
| 8. A/D voltage 2 | Oxygen Current, Beckman/YSI | |
| 9. A/D voltage 3 | Oxygen Temperature, Beckman/YSI | |
| 10. A/D voltage 4 | Transmissometer, Chelsea/Seatech | |
| 11. A/D voltage 5 | Fluorometer, WET Labs WETstar | |
| 12. A/D voltage 6 | PAR/Irradiance, Biospherical/Lux | |

Report... Help... Exit Cancel

Fluorometer, WET Labs WETstar

Serial number: WS35-736P

Calibration date: 03/30/01

Blank output: 0.052

Scale factor: 17.250

Import Export OK Cancel

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