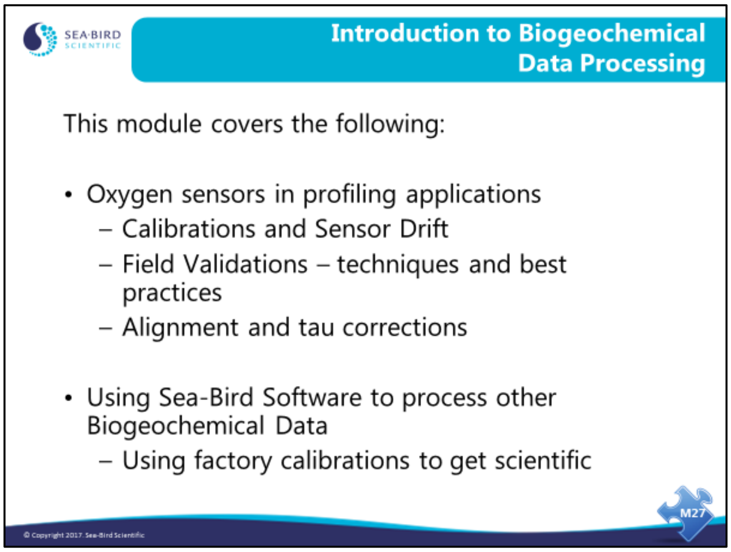
SEA·BIRD
SCIENTIFIC

Introduction to Biogeochemical Data Processing

Sea-Bird Scientific University Module 27

M27

Overview


SEA·BIRD SCIENTIFIC
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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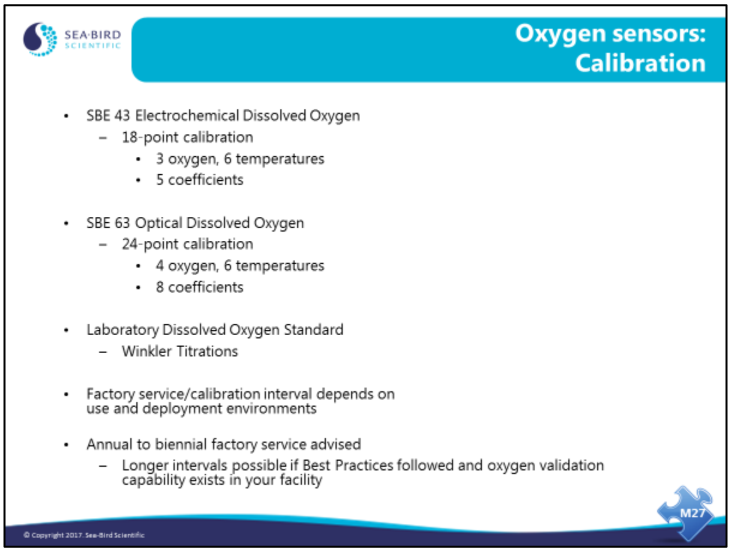
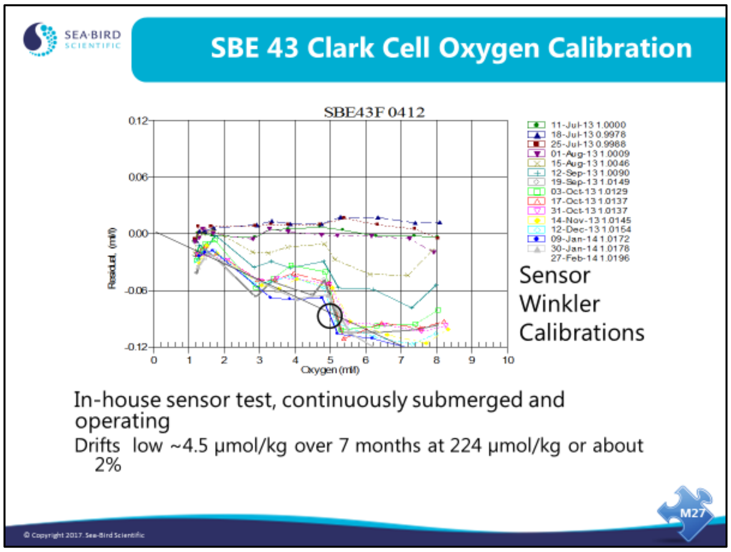
Dissolved Oxygen Calibration



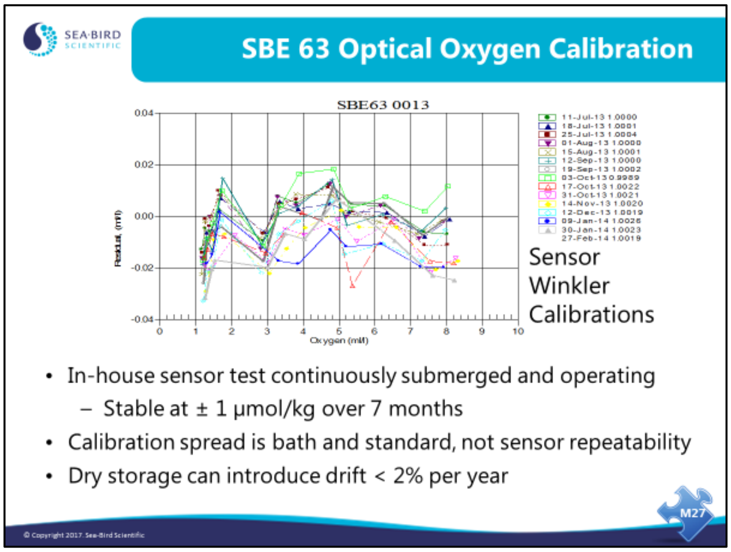
Each SBE 43 and SBE 63 is calibrated individually in a temperature-controlled bath. Bath temperatures are varied at each of 3 to 4 oxygen values, providing a comprehensive 18 to 24-point calibration. Two reference sensors in each bath are standardized against Winkler titrations weekly and monitored with 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)*

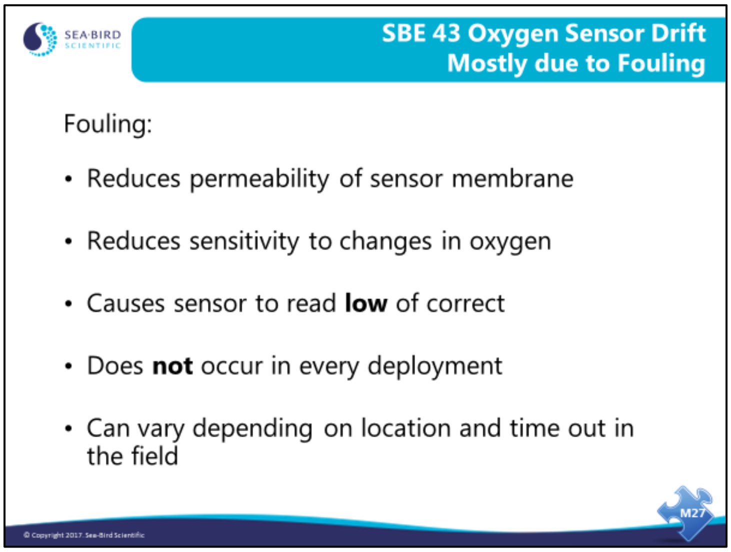


Plot indicates a slope drift of < 0.1 ml/L (~4.5 umol/kg) over seven months at saturation

Dissolved Oxygen Calibration *(continued)*



SBE 43 Dissolved Oxygen Sensor Drift

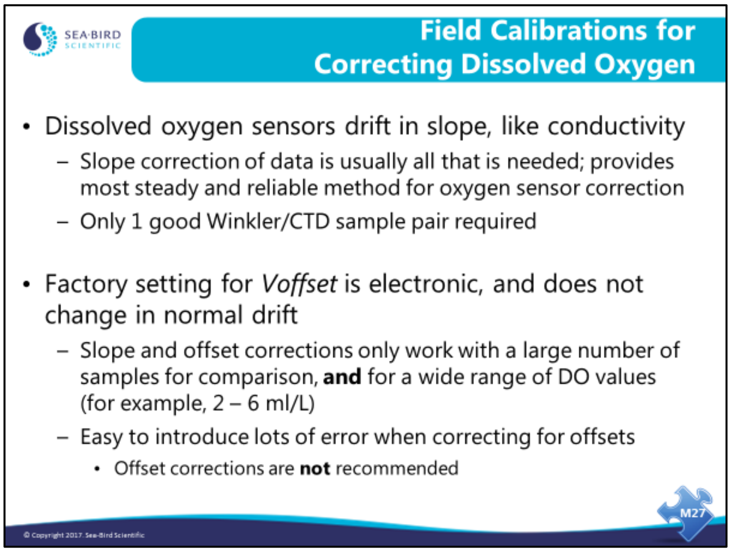


There are two mechanisms at work when it comes to SBE 43 oxygen sensor drift:

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.

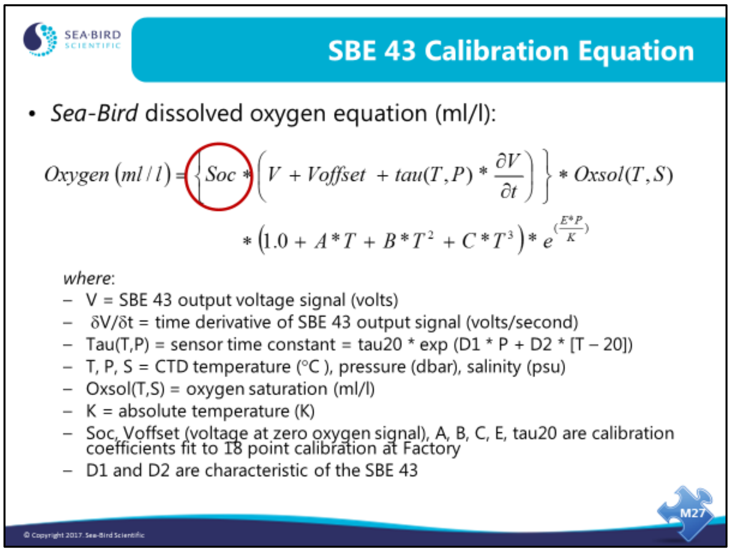
Field Calibrations for Dissolved Oxygen



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



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*.

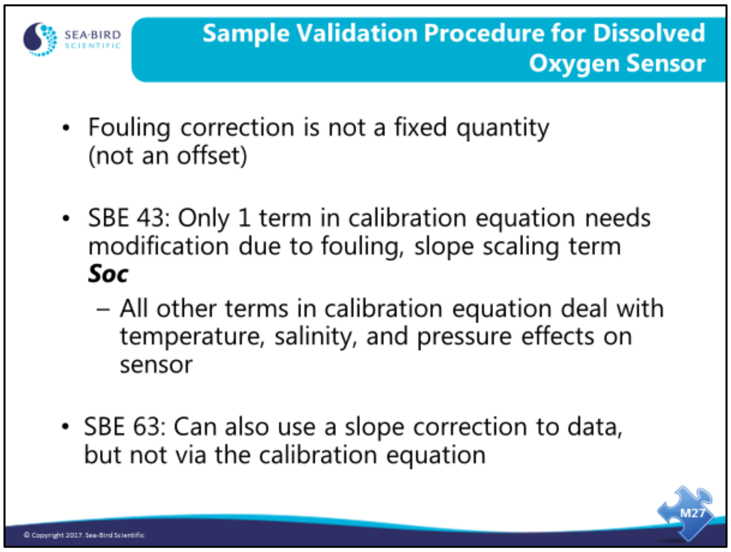
- **The calibration slope term *(Soc)*, which changes as the sensor sensitivity is modified, typically by fouling, is the coefficient we are most concerned with.**

- An electronic offset term (*Voffset*) related to the voltage output observed at a zero oxygen signal is unique to each sensor and is constant.

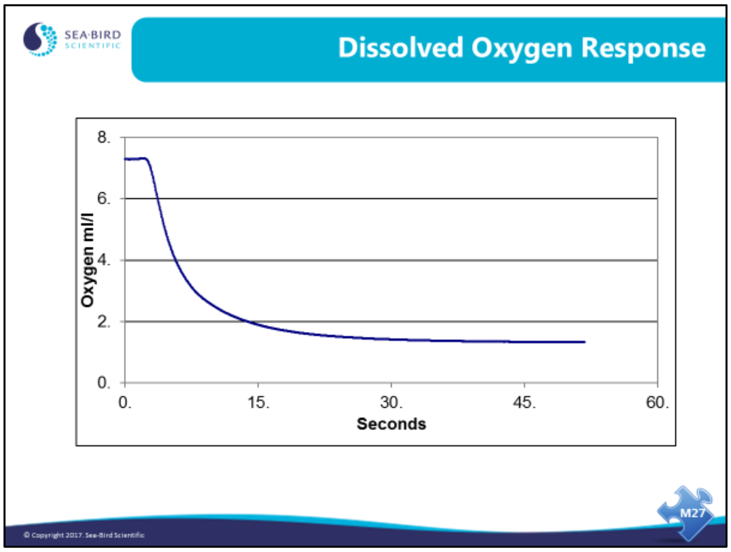
- A third-order polynomial component that compensates for changes in the sensor's sensitivity as a function of temperature remains constant.

- 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

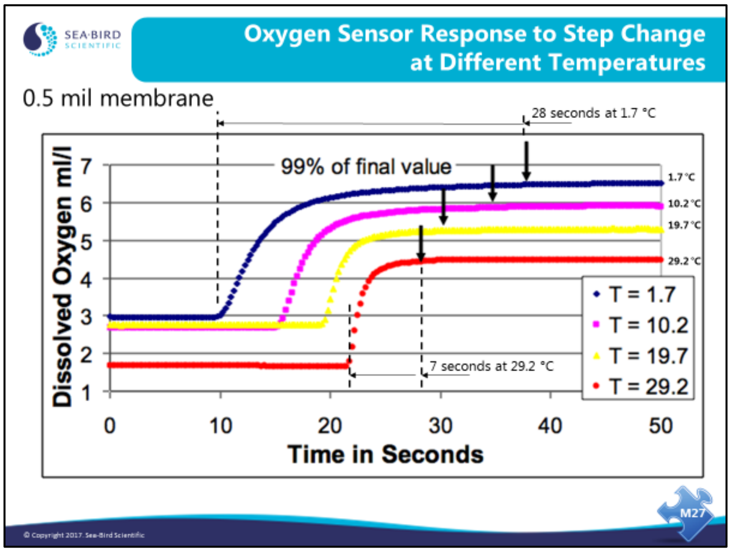


Dissolved Oxygen Sensor Response



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

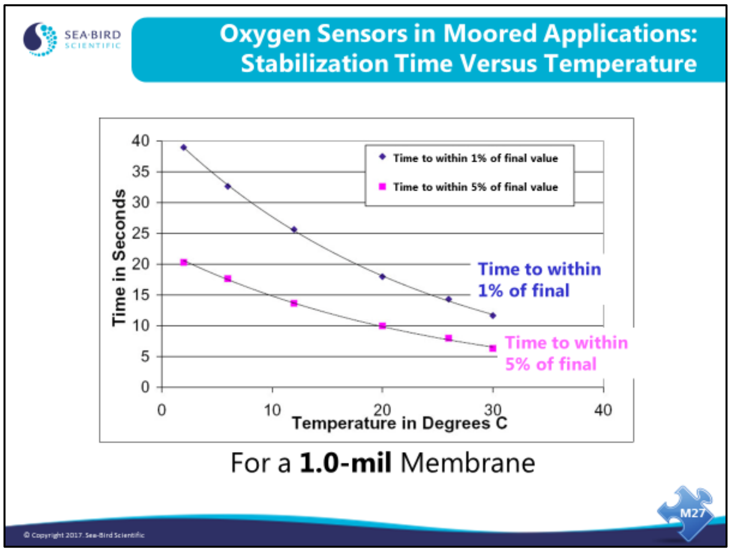
Dissolved Oxygen Sensor Response *(continued)*



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

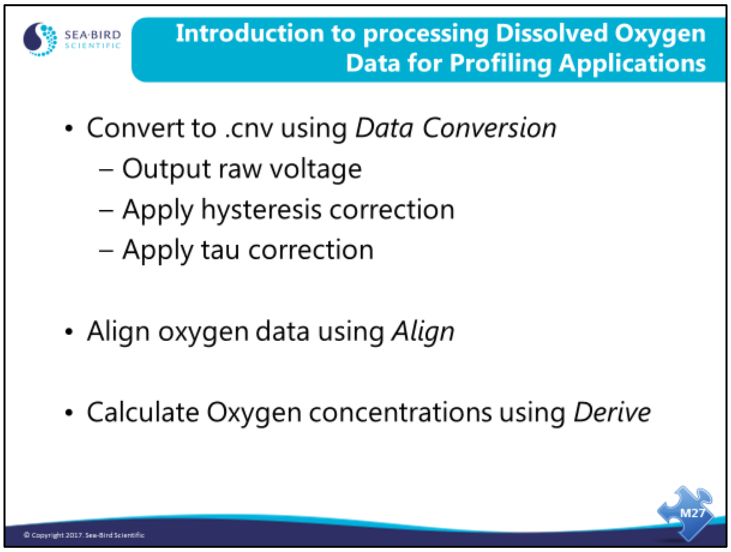
Dissolved Oxygen Sensor Response *(continued)*



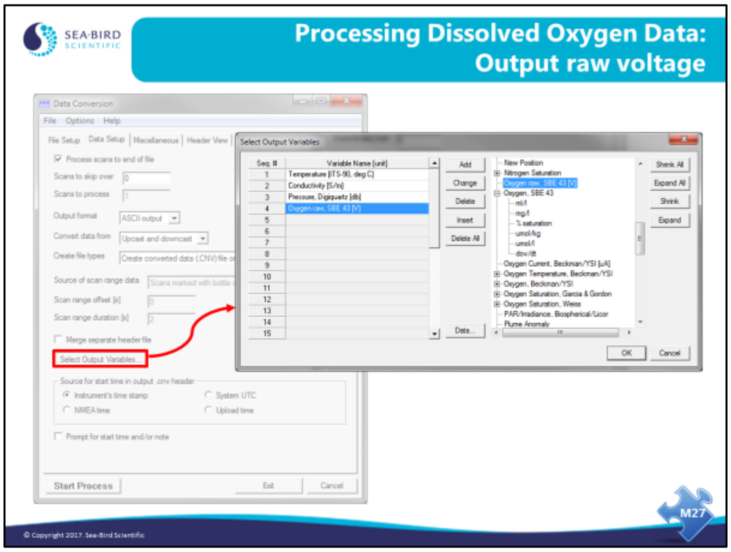
To induce a change in the oxygen sensor reading, oxygen in the environment must diffuse through a water boundary layer to the membrane surface. Next it must diffuse through the Teflon membrane that covers the electrode and into the electrolyte above the electrode. There a chemical reaction takes place 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.

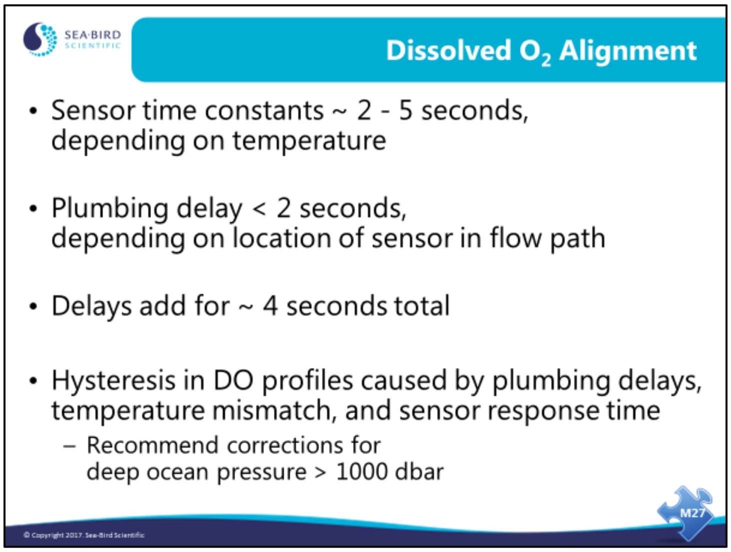
Processing Dissolved Oxygen



Removing Misalignment in Dissolved Oxygen

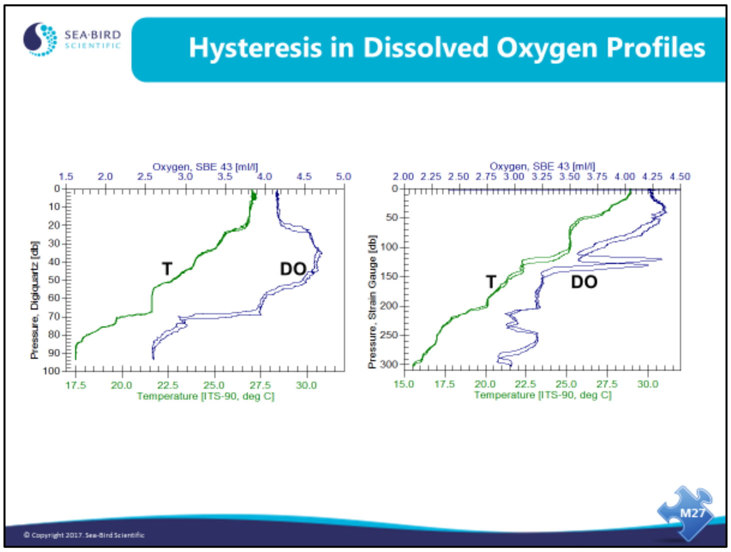


Removing Misalignment in Dissolved Oxygen *(continued)*



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

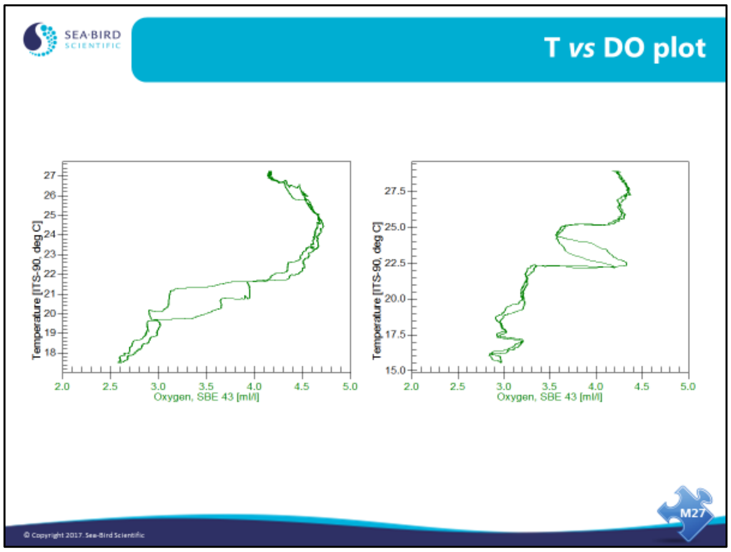
Removing Misalignment in Dissolved Oxygen *(continued)*



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.

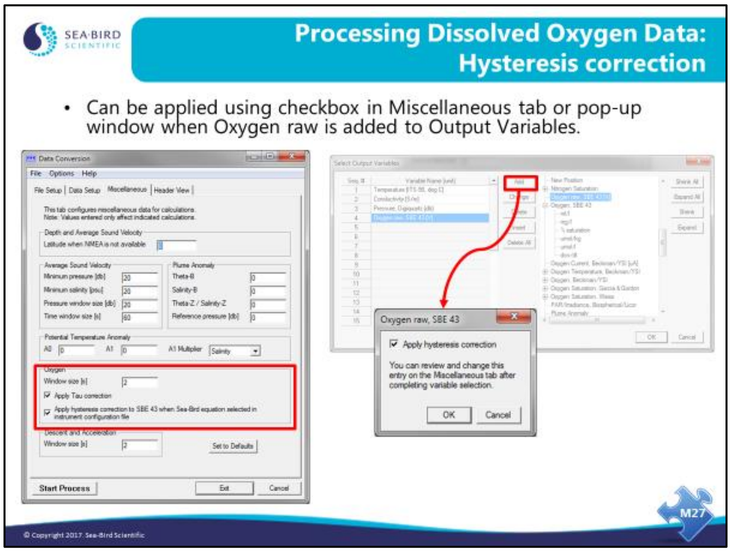
Pressure-induced hysteresis can explain differences between downcast and upcast oxygen data at depths greater than 1000 meters. For these exercises, we will not worry about deep-ocean hysteresis effects, which will be covered later in this module.

Removing Misalignment in Dissolved Oxygen *(continued)*

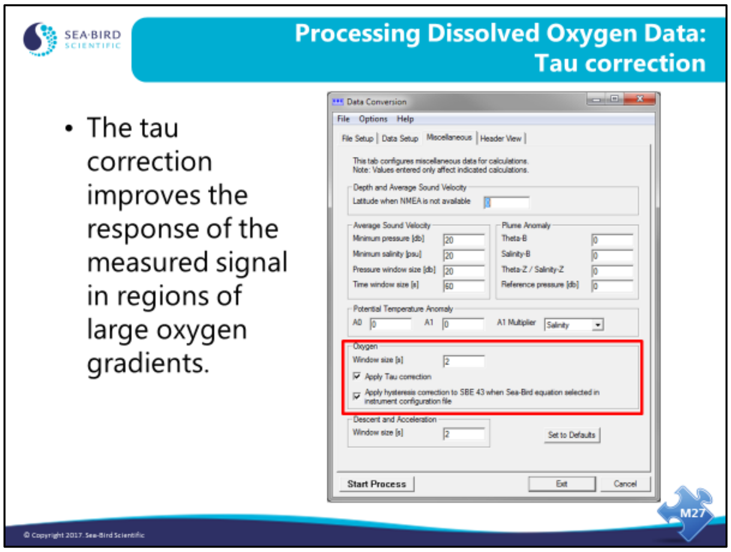


Viewing hysteresis in this manner is an effective way of eliminating the confusion of hysteresis and hydrographic phenomenon.

Removing Misalignment in Dissolved Oxygen *(continued)*



Tau Correction for Dissolved Oxygen



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

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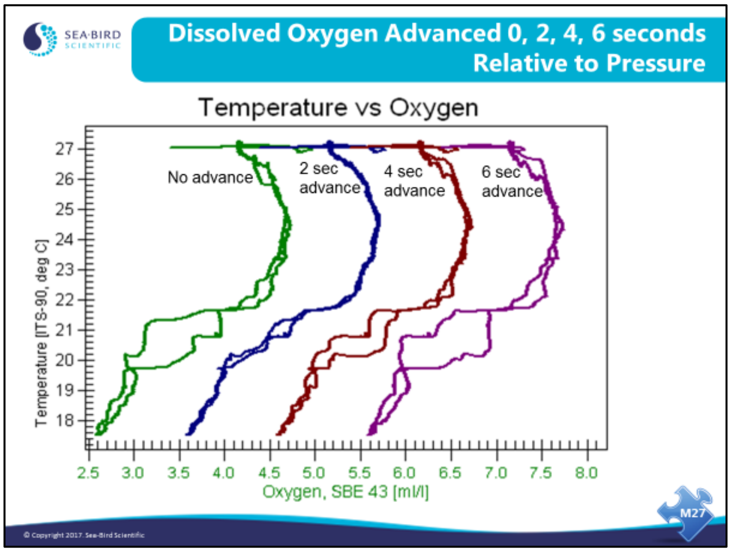
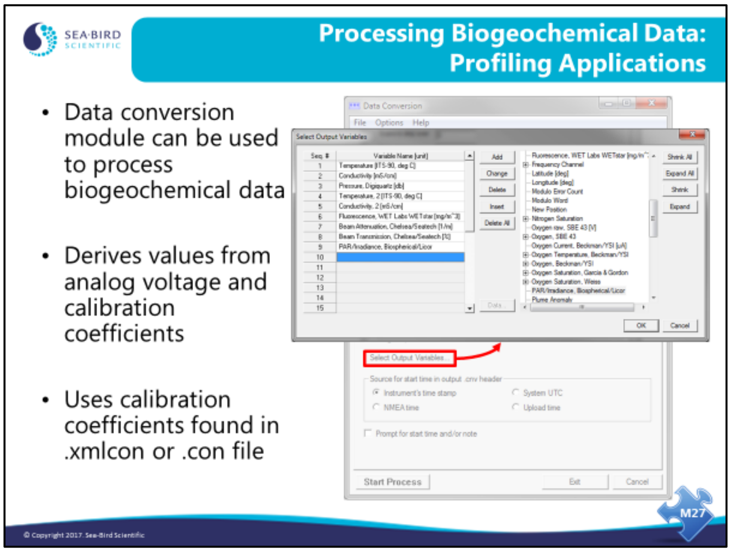
If you have time, align the data in C:\Data\Module9\AlignDO\SBE19plus\ and derive oxygen, using the same procedure.

- 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



Using Factory Calibrations to Process Biogeochemical Data