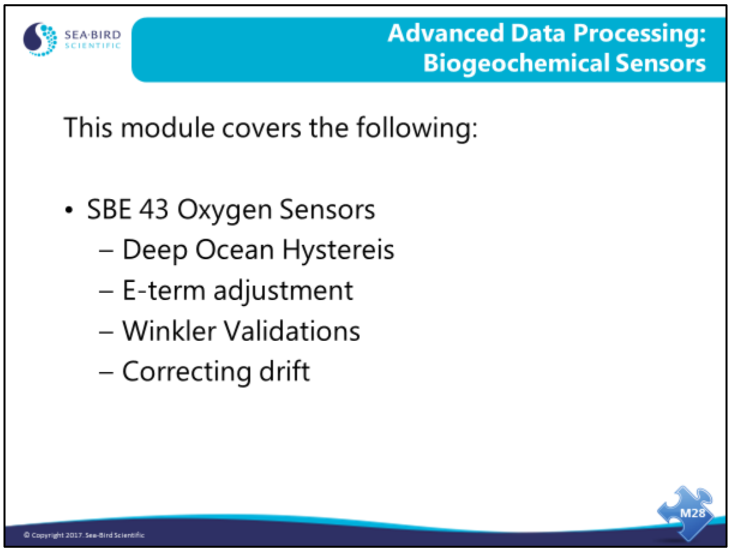
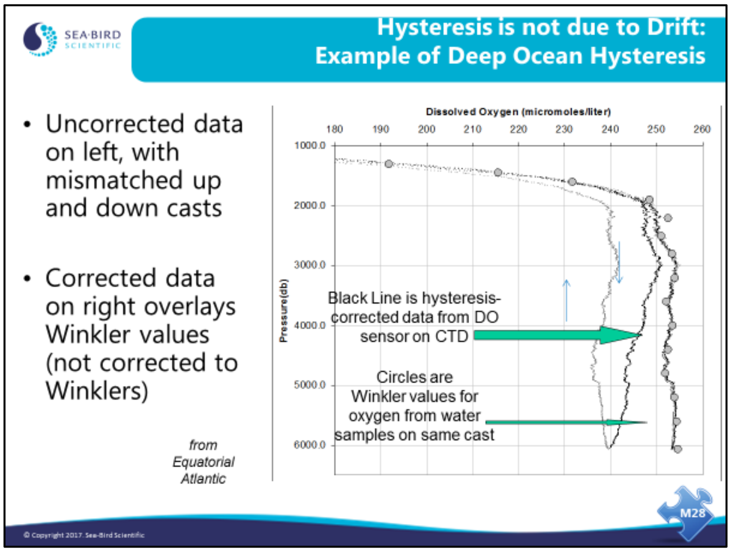
Advanced Data Processing: Biogeochemical Sensors

Sea-Bird Scientific University Module 28

Overview

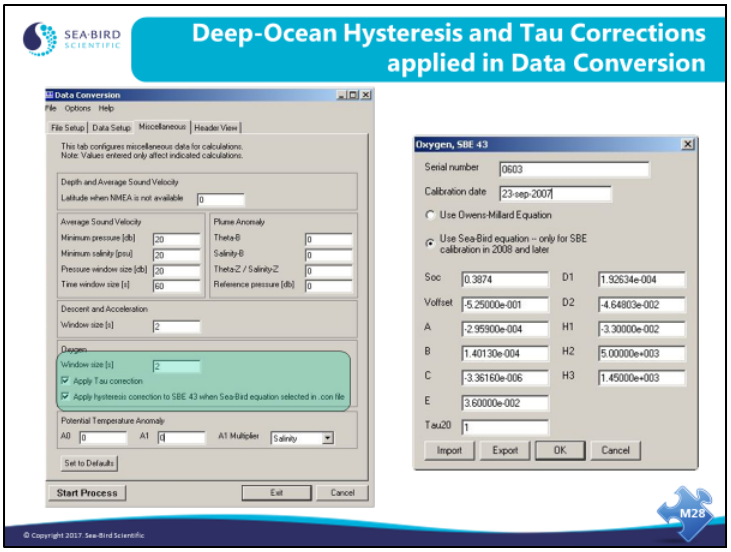

SEA·BIRD SCIENTIFIC
Advanced Data Processing: Biogeochemical Sensors
This module covers the following:
• SBE 43 Oxygen Sensors
– Deep Ocean Hystereis
– E-term adjustment
– Winkler Validations
– Correcting drift
M28

Dissolved Oxygen Deep Ocean Hysteresis



- Under high pressure, physical changes occur in gas permeable Teflon membranes that affect the permeability characteristics. The high-pressure, time-dependent effects have long time constants which ***predictably*** reduce the sensor's output.
- The deep-ocean hysteresis effect is viewed as a mismatch between CTD-DO data and bottle data and a mismatch between up and down cast DO data traces at depths below 1000 dbar.
- The effect causes sensors to read low of correct at depths 1000 dbar and greater.
- Time at depth will very slowly add to this offset, which is why the down cast oxygen values will typically be higher than the upcast oxygen trace.
  - Both the up and down cast traces can be low of the bottle data collected at corresponding depths when deep ocean hysteresis is occurring.
- The effect is modeled by a simple exponential function, so the temporal and pressure dependencies are i) predictable, and ii) correctable, and iii) require a continuous time series.
- ***NOTE:*** Deep-ocean hysteresis is separate from sensor-alignment-caused hysteresis observed throughout the water column (a mismatch due to position of sensor on the sample package).

Dissolved Oxygen Deep Ocean Hysteresis *(continued)*



A time-dependent hysteresis effect on the sensor membrane affects the membrane permeability by plasticization of the polymer membrane and modification of the ratio of crystalline and amorphous components in the membrane. This affects at all depths, but becomes significant when deeper than 1000 meters. This is not dealt with in the calibration equation term *E*. Instead, deep-ocean hysteresis is corrected for separately as it requires a series of time-dependent functions not accommodated in the Sea-Bird calibration algorithm.

To perform deep-water hysteresis corrections on your SBE 43 oxygen data, select *Apply hysteresis correction to SBE 43 when Sea-Bird equation selected in .con or .xmlcon file* on the Miscellaneous tab in the Data Conversion dialog box. Ranges and default values for the hysteresis correction are:

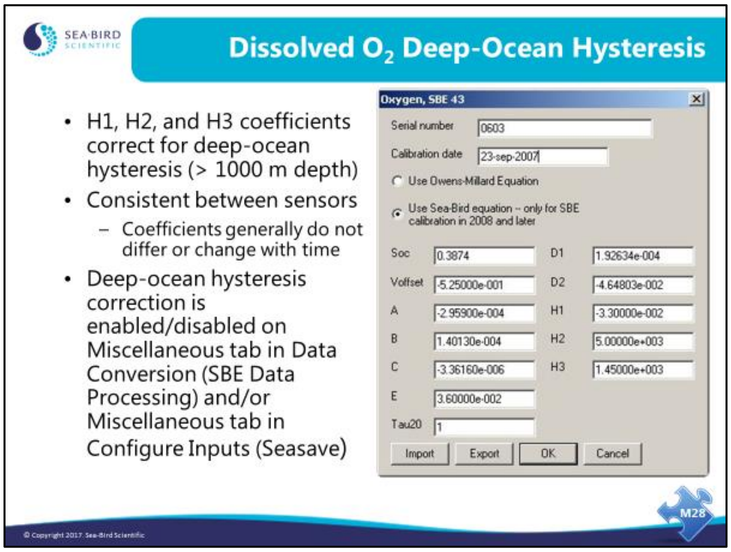
- H1 - amplitude, range -0.03 to -0.05, **default = -0.033**.
- H2 - non-linear component, does not require tuning between sensors, **default = 5000**.
- H3 - time constant, range 1200 to 2000 sec, **default = 1450 sec**.

These parameters can be adjusted if needed for high accuracy applications, but default values typically produce excellent results.

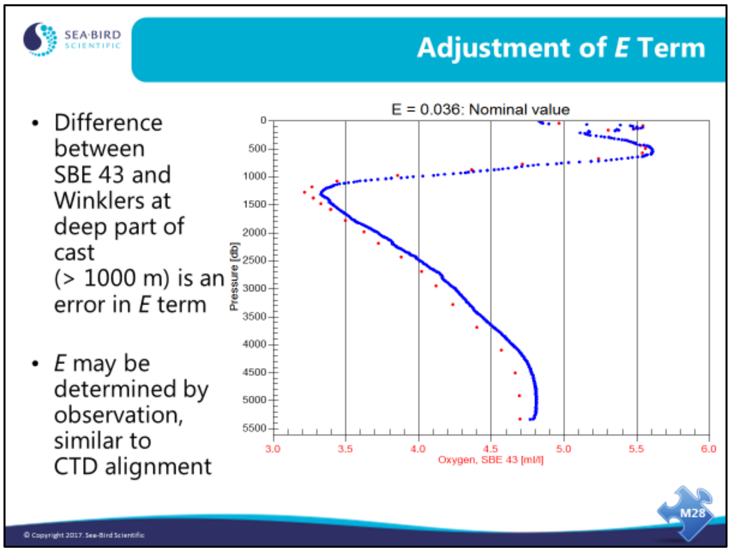
Hysteresis responses of membranes on individual SBE 43 sensors are very similar; in most cases the default parameters provide the accuracy specification of within 2% of true value. For users requiring higher accuracy (±1 μmol/kg), the parameters can be fine-tuned if a complete profile (descent and ascent) made preferably to > 3000 meters is available. Hysteresis can be eliminated by alternately adjusting H1 and H3 in the .con or .xmlcon file during comparison of the complete profile with corresponding Winkler water sample values. Once established, these parameters should be stable, and can be used without adjustment on other casts collected using the same SBE 43.

Be sure to perform hysteresis corrections to deep profile data being used to modify the *Soc* term.

Dissolved Oxygen Deep Ocean Hysteresis *(continued)*



Adjusting E in the Calibration Equation

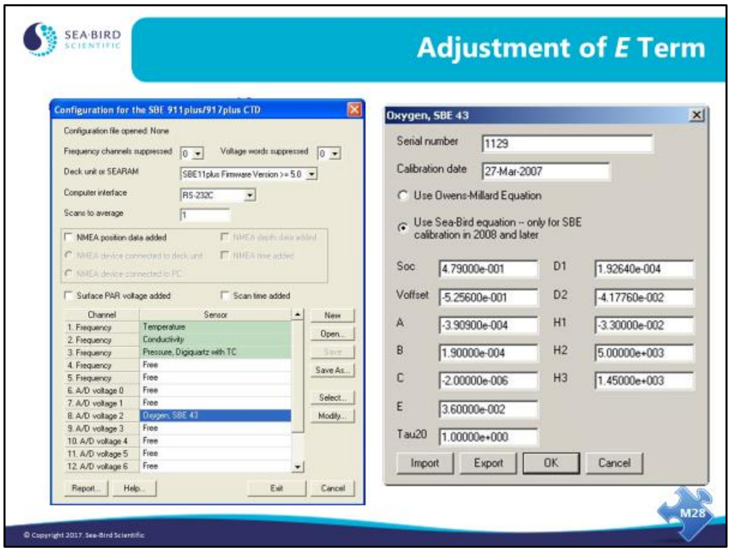


The term in the equation that corrects for pressure effects has little effect in the upper part of the profile. The slide above illustrates that as the pressure increases, the response of the instrument deviates from the Winkler titrations. We can improve the agreement of the SBE 43 and the Winkler titrations by adjusting *E*. The instantaneous effect of pressure on the sensor membrane permeability is captured in the E term of the calibration equation.

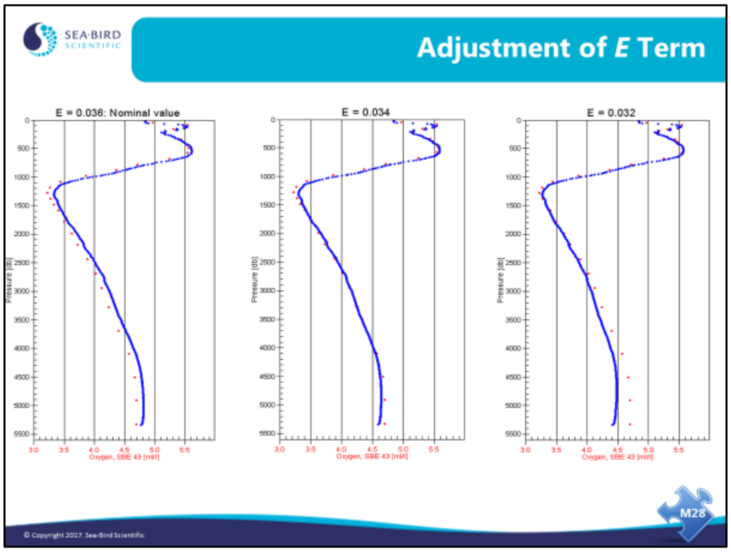
- Necessary for all profile data, regardless of deep or shallow water.

E can be adjusted so data are fit to Winkler samples after conducting hysteresis corrections

Adjusting E in the Calibration Equation *(continued)*

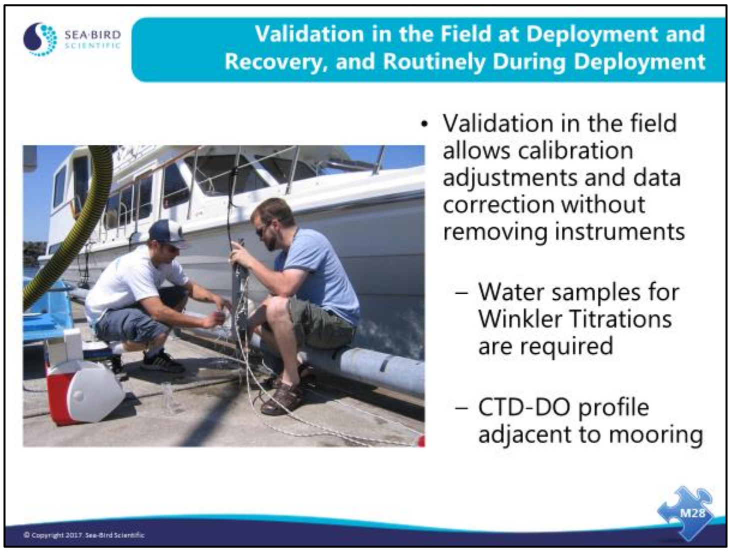


Adjusting E in the Calibration Equation *(continued)*

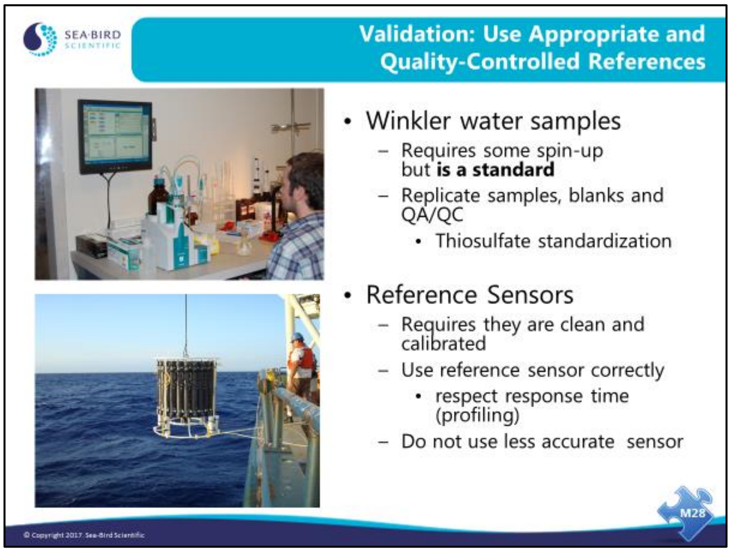


We can make the adjustment to *E* empirically. The plots above show the discrepancy between the SBE 43 calculated oxygen and the Winkler titrations with a series of *E* values. Clearly, the middle value of E = 0.034 gives the best agreement.

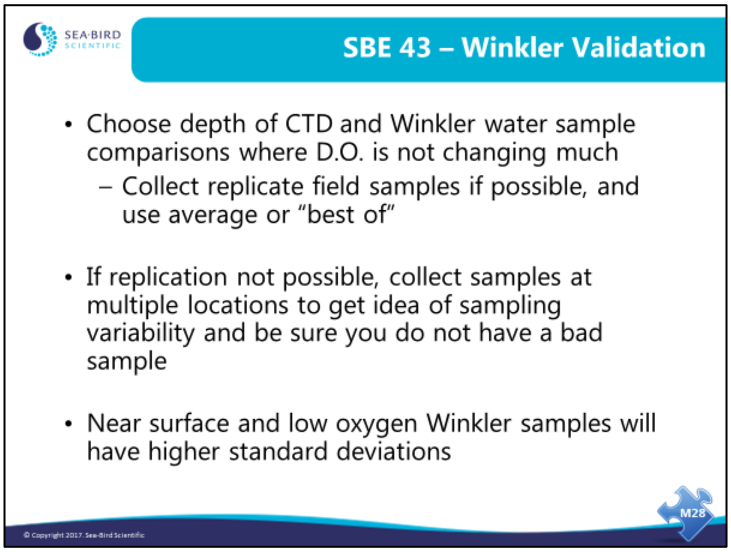
Validation in the Field



Validation in the Field *(continued)*



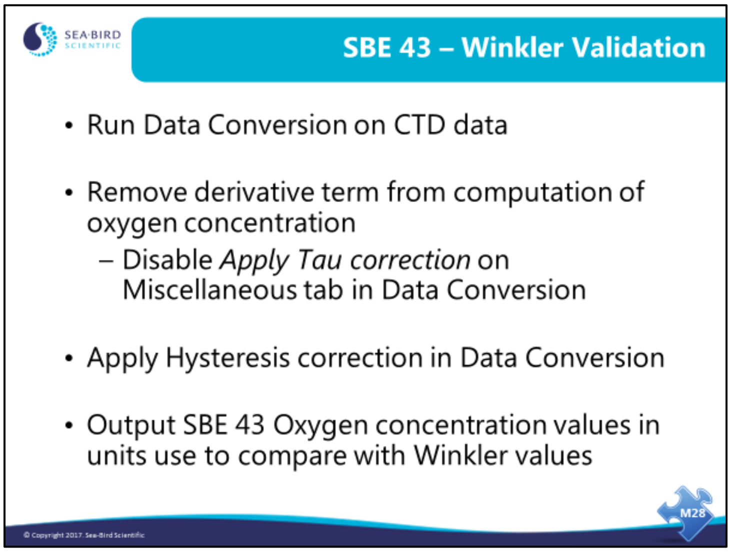
Field Calibrations – Dissolved Oxygen



Correcting SBE 43 DO Data using Field Validation Requires Care:

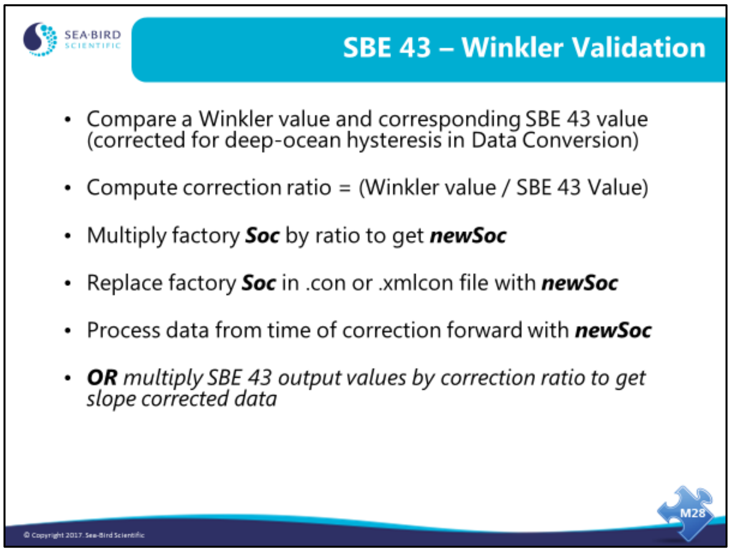
- Field validations must be carefully executed!
- Things that can contribute to sensor differences from water sample values besides sensor calibration drift or malfunction:
  - Mismatched depths between sensor and bottles
  - Internal waves
  - Non-equilibrated sensor/bottle (not long enough wait time prior to closing bottles)
  - Steep gradients over length of sampling package
  - Poor QA on Winkler titrations (chemicals, blanks, sample draw errors, bubbles in samples, analyst)

Field Calibrations – Dissolved Oxygen *(continued)*



- The tau (T,P) * δV/δt term is proportional to the first derivative of the oxygen sensor output voltage. This term is introduced to sharpen the response of the sensor to rapid changes in oxygen concentration. However, it also amplifies residual noise in the signal (especially in deep water), and in some situations this negative consequence overshadows gains in signal responsiveness. To remove the derivative term, disable *Apply Tau correction* on the Miscellaneous tab in Data Conversion; deleting tau (T,P) * δV/δt from the equation.

Field Calibrations – Dissolved Oxygen *(continued)*

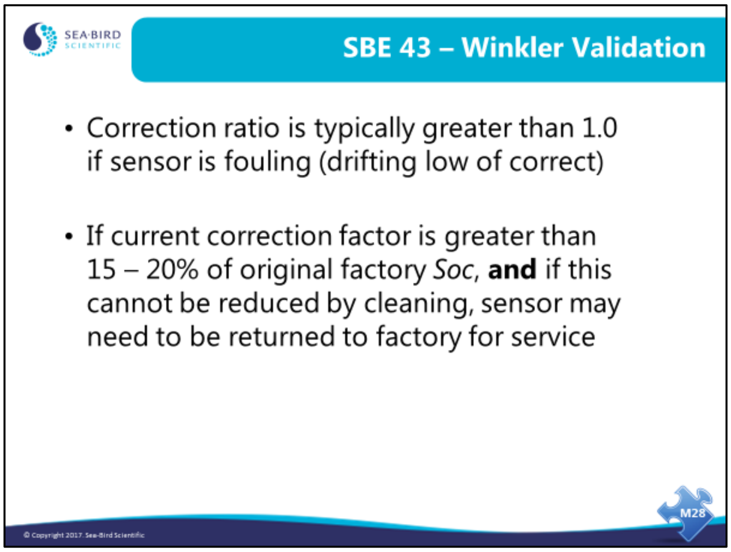


The correction ratio is typically greater than 1.0 if the sensor is fouling.

See **Application Note 64-2**

(www.seabird.com/document/an64-2-sbe-43-dissolved-oxygen-sensor-calibration-and-data-corrections).

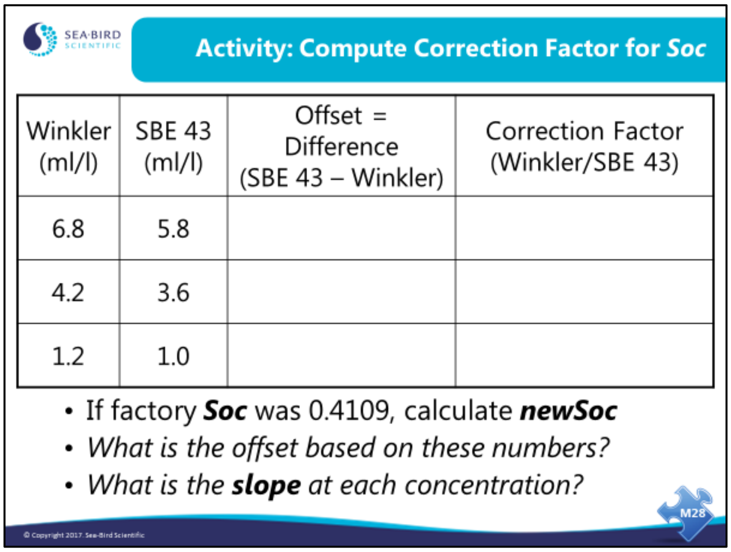
Field Calibrations – Dissolved Oxygen *(continued)*



When is a change in *Soc* indicating the sensor needs to be serviced, cleaned, or recalibrated at the factory?

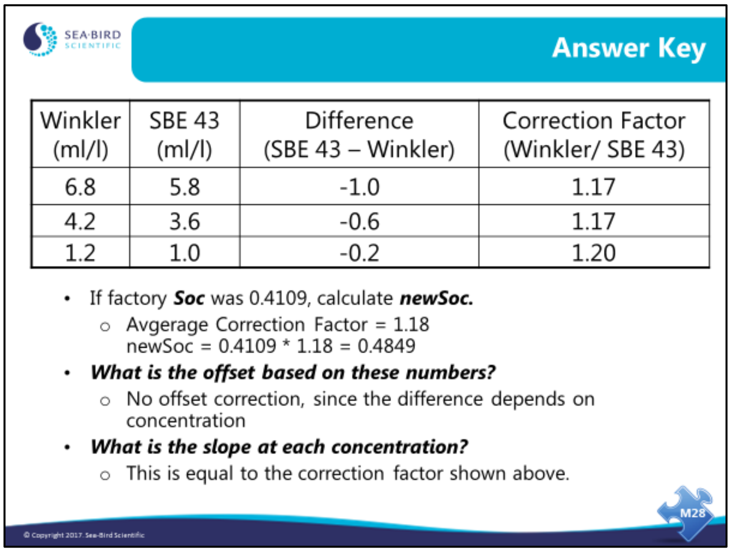
- The correction ratio is typically greater than 1.0 if the sensor is fouling as the loss of sensitivity requires increasing *Soc* to give the correct DO values.
- If the correction factor is greater than 15-20% of the original factory *Soc* (ratio of Winkler/SBE 43 ~ 1.2), and when this cannot be reduced by cleaning, the sensor may need to be returned to the factory for service.
- Other options for data correction are discussed in several papers on our website.
- An exercise in Module 12 is provided to demonstrate this method of DO data correction in a moored application.
- For additional information on SBE 43 data and corrections, see **Application Notes 64, 64-1, and 64-2** on our website.

Activity: Compute Correction Factor for *Soc*



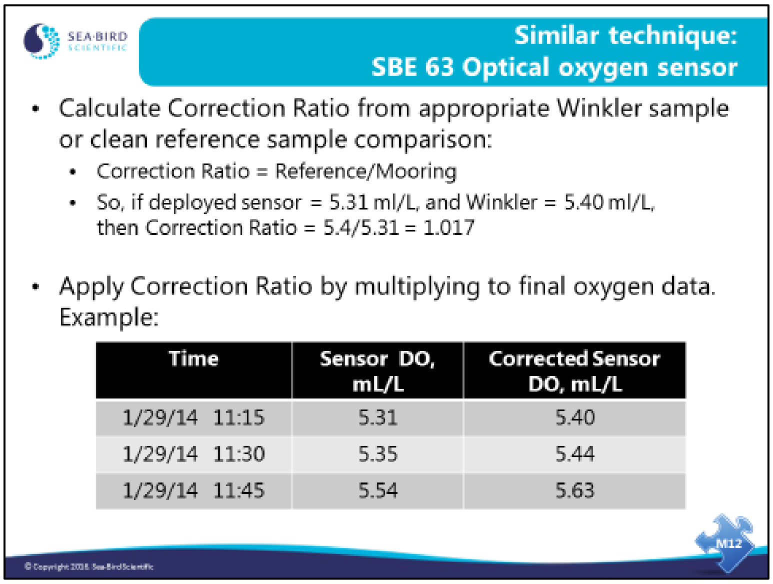
Note that the Offset (difference between SBE 43 readings and Winkler readings) is not constant, indicating that the SBE 43 is drifting by slope, not offset.

Activity: Compute Correction Factor for *Soc*

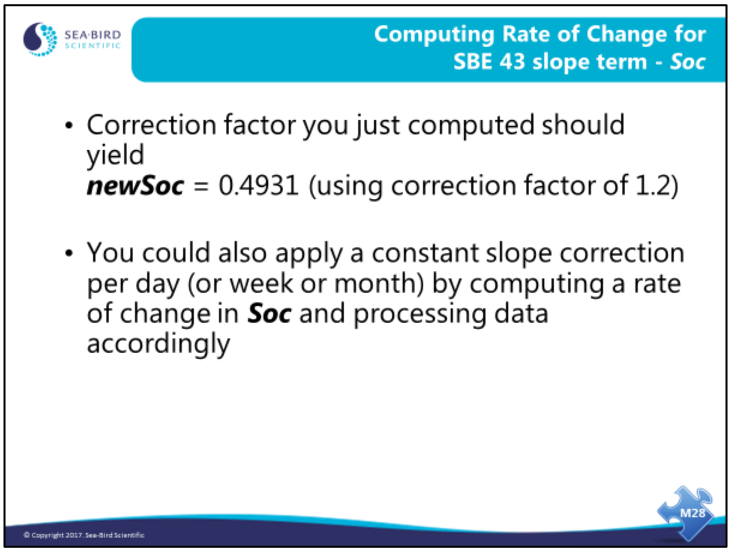


The new ***Soc*** (***newSoc***) is entered in the configuration (.con or .xmlcon) file in SBE Data Processing. The modified configuration file is used for processing measurements made after the date corresponding to the Winkler water samples.

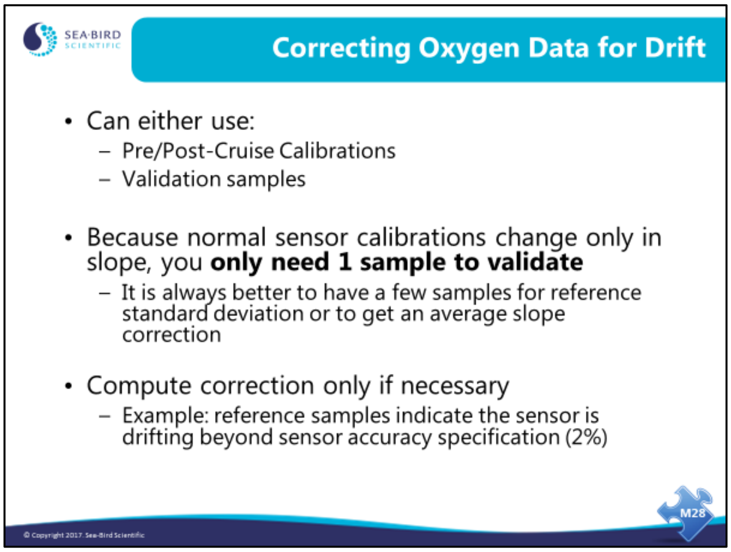
Correcting Oxygen Data: SBE 63 Optical DO Sensor



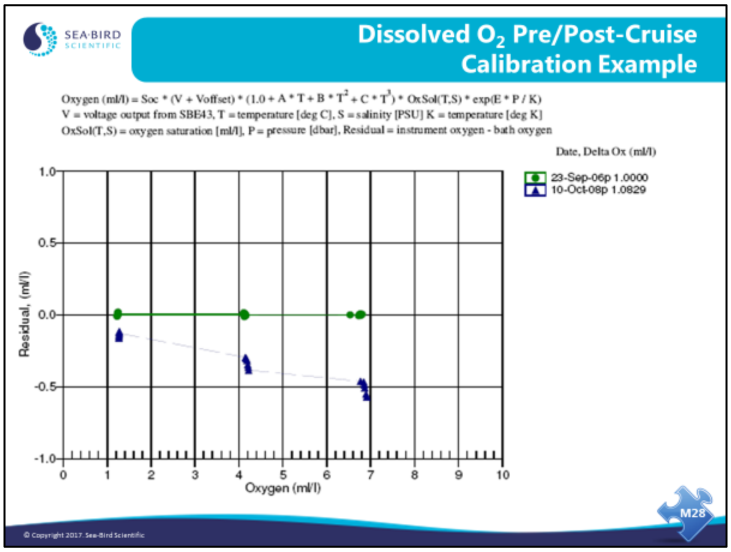
Computing Rate of Change for *Soc*



Correcting Oxygen Data for Drift

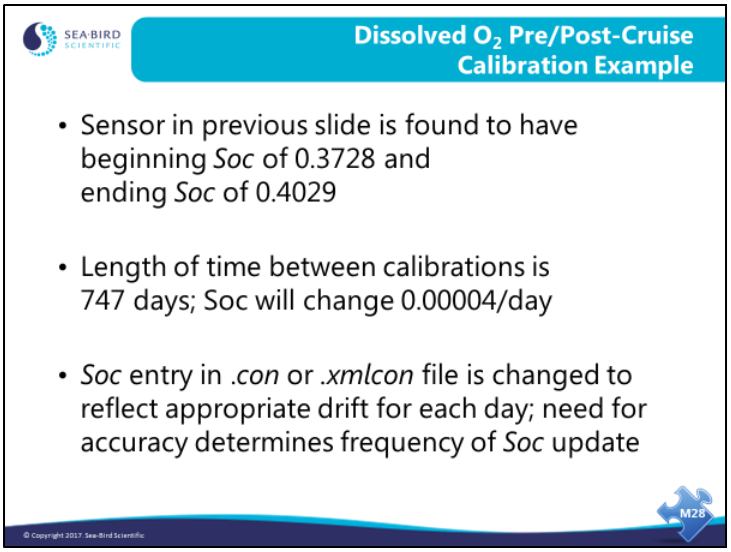


Oxygen: Using Calibrations to Improve your Data



Dissolved oxygen sensors are expected to drift in a similar manner to conductivity. For fouling and to a lesser degree chemical reasons, they lose sensitivity over time. The equation for calculating oxygen concentration from sensor output has a slope term, *Soc*, and an offset term, *Voffset*. It is expected that *Soc* will slowly increase with time, indicating a decrease in sensitivity. *Voffset* remains stable, though may vary slightly between calibrations due to fitting all coefficients to calibration bath data.

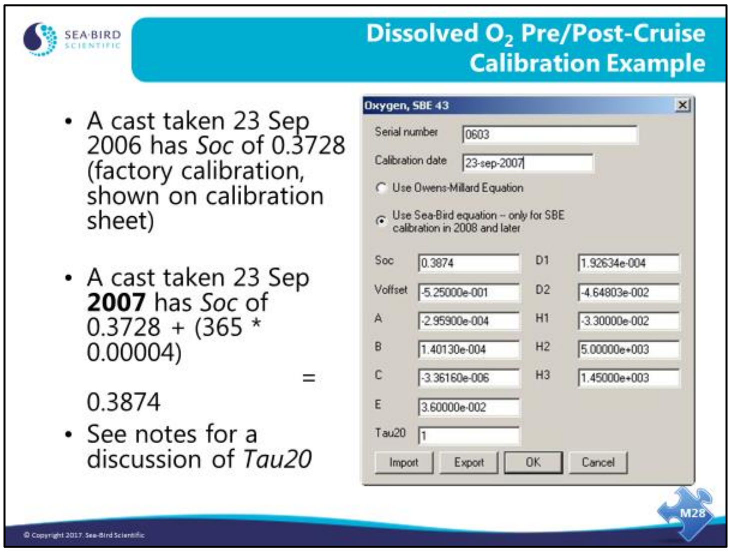
Oxygen: Using Calibrations to Improve your Data *(continued)*



The factory oxygen sensor calibration sheet provides the value for *Soc* (that portion of the calibration sheet is not shown in the previous slide).

Note that this strategy of drift correction assumes a uniform, linear change over the time between calibrations. A sensor that is handled carefully and cleaned periodically will exhibit this behavior. However, episodic fouling of the membrane by either oils or bacteria can result in a drift more exponential in nature.

Oxygen: Using Calibrations to Improve your Data *(continued)*



A word about Tau: Tau, a term in the Sea-Bird equation, relates the change in oxygen sensor voltage to dissolved oxygen concentration.

$$Oxygen\,(ml/l) = \left\{ Soc * \left(V + Voffset + tau(T,P) * \frac{\partial V}{\partial t} \right) \right\} * Oxsol(T,S)$$

$$* \left(1.0 + A*T + B*T^2 + C*T^3\right) * e^{\left(\frac{E*P}{K}\right)}$$

The parts of this equation pertinent to this discussion are:

tau(T,P) = the term we are discussing = tau20 * exp (D1 * P + D2*[T - 20])

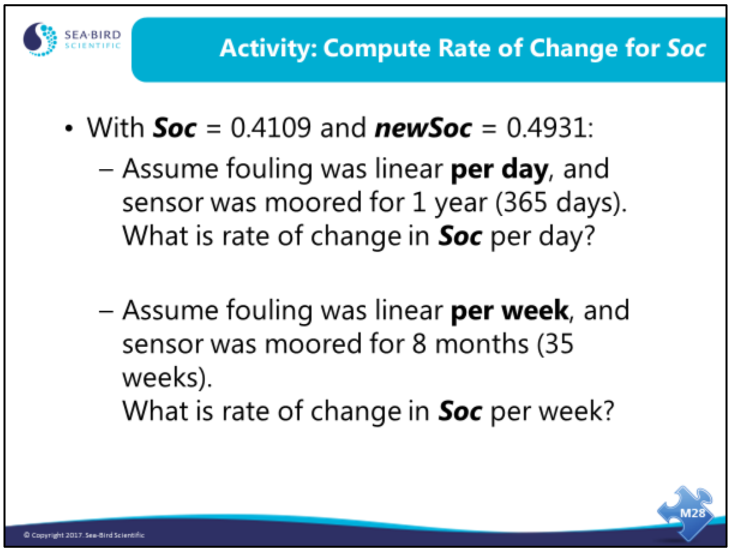
tau20 = sensor time constant tau(T,P) at 20 °C, 1 atmosphere, 0 PSU; slope term in calculation of tau(T,P)

δV/δt = the change in voltage with time

Thus, tau(T,P) sharpens the response by adding a term dependent on the change of voltage with time. While this may be helpful in regions of large oxygen gradients, it also amplifies residual noise in the signal (especially in deep water). In some situations, the negative consequence overshadows the gains in signal responsiveness. If you feel that your sensor could benefit from sharpening, feel free to experiment with tau20.

To remove the derivative term totally, disable *Apply Tau correction* on the Miscellaneous tab in SBE Data Processing's Data Conversion or Derive module (and on the Miscellaneous tab in Seasave's Configure Inputs); this deletes the term [tau(T,P) * δV/δt] from the equation.

Activity: Compute Rate of Change for *Soc*



Activity: Compute Rate of Change for *Soc*