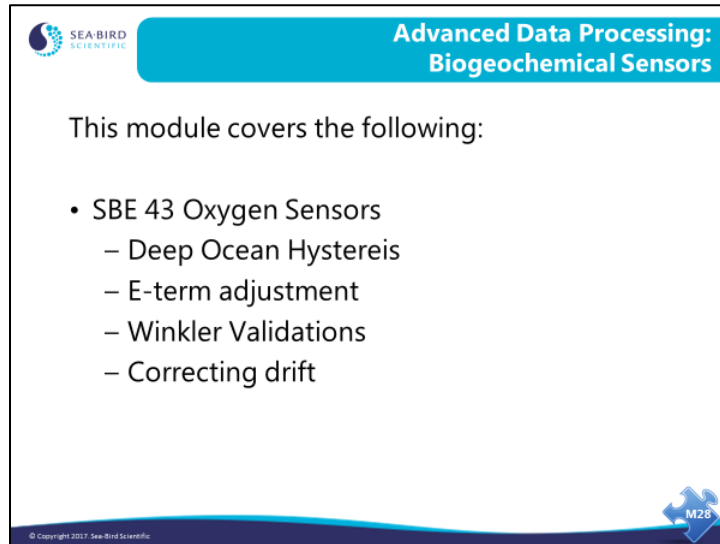




Advanced Data Processing:  
Biogeochemical Sensors  
Sea-Bird Scientific University Module 28



## Overview



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### Advanced Data Processing: Biogeochemical Sensors

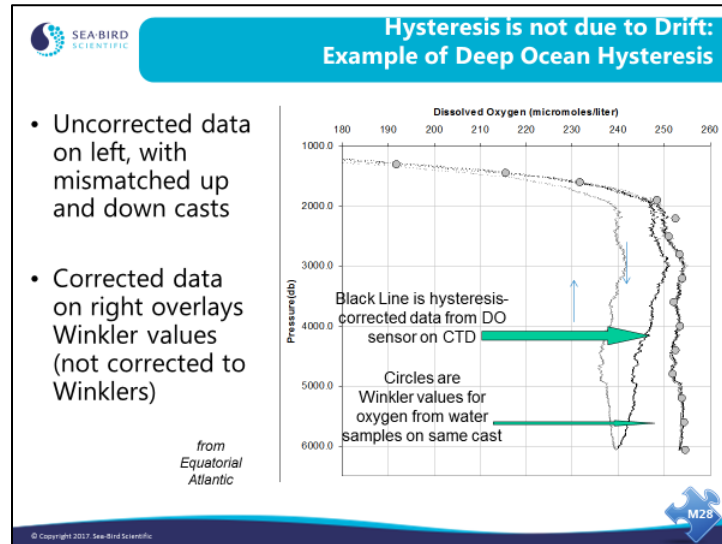
This module covers the following:

- SBE 43 Oxygen Sensors
  - Deep Ocean Hystereis
  - E-term adjustment
  - Winkler Validations
  - Correcting drift

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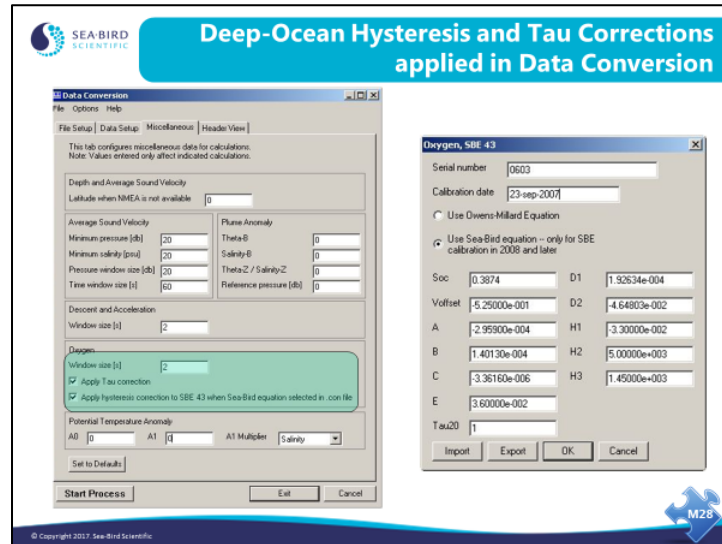
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## Dissolved Oxygen Deep Ocean Hysteresis



- 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 ( $\pm 1 \mu\text{mol/kg}$ ), 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.

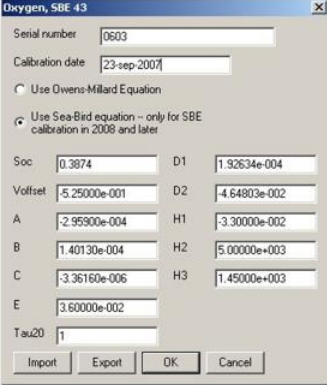
**Be sure to perform hysteresis corrections to deep profile data being used to modify the Soc term.**

## Dissolved Oxygen Deep Ocean Hysteresis (*continued*)



### Dissolved O<sub>2</sub> Deep-Ocean Hysteresis

- H1, H2, and H3 coefficients correct for deep-ocean hysteresis (> 1000 m depth)
- Consistent between sensors
  - Coefficients generally do not differ or change with time
- Deep-ocean hysteresis correction is enabled/disabled on Miscellaneous tab in Data Conversion (SBE Data Processing) and/or Miscellaneous tab in Configure Inputs (Seasave)




**Oxygen, SBE 43**

Serial number: 0603  
 Calibration date: 23-sep-2007

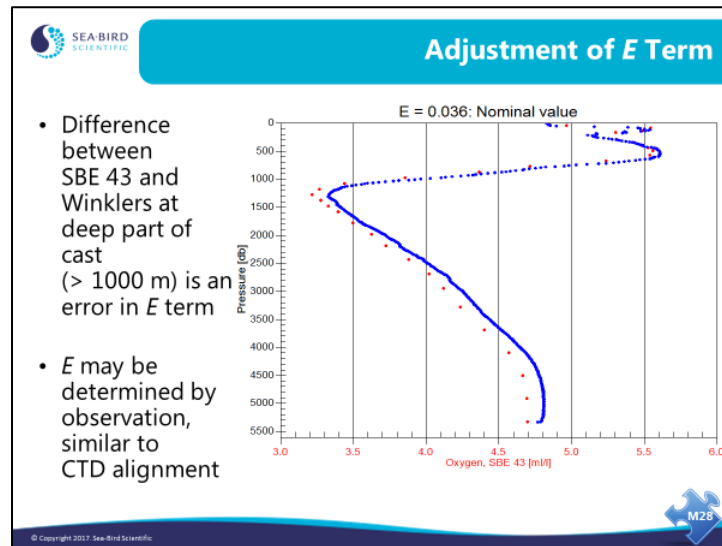
Use Ovens-Millard Equation  
 Use Sea-Bird equation - only for SBE calibration in 2008 and later

Soc	0.3874	D1	1.92634e-004
Voffset	-5.25000e-001	D2	-4.64803e-002
A	-2.95900e-004	H1	-3.30000e-002
B	1.40130e-004	H2	5.00000e+003
C	-3.36160e-006	H3	1.45000e+003
E	3.60000e-002		
Tau20	1		

Buttons: Import, Export, OK, Cancel

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## 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*)

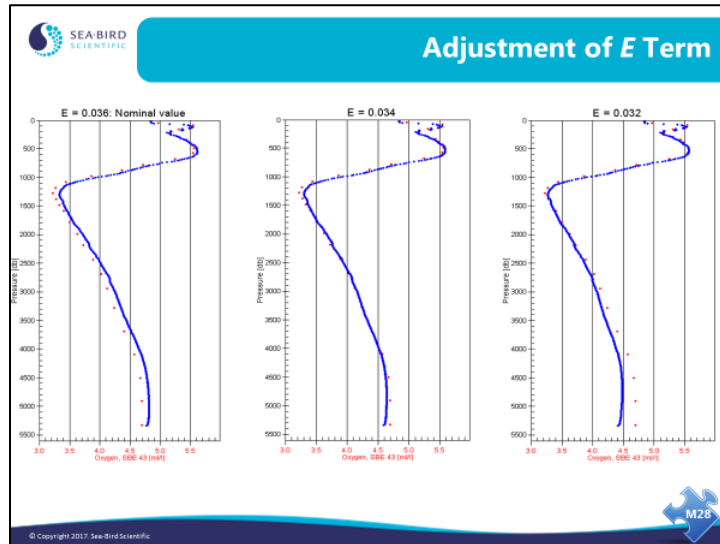
The screenshot displays two windows from the Sea-Bird Scientific software. The main window is titled "Adjustment of E Term" and is for an "Oxygen, SBE 43" sensor. It contains the following fields and values:

- Serial number: 1129
- Calibration date: 27-Mar-2007
- Use Owens-Millard Equation:
- Use Sea-Bird equation - only for SBE calibration in 2008 and later:
- Soc: 4.79000e-001, D1: 1.92640e-004
- Voffset: -5.25600e-001, D2: -4.17760e-002
- A: -3.90900e-004, H1: -3.30000e-002
- B: 1.90000e-004, H2: 5.00000e+003
- C: -2.00000e-006, H3: 1.45000e+003
- E: 3.60000e-002
- Tau20: 1.00000e+000

Buttons at the bottom include "Import", "Export", "OK", and "Cancel".

The background window, titled "Configuration for the SBE 911plus/917plus CTD", shows a list of channels with "Oxygen SBE 43" selected in channel 8. Other channels include Temperature, Conductivity, Pressure, and various voltage inputs.


## 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 at Deployment and Recovery, and Routinely During Deployment**




- Validation in the field allows calibration adjustments and data correction without removing instruments
  - Water samples for Winkler Titrations are required
  - CTD-DO profile adjacent to mooring


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## Validation in the Field (*continued*)

 Validation: Use Appropriate and Quality-Controlled References

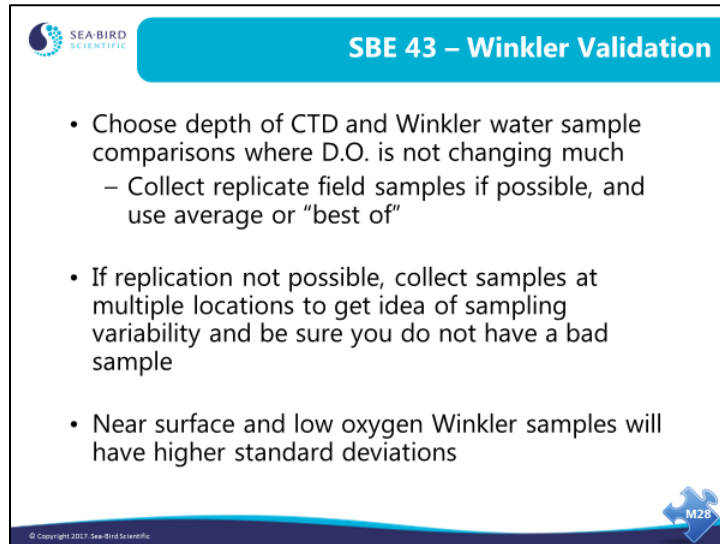


- Winkler water samples
  - Requires some spin-up but **is a standard**
  - Replicate samples, blanks and QA/QC
    - Thiosulfate standardization
- Reference Sensors
  - Requires they are clean and calibrated
  - Use reference sensor correctly
    - respect response time (profiling)
  - Do not use less accurate sensor



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## Field Calibrations – Dissolved Oxygen



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### SBE 43 – Winkler Validation

- Choose depth of CTD and Winkler water sample comparisons where D.O. is not changing much
  - Collect replicate field samples if possible, and use average or “best of”
- If replication not possible, collect samples at multiple locations to get idea of sampling variability and be sure you do not have a bad sample
- Near surface and low oxygen Winkler samples will have higher standard deviations

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### 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*)

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### SBE 43 – Winkler Validation

- Run Data Conversion on CTD data
- Remove derivative term from computation of oxygen concentration
  - Disable *Apply Tau correction* on Miscellaneous tab in Data Conversion
- Apply Hysteresis correction in Data Conversion
- Output SBE 43 Oxygen concentration values in units use to compare with Winkler values

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- The tau (T,P) \*  $\delta V/\delta t$  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) \*  $\delta V/\delta t$  from the equation.

## Field Calibrations – Dissolved Oxygen (*continued*)

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### SBE 43 – Winkler Validation

- Compare a Winkler value and corresponding SBE 43 value (corrected for deep-ocean hysteresis in Data Conversion)
- Compute correction ratio = (Winkler value / SBE 43 Value)
- Multiply factory **Soc** by ratio to get **newSoc**
- Replace factory **Soc** in .con or .xmlcon file with **newSoc**
- Process data from time of correction forward with **newSoc**
- **OR** multiply *SBE 43 output values by correction ratio to get slope corrected data*

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

## Field Calibrations – Dissolved Oxygen (*continued*)

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### SBE 43 – Winkler Validation

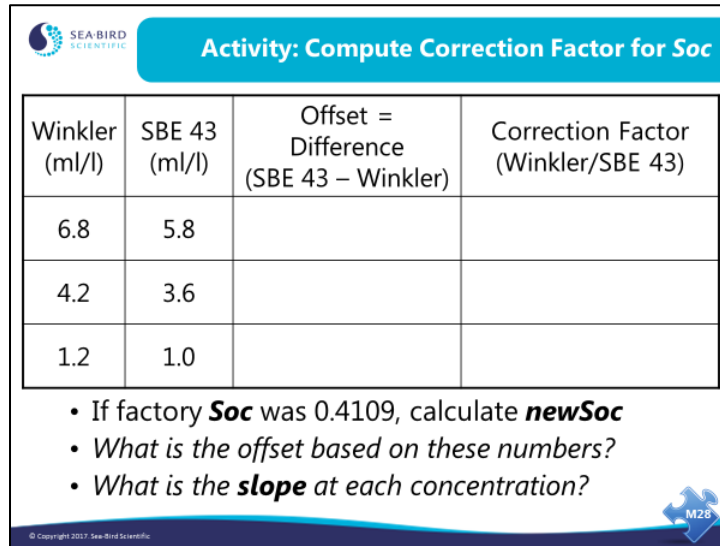
- Correction ratio is typically greater than 1.0 if sensor is fouling (drifting low of correct)
- If current correction factor is greater than 15 – 20% of original factory *Soc*, **and** if this cannot be reduced by cleaning, sensor may need to be returned to factory for service

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### 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



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Activity: Compute Correction Factor for Soc

Winkler (ml/l)	SBE 43 (ml/l)	Offset = Difference (SBE 43 – Winkler)	Correction Factor (Winkler/SBE 43)
6.8	5.8		
4.2	3.6		
1.2	1.0		


- If factory **Soc** was 0.4109, calculate **newSoc**
- *What is the offset based on these numbers?*
- *What is the **slope** at each concentration?*

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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



Answer Key

Winkler (ml/l)	SBE 43 (ml/l)	Difference (SBE 43 – Winkler)	Correction Factor (Winkler/ SBE 43)
6.8	5.8	-1.0	1.17
4.2	3.6	-0.6	1.17
1.2	1.0	-0.2	1.20


- If factory **Soc** was 0.4109, calculate **newSoc**.
  - Average Correction Factor = 1.18  
newSoc = 0.4109 \* 1.18 = 0.4849
- **What is the offset based on these numbers?**
  - No offset correction, since the difference depends on concentration
- **What is the slope at each concentration?**
  - This is equal to the correction factor shown above.

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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




**Similar technique:  
SBE 63 Optical oxygen sensor**

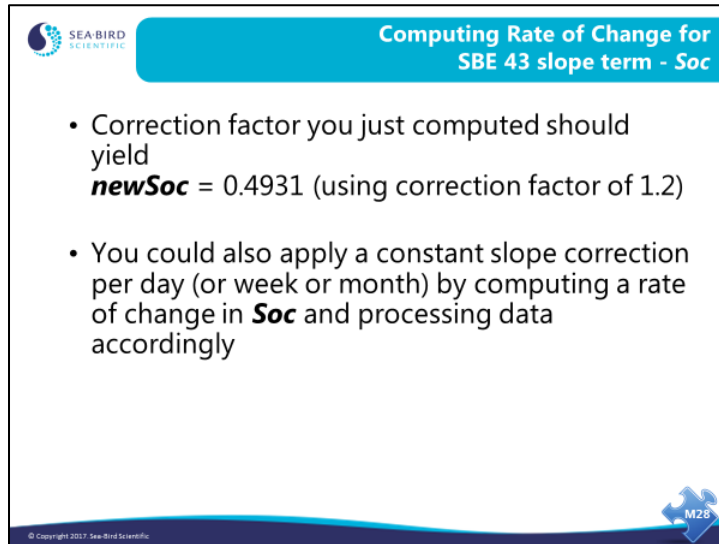
- Calculate Correction Ratio from appropriate Winkler sample or clean reference sample comparison:
  - Correction Ratio = Reference/Mooring
  - So, if deployed sensor = 5.31 ml/L, and Winkler = 5.40 ml/L, then Correction Ratio =  $5.4/5.31 = 1.017$
- Apply Correction Ratio by multiplying to final oxygen data.  
Example:

Time	Sensor DO, mL/L	Corrected Sensor DO, mL/L
1/29/14 11:15	5.31	5.40
1/29/14 11:30	5.35	5.44
1/29/14 11:45	5.54	5.63

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## Computing Rate of Change for Soc



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Computing Rate of Change for SBE 43 slope term - Soc

- Correction factor you just computed should yield  
**newSoc** = 0.4931 (using correction factor of 1.2)
- You could also apply a constant slope correction per day (or week or month) by computing a rate of change in **Soc** and processing data accordingly

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## Correcting Oxygen Data for Drift



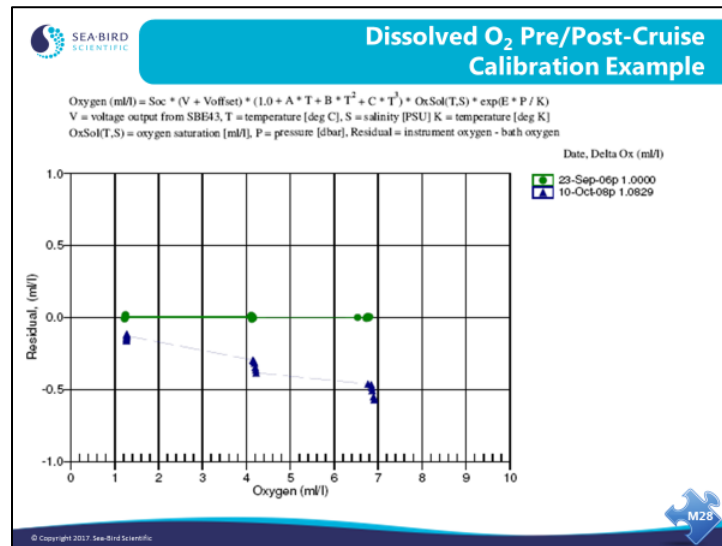
### Correcting Oxygen Data for Drift

- Can either use:
  - Pre/Post-Cruise Calibrations
  - Validation samples
- Because normal sensor calibrations change only in slope, you **only need 1 sample to validate**
  - It is always better to have a few samples for reference standard deviation or to get an average slope correction
- Compute correction only if necessary
  - Example: reference samples indicate the sensor is drifting beyond sensor accuracy specification (2%)

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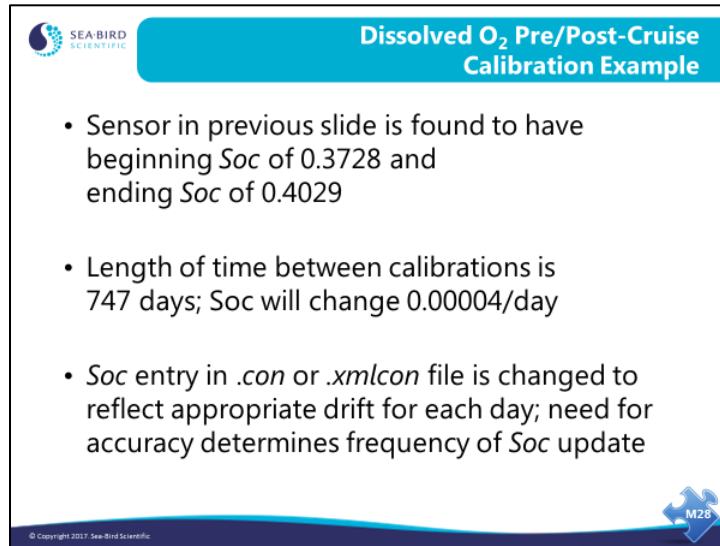


## Oxygen: Using Calibrations to Improve your Data



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 slide features a blue header with the SEA-BIRD SCIENTIFIC logo on the left and the title 'Dissolved O<sub>2</sub> Pre/Post-Cruise Calibration Example' on the right. The main content consists of three bullet points. At the bottom right, there is a blue puzzle piece icon with 'M28' written on it. At the bottom left, there is a small copyright notice: '© Copyright 2017 Sea-Bird Scientific'.

- Sensor in previous slide is found to have beginning Soc of 0.3728 and ending Soc of 0.4029
- Length of time between calibrations is 747 days; Soc will change 0.00004/day
- Soc entry in `.con` or `.xmlcon` file is changed to reflect appropriate drift for each day; need for accuracy determines frequency of Soc update

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)



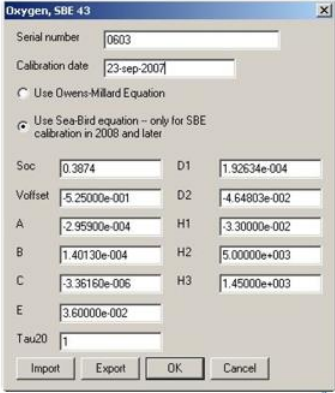
**Dissolved O<sub>2</sub> Pre/Post-Cruise Calibration Example**


- A cast taken 23 Sep 2006 has Soc of 0.3728 (factory calibration, shown on calibration sheet)
- A cast taken 23 Sep **2007** has Soc of  $0.3728 + (365 * 0.00004)$

=

0.3874

- See notes for a discussion of *Tau20*





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

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

The parts of this equation pertinent to this discussion are:

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

$\text{tau20}$  = sensor time constant  $\text{tau}(T, P)$  at 20 °C, 1 atmosphere, 0 PSU;

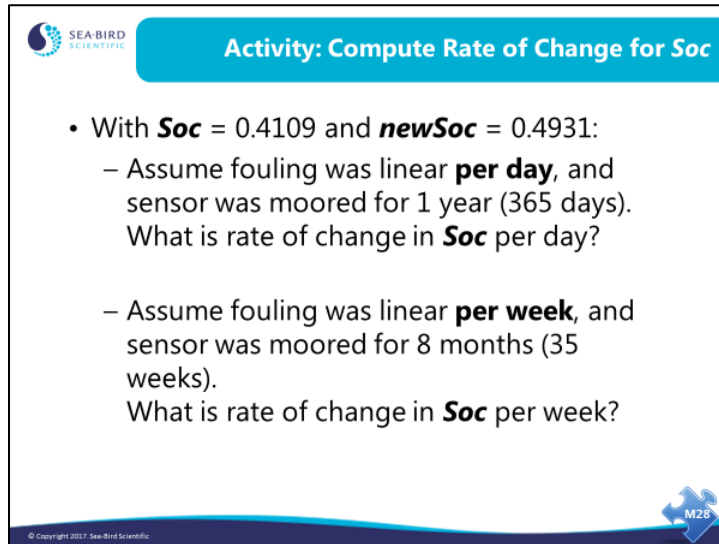
slope term in calculation of  $\text{tau}(T, P)$


$\delta V / \delta t$  = the change in voltage with time

Thus,  $\text{tau}(T, P)$  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  $\text{tau20}$ .


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  $[\text{tau}(T, P) * \delta V / \delta t]$  from the equation.

## Activity: Compute Rate of Change for Soc




 **Activity: Compute Rate of Change for Soc**

- With **Soc** = 0.4109 and **newSoc** = 0.4931:
  - Assume fouling was linear **per day**, and sensor was moored for 1 year (365 days). What is rate of change in **Soc** per day?
  - Assume fouling was linear **per week**, and sensor was moored for 8 months (35 weeks). What is rate of change in **Soc** per week?


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## Activity: Compute Rate of Change for Soc



**Answer Key:**  
**Compute Rate of Change for Soc**

- With **Soc** = 0.4109 and **newSoc** = 0.4849:
  - What is rate of change in **Soc** per day over 1 year?  
Rate of change =  $(\mathbf{NewSoc} - \mathbf{Soc}) / \# \text{ of days}$   
=  $(0.4931 - 0.4109) / 365 = 0.0002252/\text{day}$
  
  - What is rate of change in **Soc** per week over 8 months?  
– Rate of change =  $(\mathbf{NewSoc} - \mathbf{Soc}) / \# \text{ of weeks}$   
=  $(0.4931 - 0.4109) / 35 = 0.00023/\text{week}$



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