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**Dissolved oxygen data tests**

**IOL/Malina cruise 0902**

## Contents

## Problematic.

Dissolved oxygen data recorded by a SBE43 sensor connected with a Sea-Bird 911*plus* CTD probe are characterized by a systematic delay with respect to pressure. The main causes of this artefact are: 1) a long time constant of the oxygen sensor which is temperature inversely dependant; 2) a time transit of the water through the pipe (*SEASOFT-Win32 User's Manual*).

A better alignment of oxygen data in relation to pressure can also reduce hysteresis (hysteresis is a delay in the evolution of a physical or chemical parameter) of the oxygen profile. The alignment of the oxygen sensor data relative to pressure data allows to ensure that the calculations of dissolved oxygen are made using measures from the same depth (or pressure).

Sea-Bird suggests testing the "ALIGN CTD" module of the "SBE Data Processing-Win 32" software with different values in order to reduce the misalignment of the dissolved oxygen data. When oxygen and pressure data are well aligned, temperature versus oxygen plots agree between down and up profiles. (See the Module9_AdvanceDataProcessing manual and the *SEASOFT-Win32 User's Manual*). Seabird suggests for a SBE43 sensor a typical value of +5 to +10 seconds for the SBE 9*plus* underwater unit.

At the same time, Sea-Bird provides two methods (see Application Note NO. 64-2 and Training Handouts Module 8 ) to improve dissolved oxygen sensor coefficient calibration if Winkler titration data are available.

## The SBE43 dissolved oxygen equation.

Since late 2008, Sea-Bird uses a new equation called "the Sea-Bird equation" in order to compute the oxygen concentrations from a SBE43 sensor. The Sea-Bird equation is derived from the traditional Owens-Millard equation. This equation includes parameters to correct hysteresis in long deep casts (see Application Note NO. 64-3).

Sea-Bird uses a slightly modified version of the algorithm by Owens and Millard (1985) in order to calculate dissolved oxygen concentrations from the voltage output.

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

Where :

- $\frac{\partial V}{\partial t}$ = time derivative of SBE43 output signal (volts/second).
- *T* = CTD temperature (℃).
- *K* = CTD temperature (°K).
- *S* = CTD salinity (psu).
- *V* = SBE 43 output voltage signal (volts).
- $Oxsol(T,S)$ = oxygen solubility (ml/l) from temperature and salinity values using Garcia and Gordon equation.
- *Soc*, *Voffset*, $tau(T,P)$, *A, B, C* and *E* are calibration coefficients:
  - $tau(T,P)$ = sensor time constant at temperature and pressure.
  - Soc = calibration slope.
  - Voffset = electronic offset.
  - *A*, *B* and *C* terms in a polynomial and *E* term in an exponential that compensate for changes in the sensor's sensitivity.

Remark: the previous Owens and Millard algorithm uses the Weiss equation to calculate the oxygen solubility.

Assuming that the platform has been motionless during one minute or more in order to avoid dynamic corrections, the time derivative term becomes 0 and the equation can be reduced to:

$$Oxygen(ml/l) = \{Soc * (V + Voffset)\} * \phi$$

Where:

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

$$\frac{Oxygen(ml/l)}{\phi} = \{Soc * (V + Voffset)\}$$

## Calculate the new coefficients.

In a first time, we used the methods from Sea-Bird to calculate the new calibration coefficients for the SBE 43 sensor. Sea-Bird proposes 2 methods to correct dissolved oxygen concentrations from field validations.

The case 1 re-computes **only** the calibration **slope term (*Soc*)** which changes mainly with the SBE43 sensor sensitivity drift (mainly due to sensor membrane fouling). The case 2 re-computes **both** the calibration **slope term (*Soc*)** and **the electronic offset term (*Voffset*)**. As the coefficient *Voffset* is an electronic constant very accurately determined at the factory, Sea-Bird recommends to use the Slop only case in most of the time. According to Sea-Bird, the case 2 would only be performed when a large field validations are available and when the comparison concentration range is also large (about 4 to 5 ml/L for example).

For the cruise 0902, there is a unique oxygen sensor sn 0240. There are 20 Winkler titrations sampled from 4 casts: **019**, **055, 097** and **137** (see figure 1).

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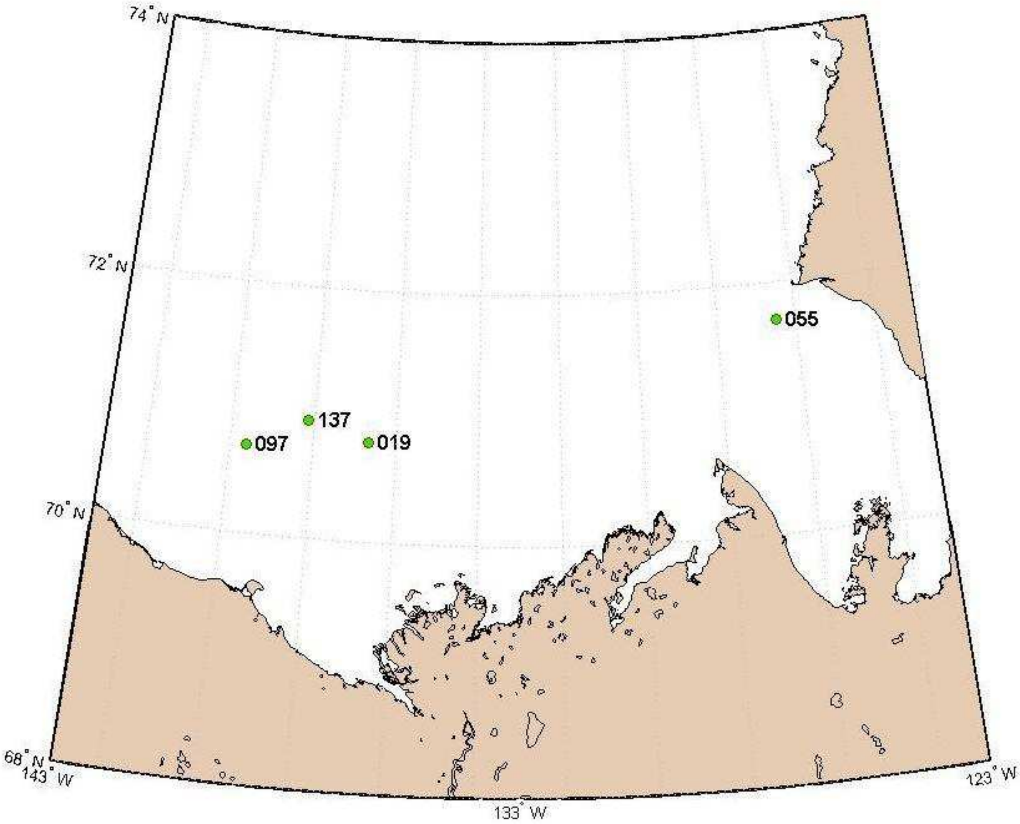
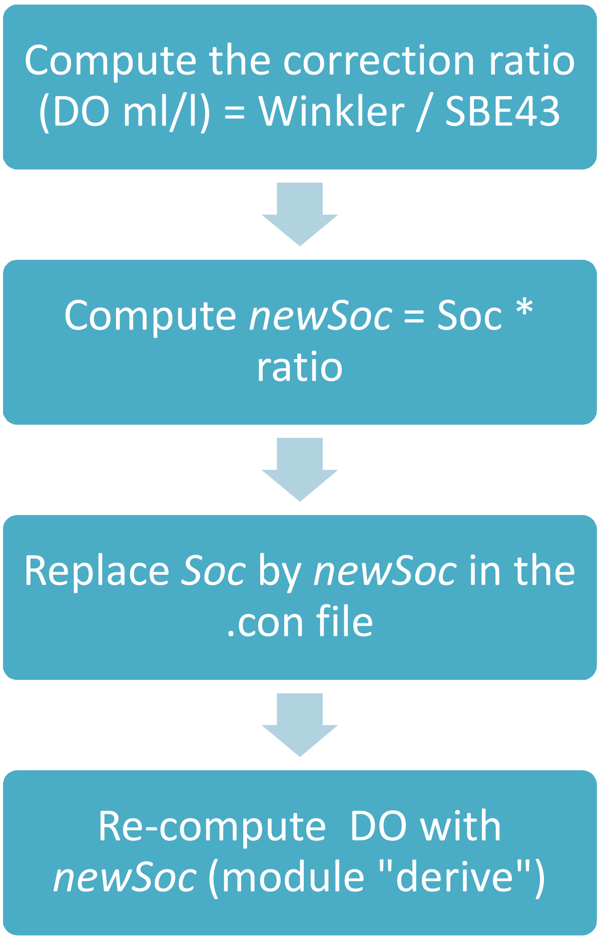



**Figure 1.** Water sample location map for calculating new coefficients for the sensor 0240.

## Case 1: *Soc* adjustment.




This approach could be done with only one reliable field validation but it would be much careful to perform the adjustment from a series of winkler data.

As the sensor's sensitivity decreases, the correction ratio is slightly greater than 1. A value close to 1.2 seems to be the limit of acceptability to get reliable data.

The results are presented in the figures 2. The standard deviation (residuals) before optimization is quite high 0.32 that could be an indication of a problem, either with the SBE43 sensor either with the Winkler titrations. The new Soc value allows to reduce the difference between the 2 set of data. The standard deviation is also better.

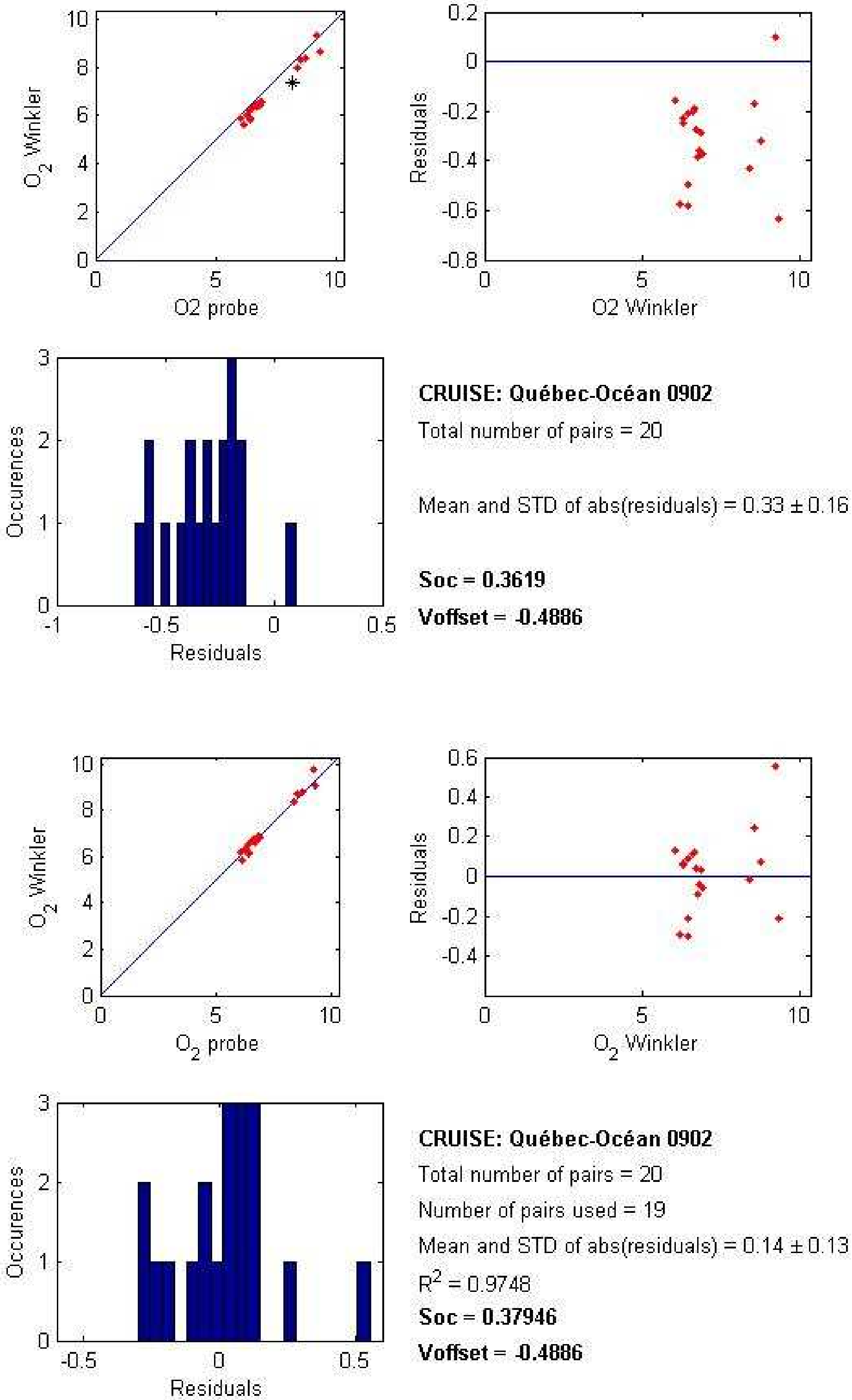
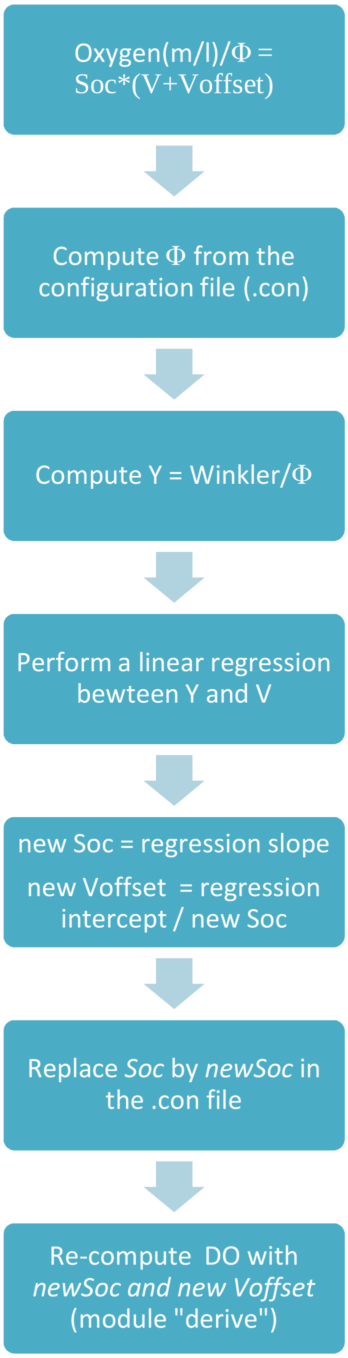



**Figure 2.** Comparison between Winkler titrations and CTD upcast data with the original (up) and the new (down) calibration coefficients for the SBE43 sensor sn 0240 using the Soc only approach.

## Case 2. *Soc* and *Voffset* adjustments.

The aim of this section is to compute new values for *Soc* and *Voffset*, the other coefficients should remain unchanged.



The results are presented in the figure 3. The figure shows that this approach gives similar results than the Soc only method. The standard deviation value is a little bit better. The new Voffset value is quite different than the original one. According to Sea-Bird, the electronic offset is very accurate and should not vary a lot. That is why, the "Soc only" option has been chosen in order to optimized the dissolved oxygen CTD data.

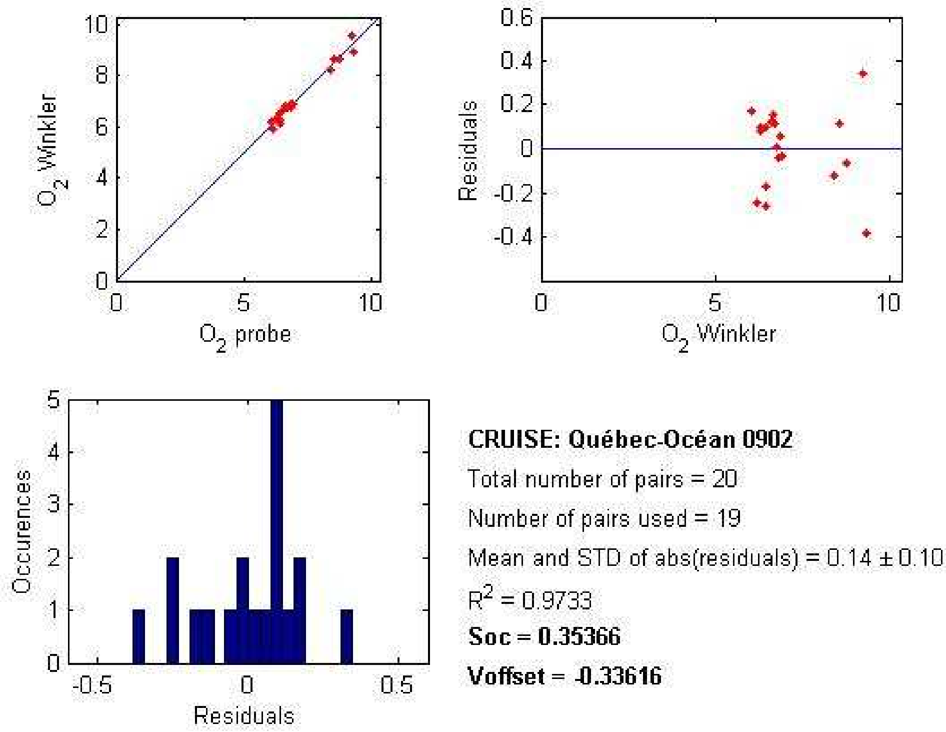
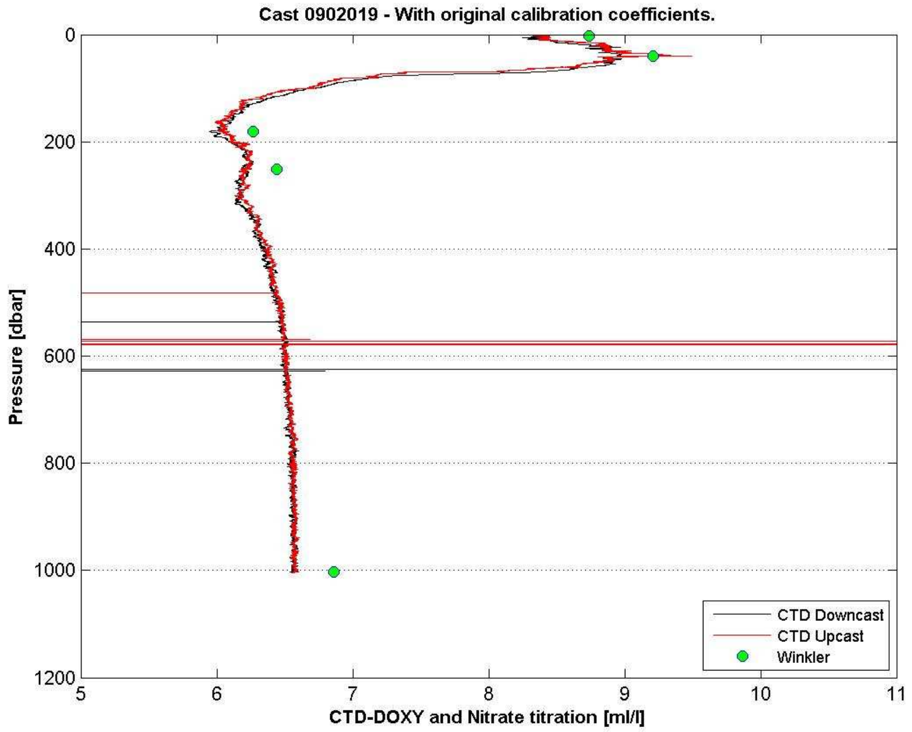



**Figure 3.** Comparison between Winkler titrations and CTD upcast data with the new calibration coefficients for the SBE43 sensor sn 0240 using the Soc and Voffset approach.

## Validation of the optimized coefficients.

The CTD dissolved oxygen data has been re-computed using the new Soc value from the "Soc only" approach. The figures 4 to 7 display the comparisons cast by cast whereas the figure 8 gathers the four descendant profiles.



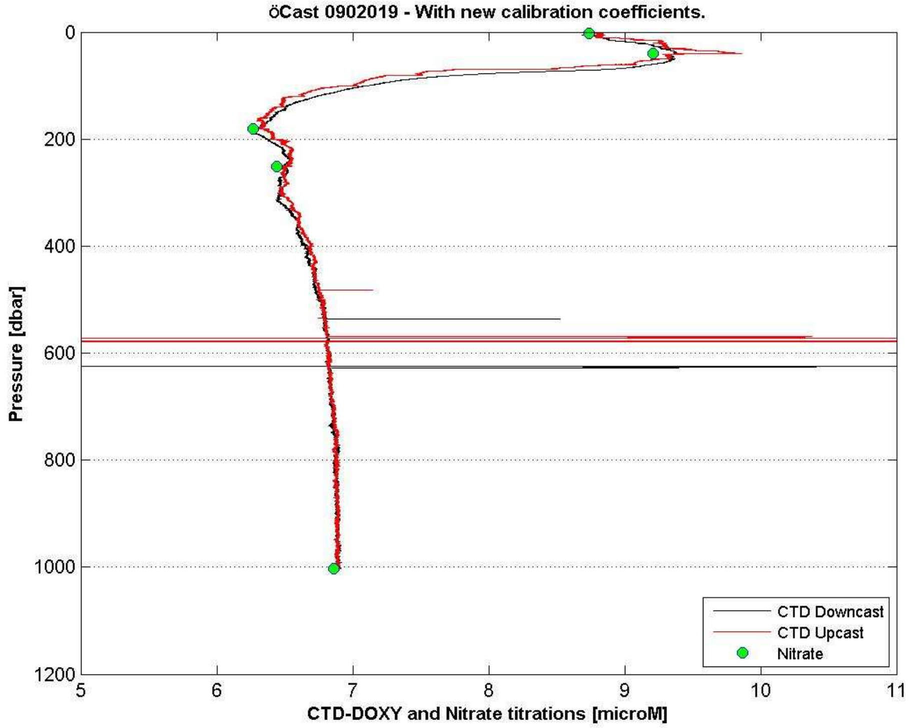
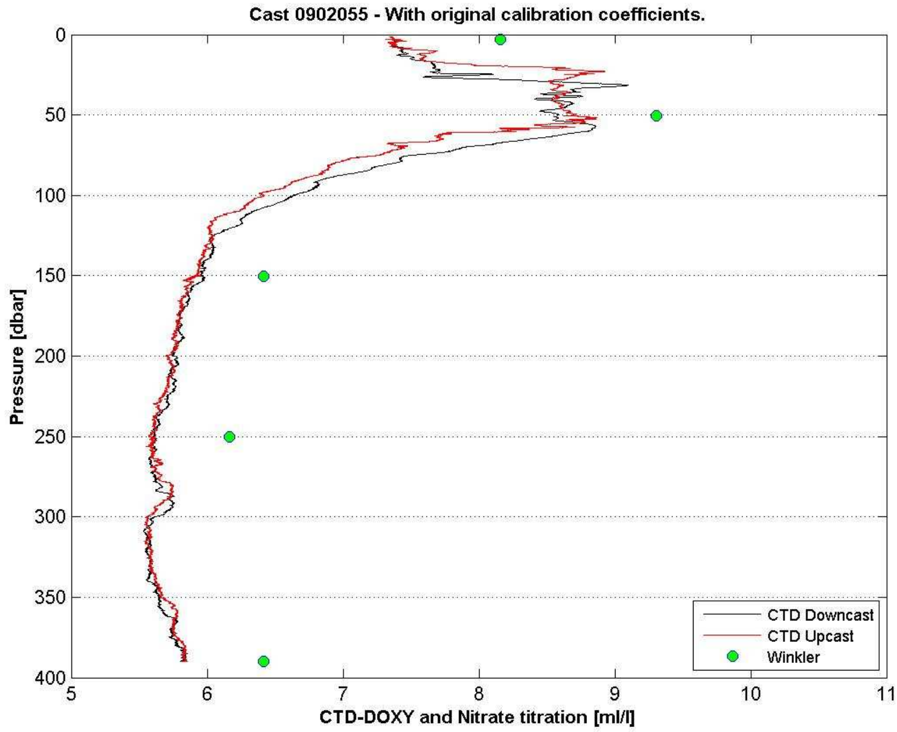




**Figure 4.** Comparison between CTD oxygen profiles computed with original and Winkler derived coefficients for the cast 019.



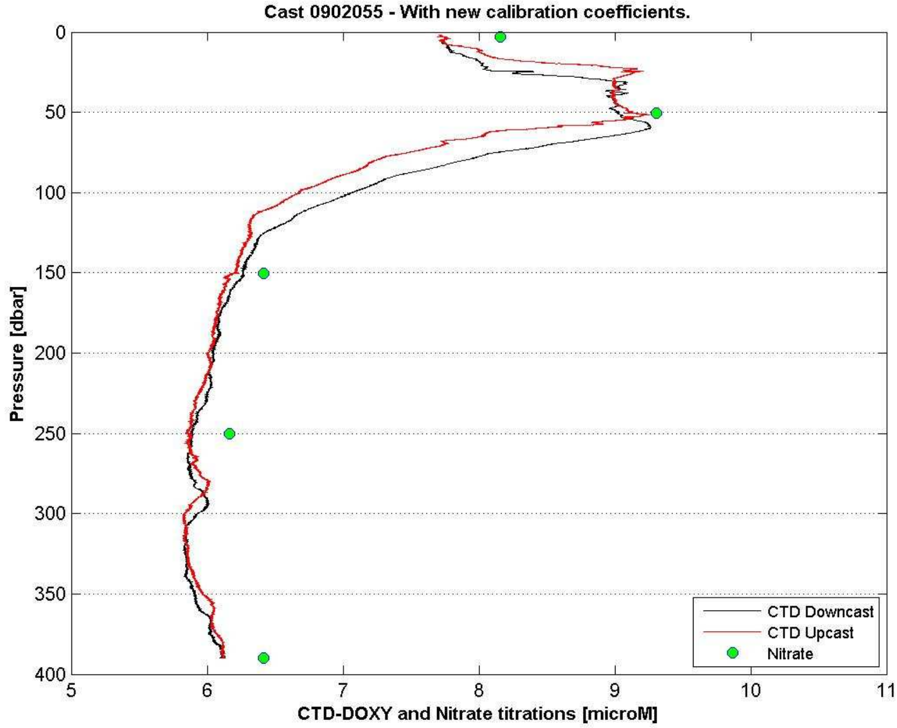




**Figure 5.** Comparison between CTD oxygen profiles computed with original and Winkler derived coefficients for the cast 055.

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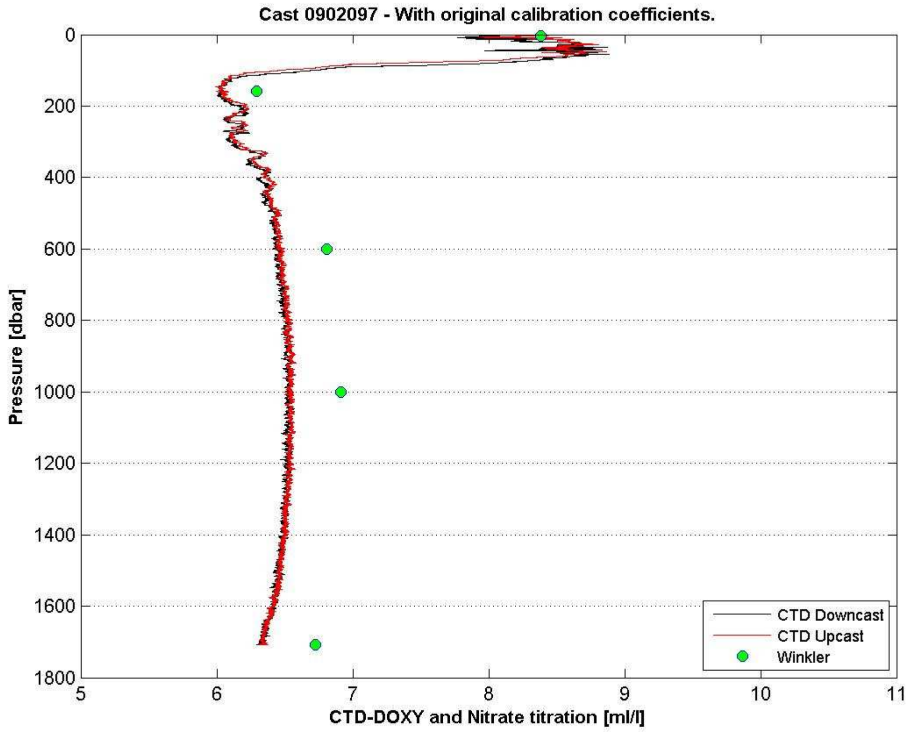


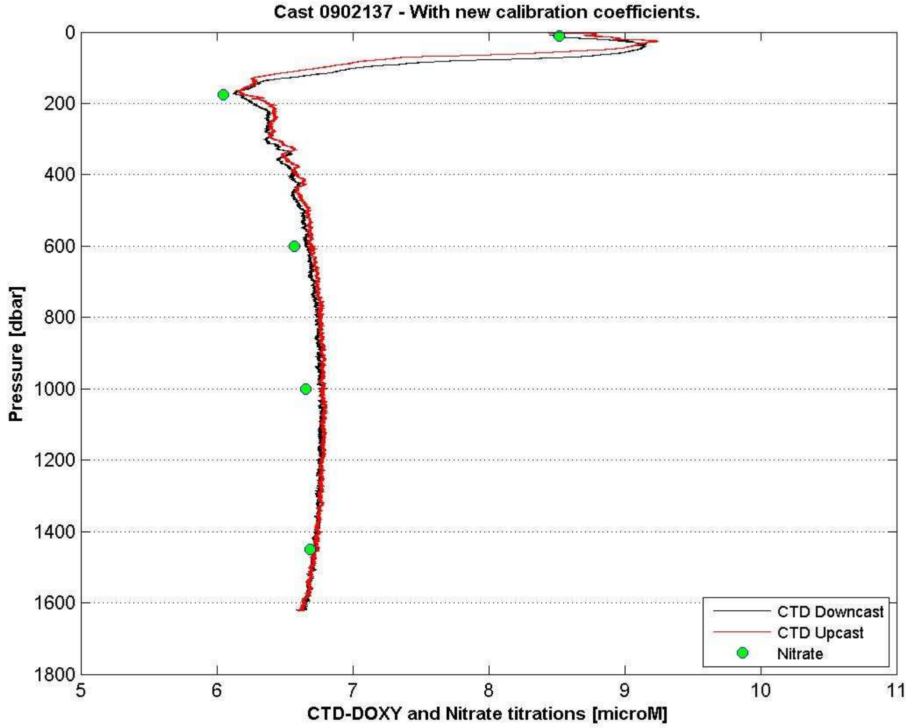
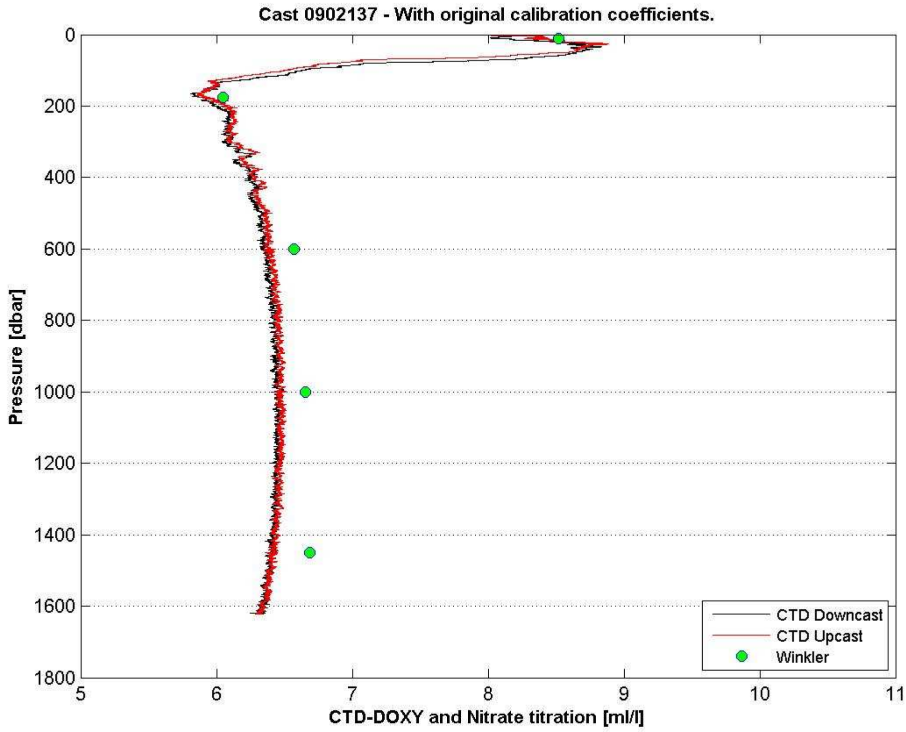




**Figure 6.** Comparison between CTD oxygen profiles computed with original and Winkler derived coefficients for the cast 137.



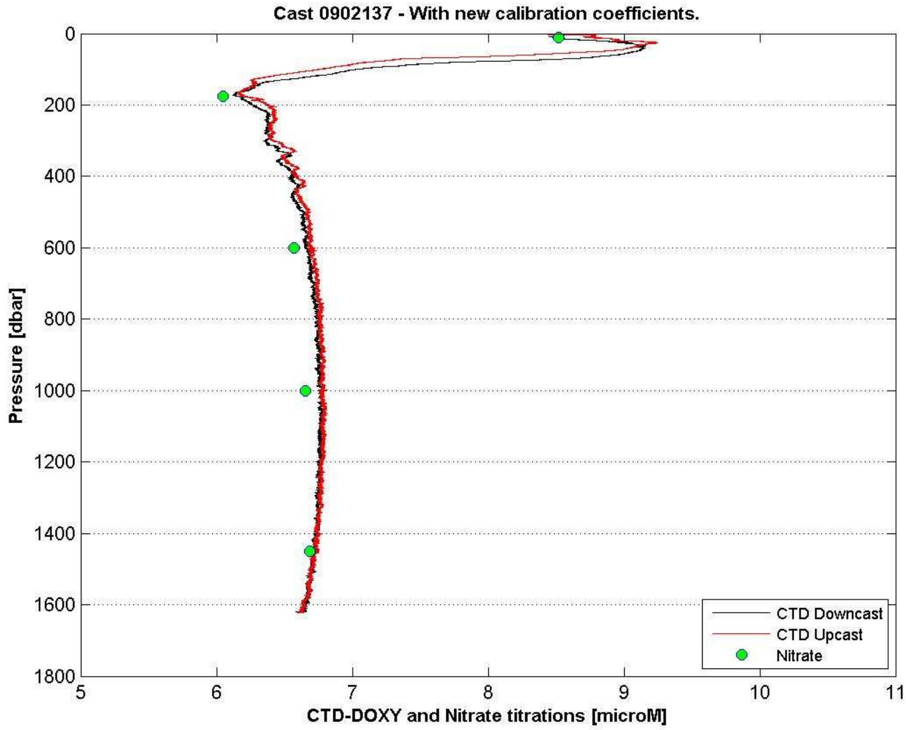
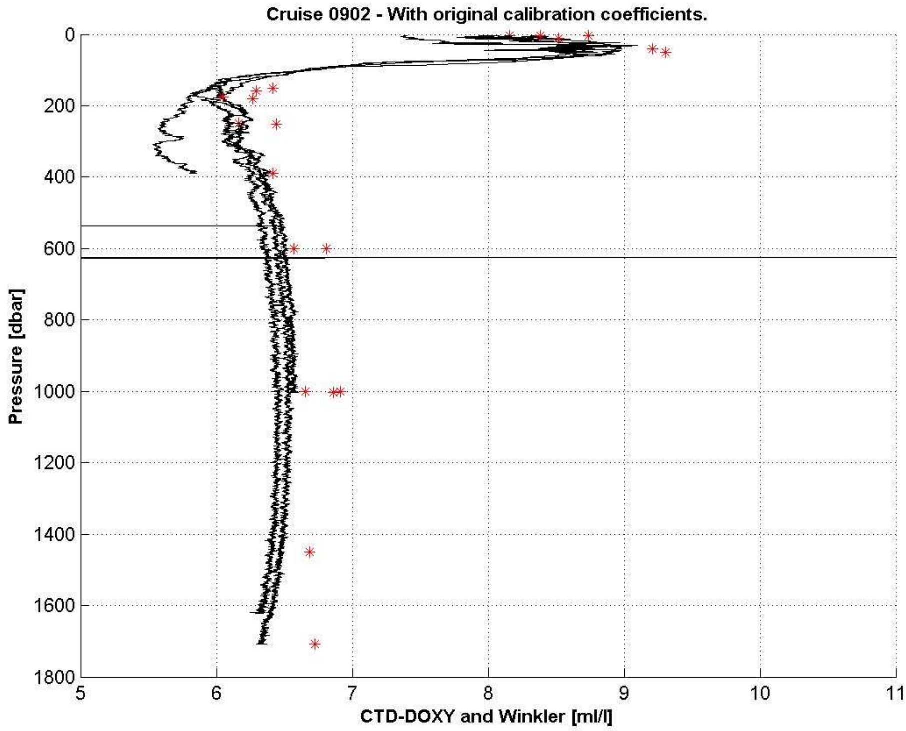




**Figure 7.** Comparison between CTD oxygen profiles computed with original and Winkler derived coefficients for the cast 075.



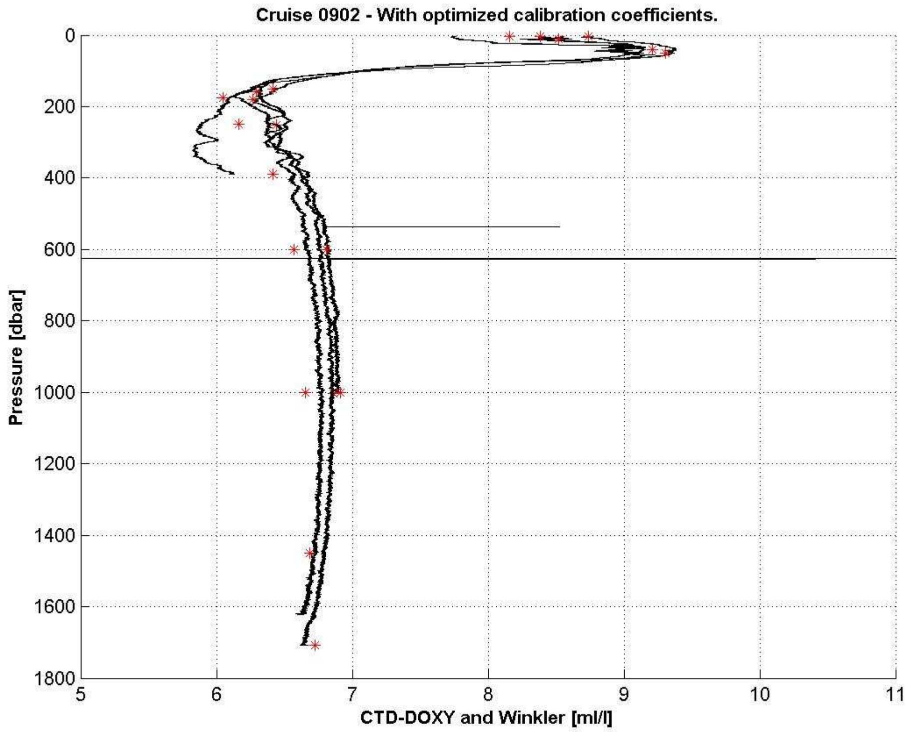




**Figure 8.** Comparison between downcast CTD oxygen profiles computed with original and Winkler derived coefficients for the 4 casts.

# Remove the O2 data misalignment.

The misalignment remove consists in testing different values through the “Align Ctd” module.

Afterwards, selected data were processed with the Sea-Bird software “SBE Data Processing-Win 32” with the following steps suggested by Sea-Bird manual.

(1) Data Conversion: “SBE 43 oxygen voltage”.
(2) Filter: pressure.
(3) Align Ctd: align selected data relative to pressure.
Oxygen Voltage, SBE 43 Advance = 0, 2, 3, 4, 5, 6, 7 and 8 seconds (for instance).
(4) Cell Thermal Mass: remove conductivity cell thermal mass effects.
(5) Derive: Oxygen, SBE 43 [ml/l], Window Size = 2 s (default value), new coefficients values.

Remark: as far as the original Owens-Millard equation is concerned, the parameter “Window Size” mentioned above has no impact on the dissolved oxygen concentration calculation as long as the coefficient *tau* is equalled to zero (see the complete equation in the Sea-Bird application note 64-2). Sea-Bird recommends to keep *tau* equalled to zero for the Owens-Millard equation.

(6) Bin Average: averages data
Bin Type ➔ decibars
Bin Size ➔ 0.2

The best alignment is evaluated by:

- Computing the correlation coefficient between the upcast and the downcast oxygen data.
- Plotting the downcast and upcast dissolved oxygen data versus the temperature data (see annex A).
- Plotting the downcast and upcast dissolved oxygen data versus the pressure data (see annex B).

The two last analyses are based on a visualisation checks and are therefore more subjective.

The following casts are added to increase the amount of data: **005**, **075, 120, 157, 177** and **190.** The results for the casts 005 and 019 could not be useful.

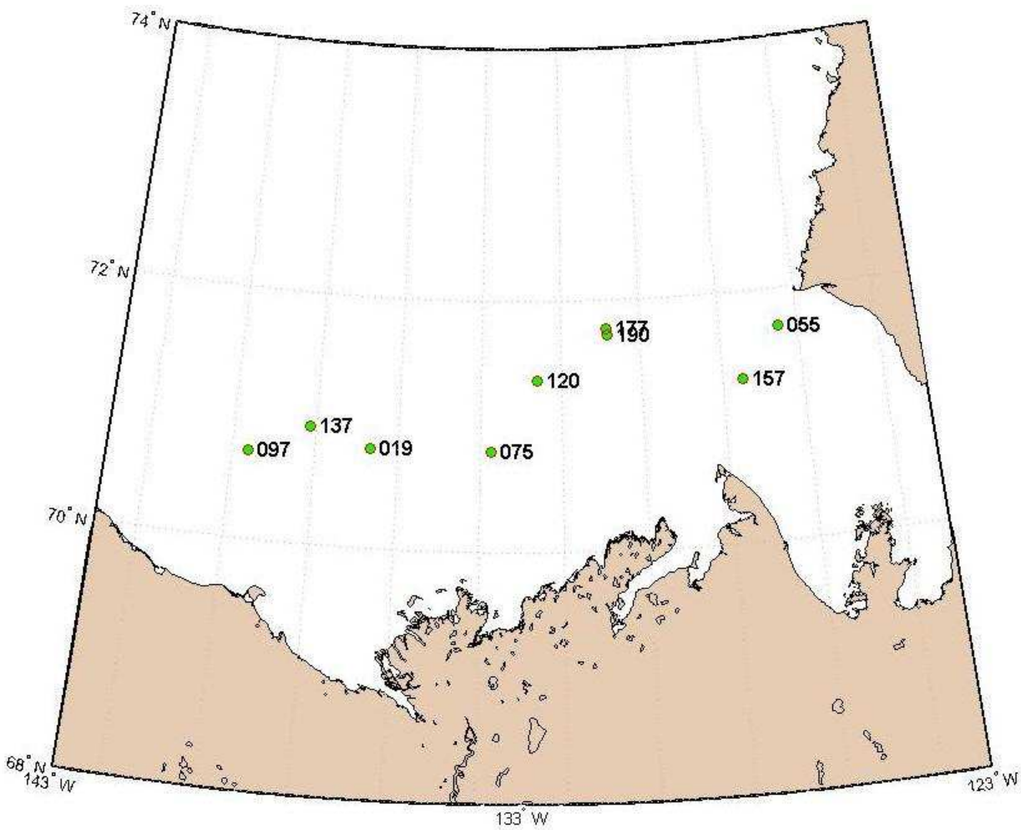



**Figure 9.** Cast location map for calculating oxygen alignment.

The best correlations (see table “Table 1”) are obtained for a correction of 7 and 8 seconds (2 and 5 times out of 7).

As far as the comparisons between oxygen versus temperature data are concerned, the best superposition is obtained mainly for correction of 4 to 6 seconds according to the casts. As far as oxygen versus pressure data are concerned, the best superposition is also obtained for a correction of 5 to 6 seconds for most of the casts.

**Table 1.** Best coefficient correlation calculated for the different alignments (0, 2, 3, 4, 5, 6, 7 and 8 seconds) for the sensor 0240.

| **Cast** | **Best Align Ctd [s]** | **$R^2$** |
|---|---|---|
| 0902055 | 8 | 0,992273 |
| 0902075 | 8 | 0,959022 |
| 0902097 | 7 | 0,988882 |
| 0902120 | 8 | 0,99101 |
| 0902137 | 8 | 0,997056 |
| 0902157 | 8 | 0,98754 |
| 0902177 | 7 | 0,984986 |

## Summary and conclusion

For this cruise, it has been decided to use the traditional Owens and Millar equation to calculate the oxygen concentration instead of the new optimized Sea-Bird equation.

The Winkler derived coefficients allow to reduce the difference between the Winkler and the CTD oxygen data. The statistics (mean and std between the Winker titrations and the SBE43 concentrations) are quite low that suggest a very good reliability of the Winkler.

As far as the alignment is concerned, the analysis shows that a correction of **5** seconds is a good compromise between all the casts and between the different depths for a specific cast.

# Annex A

**Evolution of dissolved oxygen versus temperature.**

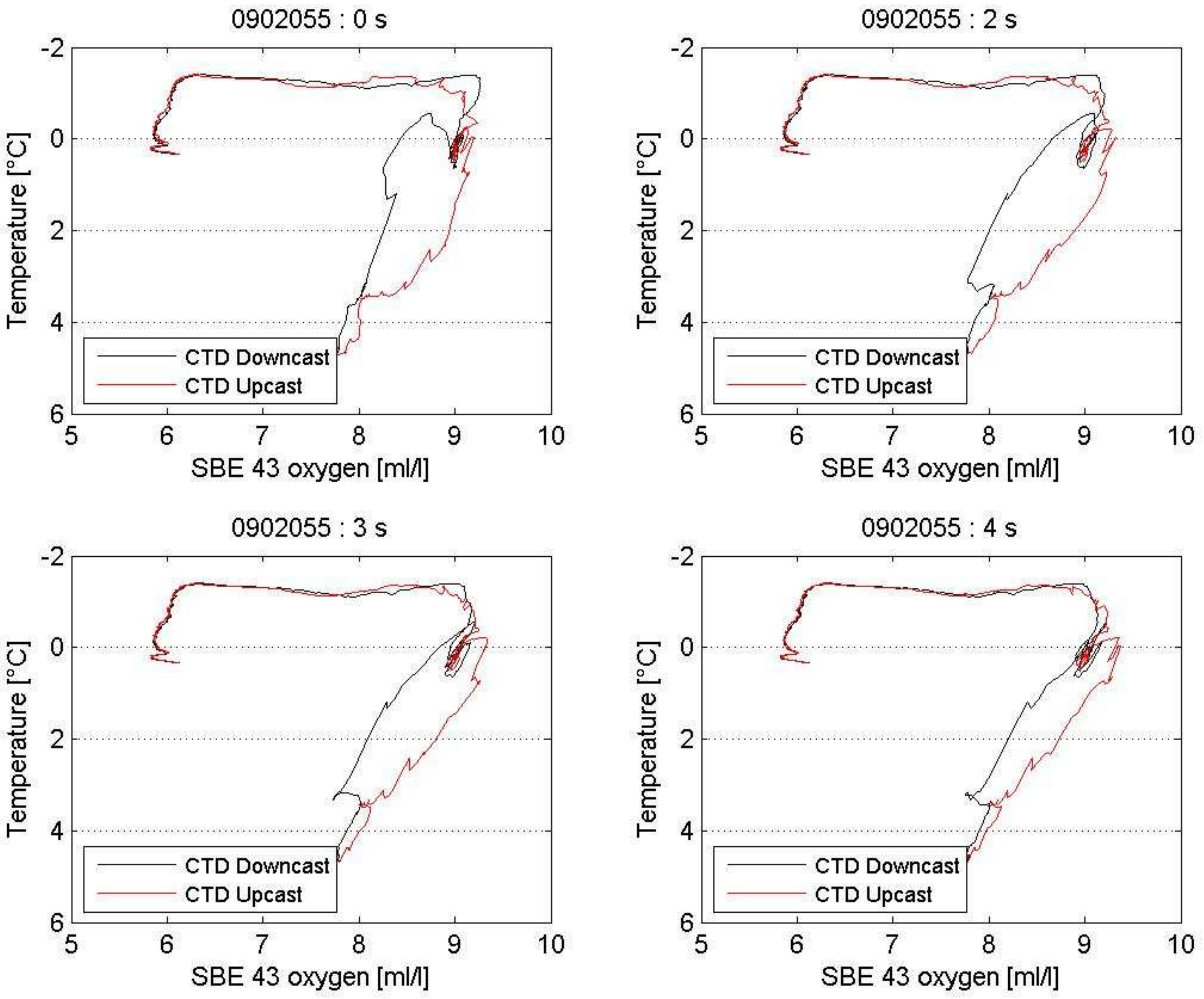



**Figure 10.** Evolution of dissolved oxygen versus temperature for the cast 055 (correction 0 to 4 seconds).

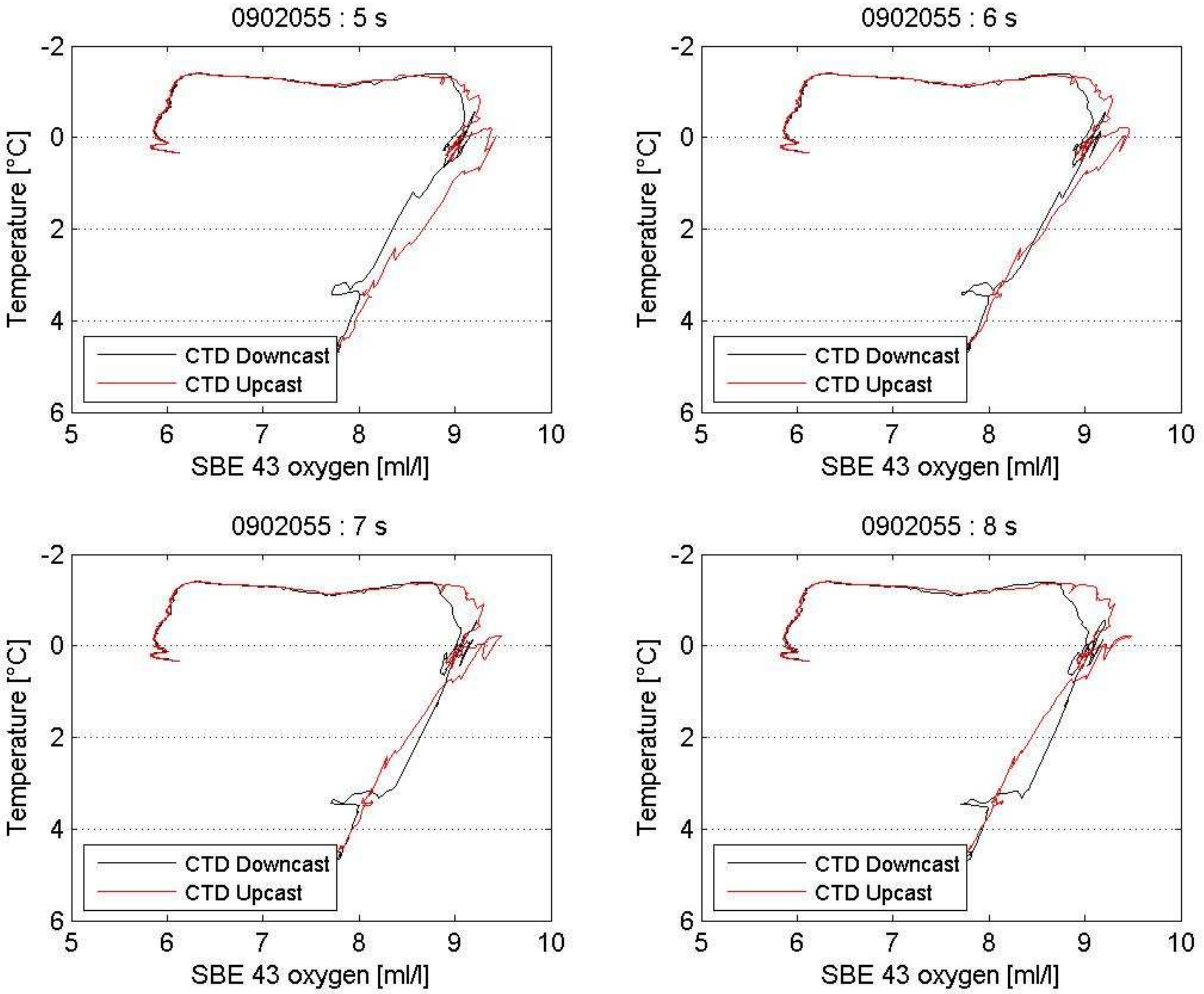



**Figure 11.** Evolution of dissolved oxygen versus temperature for the cast 055 (correction 5 to 8 seconds).

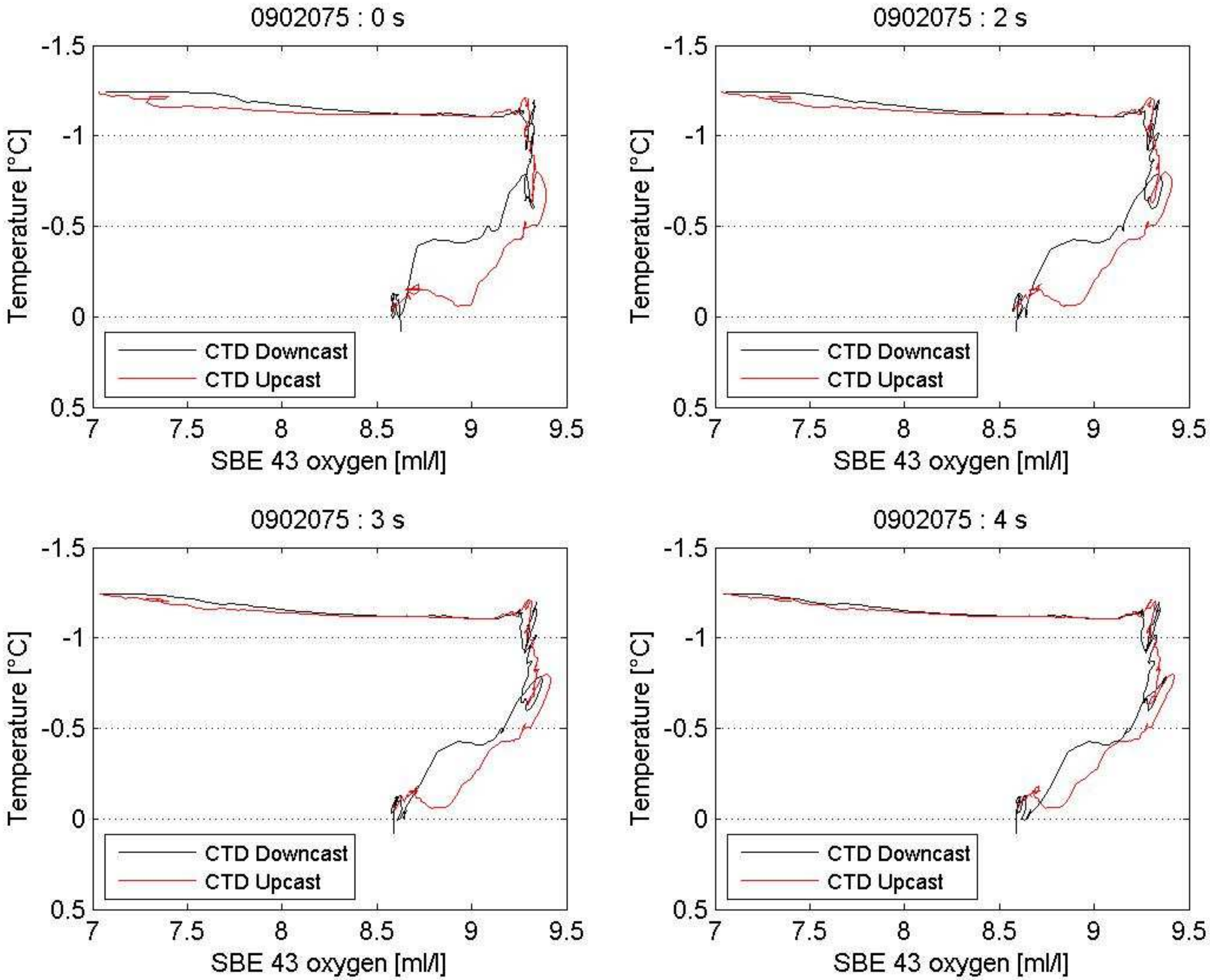



**Figure 12.** Evolution of dissolved oxygen versus temperature for the cast 075 (correction 0 to 4 seconds).

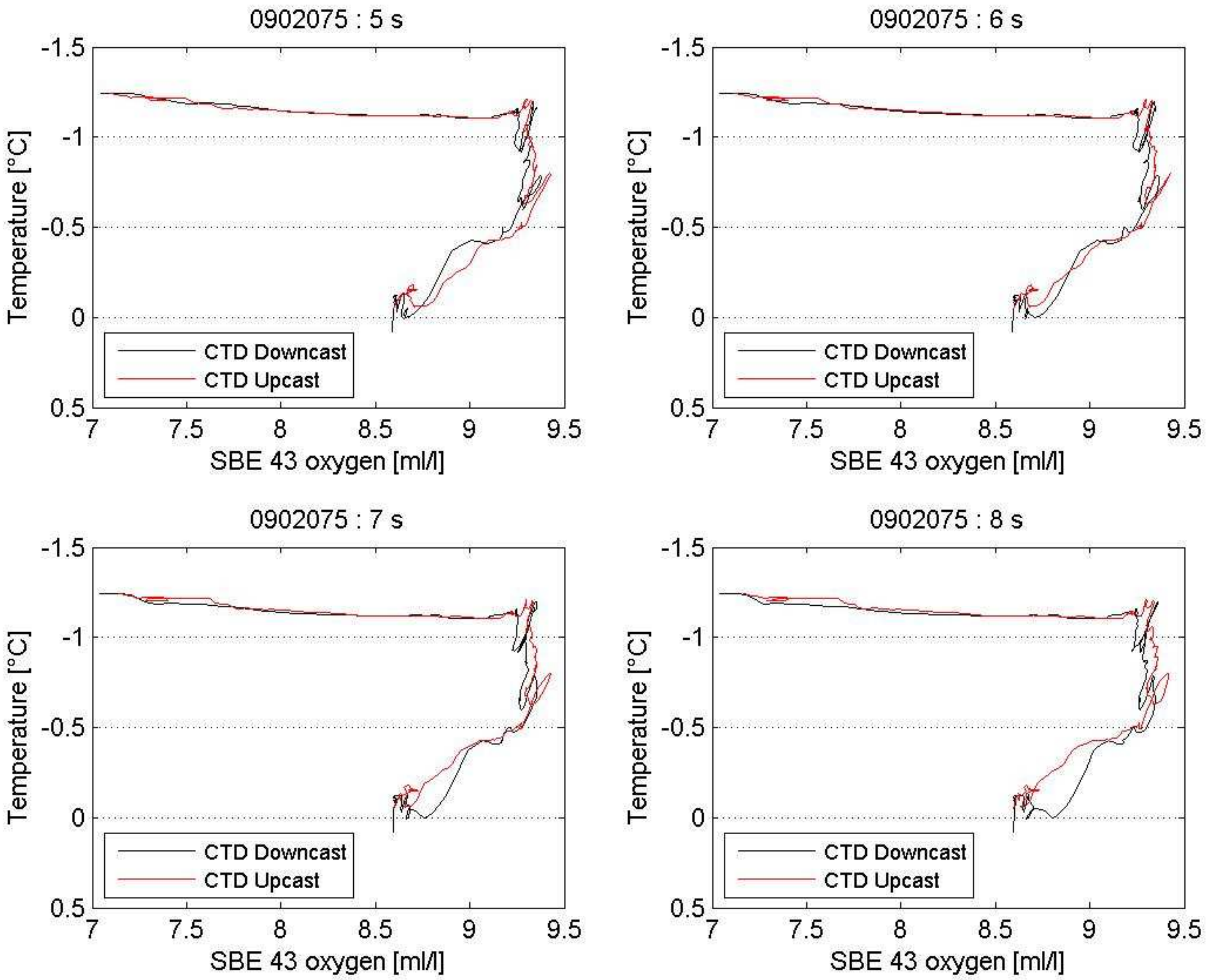



**Figure 13.** Evolution of dissolved oxygen versus temperature for the cast 075 (correction 5 to 8 seconds).

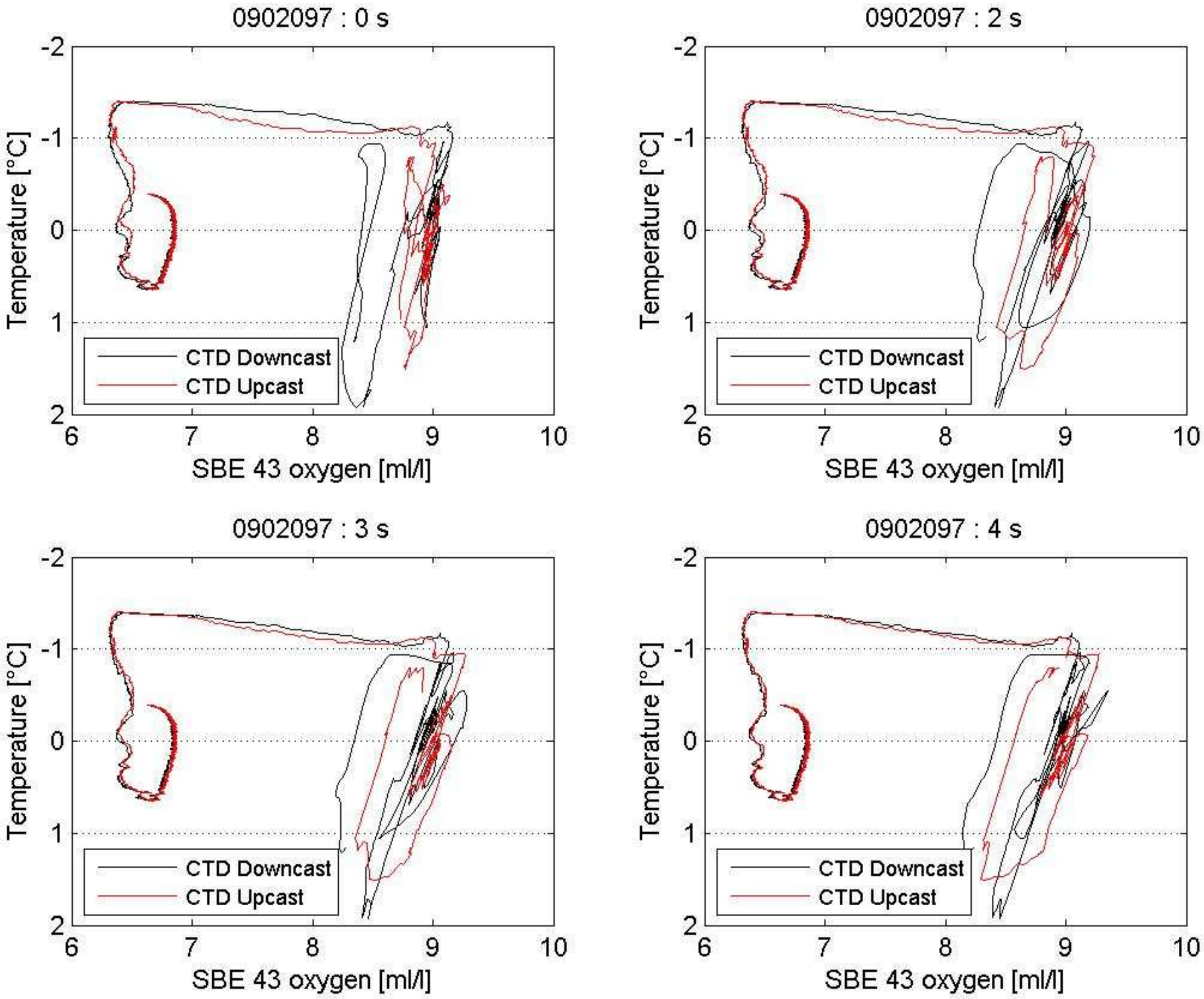



**Figure 14.** Evolution of dissolved oxygen versus temperature for the cast 097 (correction 0 to 4 seconds).

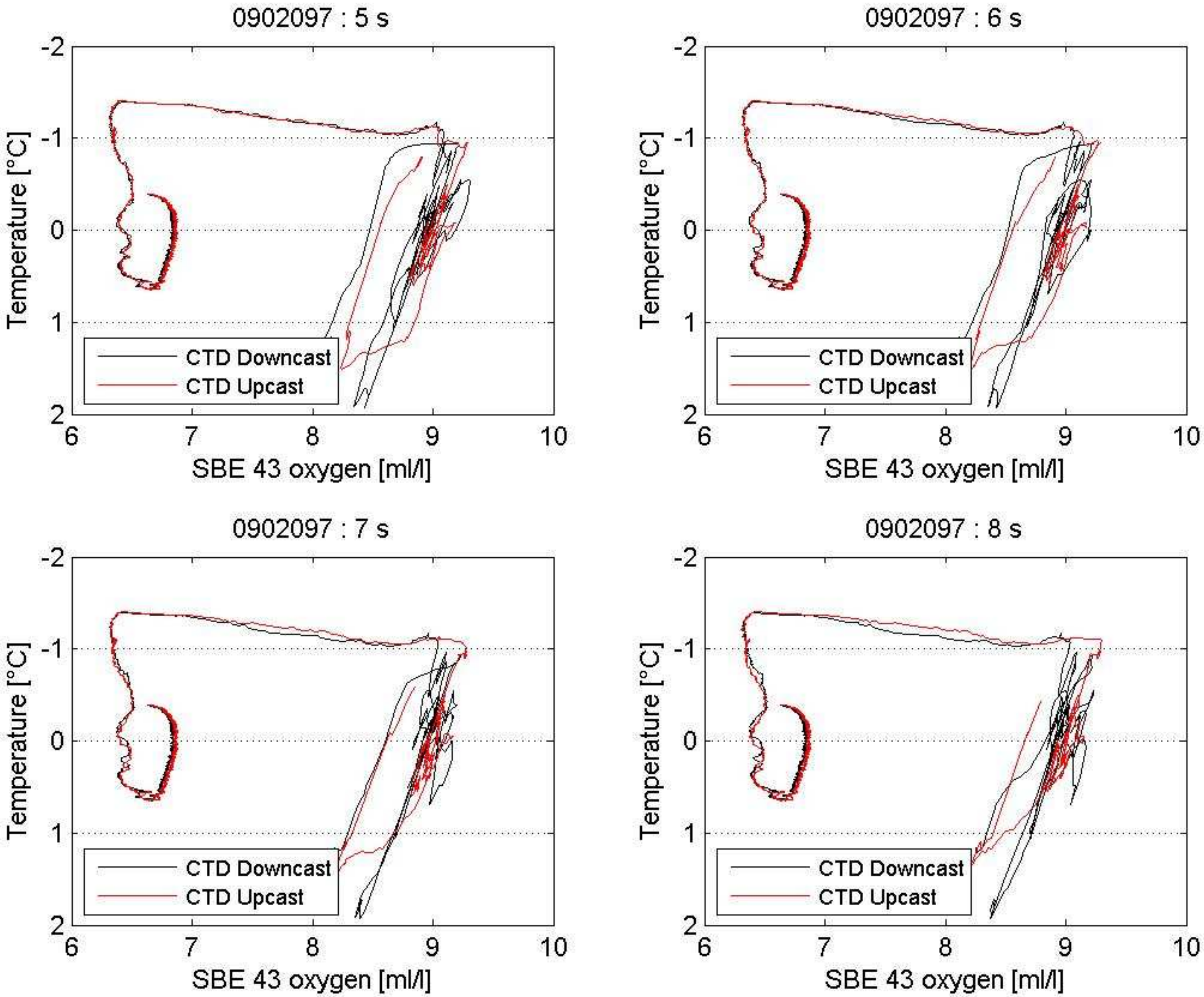



**Figure 15.** Evolution of dissolved oxygen versus temperature for the cast 097 (correction 5 to 8 seconds).

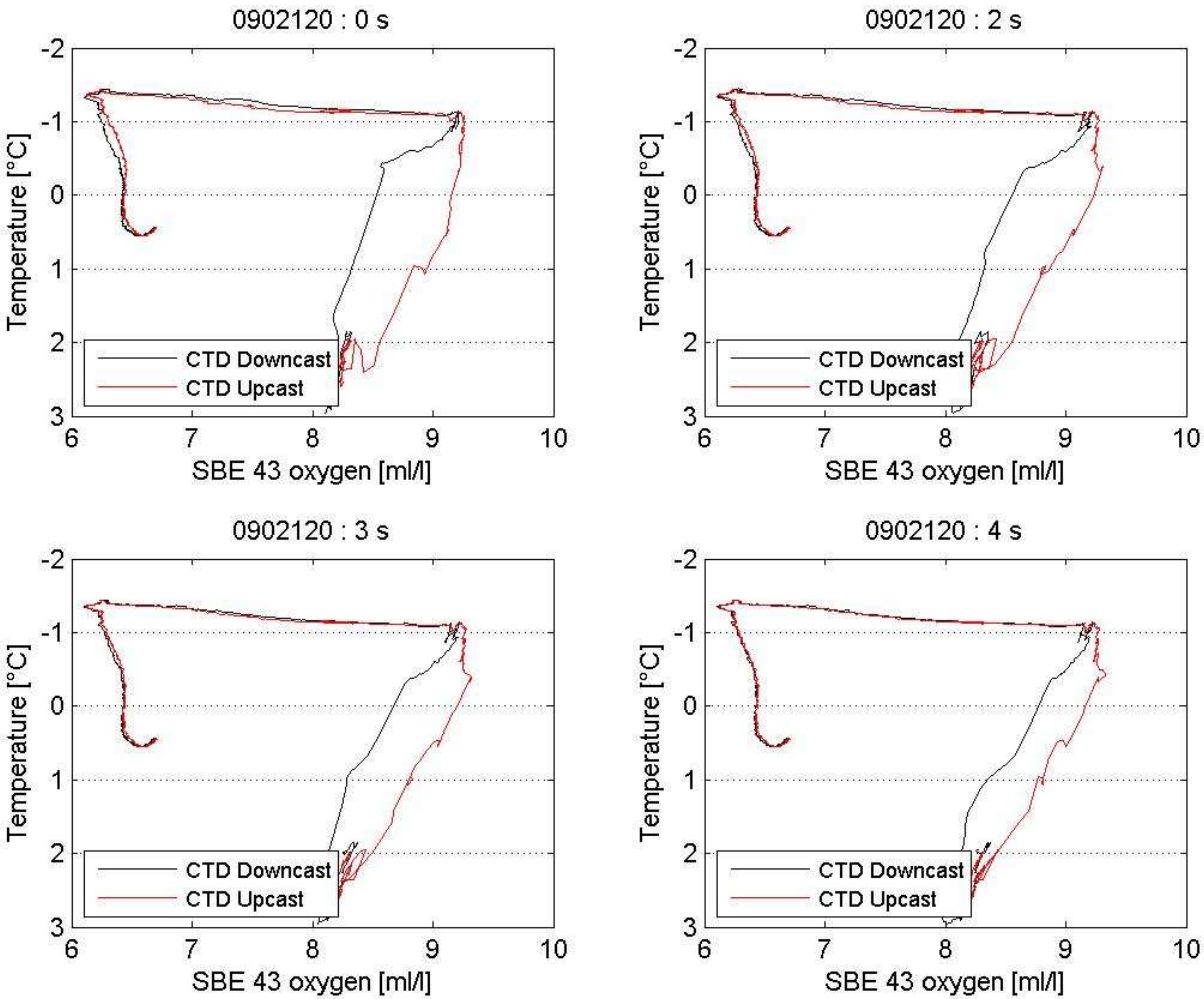



**Figure 16.** Evolution of dissolved oxygen versus temperature for the cast 120 (correction 0 to 4 seconds).

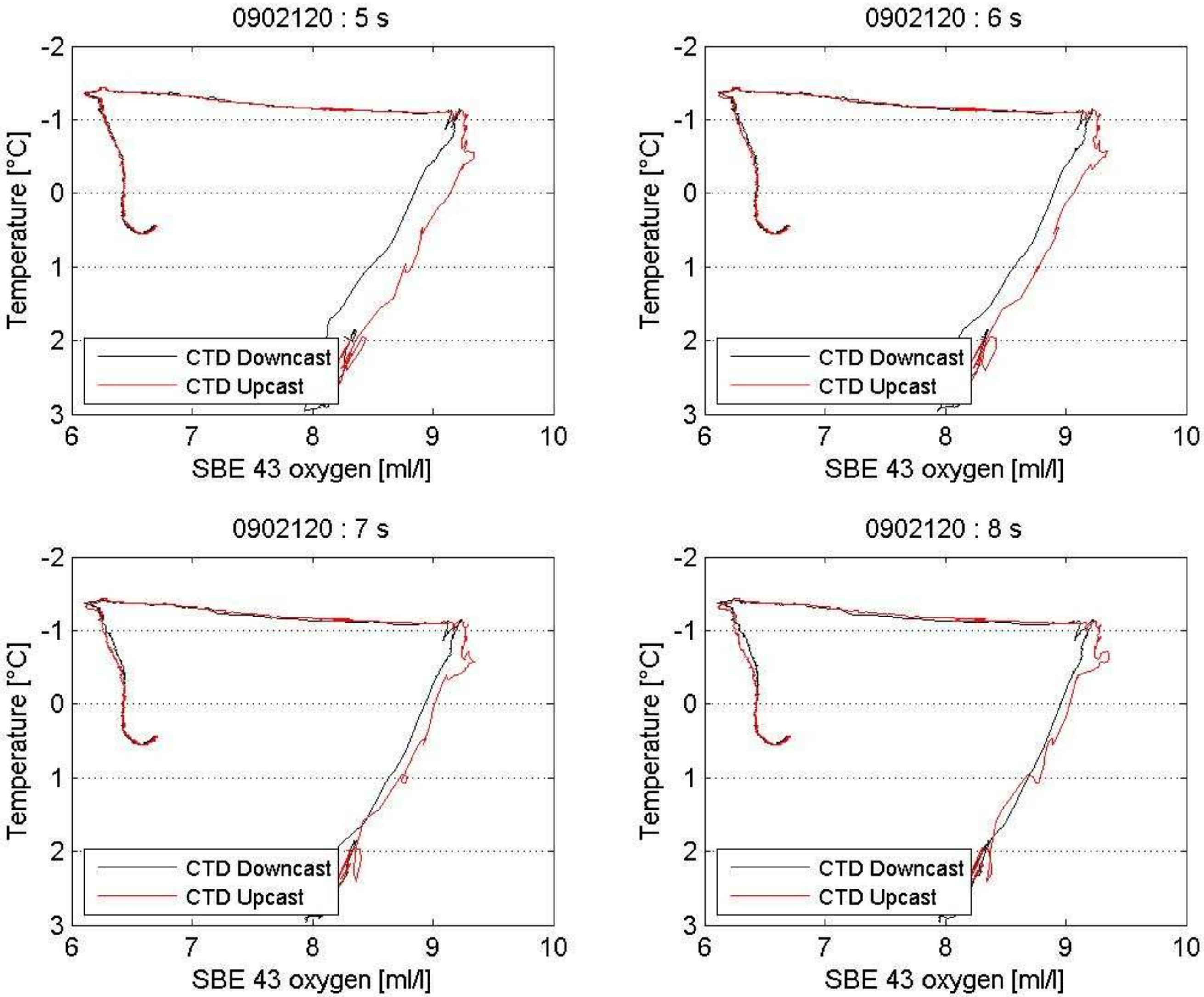



**Figure 17.** Evolution of dissolved oxygen versus temperature for the cast 120 (correction 5 to 8 seconds).

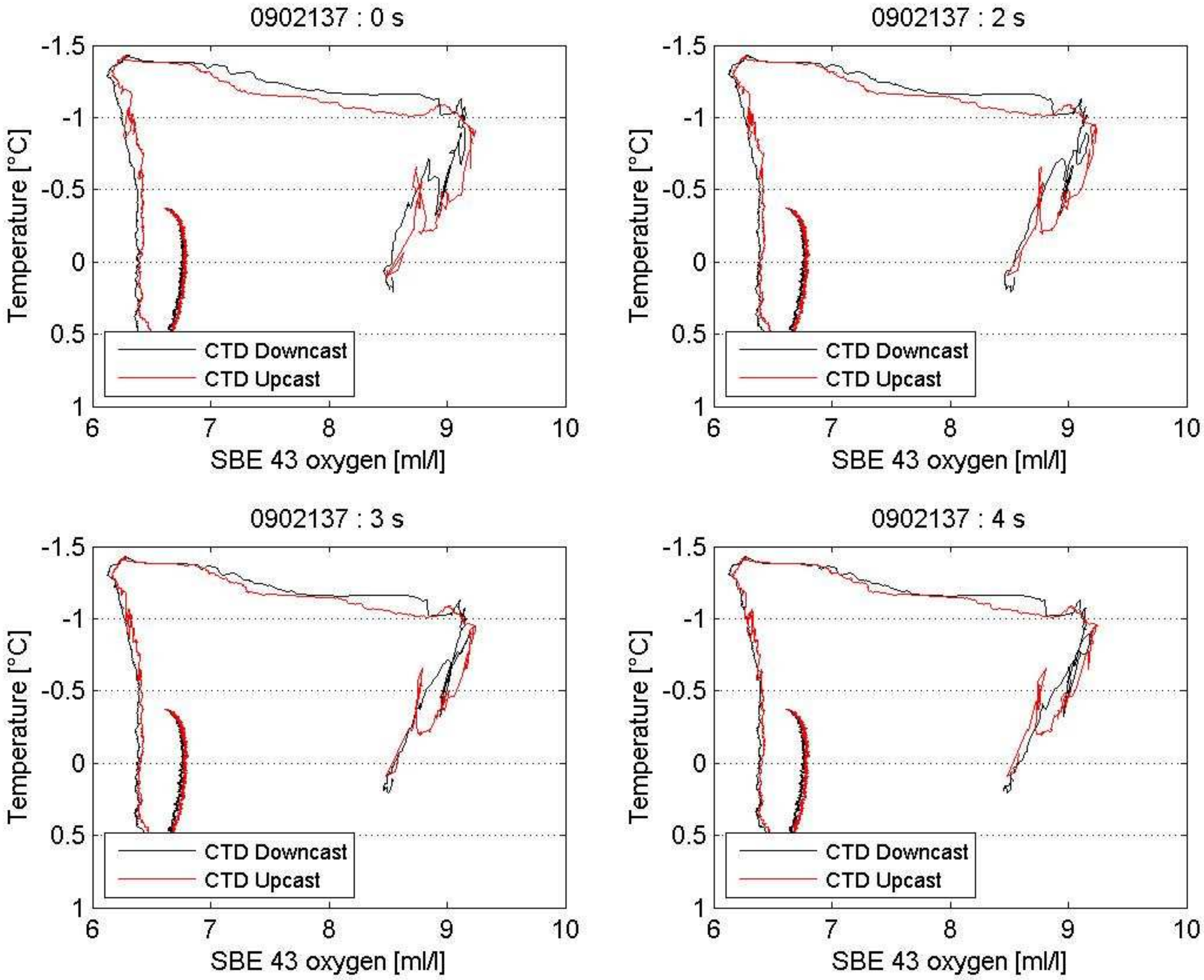



**Figure 18.** Evolution of dissolved oxygen versus temperature for the cast 137 (correction 0 to 4 seconds).

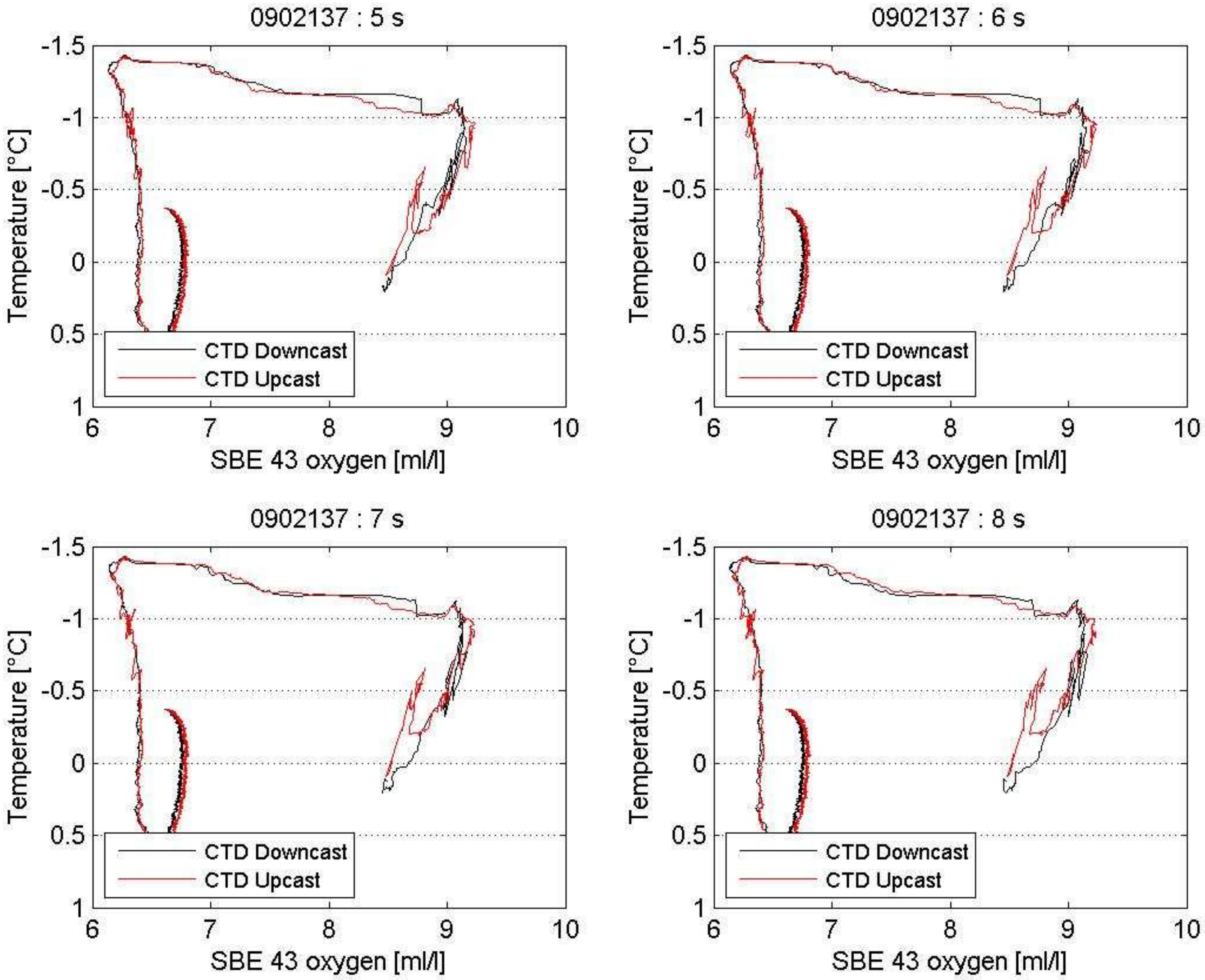



**Figure 19.** Evolution of dissolved oxygen versus temperature for the cast 137 (correction 5 to 8 seconds).

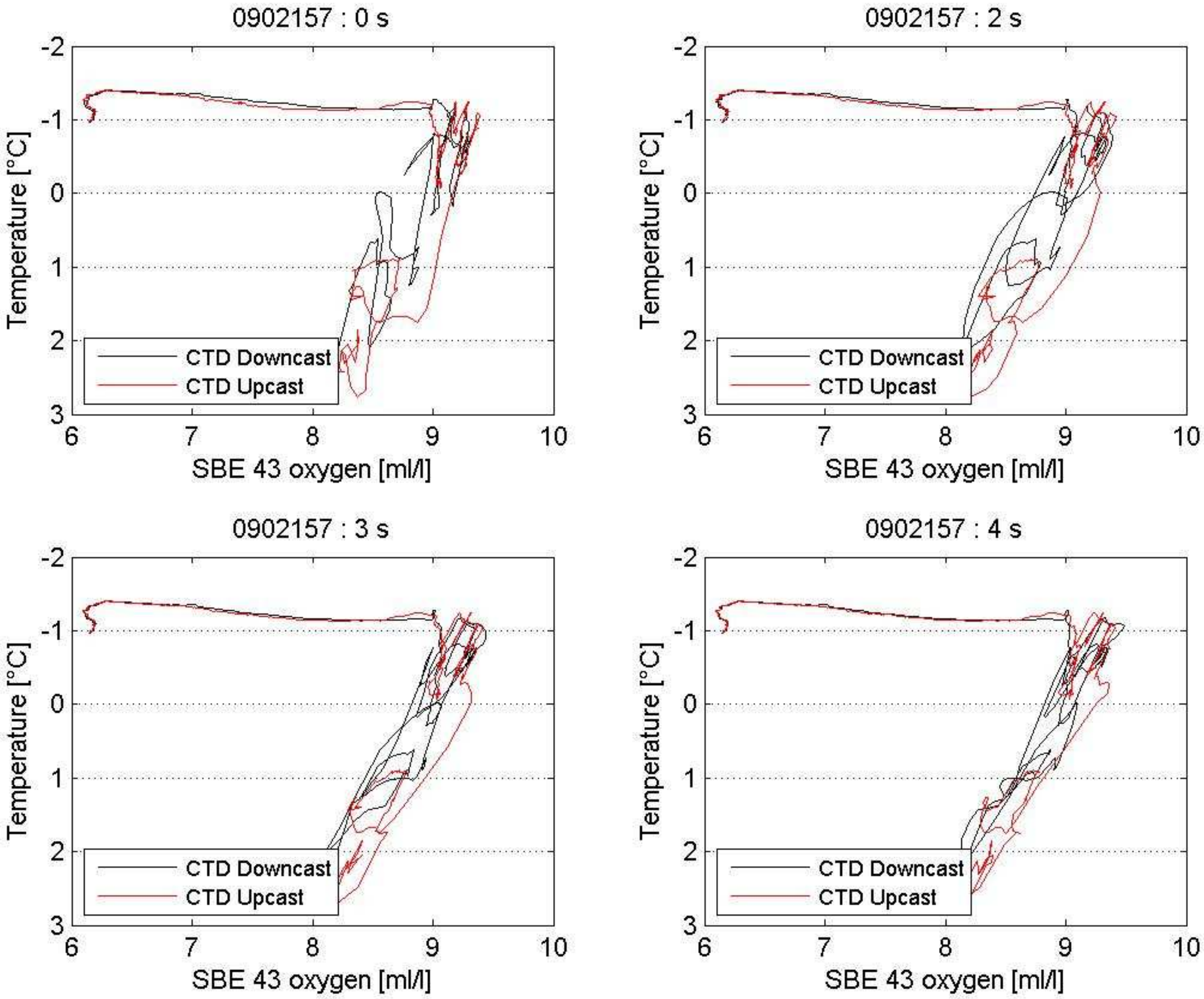



**Figure 20.** Evolution of dissolved oxygen versus temperature for the cast 157 (correction 0 to 4 seconds).

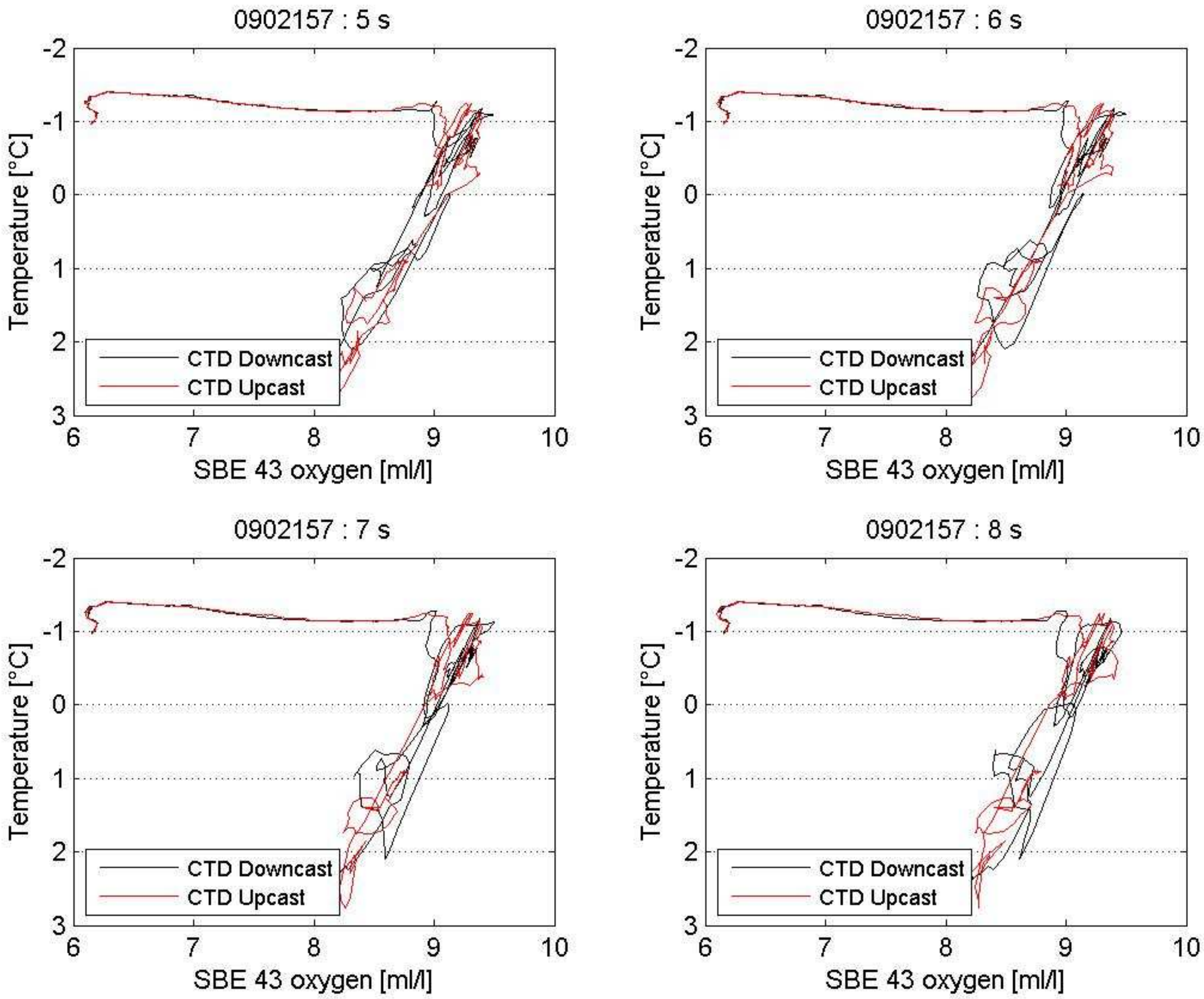



**Figure 21.** Evolution of dissolved oxygen versus temperature for the cast 157 (correction 5 to 8 seconds).

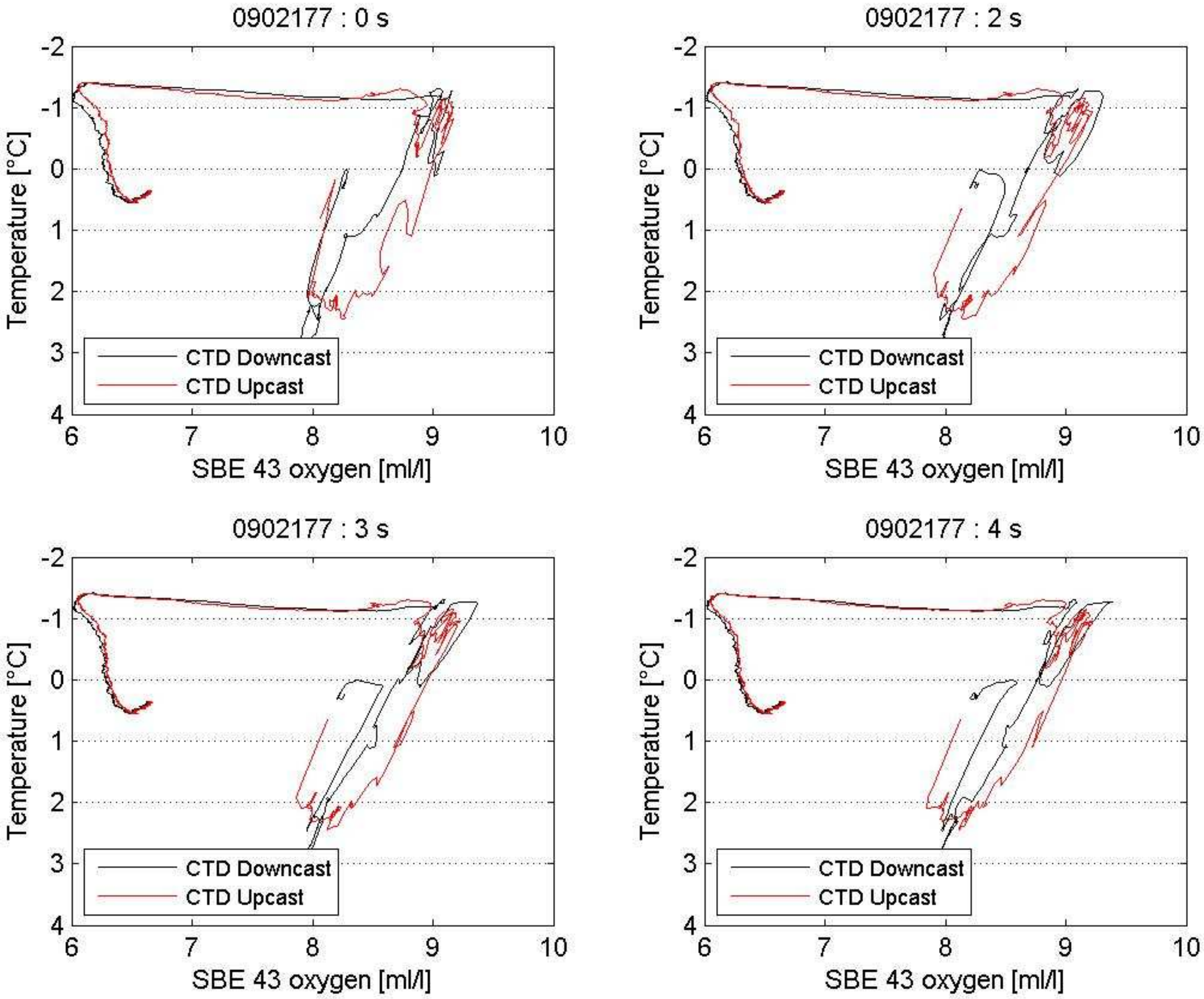



**Figure 22.** Evolution of dissolved oxygen versus temperature for the cast 177 (correction 0 to 4 seconds).

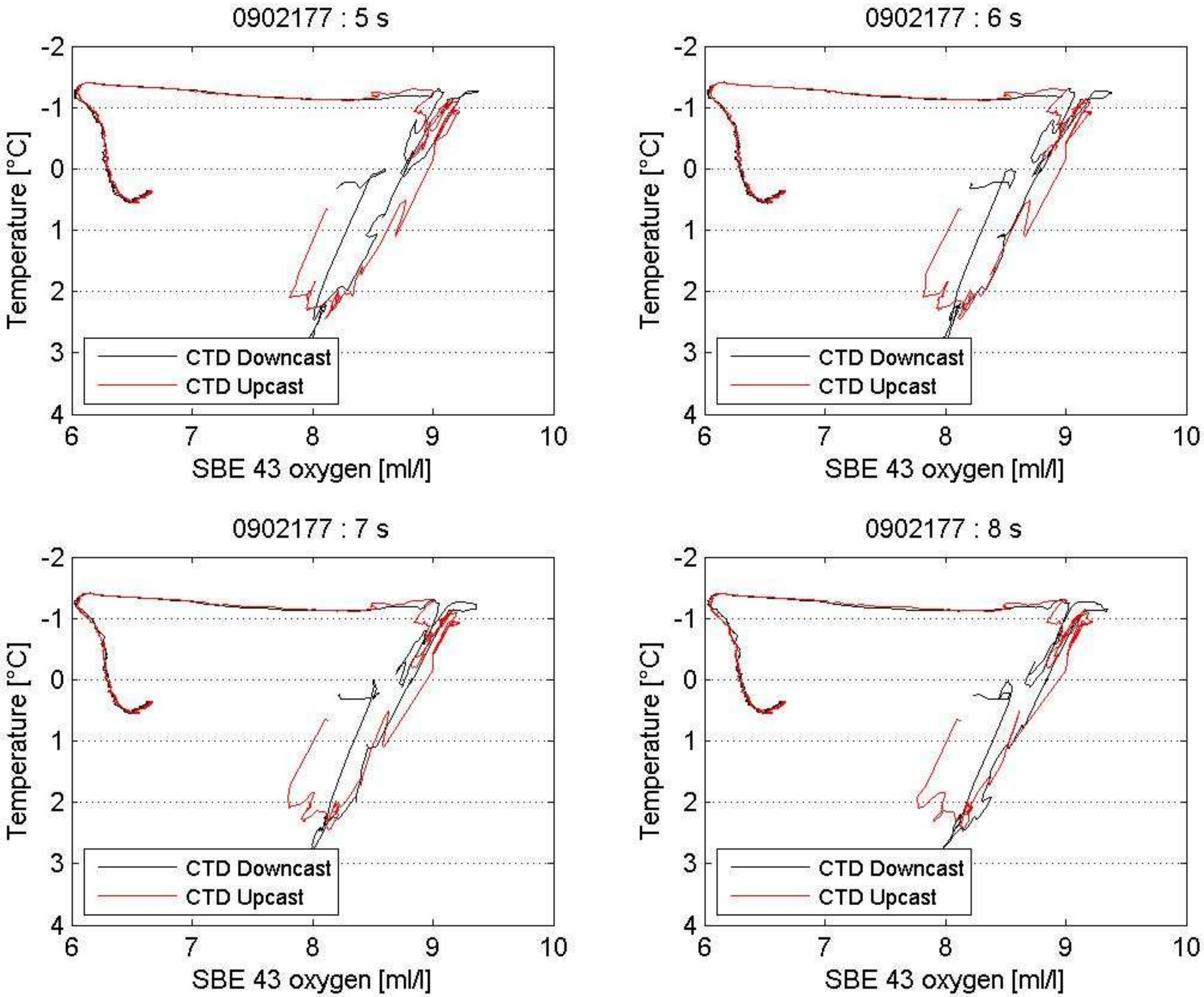



**Figure 23.** Evolution of dissolved oxygen versus temperature for the cast 177 (correction 5 to 8 seconds).

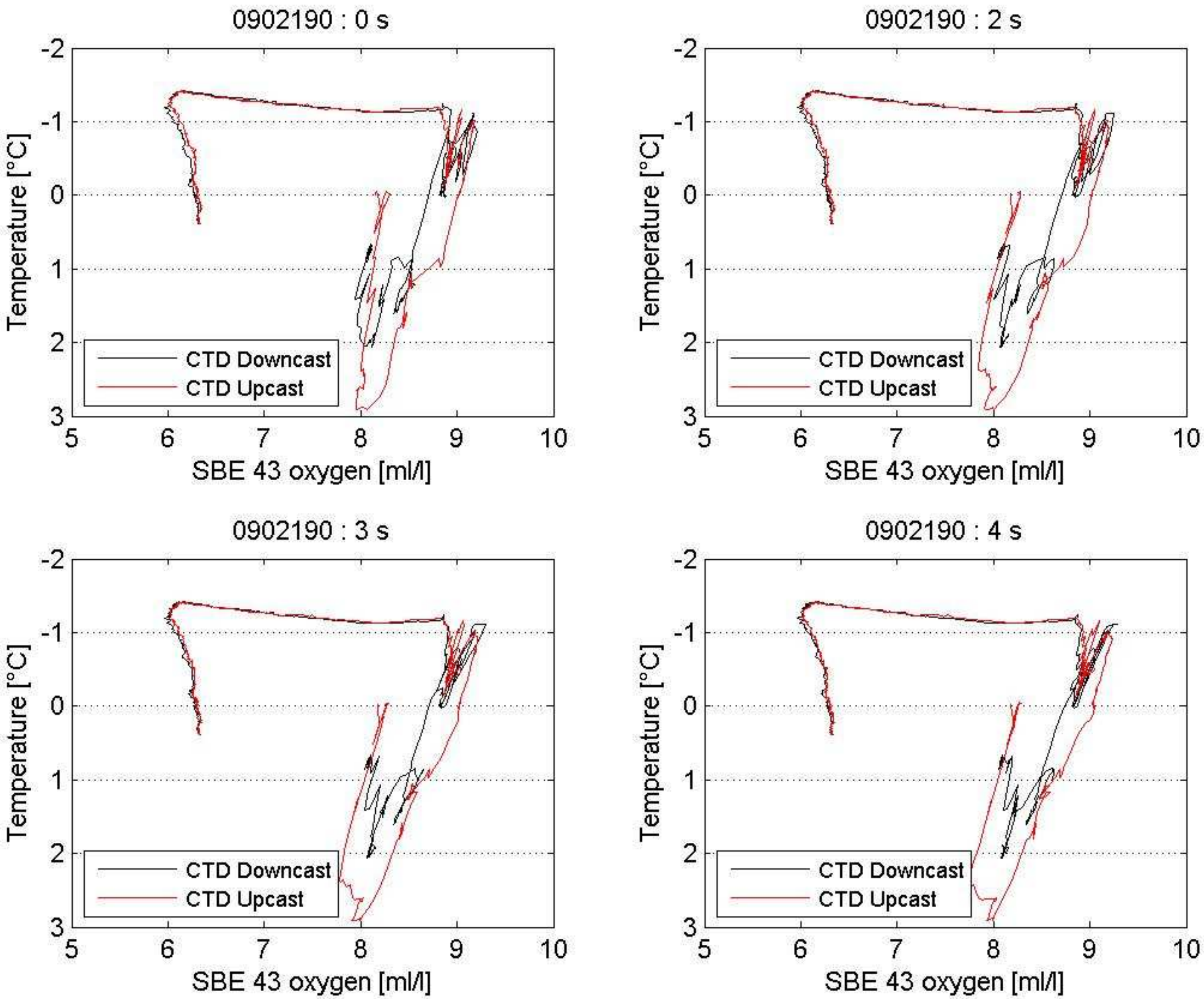



**Figure 24.** Evolution of dissolved oxygen versus temperature for the cast 190 (correction 0 to 4 seconds).

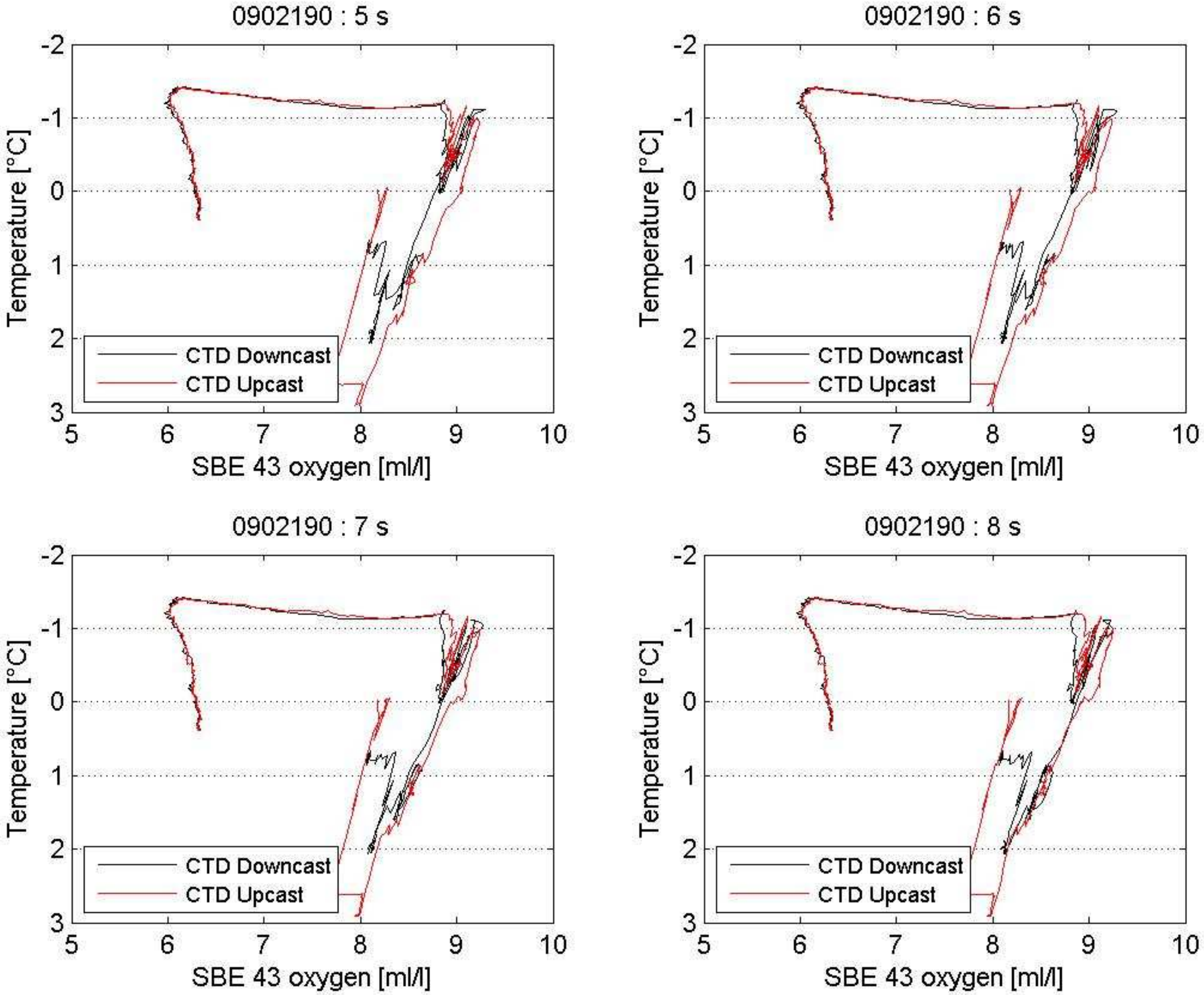



**Figure 25.** Evolution of dissolved oxygen versus temperature for the cast 190 (correction 5 to 8 seconds).

# Annex B

## Evolution of dissolved oxygen versus pressure.

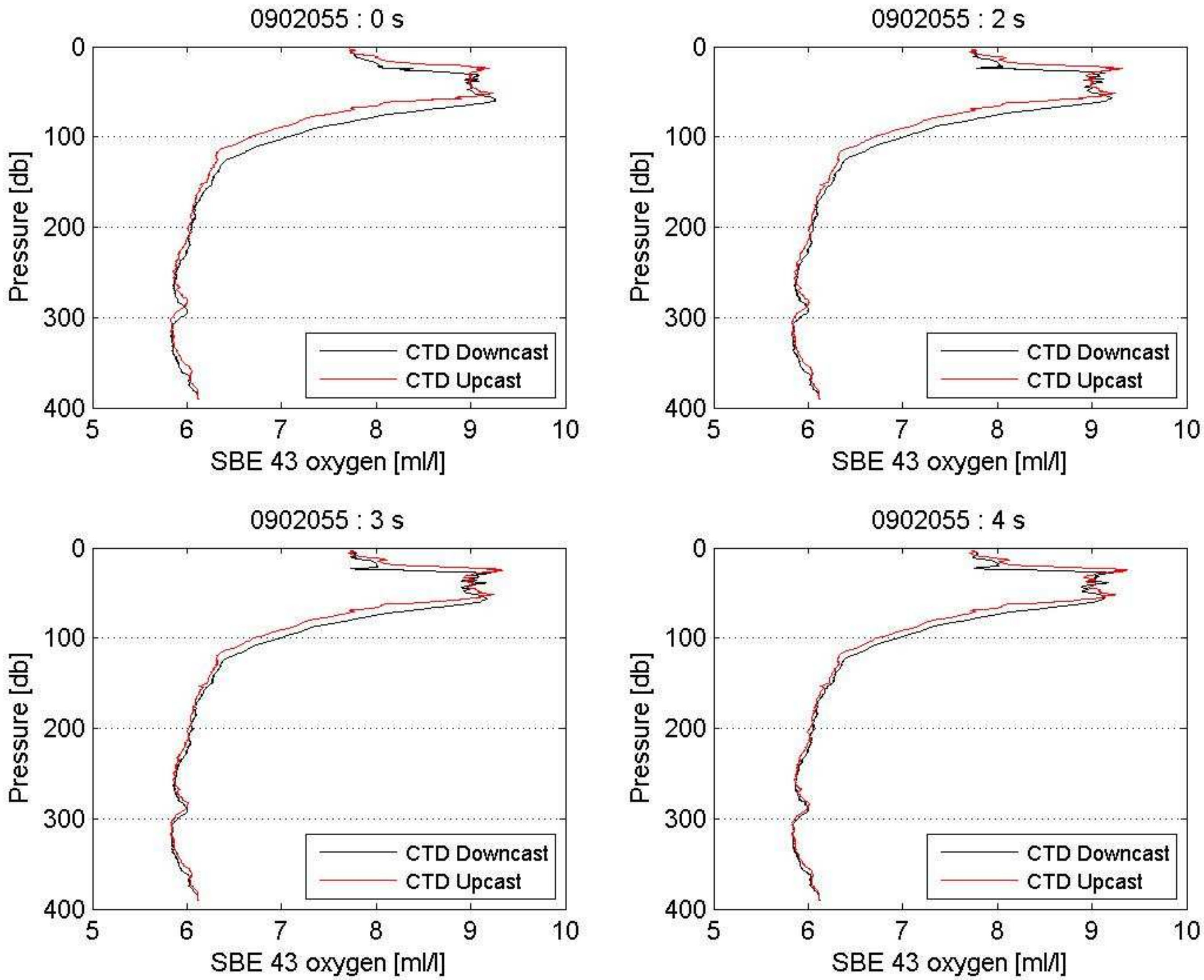



**Figure 26.** Evolution of dissolved oxygen versus pressure for the cast 055 (correction 0 to 4 seconds).

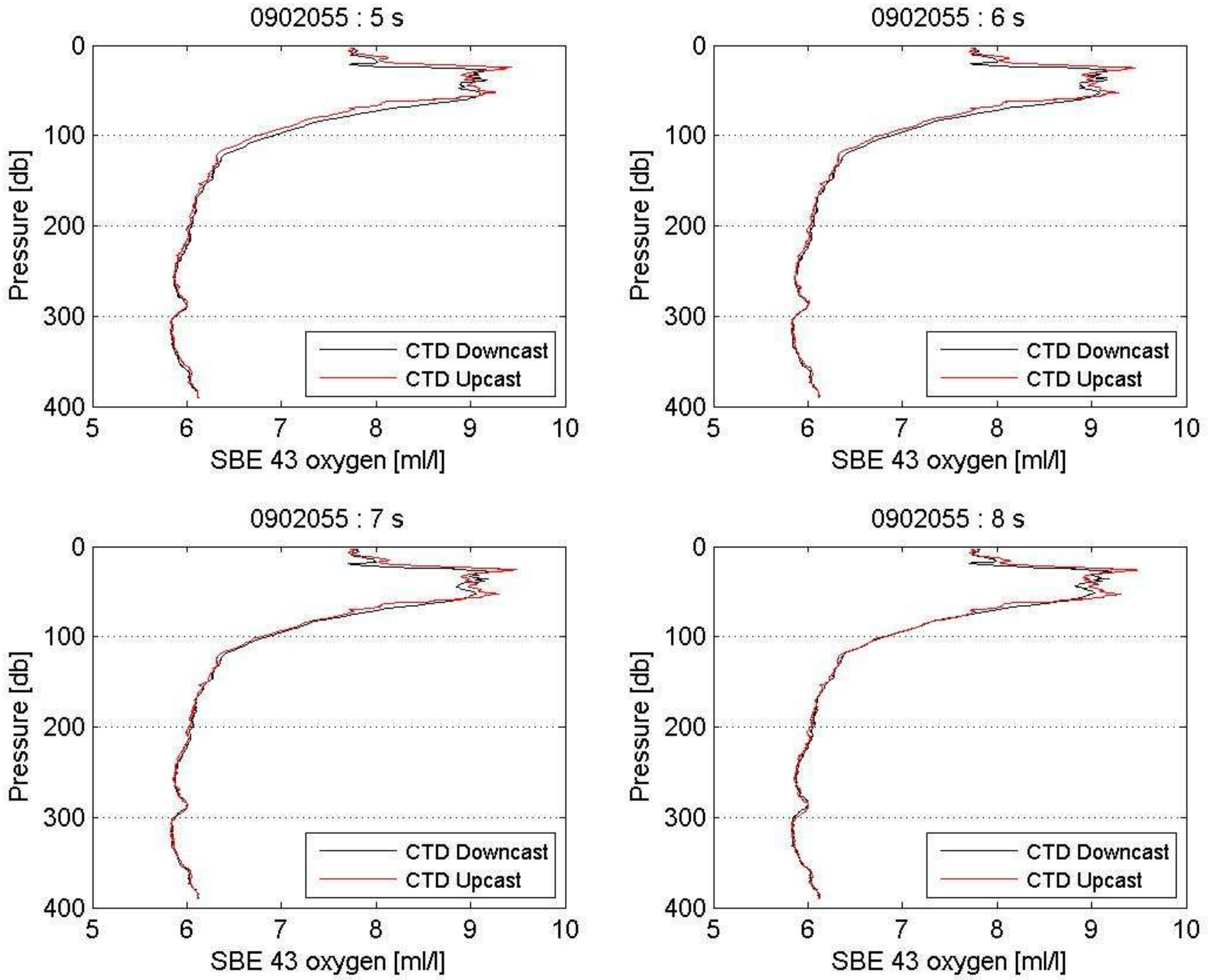



**Figure 27.** Evolution of dissolved oxygen versus pressure for the cast 055 (correction 5 to 8 seconds).

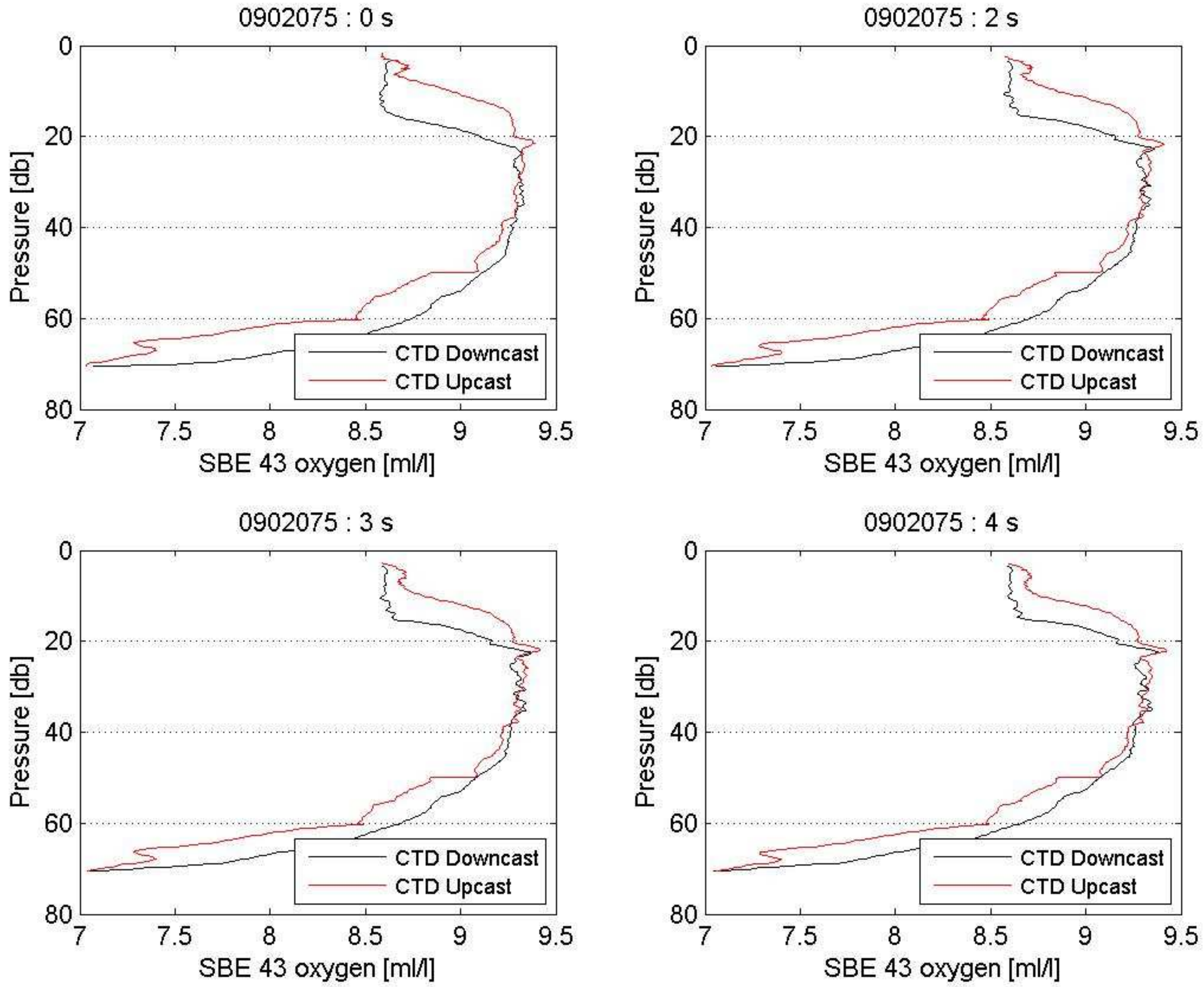



**Figure 28.** Evolution of dissolved oxygen versus pressure for the cast 075 (correction 0 to 4 seconds).

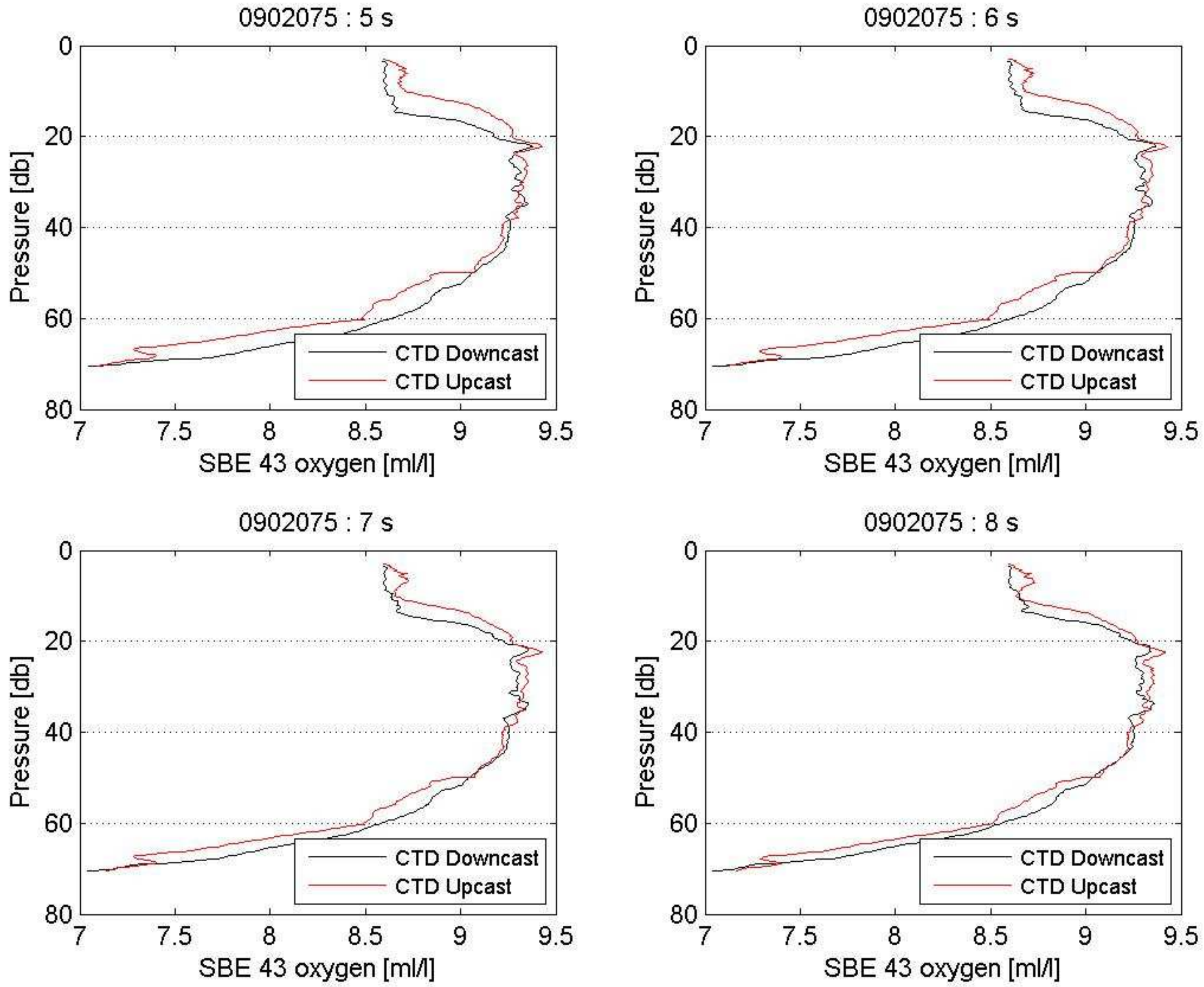



**Figure 29.** Evolution of dissolved oxygen versus pressure for the cast 075 (correction 5 to 8 seconds).

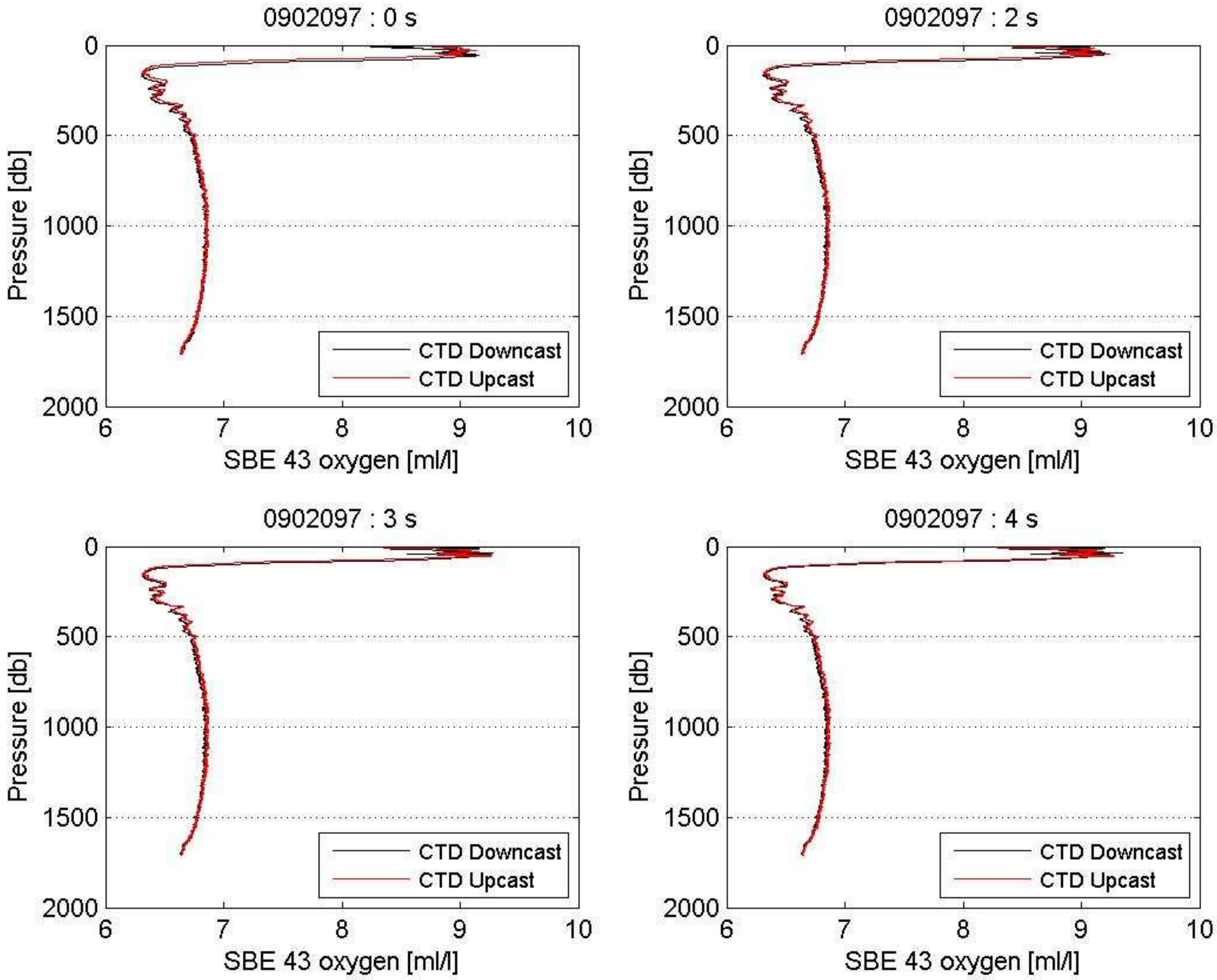



**Figure 30.** Evolution of dissolved oxygen versus pressure for the cast 097 (correction 0 to 4 seconds).

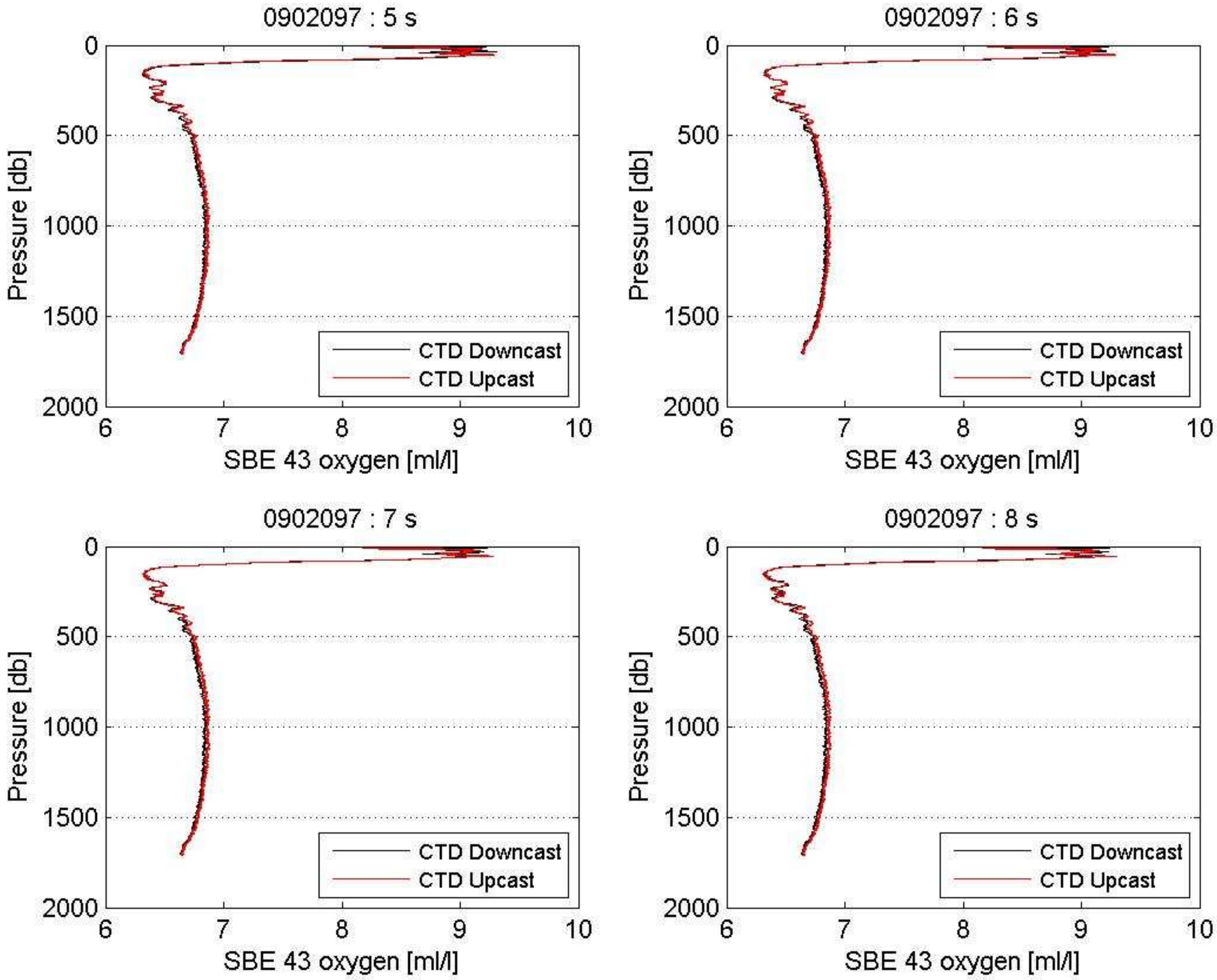



**Figure 31.** Evolution of dissolved oxygen versus pressure for the cast 097 (correction 5 to 8 seconds).

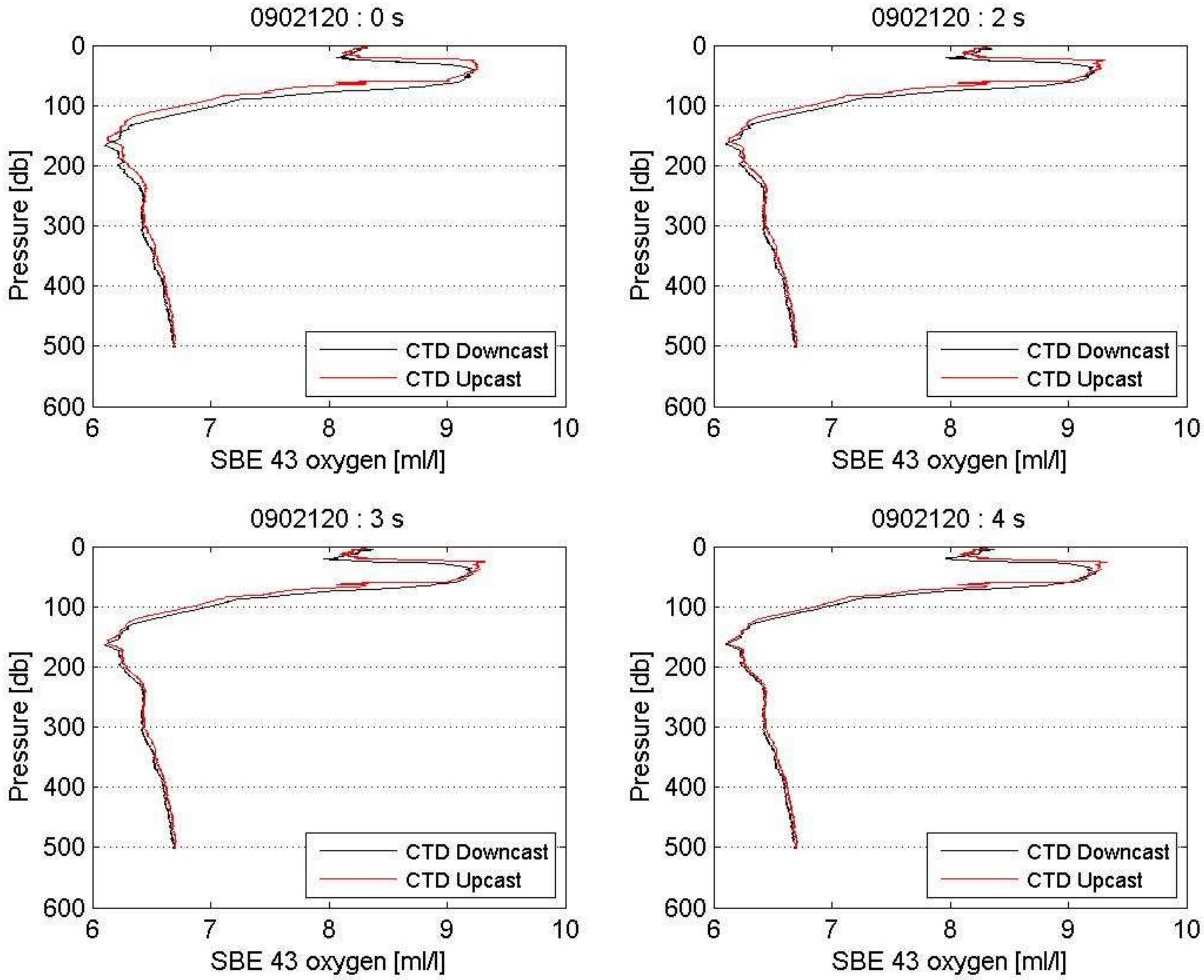



**Figure 32.** Evolution of dissolved oxygen versus pressure for the cast 120 (correction 0 to 4 seconds).

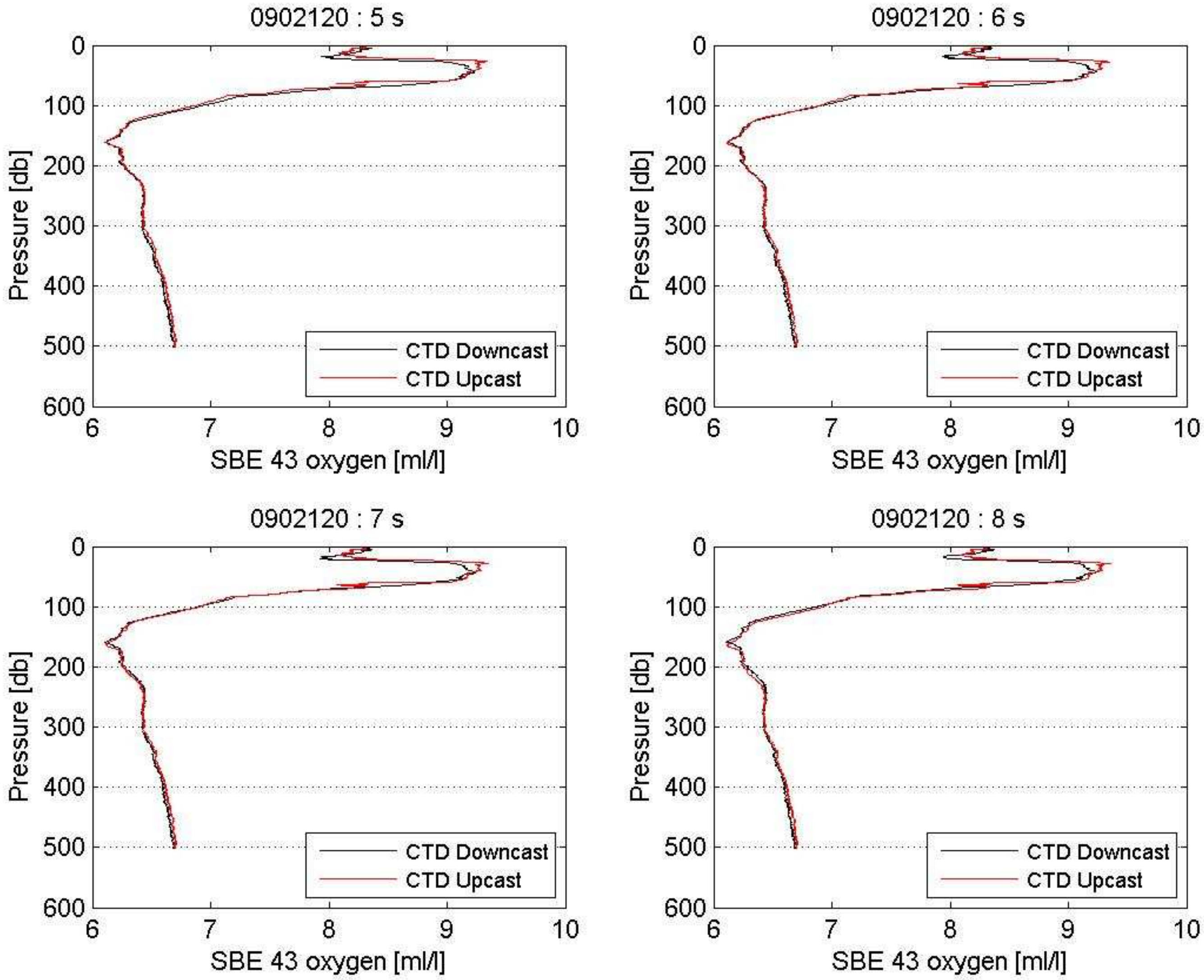



**Figure 33.** Evolution of dissolved oxygen versus pressure for the cast 120 (correction 5 to 8 seconds).

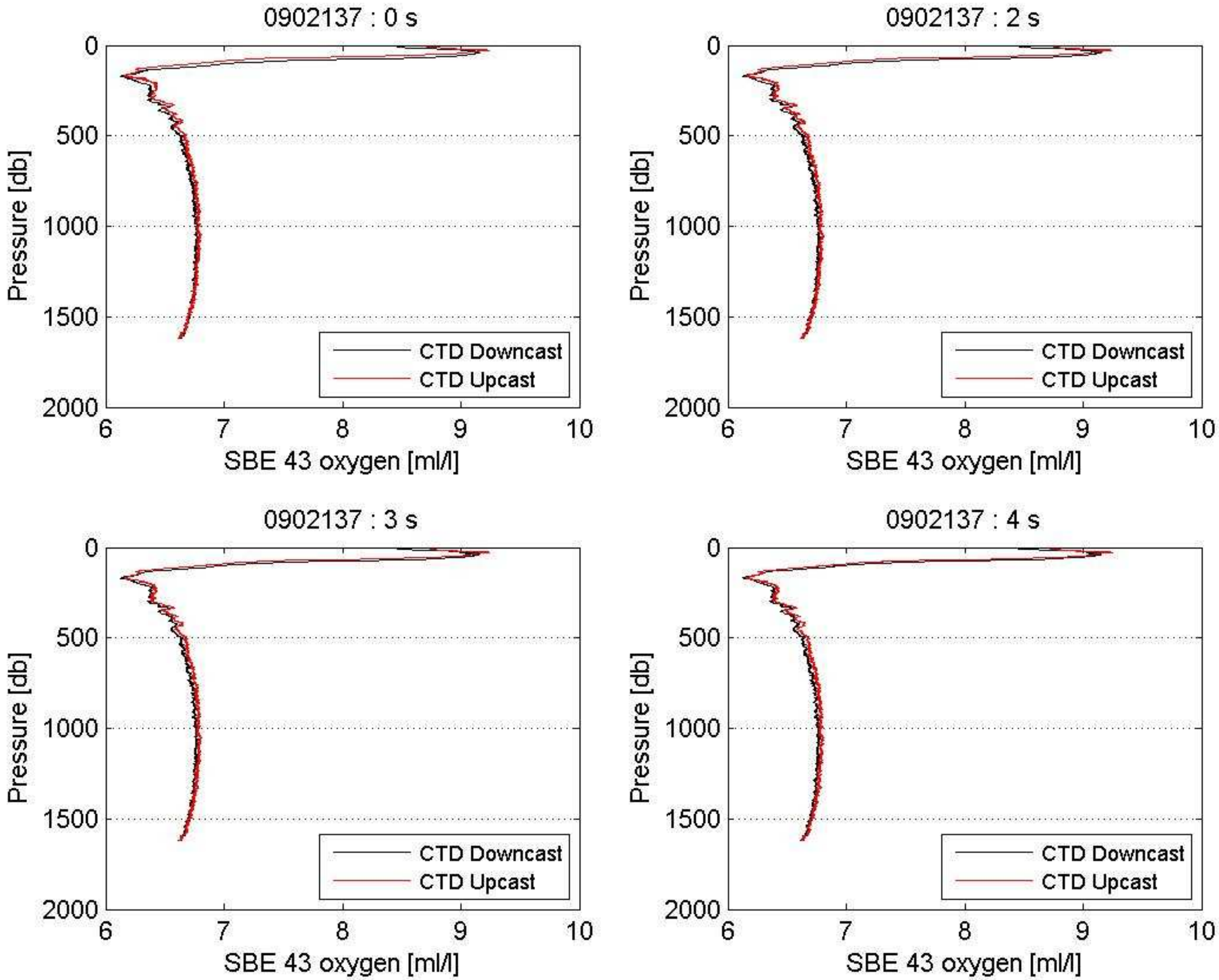



**Figure 34.** Evolution of dissolved oxygen versus pressure for the cast 137 (correction 0 to 4 seconds).

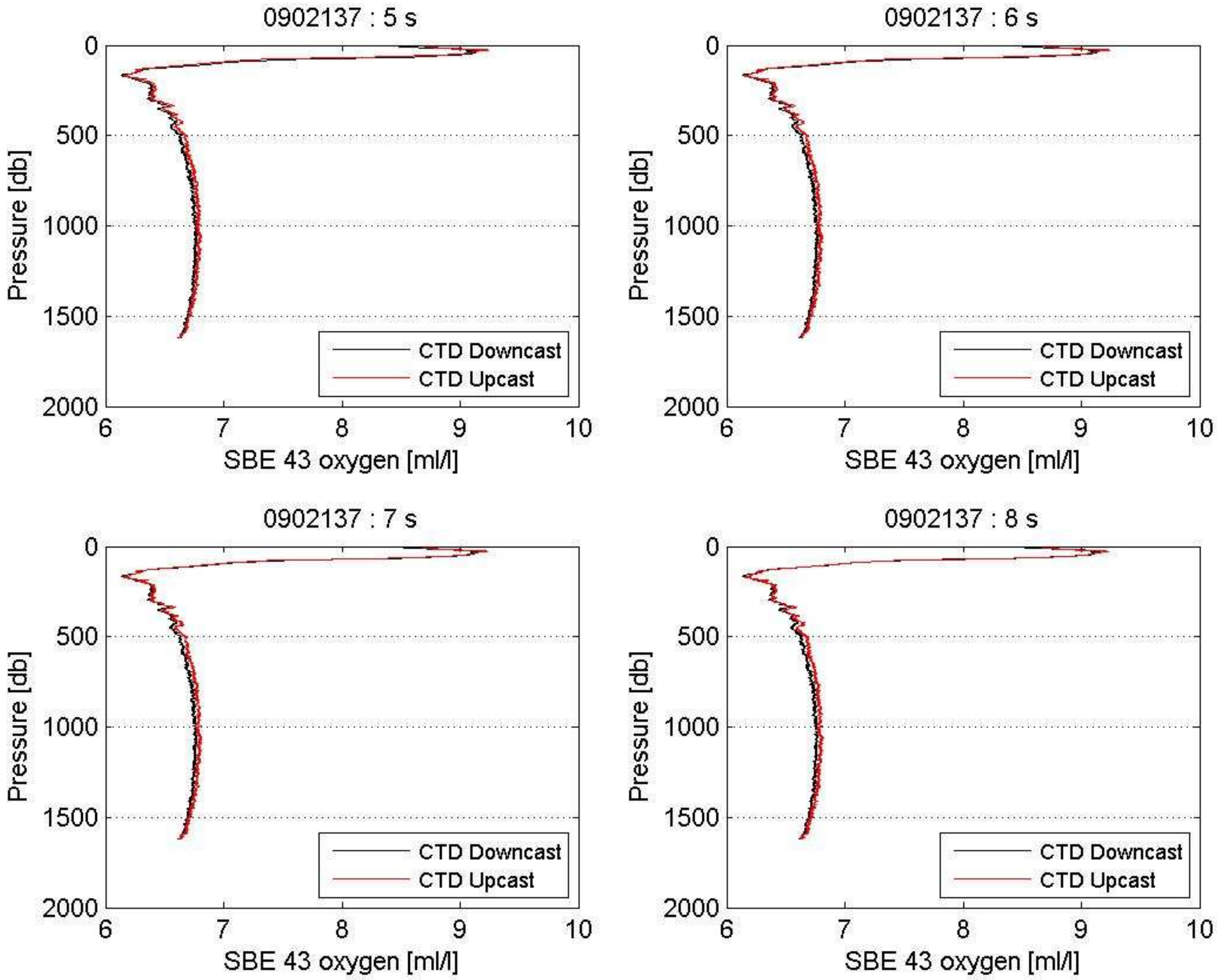



**Figure 35.** Evolution of dissolved oxygen versus pressure for the cast 137 (correction 5 to 8 seconds).

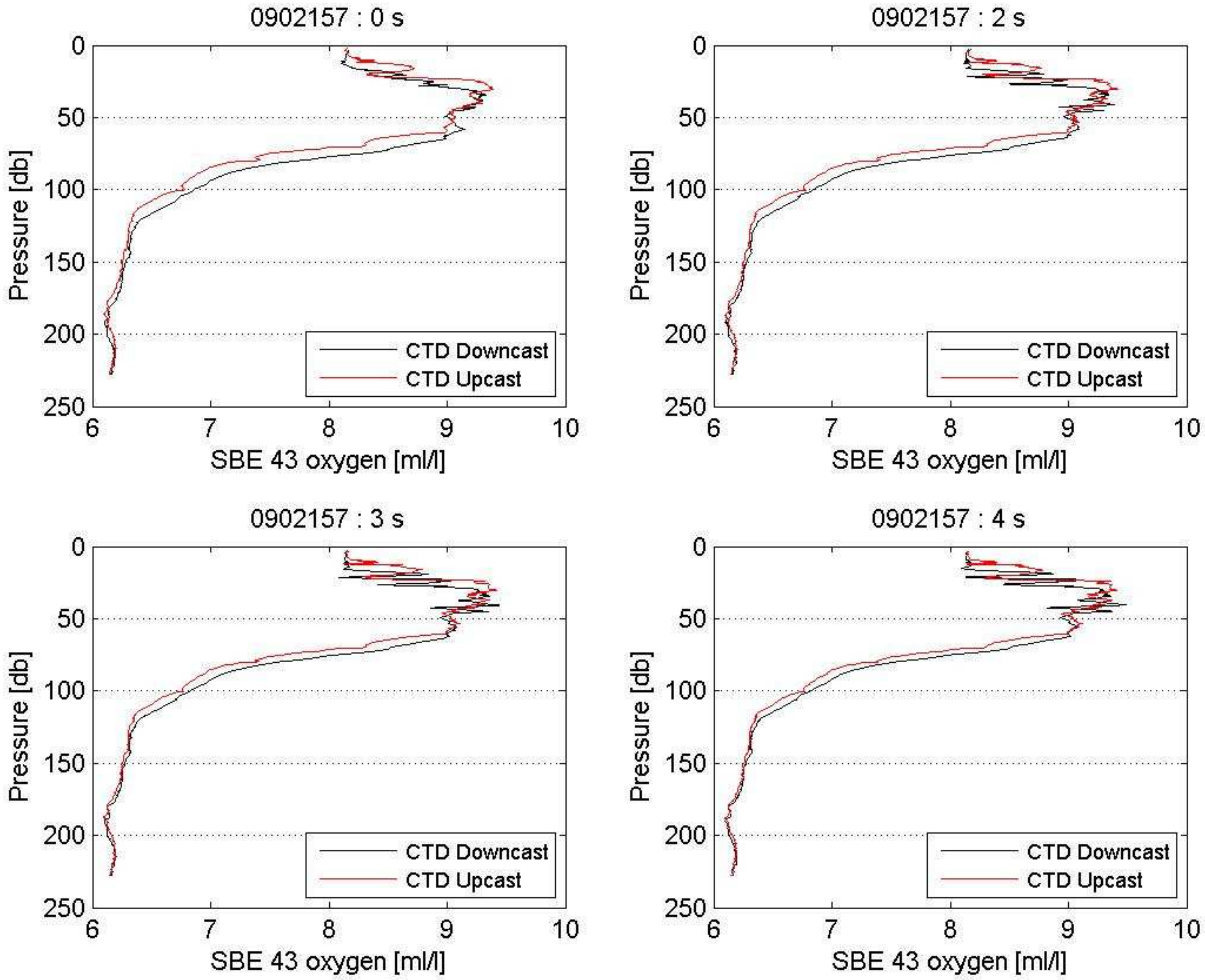



**Figure 36.** Evolution of dissolved oxygen versus pressure for the cast 157 (correction 0 to 4 seconds).

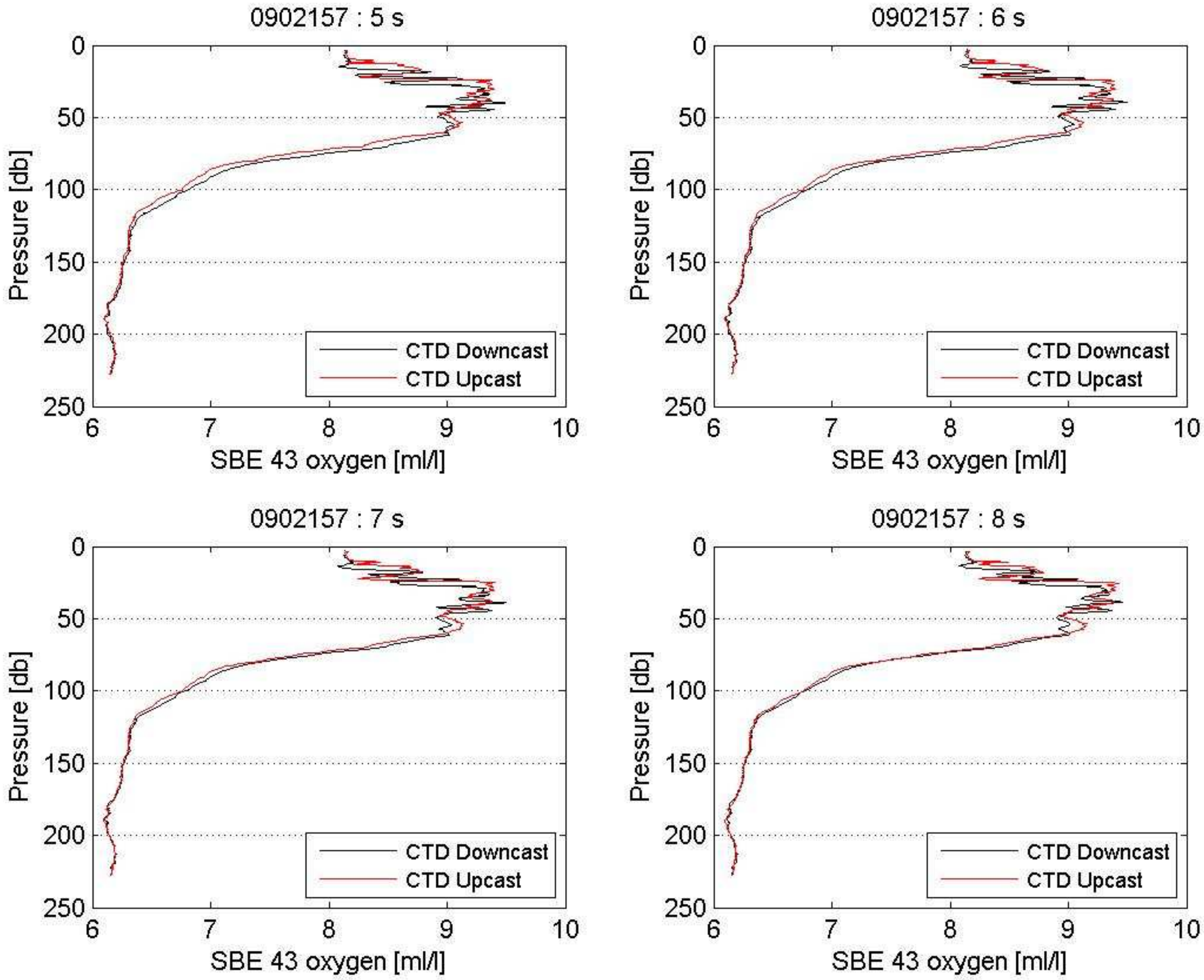



**Figure 37.** Evolution of dissolved oxygen versus pressure for the cast 157 (correction 5 to 8 seconds).

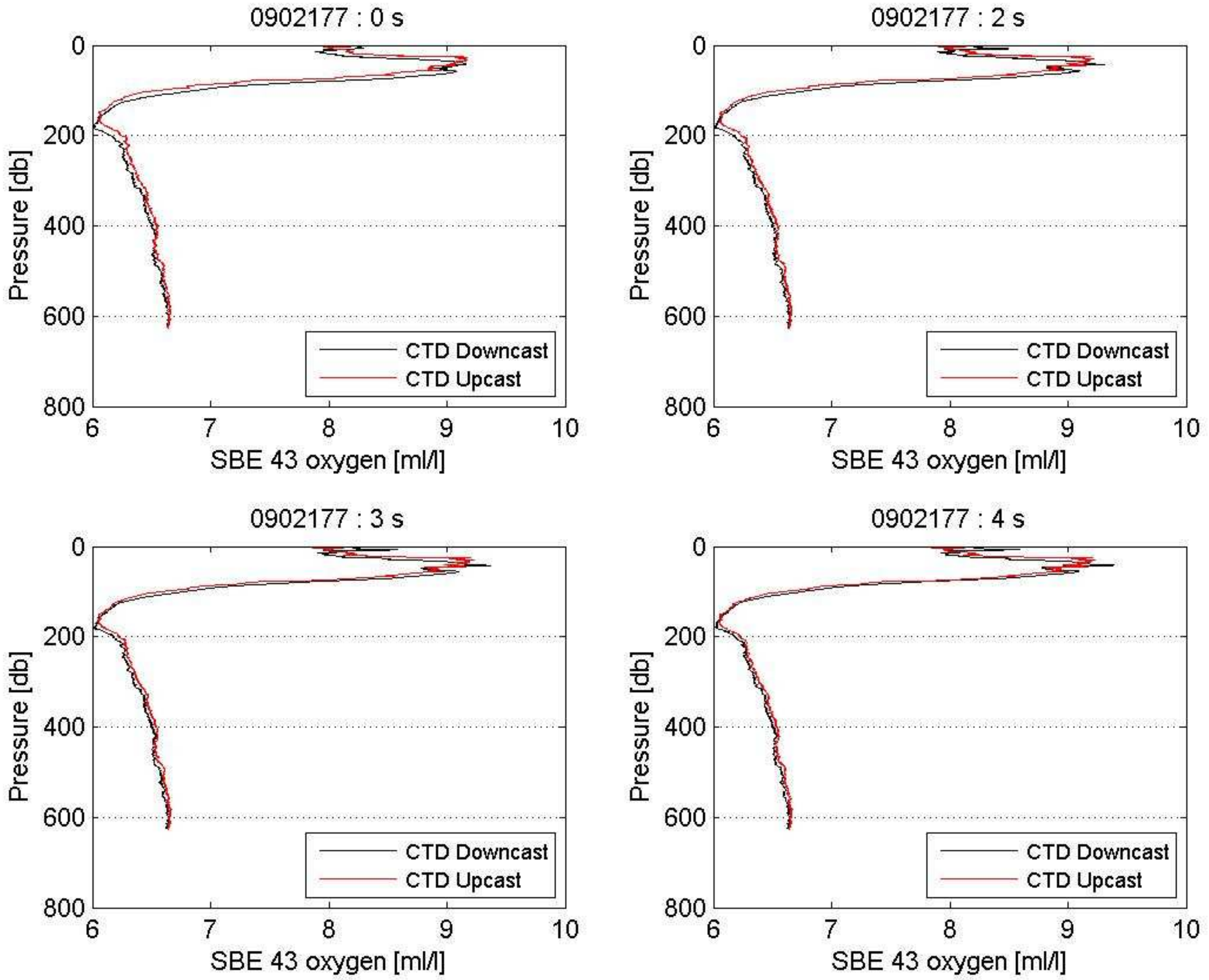



**Figure 38.** Evolution of dissolved oxygen versus pressure for the cast 177 (correction 0 to 4 seconds).

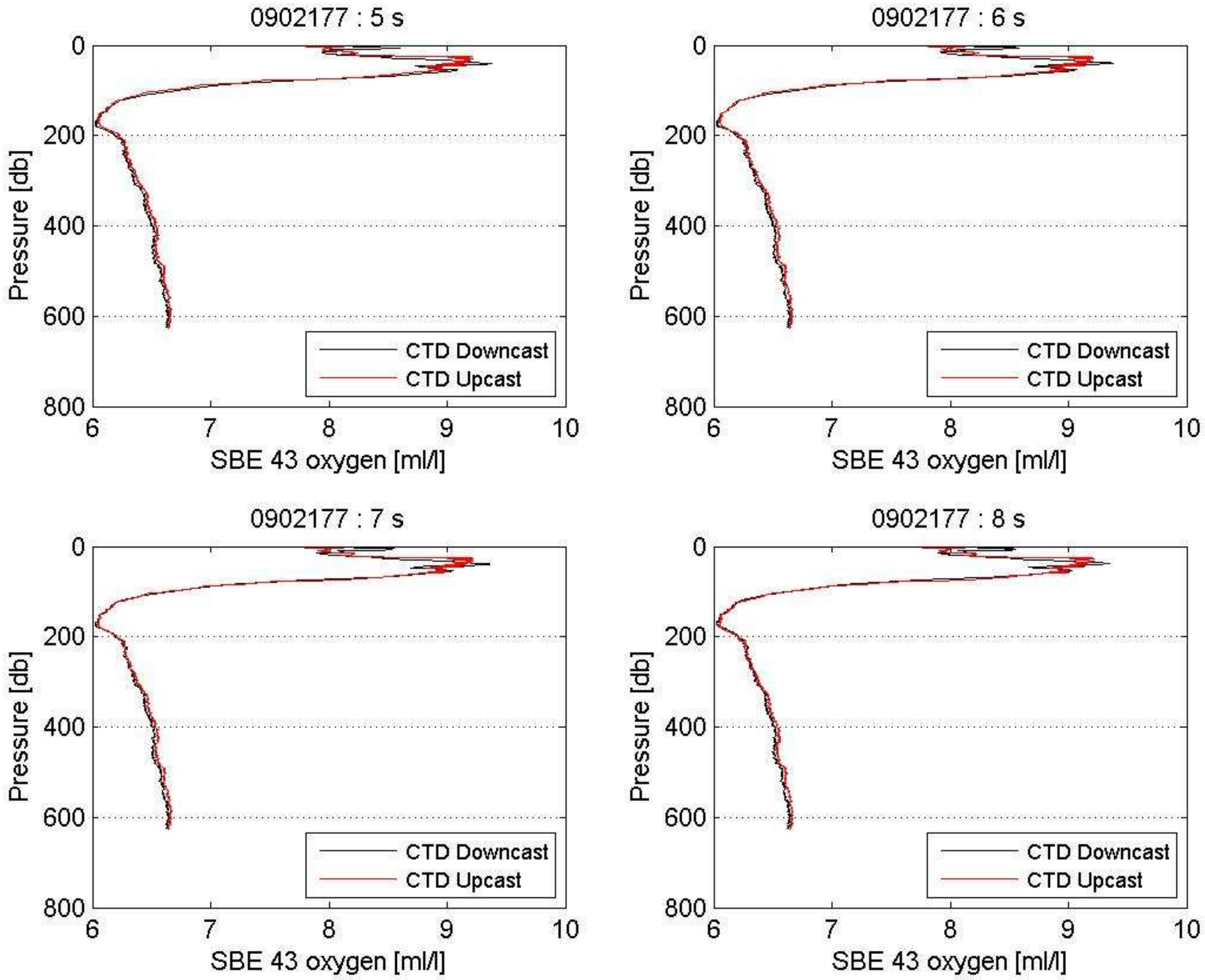



**Figure 39.** Evolution of dissolved oxygen versus pressure for the cast 177 (correction 5 to 8 seconds).

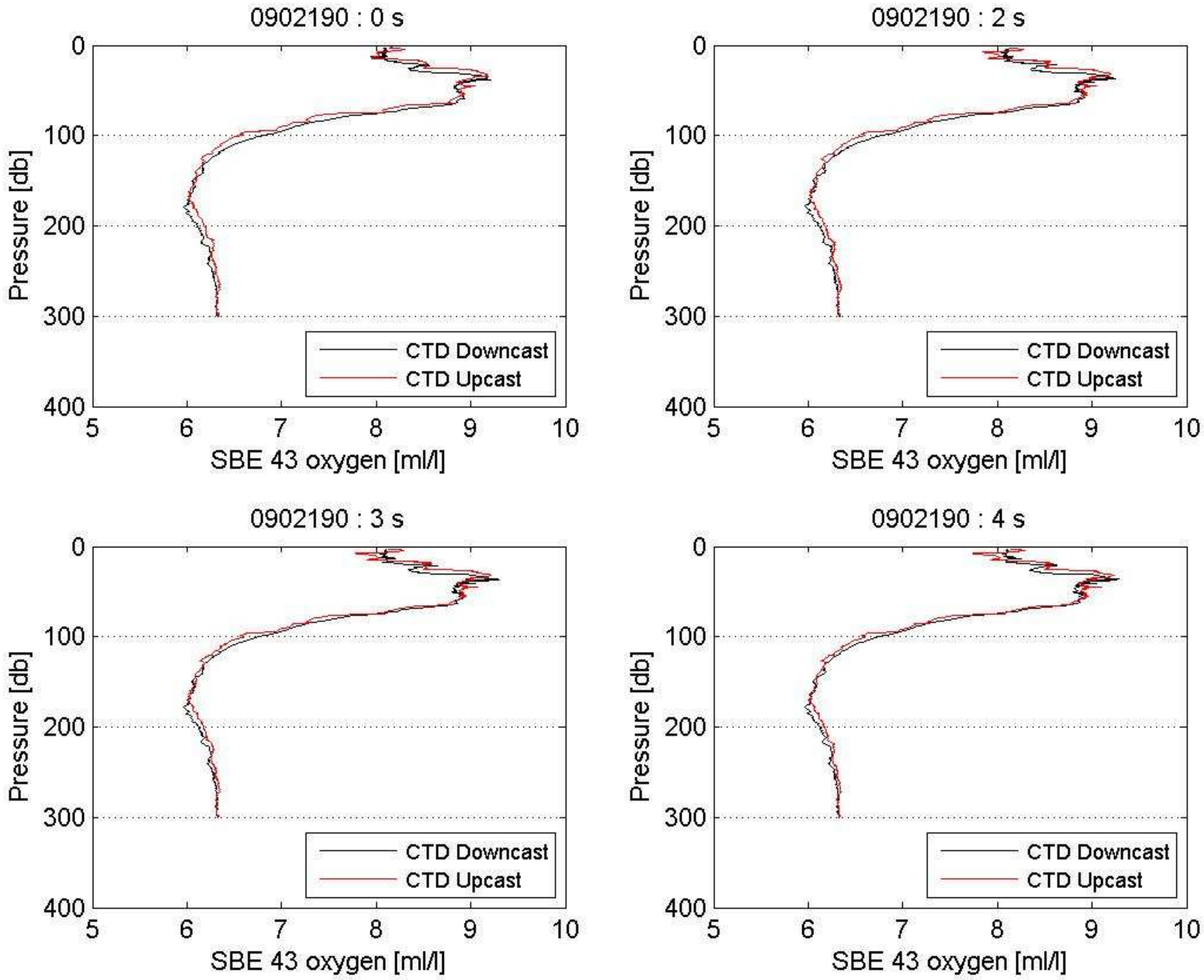



**Figure 40.** Evolution of dissolved oxygen versus pressure for the cast 190 correction 0 to 4 seconds).

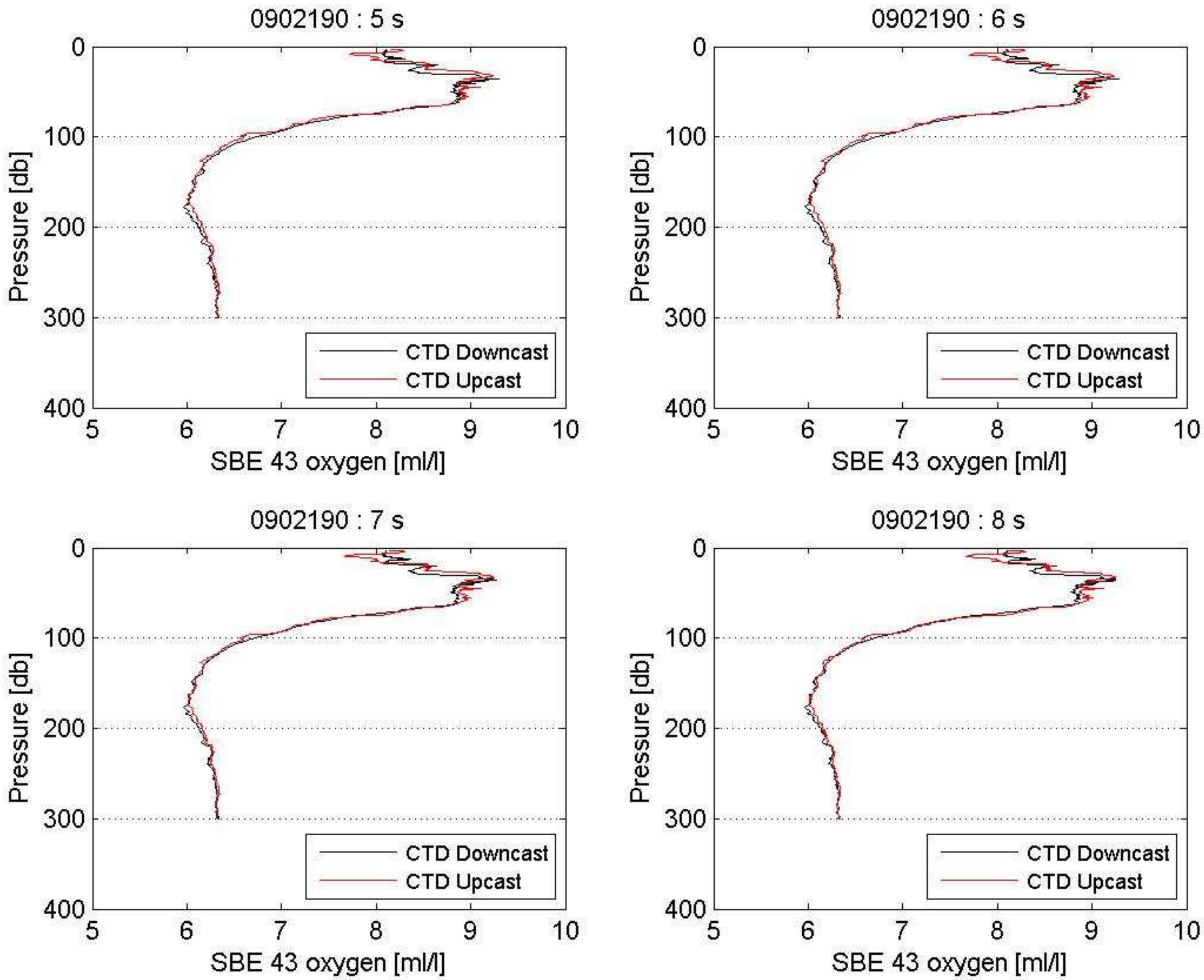



**Figure 41.** Evolution of dissolved oxygen versus pressure for the cast 083 correction 5 to 8 seconds).