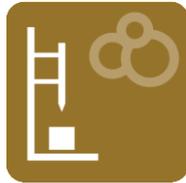# Application Note: Calculations of oxygen consumption rate using Unisense SensorTrace Profiling software.

Abstract:

This note will explain how to use SensorTrace Profiling to quantifying the consumption rate of oxygen as well as the oxygen exchange rate across the water-sediment interface, from a high resolution oxygen profile measured with an Unisense micro-profiling system. As an example we will use an oxygen micro-profile made in an organic rich sediment core collected at less than 30 cm water depth in the brackish Limfjorden in Denmark. The software uses a one-dimensional mass conservation equation for the model calculation. Before starting the analysis, we made estimates for the oxygen diffusion coefficient in all zones of the sediment, and defined boundary conditions. The model shows the activity distribution and compares the calculated profile with the actual measured profile. Using a stepwise optimization, the activity distribution is redefined until the calculated profile does not deviate from the measured profile within a statistical margin. Sum of squared error (SSE) and the p-value together with the modeled graph are used to estimate the best fit for the rate calculations.
Using SensorTrace Profiling we find that the maximum oxygen consumption rate in the sediment from Limfjorden was 2.0 nmol cm^{-3} s^{-1} and the integrated oxygen flux across the sediment – water interface, 0.09 nmol cm^{-2} s^{-1}, which are comparable rates found in similar environments.

The oxygen profile used in this note is available in the 'Unisense Data' folder under 'Demo Experiments' and you can use it for practice and to make your own rate calculations.

Figure 1 Unisense Field MicroProfiling System

Material and Method:

Sediment was collected by hand at Aggersund, Limfjorden, Denmark, in August 2015 at a water depth of about 30 cm and brought to the Unisense lab. Here the sediment core was placed into a container with brackish water (15 ‰ salinity) collected at the same location as the sediment, and stored at *in-situ* temperature, about 20°C. The water was flushed with air using an aquarium-pump and a bubble stone making sure that there was a good circulation and that a well-defined Diffusive Boundary Layer (DBL) was established just above the sediment-water interface (figure 2 and 3).

Oxygen micro-profiles were made by using a Unisense motorized MicroProfiling system and an oxygen micro-sensor with a tip-size of 50 µm (OX-50). SensorTrace Profiling was used for sensor calibration, motor control and data collection. The oxygen concentration was measured in units of µmol/L. Data was collected with 50 µm step size, 3 seconds wait and 1 second measuring time.

Figure 2 Typical micro-profiling setup in the laboratory.

Assumptions

The software uses a one-dimensional mass conservation equation (Boudreau, 1984) for the rate calculations. The model assumes steady-state conditions where transport of oxygen is occurring by diffusion and it neglects effects of e.g. burial, groundwater flow, and wave actions. Temperature and salinity should be stable – preferable similar to the *in-situ* conditions.
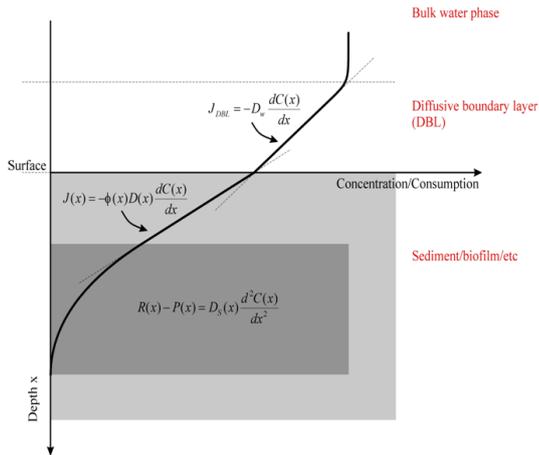
Figure 3: A typical oxygen profile in sediments with a well-mixed overlying water column, a diffusive boundary layer just above the sediment – water interface, and the sediment column. Fluxes are calculated using Fick's firs law of diffusion. Fick's second law of diffusion is used to calculated the oxygen consumption rate at different sediment depths.

Sediment water interface

In the Visualization window of SensorTrace Profiling the 0-line of the profile can be adjusted. The water – sediment is typically set to 0 µm depth. The profile with the adjusted 0-line can be used in the Activity window.

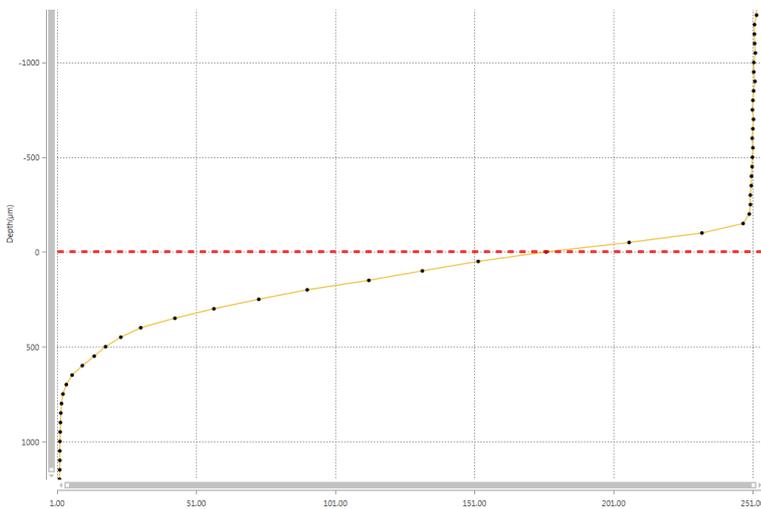*Figure 4: Oxygen micro-profile in a sediment. Use the red line to adjust the water – sediment interface.*

The interface – 0 µm depth – can sometimes be found from the oxygen profile, knowing that the oxygen diffusion in water (D_0) typically is higher than the oxygen diffusion in the sediment (Ds), giving a change in

the slope at the water – sediment interface. The sediment surface is placed at the bottom of the DBL, where the oxygen profile changes direction.

Activity

In the Activity window of SensorTrace Profiling the consumption and production rates are calculated from the oxygen micro-profile by using the one-dimensional mass conservation model. Before making the calculations the model needs various information that you have to provide:

a) A profile
b) Boundary conditions
c) Depth interval and zones
d) Diffusion coefficient of oxygen (D_s and D_0) at the different depths
e) Porosity for the Ds determination

Below we will give examples of information's that can be provided the model.

Profile: Select the profile you want consumption and flux rate calculations from.

Boundary conditions: To constrain the model, we will need two independent boundary values for the analysis. In the program you can select between 5 different pairs of boundary conditions. Example oxygen profiles where the end concentration and flux is 0, the boundary condition 'bottom conc and bottom flux' is typically used (Figure 5).
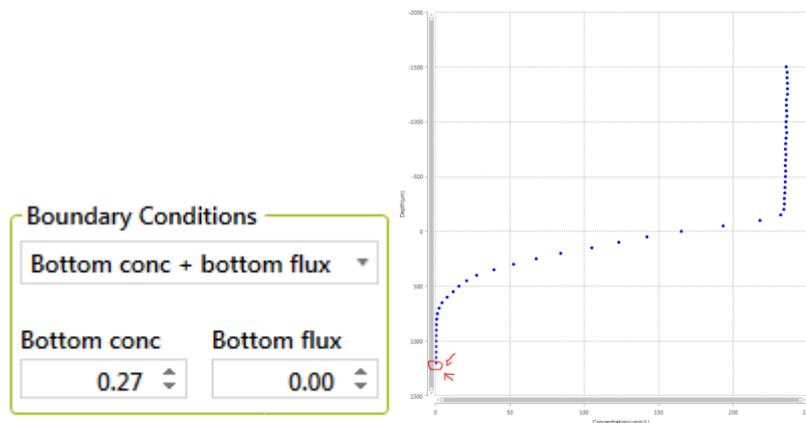

Figure 5 Boundary condition: Boundary condition "bottom conc + bottom flux"

In the sediment from Limfjorden we start with the 'bottom conc and bottom flux' boundary condition with the values 0.27 µM for bottom concentration and 0 for bottom flux, respectively.

Interval and zones: Here you define the area of the profile you want to model. It is most appropriate to calculate rates in the depth interval where a consumption or production of oxygen take place. In the model

sediments we start at the sediment – water interface (0 μm) and end where all oxygen is consumed at the bottom of the profile.

Figure 6 Settings for 'Intervals and zones'

Number of zones refer to how many volume-specific rate calculations the model should list (maximum 10 zones).   The volume-specific rate is calculated from the profile using Fick's second law of diffusion based on two or more measuring points. The appropriate number of zones can be estimated from the shape of the profile where a new zone theoretically can be made every time the profile changes its linear direction. To begin with select a high number of zones e.g. 7. After the Analysis the model highlights the most favorable number of zones based on the statistical values, SSE and p-value.

The minimum width of the volume based rate zones should be at least twice the resolution of the profile. In our model profile the resolution was 50 μm, so the minimum width should be larger or equal to 100 μm.

Diffusion rate of oxygen. In the Ds and Theta window of SensorTrace Profiling, the diffusion rate of oxygen in water (D_0) and sediment (D_s) is defined. D_0 is given in the oxygen diffusion table and is dependent on salinity and temperature. Add the same temperature and salinity as measured when you made the profile.

D_s is dependent on D_0 and porosity of the sediment (φ). The software lists three emperical formulas found in the literature, for the D_s calculations. The formula $D_s = D_0 \times \varphi$ is often used in sediment with a high porosity – like a biofilm, microbial mat and soft silty sediments. The formula $D_s = D_0 \times \varphi^2$ is typically used in sediments with lower porosity like sandy/silty sediment and compact mud. The formula $D_s = D_0/(1+3\,(1-\varphi))$ has been used in all kind of sediments. You can also manually add your own D_s value.

In the sediment from Limfjorden the overlying water had a bottom temperate of 20°C and a salinity of 15 ‰ which gives a D_0 of $2.038\ 10^{-5}\ cm^2\ s^{-1}$. D_s is calculated based on $D_s = D_0 \times \varphi$, because the sediment had a relative high porosity, of 0.8, giving a D_s of $1.63\ 10^{-5}\ cm^2\ s^{-1}$.
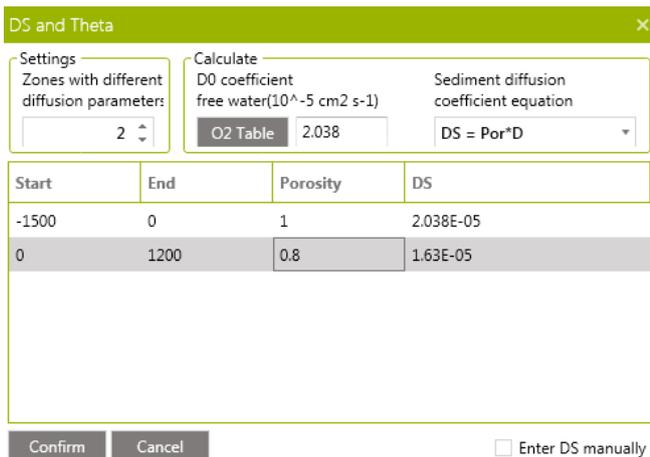
Figure 7 Settings for 'Intervals and zones'

Porosity is the correlation between the volume of void-space (like water) and the total volume of your sample. The porosity of the sediment is determined by standard geochemical analysis like water content and density measurements. If the porosity of your sample is changing with depth it is possible to calculate the oxygen diffusion rate for each depth by defining Ds for different depth intervals. In the sediment from Limfjorden we define Ds in two zones; one in the water column where $Ds = D_0 = 2.038 \ 10^{-5}$ cm^2 s^{-1} and one in the sediment where $Ds = 1.63 \ 10^{-5}$ cm^{-2} s^{-1}.

Summary of the settings

Below you find the summary of all the values we have added into the Activity window before running the model first time.

Figure 8 Oxygen microprofile and Ds calculations

Figure 9 Activity setting

When you have added all the above information you are ready to select ANALYZE. After the first analysis you have to look at the results and judge if there should be made any changes in the settings.

Results

The results of the model calculation are listed in the Statistics table and the Profile figure.

When you receive the results from the model it is important to verify if the results are scientifically correct. Below we will give you some factors you should give special attention to:

1. The yellow modeled profile
2. The volume based rate calculations
3. Zone number and statistics
4. Integrated production and consumption rates

A good model is when the yellow modeled profile is placed on top of the measured values at all depths. The green and red bars show the volume specific rate in the different depth zones.
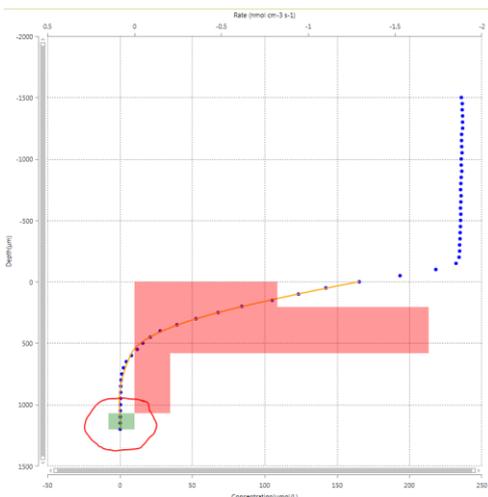

Figure 10 Modeled profile and volume based consumption and production rates after 1st Analysis.

In the statistics table the model highlights the number of optimal zones based on the sum of squared errors (SSE). The SSE is telling you how good the measured and modeled profiles fits together - the lower the SSE

value the better. The p-value indicates if the number of zones are appropriate, where a small p-value is better than a high. In the table you also find the calculated oxygen flux and the integrated oxygen consumption or production rates.

Statistics

Save solution | Export selected analysis

No. of Zones	SSE	P-Value	Top Conc (µmol/L)	Bottom Conc (µmol/L)	Top Flux (nmol cm-2 s-1)	Bottom Flux (nmol cm-2 s-1)	Integrated pr (nmol cm-2 s-
1	8842.71	0.000	125.07	0.70	0.042	0.000	-0.042
2	54.76	0.000	166.99	0.70	0.097	0.000	-0.097
3	53.79	0.494	167.49	0.70	0.098	0.000	-0.098
4	22.61	0.009	165.79	0.70	0.089	0.000	-0.089
5	18.48	0.234	165.39	0.70	0.085	0.000	-0.085

Figure 11 Statistics after 1st Analysis

In our model system the statistics shows that a model with 4 zones gives the best statistical values giving an integrated oxygen consumption rate of 0.089 nmol cm^{-2} s^{-1}.

However, from the figure, we can see that the integrated rate was based on an oxygen production rate at the bottom of the profile, which scientifically is very unlikely and values are probably an effect of the low oxygen concentrations changes and scatter in the measurements.

To avoid this uncertainty in the calculations, the depth interval was changed to maximum depth of 850 µm. At 850 µm the bottom oxygen concentration is 0.70 µM, which is added into the boundary conditions under 'Bottom concentration'.

Running Analyze again gave the following result:

Statistics

Save solution | Export selected analysis

No. of Zones	SSE	P-Value	Top Conc (µmol/L)	Bottom Conc (µmol/L)	Top Flux (nmol cm-2 s-1)	Bottom Flux (nmol cm-2 s-1)	Integrated pr (nmol cm-2 s-
1	1284.13	0.000	152.07	0.70	0.073	0.000	-0.073
2	34.71	0.000	167.88	0.70	0.101	0.000	-0.101
3	25.31	0.162	166.34	0.70	0.095	0.000	-0.095
4	8.40	0.011	165.28	0.70	0.088	0.000	-0.088
5	7.56	0.460	165.45	0.70	0.089	0.000	-0.089

Figure 12 Statistics after 2nd Analysis.

Again the model suggests an optimal zone interval of 4 giving an intergraded oxygen consumption rate of 0.088 nmol cm^{-2} s^{-1}. The SSE values is lower than in the first analysis, whereas the P-value is a bit higher.

To be able to get better statistics on the model we consider to change the boundary conditions because at a depth of 850 µm there is still oxygen and a small oxygen flux is expected in the sediment. Therefore, we

changed the boundary conditions from 'bottom conc and bottom flux' to 'Top conc + bottom conc' and made a third Analysis. The result gave an optimal zone number of 3 and an integrated oxygen consumption rate of 0,089 nmol cm^{-2} s^{-1}. The statistical values were now better than the previous solutions with a SSE value of 7.37 and a P-value of 0.001.

After trying to change other parameters (see also 'Play around' session) we decided to use the data from the 3rd analysis as our final result. We recommend to make similar calculations for minimum two more profiles from the same location.

Statistics

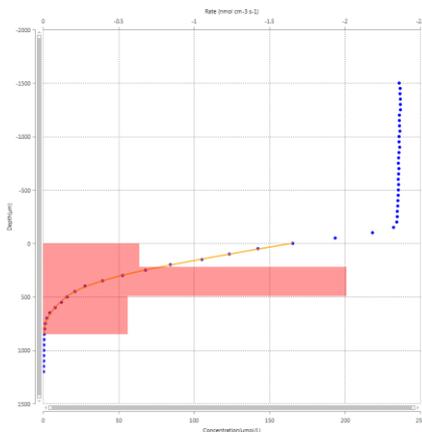| Save solution	Export selected analysis						
No. of Zones	SSE	P-Value	Top Conc (µmol/L)	Bottom Conc (µmol/L)	Top Flux (nmol cm-2 s-1)	Bottom Flux (nmol cm-2 s-1)	Integrated pr (nmol cm-2 s-
1	188.28	0.000	165.31	0.70	0.092	-0.013	-0.106
2	47.06	0.003	165.31	0.70	0.097	-0.001	-0.098
3	7.37	0.001	165.31	0.70	0.088	-0.001	-0.089
4	5.36	0.199	165.31	0.70	0.094	-0.001	-0.095
5	5.13	0.493	165.31	0.70	0.094	-0.002	-0.096

Figure 13 Statistics Analysis and model profile after 3rd analysis.

Play around

The quality of the model depends on the input data. Some input data are associated with relative high error – e.g. the porosity. To find out how large an effect the input information has on the model and the rate calculations, you can play around with the different input information.

1. Boundary conditions
2. Depth interval
3. The oxygen diffusion rate - e.g. by changing the temperature and salinity
4. Change the formula for the Ds calculation
5. Porosity

In our model a change of 2-3°C or 2-3 ‰ in the calculation of D_0 did not give an important change in our results, neither did a change in the formula from Ds = D_0 x φ to Ds = D_0 x φ^2 or changing the porosity from 0.8 to 0.85.

Final result

Using the SensorTrace Profiling software on a high-resolution oxygen profile made in an organic rich sediment core from Limfjorden in Denmark we found that the oxygen penetration rate was 950 µm and the integrated oxygen consumption rate was 0.089 nmol cm^{-2} s^{-1}. The highest volume based oxygen consumption rate, 2.008 nmol cm^{-3} s^{-1}, was found at 200 µm to 500 µm sediment depth. These oxygen consumption rates are similar to the rate found in similar organic rich sediments (e.g. Glud, 2008, Epping et al 1999).

Other solutes

The consumption and production rate of solutes like sulfide, H_2 and N_2O can also be calculated in SensorTrace Profiling from high resolution profiles. The Activity Window works in the similar way as for oxygen although the inputs might vary depending on the profile. For example, the sulfide concentration is often 0 at the surface of the sediment and high at the bottom, therefore the **boundary condition** 'top conc and top flux' of 0 is often used. The **Diffusion coefficient (D_0)** for other gasses than oxygen can be calculated from the oxygen table "Seawater and Gases Table" found www.unisense.com under support, by multiplying the table values with a constant specific for the different solutes: for H2S multiply by 0.7573, for H_2 with 1.9470 and for N_2O with 1.0049 (for more information see "Seawater and Gases Table").

References

Boudreau, B.P. 1984, On the equivalence of nonlocal and radial-diffusion models for porewater irrigation.

Epping et al 1999, Photosynthesis and dynamics of oxygen consumption in a microbial mat calculated from transient oxygen microprofiles. Limnology and Oceanography. 44(8): 1936-1948.

Glud, N. R. 2008. Oxygen dynamics of marine sediments. Marine Biology Research 4: 243-289.