Abstract

This note will explain how to use SensorTrace Profiling to quantify 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 a Unisense MicroProfiling System.

As an example we will use an oxygen microprofile 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 the boundary conditions. The model shows the rate distribution and compares the calculated profile with the actual measured profile.

Using a stepwise optimization, the rate 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 found that the maximum oxygen consumption rate in the sediment from Limfjorden was 1.25 nmol cm\(^{-3}\) s\(^{-1}\) and the integrated oxygen flux across the water–sediment interface, 0.056 nmol cm\(^{-2}\) s\(^{-1}\), which are comparable to rates found in similar environments (Glud, N. R. 2008, Epping et al 1999).

The oxygen profile used in this note is available in the ‘Unisense Data’ folder under ‘Demo Experiments’ and you can use it for practice purposes.

Material and Method

Sediment cores were 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 microprofiles were made by using a motorized MicroProfiling System and an oxygen microsensor 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.
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 – preferably similar to the in-situ conditions.

Activity

In the Activity window of SensorTrace Profiling the consumption and production rates are calculated from the oxygen microprofile 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 D_s determination

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

Profile: First select the sensor that was used to measure the profile, then select the profile.

Boundary conditions: To constrain the model, two independent boundary values are needed for the analysis. In the program you can select between 5 different pairs of boundary conditions, e.g. for oxygen profiles where the end concentration and flux deepest in the profile typically are 0 (as in the examples used here), the boundary condition ‘Bottom conc + bottom flux’ is typically used (Figure 4).

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 takes place. In the model sediments we start at the water - sediment interface (0 µm) and end where all oxygen is consumed deep down in the profile.
Max zones refers 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. Start by selecting 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 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 at least 100 µm.

**Diffusion rate of oxygen**

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

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

In the sediment from Limfjorden the overlying water had a bottom temperature of 20 °C and a salinity of 15 ‰ which gives a $D_0$ of 2.038 $10^{-5}$ cm² s⁻¹. $D_s$ is calculated based on $D_s = D_0 \times \phi$, because the sediment had a relative high porosity of 0.8, giving a $D_s$ of 1.63 $10^{-5}$ cm² s⁻¹.

**Porosity** is the ratio between the volume of void space (like water) and the total volume of your sample. The porosity of the sediment is often determined as water content. If the porosity varies with depth, increase the number of zones and define the diffusion conditions for each depth interval. In the sediment from Limfjorden we define $D_s$ in two zones; one in the water column where $D_s = D_0 = 2.038 \times 10^{-5}$ cm² s⁻¹ and one in the sediment where $D_s = 1.63 \times 10^{-5}$ cm² s⁻¹.

**Summary of settings**

Below you find the summary of all the settings we have defined in the Activity window before running the model the first time.

When you have entered all the above information click **Analyze**. After the first analysis, inspect the results and change settings to see if a better analysis can be made.
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 model is good if 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.

In the statistics table (figure 10) the model highlights the row with the optimal number of zones based on the statistics. The SSE indicates how well the measured and modeled profiles fit - the lower the SSE value the better. The P-Value may be used for selection of the best number of zones. The P-Value for n zones indicates whether increasing the number of zones from n - 1 to n resulted in a significantly improved fit.

Often P < 0.05 is used as the criterion. In Figure 10, going from 3 to 4 zones gave a significantly better fit (P = 0.010), whereas going from 4 to 5 zones did not (P = 0.456). In the table you also find the calculated oxygen flux and the integrated oxygen consumption or production rates.

In our model system 4 zones gives the best statistical values and an integrated oxygen consumption rate of 0.055 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 due to variation in data.

To avoid this, the depth interval was changed to maximum depth of 850 µm. At 850 µm the bottom oxygen concentration is 0.70 µM, which is used as the boundary conditions under ‘Bottom concentration’.

Running Analyze with these new parameters gave the following result:

Again the model suggests that 4 intervals result in the best solution (Figure 11), giving an integrated oxygen consumption rate of 0.056 nmol cm\(^{-2}\) s\(^{-1}\). The SSE values is lower than in the first analysis, whereas the P-value is a bit higher.

In an attempt to improve the fit we changed 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 + 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 0.056 nmol cm\(^{-2}\) s\(^{-1}\) (Figure 12 and 13). The statistical values were now better than the previous solutions with a SSE value of 7.81 and a P-value of 0.001.

After trying to change other parameters (see also ‘Play around’ section) 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.
The quality of the model depends on the input data. Some input data are associated with relative high uncertainty – e.g. the porosity. In order to get a feel for how sensitive the fit and the calculated rates are to the input data, we recommend to play around with the different input information - e.g.:

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 $D_s$ 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 $D_i = D_0 \times \phi$ to $D_i = D_0 \times \phi^2$ 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 was approximately 950 µm and the integrated oxygen consumption rate was 0.057 nmol cm$^{-2}$ s$^{-1}$. The highest specific oxygen consumption rate, 1.25 nmol cm$^{-3}$ s$^{-1}$, was found at approx. 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 $\text{H}_2\text{S}$, $\text{H}_2$ and $\text{N}_2\text{O}$ can also be calculated in SensorTrace Profiling from high resolution profiles. The general procedure for other solutes is the same as for oxygen, although the inputs may 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 ($D_s$) for other gasses than oxygen can be calculated from the oxygen table “Seawater and Gases Table” found under support, by multiplying the table values with a constant specific for the different solutes: for $\text{H}_2\text{S}$ multiply by 0.7573, for $\text{H}_2$ with 1.9470 and for $\text{N}_2\text{O}$ with 1.0049 (for more information see “Seawater and Gases Table”).

**References**


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