

## OXYGEN CONSUMPTION IN BENTHIC SEDIMENTS: EXPERIMENTAL ANALYSIS OF THE TEMPERATURE INFLUENCE ON SEDIMENT OXYGEN DEMAND

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*Dead organic material accumulated on the bed of a lake, reservoir or wetland often provides the substrate for substantial microbial activity as well as chemical processes that withdraw dissolved oxygen (DO) from the water column. This paper proposes to study the process of oxygen consumption in benthic sediments from Serrai Lake taking into account the temperature influence.*

**Keywords:** oxygen consumption, eutrophication, nutrient fluxes.

### 1. Introduction

Freshwater lakes are susceptible to eutrophication due to increased input of nutrients, nitrogen and phosphorus, from anthropogenic sources. Excess availability of nutrients stimulates primary production but can also have significant effects on microbial processes. Elevated primary production increases the amount of organic matter and thus increases the mineralization [1-4].

The increased mineralization consumes oxygen (O<sub>2</sub>) in the hypolimnion, leading to lake anoxia during stratification periods, favouring anaerobic microbial processes. In addition, nutrients can also affect bacterial metabolism and degradation pathways. Organic matter is predominantly degraded through microbial processes, which provide maximum energy yield. Thermodynamic energy yield from the oxidation reactions with various electron acceptors decreases in the order of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup> and CO<sub>2</sub>. For example, when nitrate is abundant organic carbon is degraded through nitrate reduction in denitrification than through methanogenesis, which is a common mode of carbon degradation in non polluted freshwater sediments [5].

Changes in degradation rates and pathways induced by eutrophication have atmospheric importance, since microbial processes produce important

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greenhouse gases carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). In freshwaters,  $\text{CH}_4$  is produced in anoxic sediments via methanogenesis and aerobically oxidized by methanotrophic bacteria if  $\text{O}_2$  is available in the sediment–water interface or water column. Thus, the  $\text{O}_2$  depletion can stimulate  $\text{CH}_4$  production in eutrophic lakes during stratifications and decrease  $\text{CH}_4$  oxidation leading to an increase in the emissions of  $\text{CH}_4$  from waters to the atmosphere [6, 13].

## 2. Materials and methods

In order to determine the fluxes oxygen profiles were performed at different temperatures.

We used microsensors made by Unisense: a miniaturized Clark-type oxygen sensor with a guard cathode designed for research applications within physiology, biotechnology, environmental sciences, and related areas.

They are based on diffusion of oxygen through a silicone membrane to an oxygen reducing cathode which is polarized against an internal Ag/AgCl anode.

The flow of electrons from the anode to the oxygen reducing cathode reflects linearly the oxygen partial pressure around the sensor tip and is in the pA range. The current is measured by a high quality pA meter. With the minute tip size, excellent response time ( $t_R < 5s$ ), and insignificant stirring sensitivity the Unisense oxygen sensor makes it possible to make reliable and fast measurements at high spatial resolution [11, 8]. The sensor is connected to a high-sensitivity picoammeter such as the Unisense PA2000 and the cathode is polarized against the internal reference. Driven by the external partial pressure, oxygen from the environment will penetrate through the sensor tip membrane and is reduced at the gold cathode surface. The picoammeter converts the resulting reduction current to a signal. The internal guard cathode is also polarized and scavenges oxygen in the electrolyte, thus minimizing zero-current and pre-polarization time [7].

Due to the extreme low currents produced in microsensors (typically 10-12 pA), only specialized picoammeters are suited for use with the microsensors. We used the picoammeter PA2000, a versatile 2-channel picoammeter designed for laboratory use with amperometric micro- and minisensors, such as Clark-type oxygen sensors.

Exposure to humidity, dust and corrosive environments (e.g. field conditions) may damage the PA2000 and shorten its performance and lifetime. The PA2000 has two channels that can be polarized independently at any level from -2.5V to +2.5V; both channels have guard connectors polarized at the same voltage as the measuring electrode.

Thus it is possible to measure signals from two different types of sensors simultaneously. The PA 2000 has a very fast signal response. It is capable of a 90% response time of 50 milliseconds, which makes dynamic measurements with a very small time resolution possible (e.g. dynamic photosynthesis measurements)

To reach the objective to precisely determine the sediment-water interface, the spatial individualization of the position of the microelectrode point it is fundamental (performed in contemporary to the measurement of the concentrations). The difficulties in such sense are manifold: the dwarfish dimensions of the diameter of point (that request high spatial resolutions), the same irregularity of the surface of sediment (and relative impossibility of univocal identification of the 'floor' of interface), the transparency of the same point (built in material glassy) [4].

For this type of analysis has been used of a digital reflex (the Nikon D1x with objective fixed nikkor AF micro 125/2.8 Ds) in endowment in the Laboratory of Hydraulic of the Department of Civil and Environmental Engineering of the Trento University. The position of the interface water-sediment is drawn by an analysis of the go off digital photos, every 500  $\mu\text{m}$  of deepening of the microelectrode, both above that inside the sediment (having had the adroitness to maintain the photographic car immovable during every test).

For every prove it tries releases for which the point results to be above the interface have allowed to draw, of the analysis in sequence, the middle number of correspondent pixel to the deep of 500  $\mu\text{m}$  of the microelectrode's point, defining so the geometric scale of the system of reference-image. The photos from which it results instead that the point of the microelectrode is penetrated inside the sediment have allowed to distinguish with evidence the exact point of infission, and therefore to define the zero of the system of reference-image. It is important to clarify that such analysis method has not guaranteed satisfying results for all the tests because of some tied up operational difficulties [14].

Sediment cores were taken from Serrai Lake, situated to a quota of 974 m on the plateau of Piné, and were kept at a constant temperature before proceeding the experiment. This lake has a surface of around 450000  $\text{m}^2$  and a middle depth of 7.5 m; is classified as eutrophic and it is periodically subject to abundant algal blooms during the spring and in the late summer. Numerous interventions have been effected for setting remedy to this situation, with the purpose to reduce to minimum the outside nutrients inputs and the inside load due to the release by the sediments, getting some results that don't seem to be enough to determine the complete recovery of the lake and the return to a mesotrophy state.

*The Fos Grant* is the principal tributary that reaches the northeast bank of the lake with varying course, strongly influenced by the atmospheric conditions.

*The Fos Maestro* reaches the lake from the southeast bank. Their origin is in the proximity of the ice stadium and is almost exclusively fed by the water used

for cooling the pressers of the refrigerant system of the stadium during the winter period. The choice of monitoring the Fos Maestro depends on the proximity of his raced to the greenhouses.

*Rio del Croz* it is a small permanent brook that goes down from the Dosso di Costalta, a not urbanized zone and poorly cultivated.

Table 1

**Principal hydrological, thermal and morphological data  
of the Serrai Lake (IASMAA)**

Basin	Fersina (Adige)
Altitude [m s.l.m.]	974
Lake surface [ $km^2$ ]	~0.45
Volume [ $m^3$ ]	~3 106
Maximum depth [ $m$ ]	18
Mean depth [ $m$ ]	7.1
Thermal classification of the lake	thermocline
Inhibitor element	phosphorus

In the summer of 1997 the phenomenon of eutrophication of the lake of the Serrai was very pronounced. The excessive concentration of nourishing in the waters has induced an abnormal algal bloom. Improvements have been effected on the situation.

The stratification of the lake always appears rather modest. The metalimnion, is individuabile in the summer months among 4 and the 7 meters with notable variations in the different years. The most elevated temperatures are been measured in 2003 with 24,5 °C at surface, while during the other years the temperature of 22°C has never been overcome. The oxygen, in the summer period, introduces very elevated values at surface and very close to anoxia at the bottom. During remixing period of the oxygen (spring), homogeneous along the whole water column, introduces normal values next to the saturation. To the autumn remixing the values are much reduced.

### 3. Experiment description and the experimental setup

It is well known that the eutrophication phenomena is related to the oxygen consumption problem so we decided to study the sediment oxygen demand in Serrai lake sediments at different temperature values, in oxic and anoxic conditions. The first step for this study was the experimental setup. A tank

was built from 15 mm glass with 50 mm isolation then some 5 mm diameter pipes were attached so that a frigorific agent could circulate and cool the water in the aquarium. The length and the depth of this tank were 0.5 m and it was supposed to have a good thermal inertia. We placed a sediment core from Serraia in the middle of that tank and we checked the temperature of the sediment, the overlying water (in the sediment core) and the basin water for a few days. We observed that in the tank water we had important thermal gradients and the same was happening in the sediment core. It was obvious that we can not control the temperature and that the cooling system we had was not efficient so we had to face the temperature control issue. We thought of reducing the dimensions of the tank, increasing the flow velocity of the frigorific agent and fill the basin with the frigorific agent (that we recirculate) instead of water. We choose a cylindrical tube of 150 mm diameter, 450 mm high with a 10 mm isolation. At the upper part we attached the 4 plastic pipes for the input of the transparent frigorific agent. We covered the sediment core with a transparent plastic lid with a 10 mm diameter whole just enough to allow the penetration of the  $O_2$  microsensor.

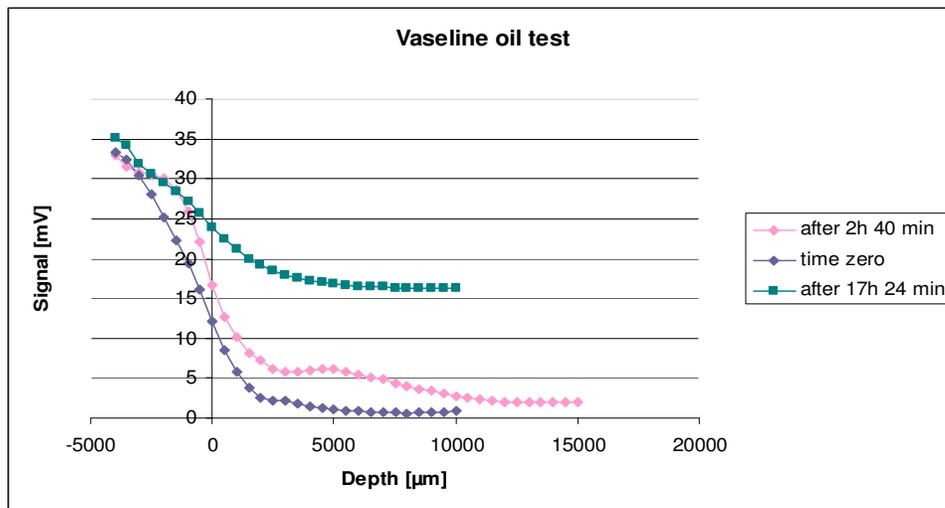


Fig. 1. Diffusion test for vaseline oil.

For the output of the frigorific agent a plastic pipe (5 mm diameter) was attached at the bottom. We tested the temperature for some days and we had a good control.

We set the temperature of the frigorific agent at 2.3 °C to reach 6.5 °C in the sediment core and we performed a first profile. The 0 point represents the sediment- water interface. From the second profile it can be seen that the oxygen

concentration is about 7 [mg/l] in the overlying water and less than 2 [mg/l] in the sediment.

In order to stop oxygen diffusion from atmosphere we tested various oils. The experiment required a chemical isolation because the oxygen probe was very fragile and the best solution we found was the silicone oil (see figure 1)

It is not completely isolating, it can be seen that the oxygen is still diffusing but comparing the first profile with the one performed after 160 minutes we realised that the differences can be negligible and that this could be a solution for our experiments. Also the values for the flux are not so high, especially for the first two profiles.

#### 4. Experimental results and discussions

A first experiment was performed at 20.8 °C and the time step between two profiles is 30 minutes (see figure 2).

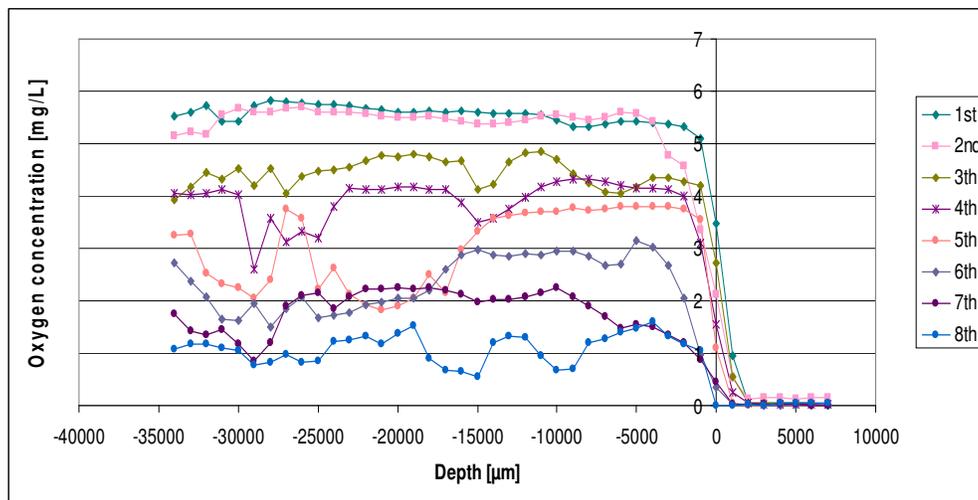


Fig. 2. Oxygen consumption profiles at 20.8°C.

The profiles were integrated and the oxygen mass and the fluxes were calculated. By the interpolation with ideal curves we concluded that a zero-order reaction fits well with our data (see figure 3).

From the slope we could determine the zero order constant rate  $k=0.0038$  and the flux evaluation for this approximation is  $J=1.149$  [mg/min·cm<sup>2</sup>]. Just to be sure that our measurements were right we repeated the test at 21°C with another sediment core that was also sampled from Serraria lake but in a different time period (June) while the one we used at 20.8 °C was sampled in may after a

strong storm that perhaps resuspended the organic matter. A rough estimation of the flux at 21°C conduces us at the value of:  $J=0,8352 \text{ [mg/min}\cdot\text{cm}^2]$ .

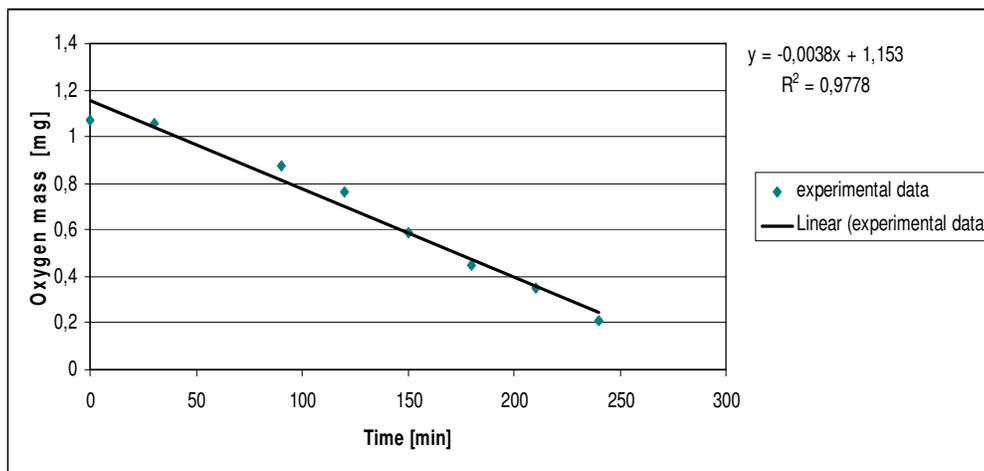


Fig. 3. Linear interpolations with a zero-order reaction curve.

This result can be compared with the previous one (obtained for 20.8°C); the small differences can be due to the difference of the temperature and to the difference of the sampling period. Because we wanted to see if the temperature influences the oxygen consumption we performed some new profiles at 5°C. In this case a second order approximation would be totally wrong but it was shown that a zero or a first order reaction fits quite well our experimental data. Using the first order approximation curve the flux was calculated:  $J=1,6958 \text{ [mg/min}\cdot\text{cm}^2]$  which is *1,475635 times more than the value of the flux we have at 20.8°C*. Because of the temperature difference we had different initial oxygen concentrations: for 20.8°C we had about 6 [mg/l] and for 5°C the initial concentration was 8 [mg/l]. This means that having different initial values we can not just compare the profiles in order to see if the temperature influences or not the oxygen consumption process. Making a difference between the oxygen mass at the initial moment and the oxygen mass we have for the last profile and taking into account the depletion time we can compare the data for these two different temperatures. At 20.8 °C 0,862702 mg of oxygen were depleted in 240 minutes and 0,613006 mg of oxygen in 330 minutes at 5°C. This means that we had a depletion rate of 0,003595 [mg/min] at 20.8°C and of 0,001858 [mg/min] at 5°C, which implies that the consumption process is accelerated by the temperature increase.

From the comparison of the experimental data we can say that the temperature definitely influences the oxygen consumption and that the

consumption rate increases with the temperature. Just to see if we obtain at least the same order of magnitude we compared these experimental results with the field data. In this calculation were considered oxygen concentration masses from 6 May 2007 until the 15<sup>th</sup> of June 2007 with the oxygenator in operation and with the oxygenator out of order; the oxygenator is situated at about 8,5 m depth. In the hypolimnion the mass of oxygen is 8101,108638 [kg] so that after a rough estimation we obtain a flux of 1,1252 [mg/day-cm<sup>2</sup>], comparable with the experimental data. Because of the oxygenator the temperature in the hypolimnion varied between 12 and 14 [°C].

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