

Respiration of Bulk Organic Matter in aquifer sediments with the Micro-OxymaxTM

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Degradation of bulk organic matter (BOM) contributes to the redox status of groundwater systems. Therefore, the potential of sandy aquifers to reduce oxidants as oxygen, nitrate and sulphate depends on their BOM content and its reactivity. (Griffioen *et al.*, (1996). Knowledge on the natural reduction capacity of aquifers has become increasingly important over the last decades, because of the excessive input of oxidants in groundwater systems, mainly by agricultural activities. Although a lot of research has been done on the degradation of organic matter in soils and marine sediments, little is known about the reactivity of BOM in aquifer sediments.

This abstract discusses the feasibility of using the Micro-Oxymax respirometer to study degradation kinetics of BOM in sandy aquifer sediments. The Micro-Oxymax continuously measures O₂ consumption, CO₂ production and temperature in the headspace of up to 80 chambers.

Materials and methods

Ten samples from various sandy Dutch aquifer sediments were selected and kept anoxic.

Duplicates were studied together with a blank that only contained tap water. Every chamber (150 ml 'Duran' bottle) was filled with about 15 g of sediment and filled up to 50 ml with tap water. The reaction vessels were connected to the closed circuit of the Micro-OxymaxTM. To stimulate BOM degradation the samples were shaken (100 rpm) and kept at a 25°C ($\pm 1^\circ\text{C}$) during the experiment. The experiment lasted 27 days and each headspace was measured sequentially in a closed circuit. It took about three hours to complete one sequence, after which the sequence was repeated. Oxygen concentrations were continuously kept saturated (~ 1.2 mmol/l at 25°C). After the experiment, the change in SO₄²⁻ and HCO₃⁻

concentrations and pH of the water in the chambers was measured.

Results and discussion

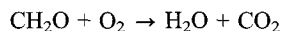
Basically, two sample types could be distinguished, using the reaction pattern in O₂ consumption and CO₂ production:

-Molar O₂ consumption was around equal to the molar CO₂ production.

-Molar O₂ consumption was much larger than CO₂ production

The observations made in these two groups will be discussed by two representative samples (sample 1 and 2).

In Fig. 1 the first sample type is illustrated. The O₂ consumption and CO₂ production is explained by the respiration of CH₂O, the simplified representation of BOM, with the overall reaction;



After a lag phase of about a day, respiration rates increase rapidly. Around day 5 respiration rates level off. The difference after day 5 in respiration rates between 1a and 1b probably reflects the natural heterogeneity of the sediment at sample scale.

TABLE 1. Analyses of water in the reaction vessels at the end of the experiment (Concentrations in mmol/l)

	Tap water	1a	1b	2a	2b
HCO ₃ ⁻	1.47	1.48	1.08	0	0
pH	8	8.03	7.05	2.36	2.39
SO ₄ ²⁻	0.17	1.45	1.84	11.7	15.5

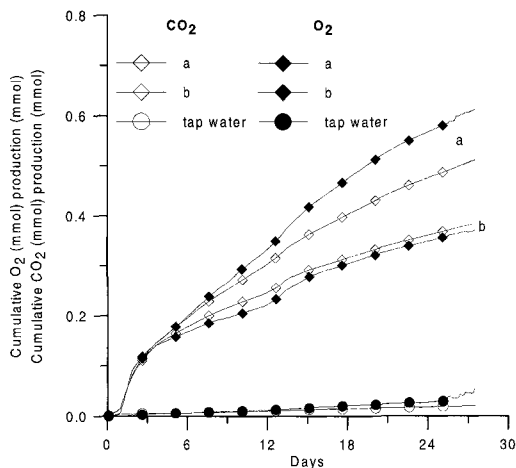


FIG. 1. Respiration of BOM in sample 1 (a and b are duplicates).

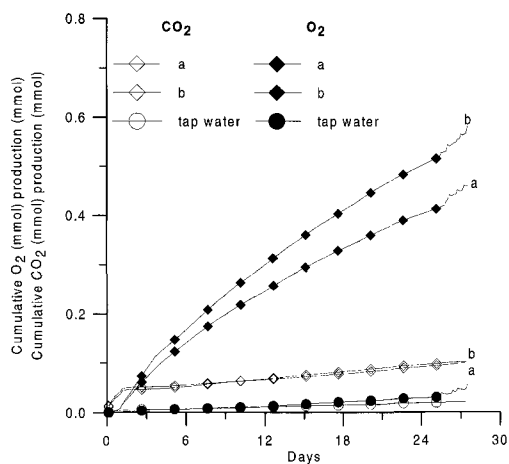


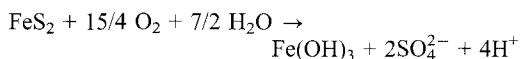
FIG. 2. O₂ consumption and CO₂ production in sample 2 (a and b are duplicates).

Around day 12 the respiration of 1a and 1b increase slightly. Since temperatures were kept constant this can be explained by organic material becoming available that was less resistant to degradation.

In Fig. 2 a different relation between the O₂ consumed and CO₂ produced is shown.

After a fast CO₂ evolution between day 0 and day 3, CO₂ production rate ceases.

The increase in SO₄²⁻ concentration and the decrease in HCO₃⁻ concentration and pH (Table 1) strongly suggests that the oxygen consumption is caused by the oxidation of iron sulphides, e.g. pyrite;



This acidifying reaction promotes carbonate dissolution resulting in CO₂ degassing. This lasted the first days of the experiment until all carbonates were dissolved.

Oxidation of dissolved organic carbon cannot account for the small CO₂ production and O₂ consumption in the tap water (Fig. 1 or 2).

Part of the O₂ 'consumption' is probably introduced by dilution of the O₂ concentrations because of the enlargement of the headspace as water vapourises.

Conclusions and further research

The Micro-Oxymax[™] respirometer proved to be an

easy and accurate method to obtain detailed respiration data.

Sandy aquifer sediments contain small amounts of organic matter (around 0.1 wt.%). In soils and marine sediments the largest part of organic carbon normally resides in the clay and silt fraction (Hedges and Oades, 1997). In a further study we will focus on determining which particle size class contains the largest part and/or the most reactive compounds of the BOM in aquifer sediments. Concentration of organic matter by physical separation might enhance experimental resolution.

In this study, indigenous bacteria only degraded half or less of the organic matter present. Extending the experiment or adding nutrients that stimulate respiration, will yield more information on the kinetic fractions present in BOM in aquifer sediments.

The acid conditions, caused by iron sulphide oxidation, inhibit potential bacterial decomposition of BOM. Raising the buffer capacity of the samples might facilitate BOM degradation after and/or during iron sulphide oxidation.

References

- Hedges, J.I. and Oades, J.M. (1997) *Org. Geochem.*, **27-7/8**, 319–61
 Griffioen, J., Lourens, A. and Van Beek, C.G.E.M. (1997) *TNO/Kiwa*, GG-R-96-89(b).