

**Supplementary material****Organic carbon burial efficiencies in sediments: The power law of mineralization revisited****Sergei Katsev<sup>1\*</sup> and Sean A. Crowe<sup>2</sup>**<sup>1</sup>*Large Lakes Observatory and Department of Physics, University of Minnesota Duluth, 2205 East 5<sup>th</sup> St., Duluth, Minnesota 55812, USA*<sup>2</sup>*Departments of Microbiology and Immunology, and Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, BC V6T1Z4, Canada**\*Corresponding author: skatsev@d.umn.edu***1. Calculation of remaining carbon fraction by integration of mineralization power law**The power law of organic matter reactivity  $k$  as a function of time  $t$ 

$$k(t) = bt^{-a}, \quad (1)$$

where  $b$  and  $a$  are constants defines the rate of organic carbon mineralization  $R$ :

$$R = \frac{dC}{dt} = -k(t)C. \quad (2)$$

Equation 2 can be integrated to obtain the fraction of organic material that remains unmineralized after a given amount of time. For  $a \neq 1$ , separation of variables and integration of

$$\frac{dC}{C} = -bt^{-a} \quad (3)$$

yields

$$C = C_0 \exp\left(\frac{-bt^{1-a}}{1-a}\right) \quad (4)$$

where  $C_0$  is the initial concentration at time  $t=0$ . For a special case of  $a=1$ , integration of Eq. (3) results in

$$C = C_0 \left( \frac{t_0}{t} \right)^b \quad (5)$$

where  $C_0$  is the concentration at time  $t_0$ .

As for the power law written in the form of Eq. (1) the time  $t=0$  results in a meaningless infinite initial reactivity, it is more practical to consider initial concentrations at some later time  $t_0$ . For organic material decomposition in the sediment, for example,  $t_0$  can correspond to the settling time (referred to as  $t_{settle}$  in the manuscript text) of organic material in the water column.  $C_0$  in that case would correspond to the amount of organic matter deposited to the sediment surface. For mineralization in the water column,  $t-t_0$  would correspond to any non-zero time that elapsed since the beginning of decomposition, e.g., after death of an organism. For a non-zero  $t_0$ , Equation 4 then becomes

$$C(t) = C(t_0) \exp \left( \frac{-b(t^{1-a} - t_0^{1-a})}{1-a} \right), \quad (6)$$

where  $t > t_0$ . The mathematical problem of infinite reactivity at  $t=0$  in Eq. (1) clearly indicates that Eq. (1) is an approximation that is expected to break down for sufficiently small times. An alternative to Eq. (1) is given, for example, by Janssen (1984) as well as Middelburg (1989) and Middelburg et al. (1993), where reactivity is written in the form

$$k(t) = b(t' + t)^{-a} \quad (7)$$

with  $t'$  as a (fitting) parameter (e.g., discussed in more detail in Arndt et al. 2013). This effectively redefines the meaning of “age” of organic material by adding an initial time parameter.

Another caveat regarding the meaning of the organic matter “age” pertains to its determination in the bioturbated zone. The depth of bioturbation in freshwater sediments is significantly shallower than in marine sediments (e.g. 2 cm in Lake Superior; Li et al. 2012), so bioturbation effects on the C age determination are restricted to a comparatively small interval. (In the original compilations of Middelburg (1989) and Middelburg et al. (1993) bioturbation was not considered.) Nevertheless, mixing of the upper sediment layers by macrofauna results in a situation where the effective age (as well as effective reactivity) at a given depth reflect a mixture of fresh and old particles. Fortunately, the effect on reactivity goes in parallel with the effect of mixing on the vertical distribution of  $^{210}\text{Pb}$ , a radioactive isotope that is commonly used for dating the age of sediment. The similarity of the two processes (exponential decrease in unsupported  $^{210}\text{Pb}$  activity and power-law decrease in organic carbon reactivity with time) is likely to decrease the bioturbation-related error in the carbon age-vs-reactivity relationship. In our compilation, we used the vertical profiles of organic carbon to determine reactivities

only below the bioturbation zone, whereas methods based on the rates of oxygen consumption (Li et al. 2012) were used within the bioturbated zone. Focusing of sediment towards the deeper regions of the lake is another factor that to some degree may affect the determination of the organic carbon age. Where sediment age is determined using a technique such as  $^{210}\text{Pb}$  dating, the age of the inorganic sediment may, in principle, differ from the age of the organic particles that rain into the sediment from directly above. This effect, perhaps, may be responsible for the observations in site-specific studies (e.g., Thomsen et al. 2004; Fig. 1) of uncharacteristically high reactivities that substantially deviate from the Middelburg line and, when projected over longer time intervals, predict unrealistically low carbon concentrations in the deeper sediment.

When the kinetics of organic matter mineralization changes, e.g. as it transitions from oxic into anoxic sediment zone, the initial concentration  $C_0$  in Eq. (4) needs to be redefined to reflect the initial concentration at the beginning of the new mineralization regime. Thus, the concentration  $C(t)$  in the anoxic sediment becomes

$$C = C_{OPD} \exp\left(\frac{-b_{anox}}{1-a_{anox}}(t^{1-a_{anox}} - t_{OPD}^{1-a_{anox}})\right) \quad (8)$$

where  $C_{OPD}$  and  $t_{OPD}$  are, respectively, the concentration and age of organic material at the oxygen penetration depth (OPD) inside the sediment column and  $a_{anox}$  and  $b_{anox}$  are the parameters for the reactivity law (Eq. 1) under anaerobic conditions. The time  $t$  is age, with the difference  $(t-t_{OPD})$  corresponding to the time the organic material spent in the anoxic sediment. The concentration  $C_{OPD}$  can be calculated similarly as

$$C_{OPD} = C_0 \exp\left(\frac{-b_{oxic}}{1-a_{oxic}}(t_{OPD}^{1-a_{oxic}} - t_{settle}^{1-a_{oxic}})\right) \quad (9)$$

where time  $t_{OPD} = t_{settle} + t_{oxic}$  includes the oxygen exposure time in the oxic water column ( $t_{settle}$ ) and in the oxic sediment layer ( $t_{oxic}$ ).  $C_0$  characterizes the amount of organic carbon at the sediment surface.

The parameters  $a$  and  $b$  in Eqs. (4,8-9) are directly obtainable from linear regression of  $\log_{10} k$  vs.  $\log_{10} t$  (Fig. 1). (In eqs. 8 and 9 the respective parameters are obtained from the linear regression fits, respectively, to data in anoxic and oxic environments, as shown in Fig. 1.) For a linear regression fit

$$\text{Log}_{10} k = b' + a' \text{Log}_{10} t, \quad (10)$$

these relations are  $a = -a'$  and  $b = 10^{b'}$ . In this manuscript, the thus obtained parameters have been used in Eqs. (9-10) to calculate the remaining unmineralized fraction of organic carbon at any time during the organic matter burial into sediment and to calculate burial efficiencies (Figs. 2-3). The burial efficiencies were calculated as  $C/C_0$ , where  $C_0$  is the organic carbon amount at the sediment-water interface and  $C$  is the amount that remains unmineralized after a given time (or at a specified depth within the sediment, where explicitly stated).

## 2. Conversion between time and depth within the sediment column and calculation of oxygen exposure time (OET)

The calculations of burial efficiencies for different sedimentation rates (SR, g cm<sup>-2</sup> y<sup>-1</sup>) (Fig. 2b and Fig. 3) required a relationship between the sedimentation rate and the duration of time that organic material spends in the oxidized sediment layer. The oxygen penetration depth (OPD, cm) was calculated from correlation with sedimentation rate (SR, g cm<sup>-2</sup> y<sup>-1</sup>) as  $OPD = 0.77 SR^{-0.53}$  (Li et al., 2012).

Conversion between time after deposition  $t$  and depth within the sediment  $x$  was done using typical surface sediment porosity of  $\phi=0.9$  and dry sediment density of  $\rho=2.65$  g cm<sup>-3</sup>:

$$t = x\rho(1-\phi) / SR \quad (11)$$

Accordingly, the oxygen exposure time (OET) in the sediment was calculated from oxygen penetration depth (OPD) as  $OET = OPD \cdot \rho \cdot (1-\phi) / SR$ . The burial efficiency was then calculated using Equations 8-9 with  $t_{oxic} = OET$ .

## SUPPLEMENTARY INFORMATION

**Supplementary Table 1. Sources of data for Fig. 1.**

<i>Lake</i>	<i>Ref.</i>	<i>Comment</i>
Baikal (Russia)	4	Water column. Assumed $U=1 \text{ m d}^{-1}$ , mixing zone 100 m. Oxic.
Bosumtwi (Ghana)	19	Sediment, anoxic.
Bouchet (France)	2	Sediment, anoxic.
Danish lakes	4	Water column. In situ incubations with $^{14}\text{C}$ . Oxic.
Elk Lake (USA)	3	Sediment, anoxic.
George (USA)	11	Sediment, anoxic.
Huron (USA)	10	Sediment, anoxic.
Kivu (Rwanda)	16	Sediment, anoxic
Loosedrecht (Netherlands)	15	Water column, oxic.
Lugano (Switzerland)	7	Water column, incubations, oxic and anoxic.
Matano (Indonesia)	This work	Sediment, anoxic
Michigan (USA)	20	Sediment, anoxic
Michigan (USA)	13	Sediment, anoxic
Michigan (USA)	11	Water column. $U=1 \text{ m d}^{-1}$ , oxic
Mirror Lake (USA)	2	Water column. In situ incubations with $^{14}\text{C}$ , oxic.
Shingobee (USA)	3	Sediment, anoxic.
Superior (USA)	8,14	Sediment, oxic and anoxic.
Superior (USA)	1	Water column. $U=0.76 \text{ m d}^{-1}$ , oxic.
Tahoe (USA)	6	Water column. Assumed $U=1 \text{ m d}^{-1}$ , mixing zone 30 m, oxic.
Victoria (Tanzania)	17	Sediment, anoxic.

### References for Supplementary Table 1

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## SUPPLEMENTARY FIGURE LEGEND

**Supplementary Figure 1. Profiles of organic carbon in lake sediments.** Red lines are calculations based on  $k(t)$  dependencies in Fig. 1, for oxic and anoxic conditions. Oxygen exposure times in sediment, organic carbon concentrations at the sediment-water interface, and effective settling times before deposition,  $t_{settle}$ , are chosen individually for better (non-unique) fit.  $t_{settle}$  accounts for settling times through oxic water column and effects of sediment resuspension; it varies between several days (in Lake Kivu, where organic matter is produced near the oxic-anoxic boundary; Pasche et al., 2010) and 20 years (in Lake Superior, where sediment resuspension is significant; Li et al., 2012). The fit lines in this figure are for illustration only and are not used in deriving the power-law parameters in Figs. 1 and 2.

**Figure 1**

