Lability of organic carbon in lakes of different trophic status

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SUMMARY
1. We used first-order kinetic parameters of biological oxygen demand (BOD), the constant of aerobic decomposition (k) and the asymptotic value of BOD (BOD_{ult}), to characterise the lability of organic carbon pools in six lakes of different trophic state: L. Naroch, L. Miastro and L. Batorino (Belarus), L. Kinneret (Israel), L. Ladoga (Russia) and L. Mendota (U.S.A.). The relative contributions of labile and refractory organic carbon fractions to the pool of total organic carbon (TOC) in these lakes were quantified. We also determined the amounts of labile organic carbon within the dissolved and particulate TOC pools in the three Belarus lakes.
2. Mean annual chlorophyll concentrations (used as a proxy for lake trophic state) ranged from 2.3 to 50.6 \mu g L^{-1}, labile organic carbon (OC_L = 0.3BOD_{ult}) from 0.75 to 2.95 mg C L^{-1} and k from 0.044 to 0.14 day^{-1}.
3. Our data showed that there were greater concentrations of OC_L but lower k values in more productive lakes.
4. In all cases, the DOC fraction dominated the TOC pool. OC_L was a minor component of the TOC pool averaging about 20%, irrespective of lake trophic state.
5. In all the lakes, most (c. 85%) of the DOC pool was refractory, corresponding with published data based on measurements of bacterial production and DOC depletion. In contrast, a larger fraction (27–55%) of the particulate organic carbon (POC) pool was labile. The relative amount of POC in the TOC pool tended to increase with increasing lake productivity.
6. Long-term BOD incubations can be valuable in quantifying the rates of breakdown of the combined particulate and dissolved organic carbon pools and in characterising the relative proportions of the labile and recalcitrant fractions of these pools. If verified from a larger number of lakes our results could have important general implications.

Keywords: biological oxygen demand, lability, lake trophic state, particulate, dissolved and total organic carbon

Introduction
The microbiologically mediated breakdown of dissolved organic carbon (DOC) and particulate organic carbon (POC) pools in aquatic ecosystems is a major factor in global carbon cycling (Kuznetsov, 1970; Odum, 1971).

The tendency of the various constituents of POC and DOC to be mineralised depends on their ‘lability’, a term that broadly describes how resistant the organic carbon components of these pools are to breakdown. The labile organic carbon (OC_L) components of DOC and POC are degraded within a relatively short period (days to weeks) by free living or attached bacteria and protists; decomposition of the refractory organic carbon (OC_R) may take much longer (Wetzel, 2001; Carlson, 2002). There is no clear distinction...
between labile and refractory organic carbon, rather
there exists a continuum of the decomposition
turnover times ranging from hours to centuries
(Sondergaard & Middleboe, 1995; Wetzel, 2001;
Carlson, 2002). Nevertheless, in early papers Birge &
Juday (1934) and Waksman (1941) had already
differentiated between labile (OC_L) and refractory
(OCR) fractions within the total organic carbon (TOC)
of natural waters.

In practice, the kinetics of OC breakdown and the
size of the OC_L fraction have been derived from
measurements of dissolved oxygen uptake and/or
bacterial biomass production in natural aquatic sys-
tems (Odum, 1971; Wetzel, 1984; Sondergaard &
Middleboe, 1995). In most aquatic systems, the DOC
pool tends to be larger and more refractory than the
POC (Wetzel, 1984; Ostapenia, 1989). We note that
most studies both in marine and freshwaters have
focused on the breakdown and utilisation of compo-
nents of the DOC pool (Sondergaard & Borch, 1992;
Sondergaard, Hansen & Markager, 1995; Carlson,
2002). At present there is relatively little information
about the various components of the TOC pool in
freshwater lakes and reservoirs, such as the propor-
tions of OC_L and OCR, or the lability of dissolved and
particulate fractions within TOC, although such data
are important for ecological modelling and a better
understanding of the functioning of these ecosystems
(Straskraba & Gnauck, 1985; Hipsey et al., 2007).

The potential effect of differing lake trophic status
on the lability of the OC pool has not been deter-
mined, although Ostapenia (1973, 1989) and Wetzel
(2001) surmised that such a relationship should exist.
In order to examine if the lability of the total organic
carbon pool was related to lake productivity, we used
data from biological oxygen demand (BOD) exper-
iments carried out in six lakes of varying trophic
status. With some notable exceptions, BOD determi-
nations have been rarely used in aquatic research to
quantify OC lability (see for freshwater systems
Fallon & Brock, 1979; Tregubova & Kulish, 1982;
Ostapenia, 1985; Delzer & McKenzie, 1999; and for
marine waters Ogura, 1972,1975; Zsolnay, 1975; Jonas
& Tuttle, 1990).

Although various oxygen demand kinetics have
been observed in BOD studies (Leonov, 1974), in most
cases these show first order decomposition kinetics:

\[
\text{BOD}_t = \text{BOD}_{ult} (1 - e^{-kt})
\]

where \(\text{BOD}_t\) (mg O_2 L^{-1}) is the biological oxygen
demand at time \(t\) (days); \(\text{BOD}_{ult}\) is the ultimate or total
BOD, asymptotic at \(t \rightarrow \infty\); and \(k\) (day^{-1}) is the reaction
constant of aerobic decomposition. The parameters of
eqn 1 have a clear interpretation: \(\text{BOD}_{ult}\) provides an
estimate of the total labile organic carbon pool (OC_L),
while \(k\) represents an estimate of lability per se, i.e. a
larger \(k\) implies a more rapid breakdown of OC. The
reciprocal of \(k\) is a measure of the turnover time of
OC_L. An additional parameter reflecting the lability
of components within the TOC pool is \(V\) (mg
O_2 L^{-1}day^{-1}), the instantaneous rate of oxygen
demand at \(t = 0\):

\[
V = \text{BOD}_{ult}k
\]

In this study, we ran BOD incubations for 20–
25 days. To our knowledge there are only few reports
concerning lability of OC based on similar, relatively
long term (15–25 days) BOD experiments [e.g. Fallon &
Brock (1979) for L. Mendota and Tregubova & Kulish
(1982) for L. Ladoga]. Here we present and analyse our
data from three lakes in Belarus, L. Naroch, L. Miestro
and L. Batorino (experiments carried out in 1979–80),
and from L. Kinneret, Israel (experiments carried
during 2005–07), together with published data for the
eutrophic L. Mendota, U.S.A. (Fallon & Brock, 1979;
Kitchell, 1992) and for the largest lake in Europe, the
oligotrophic L. Ladoga, Russia (Tregubova & Kulish,
1982), to answer the following questions:

1. What are the relative proportions of labile and
refractory organic carbon fractions within the TOC
pools of the various lakes?
2. What portion of both the dissolved and particular
fractions of the TOC is labile and what are the kinetics
of organic carbon degradation in these lakes?
3. Is there any relationship between the lability of
these organic carbon pools and lake trophic status?

Methods

The definitions and abbreviations of terms used in this
paper are listed in the Appendix.

Study sites

The Naroch Lakes consist of three connected lakes
(Batorino, surface area 6.3 km^2; Miestro, 13.1 km^2; and
Naroch itself, 79.6 km^2) in Northwest Belarus (Fig. 1). The
limnology of the Naroch Lakes has been studied

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intensively (Winberg, 1985). Much of the nutrient and pollution load from the catchment is retained in the upper lakes of the system (L. Batorino and L. Miastro). As a result, during the period described in this study (from 1979 until the mid 1980s), L. Batorino was highly eutrophic, L. Mistro moderately eutrophic and L. Naroch mesotrophic (Table 1).

Lake Kinneret (the Biblical Sea of Galilee, 170 km²) is a subtropical meso-eutrophic lake located at about 210 m below mean sea level in the northern part of the Dead Sea Rift Valley (Serruya, 1978; Fig. 1). A prominent biological feature of the lake has been the annual, late-winter spring bloom of the dinoflagellate Peridinium gatunense Nygaard (Berman et al., 1995). Since 1994, however, Peridinium blooms have appeared sporadically and there has been a steady increase of cyanobacteria in summer and autumn (Zohary, 2004).

Lake Mendota (39 km²) has become intensely eutrophic, from the beginning of the last century. The lake was a subject of large scale efforts aimed at slowing down eutrophication; from 1912 to 1958 copper sulphate was applied to reduce excessive algal growth (Pedros-Alio & Brock, 1982). Recent changes in structure and functioning suggest that the lake ecosystem has not yet stabilised (Carpenter et al., 2006).

Lake Ladoga, (17 900 km²) the largest lake in Europe was oligotrophic until the early 1960s. Since the 1970s, however, its trophic state has been mesotrophic.
From 1980, L. Ladoga showed signs of eutrophication with increased nutrient concentrations, reduced transparency and meagre fish catches, together with structural changes in its plankton, zoobenthos and fish communities. (Petrova & Terzhevik, 1992; Drabkova et al., 1996).

Major limnological characteristics of these lakes are listed in Table 1.

**BOD measurements**

We adapted the classical BOD method, widely used by water engineers (Standard Methods, 2005) but rarely applied in limnological studies, to examine the kinetics of OC degradation in a series of lakes of varying productivity. By prolonging the incubation from the traditional 5 to >20 days, and by measuring detailed time courses, we obtained information on the initial rate of O₂ uptake (reflecting the breakdown of highly labile substrates) and, in addition, estimates of BODₜₐₜₙ. For most of our experiments we used unfiltered lake water. Thus, the oxygen uptake recorded in the BOD bottles reflected the breakdown of both POC and DOC, in contrast to many published studies that have focused exclusively on DOC (e.g. Sondergaard & Middleboe, 1995; Carlson, 2002). Note that all water samples were initially brought to O₂ saturation by bubbling, thus none of the O₂ uptake observed was due to NH₄ oxidation but only to that of organic carbon compounds. Because no additional nutrients were added to the water samples, bacterial breakdown of OC may have been eventually inhibited by nutrient limitation in some cases (Standard Methods, 2005), though direct observations in L. Mendota (Fallon & Brock, 1979) did not support this possibility.

Here we present the results of BOD time series experiments made in 1979–80 at the Naroch Lakes, and during 2005–07 at L. Kinneret. In the Discussion section, we analyse these data together with similar data reported for L. Ladoga (Tregubova & Kulish, 1982) and L. Mendota (Fallon & Brock, 1979).

BOD-kinetics were obtained from the time series of oxygen demand in unfiltered, near surface lake waters. The sampling time intervals for the BOD determinations were: 2, 4, 8, 16 and 20 days and 1, 3, 5, 10, 15 and 20 (or 25) days for the Naroch Lakes and L. Kinneret respectively. All samples (15 sampling dates in each of three Naroch lakes and 14 sampling dates in L. Kinneret) were taken monthly from the lake surface water and brought to oxygen saturation by intense stirring before enclosure in BOD bottles at 20 °C in the dark. Thus the measured oxygen uptake in the BOD bottles derived solely from mineralisation of organic carbon with no sulphide and/or ammonia oxygenation. The azide modification of the Winkler method was used to determine initial and residual oxygen concentrations in triplicate BOD-bottles (Standard Methods, 2005). For experiments in L. Kinneret, potentiometric titrations were made with a high precision (±2.0 µL) 719S Metrohm Titrino titrator. We used a factor of 0.3 to convert BOD oxygen measurements (mg O₂ L⁻¹) to carbon units (mg C L⁻¹), based on a respiration coefficient of 0.8 (Winberg, 1960; Geider, 1997).

BOD-kinetic parameters [the ultimate BOD, BODₜₐₜₙ (mg O₂ L⁻¹) and the reaction constant k (day⁻¹)] were calculated with the Microsoft Excel Solver tool that

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Naroch*</th>
<th>Miastro*</th>
<th>Batorino*</th>
<th>Kinneret†</th>
<th>Ladoga‡</th>
<th>Mendota§</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area, km²</td>
<td>79.6</td>
<td>13.1</td>
<td>6.3</td>
<td>170</td>
<td>17 900</td>
<td>39</td>
</tr>
<tr>
<td>Volume, km³</td>
<td>0.71</td>
<td>0.07</td>
<td>0.02</td>
<td>4.1</td>
<td>1486</td>
<td>0.5</td>
</tr>
<tr>
<td>Secchi depth, m</td>
<td>5.1</td>
<td>1.7</td>
<td>0.78</td>
<td>3.1</td>
<td>4.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Seston concentration, mg L⁻¹</td>
<td>1.81</td>
<td>6.2</td>
<td>16.7</td>
<td>3.2</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Total organic carbon (TOC), mg L⁻¹</td>
<td>5.38</td>
<td>8.71</td>
<td>14.6</td>
<td>5.08</td>
<td>10.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Particulate organic carbon (POC), mg L⁻¹</td>
<td>0.49</td>
<td>1.68</td>
<td>4.81</td>
<td>1.48</td>
<td>0.7</td>
<td>1.78</td>
</tr>
<tr>
<td>Dissolved organic carbon (DOC), mg L⁻¹</td>
<td>4.89</td>
<td>7.03</td>
<td>9.75</td>
<td>3.6</td>
<td>9.6</td>
<td>4.52</td>
</tr>
<tr>
<td>Chlorophyll (Chl), µg L⁻¹</td>
<td>4.9</td>
<td>20.0</td>
<td>50.1</td>
<td>18.0</td>
<td>2.3</td>
<td>50.6</td>
</tr>
<tr>
<td>Primary production, g C m⁻² year⁻¹</td>
<td>80</td>
<td>180</td>
<td>170</td>
<td>650</td>
<td>51</td>
<td>720</td>
</tr>
</tbody>
</table>

*Ostapenya (2000); †Serruya (1978); Berman et al. (1995); Yacobi (2006); ‡Petrova (1982); §Fallon & Brock (1979); Pedros-Alio & Brock (1982).
uses the Generalised Reduced Gradient (GRG2) non-linear optimisation code assuming first order kinetics (eqns 1 & 2). The goodness-of-fit of the approximated kinetic curves was determined by the square of the correlation between experimental and calculated data. For L. Ladoga (Tregubova & Kulish, 1982) and L. Mendota (Fallon & Brock, 1979), $BOD_{ult}$ and $k$ were estimated graphically by the method of Thomas (1950).

The instantaneous rate $V$ (mg O$_2$ L$^{-1}$ day$^{-1}$) was calculated in two ways: as $kBOD_{ult}$ (eqn 2) and as instantaneous oxygen demand on day 1.

**BOD in 0.8 μm filtered lake water**

For the Naroch lakes, BOD was determined simultaneously in both unfiltered and 0.8 μm pre-filtered water samples. Despite obvious changes brought about by filtration of the water samples, such as the loss of potential microbial substrates caused by removal of organic particles, algae and protists, this approach has been widely used in studies of lability of DOC (Wetzel et al., 1972; Lee & Wakeham, 1992; Sondergaard & Middleboe, 1995; Jonas, 1997). Oxygen demand in the filtered water samples was presumably due to the activity of free living bacteria utilising dissolved organic matter (Fallon & Brock, 1979; Sondergaard & Middleboe, 1995; Weiss & Simon, 1999).

We assumed the additive character of the separate components in the labile TOC pool (i.e. TOC$_L$ = POC$_L$ + DOC$_L$). Therefore, in these experiments, the parameters of BOD-kinetics associated with particulate POC were obtained from the curves calculated by difference:

$$BOD_p(t) = BOD_{ultp}(1 - e^{-kt})$$
$$= BOD_{ult}(1 - e^{-kt}) - BOD_{ultd}(1 - e^{-kt})$$  \(3\)

$$BOD_{ultp} = BOD_{ult} - BOD_{ultd}$$  \(4\)

where $BOD_p$ and $BOD_{ultp}$; $BOD_d$ and $BOD_{ultd}$ are BOD parameters derived from the POC and DOC fractions, respectively.

**Chlorophyll and lake trophic status**

Mean annual chlorophyll concentrations were used as a proxy for lake trophic status. Chlorophyll was measured fluorometrically (Holm-Hansen et al., 1965) in L. Kinneret (Yacobi, 2006), and spectrophotometrically (Strickland & Parsons, 1965) in the Naroch Lakes, L. Mendota (Fallon & Brock, 1979) and L. Ladoga (Tregubova & Kulish, 1982). The relationship between the trophic status of the lakes and BOD kinetics was determined by regressing annual averaged values of BOD parameters against the respective chlorophyll concentrations.

**Particulate and dissolved organic carbon (POC and DOC)**

For the Naroch Lakes, POC was determined by dichromate digestion of the particulate matter collected on GF/F filters (Ostapenia, 1985). POC in L. Kinneret was estimated as half the loss on ignition at 550 °C of seston collected on GF/F filters. Recent determinations of POC with a CHN-analyser gave good agreement between these two methods (W. Eckert, unpubl. data). We used literature values for POC and DOC in L. Ladoga (Petrova, 1982) and L. Mendota (Fallon & Brock, 1979). DOC concentrations in the Naroch Lakes were measured with dichromate digestion (Ostapenia, 1965), and in L. Kinneret by the wet combustion method with an Model 1010 Organic Carbon Analyser (OI-Analytical, College Station, Texas, U.S.A.).

**Results**

Averaged annual values for $BOD_{ult}$, $k$ and $V$ for all the lakes considered in this study are shown in Table 2.

**BOD kinetics**

The calculated BOD first order kinetic curves were close to those given by the experimental data ($r^2$ ranged from 0.92 to 1.00; slope of the regression close to 1). In many cases, the uptake of the oxygen remained linear up to 20 days, indicating that the actual BOD$_{ult}$ was much higher than estimates based on the frequently assumed value of $BOD_{ult} = 1.5BOD_5$ (Scopintsev, 1978; Jonas & Tuttle, 1990). This observation limited our use of results from studies of BOD dynamics and their relationship to chlorophyll in Chesapeake Bay (Jonas & Tuttle, 1990; Jonas, 1997) because, in these cases, only BOD$_5$ tests were carried out.

**Naroch Lakes**

BOD kinetic parameters in these lakes showed no clear seasonality during our study (Fig. 2). Averaged...
concentrations of OC$_L$ (estimated as 0.3BOD$_{ult}$) ranged from 0.41 (L. Naroch) to 4.83 mg C L$^{-1}$ (L. Batorino), in most cases being greater in the latter, more productive lake (Fig. 2). A similar pattern was observed for $V$, the instantaneous rate of oxygen demand at $t = 0$, which varied from 0.2 to 0.64 mg O$_2$ L$^{-1}$day$^{-1}$. The highest $k$-value (0.126 day$^{-1}$) was obtained for L. Naroch while the minimum (0.008 day$^{-1}$) was recorded in L. Batorino.

**L. Kinneret**

As for the Naroch Lakes, there was no clear seasonal trend in the BOD kinetic parameters in L. Kinneret (Fig. 3). BOD$_{ult}$ ranged from 2.34 to 21.28 mg O$_2$ L$^{-1}$, $k$ from 0.02 to 0.13 day$^{-1}$, and $V$ from 0.11 to 1.07 mg O$_2$ L$^{-1}$day$^{-1}$. Exceptionally high values of BOD$_{ult}$ (21.28 mg O$_2$ L$^{-1}$ = 6.3 mg C L$^{-1}$) and $V$ (1.07 mg O$_2$ L$^{-1}$ day$^{-1}$ = 0.31 mg C L$^{-1}$ day$^{-1}$) were measured during an intense phytoplankton bloom of the dinoflagellate *Peridinium* in spring 2006 but because of large seasonal variability, the average annual values were not significantly affected. In this water sample, OC$_L$ comprised about half of the entire OC pool. We have not included these data in Fig. 4 because they reflect an extreme situation within a very dense *Peridinium* patch. A summary of all the BOD kinetic parameters measured by us in the Naroch Lakes and L. Kinneret, and those reported by Tregubova & Kulish (1982) for L. Ladoga and by Fallon & Brock (1979) for L. Mendota is given in Table 2.

The values of $V$, calculated either as the product of $k$BOD$_{ult}$ (eqn 2) or measured as instantaneous oxygen demand on day 1, were very similar ($r^2 = 0.93$, slope = 0.98 ± 0.04, $P < 0.001$).

**BOD-kinetic parameters in filtered water: Naroch Lakes**

In order to examine the relative lability of POC and DOC components of the TOC pool, BOD experiments with both unfiltered and pre-filtered (0.8 lm) water were made in the Naroch Lakes experimental series. In calculating BOD-kinetics for these components of the TOC pool we assumed the additivity of these parameters (eqns 3 & 4). BOD-kinetic parameters for DOC and POC in the Naroch Lakes are summarised in Table 3.

Similarly to unfiltered water, BOD$_{ult}$ and $V$ values obtained for filtered water samples were on average higher in more productive lakes (Table 3; Fig. 4). BOD$_{ult}$ in L. Batorino was significantly larger ($P < 0.05$, $n = 15$) than in Lakes Naroch and Miastro. The variability (as coefficient of variation) of the instantaneous rate of oxygen demand at $t = 0$ ($V$) in eutrophic L. Batorino was greater than in mesotrophic L. Naroch (from 0.06 to 0.25 and from 0.06 to 0.50 mg O$_2$ L$^{-1}$day$^{-1}$, respectively). In all three lakes, the reaction constant ($k$) varied within a 10-fold range (0.02 to 0.20 day$^{-1}$) with no statistical differences between the lakes ($P < 0.1$, $n = 15$).

### Table 2 BOD-kinetic parameters in Naroch Lakes, Lake Kinneret, and Lakes Ladoga and Miestro: average and coefficient of variance (in brackets), and range [square brackets]; $n$ = number of experimental series

<table>
<thead>
<tr>
<th>Lakes</th>
<th>Variables</th>
<th>BOD$_{ult}$ mg O$_2$ L$^{-1}$</th>
<th>$k$ day$^{-1}$</th>
<th>$V$ mg O$_2$ L$^{-1}$ day$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naroch ($n = 15$)</td>
<td></td>
<td>2.44 (0.41)</td>
<td>0.095 (0.34)</td>
<td>0.26 (0.48)</td>
</tr>
<tr>
<td>Miastro ($n = 15$)</td>
<td></td>
<td>5.37 (0.46)</td>
<td>0.072 (0.46)</td>
<td>0.35 (0.35)</td>
</tr>
<tr>
<td>Batorino ($n = 15$)</td>
<td></td>
<td>11.7 (0.43)</td>
<td>0.043 (0.62)</td>
<td>0.37 (0.42)</td>
</tr>
<tr>
<td>Kinneret ($n = 14$)</td>
<td></td>
<td>4.55 (0.34)</td>
<td>0.058 (0.34)</td>
<td>0.21 (0.51)</td>
</tr>
<tr>
<td>Ladoga* ($n = 6$)</td>
<td></td>
<td>5.24 (0.30)</td>
<td>0.140 (0.284)</td>
<td>0.69 (0.25)</td>
</tr>
<tr>
<td>Mendota† ($n = 10$)</td>
<td></td>
<td>10.16 (0.40)</td>
<td>0.041 (0.74)</td>
<td>No data</td>
</tr>
</tbody>
</table>

*Published data by Tregubova & Kulish (1982).
†Published data by Fallon & Brock (1979).
‡Not included in averaging.
Organic carbon pools

In the six lakes covered by this study, annual average DOC ranged from 67% to 93% of TOC. DOC/POC ratios varied widely in the lakes studied: from 2.0 in L. Batorino to 14.5 in L. Ladoga (Table 4). The proportion of POC in the entire TOC pool increased from 7% to 33% with increasing lake trophic status as reflected by chlorophyll concentrations (Table 4). By contrast, the percentage of OC_L in TOC varied only twofold (from 14% to 27%) and the refractory organic carbon fraction (OC_R) varied from 73% to 83% of TOC (Table 4).

Discussion

Despite wide use of the term ‘lability’ in respect to the breakdown of organic matter in aquatic systems, there does not appear to be a commonly accepted quantitative definition of this term in the literature. Wetzel (1992) and Hendrickson et al. (2007) suggested characterising lability by the value of the first rate decay constant k, defining ‘labile’ and ‘refractory’ organic matter as having k values of 0.075–0.094 and 0.001–0.002 day\(^{-1}\), respectively. Ostapenia (1985) proposed quantifying the lability of TOC as the ratio of BOD\(_{ult}\)/TOC and showed that, for the Naroch Lakes, the labile fraction ranged from 12 to 21% of TOC. He also found that POC_L accounted for about 50% of POC in mesotrophic L. Naroch, but was significantly lower in more productive L. Miestro and L. Batorino (20 and 17%, respectively). Here we propose that the ‘lability’ of organic carbon pools may be quantitatively defined with two parameters: (i) by the concentration of OC_L (estimated as BOD\(_{ult}\)), and (ii) by k (the rate constant of aerobic decomposition of OC_L).

The variability of lake-averaged values of k in this study was greater than the range (from 0.02 to 0.05 day\(^{-1}\)) suggested by Wetzel (1992) and Hendrickson et al. (2007) for a wide range of lakes. Here, values of k ranged from 0.041 day\(^{-1}\) in hyper-eutrophic L. Mendota to 0.14 day\(^{-1}\) for oligo-mesotrophic L. Ladoga and was correlated (P < 0.005) with average, annual lake chlorophyll concentrations (Fig. 5).

The average concentration of OC_L in the lakes studied varied from 0.73 to 3.05 mg C L\(^{-1}\) with an overall trend of increase with lake trophic state (Fig. 5). A close relationship between chlorophyll
concentrations and oxygen demand (as BOD$_5$) has been reported for several aquatic ecosystems (Zsolnay, 1975; Fallon & Brock, 1979; Jonas & Tuttle, 1990). This relationship was also used previously to estimate specific respiration rates (Ostapenia, 1989; Parparov et al., 1998). However, to the best of our knowledge, a direct significant relationship between OCL and lake trophic status (Fig. 5) has not been reported previously.

Ostapenia (1985, 1989) analysed data for lakes worldwide and found the following empirical regression ($r^2 = 0.93$, $n = 23$, $P < 0.01$):

$$\log \frac{\text{DOC}}{\text{POC}} = \left(1.33 \pm 0.05\right) - \left(0.47 \pm 0.03\right) \log \text{Chl}$$ (5)

Ostapenia’s (1985, 1989) data for three Naroch Lakes, supplemented with the data for L. Kinneret and L. Ladoga, confirm a similar, significant inverse relationship between the ratio of DOC/POC and Chl (Fig. 6). Therefore, it is not surprising that $k$ also correlated well with DOC/POC (Fig. 6) within the DOC/POC range from 2.0 to 14.5. The results shown in Figs 5 & 6 indicate that OCL and $k$ show significant correlations with both lake trophic state (as Chl) and with the ratio DOC/POC. This finding suggests that annual average values for Chl or DOC/POC could be used for estimating TOC lability when direct determinations based on BOD-kinetics are unavailable.

Table 3 Naroch Lakes: BOD-kinetic parameters in 0.8 μm filtered water (DOC) and calculated average values for POC. Average of 15 experimental series (coefficient of variation in brackets)

<table>
<thead>
<tr>
<th>Variables</th>
<th>L. Naroch</th>
<th></th>
<th>L. Miastro</th>
<th></th>
<th>L. Batorino</th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>DOC</td>
<td>POC</td>
<td>DOC</td>
<td>POC</td>
<td>DOC</td>
<td>POC</td>
</tr>
<tr>
<td>BOD$_{ult}$, mg O$_2$ L$^{-1}$</td>
<td>2.02 (0.21)</td>
<td>1.60</td>
<td>2.27 (0.09)</td>
<td>3.43</td>
<td>3.91 (0.32)</td>
<td>11.4</td>
</tr>
<tr>
<td>$k$, day$^{-1}$</td>
<td>0.052 (0.52)</td>
<td>0.054</td>
<td>0.068 (0.48)</td>
<td>0.049</td>
<td>0.061 (0.65)</td>
<td>0.043</td>
</tr>
<tr>
<td>$V$, mg O$_2$ L$^{-1}$ day$^{-1}$</td>
<td>0.12 (0.07)</td>
<td>0.10</td>
<td>0.18 (0.42)</td>
<td>0.16</td>
<td>0.20 (0.51)</td>
<td>0.37</td>
</tr>
</tbody>
</table>

n.d., no data.

Parparov et al., 1998). However, to the best of our knowledge, a direct significant relationship between OCL and lake trophic status (Fig. 5) has not been reported previously.

Ostapenia (1985, 1989) analysed data for lakes worldwide and found the following empirical regression ($r^2 = 0.93$, $n = 23$, $P < 0.01$):

$$\log \frac{\text{DOC}}{\text{POC}} = \left(1.33 \pm 0.05\right) - \left(0.47 \pm 0.03\right) \log \text{Chl}$$ (5)

Ostapenia’s (1985, 1989) data for three Naroch Lakes, supplemented with the data for L. Kinneret and L. Ladoga, confirm a similar, significant inverse relationship between the ratio of DOC/POC and Chl (Fig. 6). Therefore, it is not surprising that $k$ also correlated well with DOC/POC (Fig. 6) within the DOC/POC range from 2.0 to 14.5. The results shown in Figs 5 & 6 indicate that OCL and $k$ show significant correlations with both lake trophic state (as Chl) and with the ratio DOC/POC. This finding suggests that annual average values for Chl or DOC/POC could be used for estimating TOC lability when direct determinations based on BOD-kinetics are unavailable.

Table 4 Annual average chlorophyll concentrations, percentages (%) of dissolved DOC and particulate POC in TOC pools, and of labile and refractory fractions in the DOC and POC pools (for the Naroch Lakes only)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lakes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ladoga</td>
</tr>
<tr>
<td>Chl, μg L$^{-1}$</td>
<td>2.3</td>
</tr>
<tr>
<td>DOC/TOC</td>
<td>93</td>
</tr>
<tr>
<td>POC/TOC</td>
<td>7</td>
</tr>
<tr>
<td>OCL$_{ld}$/TOC</td>
<td>15</td>
</tr>
<tr>
<td>OCR$_{ld}$/TOC</td>
<td>8</td>
</tr>
<tr>
<td>OCL$_{ld}$/DOC</td>
<td>n.d.</td>
</tr>
<tr>
<td>OCR$_{ld}$/DOC</td>
<td>n.d.</td>
</tr>
<tr>
<td>OCL$_{ld}$/POC</td>
<td>n.d.</td>
</tr>
<tr>
<td>OCR$_{ld}$/POC</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

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Despite the limited number of lakes investigated in this study, the data presented in Figs 5 & 6 clearly show the opposing trends of the lability parameters \( \text{OC}_L \) and \( k \). Although the concentration of labile organic carbon, \( \text{OC}_L \) (estimated from BOD ult) tended to be higher in more productive lakes, the actual rate of \( \text{OC}_L \) breakdown (\( k \)) in such lakes was slower than in less productive lakes. We hypothesise that higher trophic status is accompanied with an increase of organic carbon concentrations but, at the same time, with a decrease in the lability of this pool. Lowering of \( \text{OC}_L \) lability may be related to the frequent dominance in eutrophic lakes of cyanobacteria (Wetzel, 2001) that are relatively less metabolically active than other planktonic autotrophs (Parparov et al., 1998).

**BOD in unfiltered and filtered lake water**

The lability of DOC in filtered water was studied using BOD-kinetics only in the three Naroch Lakes. Nevertheless, the present data provide important, initial information about partitioning of labile organic carbon between the dissolved and particulate organic carbon pools in lakes of different productivity. With increasing chlorophyll concentrations from L. Naroch to L. Batorino, both the dissolved and particulate fractions of \( \text{OC}_L \) within TOC increased. In contrast, the decay constant (\( k \)) for the dissolved and particulate fractions of \( \text{OC}_L \) had similar values and varied insignificantly (Table 3). Thus, in these lakes, both dissolved and particulate fractions of \( \text{OC}_L \) appeared to have similar rates of aerobic breakdown.

The concentrations of the dissolved and particulate \( \text{OC}_L \) relative to their respective DOC and POC pools were estimated by the ratios of BOD ult/d/DOC and BOD ult/p/POC (where BOD ult/d and BOD ult/p are the ultimate BOD values obtained from eqns 3 & 4 for dissolved and particulate \( \text{OC}_L \) respectively). The percentage of the labile organic carbon fraction in DOC varied within narrow limits, from 10% to 12% (Table 4), in good correspondence with the data reported from measurements of bacterial production and DOC depletion in L. Michigan (Laird & Scavia, 1990) and L. Constance (Weiss & Simon, 1999); see also
reviews by Sondergaard & Borch (1992) and Sondergaard & Middleboe (1995). The percentage of the labile organic carbon fraction in POC (27–55%) was significantly higher than in DOC and did not appear to be related to the lake trophic status (Table 4).

In conclusion, data from long-term (>20 days) BOD experiments have allowed us to estimate the lability of the organic carbon pools in six lakes of varying trophic status. The average concentration of the labile organic carbon (OC_L) in these lakes varied from 0.75 to 2.95 mg C L\(^{-1}\), while the constant of the aerobic decomposition (k) ranged from 0.044 to 0.14 day\(^{-1}\). Our data showed that, as lake trophic status increased, there were greater concentrations of OC_L, although k (the actual breakdown rate of the labile carbon pool) decreased. In all cases, OC_L was a minor component of the TOC pool (on average about 20%), irrespective of lake productivity. In all the lakes, most (c. 80%) of the DOC pool was refractory, agreeing with published data obtained from measurements of bacterial production and DOC depletion (Laird & Scavia, 1990; Sondergaard & Middleboe, 1995; Weiss & Simon, 1999). In contrast, a larger fraction (27–55%) of the POC pool was labile. The relative amount of POC in the TOC pool tended to increase with increasing lake trophic status.

Long-term BOD incubations as used here can provide valuable data for quantifying the rates of breakdown of the combined particulate and dissolved organic carbon pools and to characterise the relative proportions of labile and recalcitrant fractions of these pools. If verified from a larger number of lakes our results could have important general implications.

Acknowledgments

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References


**Supporting Information**

Additional Supporting Information may be found in the online version of this article:

**Appendix S1.** List of acronyms for parameters used in this study.

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