The role of biogeochemical cycling for the formation and preservation of varved sediments in Soppensee (Switzerland)

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Abstract

We analyzed seasonally aggregated observations of temperature, conductivity, dissolved oxygen and dissolved inorganic carbon from Soppensee (District of Lucerne, Switzerland) for the yrs 1980 to 1993. Holomictic Soppensee is characterized by a strong summer stratification with a thin epilimnion separated from an anoxic hypolimnion by a strong pycnocline formed by thermal and chemical gradients. A vertical one-dimensional model was developed to simulate the observed seasonal cycles of carbon and oxygen. The processes of net community production, mineralization of organic matter, precipitation and dissolution of calcite, gas exchange, in- and outflow, sedimentation and vertical eddy diffusion are included. According to the model, the annual net community production is estimated to about $110 \text{ g C m}^{-2} \text{ yr}^{-1}$ and the annual net primary production to about 330 to $440 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is a typical value for eutrophic lakes. A mass balance of the carbon cycle indicates that most of the inflow comes from groundwater which is super-saturated with respect to atmospheric CO_2 . Therefore the surface waters exhibit a large capacity for calcite precipitation. The results of the model are used to constrain the conditions that favor the formation of varved sediments in Soppensee during thousands of yrs. Model calculations show that the deep waters would still turn anoxic even if the sedimentation rate of organic matter were decreased to 25%. Several physical factors such as biogenic stabilization of the deep waters due to calcite dissolution and low input of wind energy are responsible for the long term anoxia in Soppensee.

Introduction

Sediment cores from marine and fresh water environments have revealed a plethora of information about past climates and their variability and hence have contributed greatly to our understanding of climate in general. However, the interpretation of these records is often not straightforward but requires a detailed understanding of how climate signals are modified and ultimately preserved in the sediments. In the case of sediment records of biogeochemical properties, one has to take into account that the fate of organic and inorganic matter deposited at the sediment-water interface is closely coupled to the biogeochemical cycling of carbon and oxygen in the overlying water column. Thus, in order to interpret a sedimentary record, the

processes in the water column and at the sediment water interface have to be well understood. We investigated these biogeochemical processes and their link to the sediment record in Soppensee, a small lake located 20 km northwest of Lucerne on the Central Swiss Plateau (Figure 1). Soppensee is a kettle lake about 800 m long and 400 m wide with a maximum water depth of 27 m. The lake drains a 1.6 km^2 catchment, and was formed towards the end of the last glaciation (Lotter, 1989). Sediment cores taken from Soppensee have yielded information on the environmental history of the last 15,000 yrs (Lotter, 1989). An outstanding characteristic of the sediment record is the existence of varved sediments over several thousand years (Lotter, 1989). This indicates very stable conditions of the sedimentation cycle and of the redox conditions

Figure 1. Map of Switzerland indicating the geographical location of the Soppensee and bathymetric map of Soppensee as determined by Lotter (1989).

at the sediment surface. This stability occurred despite significant changes in climate and environmental conditions over the periods when the varved sediments were deposited.

The purpose of this paper is to investigate the biogeochemical processes and conditions that led to the formation and preservation of laminated sediments in Soppensee. To this end, we first study the seasonal cycles of carbon and oxygen in this lake by means of a vertical one-dimensional model. This model permits us to quantify the coupling of these biogeochemical cycles with the sediment process (Quay et al., 1986; Hollander, 1989). Results of this model are then used to constrain the conditions favorable for the formation and preservation of laminated sediments in Soppensee.

Observation of the seasonal cycle

The set of seasonal data analyzed in our modeling study will be briefly described first. This data set was obtained at the position of maximum depth in the center of Soppensee (Figure 1). A summary of the main characteristics of the lake can be found in Table 1. This station was irregularly occupied from 1979 to 1993 resulting in a total of 28 hydrographic casts that include at least temperature and conductivity. The concentration of dissolved oxygen, alkalinity and pH were determined 23 and 17 times, respectively. Occasionally, nutrients, trace metals, methane and hydrogen sulfide were included. Starting in 1990, the hydrographic casts were augmented by fine-scale CTD

(conductivity, temperature, depth) profiles. The full data set including a discussion of the precision of the data is presented by Gruber (1993).

Because of the very irregular occupation of the station, the data were seasonally aggregated without regard to inter-annual variability. The aggregated seasonal cycles of temperature (including epilimnion depth), conductivity and dissolved oxygen are presented in Figures 2a to 2c. Figure 2d shows the seasonal cycle of dissolved inorganic carbon (DIC) defined as the sum of all inorganic carbon species (H_2CO_3^* , HCO_3^- and CO_3^{2-}).

We estimated the depth of the epilimnion for each CTD profile on the basis of density calculated from temperature and conductivity. The base of the epilimnion was defined arbitrarily as the depth having an increase in density of $\Delta\rho = 0.05 \text{ kg m}^{-3}$ relative to the surface value. Visual inspection showed that this method gave in general good results with the exception of profiles taken in early spring.

Lake temperature (Figure 2a) exhibits a seasonal cycle which is typical for this latitude. Favored by a relatively wind-protected location and a trophy-related high light attenuation, the surface layers of the lake are warming rapidly in spring. Subsequently, a strong thermal stratification develops in summer with a maximum temperatures in the epilimnion of more than 25°C observed in July and August. During summer the depth of the epilimnion stays rather constant at about 3 to 4 m. Afterwards the cooling period starts with a slow convective erosion of the stratification and subsequent deepening of the thermocline. At the end

Table 1. Summary of parameters used in the seasonal model of Soppensee

Symbol	Definition	Value or range	Type of parameter, evaluation and source
A	Isobath area	0–236000 m ²	Bathymetric map from Lotter (1989)
V	Volume of lake	2.9·10 ⁶ m ³	Calculated from isobath area
h _{epi}	Epilimnion depth	3–27 m	Time series: determined from density profiles of the yrs 1979 to 1993
r	Hydraulic rate: defined as Q _{out} /V	8.9·10 ⁻⁴ d ⁻¹	From Stadelmann, pers. comm.
Q _{out}	Annual mean outflow	2600 m ³ d ⁻¹	Estimate based on the assumption of constant DIC pool size
DIC _{in}	Concentration of DIC in the inflow	5.7 mM	Saturation for inflow into the epilimnion
O ₂ ⁱⁿ	Concentration of O ₂ in the inflow	0.22–0.35 mol m ⁻³	Estimate based on the assumption of constant Ca pool size
Ca ⁱⁿ	Concentration of Ca in the inflow	2.2 mol m ⁻³	Profile: calculated by temperature budget method from data of the yrs 1990 to 1993
K _z	Vertical eddy diffusivity	0.5–2·10 ⁻⁶ m ² s ⁻¹	Time dependent profile: extrapolation of value from 30/31.7.1992
NCP	Zero order rate of net community production	0–0.015 mol m ⁻³ d ⁻¹	Redfield ratio lowered because of possible use of ammonia as nitrogen source
PQ	Photosynthetic quotient (oxygen to carbon ratio)	1.2 mol O ₂ (mol C) ⁻¹	Time dependent profile: determined from the sedimentation rate in sediment core 89–23
R	Zero order rate of calcite formation	0–0.015 mol m ⁻³ d ⁻¹	Estimates from Swiss lakes (Karagounis, 1992)
k _{min}	First order rate of POC mineralization	0.02 d ⁻¹	Time series: calculated from estimated β _{CO2} and observed seasonal cycle of pCO ₂
I _s	Surface CO ₂ gas exchange flux	–0.05–0.0004 mol m ⁻² d ⁻¹	Time series: estimated by the formula of Wanninkhof (1992)
β _{O2}	Gas exchange velocity for oxygen	0.20–0.35 m d ⁻¹	Time series: estimated by the formula of Wanninkhof (1992)
β _{CO2}	Gas exchange velocity for CO ₂	0.15–0.30 m d ⁻¹	Time series: calculated by formula of Weiss (1970)
O ₂ [*]	Oxygen saturation concentration	0.22–0.35 mol m ⁻³	Time series: calculated from the discrepancy between observed and simulated sedimentation rate.
F _{min}	Sediment flux by mineralization of POC	0.008–0.026 mol m ⁻² d ⁻¹	Time series: estimated from observed Ca accumulation in hypolimnion
F _{diss}	Sediment flux by dissolution of calcite	0.0058 mol m ⁻² d ⁻¹	Estimates from other Swiss lakes (Bloesch & Sturm, 1986) etc.
V _{POC}	Sedimentation velocity of POC	1.5 m d ⁻¹	Estimates from other Swiss lakes (Bloesch & Sturm, 1986) etc.
V _{CaCO3}	Sedimentation velocity of calcite	1.5 m d ⁻¹	

of the year the lake reaches the state of convective overturn which lasts typically until the beginning of March. This period of deep mixing can be interrupted by short periods of inverse temperature stratification or by ice cover. Soppensee can therefore be regarded as being at least partly holomictic.

The conductivity κ₂₀ (conductivity standardized to 20 °C) is mainly determined by Ca²⁺ and HCO₃⁻. It varies in the epilimnion between approximately 330 μS cm⁻¹ in winter and 200 μS cm⁻¹ in midsummer (Figure 2b). At intermediate depths the conductivity stays rather constant at about 330 μS cm⁻¹, whereas an increase to about 390 μS cm⁻¹ can be observed in the deep hypolimnion in late fall.

The concentration of oxygen (Figure 2c) exhibits a very distinct seasonal cycle. In March, at the beginning of the stratification period, the concentration of dissolved oxygen is slightly supersaturated (12 mg O₂ l⁻¹) in the epilimnion, whereas the concentrations in the hypolimnion are lower, but above 7 mg O₂ l⁻¹. This vertical gradient during a period of convective mixing is a consequence of high consumption in the deeper layers compared to the supply by vertical mixing. With the onset of stratification, O₂ in the hypolimnion is rapidly used up by the oxidation of organic matter, and in May the water below 10 m contains less than 1 mg O₂ l⁻¹. The anoxic period in the hypolimnion lasts until the end of the yr, when oxygen is replenished by convective

Figure 2. Isolines of the seasonally aggregated data from the yrs 1980 to 1993 in Soppensee; (a) temperature [$^{\circ}\text{C}$] together with the epilimnion depth; (b) conductivity κ_{20} [$\mu\text{S cm}^{-1}$]; (c) dissolved oxygen [mg l^{-1}]; (d) dissolved inorganic carbon (DIC) [mmol l^{-1}]. The data (supplied by P. Stadelmann, pers. comm) were aggregated without regard of inter-annual variability. Dots indicate observations. The isolines were obtained by interpolating the data linearly on a grid of 50 by 50 points.

Figure 2. Continued.

mixing. Due to high biological production, the oxygen concentrations in the epilimnion are supersaturated during the whole summer with maximum supersaturation up to 80% at the end of July. Diminishing production and mixing with the underlying anoxic water decrease the O_2 concentration subsequently. In October the epilimnion becomes finally undersaturated. Gas exchange with the atmosphere replenishes the oxygen reservoir during winter.

The concentration of dissolved inorganic carbon (DIC) was calculated from the observations of pH, alkalinity and temperature using thermodynamic relationships established by Dickson & Millero (1987). The seasonal cycle of DIC is qualitatively similar to that of conductivity, because conductivity is mainly determined by the concentration of bicarbonate (HCO_3^-), the predominant species of DIC at the observed pH (Figure 2d). In spring the concentration of DIC is about 3.3 mM in the whole lake. The concentrations in the epilimnion decrease afterwards to minimum values of about 2 mM observed in July and August, whereas the concentrations in the hypolimnion stay relatively constant. This decrease is caused by the combined effect of consumption of CO_2 by photosynthesis and the biogenically induced formation of calcite ($CaCO_3$). Afterwards DIC increases slowly to the winter values of about 3.3 mM by inflow, gas exchange and vertical mixing. In the hypolimnion, however, DIC shows a strong increase at the end of the yr to concentrations above 4.5 mM. This is paralleled by a similar increase in conductivity (Figure 2b). We assume this accumulation of DIC to be caused by mineralization of organic matter and dissolution of calcite. Convective mixing at the end of the yr destroys this hypolimnetic maximum.

A model of the seasonal carbon and oxygen cycle

Outline of the model

We have chosen an adaptation of the model CHEMSEE (Ulrich, 1991) to represent the seasonal cycle of oxygen and DIC. This vertical one-dimensional vertical model was developed to investigate the fate of chemical substances in lakes and allows to define interactively variables of different types as well as processes that act on these variables. This model needs as input the morphometry of the lake, vertical eddy diffusivity, epilimnion depth, as well as in- and outflow.

The model used here is schematically depicted in Figure 3. The upper compartment represents the epilimnion and is in direct contact with the atmosphere. The epilimnion, which is assumed to be homogeneously mixed, is underlain by the density stratified water of the meta- and hypolimnion. The thickness of the epilimnion varies as specified by the observations presented in Figure 2a.

Five dynamic variables in the water column have been defined for this study: DIC, O_2 , dissolved calcium (Ca), living and dead biomass (POC) and calcite ($CaCO_3$). The first three variables describe dissolved components whereas the latter two represent solid phases. Vertical eddy-diffusion, outflow and sedimentation are modeled by the standard procedures of CHEMSEE. In addition we have identified the following processes affecting the concentration profiles of the five dynamic variables:

- (1) Gas exchange transfers inorganic carbon and oxygen between the epilimnion and the atmosphere according to the difference of the partial pressure between air and water. Since the gas exchange of carbon depends only on the concentration of dissolved CO_2 rather than DIC, the transfer of CO_2 through the air-water interface is calculated independently.
- (2) The exchange of carbon between DIC and the living biomass is approximated in the model by the net community production over a diurnal cycle. This process, restricted to the upper layers of the lake, consumes DIC and produces POC and O_2 .
- (3) During sedimentation POC is remineralized to DIC by heterotrophic organisms.
- (4) From late spring to early summer $CaCO_3$ is formed in the epilimnion, which is assumed to settle to the sediment without dissolution in the water column. A fraction of the calcite is dissolving at the sediment surface during the stagnation period.
- (5) A fraction of the POC that reaches the sediment surface is oxidized by O_2 to DIC.

The processes of net community production and mineralization of POC are coupled to the production or consumption of oxygen by a fixed stoichiometry. In our study this stoichiometric factor is called photosynthetic quotient PQ, which is defined as the ratio of oxygen released to the water per carbon fixed in biomass during photosynthesis (Table 2, eq. 2). Due to the lack of analytical data, we did not consider the possible formation of methane and other reduced substances during the anoxia in the hypolimnion.

The mathematical model is presented in Table 2 in form of differential equations for each of the five

Figure 3. Schematic representation of the vertical one-dimensional model of the seasonal carbon and oxygen cycle. The upper compartment represents the seasonally varying epilimnion, which is underlain by a meta- and hypolimnion. The model is depicted in mathematical form in Table 2.

dynamic variables. In order to solve these differential equations numerically, they were transformed into their discrete equivalents by the control volume approach. For further details of the discretization we refer to Ulrich (1991).

Parameterization of the model

A summary of the values of the model parameters is presented in Table 1 together with the source of data or a short description of their evaluation.

The lake area ($A(z)$) as a function of depth was taken from the bathymetric map in Lotter (1989). The annual mean outflow Q_{out} in 1981 was determined to about $0.03 \text{ m}^3 \text{ s}^{-1}$ (Stadelmann, pers.comm.). This equals the mean inflow Q_{in} with the assumption of a constant surface level. Most of the inflow enters the lake as groundwater.

The vertical eddy diffusivity K_z was estimated by the temperature budget method from continuous measurements of a thermistor chain, deployed from March to June and from August to December 1990. Since K_z showed little seasonality, an average profile was formed with values ranging from $0.5 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 5 to 10 m depth to $2 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 10 to 27 m depth.

The flux of DIC and Ca from the sediment by dissolution of calcite, F_{diss} , was estimated from the accumulation of dissolved calcium in the hypolimnion during the stratification period. By further assuming that dissolution of calcite takes place only from August

to December, we calculated for F_{diss} a value of $5.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ for these 150 days. F_{diss} was set to zero for the rest of the year. This relatively small value is supported by Weber (1981) who found no evidence for large dissolution of calcite in Greifensee. Calcite dissolution rates of $0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ were calculated from pore-water profiles in Sempachersee (Urban et al., 1997). To estimate the rate of calcite formation R , we assumed that the formation takes place only during a period of about 100 days in late spring to early summer. This assumption is supported by many observations (e.g. Kelts & Hsü, 1978) and is also documented in the varved sediments of Soppensee (Lotter, 1989). We estimated the rate of calcite formation based on the yearly sedimentation rate measured on core 89–23 (Sturm, pers.comm) which was taken at the deepest point of the lake. The annual sedimentation rate was found to be about $3.5 \text{ mol CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ in the yrs before 1989. Including the dissolution of calcite at the sediment surface and assuming that the formation of calcite takes place only in the epilimnion, extending over 3 meters, we calculated an R of $15 \text{ mmol m}^{-3} \text{ d}^{-1}$ during these 100 days. The analysis of a sediment trap which was exposed from 29.7.92 to 6.8.92 at a depth of 15m, yielded a calcite formation rate of about $14 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the epilimnion. This is only about a third of our estimate but seems to be reasonable, because the exposition period of the sediment trap lies at the end of the calcite formation period.

Table 2. Differential equations for DIC, O₂, POC, Ca and CaCO₃ in the seasonal model

Differential equation for DIC: (mol m⁻³ d⁻¹)

$$\frac{\partial \text{DIC}}{\partial t} = r \cdot (\text{DIC}^{\text{in}} - \text{DIC}) + \frac{1}{A} \cdot \frac{\partial}{\partial z} \cdot K_z \cdot A \cdot \frac{\partial \text{DIC}}{\partial z} - \text{NCP} - R + k_{\text{min}} \cdot \text{POC} + \frac{1}{h_{\text{epi}}} \cdot I_s + \frac{dA}{A \cdot dz} \cdot (F_{\text{min}} + F_{\text{diss}}) \quad (1)$$

Differential equation for O₂: (mol m⁻³ d⁻¹)

$$\frac{\partial \text{O}_2}{\partial t} = r \cdot (\text{O}_2^{\text{in}} - \text{O}_2) + \frac{1}{A} \cdot \frac{\partial}{\partial z} \cdot K_z \cdot A \cdot \frac{\partial \text{O}_2}{\partial z} + \text{PQ} \cdot \text{NCP} - \text{PQ} \cdot k_{\text{min}} \cdot \text{POC} + \frac{1}{h_{\text{epi}}} \cdot \beta_{\text{O}_2} \cdot (\text{O}_2^* - \text{O}_2) - \text{PQ} \cdot F_{\text{min}} \cdot \frac{dA}{A \cdot dz} \quad (2)$$

Differential equation for POC: (mol m⁻³ d⁻¹)

$$\frac{\partial \text{POC}}{\partial t} = -r \cdot \text{POC} + \frac{1}{A} \cdot \frac{\partial}{\partial z} \cdot K_z \cdot A \cdot \frac{\partial \text{POC}}{\partial z} - v_{\text{POC}} \cdot \frac{\partial \text{POC}}{\partial z} + \text{NCP} - K_{\text{min}} \cdot \text{POC} \quad (3)$$

Differential equation for Ca: (mol m⁻³ d⁻¹)

$$\frac{\partial \text{Ca}}{\partial t} = r \cdot (\text{Ca}^{\text{in}} - \text{Ca}) + \frac{1}{A} \cdot \frac{\partial}{\partial z} \cdot K_z \cdot A \cdot \frac{\partial \text{Ca}}{\partial z} - R + F_{\text{diss}} \cdot \frac{dA}{A \cdot dz} \quad (4)$$

Differential equation for CaCO₃: (mol m⁻³ d⁻¹)

$$\frac{\partial \text{CaCO}_3}{\partial t} = -r \cdot \text{CaCO}_3 + \frac{1}{A} \cdot \frac{d}{dz} \cdot K_z \cdot A \cdot \frac{d \text{CaCO}_3}{dz} - v_{\text{CaCO}_3} \cdot \frac{\partial \text{CaCO}_3}{\partial z} + R \quad (5)$$

Unfortunately there is no data available about measurements of *biological production*. Gruber (1993) estimated the daily net primary production on 31.7.92 to about $1300 \pm 250 \text{ mg C m}^{-2} \text{ d}^{-1}$ on the basis of measurements of the diurnal cycle of DIC and oxygen and a model study. Assuming a recycling efficiency of 3 to 4, a representative value for eutrophic lakes (Bloesch et al., 1977), the daily net community production must be in the order of 300 to 400 mg C m⁻² d⁻¹, which equals to 0.025 to 0.033 mol m⁻² d⁻¹. We assumed that this value, which is supported by the analysis of the POC flux inferred from the sediment trap, is representative for late summer and that the vertically integrated net community production is somewhat higher in spring (0.045 mol m⁻² d⁻¹). For the rest of the yr the assumption was made that net community production shows a seasonal cycle similar to that of the solar radiation. Our tentative estimate of the seasonal cycle of net community production is

shown in Figure 4. According to this seasonal cycle, the annual integrated net community production is about 9.2 mol C m⁻² yr⁻¹ or 110 g C m⁻² yr⁻¹.

The *photosynthetic quotient PQ* was chosen to be 1.2. This is somewhat lower than the Redfield ratio of 1.3, because of the possible utilization of ammonia as nitrogen source (Stumm & Morgan, 1981). We lack observations in Soppensee to estimate k_{min} , the *rate of mineralization of POC* in the water column. We employed a value of 0.02 d⁻¹, an average of the rates found by the modeling studies of Karagounis (1992) for Lago Lugano and Greifensee and of Imboden (1984) for Zugersee. However, observations based on sediment traps (Bloesch & Sturm, 1986; Bloesch & Uehlinger, 1990) show no evident mineralization of settling particles in the hypolimnetic water column. For the *sedimentation velocities* of POC (v_{POC}) and calcite (v_{CaCO_3}) we have adopted a value of 1.5 m d⁻¹, a typical value found in Swiss lakes (Bloesch & Sturm, 1986; Beer et al., 1989; Karagounis, 1992).

We estimated the *gas exchange velocity of oxygen* (β_{O_2}) and of *carbon dioxide* (β_{CO_2}) using the empirical relationship between wind speed and gas exchange velocity proposed by Wanninkhof (1992) for average wind speeds. Lacking direct observation of wind speed at Soppensee we estimated them on the basis of observations performed by Heeb (1991) in the yrs 1986 to 1988 and measurements at the automatic meteorological station (ANETZ) Lucerne-Allmend (SMA, 1979–1987). We calculated an annual average for the gas exchange velocity of carbon dioxide (β_{CO_2}) of $0.24 \pm 0.04 \text{ m d}^{-1}$ and of oxygen (β_{O_2}) of $0.27 \pm 0.04 \text{ m d}^{-1}$. The estimate for oxygen is in good agreement with estimates in other low-wind lakes (Scheidegger et al., 1994).

The *surface input* I_s of CO₂ by gas exchange in (mol m⁻² d⁻¹) was evaluated independently of the model and used as an input function. Its value for each time step it is calculated by

$$I_s(t) = \beta_{\text{CO}_2}(t) \cdot \alpha_{\text{CO}_2}(t) \cdot [\text{pCO}_{2\text{atm}} - \text{pCO}_{2\text{epi}}(t)] \quad (1)$$

where α_{CO_2} denotes the solubility of CO₂ in water (mol m⁻³ ppm⁻¹), $\text{pCO}_{2\text{atm}}$ the atmospheric concentration of CO₂ (ppm) and $\text{pCO}_{2\text{epi}}$ the partial pressure of CO₂ in the surface water (ppm). We have adapted the formula of Weiss (1974) for the calculation of the CO₂ solubility. The atmospheric concentration of CO₂ was chosen to be 350 ppm, the average between 1980 to 1992 (Keeling et al., 1989). The partial pressure of CO₂ in the surface water ($\text{pCO}_{2\text{epi}}$) was calculated from the observations of pH, alkalinity and temperature using

Figure 4. Seasonal cycle of the vertically integrated net community production (NCP) as assumed for the seasonal carbon and oxygen model. Inset shows the assumed vertical profile for net community production.

the thermodynamic relationships of Dickson and Millero (1987).

The flux of carbon from the sediment caused by mineralization of POC, $F_{\min}$, was estimated by the difference of the POC sedimentation rate observed in the sediment and the amount of POC that reaches the sediment surface as simulated by our model. The observed POC sedimentation rate was determined from core 89–23 (Sturm, pers.comm.) to be $3.5 \text{ mol C m}^{-2} \text{ yr}^{-1}$. For the seasonal structure of $F_{\min}$, we assumed a stepfunction which is proportional to the amount of POC arriving at the sediment and is slightly modulated by the observation of high accumulation rates in the deep water in fall. Thus, $F_{\min}$ varies stepwise between $0.026 \text{ mol m}^{-2} \text{ d}^{-1}$ during early spring, $0.012 \text{ mol m}^{-2} \text{ d}^{-1}$ during summer, $0.016 \text{ mol m}^{-2} \text{ d}^{-1}$ in late fall and $0.008 \text{ mol m}^{-2} \text{ d}^{-1}$ in winter and has an annual average of $0.013 \text{ mol m}^{-2} \text{ d}^{-1}$.

The mean concentrations of DIC and Calcium in the inflow (DIC^{in} and Ca^{in}) were estimated on the basis of budget calculations with the implicit assumption of steady state over the annual cycle. According to these calculations DIC^{in} was estimated to about 5.7 mM and Ca^{in} to about 2.2 mM. For oxygen the assumption was made that the inflow is in equilibrium with the atmosphere.

Simulation

The simulation of the seasonal cycle of DIC, O_2 , POC, Ca and CaCO_3 started in spring at day 60 and the model was

run for 365 days until the next year at day 425. The vertical resolution was fixed to 1 m, which resulted in 27 boxes. The model was integrated forward in time using the Euler method and with a variable time step ranging from 0.1 to 0.2 days. The observed profiles of 3. March 1980 were used as initial conditions for DIC and oxygen. For initial Ca, a constant profile of 1.5 mM was assumed.

Results of the model

The simulated seasonal cycles for dissolved oxygen and DIC in the standard case are shown in Figure 5. We do not present the data of POC, CaCO_3 and Ca because no observations of these components are available. In Figure 6 we show the annual carbon budget for Soppensee as inferred from our model.

The comparison of the simulated seasonal cycle of oxygen to the observed one reveals good agreement for the general features of the cycle (Figure 5a). The model simulated properly the formation of the anoxic hypolimnion during summer, but it failed to calculate correctly the rapid development of the anoxia in spring and early summer. The simulated cycle exhibits also the buildup of high concentrations ($> 13 \text{ mg O}_2 \text{ l}^{-1}$) in the epilimnion during summer, but the model overestimates the maximum O_2 concentrations ($> 15 \text{ mg O}_2 \text{ l}^{-1}$).

The simulated seasonal cycle of DIC is also in good agreement with the observed cycle, although a precise comparison is not possible because of the scatter and the scarcity of the data (Figure 5b). The model simulates successfully the development and the duration

Figure 5. Isolines of the seasonal cycles of (a) dissolved oxygen and; (b) dissolved inorganic carbon as simulated by the model. For easier comparison with the observations in Figure 2c and 2d, the same levels for the isolines were chosen.

of the epilimnion minimum in midsummer that is generated by high net community production and the formation of calcite. In the hypolimnion, however, the agreement is worse. The model is able to simulate the developing DIC maximum at the end of the yr, but the evolution is gradual in the model whereas the observations show a rapid increase between September and October.

The carbon budget calculation (Figure 6) shows that inflow and outflow with 24 and 12 mol m⁻² yr⁻¹ are quantitatively the most important processes over the yr. Net community production transforms about 9.2 mol m⁻² yr⁻¹ DIC to organic carbon. According to the model, 1.0 mol m⁻² yr⁻¹ POC is mineralized during settling, whereas 4.7 mol m⁻² yr⁻¹ is mineralized at the sediment surface. Only 3.5 mol m⁻² yr⁻¹ are finally stored as organic carbon in the sediment. About 5 mol m⁻² yr⁻¹ is escaping from the lake to the atmosphere by gas exchange. Over the annual cycle, about 4.4 mol m⁻² yr⁻¹ calcite is formed in the epilimnion. Thereof, about 0.9 mol m⁻² yr⁻¹ is being dissolved at the sediment, and 3.5 mol m⁻² yr⁻¹ is deposited finally in the sediment.

We performed sensitivity studies to evaluate the influence of different parameters on the model results. The modeled seasonal cycles of DIC and O₂ reacted

sensitively to variations in the photosynthetic quotient, net community production and gas exchange velocity, whereas changes in the mineralization rate had only small effects on these results. In summary, the model is able to simulate correctly the major characteristics of the average seasonal cycles of DIC and oxygen in Soppensee, although many of the model parameters had to be estimated on a relatively weak basis.

Discussion

The most striking characteristic of Soppensee is the long history of anoxic deep waters which is recorded as annual varves over thousands of yrs. In this section we use the results from the dynamic model of the biogeochemical cycles in order to demonstrate that the interaction of several factors is creating favorable conditions for the genesis and the preservation of varved sediments in Soppensee.

First, we outline the special features of the *carbonate system* in this lake and its role in varve formation. Second, we estimate the *primary production* which is at present necessary to maintain anoxic deep waters. Finally, we discuss the internal and external *physical*

Figure 6. Mean annual carbon budget for Soppensee in the yrs from 1980 to 1993 according to independent estimates and the calculations of the seasonal model. Normal printed values have units of [mol m⁻² yr⁻¹], whereas values printed in *italic* refer to the whole lake and have units of [10⁵ mol yr⁻¹].

factors that influenced deep water mixing and anoxia during the last 15,000 yrs.

DIC - input and calcite sedimentation

In order to maintain steady state, the observed deposition rates of POC and CaCO_3 require sufficient input of DIC and Ca into the lake. The calculated mean input concentration of 5.7 mM DIC and 2.2 mM Ca are relatively high. Pure water in equilibrium with CaCO_3 and an atmospheric pCO_2 of 350 ppm contains about 1 mM DIC and 0.5 mM Ca (Stumm & Morgan, 1981). The supersaturation of the inflow with respect to atmospheric CO_2 indicates that groundwater entries play a significant role in Soppensee. The model calculation showed that the magnitude of ground water input into the hypolimnion has to be small, since the characteristics of the seasonal cycles were simulated correctly with all the inflow going into the surface waters. The concentrated inflow of alkalinity and Ca into the epilimnion obviously provides the basis for the intense calcite precipitation in Soppensee.

The mass balance in Figure 6 indicates that about $4.4 \text{ mol m}^{-2} \text{CaCO}_3$ is formed in the epilimnion during spring to early summer, which settles rapidly to the sediment. This is a large calcite flux: A time series of sediment trap data from Sempachersee results in an average CaCO_3 sedimentation of $2.3 \text{ mol m}^{-2} \text{ yr}^{-1}$ (Urban et al., 1997). Stabel (1986) estimated for the less productive Lake Constance an authigenic calcite precipitation of $1.9 \text{ mol m}^{-2} \text{ yr}^{-1}$. The combination of high productivity and groundwater inflows in Soppensee results in calcite precipitation rates which are higher than those of large eutrophic lakes.

Remineralization of organic carbon at the sediment surface produces carbonic acid that may dissolve some calcite. However, our model results indicate that 80% of the precipitated calcite is buried. Other studies in Greifensee and Sempachersee (Weber, 1981; Hollander, 1989; Urban et al., 1997) also found that only a small fraction of calcite is dissolved. Since H_2CO_3 is formed as a product of the degradation process under oxic as well as under methanogenic situations, the coupling between the dissolution of calcite and the remineralization exists in both conditions. The sedimentary record of Soppensee shows a highly variable sedimentation rate of calcite and a rather constant sedimentation rate of organic carbon (Sturm, 1993). Since CaCO_3 dissolution is linked to the remineralization of POC, these observations cannot be explained by changes in diagenetic processes only. However, they may also

reflect changes in the DIC and Ca concentrations of the inflowing groundwater, which are governed by changes in precipitation and vegetation.

Primary production, anoxia and burial of organic carbon

The most important criteria for the genesis and preservation of varved sediments is the existence of anoxic conditions in the sediment and at the sediment surface (O'Sullivan, 1983), which is usually coupled to anoxic bottom water. A good example for this criteria is the well preserved history of recent eutrophication in many Swiss lakes (Weber, 1981; Züllig, 1988), where the onset of seasonal varves is clearly linked to the formation of anoxic hypolimnion water. The oxygen content in the hypolimnion reflects a delicate balance between consumption of oxygen by remineralization and transport by mixing. Anoxic conditions are generated when either consumption is high or supply by mixing is insufficient. In lakes the largest fraction of organic matter is remineralized at the sediment surface. Therefore the deep part of the hypolimnion is more affected by oxygen consumption because of a higher ratio of sediment surface to water volume. Therefore, depending on the geometry of the lake, anoxic conditions can already be generated with relatively small O_2 consumption rates, and thus, also small primary production.

Net community production was estimated to be about $9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ or about $110 \text{ g C m}^{-2} \text{ yr}^{-1}$. We assumed implicitly in our model that net community production is equal to the flux of organic carbon out of the euphotic zone (export production). Therefore our estimate of net community production can be compared to primary production estimates in other lakes by assuming that the recycling efficiency is about 3 to 4 (Bloesch et al., 1977). A further possibility to estimate the annual primary production was established by Fricker (1980) by relating the spring overturn concentration of phosphorus to the annual net primary production. Applying his formula with the corresponding phosphorus concentration of about 0.06 mg P l^{-1} , we estimated for Soppensee an annual net primary production of about $280 \pm 90 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($23 \pm 7 \text{ mol C m}^{-2} \text{ yr}^{-1}$). This estimate indicates that the model result of $385 \pm 55 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($32 \pm 5 \text{ mol C m}^{-2} \text{ yr}^{-1}$) is rather too large than too small.

The model calculations for the whole lake showed that out of $8.2 \text{ mol m}^{-2} \text{ yr}^{-1}$ of organic carbon arriving at the sediment surface, about $4.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ is

mineralized and about $3.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ is buried in the sediment. For the water masses below 10 m, the remineralization at the sediment surface together with the relatively small mineralization in the water column leads to an annual oxygen consumption of $8.7 \cdot 10^5 \text{ mol O}_2 \text{ yr}^{-1}$. The hypothetical oxygen inventory at saturation in the water masses below 10 m is only $3.5 \cdot 10^5 \text{ mol O}_2$. Therefore under present day conditions the oxygen demand could decrease by a factor of two and the hypolimnion would still develop anoxia. Model calculations with reduced export production showed that even at 25% of the present value, the deepest part of the lake still becomes anoxic during the stagnation period due to the high ratio of sediment surface to volume and insufficient supply of oxygen by vertical mixing.

Only a minor part of the organic carbon that is produced by photosynthesis in the epilimnion is finally buried in the sediment. At present only a fraction of about 10% of the estimated net primary production is deposited as organic carbon. This value seems to be typical for eutrophic lakes (Bloesch et al., 1977). The magnitude of this fraction depends mainly on two factors: The recycling efficiency within the euphotic zone and the amount of organic carbon that is mineralized at the sediment surface. In marine ecosystems the recycling efficiency was shown to be dependent on the trophic state as indicated by the nitrate concentrations (Eppley, 1989; Sathyendranath, 1991). Oligotrophic systems tend to be much more economic (high recycling efficiency), whereas eutrophic systems have a much smaller recycling efficiency. We expect also that the fraction of organic carbon that is remineralized at the sediment surface is increasing with decreasing flux, because of a smaller burial rate and a better balance between oxygen consumption and supply. Therefore we assume that the deposition rate of organic carbon in the sediment is varying over-proportionally with changes in net primary production. However, over the last 10,000 yrs the burial rate of organic carbon has been remarkably constant varying only within a factor of two (Sturm, pers. comm.) We conclude that Soppensee probably remained in the meso- to eutrophic range since the last glaciation.

Mixing and anoxia

The turbulent flux of oxygen to the bottom water depends on the input of kinetic energy by wind stress and on the water column stability. Whereas the effect of kinetic energy input is mainly determined by external

factors such as wind exposition and, especially for small lakes, by the surrounding vegetation, the water column stability reflects internal as well as external factors. The water column stability N^2 is defined as:

$$N^2 = -\frac{g}{\rho} \cdot \frac{\partial \rho}{\partial z} = g \cdot \left(\alpha \cdot \frac{\partial T}{\partial z} - \gamma_{\kappa} \cdot \frac{\partial \kappa_{20}}{\partial z} \right) \quad (2)$$

where g denotes the acceleration due to gravity (m s^{-2}), ρ the density (kg m^{-3}), z the water depth (m; positively upwards), α the thermal expansivity of water (K^{-1}) and γ_{κ} the relative change of density per unit conductivity ($\text{cm } \mu\text{S}^{-1}$). As shown by equation (2), stability is composed of two terms, given by the local temperature and conductivity gradients $\partial T / \partial z$ and $\partial \kappa_{20} / \partial z$, respectively. The latter is strongly influenced by remineralization and dissolution at the sediment and the corresponding flux of dissolved substances from the sediment into the water. When mixing is low, ions can accumulate in the bottom water and hence produce a biogenic density stratification of the water column. The increase of the water column stability reduces mixing which in turn increases the accumulation of the remineralization products and finally leads to a higher static stability. This positive feedback loop can only be interrupted during periods of low thermal stability in winter by the input of high kinetic energy as for example by a passing storm.

Remineralization of organic matter and the dissolution of calcite are generating a high flux of DIC ($5.6 \text{ mol m}^{-2} \text{ yr}^{-1}$) and calcium ($0.9 \text{ mol m}^{-2} \text{ yr}^{-1}$) from the sediment to the hypolimnion during the stratification period supporting the biogenic density stratification in the bottom layer. By using a simplified model of internal waves (Münnich et al., 1992), we estimated the average velocity of bottom currents based on data of a thermistor chain, moored during 1990. This allows to calculate roughly the level of turbulence in the bottom layer. The rate of production of turbulence by these currents can then be compared to the salt induced water column stability N^2 (Wüest, 1994). This comparison shows that the bottom currents are too slow to mix the benthic boundary layer and also too slow to induce resuspension of deposited particulate matter (Gloor et al., 1994). These calculations are consistent with CTD data, where no evidence for the existence of well mixed benthic boundary layers was found. The accumulation of dissolved substances not only reduces the supply of oxygen to the hypolimnion but also prolongs effectively the stratification period. Deep mixing in

winter lasted on average about 100 days during the observation period (1979–1993). Since the oxygen demand at the sediment surface is also high during convective mixing, the sediment surface stays anoxic even when the concentration of oxygen in the overlying water is well above zero. The possible formation of ice cover during winter, as it was probably more common in the colder years before 1980, further reduces the oxygen supply by intercepting the gas exchange between atmosphere and lake.

In Soppensee the present input of kinetic energy by wind is low as observed by the small excitation of internal waves. Since the lake surface is so small, we can expect that the wind stress onto the lake water depends on the density and height of the surrounding vegetation. Therefore we expect less turbulent mixing and also longer periods of stagnation and consequently stronger anoxia in the hypolimnion during periods of denser vegetation. Since the pollen diagrams indicate that Soppensee was surrounded by forests until 2000 BP (Lotter, pers. comm.), it seems plausible that Soppensee has experienced very long periods during which the deepest part remained completely stratified during the whole year.

Conclusions

The seasonal cycles of DIC and O_2 in Soppensee are the result of a complex interaction of the processes of net community production, remineralization of POC, formation and dissolution of calcite ($CaCO_3$), in- and outflow, gas exchange and vertical eddy diffusion. We incorporated these processes into a simple vertical one-dimensional biogeochemical model in order to simulate the seasonal cycles of DIC and O_2 and to establish an annual carbon budget. Production of organic matter and biogenically induced calcite formation in the epilimnion are generating high vertical gradients of dissolved substances during the summer stratification period by removing DIC and calcium from the surface and partially releasing it into the hypolimnion. The high vertical gradients of dissolved substances are only partially reduced by vertical diffusion and gas exchange and lead to an increased density stabilization of the water column. High concentrations of DIC and calcium in the inflows are necessary to maintain the high calcite formation rates, indicating that groundwater is the dominant source of the inflowing water. The biologically increased stabilization suppresses turbulence and prolongs the

stratification period and hence the duration of anoxia in the bottom water. The formation and preservation of varved sediments in Soppensee is strongly coupled to these processes. According to our hypothesis, the existence of these varves over very long periods reflects the interaction of low external forcing by wind with internal biologically formed static stability. As shown by our model calculations, Soppensee would develop anoxic bottom water even when primary production was reduced to 25%.

Soppensee is a good example to demonstrate how chemical, physical and biological processes are interacting in a complex manner. Interpretation of changes in the sedimentary record in the past requires knowledge of these complex interactions. Dynamic models may help us to integrate the views from different disciplines.

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