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ORIGINAL PAPER

## Abrupt onset of carbonate deposition in Lake Kivu during the 1960s: response to recent environmental changes

Natacha Pasche · Georges Alunga · Keely Mills ·  
Fabrice Muvundja · David B. Ryves · Michael Schurter ·  
Bernhard Wehrli · Martin Schmid

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**Abstract** This study interprets the recent history of Lake Kivu, a tropical lake in the East African Rift Valley. The current gross sedimentation was characterized from a moored sediment trap array deployed over 2 years. The past net sedimentation was investigated with three short cores from two different basins. Diatom assemblages from cores were interpreted as reflecting changes in mixing depth, surface salinity and nutrient availability. The contemporary sediment trap data indicate seasonal variability, governed by diatom blooms during the annual mixing in the dry season, similar to Lakes Malawi and Tanganyika. The ratio of settling fluxes to net

sediment accumulation rates implies mineralization rates of 80–90% at the sediment–water interface. The sediment cores revealed an abrupt change ~40 years ago, when carbonate precipitation started. Since the 1960s, deep-water methane concentrations, nutrient fluxes and soil mineral inputs have increased considerably and diatom assemblages have altered. These modifications probably resulted from a combination of three factors, commonly altering lake systems: the introduction of a non-native fish species, eutrophication, and hydrological changes inducing greater upwelling. Both the fish introduction and increased rainfall occurred at the time when the onset of

N. Pasche (✉) · B. Wehrli  
Department of Surface Waters, Research  
and Management, Eawag, Swiss Federal Institute  
of Aquatic Science and Technology,  
6047 Kastanienbaum, Luzern, Switzerland  
e-mail: Natacha.Pasche@eawag.ch

B. Wehrli  
e-mail: Bernhard.Wehrli@eawag.ch

N. Pasche · B. Wehrli  
Institute of Biogeochemistry and Pollutant Dynamics,  
ETH, Swiss Federal Institute of Technology,  
8092 Zürich, Switzerland

G. Alunga · F. Muvundja  
Institut Supérieur Pédagogique, Bukavu,  
Democratic Republic of the Congo  
e-mail: georgesalunga@yahoo.fr

F. Muvundja  
e-mail: amisimuv@yahoo.fr

K. Mills · D. B. Ryves  
Department of Geography, Loughborough University,  
Leicestershire LE11 3TU, UK  
e-mail: k.mills@ballarat.edu.au

D. B. Ryves  
e-mail: D.B.Ryves@lboro.ac.uk

*Present Address:*  
K. Mills  
School of Science and Engineering, University  
of Ballarat, Ballarat, Victoria 3353, Australia

M. Schurter · M. Schmid  
Department of Surface Waters, Research  
and Management, Eawag, Swiss Federal Institute  
of Aquatic Science and Technology, 6047  
Kastanienbaum, Luzern, Switzerland  
e-mail: Michael.Schurter@eawag.ch

M. Schmid  
e-mail: martin.schmid@eawag.ch

carbonate precipitation was observed, whereas catchment population growth accompanied by intensified land use increased the flux of soil minerals already since the early twentieth century due to more intense erosion.

**Keywords** East Africa · Nutrients · Net and gross sedimentation · Carbonates · Diatoms · Ecological change · Tanganyika sardine

## Introduction

Situated in East Africa and influenced by two active volcanoes, Lake Kivu has experienced dramatic changes in its history (Haberyan and Hecky 1987). It was 300 m below its present level from 10,000 to 7,000 years BP and transformed into a deep lake around 6,000 years BP. About 5,000 years BP carbonate deposition ceased and diatom communities were completely modified in a short time. These dramatic changes were attributed to volcanism and hydrothermal activities (Haberyan and Hecky 1987). Increased aridity resulted in a temporary closure of Lake Kivu between ~3,500 and 1,400 years BP. In modern Lake Kivu, dissolved gases in the deep water are estimated at 60 km<sup>3</sup> CH<sub>4</sub> and 300 km<sup>3</sup> CO<sub>2</sub> (at 0°C and 1 atm). Recent studies indicate an increase in methane concentrations by 15% during the last 30 years (Schmid et al. 2005), which might have resulted from one or several environmental changes. First, gross sedimentation may have increased due to the fast-growing population, intensified land use and erosion of the steep catchment slopes. Second, the introduction of *Limnothrissa miodon* (the Tanganyika sardine) in 1960 altered the food web by eliminating the *Daphnia* communities (Dumont 1986). Third, intensified rainfall may have increased the subaquatic inflows, resulting in an increased transport of nutrients to the surface layer.

The present study aimed at assessing the importance of these three processes for recent changes in nutrient cycling and methane production. For this purpose, sediment cores representing the last 200–300 years of the history of the lake as well as material collected in sediment traps were analyzed both for chemical composition and diatom assemblages.

## Study site

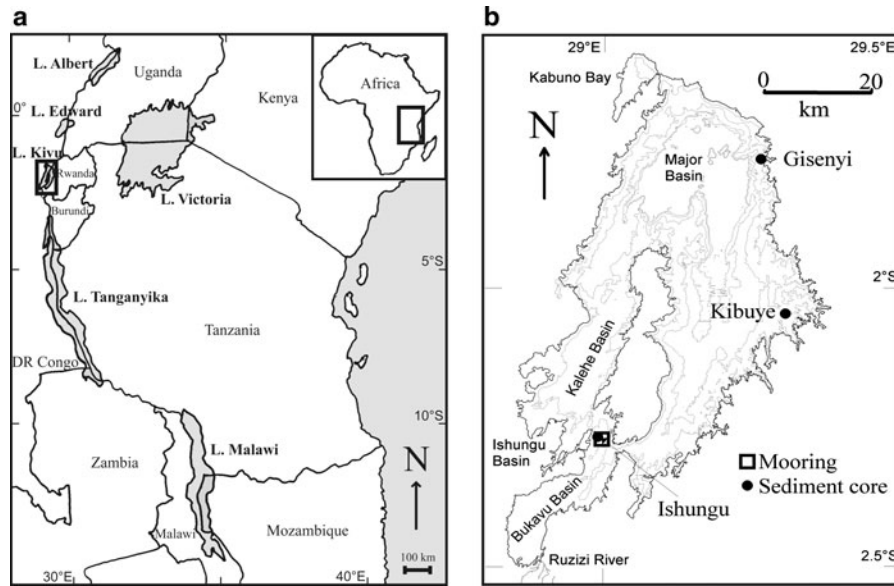
Lake Kivu is located in the East African Rift Valley, between the Republic of Rwanda and the Democratic Republic of the Congo. At an elevation of 1,463 m, it has an area of 2,370 km<sup>2</sup>, a volume of 580 km<sup>3</sup> and a maximum depth of 485 m (Schmid et al. 2004; Tietze 1978). The lake (Fig. 1) consists of a major and four smaller basins (Botz et al. 1988). Subaquatic springs enter below 180 m depth, with an estimated flow of 1.3 km<sup>3</sup> yr<sup>-1</sup> (Schmid et al. 2005). More than 127 rivers enter the lake (2.4 km<sup>3</sup> yr<sup>-1</sup>) from the catchment (5,097 km<sup>2</sup>), and the Ruzizi River (3.6 km<sup>3</sup> yr<sup>-1</sup>) is its outflow (Muvundja et al. 2009). Precipitation (3.3 km<sup>3</sup> yr<sup>-1</sup>) is nearly equal to lake-surface evaporation (3.4 km<sup>3</sup> yr<sup>-1</sup>). The water inputs and outputs (7 km<sup>3</sup> yr<sup>-1</sup>) are thus in equilibrium (Muvundja et al. 2009). The oxycline varies seasonally from 30 m in the stratified rainy season to 60 m in the dry windy season (June–September).

## Methods

### Sites, coring and sediment trap sampling

Gravity sediment cores (Fig. 1) were taken in May 2006 at Kibuye (2°02.886'S, 29°18.307'E, 190 m depth) and Ishungu (2°16.077'S, 28°59.374'E, 175 m depth) and in May 2007 at Gisenyi (1°46.383'S, 29°15.763'E, 155 m depth). Due to high gas concentrations, undisturbed cores could only be taken above 200 m depth. The three cores were transported to the Eawag laboratories in Switzerland, where they were sectioned at 0.5-cm intervals. Samples were frozen and lyophilized. Dried samples were ground and homogenized. Unfortunately, the Gisenyi core lost its uppermost section, as assessed by the <sup>10</sup>Be absence in the first layer.

One sediment trap mooring was set in Ishungu Basin from May 2006 to January 2008 (Fig. 1). Sediment traps consisting of two perspex cylinders (diameter 9.2 cm, length 100 cm) were placed at 4 different depths (50, 90, 130 and 172 m). Trap material was collected monthly with overlying water into 250-ml bottles. Frozen samples were transported to Eawag. Lyophilized samples were weighed, ground and homogenized. During freeze-drying, salts contained in the lake water contaminated our sediment



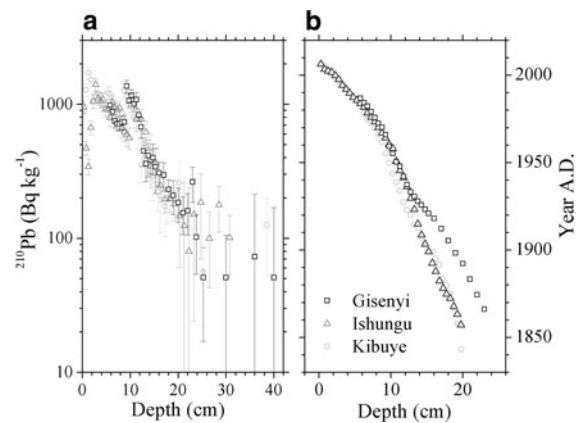
**Fig. 1** **a** Map of Africa with an enlargement on the Great Lakes in Eastern Africa, adapted from Sarmiento et al. (2007). **b** Map of Lake Kivu showing the location of the sediment cores (circles) and the sediment traps (rectangle). The Kibuye sediment core (2°02.886'S, 29°18.307'E, 190 m depth) and the

Gisenyi sediment core (1°46.383'S, 29°15.763'E, 155 m depth) were taken in the deep basin. In the Ishungu basin, the mooring with the sediment traps (02°16.255'S, 28°59.780'E) was fixed close to the coring site (2°16.077'S, 28°59.374'E, 175 m depth)

samples. The water contribution was estimated by assuming that the measured  $\text{Na}^+$  stemmed only from the water phase. The other water components (Ca, Mg, K, Cl, TIC, TN, TP, Sr and Mn) were corrected based on their molar ratios with  $\text{Na}^+$  at the given depth in the water column (Pasche et al. 2009). TIC was corrected with the molar ratio between  $\text{Na}^+$  and alkalinity ( $\text{HCO}_3^-$ ) and with a factor accounting for the formation and subsequent loss of  $\text{CO}_2$  during the precipitation of carbonates of Ca and Mg.

Dating

The cores were dated using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities measured by  $\gamma$ -counting in a well-type Ge-Li bore-hole detector. As sedimentation rates showed two distinct slopes (Fig. 2), a constant rate of supply model was applied (Appleby and Oldfield 1978). The supported  $^{210}\text{Pb}$  was calculated as the average background activity below 20 cm, where  $^{210}\text{Pb}$  remained constant. This supported  $^{210}\text{Pb}$  varied from 60  $\text{Bq kg}^{-1}$  for Gisenyi to 133  $\text{Bq kg}^{-1}$  for Ishungu. In Kibuye, supported  $^{210}\text{Pb}$  was calculated from  $^{226}\text{Ra}$  activities, equalling 104  $\text{Bq kg}^{-1}$ . The  $^{210}\text{Pb}$  supply averaging 330  $\text{Bq m}^{-2} \text{yr}^{-1}$  represents a high



**Fig. 2** **a**  $^{210}\text{Pb}$  activities in three different sediment cores measured in  $\text{Bq kg}^{-1}$ . Error bars represent accuracy of each measurement. The data from the Gisenyi sediment core were shifted by 5.5 cm, as the upper part of the sediment core was lost during sampling. **b** Age model applied for three different sediment cores

atmospheric flux probably explained by the lake's remoteness from oceanic influence and the abundant rainfall (Appleby et al. 2001).  $^{210}\text{Pb}$  can only be used to date ages <150 years. Sedimentation rates before 1850 were set to the steady average of the deeper unit.  $^{137}\text{Cs}$  activity peaks could not be detected.

Fluxes and dates before ~1850 should therefore be treated with some caution.

### Analytical methods

Total carbon (TC) was measured using a combustion CNS elemental analyzer (VARIO Co and EuroVector Co). TIC was analyzed as CO<sub>2</sub> by coulometry (UIC Coulometrics) after acidification with 3 M HCl. TOC was calculated as the difference between TC and TIC. For TN and TP, sediment material digested for 2 h at 121°C with peroxydisulfate solution was analyzed photometrically using a flow-injection analyzer (FIA, Procon AG). TOC, TIC, TP and TN were measured in the three cores and all trap samples. For quantitative mineral analysis on the Kibuye core and on every trap samples, major and trace elements were measured using X-fluorescence (UniQuant). The sum of carbonates and organic content was determined by loss on ignition at 1,100°C for 2 h.

Biogenic silica was measured using the single-step wet-alkaline leach method (Ohlendorf and Sturm 2008) for the Kibuye core and in the trap material at 90 m. Freeze-dried material was transferred to a Teflon crucible and treated with 10 ml 1 M NaOH. After digestion for 3 h at 90°C, the centrifuged aliquot was treated with 0.075 M HNO<sub>3</sub> and BSi was measured within 24 h by inductively-coupled plasma, optical-emission spectroscopy (ICP-OES/Spectro-Ciros). Simultaneous determination of aluminium and sodium allowed correcting (1:2 for Al:Si) for Si derived from silicate mineral dissolution (Ohlendorf and Sturm 2008).

Samples were prepared for diatom analysis for the Kibuye core and on trap material at 90 m following the water bath method of Renberg (1990). Diatom concentrations were estimated by adding a known number of inert microspheres (Battarbee and Kneen 1982) and slides were mounted in Naphrax. At least 300 frustules per sample were counted in transects under oil-immersion phase-contrast light microscopy (Leica DMRE microscope) at ×1000 magnification. General (Germain 1981; Krammer and Lange-Bertalot 1986, 1988, 1991a, 1991b) and regional floras (Cocquyt 1998; Gasse 1986) were consulted to identify to species level. Preservation was assessed using the F index (Ryves et al. 2001), the fraction of valves showing no signs of dissolution under light microscopy compared to the total number of valves.

The diatom data were divided into assemblage zones using optimal sum of squares partitioning (Birks and Gordon 1985) by the program ZONE (version 1.2; Juggins 2002), and detrended correspondence analysis was used to highlight the main underlying patterns of variation (ter Braak 1995). Ordinations were implemented using CANOCO 4.54 (ter Braak and Šmilauer 2002).

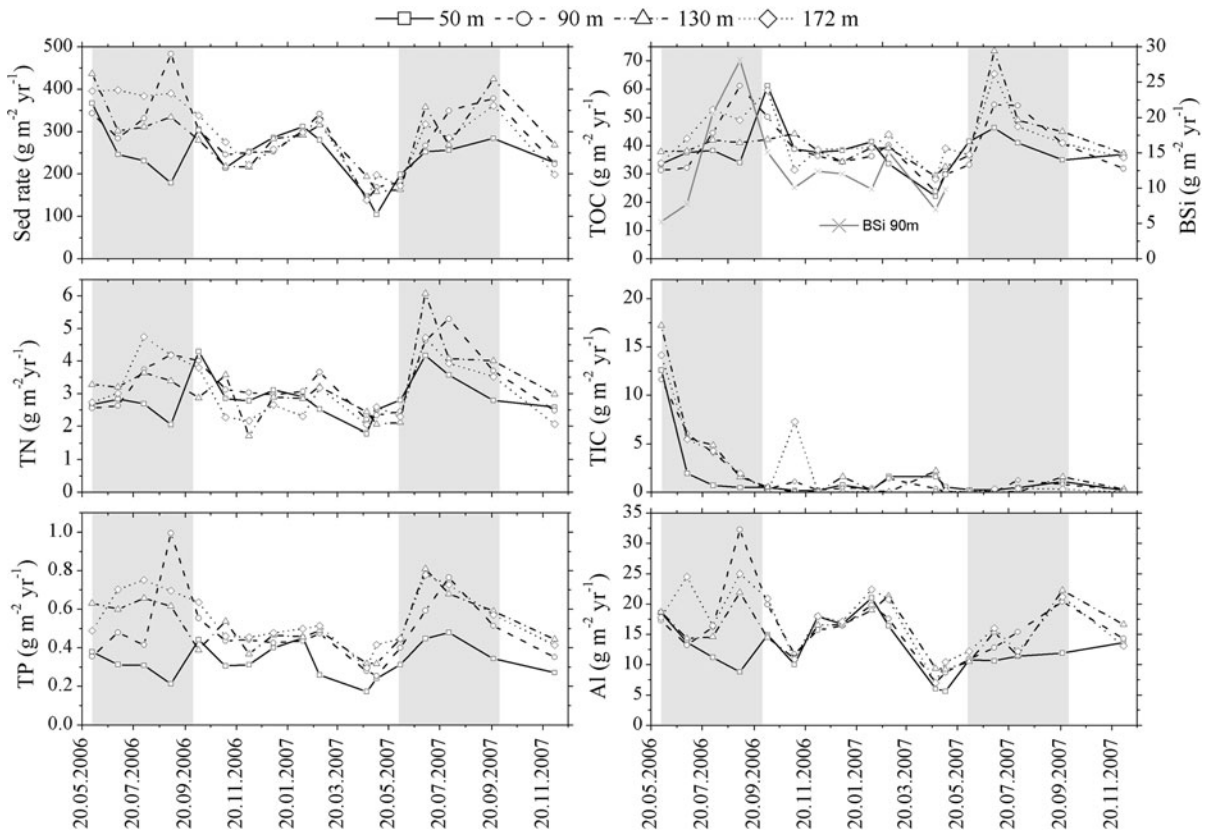
Quantitative diatom conductivity reconstructions were inferred using the European Diatom Database website (EDDI, <http://craticula.ncl.ac.uk/Eddi/jsp/>). Modern analogue matching of full samples with conductivity datasets showed that the closest analogues were from the East and North African subset, which was applied to fossil diatom assemblages using a weighted-averaging model with inverse de-shrinking ( $WA_{inv} : r_{jack}^2 = 0.758$ , RMSEP = 0.44 log units). Goodness-of-fit is assessed by considering the minimum dissimilarity coefficient between the fossil sample and the training set (Juggins 2001). All quantitative reconstructions using diatom data were carried out using the ERNIE software package within EDDI.

## Results

### Contemporary gross sedimentation

Material collected in sediment traps varied seasonally with maximum fluxes during annual mixing between June and September. TOC, TN, TP and BSi fluxes were maximal between August and October in 2006 and between July and August in 2007 (Fig. 3). The OM peak was higher in 2007 than in 2006. These maxima occurred during the dry season, when mixing induced by stronger winds and evaporation lowers the oxycline below 50 m depth. TIC was high at the beginning of the measurement period in June 2006 but then remained at low levels.

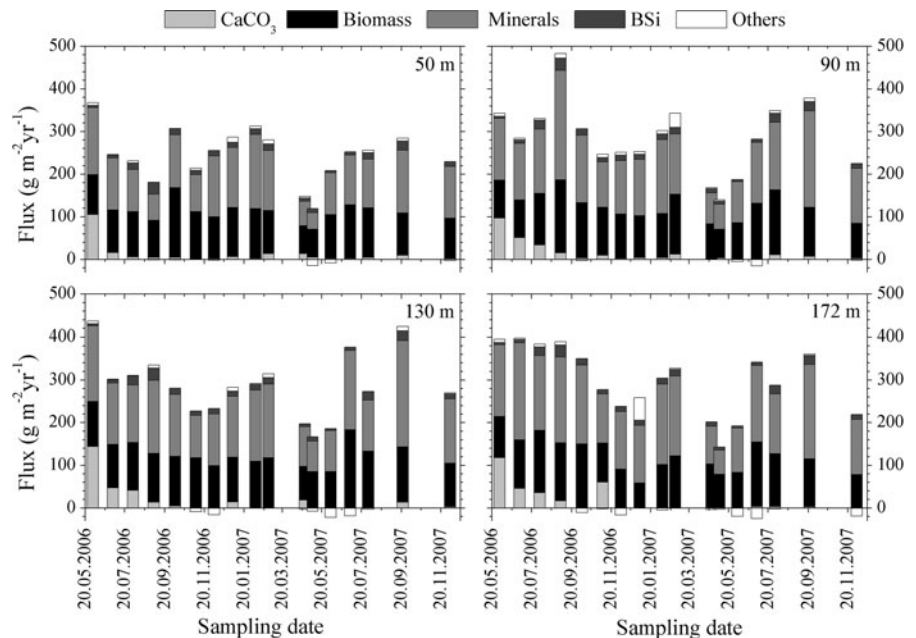
A mass balance for the different fractions observed in sediment traps was established (Fig. 4). CaCO<sub>3</sub> was determined as the average between TIC and CaO measurements. OM was calculated as the average between the sum of TOC, TN, TP, as well as O and H using the Redfield ratio, and a determination from the loss on ignition minus the loss of CaCO<sub>3</sub> as CO<sub>2</sub>. BSi and total minerals were measured directly. BSi was measured only at 90 m and reported for the other



**Fig. 3** Sedimentation rates and fluxes of nutrients (TOC, TP, TN), carbonates and aluminium measured in the four sediment traps (50, 90, 130 and 172 m) on the Ishungu mooring.

Biogenic Si at 90 m is illustrated in the TOC graph. The grey shading represents the dry seasons from June to September

**Fig. 4** Composition of material collected in sediment traps at 50, 90, 130 and 172 m on Ishungu mooring partitioned between carbonates (light grey), biomass (black), biogenic silica (grey) and minerals (dark grey). The fraction “others” (white) corresponds to the rest in order to agree with the sedimentation rate



**Table 1** Fluxes of sediment components for the three sediment cores and sediment traps from four depths (50, 90, 130 and 172 m), as well as molar ratios between TOC, TN and TP

	Sed. rate (g m <sup>-2</sup> year <sup>-1</sup> )	Fluxes (g m <sup>-2</sup> year <sup>-1</sup> )				Molar ratio		
		TIC	TOC	TN	TP	TOC:TN	TOC:TP	TN:TP
Sediment cores (Depth range cm)								
Ishungu 0–10	226	5.92	7.2	0.83	0.136	15	164	11
Kibuye 0–8.5	212	8.41	12.8	0.60	0.108	25	300	12
Gisenyi 0–3.5	351	21.12	16.6	1.00	0.180	19	238	12
<b>Average white layer</b>	<b>263</b>	<b>11.81</b>	<b>12.2</b>	<b>0.81</b>	<b>0.141</b>	<b>20</b>	<b>234</b>	<b>12</b>
Ishungu 10–31.5	76	0.93	3.4	0.41	0.045	10	144	14
Kibuye 8.5–39	65	0.53	9.0	0.33	0.037	32	627	20
Gisenyi 3.5–43	125	1.74	17.8	0.73	0.094	28	538	19
<b>Average brown layer</b>	<b>89</b>	<b>1.06</b>	<b>10.1</b>	<b>0.49</b>	<b>0.059</b>	<b>23</b>	<b>436</b>	<b>17</b>
Ratio white/brown	3.0	11	1.2	1.6	2.4	0.85	0.54	0.67
Sediment traps (Depth m)								
50	244	1.41	38.1	2.88	0.332	16	305	20
90	285	1.94	39.6	3.16	0.467	15	230	16
130	284	2.37	41.2	3.13	0.511	16	215	14
172	292	2.34	42.8	3.07	0.548	17	204	12
<b>Average 90–172</b>	<b>287</b>	<b>2.22</b>	<b>41.2</b>	<b>3.12</b>	<b>0.509</b>	<b>16</b>	<b>216</b>	<b>14</b>

For sediment cores, the first layer contained the white laminae (white layer), which were absent from the second unit (brown layer). Fluxes from sediment traps are averaged over 2 years, representing 17 samples per depth from Ishungu basin sediment traps

depths of the same sampling date. The total of these four components agreed within 2% with the sedimentation rate. The main constituents were minerals (50%) and biomass (40%). Minerals showed a slight minimum from mid-April to mid-June. Biomass and BSi had maxima from mid-June to mid-October, while CaCO<sub>3</sub> was important only in June 2006. OM fluxes were constant throughout the water column, whereas fluxes of soil minerals and CaCO<sub>3</sub> were smaller at 50 m (Table 1). Cooler and heavily loaded stream water probably intrudes occasionally below 50 m.

Diatoms (Fig. 5) were analysed on monthly collections at 90 m from May 2006 to 2007. Diatom preservation was excellent. Diatom concentrations were highest from June to August 2006 and April to May 2007. All samples were dominated by *Nitzschia lancettula* Müll., with seasonal appearances of *N. bacata* Hust., *N. tropica* Hust., *N. graciliformis* Lange-Bert. & Sim. and *Fragilaria danica* (Kütz.) Lange-Bert. There were low but persistent occurrences of periphytic taxa, notably *Amphora pediculus* (Kütz.) Grun. and *Encyonema muelleri* (Hust.) Mann, but no *Chaetoceros* cysts or *Urosolenia* Round and

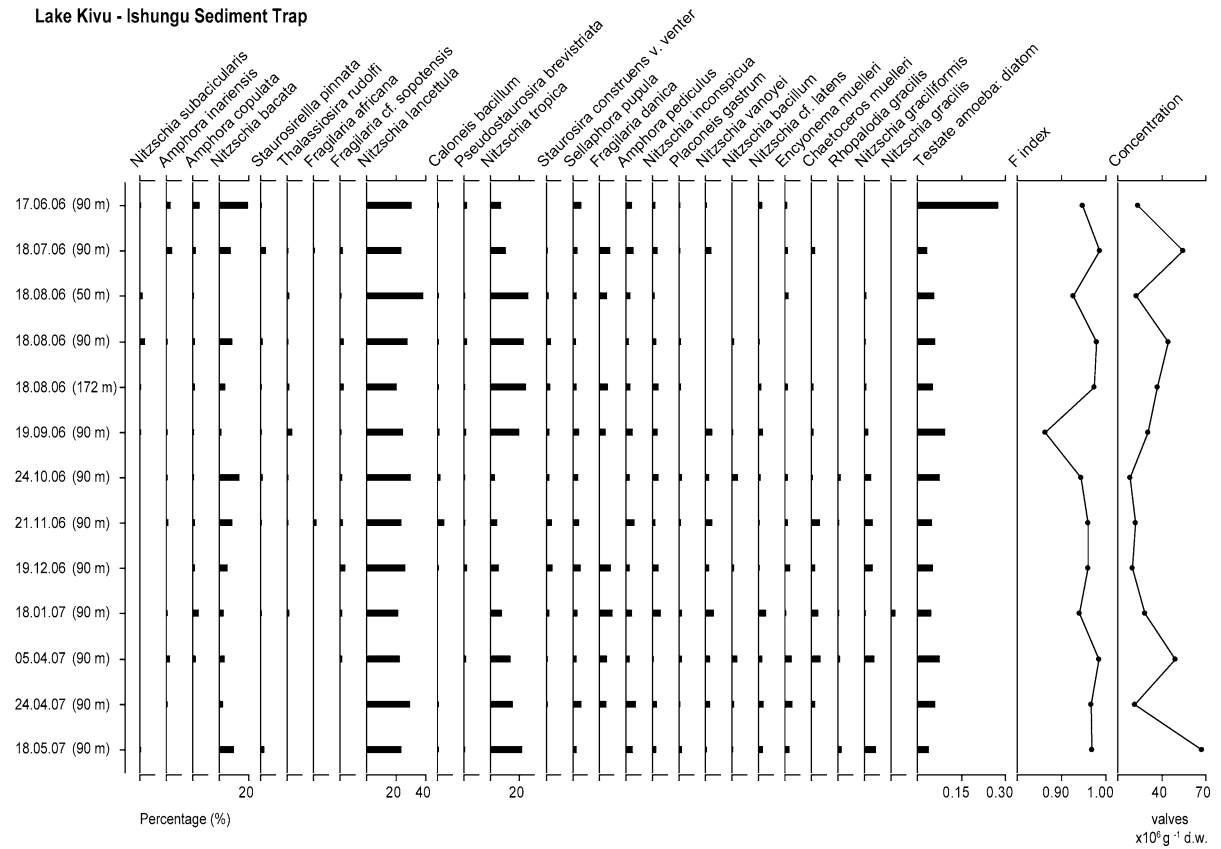
Crawford spp. (Sarmiento et al. 2007) were seen. Testate amoebae remains were always present with the testate amoebae:diatom ratio (TA:D) <0.1, except for June 2006 (0.25). In combination with low abundances of *N. tropica* and *F. danica* and significant amounts of pennate taxa, this high TA:D ratio suggests substantial transport of littoral sediments to the trap during May to June 2006.

#### Past sediment accumulation

#### *Sedimentation rates and visual description*

An abrupt transition from non-laminated dark to white laminae was visible in the upper cores. The logarithmic <sup>210</sup>Pb activities revealed two distinct slopes separated at the depth of this transition (Fig. 2). The shallower slope averaged 0.33 cm yr<sup>-1</sup>, whereas the deeper slope was 0.18 cm yr<sup>-1</sup>. This extreme shift is caused by a sudden onset of carbonate accumulation, diluting <sup>210</sup>Pb activity and increasing sedimentation rates. For the Gisenyi core, this pattern was reproduced assuming a loss of the top





**Fig. 5** Diatom assemblages of Lake Kivu sediment traps. All species >2% in any one sample are displayed. The ratio of testate amoebae scales to diatoms is displayed alongside the diatom preservation index (F index) and diatom concentrations

5.5 cm (Fig. 2). The constant rate of supply model indicated that mass accumulation rates increased by three-fold (Table 1). The transition occurred, within dating uncertainties, in the early 1960s.

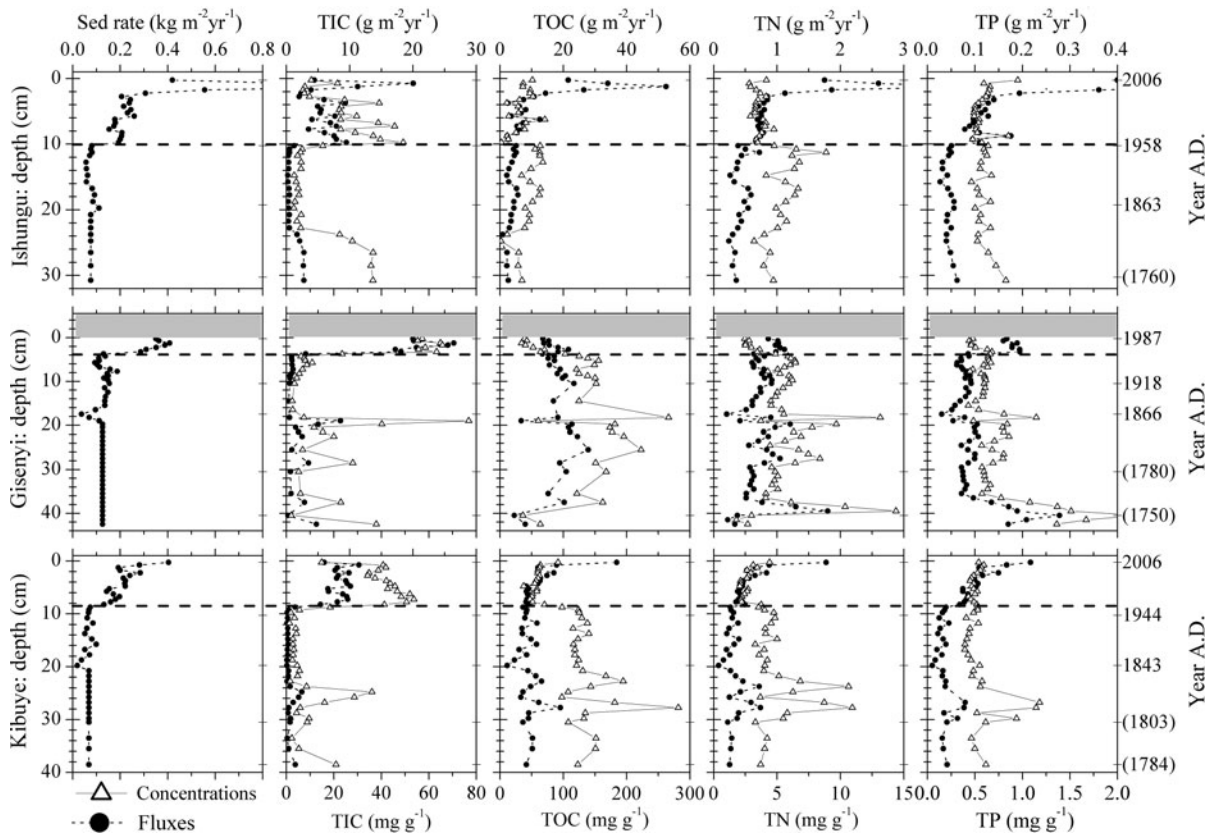
*Main component concentrations*

Concentration profiles of C, N, P (Fig. 6), BSi and minerals (Fig. 7) reflected changes between these two layers. TIC increased abruptly at their transition. TOC and TN were less concentrated in the white layer, while TP remained constant. The N:P ratio was lower in the upper layer. In the earlier record (<1850), two OM peaks separated by a TIC peak were observed in the Kibuye and Gisenyi cores (Fig. 6). For the Kibuye core, BSi concentrations have decreased since 1960. Elements linked to the carbonate cycle (Ca, Sr, Ba) showed a clear increase in the white layer, while indicators for soil minerals (Si, Al, Ti) showed a gradual increase from 30 cm

depth upwards. Mg, K and Mn remained constant, while Fe and S slightly increased in parallel, which indicates an increased precipitation of FeS.

*Main component fluxes*

Fluxes, derived from sedimentation rates and concentrations, increased for most constituents since the 1960s (Fig. 6). To quantify the changes, the average fluxes in the carbonate layer were compared to those before 1960 (Table 1). TIC accumulation was 10 times higher in the last 40 years, TP fluxes more than doubled, while TN increased by 60%. TOC fluxes were less consistent; recent fluxes increased by 100 and 40% and decreased by 7% in the Ishungu, Kibuye and Gisenyi cores, respectively. The lithogenic fraction has increased 3.5 times in the last 40 years (Fig. 7). Carbonate forming elements increased 14, 26 and 20 times for Ca, Sr and Ba, respectively. The Si, Al, Ti, Fe and S fluxes were augmented by factors



**Fig. 6** Concentrations (continuous lines with triangles,  $\text{mg g}^{-1}$ ), sedimentation rates (dashed lines with circles,  $\text{kg m}^{-2} \text{yr}^{-1}$ ) and fluxes of nutrients (dashed lines with circles,  $\text{g m}^{-2} \text{yr}^{-1}$ ) for the three different sediment cores taken at the positions shown in Fig. 1. The horizontal dashed lines represent the lower limit of the layer containing white laminae (10 cm for Ishungu, 3.5 cm for Gisenyi and 8.5 cm for Kibuye sediment core). Dates

extrapolated outside the range of Pb dating are given in parentheses. Some peak values are not shown (Ishungu: sedimentation rates of  $0.93 \text{ kg m}^{-2} \text{yr}^{-1}$  at 0.75 cm and  $1.46 \text{ kg m}^{-2} \text{yr}^{-1}$  at 1.25 cm, TN flux of  $4.25 \text{ g m}^{-2} \text{yr}^{-1}$  at 1.25 cm and TP fluxes of  $0.55 \text{ g m}^{-2} \text{yr}^{-1}$  at 0.75 cm and  $0.96 \text{ g m}^{-2} \text{yr}^{-1}$  at 1.25 cm; Gisenyi: TP concentration of  $2.23 \text{ mg g}^{-1}$  at 40.5 cm)

of 3.2, 4.4, 4.0, 3.2 and 4.2, respectively. A mass balance for the different fractions observed in the Kibuye core was established (Fig. 7) and clearly indicates a large increase in the carbonate and mineral fluxes during the last 40 years.

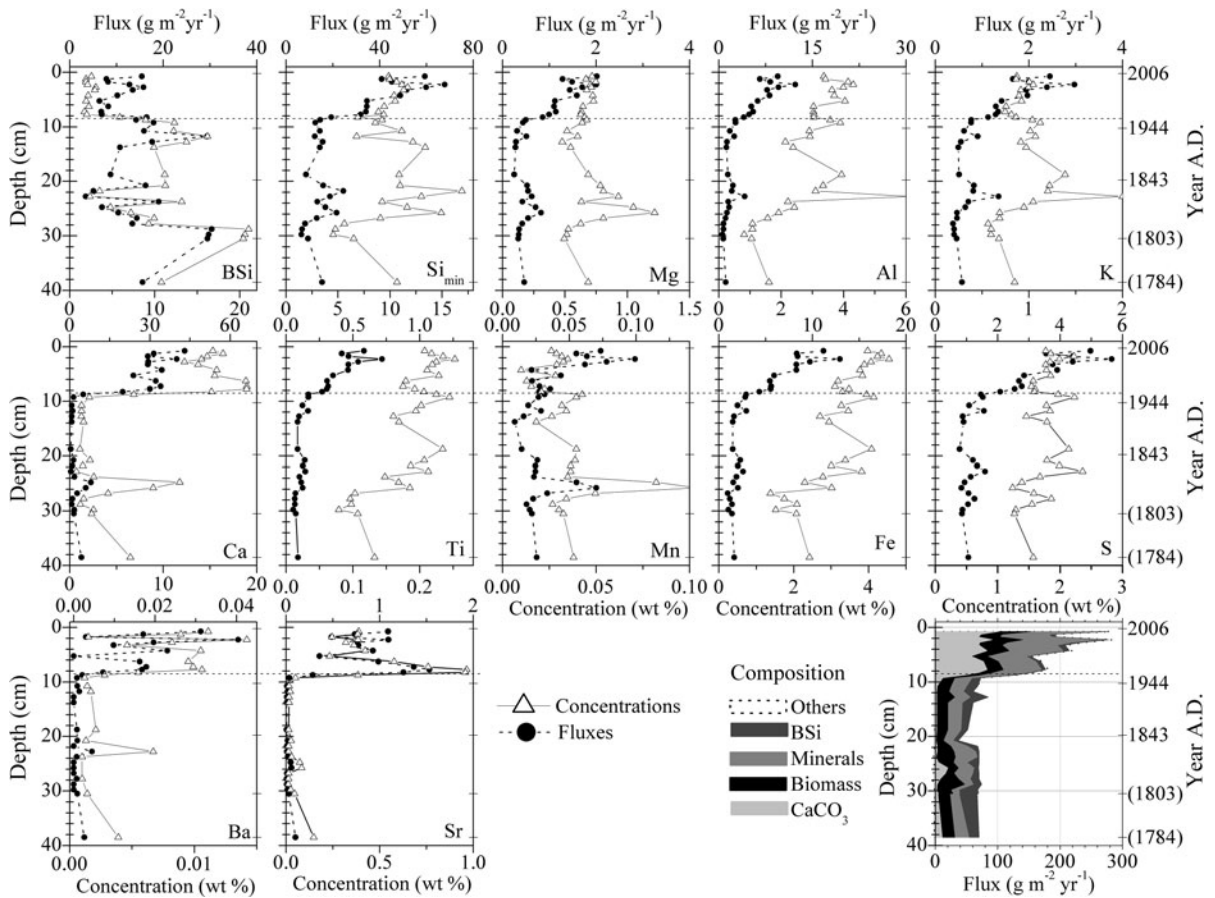
#### Diatom analyses

Diatom analyses of the Kibuye core recorded 83 species (Fig. 8). Five diatom assemblage zones were identified (Kiv-1–Kiv-5). The deepest layer (zone Kiv-1) is dominated by facultative plankton and periphyton, with only a few truly planktonic taxa present, notably long, thin *Nitzschia* species (*N. bacata*, *N. graciliformis*, *N. confinis* Hust.) and *Chaetoceros muelleri* Lemm. There are important

contributions from periphytic taxa (especially *Rhopalodia gibba* (Ehr.) Müll., ~15% of the assemblage at 34 cm). The testate amoeba to diatom ratio (TA:D) is low, while the F index is very high with high BSi fluxes but relatively low diatom flux. Diatom-inferred (DI) conductivity is around  $1,250 \mu\text{S cm}^{-1}$ .

Zone Kiv-2 contains an assemblage dominated by a short, broad *Nitzschia* species, which we call here *Nitzschia* aff. *obsoleta* Hust., with important contributions from *N. bacata* and *N. tropica*. At 25.5 cm, *Cyclostephanos dubius* (Fricke) Round and *Stephanodiscus parvus* Stoermer and Håk. appear for the only time in the record, with a peak in *Chaetoceros muelleri* (7%), the reappearance of periphytic taxa, and an increased TA:D. Preservation is good, but reaches its lowest value at 25.5 cm, while diatom





**Fig. 7** Concentrations (continuous lines with triangles) and fluxes of different elements (dashed lines with circles,  $\text{g m}^{-2} \text{yr}^{-1}$ ) measured by X-ray fluorescence for the Kibuye sediment core, and composition partitioned between carbonates, biomass, biogenic silica and minerals. The horizontal

dashed lines represent the lower limit of the layer containing white laminae (8.5 cm). The fraction “others” corresponds to the rest in order to agree with the sedimentation rate and is hardly visibly on this scale. Dates extrapolated outside the range of Pb dating are given in parentheses

fluxes remain low for much of this zone with BSi fluxes falling from maximum values at the base of the zone. DI-conductivity is generally  $\sim 1,000 \mu\text{S cm}^{-1}$ , but rises to  $4,000 \mu\text{S cm}^{-1}$  at 25.5 cm. Conductivity information for *Nitzschia aff. obsoleta* is not available within the EDDI database, hence we do not infer a value for samples where this species is present  $>40\%$ .

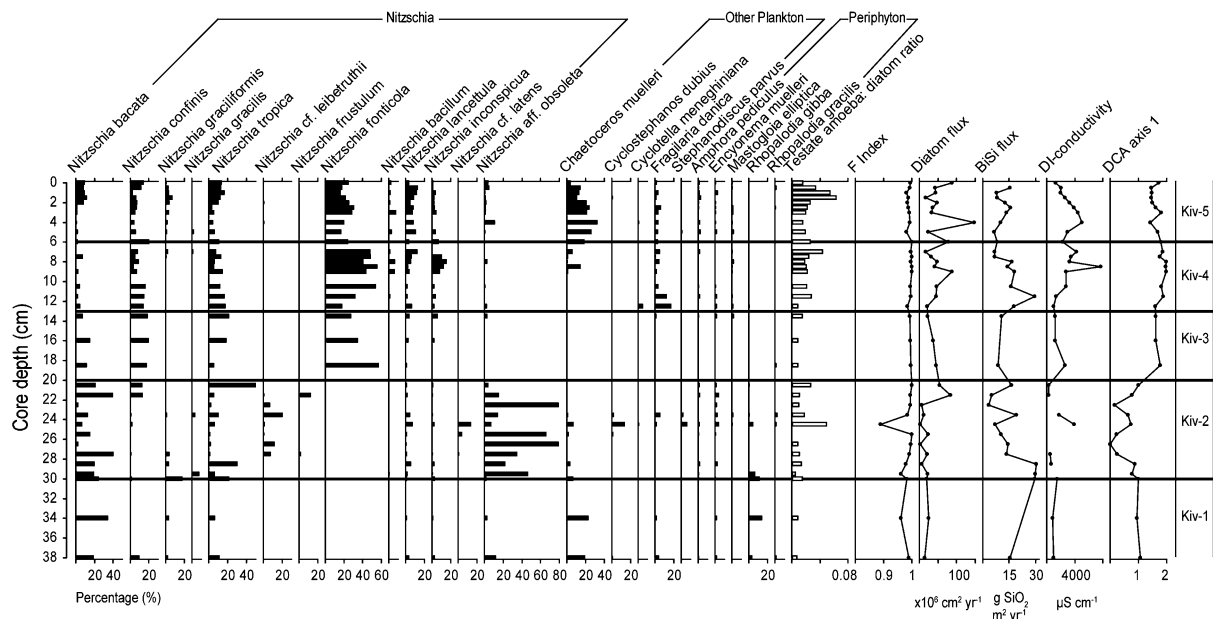
Kiv-3 is again dominated by *Nitzschia* taxa (*N. fonticola* (Grun.), *N. confinis*, *N. bacata* and *N. tropica*). DI-conductivity is  $\sim 2,000 \mu\text{S cm}^{-1}$  while diatom preservation and flux are both high and BSi fluxes are moderate.

Zone Kiv-4 is dominated by *Nitzschia fonticola*, with *N. confinis*, *N. tropica*, *N. inconspicua* Grun. and *F. danica* all important (the latter especially at the base

of the zone), and *Chaetoceros muelleri* reappearing. Preservation is good but diatom flux is variable, and TA:D increases. DI-conductivity rises to  $\sim 4,000 \mu\text{S cm}^{-1}$  (with a possibly anomalous peak at  $\sim 8,000 \mu\text{S cm}^{-1}$ ), while BSi fluxes fall from high values (coincident with the appearance of *Fragilaria danica*).

The most recent zone, Kiv-5, is dominated by a wide range of *Nitzschia* species and *Chaetoceros muelleri*, with *Amphora pediculus*, *Encyonema muelleri* and *Fragilaria danica* significant. The TA:D reaches its maximum in the core, with diatoms well preserved but with variable flux. DI-conductivity falls from higher values at the base of the zone, but surface sediment values agree well with recent observations in the lake (Sarmiento et al. 2006) of around  $1,200 \mu\text{S cm}^{-1}$ .

Lake Kivu - Kibuye Sediment Core (Kivu 3 - 09.06.06)



**Fig. 8** Diatom stratigraphy from Lake Kivu (Kibuye sediment core). All species >2% in any one sample are displayed. The diatom taxa have been grouped into ecological/habitat types and the sequence is split into assemblage zones Kiv-1–5. The ratio of testate amoebae scales to diatoms is displayed

## Discussion

### Degradation at the sediment-water interface

The constant fluxes of organic matter throughout the water column demonstrate minor degradation. Lake Malawi traps (Pilskałn 2004) also demonstrated maximum fluxes during the dry and windy season, when upwelling induces high algal production. BSi fluxes were similarly high during mixing and disappeared in the rainy season. Carbonate fluxes were characterized in both lakes by precipitation events, but were higher in Lake Kivu.

The degradation at the sediment-water interface was estimated by comparing fluxes observed in traps and cores (Table 2). Gross sedimentation is the average of the fluxes observed at 90, 130 and 172 m depth over 2 years. Net sedimentation is the average of the fluxes calculated for the carbonate layer of the Ishungu core. These comparisons indicate that OM is highly degraded; 74% for TN, 73% for TP and 83% for TOC. Similar degradation ratios were reported for temperate lakes (Bloesch et al. 1977;

alongside the diatom preservation index (F index), diatom concentrations and the axis 1 sample scores from Detrended Correspondence Analysis (DCA). Diatom-inferred conductivities are based on the East and North African dataset for salinity in EDDI

Lehmann et al. 2002). BSi is also partly (18%) re-dissolved. Surprisingly, TIC gross sedimentation represents only 40% of the net sedimentation. Carbonate sedimentation is characterized by short spikes, manifested by individual thin white layers in the upper part of the sediment cores, and our observations were obviously not representative for the average fluxes in the last decades.

Comparison with internal loading of nutrients (Pasche et al. 2009) suggests that gross sedimentation is underestimated by 50–70%. Indeed, primary production varies significantly between years, and in situ measurements of chlorophyll *a* and phytoplankton counts (J.-P. Descy, pers. commun., 2009) suggest that primary production, and especially the biomass of large diatoms during the deployment of the traps were far below the average for 2002–2005 (Sarmiento et al. 2006). In steady state, degradation at the sediment-water interface should be similar to internal loading (Table 2), allowing the correction of gross sedimentation. The measured gross sedimentation over 2 years was only 55% for TOC, 51% for TP, 32% for TN and 53% for BSi of the estimated

**Table 2** Degradation at the sediment/water interface determined by the comparison between the annual averaged flux in the sediment trap from 90 to 172 m and the average of the white layer from the Ishungu core, taken at the same location

	Sed. rate (g m <sup>-2</sup> year <sup>-1</sup> )	TOC (g m <sup>-2</sup> year <sup>-1</sup> )	TP (g m <sup>-2</sup> year <sup>-1</sup> )	TN (g m <sup>-2</sup> year <sup>-1</sup> )	BSi (g m <sup>-2</sup> year <sup>-1</sup> )
Gross sedimentation (avg. 90–172 m)	287	41	0.51	3.1	6.1
Net sedimentation (Ishungu core)	223	7	0.14	0.8	5.0
Degradation at the sediment water Interface	60	34	0.37	2.3	1.1
Internal loading			0.86	8.9	6.4
Corrected long-term gross sedimentation, required to balance internal loading			1.00	9.7	11.4
Difference between corrected and measured gross sedimentation			0.49	6.6	5.3

This degradation is compared with internal loading of nutrients (Pasche et al. 2009). Gross sedimentation was recalculated to balance the internal loading. These calculations compare the required long-term gross sedimentation with the lower gross sedimentation measured during our 2 year sampling time

long-term gross sedimentation. These lower values seem to reflect the atypically low diatom concentrations during the exposure time rather than degradation within the traps. Indeed, diatom preservation in Kivu's sediments and traps is excellent, as expected in an anoxic hypolimnion with low pH and high dissolved silica (Ryves et al. 2006).

#### Diatom ecology and paleoecology

The sediments are dominated by *Nitzschia* species, several of which are specific to tropical or African regions (Sarmiento et al. 2006), and since the 1970s, *Chaetoceros muelleri* has become significant. *Chaetoceros* and *Nitzschia* have been present for the last 6,000 years (Haberyan and Hecky 1987), while the present-day phytoplankton of Kivu is similar to Lake Victoria prior to its human-induced nutrient changes (Sarmiento et al. 2006). The long, thin *Nitzschia* group of Kivu are good competitors at high Si:P ratio and are always dominant; centrics (*Stephanodiscus*) that compete best at lower Si:P are rare (Sarmiento et al. 2006), while *Aulacoseira* Thwaites (which also require high Si:P) are absent, perhaps because of high sinking rates under stratified conditions, and the elevated salinity. However, surveys (Hecky and Kling 1987; Sarmiento et al. 2007) and trap material from Ishungu (Fig. 4) did not record *Chaetoceros*, despite its importance in the upper Kibuye core (Fig. 8).

Several changes in the diatom assemblages were observed in the recent sediment record. Their

interpretation is complicated by mixing regimes affecting the Si:P ratio (Kilham et al. 1986). Because P is mainly supplied to the epilimnion by internal recycling, while external inputs contribute significantly to Si inputs (Muvundja et al. 2009), longer stratified periods lead to high Si:P ratios in the epilimnion, while deeper mixing lowers surface Si:P ratios and potentially increases salinity. Changes in DI-conductivity should therefore be viewed with caution, as certain key taxa may be driven more by the Si:P ratio than by salinity. The general dominance of long, thin *Nitzschia* species and the obligate N-heterotroph *N. fonticola* (linked to *Microcystis* blooms; Kilham et al. 1986) for much of the record is indicative of water column stability with a reduced mixing regime (Stager et al. 1997). For example, *Nitzschia bacata* has been shown to form near-surface populations under daily stratification (Sarmiento et al. 2006; Stager et al. 2003, 2005).

Below ~30 cm, diatom samples contain an unusually low abundance of plankton (<50% on average), with significant occurrence (>10%) of both *Chaetoceros* and benthic *Rhopalodia* (Haberyan and Hecky 1987). This might indicate a lower lake level, increased surface salinity and closer near-shore habitats, with deeper mixing, and reduced Si:P ratio. Under this hypothesis, this may reflect regionally dry conditions from around 200–500 years ago, seen at Lakes Tanganyika and Edward (Russell and Johnson 2005; Stager et al. 2009) and smaller lakes in the western rift (Russell and Johnson 2007; Bessems et al. 2008). Alternatively, these sediments may

represent a turbidite deposit from shallower waters, although diatom preservation is very good and TA:D ratio remains low. Further cores from shallow sites in Kivu are needed to differentiate between these hypotheses.

Between 20 and 29 cm, declines in *Rhopalodia* and *Chaetoceros* and high abundance of smaller *Nitzschia* may imply higher water level. Diatom fluxes are generally low, while sustained increases in TA:D suggest increased catchment erosion, and/or littoral sediment transport (Haberyan and Hecky 1987). Within this zone, at ~25 cm, a short-lived perturbation appears in the diatom record characterized by low Si:P taxa (*Cyclostephanos dubius* and *Stephanodiscus parvus*), increased TA:D ratio, high proportion of littoral diatoms, minor peaks in the saline taxa *Thalassiosira rudolfi* (Bachm.) Hasle and *Chaetoceros* spp. and increased DI-conductivity of surface waters. This is paralleled by increased TOC, TN and TP in the cores (Fig. 6). This combination tempts us to speculate that deep water mixing may have been maximal at this time, bringing more saline water, with low Si:P, to the surface, while overall reduced plankton productivity allowed transport from near-shore sediments to provide a littoral signal to the core site. Alternatively, these observations may reflect greater littoral and catchment inwash from higher precipitation across the region, reflecting the widespread return to wetter conditions across East Africa during the 1800s (Stager et al. 2005, 2009; Bessems et al. 2008).

The replacement with *N. fonticola* agg. (~18 cm) may indicate continuing high lake level, stable stratification and shallow mixing under N limitation. Continued dominance of *N. fonticola* until the present day suggests these conditions persisted, with the appearance of *Fragilaria danica* at ~13 cm suggesting maximum Si:P ratio in the record and the re-appearance of *Chaetoceros* at around 9 cm (1960s).

A third major change in the diatom stratigraphy occurred 1970, coincident with the onset of carbonate accumulation (Fig. 6). This recent period is dominated by the planktonic, freshwater *Nitzschia fonticola* and *N. lancettula*. Stager et al. (2005) report the latter taxon in cores from Lake Victoria at times when the lake was deep and very fresh. The large increase in testate amoebae scales throughout this section is indicative of increased catchment inwash as recorded elsewhere in East Africa over this period (Mills 2009).

Between 1970 and 2006, there is also a substantial peak in *Chaetoceros*, probably indicating higher salinity or changes in Si:P. *Chaetoceros* is found only in more saline lakes (EDDI database) or coastal waters, and *Chaetoceros muelleri* has a high conductivity optimum within the EDDI training set. Their dominance in mid-Holocene sediments from Kivu implied surface salinity of 3 ppt (Haberyan and Hecky 1987). However, the similarity of recent salinity profiles to those from the 1970s (Tietze 1978; Schmid et al. 2005) and a consistently high lake level argue against a significantly higher surface salinity in the last few decades, especially at the inferred value of 4,000  $\mu\text{S cm}^{-1}$ . In the Baltic, increases in *Chaetoceros* are often indicative of anthropogenic nutrient enrichment (Ryves et al. 2004). We propose that *Chaetoceros* does indeed reflect slightly increased salinity, but is rather more an indicator of low Si:P, similarly to *Stephanodiscus/Cyclostephanos* in fresh conditions. Lowering surface Si:P ratios may have been induced by recent nutrient inputs from the catchment, and increased upwelling of more saline, low Si:P deep waters.

#### Major changes in sedimentation during the last 40 years

The most sudden change is the onset of carbonate precipitation in the early 1960s. Calcite was nearly absent in the sediment prior to this and its accumulation suddenly increased by 11-fold. In the last 40 years, fluxes slightly increased for TOC (20%) and TN (60%) but more than doubled for TP (Table 1). Total mineral accumulation increased by a factor of 3.5 and positive trends were observed for soil tracers and elements co-precipitating with carbonates.

The sudden onset of carbonates was probably induced by higher primary productivity. In Lake Kivu, the water above 60 m is oversaturated related to calcite and the saturated deep-water prevents any re-dissolution (Pasche et al. 2009). Even if the water is oversaturated, nucleation is necessary to start the precipitation process, often linked to phytoplankton activity (Dittrich and Obst 2004; Stabel 1986). Carbonates in older sediments (Botz et al. 1988) were identified as primary precipitates (aragonite, monohydrocalcite) and diagenetic products (siderite, calcite, and dolomite). Aragonites ( $\delta^{13}\text{C} = 4\text{--}6\text{‰}$ ) precipitated (Botz et al. 1988) in isotopic equilibrium

with the lake water bicarbonate ( $\delta^{13}\text{C} = 4.8\text{‰}$ ). In comparison, recent carbonates are isotopically heavier ( $\delta^{13}\text{C} = 6.1\text{--}7\text{‰}$ ), which might indicate more intense primary production.

Three major hypotheses could explain the abrupt changes around 1960: food web modifications, increased external nutrient inputs, or more intense upwelling via subaquatic sources. We discuss each in turn.

#### Top-down effects due to the introduction of *Limnothrissa miodon*

Changes could have been caused by an increased top-down control after the introduction of the first pelagic and planktivorous fish, *Limnothrissa miodon* (the Tanganyika sardine). This non-native fish was introduced in Lake Kivu in 1958–1960. This new predator eliminated the efficient grazer, *Daphnia curvirostris* (Dumont 1986), which was replaced by less efficient cyclopoid copepods (Isumbisho et al. 2006), reducing top-down control on phytoplankton (Sarmiento et al. 2006). Elsewhere, increased primary production has often triggered carbonate precipitation (Hodell et al. 1998; Teranes and McKenzie 1999). The recycling of nutrients in the epilimnion and their export could also have changed due to the shift in zooplankton communities. Increased primary production is, however, difficult to demonstrate due to the lack of historic data. However, our sediment core analyses suggest an enhanced export production, especially of P (Table 1). This change in recycling might have resulted from the shift in zooplankton dominance: *Daphnia* favours nutrient recycling (Bossard and Uehlinger 1993; Darchambeau et al. 2005), while copepods export P through faecal pellets. Reduced pressure on smaller pelagic diatoms may explain increases in *Nitzschia lancettula* and *N. inconspicua* since the 1950s (Haberyan 1985). These food web changes may have occurred rapidly and could have triggered the carbonate onset around the time of *Limnothrissa*'s introduction.

#### Bottom-up effects due to increased external nutrient inputs

The increased erosion due to deforestation over the last decades has amplified sediment load to the lake, explaining the increase in periphytic diatoms and

terrestrial testate amoebae, and supplying abundant nucleation sites for carbonate precipitation. P sedimentation could have been amplified via the flux of P-rich soil particles, decreasing the N:P ratio. Increased nutrient loading, accentuated by direct inputs from the fast-growing population, could accelerate lake productivity, alter the Si:P ratio in the epilimnion, and affect both pH and the supersaturation of  $\text{CaCO}_3$ .

The population in the catchment has increased steeply to 2.1 million over the last decades (Muvundja et al. 2009). Enhanced anthropogenic activities and the lack of sewage treatment have increased external nutrient inputs to Lake Kivu. An increase in nutrients would induce enhanced primary production, as indicated by the appearance in the last 40 years of *Chaetoceros muelleri*. Unfortunately, no historic data are available for comparison. But recent analyses (Muvundja et al. 2009) demonstrate that external nutrient inputs contribute only a minor part (10% soluble reactive P, 25% dissolved N, 45% dissolved Si) to the total loading, dominated by upwelling (Pasche et al. 2009). Even if the external nutrient loading has increased, this anthropogenic influence may represent only a small change to the nutrient budget of the epilimnion.

Allochthonous material reaching Lake Kivu might have been enhanced by soil erosion in the deforested catchment area. The Kibuye core reveals a three-fold increase in soil minerals during the last 40 years. The larger TP fluxes might be explained by the extremely high TP loads in rivers (Muvundja et al. 2009). Similar catchment disturbance was also reported for Lake Tanganyika, where sedimentation rates in deltas dramatically increased in the early 1960s (McKee et al. 2005), due to extraordinary rainfalls in 1961–62. TOC fluxes also increased in mid-twentieth century, driven by allochthonous OM and increased near-shore productivity (Palacios-Fest et al. 2005). In Lake Malawi, anthropogenic impacts may have increased external nutrient loading by 50% (Hecky et al. 2003).

In summary, population increase and catchment deforestation have led to growing external nutrient inputs, although these sources contribute only a small fraction of the internal loading (Muvundja et al. 2009). In contrast, erosion was clearly responsible for the increased fluxes of adsorbed P and soil minerals in near-shore sediment cores.



## Hydrological changes

Hydrological changes in East Africa have been documented for several lakes (Nicholson and Yin 2001; Ryner et al. 2008). In Lake Kivu, subaquatic springs contribute about 20% of total water inputs and drive a slow upwelling (Schmid et al. 2005). An increase in the subaquatic discharge could deliver more nutrients and  $\text{Ca}^{2+}$  to the epilimnion by upwelling, inducing higher primary production, lower Si:P ratios,  $\text{CaCO}_3$  precipitation and higher salinity.

The water levels of the African Great Lakes are sensitive to climatic conditions, and the water budgets of Lakes Victoria and Tanganyika have been used to reconstruct past climate. In the twentieth century, these lakes rose rapidly after the extreme rainfalls from 1961 to 1964 followed by high water level until 1990 (Nicholson 1999; Nicholson and Yin 2001). The water level of Lake Kivu was 0.44 m higher during 1965–1993 compared to 1945–1960. Annual rainfall from meteorological stations in the catchment were about 100 mm higher in 1962–90 than in 1932–61 (Rwanda Meteorological Service), representing 20% of the whole catchment discharge. Supposing enhanced subaquatic discharge, more salts and  $\text{Ca}^{2+}$  would be delivered to the surface by upwelling. These changes could induce higher primary production, carbonate precipitation and a shift toward diatoms typical of lower Si:P, and more saline conditions. In addition, a strengthening of the main chemocline has been observed since 1972 (Schmid et al. 2010), probably resulting from increased discharge from subaquatic springs.

In summary, the rise in lake level between 1960 and 1993 resulted from an increase in rainfall, ultimately feeding the subaquatic sources. Higher subaquatic discharge may have enhanced the upwelling of nutrients and salts to the epilimnion, leading to higher primary production and a shift towards more saline diatoms.

## Conclusions

In permanently stratified lakes, the seasonal deepening of the mixed layer releases nutrients from their nutrient-rich deep waters. Consequently, gross sedimentation in Lake Kivu showed a seasonal maximum coinciding with the primary production peak during

the dry season. Mineralization at the sediment water interface released 80–90% of the nutrients and organic carbon, and 56% of biogenic silica, back into the water column.

Sediment cores revealed an onset of  $\text{CaCO}_3$  accumulation 40 years ago, accompanied by nutrient increases, and a shift towards more saline diatoms with lower Si:P requirements. These changes probably resulted from ecosystem modifications, occurring around 1960. First, the introduced *Limnothrissa miodon* reduced the zooplankton communities, allowing increased phytoplankton populations and changing algal community dynamics. Second, the increasing population in the catchment might have induced eutrophication by catchment disturbance, soil inwash and effluent inputs. Third, stronger upwelling fed by enhanced subaquatic springs delivered more nutrients to the surface water, sustaining higher primary production. However, we were not able to determine which of these mechanisms, or which combination of mechanisms, is the actual dominant cause. Further investigations, such as long-term sediment trap data or analyses of  $\text{CaCO}_3$  minerals might help to elucidate the trigger for  $\text{CaCO}_3$  precipitation.

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