Doctoral Thesis

Effect of large dams in the Zambezi River Basin: Changes in Sediment, Carbon and Nutrient Fluxes

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Manuel J. Kunz

Effect of Large Dams in the Zambezi River Basin: Changes in Sediment, Carbon and Nutrient Fluxes

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Effect of Large Dams in the Zambezi River Basin: Changes in Sediment, Carbon and Nutrient Fluxes

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Doctor of Sciences

presented by
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2011
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Summary

The history of intensive river damming during the last 100 years promoted hydroelectricity, irrigation and flood control, but also resulted in serious environmental problems. By altering the flow regime of rivers, dams influence the transport of particles, carbon (C), and nutrients from land to ocean. This impact on biogeochemical cycles is aggravated by reservoir-internal processes, such as primary production, mineralization, and greenhouse gas emissions. Consequently, dam operations often lead to deterioration of downstream ecosystems. Despite these problems, hydropower represents a valid option for economic development in Sub-Saharan river basins, where only \( \sim 5\% \) of the large potential for hydropower is being exploited.

Against this background, this study investigated the impacts of river damming in the Zambezi River Basin (ZRB), the fourth largest river basin in Africa. The Zambezi is already affected by several large dams, and it has been suggested to expand hydropower generation. We hypothesized that dam impacts on sediment transport, and C, nitrogen (N), and phosphorus (P) cycling in the ZRB is large relative to pre-dam conditions. This hypothesis was tested by investigating two large reservoirs in the ZRB, Lake Kariba and Itezhi-Tezhi. We aimed to quantify the removal, internal processing and the changes in downstream loading of sediment, C, N, and P, under current, historic and future conditions. For this purpose, we (i) investigated the geochemistry of sediment records of Lake Kariba; (ii) compiled mass balances of C, N, and P for Itezhi-Tezhi reservoir based on water column and sediment analyses, and on numerical modeling of lake-internal biogeochemical processes; and (iii) estimated methane (CH\(_4\)) production and emissions through the relevant pathways in Lake Kariba.

Our results of the geochemical measurements on Lake Kariba sediments revealed large variability in the sediment regime, both in time (downcore direction) and in space (across sampling sites). \( \delta^{13}\)C and C:N values were used to assess the relative contributions of allochthonous and autochthonous organic matter, the latter accounting for \( > 45\% \) of lacustrine organic matter sedimentation. Allochthonous organic matter inputs were highest in deltaic deposits, and were present as discrete flood layers of varying thickness in la-
custrine cores. Overall sediment loads amounted to $4 \times 10^6$ t yr$^{-1}$ (700 g m$^{-2}$ yr$^{-1}$). The associated $120 \times 10^3$ t C yr$^{-1}$ (23 g C m$^{-2}$ yr$^{-1}$) represent $\sim$1% of global organic C burial in reservoirs, which is less than expected, as Lake Kariba covers $\sim$2% of the total global surface area of reservoirs. N and P removal efficiencies were 70 and 90%, respectively.

The quantification of C, N, and P mass balances and numerical modeling of biogeochemical cycling illustrated the importance of Itezhi-Tezhi reservoir in altering the riverine transport of these substances. Sediment accumulation rates increased exponentially from the dam to the mouth of the major inflow, and integrating this relationship over the entire reservoir surface allowed estimating total sediment accumulation ($330 \times 10^3$ t yr$^{-1}$), as well as C, N and P net sedimentation ($16 \times 10^3$, $1.5 \times 10^3$ and 200 t yr$^{-1}$, respectively). In comparison with N and P input and output loads, removal rates of 50% for N and 60% for P resulted. From numerical modeling of the reservoir’s biogeochemistry we estimated a mesotrophic primary production rate of 280 g C m$^{-2}$ yr$^{-1}$, of which 27% originated from N fixation. C, N and P incorporated into organic matter during primary production were efficiently recycled within the reservoir (N and P recycling factors $\sim$9). Consequently, although biological C fixation resulted in an input load comparable to riverine inputs, autochthonous organic C output loads accounted for only 20% of total C outputs. Scenario modeling runs incorporating deep water releases predicted $\sim$30% lower organic C outputs, an increase of dissolved N and P outputs by a factor of $\sim$4 and $\sim$2, respectively, and the potential of anoxia in the outflow during up to four months.

Littoral zones of Lake Kariba directly influenced by secondary tributaries were found to be major emitters of CH$_4$. The related total emission rates of $\sim$1 g m$^{-2}$ d$^{-1}$ were two orders of magnitude higher than in littoral areas distant from inflows and in the pelagic. In such emission hot spots, ebullition was the most efficient emission pathway, varying largely in magnitude and frequency. Hot spot ebullition was also identified as the most important emission pathway in a CH$_4$ mass balance for the deepest subbasin of the reservoir, whereas surface diffusion and outgassing in the turbine outflow were relatively low.
Zusammenfassung


Die Resultate der geochemischen Messungen in Karibas Sedimenten zeigten eine grosse Variabilität in der Sedimentablagerung, sowohl zeitlich (innerhalb eines Sedimentkerns) als auch örtlich (zwischen den verschiedenen Probenahmenstellen). Anhand der δ¹³C- und den C:N-Werten des organischen C konnten wir die relativen Beiträge an allochthonen und autochthonen Sedimenten zum totalen organischen Material abschätzen, wobei der autochthone Beitrag > 45% der see-internen Sedimentation des organischen Materials ausmachte. Allochthone Einträge an organischem Material waren am höchsten in den Delta-Ablagerungen der Zuflüsse. Zusätzlich erschienen sie als diskrete Flut-Schichten in den lakustrinen Sedimentkernen. Die gesamte abgelagerte Sedimentfracht lag im Bereich von $4 \times 10^6$ t yr⁻¹ (700 g m⁻² yr⁻¹). Der damit verbundene C-Einbau ins Sediment von $120 \times 10^3$ t C yr⁻¹ (23 g C m⁻² yr⁻¹) entspricht ~1% der globalen C-Senke in Stauseen. Dies ist weniger als erwartet, da die Fläche des Kariba ~2% der globalen Stauseefläche ausmacht. Die Einlagerungen von N und P ins Sediment waren mit 70% und 90% der Nettozuflüsse hoch.

Die Quantifizierung der C-, N- und P-Massenbilanzen und die Modellierung der biogeochemischen Kreisläufe illustrierten die Wichtigkeit des Itezhi-Tezhi-Stausees für die Veränderung des Transports dieser Substanzen durch die Flüsse. Die Sedimentakkumulationsraten nahmen vom Staudamm zur Mündung des Hauptzuflusses exponentiell zu, und Integration dieser Funktion über die gesamte Stauseefläche ermöglichte es, die gesamte Sedimentakkumulation ($330 \times 10^3$ t yr⁻¹), sowie C-, N- und P-Nettosedimentation ($16 \times 10^3$, $1.5 \times 10^3$, beziehungsweise 200 t yr⁻¹) abzuschätzen. Im Vergleich mit N- und P-Einträgen und -Abflussfrachten wurden Verlustraten von 50% für N und 60% für P abgeschätzt. Mithilfe der Modellierung der biogeochemischen Prozesse errechneten wir eine mesotrophe Primärproduktionsrate von $280$ g C m⁻² yr⁻¹, von der 27% von der N-Fixierung stammten. Die während der Primärproduktion ins organische Material eingelagerten C-, N- und P-Anteile wurden innerhalb des Stausees effizient rezykliert (N- und P-Rezyklierungsfaktoren ~9). Folglich trug der autochthone C-Abfluss nur 20% zum totalen C-Abfluss bei, obwohl die biologische C-Fixierung in einem Eintrag vergleichbar mit dem der Zuflüsse resultierte. Die Szenario-Modellierung, die Tiefenwasserabflüsse miteinbezog, sagte um ~30% tiefere organische C-Abflüsse, einen Anstieg der gelösten N- und P-Abflüsse um den Faktor ~4, beziehungsweise ~2 und potenziell anoxische Bedingungen im Ausfluss während bis zu vier Monaten voraus.

Ufernahe Zonen des Kariba-Sees, welche direkt durch sekundäre Zuflüsse beeinflusst sind, konnten als die Hauptemitter von CH₄ identifiziert werden. Die entsprechenden
Emissionsraten von $\sim 1 \text{ g m}^{-2} \text{ d}^{-1}$ sind zwei Größenordnungen grösser als in ufernahen Zonen ohne Zuflüsse oder im Pelagial. In solchen “Emissions-Hotspots” war das Ausgasen von Blasen der wichtigste Austragungspfad; die Variabilität des Ausmasses und der Frequenz waren aber sehr gross. Das Ausgasen von Blasen in Hotspots wurde in einer $\text{CH}_4$-Massenbilanz für das tiefste Becken des Kariba als wichtigsten Austragungspfad identifiziert, im Gegensatz zu den relativ geringen Verlusten via Oberflächendiffusion und via Ausgasen im Turbinenabfluss.
Zusammenfassung
Chapter 1

Introduction
1.1 The effect of dams

Economic development is closely linked to the availability of energy. Hence, generating sufficient energy in less developed regions of the world is of key interest (United Nations, 1993). To reach this goal in a sustainable way, renewable energy sources are to be favored. Against this background, hydropower generation is an attractive option on the African continent, given the clear need for development. Moreover, only < 5% of the African hydropower potential is being exploited, resulting in a production of $\sim50,000 \text{GWh yr}^{-1}$. This production of the entire continent is extremely low: it is in the same range as the hydropower production of the small country of Switzerland. The annual electricity consumption per capita in African households is $< 80 \text{kWh}$, again being very low in comparison to developed countries (e.g., Norway: 26,000 kWh; Bartle, 2002).

On average, hydropower schemes have met their targeted economic performance by producing the expected amount of electricity (World Commission on Dams, 2000). Yet this economic benefit was accompanied with negative effects on the environment and for the local populations. The report by the World Commission on Dams (2000) summarizes the negative effects on the environment as ecosystem and habitat degradation, decreased biodiversity, affected water quality and natural flooding of the wetlands and flood plains, and increased greenhouse gas emissions. Primarily, these negative ecosystem effects are related to the altered flow regime (Poff et al., 2010). Along with this hydrologic effect, riverine transport of particulate matter is greatly affected. In a global context, the particle load to the oceans has decreased by at least 50% due to dam operations, with certain river basins exhibiting a trapping efficiency of $> 80\%$ (Vörösmarty et al., 2003). The resulting deficit in suspended matter downstream of dams leads to erosion of the channel bed and the river banks, which adversely affects riparian ecosystems (Kondolf, 1997). This relationship between river damming and downstream effects have also been reported for African rivers (Snoussi et al., 2007).

In line with the reduced sediment transport due to river damming, the delivery of carbon (C) and nutrients to the oceans is also subject to change. Accumulation of sediments in reservoirs increased the burial of C in inland waters (Dean and Gorham, 1998), thus playing a prominent role in the global C cycle (Cole et al., 2007). Similar to C, reservoirs affect the nitrogen (N) cycle by, on the one hand, enhancing primary production and high N-fixation rates (Dumont et al., 2005). On the other hand, reservoirs are important sinks by removing N to the sediments, and by emitting $\text{N}_2$ formed by denitrification (Harrison et al., 2009). In a global context, $\sim50\%$ of total N inputs to the freshwater aquatic system are removed by rivers, lakes, and reservoirs, with reservoirs removing $\sim5\%$ of these inputs (Wollheim et al., 2008). This study, however, did not consider wetlands, which are known
1.2. The Zambezi River Basin

The Zambezi River Basin (ZRB; Figure 1.1) is an interesting system for studying dam-related negative effects on the environment in an economically less developed region. The rapid population growth in the ZRB (2.9%; Chenje, 2000; Mpande and Tawanda, 1996) accentuates needs for food production, irrigation, and energy generation. For all these needs, dams may help meeting the increasing demands. In terms of energy, hydropower is already being generated at several large dams in the ZRB, and there are numerous new
projects planned for further exploitation (Shela, 2000; Figure 1.1, Table 1.1). Current planning includes five large (capacity > 1 GW; Figure 1.1) dams along the main stem and more than 30 smaller dams (< 1 GW) within the ZRB. If realized, these hydropower schemes will substantially increase energy production, and may therefore support economic development in the ZRB. For instance, Mozambique has a current per capita energy consumption of 76 kWh yr\(^{-1}\), which could potentially be increased to 2,080 kWh yr\(^{-1}\) if the entire hydropower potential would be exploited (Bartle, 2002). The latter value translates to 240 W capita\(^{-1}\) being still far below the sustainability goal for developed countries of 2,000 W capita\(^{-1}\) (Jochem, 2004).

The Zambezi drains a catchment of 1.4 million km\(^2\) (Vörösmarty and Moore, 1991) that is shared by eight riparian countries (Shela, 2000; Figure 1.1). The catchment annually receives rainfall of 400 to 1,400 mm on average (Soils Incorporated, 2000). There is a gradient in precipitation from the wetter northern part to the relatively dry southern part. In addition to a high spatial variability, the amount of rainfall varies seasonally and inter-annually (Hachigonta and Reason, 2006). Due to high evaporation losses, the catchment produces only 70 mm yr\(^{-1}\) of runoff annually (~6% of precipitation; Soils Incorporated, 2000). This amounts to a total discharge of 110 km\(^3\) yr\(^{-1}\), making the Zambezi River the largest African river draining into the Indian Ocean (Soils Incorporated, 2000; Vörösmarty and Moore, 1991).

The negative effects of the existing dams on the riverine ecosystems are concentrated in the impounded lower stretch of the Zambezi River (Figure 1.1). Dam-induced hydrological changes are apparent, especially downstream of Cahora Bassa Dam (Beilfuss and Dos Santos, 2001; Vörösmarty and Moore, 1991). As a direct effect, the decrease in riverine sediment transport resulting from river damming is already substantial, as illustrated in a global modeling study by Vörösmarty et al. (2003) that estimated a sediment removal efficiency of 80 to 100%, making the ZRB one of the most severely affected river basins worldwide. However, while this study estimates overall sediment loading to the ocean, the effectiveness of the particle sinks, i.e., the reservoir sediments, in retaining particles and associated C and nutrients has not been quantified. Global modeling studies predict also high nutrient removal rates in the ZRB, e.g., for N (Harrison et al., 2009). However, this study lacks ground-truthing data for tropical regions, such as Sub-Saharan Africa, as predictions are extrapolated from relative sparse datasets collected in South America. Moreover, it is largely unknown how reservoir-internal processes, such as primary production and mineralization of OM influence the loads of sediment, C and nutrients in rivers. These various changes to the hydrology and the biogeochemical cycles in the ZRB resulted in unwanted environmental effects endangering vulnerable and valuable ecosystems (Seyam et al., 2001; Figure 1.1). Of particular importance are morphological and
ecological changes downstream of Lake Kariba and Cahora Bassa (Attwell, 1970; Guy, 1981; Ronco et al., 2009), limnological changes in Lake Cahora Bassa (Bond and Roberts, 1978; Bond et al., 1978; Hall et al., 1976, 1977), and the degradation of the Zambezi delta (Beilfuss and Davies, 1999; Beilfuss and Dos Santos, 2001; Scodanibbio and Mañe, 2005) and the Kafue Flats (Mumba, 2007; Obrdlik et al., 1989).

Our work focussed on two large reservoirs in the ZRB, Lake Kariba and Itezhi-Tezhi (Figure 1.1). These two reservoirs were chosen as examples to study dam-induced changes in biogeochemical cycles in the ZRB. A detailed description of the two reservoirs follows.

<table>
<thead>
<tr>
<th>Dam</th>
<th>Completion</th>
<th>Capacity</th>
<th>Reservoir</th>
<th>Drainage area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Year)</td>
<td>(MW)</td>
<td>A (km²)</td>
<td>V (km³)</td>
</tr>
<tr>
<td>Kariba</td>
<td>1959</td>
<td>1,320e</td>
<td>5,250e</td>
<td>160</td>
</tr>
<tr>
<td>Cahora Bassa</td>
<td>1974</td>
<td>2,075c</td>
<td>2,700c</td>
<td>73</td>
</tr>
<tr>
<td>Itezhi-Tezhi</td>
<td>1977</td>
<td>120h</td>
<td>370i</td>
<td>5</td>
</tr>
<tr>
<td>Kafue Gorge</td>
<td>1971</td>
<td>900c</td>
<td>800–1,600i</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a Locations are given in Figure 1.1
b Beilfuss and Dos Santos (2001)
c Gandolfi et al. (1997)
d Hydraulic residence time; estimated from mean inflows to reservoirs (Beilfuss and Dos Santos, 2001)
e Soils Incorporated (2000)
f At Kariba North Bank power station, additional turbines are currently being installed adding 360 MW capacity
g Coche (1974)
h Projected capacity, power station is currently being installed (Scott Wilson Piésole, 2003a)
i Obrdlik et al. (1989)
j Scott Wilson Piésole (2003b)
k Kapetsky and Petr (1984)
1.3 Lake Kariba

Lake Kariba is the largest reservoir in the ZRB, and one of the largest reservoirs worldwide (Figures 1.1, 1.2 and 1.3, Table 1.1). The dam was constructed within 3.5 yr and closed in 1958, shortly after the highest ever recorded flood had caused considerable damage to the uncompleted dam structure (Anderson et al., 1960). During the subsequent four years of filling, the lake reached its final volume of 160 km$^3$ and a surface area of 5,250 km$^2$. 

Figure 1.1: Map of the Zambezi River Basin illustrating the location of the major rivers, existing and projected hydropower dams, and important wetlands.
translating to a mean depth of $\sim$30 m. Like other reservoirs, Lake Kariba has an elongated shape and is highly dendritic, resulting in a long shoreline of $\sim$2,100 km (Coche, 1974; Figure 1.2). The up to 100 m deep lake is fed by tributaries draining $\sim$50% of the Zambezi catchment. The Zambezi River provides $\sim$80% of the total inflow (mean $\sim$60 km$^3$ yr$^{-1}$), the Sanyati River $\sim$8%, and the remaining share is delivered by small, seasonally flowing tributaries (Marshall, 1988). Total inflow varied between 16 km$^3$ yr$^{-1}$ in 1995/96 and 98 km$^3$ yr$^{-1}$ in 1957/58 (Beilfuss and Dos Santos, 2001), reflecting the high interannual variability in precipitation in the catchment. Net evaporation losses from the reservoir are 0.96 m yr$^{-1}$ ($\sim$5 km$^3$ yr$^{-1}$) on average, which equal $\sim$10% of mean total inflow (Beilfuss and Dos Santos, 2001).

The operation of the dam has greatly altered the discharge regime downstream of the dam. Low flow discharge has increased by a factor of three, and peak flow has been reduced by 40% compared to pre-dam conditions (Beilfuss and Dos Santos, 2001). The
outflow from the reservoir is used to operate turbines, whose intakes are located in a zone of \( \sim 13-33 \text{ m depth} \), the approximate depth of the thermocline during the stratified period (Anderson et al., 1960). Excess discharge in years with exceptionally high runoff is spilled through six gates located in \( \sim 30 \text{ m depth} \) (Figure 1.3). The Zambian and the Zimbabwean producers share a total hydropower capacity of 1,320 MW (Soils Incorporated, 2000). The mean production of hydroelectricity amounted to 5,200 GWh yr\(^{-1}\) for the period between 1960 and 1984 (Beilfuss and Dos Santos, 2001). Turbine extensions currently being installed at the North Bank Power Station will add 360 MW to the Zambian capacity, and a 250–360 MW extension is planned for the South Bank.

Negative effects for downstream ecosystems caused by the altered discharge regime downstream of Kariba Dam were identified at a relatively early stage. Attwell (1970) related increased pressure on the vegetation, erosion of silt deposits, and the degradation of the floodplain ecosystems in general to a more leveled out river discharge. Moreover, the author envisioned an aggravation of this problem due to further hydrologic changes induced by the upcoming regulation of the Kafue River (see below). Monitoring of river bank erosion in the Mana Pools floodplain downstream of Kariba Dam (Figure 1.1) showed that flood releases from the dam led to net land losses, as the deposition of sediments was diminished (Guy, 1981). Although these studies postulated that upstream sediment trapping was the most likely cause for the observed erosion, a quantification of the sediment accumulation in Lake Kariba was not carried out so far. Similarly, Bolton (1984) only assumed that the largest proportion of sediment loads transported to Lake Kariba are retained behind the dam.

Since the creation of Lake Kariba, several limnological studies have investigated the physico-chemistry of the lake. Lake Kariba has been described as nutrient-poor and monomictic, with the formation of an anoxic hypolimnion during the stratified period (Balon, 1978; Coche, 1974). The main motivation for limnological research was to explore the potential for fisheries (Balon and Coche, 1974; Begg, 1970; Coche, 1968; Harding, 1961, 1964). Although productivity increased during an initial eutrophication period of approximately four years, the lake soon after reached an oligotrophic state, limiting the fisheries potential (Coche, 1974; Marshall, 1988). To increase fish production in Lake Kariba, the freshwater sardine *Limnothrissa miodon*, native to Lake Tanganyika, was successfully introduced (Balon and Coche, 1974; Marshall, 1982, 1988; Mtada, 1987). In this context, more recent studies investigated the interactions of this and other species with the rest of the food web, such as plankton communities (Hancock, 1979; Marshall, 1991; Masundire, 1994, 1997; Ramberg, 1984; Ramberg et al., 1987), and explored the significance of potential causes of fluctuating fishing yields (Chifamba, 2000; Ndebele-Murisa et al., 2010; Phiri et al., 2007; Tweddle, 2010). An additional interest in nutrient cycling in Lake Kariba
Figure 1.3: Pictures of Kariba Dam taken (a) from the Zimbabwean side in June 2009 showing the six spillgates, and (b) below the dam on the Zambian side at the beginning of the spilling period in January 2011. Total discharge during this period was $\sim 4,500 \text{ m}^3 \text{ s}^{-1}$, with the two open spillgates contributing $\sim 1,500 \text{ m}^3 \text{ s}^{-1}$.
emerged from the massive spreading of aquatic weeds (Mitchell, 1969, 1973). Although these topics are clearly linked to lake-internal and basin-wide biogeochemical fluxes, there is a lack of systematic investigation of these cycles. In addition to the occurrence of aquatic weeds jeopardizing power generation (Balon, 1978), other environmental issues were the center of focus (Tumbare, 2008), such as the pollution with pesticides (Berg, 1995), and the potential of heavy metal pollution due to mining activities in the catchment (Nakayama et al., 2010; Tomasik et al., 1995).

1.4 Itezhi-Tezhi reservoir

Itezhi-Tezhi reservoir (dam closure in 1978) is located in the lower Kafue River Basin, Zambezi’s largest tributary (Figures 1.1, 1.4 and 1.5). It is part of the Kafue hydropower scheme, in which it serves as a retention basin for the downstream Kafue Gorge Dam (dam closure in 1971; Table 1.1; Scott Wilson Piésold, 2003b). Itezhi-Tezhi Dam discharges surface water through three spillgates (Figure 1.5), or bottom water through a tunnel at \( \sim 40 \text{ m} \) depth in the rare case when the water level drops \( \sim 8 \text{ m} \) below normal operating level (ZESCO, personal communication). The hydropower station at Kafue Gorge has an installed power capacity of 900 MW (Beilfuss and Dos Santos, 2001), producing 6,100 GWh yr\(^{-1}\) on average (Scott Wilson Piésold, 2003a). The hydropower scheme will be extended in the next few years with the installation of turbines at Itezhi-Tezhi allowing for additional energy production at 120 MW (Scott Wilson Piésold, 2003a). For this purpose, diversion tunnels are already existing, whose intakes will withdraw bottom water from the deepest site of the reservoir to 17 m above bottom (ZESCO, personal communication).

The total inflow to Itezhi-Tezhi reservoir accounts for \( \sim 8 \text{ km}^3 \text{ yr}^{-1} \), thus flushing the reservoir volume of \( 5.4 \text{ km}^3 \) in less than 1 yr (Table 1.1; Obrdlik et al., 1989). The reservoir has a maximum surface area of 364 km\(^2\), and a mean depth of \( \sim 15 \text{ m} \). Basic physicochemical data about the reservoir is limited to a few point measurements of oxygen, conductivity and major ions (Obrdlik et al., 1989). Given its importance for fisheries – despite its 14 times smaller surface area, the reservoir yields approximately a fourth of the production in Lake Kariba, the latter being similar to the total fishing yields of the entire Kafue River Basin (Tweddle, 2010) – its productivity might be substantially higher than Lake Kariba’s. Similar to Lake Kariba, *Limnothrissa miodon* was successfully introduced to Itezhi-Tezhi reservoir in 1992 (Tweddle, 2010).

Itezhi-Tezhi reservoir constitutes an excellent example to study negative effects of dams on downstream ecosystems. The Kafue hydropower scheme has strongly altered the hydrologic conditions in the Kafue Flats, a large floodplain type wetland enclosed by the
two dams (Figures 1.4 and 1.6). In comparison to flow conditions without dams, the peak discharge to the Kafue Flats in March has decreased by $\sim 30\%$ (720 vs. 480 m$^3$/s$^{-1}$), and the minimum discharge has increased by a factor of $\sim 3$ (50 vs. 150 m$^3$/s$^{-1}$, Mumba and Thompson, 2005; Figure 1.7). As a result of these hydrologic changes, a smaller total area of the Kafue Flats is flooded during the wet season. On the other hand, the flooded area during the dry season has increased from 300 to 1,500 km$^2$, which is equivalent to a 20% loss in flood recession area (Acreman et al., 2000). Finally, a larger area remains constantly inundated throughout the year, mostly due to the backwater effect of the Kafue Gorge Dam (Mumba and Thompson, 2005).
Chapter 1. Introduction

Figure 1.5: Picture of Itezhi-Tezhi Dam with its spillgates discharging surface water from the reservoir (courtesy of R. Beilfuss, reprinted with permission).

Figure 1.6: Picture of the Kafue Flats downstream of Itezhi-Tezhi reservoir (courtesy of R. Beilfuss, reprinted with permission).
1.4. Itezhi-Tezhi reservoir

As a consequence of decreased seasonal flood dynamics in the Kafue Flats, specialized plant and animal species find less ideal conditions, and invasive species have spread (ECZ, 2004; McCartney and Houghton-Carr, 1998; Mumba, 2007; Mumba and Thompson, 2005). This development endangers the rich biodiversity of this unique ecosystem (Acreman et al., 2000), and altered nutrient availability has been identified as a potential cause for the shift in species distribution (Schepp, 1985). To mitigate these negative effects, artificial flood releases were suggested to mimic the natural flooding pattern during the wet season (Gandolfi et al., 1997; McCartney and Houghton-Carr, 1998; Schelle and Pittcock, 2005; Sinyangwe and Stephenson, 2005). As hydrologic changes after dam closure were identified as main cause for the ecological degradation (Mumba and Thompson, 2005), these measures may indeed help in improving the state of the floodplain. Besides the hydrologic alterations, it remains largely unclear how changes in particle, C and nutrient cycling and transport due to dam operations have influenced the floodplain ecosystem, although these effects were identified to be potentially significant (Mumba and Thompson, 2005). So far, findings from the few studies about the effect of damming at Itezhi-Tezhi on the downstream water quality only indicate less pronounced seasonal differences compared to the pre-dam situation (Obrdlik et al., 1989; Salter, 1985).

Additional pressure on the environment in the Kafue River Basin originates from two main sources: (i) localized high nutrient loads from intensive agriculture and (ii) heavy-metal pollution due to mining activities (Kambole, 2003). High nutrient loads may have led to infestations with water hyacinths in the lower Kafue Flats (Alsterhag and Petersson, 2004).

![Figure 1.7: The hydrologic impact of Itezhi-Tezhi reservoir is illustrated by the difference in the mean discharge of the Kafue River upstream of the dam (blue curve, measured at Hook Bridge from 1973–2009, 30 day moving average of daily means) and at the dam outflow (red curve, 1978–2009; ZESCO, unpublished data). As a consequence of the dam, the discharge to the downstream Kafue Flats decreased by ~30% in the rainy season, and increased by a factor of ~3 in the dry season.](image-url)
2004), requiring pollution control measures (Sinkala et al., 2002). Mining activities (mainly producing copper and cobalt) predominantly take place in the upper Kafue, draining the Copper Belt province in Zambia. Due to mine effluents discharging into the Kafue River, high copper and cobalt concentrations reaching values 100 times higher than natural were found (Pettersson and Ingri, 2001). Consequently, these elements accumulated in aquatic organisms and sediments (Choongo et al., 2005; Norrgren et al., 2000; von der Heyden and New, 2005). Some studies suggested a trend to lower pollution in Itezhi-Tezhi reservoir and the Kafue Flats (Mwase, 1998), indicating efficient removal of particle bound heavy metals in upstream river reaches and wetlands. On the other hand, a recent study found high concentrations of Cu in fish from Itezhi-Tezhi reservoir (Nakayama et al., 2010).

1.5 Scope of this thesis – biogeochemical effects of large dams

We hypothesize that, large dams in general, and specifically Lake Kariba and Itezhi-Tezhi reservoir, disrupt the riverine transport of sediment, carbon (C), nitrogen (N) and phosphorus (P) by both physical removal and by changing biogeochemical cycles, therefore causing negative effects in the downstream ecosystems. Based on this overall hypothesis, the present study explores the following more specific hypotheses:

- Dams act as barriers for significant portions of particles, and particle-associated C, N, and P. These retained substances are of allochthonous origin, as well as stemming from lacustrine primary production. As a consequence of the removal within the Itezhi-Tezhi reservoir, availability of particles, C, N, and P is substantially reduced in valuable downstream wetlands, in particular the Kafue Flats, the Mana Pools floodplain and the Zambezi delta (Figure 1.1).

- Reservoirs act as biogeochemical reactors, thus fostering biological fixation of C and N, and biological incorporation of inorganic N and P into autochthonous OM, mineralizing allochthonous and autochthonous OM, and emitting CH₄.

1.6 Approach and outline

Our approach included intensive field investigations of Lake Kariba and Itezhi-Tezhi reservoirs followed by detailed system analyses of both reservoirs. In addition, we applied a
numerical model to simulate the lake-internal biogeochemical processes of Itezhi-Tezhi reservoir. In particular, we aimed at:

- a detailed examination of the sediment records in the two reservoirs. This allowed quantifying the current and historic removal of particles, C, N, and P. Therefore, an accurate estimate of the removal capacity of the reservoirs for these substances could be given. By collecting sediment cores at different locations along the thalweg of the original river channels, we accounted for spatial variability of sediment deposition. Moreover, the geochemical signal of OM deposits yielded information about the source composition.

- calculating C, N, and P mass balances based on estimated input and output loads, reservoir-internal fluxes, such as system new production, and sediment accumulation, for assessing the fate and the overall change in riverine transport of these substances to downstream wetlands due to dam operation.

- biogeochemical modeling. The model was used to evaluate Itezhi-Tezhi reservoir’s current and future role on particle, C, N, and P retention, cycling, and downstream river transport. Additionally, the model improved our mechanistic understanding of the reservoir-internal biogeochemical processes, and enabled us to evaluate the effect of future dam management strategies on downstream C, N, and P transport, as well as oxygen concentrations in the river.

- quantifying \( \text{CH}_4 \) production and release through all important pathways (i.e., ebullition, diffusion across the water surface-atmosphere interface, and outgassing) in Lake Kariba. A particular focus was placed on ebullition from littoral zones, which were expected to contribute substantially to overall emissions due to riverine OM inputs.

The following three Chapters 2, 3 and 4 are individual manuscripts that have been published or submitted to international, peer-reviewed journals (Journal of Geophysical Research – Biogeosciences, Water Resources Research, and Environmental Science and Technology, respectively). A brief overview of the contents of these chapters follows.

**Chapter 2: Sediment accumulation and carbon, nitrogen, and phosphorus deposition in the large tropical reservoir Lake Kariba (Zambia/Zimbabwe)**

In this chapter, we quantified sediment, C, N, and P accumulation, including historic changes and spatial variability, using sediment cores from Lake Kariba. Geochemical
signatures ($\delta^{13}$C, C:N) suggest that autochthonous sources account for $> 45\%$ of the accumulating OM in lacustrine sediments. Allochthonous sediment, on the other hand, was present in discrete layers of flood deposits. The overall accumulation rate of sediment was on the order of $\sim 4 \times 10^6$ t yr$^{-1}$. Associated OC accumulation ($\sim 20$ g C m$^{-2}$ yr$^{-1}$) is less than the global mean in reservoirs, and accounted for $\sim 1\%$ of globally buried OC in reservoir sediments. Total N and P were efficiently removed from the system ($\sim 70\%$ and $\sim 90\%$ of inputs). The resulting reduction in riverine transport of C, N, and P is likely to have adverse impacts in downstream wetlands.

Chapter 3: Impact of a large tropical reservoir on riverine transport of sediment, carbon and nutrients to downstream wetlands

This chapter summarizes the system analysis of Itezhi-Tezhi reservoir which was based on sediment records, estimates of input and output loads, and water column measurements. The resulting OC, N, and P mass balances revealed that substantial portions of these substances are removed from the riverine transport, either by sediment deposition or by reservoir-internal biogeochemical cycling. Biogeochemical model results suggested that considerable primary production was taking place, as well as quantitatively important related processes, such as N fixation, mineralization of autochthonous OM, and denitrification. Future scenario modeling suggested that outputs through newly installed turbines powered by hypolimnetic water may cause temporal anoxia in the outflow, decrease OC outputs, and increase dissolved inorganic N and P outputs from the reservoir.

Chapter 4: Spatial heterogeneity of methane ebullition in a large tropical reservoir

We investigated CH$_4$ emissions from Lake Kariba using an echosound device for measuring ebullition fluxes, diffusion chambers for measuring surface emissions, sediment pore-water cores for estimating sediment-water diffusion, and water-column concentration measurements for estimating seasonal hypolimnetic accumulation and surface and downstream outgassing. The study compared emissions from littoral zones receiving different amounts of OM inputs with emissions from lacustrine zones and the potential of downstream outgassing. Ebullition near tributary deltas was clearly the dominant emission pathway, suggesting its importance for overall CH$_4$ emissions from Lake Kariba.
Chapter 2

Sediment accumulation and carbon, nitrogen, and phosphorus deposition in the large tropical reservoir Lake Kariba (Zambia/Zimbabwe)

Manuel J. Kunz, Flavio S. Anselmetti, Alfred Wüest, Bernhard Wehrli, Adrian Vollenweider, Silvan Thüring, David B. Senn
Abstract

Large dams affect the aquatic continuum from land to ocean by accumulating particles and nutrients in their reservoirs. We examined sediment cores to quantify sediment, organic carbon (OC), nitrogen (N), and phosphorous (P) accumulation, and to examine historic changes and spatial variability in the sedimentation pattern in Lake Kariba, the largest hydropower reservoir in the Zambezi River Basin (ZRB). Sediment characteristics (concentrations of OC, N, P; δ¹³C and δ¹⁵N; wet bulk density) showed large variability both with sediment depth and between cores. While organic matter (OM) in river deltas was primarily allochthonous in origin, OM characteristics (δ¹³C, C:N) in lacustrine sediments suggest that autochthonous sources account for > 45% of the OM that accumulates over large areas of the lake. At the same time, the relative contribution of allochthonous material within individual layers of lacustrine cores varied considerably with depth due to discrete flood deposits. The overall sediment accumulation rate in Lake Kariba is on the order of 4 × 10⁶ t yr⁻¹, and the estimated OC accumulation of 120 × 10³ t C yr⁻¹ accounts for ~1% of globally buried OC in reservoirs. In addition, mass balance calculations revealed that approximately 70% and 90% of incoming total N and P, respectively, are eliminated from the water column by sedimentation (N, P) and denitrification (N). Since Lake Kariba attenuates flow from ~50% of the ZRB, these OC, N, and P removals represent a drastic reduction in nutrient loadings to downstream riparian ecosystems and to the coastal Indian Ocean.

Keywords  Reservoir sediments, Zambezi River, sediment accumulation, nutrient trapping, organic carbon, dam impacts

2.1 Introduction

While large dams are constructed to provide socioeconomic benefits in the form of hydropower, water storage and flood control, they typically also have major adverse impacts on ecosystem services (Rosenberg et al., 2000; World Commission on Dams, 2000). These impacts result from a range of factors, including highly altered flow regime (Richter et al., 1996), trapping of particles (Vörösmarty et al., 2003; Walling, 2006) and associated nutrients (Bosch, 2008; Bosch and Allan, 2008; Haregeweyn et al., 2008; Harrison et al., 2009; Teodoru and Wehrli, 2005) and altered water quality and nutrient dynamics (Friedl and Wüest, 2002; Matzinger et al., 2007a). Globally, dams have dramatically changed the transfer of particles from land to ocean, decreasing particle loads to the ocean by > 50%
2.1. Introduction

(Vörösmarty et al., 2003). Furthermore, reservoirs are considered to play an important role in the global carbon (C) cycle (Battin et al., 2009), by burying a large fraction of terrestrial organic C (OC) that would otherwise reach the oceans (Cole et al., 2007; Dean and Gorham, 1998; Downing et al., 2008; Stallard, 1998), and by emitting greenhouse gases such as CO$_2$ and CH$_4$ (Alin and Johnson, 2007; DelSontro et al., 2010; Tranvik et al., 2009).

Less economically developed regions of the world have considerable untapped hydropower potential (Bartle, 2002; Hydropower and Dams, 2001). This is particularly true in Africa, where only ~5% of the existing hydropower potential is being utilized (Bartle, 2002; Hydropower and Dams, 2001) and where ongoing economic development drives the planning for new dams (McCartney, 2009). Sparse biogeochemical data in such developing regions limit the ability to reliably evaluate the ecological impacts of existing and proposed dams.

The Zambezi River Basin (ZRB) is a particularly relevant example. The Zambezi is the fourth largest river in Africa (area = 1,400,000 km$^2$; average runoff Q = 6,980 m$^3$ s$^{-1}$; Latrubesse et al., 2005) and is highly fragmented by large hydropower structures (Shela, 2000). The hydrology of the system has been extensively studied (Beilfuss and Dos Santos, 2001; Vörösmarty and Moore, 1991) and there is evidence of massive disturbances to downstream ecosystems, particularly due to altered flooding regimes (Beilfuss and Davies, 1999), as well as river-bank and coastal erosion (Guy, 1981; Scodanibbio and Mañez, 2005). While several studies have investigated the basic limnology during the early stages of the reservoirs (e.g., Coche, 1974) and lake productivity and fisheries potential (e.g., Marshall, 1979), there has been only limited exploration of the biogeochemical impacts of the ZRB’s reservoirs on downstream systems (Attwell, 1970; Ronco et al., 2009). Moreover, only 30% of the ZRB’s hydropower capacity is currently being utilized, and several new large dams are in various stages of advanced planning (McCartney, 2009; Shela, 2000). Thus, there is a critical need to understand the current biogeochemical impacts, as these new dams will exert further pressure on the environment.

The goal of this study was to quantify the current and historic impact of Lake Kariba (Zambia/Zimbabwe), the largest reservoir in the ZRB, on the downstream transport and the cycling of particles, OC, nitrogen (N), and phosphorus (P). Lake Kariba, one of the world’s largest reservoirs by volume (volume = 157 km$^3$, area = 5,364 km$^2$, maximal depth = 97 m, Coche, 1968; Magadza, 2006), is the first of two reservoirs along the Zambezi main stem and regulates runoff from 667,000 km$^2$ or 49% of the ZRB (Magadza, 2006). Although negative downstream effects of Kariba Dam have been documented (Attwell, 1970; Soils Incorporated, 2000), the potential causes have not been examined in details,
and neither sedimentation nor removal of C, N and P in Lake Kariba have been sufficiently characterized. We examined the sediment record of Lake Kariba by analyzing physical and chemical properties of sediment cores collected at ten locations and of sediment-trap material, and used these archives to explore the following questions: (i) What is the magnitude of sediment trapping in Lake Kariba, and how do sedimentation and sediment composition vary spatially and temporally? (ii) To what extent does Lake Kariba influence C cycling by burying and mineralizing allochthonous OC and fixing new (autochthonous)

Figure 2.1: Bathymetric map of Lake Kariba with interbasin boundaries indicated by dashed lines (adapted from Coche, 1974). Lake Kariba is located on the border between Zambia and Zimbabwe, in the middle Zambezi (see inset). Sediment coring sites are indicated by dots; major inflows and the outflow at the dam are marked by black arrows. Sediment traps were moored at station B99 in front of the dam. The grey shaded area delineates the lacustrine sedimentation area (see text).
2.2. Study site

After dam closure in 1958, Lake Kariba (Figure 2.1) filled over a period of five years. The mean total inflow is $\sim 60 \text{ km}^3 \text{ yr}^{-1}$, resulting in a residence time of $\sim 3 \text{ yr}$ (Marshall, 1988). The Zambezi accounts for $\sim 80\%$ of inflowing water, while the Sanyati River, which enters closer to the dam from the south (Figure 2.1), accounts for $\sim 8\%$ (Marshall, 1988). Coche (1974) described the lake’s highly dendritic shape encompassing numerous isolated bays (shoreline length $\sim 2,000 \text{ km}$) and its morphobathymetry, featuring four distinct subbasins (basins I to IV, Figure 2.1). The lake is described as warm, nutrient-poor and monomictic (Marshall, 1988). Annual flooding occurs between November and May during and after the rainy season (Karenge and Kolding, 1995), followed by a dry period of cooling, triggering complete deep convective mixing in July. Subsequently, thermal stratification is re-established.

2.3 Methods

2.3.1 Sample collection and preparation

Sediment cores from ten sites (Figure 2.1) were retrieved during three field campaigns (July 2007, May 2008, and February 2009) using a gravity corer (UWITEC) equipped with 6.3 × 60 cm PVC tubes. The tubes were immediately sealed after sampling to minimize disturbance during transport. Cores were transported upright and, upon arrival at the laboratory, stored at 4°C until further processing.

Wet bulk density (WBD) was measured with gamma-ray attenuation on whole cores with a Geotek Multisensor core logger at a downcore resolution of 5 mm. Cores were split vertically, and digital photographs were taken from fresh surfaces after opening. Subsequently ($\sim 1 \text{ h}$ after opening), color reflectance of normal light on the split core surface was measured using a Jai CV L105 e CCD Colour Line Scan Camera at a downcore resolution of 140 pixel cm$^{-1}$.

The working halves of the cores of the 2007 and 2008 campaigns were subsampled at 1-cm depth intervals (cores B21, B55, B56, B58; Figure 2.1), or from similarly colored layers (B11, B41, B51, B61, B99; Figure 2.1) to investigate characteristics of individual layers.
Additionally, samples from pure colored (i.e., black versus bright) layers were collected from supplementary cores retrieved from stations B21, B31 and B99 during the 2009 field campaign. All samples were freeze-dried until they reached constant mass, homogenized and stored in plastic boxes. The mass of dried material from a core depth increment divided by the increment volume was calculated to give dry bulk density, which was used for calculating mass accumulation rates.

To estimate gross autochthonous sedimentation rates, sediment traps (collecting area = 66 cm$^2$) were moored at site B99 (Figure 2.1), at 2.8, 55.6 and 61.7 m above the bottom between July 2007 and June 2009. This station, which was located the furthest distance from major inflows, was selected to maximize the relative contribution of autochthonous material to the traps. Traps were recovered in May 2008, February 2009 and June 2009. Samples were frozen within 5 h after collection. Prior to analysis, the samples were freeze-dried, weighed, and homogenized.

In addition to sediment sampling, water samples were collected during the three field campaigns. To estimate nutrient discharges through the outflow we collected water samples at B99 (Figure 2.1) throughout the water column and specifically at depths of the turbine intakes (i.e., between 7 and 44 m depth). Water samples were also collected at all stations depicted in Figure 2.1 at 5 to 10-m depth resolution for measuring pH and alkalinity by endpoint titration.

### 2.3.2 Sample analysis

Elemental composition (C, N) and stable-isotope ratios ($\delta^{13}$C, $\delta^{15}$N) were measured using a 6890N Elemental Analyzer (Agilent Technologies) coupled with an Isoprime continuous flow isotope-ratio mass spectrometer (Micromass). Stable-isotope ratios were expressed in the $\delta$-notation using the Vienna Pee Dee Belemnite and atmospheric N$_2$ as standards. Reproducibility for replicate measurements was better than 3% and 5% for total C (TC) and total N (TN), respectively, and 0.1‰ and 1.0‰ for $\delta^{13}$C and $\delta^{15}$N, respectively.

Based on the catchment geology, allochthonous inorganic C (IC) input to the sediments was expected to be low (Coche, 1974). We confirmed this by analyzing both IC and OC on more than 50% (n = 137) of all samples across all cores and depositional environments in two ways: by directly analyzing OC on samples acidified with 12% HCl using the elemental analyzer; M"{u}ller and Gastner, 1971; Yamamuro, 2000, and indirectly by subtracting TIC (measured using a UIC Inc. CM 5012 CO$_2$ coulometer; M"{u}ller and Gastner, 1971) from TC. The comparison of TC and OC revealed that 98 ± 3% of TC was OC. A similar analysis comparing $\delta^{13}$C of acidified and untreated samples showed small (< 1.0‰) and
nonsystematic differences. Hence, we hereafter use measurements performed on untreated samples for OC concentrations and OC-\( \delta^{13} \)C.

Total P (TP) concentrations of sediment and supplementary water samples were determined photometrically on a Procon flow analyzer after digesting the samples with K\(_2\)S\(_2\)O\(_8\) at 120°C for 2 h (DEW, 2004). Reproducibility for replicate measurements was better than 5%.

To examine the fining of allochthonous particles with increasing distance from river mouths, grain-size distribution was measured on wet sediment samples by laser diffraction (Malvern Mastersizer 2000). For this analysis, only samples from the transect towards Sanyati (cores B55, B56 and B58) were used.

Core B55 was selected for radionuclide dating as it visually had the best preserved layering. Hence, B55 served as an example core for establishing the chronology of Lake Kariba. Gamma spectrometric measurements for \(^{210}\)Pb (at 46.5 keV) and \(^{137}\)Cs (at 662 keV) were carried out on well-type GeLi-detectors. \(^{210}\)Pb activities showed erratic depth profiles. Therefore, only \(^{137}\)Cs data were used for chronological interpretation.

### 2.4 Results

#### 2.4.1 Sediment stratigraphy

Station B55 is located in a deep (\(\sim 80 \text{ m}\)) and clearly lacustrine zone of Basin IV, situated \(\sim 30 \text{ km}\) from the Sanyati, Kariba’s second largest tributary. We expected that B55’s location would allow its sediments to record both allochthonous and autochthonous inputs, and used core B55 for the initial description and characterization of sediment stratigraphy. From WBD measurements, two major sections could be distinguished (Figure 2.2a). Sediments in the top \(\sim 15 \text{ cm}\) are characterized by a low density of \(\sim 1 \text{ g cm}^{-3}\). Below 15 cm, the density increases sharply over a 1-cm transition zone to values between 1.6 and 1.8 g cm\(^{-3}\). We interpret the sharp density gradient as marking the transition between predam and postdam (i.e., the reservoir filling period) deposits, an observation that is consistent with other geochemical data described below. Density variations were small in the postdam deposits, except for the section between 4.5 and 7.0 cm depth, containing slightly denser material (Figure 2.2a).

Within the postdam sediments, a sequence of differently colored layers (light brown, black, and intermediate gray-brown) of varying thickness could be visually distinguished in the core (Figure 2.2b). The color layering of the postdam sediments was confirmed by vari-
Figure 2.2: Stratigraphy and chronology of core B55 (Figure 2.1) illustrated by (a) depth profiles of WBD (blue) and $^{137}$Cs activity (red); (b) photograph of sediment core with superimposed color reflectance ($L^*$, white line); (c) four lithotypes are distinguished in the postdam section indicated by different colors; and (d) Zambezi discharge at Victoria Falls. Sediment layers were dated based on the abrupt change in WBD, bomb fallout signals in $^{137}$Cs activity, and their relation to discharge peaks at Victoria Falls (blue lines connecting panels c and d). Lower parts of the predam sediments (18 to 29 cm) are not shown in this figure (see Figure 2.3). The core photograph was optimized for brightness and contrast. Note the reflections in the photograph due to the wet, freshly cut surface, which also affected absolute $L^*$.

The local $L^*$ maxima ($\sim 65$) and local minima ($\sim 30$ to $45$) coincide with bright and black layers, respectively. We interpreted the layering, and the varying layer thicknesses, as resulting from seasonal or interannual variations in color reflectance $L^*$ (white line in Figure 2.2b).
variations in the loadings from different sediment sources, i.e., seasonal or interannual variations in flood-induced, allochthonous sediment inputs versus internal primary production yielding autochthonous sediment inputs. The geochemical signatures of the respective layers support the notion of differing relative contributions from allochthonous and autochthonous OM sources, as described in the following section. Based on this analysis of sediment density, L*, and color or brightness, we defined four lithotypes to describe the core’s stratigraphy in the postdam section (Figure 2.2c): (i) black colored, (ii) bright colored, (iii) intermediate colored, and (iv) transitional density. Lithological variations in the predam sediments were not further explored because they are unrelated to the dam.

Cores B21, B31, B61, B41, and B51 showed similar sequences of the four lithotypes in the postdam section, and the sharp increase in density to the predam section (Figure 2.3, top). Cores B99 and B56 also exhibited the color stratigraphy; however, they do not have sharp basal increases in density, indicating that the corer did not penetrate through the entire postdam deposits and did not reach the predam sediments at these sites. Cores B11 and B58 were different from all other cores in that they were visually homogeneous over their entire thickness with no color-variation of layers and higher but relatively constant WBD (Figure 2.3, top).

### 2.4.2 Chemical and isotopic composition

Substantial differences in the geochemical composition of the sediments from Lake Kariba were evident, both between cores and within individual vertical profiles (Figure 2.3, bottom and Figure 2.4). OC concentrations in postdam sections of the lacustrine cores (B21, B31, B61, B41, B51, B99, B55, and B56) were significantly (p < 0.001, ANOVA) greater than OC concentrations in their respective predam sections, as well as in cores taken in areas close to the inflows, hereafter referred to as “riverine” cores (B11 and B58). postdam layers also had significantly higher TN and TP concentrations and significantly lower δ¹³C and C:N than predam and riverine sediments (p < 0.001, ANOVA; Figure 2.4). However, predam sediments and riverine cores only differed significantly in their OC levels (p < 0.001), and not in other parameters (p > 0.2). Although mean δ¹⁵N values of lacustrine postdam sediments were significantly lower than lacustrine predam sediments (Figure 2.4; Figure A.1, available as auxiliary material in Section 2.8), the lacustrine postdam samples did not differ significantly (p = 0.8; Figure 2.4) from riverine samples, suggesting that riverine influence is not reflected in this parameter. The difference between riverine and lacustrine sediments was, however, evident in grain-size measurements, which showed a clear fining from B58 to B55 (Figure A.2, available as auxiliary material). Median grain size decreased from 13.8 ± 2.6µm at B58 to 2.6 ± 0.4µm in postdam deposits at B55.
Chapter 2. Kariba sediments

Data from a shorter core retrieved at B21 in 2007, data from core retrieved at B21 in 2009 shading indicates lithotype as shown in Figure 2.2. Correlated layers are indicated by blue lines, dashed lines depict uncertain correlations. Color δ/one.three.C (‰) = 26.0 C:N max δ/one.three.C (‰) = 19.5 C:N max

Figure 2.3: Core stratigraphy and depth profiles of WBD (top), and depth profiles of OC, TN, TP, C:N and TNOC δ/one.three.C (‰)
2.4. Results

In comparison, predam sediments at B55 consisted of significantly coarser material (Welch Two Sample t-test, \( p < 0.001 \), median = 46.2 ± 11.3\( \mu \)m).

The elemental and isotopic composition of sediment-trap material differed considerably from postdam sediment-core samples. In particular, OC and TN concentrations in sediment trap material were significantly \(( p < 0.001 )\) greater than in postdam sediments, and \( \delta^{13}C \) and C:N were lower (Figure 2.5, Table 2.1). Based on the higher masses collected between 2007 and 2008, and the lower OC and TN concentrations (Table 2.1), it is likely that the traps collected a high portion of flood-derived matter during this period. Therefore, we used the 2008/2009 samples for subsequent calculations related to the composition and sedimentation of autochthonous material.

Despite the clear layering in the postdam sediments, there are few readily apparent correspondences between the vertical profiles of the postdam sediments’ chemical compo-
Figure 2.5: Scatter-plots of $\delta^{13}$C against OC (a) and $\delta^{13}$C against C:N ratio (b). Filled symbols denote samples from predam deposits or from riverine cores. Open symbols denote core and sediment trap samples from postdam period. For the latter, high OC, low C:N ratios and low $\delta^{13}$C values indicate low contents of allochthonous matter. Points highlighted by shaded ellipses have a maximal allochthonous signature within the samples of the respective core, and therefore are most likely flood deposits. The black boxes encompass the two hypothetical end members of sediment sources (i.e., sediment trap samples for autochthonous organic matter (OM), predam sediments and riverine cores for allochthonous OM).

Table 2.1: Summary of sediment trap data

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<tr>
<th>Period</th>
<th>Mass (mg ± 1σ)</th>
<th>Sedimentation rate (g cm$^{-2}$ yr$^{-1}$ ± 1σ)</th>
<th>OC (mg g$^{-1}$ ± 1σ)</th>
<th>TN (mg g$^{-1}$ ± 1σ)</th>
<th>$\delta^{13}$C (‰ ± 1σ)</th>
<th>C:N (mol mol$^{-1}$ ± 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul 2007 to May 2008</td>
<td>17 ± 7</td>
<td>0.31 ± 0.12</td>
<td>39.7 ± 5.2</td>
<td>5.1 ± 0.7</td>
<td>−26.4 ± 0.0</td>
<td>9.1 ± 0.1</td>
</tr>
<tr>
<td>May 2008 to Jun 2009</td>
<td>6 ± 2</td>
<td>0.08 ± 0.03</td>
<td>75.5 ± 7.8</td>
<td>9.5 ± 1.3</td>
<td>−28.8 ± 0.8</td>
<td>9.3 ± 0.5</td>
</tr>
</tbody>
</table>

sitions (Figure 2.3, bottom) and their visual stratigraphy (Figure 2.3, top). We suspected that this limited correspondence resulted from the relatively coarse sub-sampling (1 cm) compared to the thickness of many of the dark layers, which was unavoidable in many cases because of the extremely thin layering (millimeters). Subsequent measurements of
lithologically pure layers (black versus bright) from the 2009 cores showed that geochemical differences between the black and bright lithotypes were indeed apparent (Figure 2.6). Pure black layers had significantly higher (p < 0.01) OC and TN concentrations, and significantly lower (p < 0.001) δ¹³C values than bright layers; mean C:N values, however, did not differ significantly (p = 0.2, 11.3 ± 1.3 and 10.4 ± 1.3, respectively). Further, when combining measurements from all cores and sediment traps in plots of δ¹³C against OC and C:N, distinct groupings and systematic variations become evident (Figure 2.5). predam sediments and samples from riverine cores grouped together and displayed the highest values for δ¹³C and C:N and the lowest OC concentrations. Sediment-trap material plotted at the opposite end of Figure 2.5 having the lowest values for δ¹³C and C:N and the highest OC concentrations. postdam sediments from lacustrine cores were distributed between these two end-member groups (Figure 2.5). Within Figure 2.5, several postdam sediment layers plotted separately from other layers in the same core (e.g., core B41 2.2 to 2.9 cm; B99 4.4 to 4.7 cm; B55 4.7 to 5.3 cm), shifted toward riverine or predam sediments. These layers also had locally distinct TN and TP concentrations, higher WBD (Figure 2.3), and higher mean grain size (Figure A.2, available as auxiliary material).

![Figure 2.6: Box plot of OC, TN and δ¹³C in pure lithotypic samples from the postdam sections of cores B21, B31 and B99 retrieved in February 2009 (black layers n = 7, bright layers n = 11). Bright layers contain substantially less OC and TN, and are isotopically heavier than black layers indicating the relatively large contribution of allochthonous OM in the flood-derived bright layers.](image)

### 2.4.3 Age model and sediment accumulation rates

The layered sediment structure and three key time horizons were used to develop an age model for the postdam section of core B55. A first time horizon was defined by the core surface, dating to core retrieval in 2008. Second, the bottom of the low to
high density transition zone (15.7 cm), which coincided with the onset of the lacustrine depositional regime, was set to the year of dam closure, 1958. For the third time horizon, the $^{137}\text{Cs}$ peak at 12.5 cm depth (Figure 2.2a) was matched with the historic maximum of atmospheric fallout from nuclear weapons testing in 1963. It should be noted that considerable uncertainty may be associated with the $^{137}\text{Cs}$-derived time horizon, as the erratic $^{210}\text{Pb}$ profiles point to irregular supply of allochthonous radiogenic isotopes.

Building on the interpretation that dark autochthonous sediment was intercalated by brighter flood layers deposited during intense annual runoff events in the Zambezi, long-term discharge records of the Zambezi at Victoria Falls (∼150 km upstream of Lake Kariba; Figure 2.2d; Zambezi River Authority, 2010), were used to approximately date some individual layers by attributing bright and dark layer pairs to hydrological years (blue lines in Figure 2.2c and d). The large variation of discharge (Figure 2.2d) reflects interannual differences of the flood amplitude during the wet season. Over the first 22 yr after dam construction (1958 to 1980), which was an above-average wet period, bright and black layer pairs could be identified for almost every year. Discharge records show that after 1980 the upper Zambezi experienced a period when drier conditions prevailed. Layering also became less pronounced after 1980, and relatively thick intermediate-colored bands are present. We interpret the gap in the sequence of flood-derived layers as having resulted from the absence of major floods, and lower particle loads to Lake Kariba. The prolonged absence of clear layers made layer identification and dating after 1980 more difficult.

Sediment accumulation rates for dated layers in core B55 were estimated based on this age model. The mean mass accumulation rate recorded at B55 over the 50 yr was 0.07 g cm$^{-2}$ yr$^{-1}$. However, interannual variability in sediment accumulation rates inferred from dated layers was considerable. The highest sediment accumulation rates occurred shortly after dam closure (1958 to 1961) and during major floods (hydrological years 1962/1963, 1975/1976, 1977/1978, 2006/2007, maximum = 0.21 g cm$^{-2}$ yr$^{-1}$). Minimum sedimentation rates appear to have been as low as 0.01 g cm$^{-2}$ yr$^{-1}$ (years 1972/1973, 1981/1982, 1995/1996).

Based on core photographs, there was strong correspondence between the layering patterns in core B55 and the patterns in cores from other near-by stations, in particular B51 and B99 (blue lines, Figure 2.3, top). Inter-core similarities could also be discerned over longer transects (B21 to B99, B56 to B99). Layering was not equally preserved in cores closer to the Zambezi inflow, where density currents have more energy. Consequently, flood layers may have amalgamated, or erosional features may have occurred, ultimately causing incomplete successions of flood layers. Nonetheless, considering the large distances between stations, clear correspondence between some layers across multiple stations sug-
gests some major depositional events are felt at the entire lake scale. At the same time, the substantial differences in chemistry and stratigraphy between riverine sediments and postdam lacustrine sediments and between some postdam lacustrine cores clearly show that sedimentation in Lake Kariba is spatially heterogeneous and flood-dominated.

2.5 Discussion

2.5.1 OM provenance: allochthonous vs. autochthonous sources

The chemical composition of OM can be used to differentiate between allochthonous and autochthonous sources to sediments (Meyers and Teranes, 2002). OM derived from vascular plant material can in general be distinguished from algal biomass by a higher C:N (> 20 versus 8 to 10; Meyers and Teranes, 2002). In addition, OM from C4 plants and OM from phytoplankton differ considerably in their δ\(^{13}\)C ranges (−10 to −15‰, and −20 to −30‰, respectively; Meyers and Lallier-Verges, 1999; Meyers and Teranes, 2002). In combination, these two factors cause higher C:N and isotopically heavier OC in sediment as the proportion of OM from allochthonous sources increases. In turn, relatively lower C:N and lower δ\(^{13}\)C values indicate a higher proportion of algal OM in the sediments. Early diagenesis of OM in sediments can also cause shifts in C:N and δ\(^{13}\)C of bulk OM; however, changes in C:N and δ\(^{13}\)C due to OM transformations tend to be relatively small compared to the large differences between end-member compositions (Lamb et al., 2006).

The separation of postdam sediment layers along the continuums in Figure 2.5 is consistent with the mixing of sediment material from autochthonous and allochthonous sources. The high C:N and δ\(^{13}\)C values and relatively low OC concentrations in the predam sediments of lacustrine cores, and over the entire depth of the riverine cores, are consistent with primarily allochthonous OM (Figure 2.5). As expected, the composition of sediment trap material (low C:N and δ\(^{13}\)C values) is consistent with it containing a high proportion of algal material, and thus autochthonous OM. Although the measured C:N and δ\(^{13}\)C are typical for algal biomass, Redfield-type algal OM has an OC content of ∼400 mg g\(^{-1}\). The measured OC concentration range of 65 to 100 mg g\(^{-1}\) in sediment-trap material may point to dilution by some OC-poor allochthonous particles, or by silica-rich and thus relatively carbon-poor autochthonous material (e.g., diatoms). Given the distance of station B99 from the major inflows and the fairly distinct signature of trapped material (Figure 2.5), for subsequent calculations we considered the sediment trap material to be reasonably representative of autochthonous OM composition in terms of C:N and δ\(^{13}\)C.
We applied a simple mixing model (Waterson and Canuel, 2008) to estimate the relative contributions of allochthonous and autochthonous OM in the lacustrine postdam sediments of Lake Kariba. In this model, mean C:N and $\delta^{13}C$ values of predam and riverine samples were used to represent the allochthonous end-member composition ($16 \pm 1$, $-19.9 \pm 0.8^{\circ}e$, respectively). Sediment trap samples (2007/8 period excluded, see above) were used to represent the autochthonous end-member composition (means: $9.1 \pm 0.6$ and $-28.8 \pm 0.8^{\circ}e$, respectively). Solving the mixing equations (Fry, 2006):

$$\delta^{13}C_{\text{postdam}} = (1 - f_{\text{auto}}) \cdot \delta^{13}C_{\text{allo}} + f_{\text{auto}} \cdot \delta^{13}C_{\text{auto}}$$

for

$$f_{\text{auto}} = \frac{\delta^{13}C_{\text{postdam}} - \delta^{13}C_{\text{allo}}}{\delta^{13}C_{\text{auto}} - \delta^{13}C_{\text{allo}}}$$

yields $f_{\text{auto}} = 59 \pm 30\%$ for the mean postdam sediments of the lacustrine cores ($\delta^{13}C_{\text{postdam}} = -25.0 \pm 1.8^{\circ}e$). Calculating $f_{\text{auto}}$ using C:N instead of $\delta^{13}C$ results in $f_{\text{auto}} = 58 \pm 21\%$ (mean $C:N_{\text{postdam}} = 11.8 \pm 1.9$). Hence, in the lacustrine cores, on average $\sim 60\%$ of the OM in postdam sediments was of autochthonous origin, and $\sim 40\%$ of allochthonous OM. As sediment-trap material contained some allochthonous contribution, and therefore had a lower C:N ratio than pure algal OM, we also calculated $f_{\text{auto}}$ using a Redfield C:N ratio of 106:16 for $C:N_{\text{auto}}$. In this lower-end scenario for lacustrine cores, $f_{\text{auto}}$ decreased to 45%.

The approach used here, employing OC-$\delta^{13}C$ and C:N, may serve as a fairly simple method for quantifying autochthonous OC contributions in other lakes and reservoirs. In general, data on the relative contributions of allochthonous and autochthonous OC to lake sediments are sparse (Alin and Johnson, 2007) but important for estimating the anthropogenic effects of river damming on the global C cycle (Downing et al., 2008). The $f_{\text{auto}}$ value of $> 45\%$ was estimated for the lacustrine sedimentation zone in Lake Kariba. If deltaic sedimentation were included to estimate a whole-lake weighted average $f_{\text{auto}}$, the value would be lower, moving in the direction of the global mean of $f_{\text{auto}} < 12\%$ for allochthonous and autochthonous OC fluxes to reservoir sediments (Stallard, 1998). Additionally, the higher $f_{\text{auto}}$ we obtained for Lake Kariba may be due to low allochthonous OC contributions, which may be expected due to erosion of OC-depleted Kalahari Sands (Wang et al., 2007), the dominant soil type in the Kariba catchment (Coche, 1974). This assessment is consistent with the observations by De Junet et al. (2009), who also described relatively high autochthonous contributions to the sediments of a tropical reservoir in South America.
2.5.2 Sediment accumulation in Lake Kariba

Given the event-driven and spatially heterogeneous depositional environment in Lake Kariba, we employed multiple approaches to quantify sediment accumulation. For a first estimate of reservoir-wide sediment accumulation, we used mean sediment-core data (dry bulk density and postdam sediment thickness) and particle concentrations in the tributaries (Zambezi River Authority (ZRA), unpublished data), and assumed uniform sediment distribution. This approach yielded sediment accumulation rates in the range of $\sim 3$ to $\sim 8 \times 10^6$ t yr$^{-1}$ (Table 2.2).

Table 2.2: Summary of sediment accumulation rates based on the assumption of a uniform sediment distribution

<table>
<thead>
<tr>
<th>Approach</th>
<th>Sedimentation accumulation rate $(10^6$ t yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Mean sediment accumulation rate, area below Mud Deposition Boundary</td>
<td>4.1</td>
</tr>
<tr>
<td>Depth (Rowan et al., 1992)</td>
<td></td>
</tr>
<tr>
<td>(ii) Mean sediment accumulation rate, area below epilimnion</td>
<td>3.1</td>
</tr>
<tr>
<td>(iii) Linearly increasing sediment accumulation rate to the base of the epilimnion; constant rate below, whole lake surface area (5.364 km$^2$)</td>
<td>7.5</td>
</tr>
<tr>
<td>(iv) Sediment load estimated from TSS data for Sanyati mouth (Zambezi River Authority, unpublished data, 2010), scaled up to match total inflows, removal rate 100%</td>
<td>6.5</td>
</tr>
</tbody>
</table>

These estimates, however, do not consider the complex depositional processes in reservoirs (Shotbolt et al., 2005). To obtain a more physically-based and nuanced estimate, we developed a refined sedimentation model that takes into account the morphology of Lake Kariba, and considers two main sedimentation zones (Figure 2.1; for a detailed description see appendix in Section 2.8.2): (i) the thalweg area (up to 10-km wide) following the original river channels, in which density currents deposit allochthonous sediment as distinct flood layers in addition to autochthonous sediments; (ii) the littoral zones, unaffected by density currents and therefore only collecting autochthonous sediments. Following this approach, the thickness of flood layers accounted for 23, 42, 30 and 30% of postdam section in basins IV, III, II and I, respectively. Near the Zambezi and Sanyati inflows, the transition between pre- and postdam sections were not captured in the sediment cores (Figure 2.3). Hence, using the lengths of B11 and B58 cores underestimates the true sedimentation rates there. The resulting estimated total sediment accumulation rate in both the littoral and lacustrine zones summed to $3.7 \times 10^6$ t yr$^{-1}$ (Table 2.3), which is comparable to the range estimated above assuming uniform settling across the lake ($\sim 3$ to $\sim 8 \times 10^6$ t yr$^{-1}$), but may underestimate the accumulation in river deltas.
Table 2.3: Summary of sediment accumulation rates based on the lacustrine-littoral sediment model

<table>
<thead>
<tr>
<th>Basin</th>
<th>Sedimentation rate (g cm(^{-2}) yr(^{-1}))</th>
<th>Dry bulk sediment density (g cm(^{-3}))</th>
<th>Area (km(^2))</th>
<th>Sediment accumulation rate (10(^6) t yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.91</td>
<td>1.8</td>
<td>34</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td>1.1</td>
<td>66</td>
<td>0.5</td>
</tr>
<tr>
<td>II</td>
<td>0.18</td>
<td>0.2</td>
<td>339</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>0.2</td>
<td>346</td>
<td>0.4</td>
</tr>
<tr>
<td>III</td>
<td>0.03</td>
<td>0.1</td>
<td>492</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.1</td>
<td>1,555</td>
<td>0.3</td>
</tr>
<tr>
<td>IV</td>
<td>0.06</td>
<td>0.2</td>
<td>500</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.2</td>
<td>2,049</td>
<td>1.0</td>
</tr>
<tr>
<td>Total</td>
<td>0.07</td>
<td></td>
<td>5,381</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Both estimates of total sediment accumulation are consistent with an earlier study (Bolton, 1984) that estimated a sediment accumulation rate of 7 \(\times\) 10\(^6\) t yr\(^{-1}\) in Lake Kariba, based on erosion rates in Zimbabwean catchments, and assuming that most of the sediments produced upstream of Victoria Falls are trapped in large upstream wetlands (i.e., Barotse Plains and Chobe Swamps). Milliman and Meade (1983) estimated a sediment yield of 35 t km\(^{-2}\) yr\(^{-1}\) for the entire ZRB. Applying this yield to the Kariba catchment downstream of Victoria Falls (area = 1.7 \(\times\) 10\(^5\) km\(^2\); Bolton, 1984) results in a comparable sediment load of 6 \(\times\) 10\(^6\) t yr\(^{-1}\) to Lake Kariba, again of comparable magnitude to the above mentioned estimate based on our sediment cores. Bolton (1984) asserted that a safe estimate for an upper bound erosional sediment yield may be an order of magnitude higher than the measured values, and arrived at a sediment accumulation range of 7 to 70 \(\times\) 10\(^6\) t yr\(^{-1}\). Applying a similar factor to our sediment accumulation rate, we obtained a range of 3 to 30 \(\times\) 10\(^6\) t yr\(^{-1}\). Since our sedimentation model is better constrained in the lacustrine zone, any difference between the best estimate (3.7 \(\times\) 10\(^6\) t yr\(^{-1}\)) and the maximum estimate (30 \(\times\) 10\(^6\) t yr\(^{-1}\)) would arise primarily through material accumulating in the deltas. Assigning this additional sedimentation entirely to the Zambezi and Sanyati deltas in Lake Kariba, and estimating the delta areas to be on the order of 200 and 50 km\(^2\), respectively, results in a sedimentation rate of \(\sim\)10 cm yr\(^{-1}\) in these deltas. This value is not unreasonable; however, based on the available data, sediment accumulation rate estimates in the deltas cannot be further constrained.
2.5.3 Organic carbon cycling and sedimentation

Using sediment accumulation rates and OC concentrations, the rate of net OC accumulation in the sediments was estimated to be $120 \times 10^3$ t yr$^{-1}$ (range = 100 to $800 \times 10^3$ t C yr$^{-1}$, Table 2.4). The estimate of $f_{auto} > 45\%$ across the lacustrine areas indicates that Lake Kariba, in addition to trapping allochthonous OC, has altered OC cycling in the ZRB by fostering autochthonous primary production, and removing some of this OC to the sediments. The estimated Kariba net OC accumulation rate is on the order of 1% of the global OC burial in reservoirs given by Dean and Gorham (1998). This proportion is somewhat less than expected, as Lake Kariba covers ~2% of the total global surface area of reservoirs (Downing et al., 2006). The net OC accumulation rate translates to a flux of 23 (range = 19 to 150) g C m$^{-2}$ yr$^{-1}$. Comparing this estimate to mean C-burial in reservoirs worldwide (400 g C m$^{-2}$ yr$^{-1}$; Dean and Gorham, 1998), and in eutrophic reservoirs in Iowa, USA (148 to 17,000 g C m$^{-2}$ yr$^{-1}$; Downing et al., 2008), Lake Kariba appears to accumulate OC at a low rate, even when maximum estimates are considered. The relatively low OC accumulation is not necessarily surprising since Kariba is oligotrophic and drains a catchment dominated by soils with low OC contents and high OM mineralization rates (Coche, 1974; Wang et al., 2007). Assuming a low OC concentration of ~0.5% (Wang et al., 2007) in allochthonous sediment, and an allochthonous sediment input of $3.7 \times 10^6$ t yr$^{-1}$ (range = 3 to $30 \times 10^6$ t yr$^{-1}$, see above), the allochthonous OC input would amount to $19 \times 10^3$ t C yr$^{-1}$ (15 to $150 \times 10^3$ t C yr$^{-1}$). This value represents gross allochthonous OC input prior to any mineralization, and is thus an overestimate in that respect. Nevertheless, it is considerably lower than our estimated total OC accumulation of $120 \times 10^3$ t C yr$^{-1}$ (range = 100 to $800 \times 10^3$ t C yr$^{-1}$), and further highlights the relative importance of autochthonous OC contributions to the sediment.

Table 2.4: Summary of sediment, OC, TN and TP accumulation rates$^a$

<table>
<thead>
<tr>
<th>Accumulation rate</th>
<th>Sediment ($10^6$ t yr$^{-1}$)</th>
<th>OC ($10^3$ t C yr$^{-1}$)</th>
<th>TN ($\text{TN}_{\text{sed}}$) ($10^3$ t N yr$^{-1}$)</th>
<th>TP ($\text{TP}_{\text{sed}}$) ($10^3$ t P yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lacustrine and littoral zones in basins I to IV</td>
<td>3.7</td>
<td>120</td>
<td>12</td>
<td>4.1</td>
</tr>
<tr>
<td>Range</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>3.0</td>
<td>100</td>
<td>11</td>
<td>3.8</td>
</tr>
<tr>
<td>Maximum</td>
<td>30</td>
<td>800</td>
<td>62</td>
<td>17</td>
</tr>
</tbody>
</table>

$^a$ Based on our estimated sediment accumulation rates for lacustrine and littoral zones. Minimum and maximum values are estimated based on a sediment accumulation range of 3 to $30 \times 10^6$ t yr$^{-1}$ (see text). Multiplying sediment accumulation rates with mean concentrations of OC, TN and TP resulted in respective accumulation rates.
The net OC accumulation in the sediment comprises the fraction of gross OC settling in the basin that is not mineralized within the water column or after deposition (Figure 2.7). The mean gross OC accumulation rate, estimated from the sediment traps, was $61 \pm 10 \text{ g C m}^{-2} \text{ yr}^{-1}$. We compared this estimate with the mean net OC accumulation rate of the lacustrine zone of Basin IV ($= 24 \pm 9 \text{ g C m}^{-2} \text{ yr}^{-1}$), which was calculated based on the OC accumulation rates for cores B41, B51, B55, B61, and B99 (Figure 2.1). Based on these estimates, the burial efficiency ($BE$) of OC, defined as the net OC accumulation rate divided by the gross OC accumulation rate, is 41%. This value compares well with a calculated $BE$ of 45% estimated from the relationship

$$BE = 32.1 + 27.9 \cdot \log(Sedimentation \ rate \cdot \text{mm}^{-1} \cdot \text{yr})$$

(2.3)
given by Sobek et al. (2009) using a mean sedimentation rate of 3 mm yr$^{-1}$ for Lake Kariba. Both $BE$ values of 41% and 45% are specific to lacustrine zones. $BE$ in the deltaic areas would be higher due to greater sedimentation rates and the likelihood that the allochthonous OM, which predominates there, is more refractory than newly produced autochthonous OM. We also calculated the $BE$ using a relationship developed for large natural lakes in relation to their latitude given by (Alin and Johnson, 2007) and obtained a value of 1.7%. This value substantially underestimates the actual fraction of OC buried, and suggests that large tropical reservoirs such as Lake Kariba may have different characteristics than large natural lakes at low latitudes.

Given that Lake Kariba acts as an efficient trap for allochthonous particles and OC, we hypothesized that it is a net heterotrophic system (Staehr et al., 2010; Tranvik et al., 2009), i.e., that respiration exceeds gross primary production, and as a result water column concentrations of OC mineralization products, CO$_2$ and CH$_4$, accumulate beyond saturated levels (Sobek et al., 2005). Net heterotrophic systems are net sources of CO$_2$ (and potentially CH$_4$) to the atmosphere (Cole et al., 1994). Other studies have observed in particular that tropical lakes (Marotta et al., 2009) and reservoirs (Abril et al., 2005) emit substantial amounts of these greenhouse gases. Water column measurements in Lake Kariba from 2007 to 2009 revealed that CO$_2$ was indeed oversaturated by 350 to 1,100%, indicating that Lake Kariba is clearly net heterotrophic. Similarly, all observed CH$_4$ concentrations exceeded saturation by $> 500\%$ (DelSontro et al., 2011).

### 2.5.4 Nitrogen cycling and sedimentation

The creation of Lake Kariba also impacted the downstream transport of fixed N, as evidenced by the accumulation of N in sediments. To quantify TN removal and changes in N cycling, we applied a steady-state box model for Lake Kariba that balanced TN sources
2.5. Discussion

Figure 2.7: Schematic of input, internal and output loads (in 10^3 t yr) used in OC, TN and TP budget calculations, as well as resulting OC burial efficiency, and TP and TN removal rates (%). Numbers are best estimates, and, if available lower and upper bonds.

$$TN_{in} + TN_{fix} = TN_{out} + TN_{denit} + TN_{sed}$$ (2.4)

where inputs are given by the sum of riverine loads ($TN_{in}$) and N fixation ($TN_{fix}$), and losses by outflow ($TN_{out}$), denitrification ($TN_{denit}$), and net N accumulation in the sediment ($TN_{sed}$). The best estimate of $TN_{sed}$ was $12 \times 10^3$ t N yr$^{-1}$, with lower and upper bounds of 11 to 62 $\times 10^3$ t N yr$^{-1}$ (Table 2.4). $TN_{out}$ was calculated using the mean outflow concentration of 340 µg TN l$^{-1}$ and a mean discharge of 42 km$^3$ yr$^{-1}$ (Beilfuss and Dos Santos, 2001), yielding a value of $14 \times 10^3$ t N yr$^{-1}$. Low $\delta^{15}$N and relatively high C:N of sediment trap samples (Figure 2.3, Table 2.1) are consistent with N deficiency (Das et al., 2008; Talbot, 2001). The low $\delta^{15}$N, along with low N:P, may also suggest that N fixation is taking place (Figure A.1; available as auxiliary material). This is in accordance with evidence of annual cyanobacteria blooms during the rainy season (Ramberg et al., 1987) and measured N fixation rates ranging from 0.04 to 0.2 g N m$^{-2}$ yr$^{-1}$ (Moyo, 1997). However, extrapolating these rates to the entire lake area results in an estimate for $TN_{fix}$ of 0.2 to 1.1 $\times 10^3$ t N yr$^{-1}$, which is 10 to 50 fold lower than $TN_{sed}$ (Table 2.4). Thus, N fixation appears to be a relatively unimportant source of fixed N to the system. The denitrification loss for Basin IV was calculated as the difference between the mean gross TN sedimentation rate ($= 7.7 \pm 2.5$ g N m$^{-2}$ yr$^{-1}$, based on sediment trap data) and the mean
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net TN accumulation rate at B41, B51, B55, B61 and B99 (\(= 2.5 \pm 1.0 \text{ g N m}^{-2} \text{ yr}^{-1}\)). Extrapolated to the entire lake surface, this difference of \(5.2 \pm 3.6 \text{ g N m}^{-2} \text{ yr}^{-1}\) results in a denitrification estimate \(TN_{\text{denit}}\) of \((28 \pm 19) \times 10^3 \text{ t N yr}^{-1}\), which compares well with the difference between gross TN sedimentation and \(TN_{\text{sed}}\) (\(= 29 \times 10^3 \text{ t N yr}^{-1}\); Table 2.3). Hence, denitrification appears to be an important TN sink (\(\sim 50\%\) of all TN losses).

Based on equation (2.4), we calculated the fraction of TN inputs that are removed within the reservoir:

\[
f_{TN, \text{rem}} \approx \frac{TN_{\text{sed}} + TN_{\text{denit}}}{TN_{\text{in}} + TN_{\text{fix}}} \approx \frac{TN_{\text{sed}} + TN_{\text{denit}}}{TN_{\text{out}} + TN_{\text{denit}} + TN_{\text{sed}}} \quad (2.5)
\]

Using best estimates for \(TN_{\text{sed}}\) (\(12 \times 10^3 \text{ t N yr}^{-1}\)), \(TN_{\text{out}}\) (\(\sim 14 \times 10^3 \text{ t N yr}^{-1}\)), and \(TN_{\text{denit}}\) (\(\sim 29 \times 10^3 \text{ t N yr}^{-1}\)), we obtained \(f_{TN, \text{rem}} = 74\%\). Two thirds of this N removal originated from denitrification and one third from net sediment accumulation. This 74% removal efficiency places Lake Kariba at the upper end of observed values for tropical reservoirs (0.04 to 70%; Harrison et al., 2009). On the other hand, \(TN_{\text{sed}} + TN_{\text{denit}}\) translates to an areal rate of \(7.7 \text{ g N m}^{-2} \text{ yr}^{-1}\), which is \(\sim 3\)-fold smaller than the global mean reservoir N removal rate (Harrison et al., 2009), and thus overall N loading to and removal by Lake Kariba are relatively low. There is substantial uncertainty associated with this N removal estimate due to the lack of direct measurements of N fixation and denitrification, and the uncertainty related to deltaic sedimentation. Nonetheless, our results suggest an efficient N removal in Lake Kariba, and thus a substantial decrease in the delivery of N to downstream systems.

2.5.5 Phosphorus cycling and sedimentation

The cycling and removal of TP in Lake Kariba were explored following a similar approach as described for TN by adjusting equations (2.4) and (2.5). Using a mean outflow concentration of \(14 \mu \text{g TP l}^{-1}\) and a mean discharge of \(42 \text{ km}^3 \text{ yr}^{-1}\) (Beilfuss and Dos Santos, 2001), \(TP_{\text{out}} = 0.6 \times 10^3 \text{ t P yr}^{-1}\). Based on the estimated TP accumulation rates (\(TP_{\text{sed}} = 4.1 \times 10^3 \text{ t P yr}^{-1}\), range = 3.8 to \(17 \times 10^3 \text{ t P yr}^{-1}\), Table 2.4), \(f_{TP, \text{rem}} = 87\%\) (range = 86 to 97%). Global scale models predict that only 13% of riverine transported particulate P is trapped in regulated basins worldwide; the prediction for Africa is 18% (Beusen et al., 2005). The relatively high P removal potential found in our study is however reasonable given the long hydraulic residence time (\(\sim 3\) yr) and high sediment removal potential of Lake Kariba (Beusen et al., 2005; Vörösmarty et al., 2003). Magadza (1992) also predicted a high P removal capacity of Lake Kariba, although the magnitude of that study’s P loads were considerably lower than our combined sinks (factor of 4), perhaps suggesting a substantial underestimate.
2.6 Conclusions

Our observations illustrate that Lake Kariba has substantially altered the downstream transport of particles, carbon (C) and nutrients in the Zambezi (Figure 2.7). Sediment accumulation rates and organic matter signatures were found to vary strongly within and between sediment sampling sites. These variations are attributed to annual flood deposits, which delivered large amounts of allochthonous matter to the lake. Thicknesses of these flood deposits vary interannually depending on the discharge of the tributaries. The estimated annual sediment retention was $\sim 4 \times 10^6$ t yr$^{-1}$, and the net accumulation rates of organic C, nitrogen (N) and phosphorus (P) are on the order of $\sim 100 \times 10^3$ t C yr$^{-1}$, $\sim 11 \times 10^3$ t N yr$^{-1}$ and $\sim 4.1 \times 10^3$ t P yr$^{-1}$, respectively. This P accumulation rate in Kariba’s sediments corresponds to 87% removal efficiency of total P inputs. The N removal efficiency was found to be somewhat lower (74%), with important contributions from both denitrification and sediment accumulation. The removal of particles in the reservoir in general undoubtedly contributes to net bank and channel erosion downstream of the dam. In addition, the decreases of riverine C, N and P transport, downstream ecosystem may have adverse biogeochemical impacts, especially considering that Lake Kariba attenuates the flow from $\sim 50\%$ of the Zambezi Basin. For example, sensitive ecosystems, such as floodplains, may experience ecological changes due to altered nutrient availability. Similarly, flood-recession agriculture and coastal fisheries may be jeopardized due to nutrient deficiencies. These impacts are of special concern in developing countries owing to the generally OC and nutrient depleted soils and the limited availability of fertilizers.

In a broader context, the OC accumulation rate of $\sim 20$ g C m$^{-2}$ yr$^{-1}$ is lower than the global mean for reservoirs. Nevertheless, the retained mass of OC in such a large lake contributes substantially to the anthropogenically-induced shift in C burial on land instead of in the oceans.

2.7 Acknowledgements

The project was funded as part of the ADAPT project of the Competence Center Environment and Sustainability (CCES) and obtained additional support from Eawag. We thank the staff of the Zambezi River Authority Tedious Gumi, Clement Mukosa, Pherry Mwiinga, Mavis Nawa, and Evis Siamachoka at Lusaka and Kariba Town for logistical support, and the Eawag staff Christian Dinkel, Daniel Ineichen, Ruth Stierli, Leticia Stojkovski, and Alois Zwyssig for field and laboratory assistance. An earlier version of the
manuscript could be improved significantly thanks to the helpful comments by two anonymous reviewers.
2.8 Appendix

2.8.1 Supplementary figures

Figure A.1: Downcore profiles of $\delta^{15}$N and N:P from selected cores.

Figure A.2: Plot of grain size distribution (Beierle et al., 2002) of the cores B55, B56 and B58. Median grain size (open dots) increases with decreasing distance from the mouth of the Sanyati River, and with depth at B55 reflecting the transition to predam sediments. The layer at $\sim$5.5 cm depth contains slightly coarser matter compared to average postdam sediments at B55.
2.8.2 Extended methods: Sedimentation model for Lake Kariba

The complexity of sediment deposition in reservoirs (Shotbolt et al., 2006) and the large size of Lake Kariba require a more nuanced approach to estimate lake-wide sediment accumulation than the simplistic approaches often applied in lakes. For instance, extrapolating sediment accumulation rates derived from sediment cores collected at the center of a reservoir to littoral areas may lead to considerable bias. Given the limited information on the spatial heterogeneity of sediment deposition in Lake Kariba, we based our estimate of total sediment accumulation on four assumptions: (i) We assume that major tributaries create density currents during seasonal flood events. Density currents have been shown to be the most important contributors of allochthonous sediments to reservoirs (De Cesare et al., 2001; Fan, 1986). (ii) We assume that the density currents act as underflows that flow along the thalweg of the original river channel. As they distribute over the lake bottom, i.e., the original valley floor, particles settle forming distinct flood layers in the sediment records of the respective areas. (iii) The dividing line defining the lake bottom, and thus the area where the density currents take effect, was constrained by the availability of bathymetric data provided by Coche (1974). The respective zone was defined as the area with a water depth > 55, > 40, > 25 and > 15 m in basins IV, III, II and I, respectively (i.e., below the second deepest contour lines; Figure 2.1). (iv) In contrast to allochthonous sediments, we assume spatial heterogeneity in autochthonous sedimentation to be negligible based on small spatial variation of primary production (Kimmel et al., 1990). As a consequence of these assumptions, flood layers are restricted to the thalweg area, with no flood deposits occurring in the littoral zones. On the other hand, accumulation of autochthonous sediments is evenly distributed over the lake. Hence, littoral sediment accumulation rates were estimated from the accumulation rates in the thalweg area excluding the allochthonous contributions. The areal sediment accumulation rate for each sub-basin (Figure 2.1) was calculated from the thickness of the sediment sections divided by the elapsed time between dam closure and core collection and divided by the mean dry bulk density. Multiplication of the areal sediment accumulation rates with the sediment surface areas of the thalweg and littoral sedimentation areas of each sub-basin resulted in the total mass of annually accumulated sediment.
Chapter 3

Impact of a large tropical reservoir on riverine transport of sediment, carbon and nutrients to downstream wetlands

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submitted to Water Resources Research, under revision
Abstract

Large dams are widely acknowledged to have major ecological and biogeochemical impacts on downstream ecosystems such as wetlands and riparian habitats. We examined the sediment removal and carbon (C), nitrogen (N), and phosphorus (P) cycling in Itezhi-Tezhi reservoir (ITT), which is located upstream of the Kafue Flats wetland in the Zambezi River Basin and has a surface area of 364 km$^2$ and a hydraulic residence time $\sim$0.7 yr. C, N, and P removal were estimated based on a transect of sediment cores, and a mass balance approach and a numerical biogeochemical reservoir model were applied to estimate N and P removal efficiencies, organic C mineralization, primary production, and N fixation. Since dam closure in 1978, $330 \times 10^3$ t of sediment and $16 \times 10^3$, $1.5 \times 10^3$, $200$ t of C, N, and P, respectively, have accumulated annually in ITT sediments. Approximately 50% of N inputs and 60% of P inputs are removed by the reservoir, illustrating its significant role in decreasing river-transported nutrients to the downstream Kafue Flats floodplain. The biogeochemical model predicted substantial primary production in ITT ($\sim$280 g C m$^{-2}$ yr$^{-1}$), and significant N-fixation ($\sim$30% for the total primary production) was required to support primary production due to marginal inputs of inorganic N. Model simulations indicate that future hydropower development in the reservoir, involving the installation of turbines driven by hypolimnetic water, will likely result in the delivery of low-oxygen waters to downstream ecosystems and increased outputs of dissolved inorganic N and P by a factor of $\sim$4 and $\sim$2, respectively.

Keywords Zambia, biogeochemical reservoir modeling, sediment retention, dam impacts on downstream ecosystems

3.1 Introduction

Inland waters are important at regional and global scales as regulators of sediment, carbon and nutrient transport from land to ocean (Cole et al., 2007; Seitzinger et al., 2005; Vörösmarty et al., 2003). In the last century, anthropogenic activities have substantially affected this transport, mainly through the construction of $\sim$45,000 dams. The dams and their reservoirs have increased the retention of suspended sediments, with an estimated particle retention of 50% of natural loads to the oceans (Vörösmarty et al., 2003; Walling, 2006). Among inland waters, reservoirs are now the most important organic carbon (OC) sinks through sediment burial ($\sim$80% of the total load of $0.2 \times 10^9$ t C yr$^{-1}$), and the most important contributor to CO$_2$ emissions ($\sim$40% of the total estimate of $0.8 \times 10^9$ t C yr$^{-1}$;
3.1. Introduction

Cole et al., 2007). Similarly, a substantial portion of in-land removal of nitrogen (N) takes place in reservoirs (∼30% of the total global estimate of ∼20 × 10^6 t N yr⁻¹; Harrison et al., 2009). Finally, reservoir sediments have been shown to efficiently trap phosphorus (P) (Beusen et al., 2005; Bosch, 2008; Bosch and Allan, 2008; Haregeweyn et al., 2008). Despite these global trends, individual dams may act temporally as nutrient sources (Teodoru and Wehrli, 2005). The disrupted transport of sediment, C, N, and P has profound consequences for downstream ecosystems, including sensitive wetlands and deltaic systems (McCartney, 2009; World Commission on Dams, 2000).

While the global rate of large dams construction has slowed, planning for and construction of new dams in economically-developed regions, and Sub-Saharan Africa in particular, continue (Bartle, 2002; Hydropower and Dams, 2001). In these river basins, dam-related impacts will be superposed on predicted increases in anthropogenic loading of dissolved N and P in river basins draining economically-developing regions (Dumont et al., 2005; Harrison et al., 2005).

Meanwhile, our knowledge about how subtropical and tropical ecosystems will respond to and process higher nutrient loads is limited because of a lack of data on baseline conditions and limited biogeochemical studies in these systems. Global biogeochemical models are better constrained in temperate regions, and have greater predictive power in economically-developed regions (Seitzinger et al., 2010). Moreover, such studies focus on riverine transport to the coasts and depend on relatively coarse parameterizations of biogeochemical processes within the basins. Given the importance of reservoirs in altering biogeochemical cycles and in affecting downstream ecosystems (Richter et al., 2010), there is a strong need for studies aimed at improving the understanding of biogeochemical processes in tropical reservoirs (Dumont et al., 2005).

Against this background, the Zambezi River Basin (ZRB, Southern Africa; Figure 3.1) is a particularly interesting example. The ZRB, the fourth largest river basin in Africa is already highly fragmented by four large hydropower schemes. Only around 20% of the ZRB’s hydropower potential is currently being utilized, and there are several new dams or dam expansions at various stages of advanced planning (Denconsult, 1998; Shela, 2000). Economic development, population growth and dam construction in the ZRB will most likely result in a shift towards a more industrialized river system with higher dissolved and decreased particulate nutrient transport (Yasin et al., 2010). Dam-induced impacts on ecosystems in the ZRB, as well as socioeconomic aspects of water resources management, are being examined within the African Dams Project, which includes the present study (http://www.cces.ethz.ch/projects/nature/adapt/).
We explored the effects of tropical reservoirs on biogeochemical cycles by studying Itezhi-Tezhi reservoir (ITT) located in the lower Kafue River, the largest tributary of the Zambezi River (Figure 3.1). Dam operation at Itezhi-Tezhi has caused negative ecological impacts in the Kafue Flats (Figure 3.1), a high-value and vulnerable floodplain ecosystem situated immediately downstream of the dam (Mumba and Thompson, 2005). While hydrologic changes after dam closure have been identified as a main cause for the ecological degradation (McCartney and Houghton-Carr, 1998; Mumba and Thompson, 2005), there has been limited systematic research into dam-induced changes to particle, C, N and P loads. The goals of this study were to quantify the removal of particles, C, N, and P by ITT, and estimate alterations to C and nutrient cycling through internal processes.
3.2 Study site

within the reservoir. Sediment cores were collected at multiple locations throughout the reservoir to quantify sedimentation and the accumulation of C, N, and P in sediments. Water column measurements of dissolved oxygen (DO), temperature, and nutrients over an annual cycle were used to assess internal cycling. Basic mass balances were estimated for C, N, and P, and a biogeochemical numerical model was developed to simulate internal cycling of C, N, and P under current operating conditions. The model was also used to predict changes in water quality under future changes to operating rules due to new turbine installations.

Figure 3.2: Daily mean discharge of the inflow (\(Q_{\text{hook}}\), grey lines; measured at Hook Bridge, Figure 3.1) and the outflow (\(Q_{\text{spill}}\), black lines; at the dam) of ITT for the simulation period (2008/2009, solid lines), and the 1978 to 2009 averages (dashed lines). The shaded area depicts the design discharge level for the planned turbines (306 m\(^3\) s\(^{-1}\)).

3.2 Study site

ITT was formed after damming of the Kafue River in 1978 for the main purpose of providing additional discharge to the downstream Kafue Gorge Dam (Figure 3.1) during the dry season (Obrdlik et al., 1989). The reservoir has a surface area of 364 km\(^2\), a volume of 5.4 km\(^3\) and maximal depth of 50 m at upper storage level (McCartney and Houghton-Carr, 1998; Obrdlik et al., 1989). With a mean outflow of 250 m\(^3\) s\(^{-1}\) (ZESCO, unpublished
data, 2009; Figure 3.2), the hydrologic residence time is \( \sim 0.7 \) yr. Little is known about ITT’s biogeochemistry; Obrdlik et al. (1989) described the reservoir as oligotrophic.

Under current operating conditions, water is almost exclusively discharged from the surface through spillways, with rare bottom water withdrawals during low storage (ZESCO, unpublished data, 2009). In the near future, turbines will be installed in existing diversion tunnels, and bottom water releases will be used to generate hydropower (Scott Wilson Piésold, 2003b).

### 3.3 Methods

#### 3.3.1 Field measurements and sampling

Sampling campaigns took place between July 2007 and June 2009 during nine field campaigns at stations along the thalweg of the two major inflows (Figure 3.1 and Table B.1, available as auxiliary material in Section 3.8.2). To analyze water quality, we collected water samples at 5 to 10 m depth resolution using a five-liter Niskin bottle. Kafue River water was sampled upstream of ITT at Hook Bridge (80 km upstream of its mouth), and immediately downstream of the dam at station K1 between April 2008 and February 2009 (Figure 3.1). Water samples for nutrient analysis were stored in PE containers, cooled immediately after collection, and frozen within 5 h. To analyze dissolved fractions we filtered the water samples immediately after collection using cellulose-acetate disc filters pre-rinsed with nanopure water and a poresize of 0.45 µm (FP30/0.45CA, Whatman). pH was measured with a Metrohm pH meter. For measuring dissolved methane (CH\(_4\)), water was collected in air-tight glass vials and poisoned with copper dichloride (CuCl\(_2\)).

Profiles of temperature, DO, conductivity, and turbidity were recorded using a conductivity-temperature-depth probe (CTD; CTD60M, Sea and Sun Technologies). Absolute DO concentrations were determined with the Winkler method for CTD oxygen calibration. Continuous records of water temperature were obtained from three thermistors (Minilog, Vemco; logging frequency = 1 h) moored at station IT1 (Figure 3.1). The position of the uppermost thermistor was 6 m below surface level with two additional loggers located at 2 m and 34 m height above the bottom (i.e., at 48 and 16 m depth relative to the maximum surface level, respectively).

Sediment cores were collected at eight sites along the thalweg of the original river channels (Figure 3.1) in July 2007 and May 2008 using a gravity corer (UWITEC) equipped with 6.3 × 60 cm PVC tubes. To minimize disturbance during transport, the tubes were immediately sealed and kept upright. After shipping, cores were stored at 4°C until
3.3. Methods

Wet bulk density (WBD) was measured on integral cores with a core logger (Multisensor, Geotek) at a 5-mm downcore resolution. Subsequently, cores were split vertically, photographed, and subsampled at 1-cm depth intervals. These samples were freeze-dried, homogenized and retained in plastic containers for geochemical analysis. Mass of dried samples divided by the volume of the respective core segment resulted in the dry bulk density of the sediment sample.

Cylindrical sediment traps were moored at site IT1 (Figure 3.1) between May 2008 and June 2009 at 10, 25, and 38 m height above the bottom. Sediment was collected in October 2008, February 2009 and June 2009 (i.e., after four to five months of deployment). The samples were transported frozen, freeze-dried, weighed and homogenized prior to geochemical analyses.

3.3.2 Sample analysis

Water samples were analyzed colorimetrically for the dissolved inorganic N (DIN) species $\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{NH}_4^+$, and soluble reactive P (SRP) by applying standard methods (DEW, 2004). After introducing a 25% headspace volume of $\text{N}_2$, dissolved CH$_4$ was measured on a gas chromatograph (6890N, Agilent) equipped with a flame ionization detector.

Total N (TN) and total P (TP) of water, sediment core and sediment trap samples were measured photometrically after a $\text{K}_2\text{S}_2\text{O}_8$ digestion at 120°C for two hours (DEW, 2004). TN concentrations were only further considered for water samples. Total C (TC) and TN and C stable-isotope composition ($\delta^{13}\text{C}$; expressed in the δ notation according to Vienna Pee Dee Belemnite) of sediment samples was determined with an Elemental Analyzer (NC2500, Thermaquest) coupled with a continuous flow isotope-ratio mass spectrometer (Isoprime, Micromass). Measurements of inorganic C (CM 5012 CO$_2$ coulometer, UIC Coulometrics) on ~20% of all sediment samples confirmed that TC mainly consisted of organic C (> 99%). Hence, measured TC was hereafter considered as total organic C (TOC) and isotopic ratios as OC-$\delta^{13}\text{C}$.

3.3.3 Biogeochemical reservoir modeling

To model reservoir-internal biogeochemical cycles, we adopted existing models developed by Omlin et al. (2001a,b), which have been successfully applied to various lake types (Mieleitner and Reichert, 2006), and used for scenario modeling (Matzinger et al., 2007a,b). The model AQUASIM (Reichert, 1994) allows one to simulate the key variables temperature (T), $\text{NO}_3^-$, $\text{NH}_4^+$, DO, SRP, total phytoplankton, total zooplankton, and dead organic
matter (OM), and includes the reservoir-internal processes of growth, respiration, and death of phytoplankton and zooplankton, P removal by adsorption to sinking particles, and water column and sediment mineralization.

In a first step, our version of the AQUASIM model (hereafter called “RES1”) was adapted to the physical conditions of ITT. ITT’s mixing and thermal stratification were parameterized by adopting separate diffusivities for the epilimnion, the metalimnion and the hypolimnion to fit measured T profiles over the course of 1 yr. Inflow and outflow hydrographs were based on daily discharge data (ZESCO, unpublished data, 2009; Figure 3.2). Imbalanced in- and outflows are compensated for by AQUASIM since the software does not allow variable surface water levels.

In a second step, we applied changes to biogeochemical parameters and processes. The sediment was parameterized according to the approach by Matzinger et al. (2007b), who approximated sediment mineralization with processes taking place at the sediment-water interface. Since anthropogenic nutrient loadings to ITT are expected to be lower than in the lakes of the original models, we anticipated stronger nutrient limitation of phytoplankton growth, particularly in terms of a relatively low DIN availability. We therefore introduced a process modeling N-fixation according to the approach by Kiirikki et al. (2001).

An anticipated difference between ITT and previously simulated lakes and reservoirs was the relatively high proportion of allochthonous material loaded to ITT whose elemental composition and lability are likely to differ substantially from autochthonous produced OM. We therefore separated allochthonous from autochthonous degradable OM allowing us to monitor the relative effects of the two sources for internal cycling. Furthermore, we assumed that the OM accumulating in the sediments remains available for mineralization over extended periods, according to the multi-G model of OM mineralization due to varying degradability (Berner, 1980; Westrich and Berner, 1984). This leads to a constant production of reduced substances that exert a DO demand during aerobic conditions. To integrate this DO demand into RES1, we introduced an additional process (hereafter referred to as “background mineralization”) that accounts for the oxidation of reduced substances by consuming DO (e.g., for the oxidation of CH\textsubscript{4}, NH\textsubscript{4}+, S(–II), and reduced dissolved metals). The areal background mineralization rate, which was allowed to vary with depth depending on the sediment area to water volume of a given depth increment, was quantified by estimating the difference between measured DO depletion and the DO calculated depletion from mineralization of newly deposited allochthonous and autochthonous OM (see appendix in Section 3.8.4 for a more detailed description of this process).
RES1 was calibrated using measured depth profiles of NO$_3^-$, NH$_4^+$, DO, SRP during the hydrologic year 2008/2009, starting on 1st of August after the deep mixing period, as well as losses of C, N and P to the sediment and through the spillways. The model architecture and the calibration procedure are described in detail in the auxiliary material (Section 3.8.4).

For evaluating the future changes in riverine C, N, and P transport induced by bottom water releases through turbines, we conducted model runs incorporating a second deep-water outlet in addition to surface water spillage. According to the planned operation rules, a maximum of 306 m$^3$s$^{-1}$ can be turbinated (Scott Wilson Piésold, 2003b). Hence, if available, this amount of discharge was diverted through the turbine outlet in RES1, and excess discharge was spilled from the surface. Hydrographs for the simulation period are illustrated in Figure 3.2.

### 3.4 Results

#### 3.4.1 Sediment, carbon and nutrient deposition

Net accumulation of solids, OC, N and P in ITT’s sediments was quantified based on data from sediment cores collected at the eight stations listed in Table 3.1. The lengths of the entire cores varied between 12 cm (IT4) and 57 cm (IT6). Cores collected at IT1, IT2, IT7, IT10 and IT11 featured dark, blackish sediment with intermittent lighter bands, layered on top of homogenously colored, lighter gray deposits (Figure B.1, available as auxiliary material in Section 3.8.1). This zone of distinct color change coincided with a strong downcore increase in WBD, decreasing OC, TP and TN concentrations, and increasing C:N and $\delta^{13}$C values (Figures 3.3 and B.2). Altogether, these abrupt changes in the sediment core profiles indicate that there was a shift in the sedimentation regime from pre-dam to lake-like conditions that would have occurred around 1978, the year of dam closure. Based on the cores’ compositional changes and locations (> 10 km distance from main river inlets; deep areas of ITT), they are hereafter referred to as lacustrine cores, and the two vertical sediment sections are called “pre-dam” and “post-dam”.

In cores collected at stations closest to the main river inlets (IT4, IT6, and IT9), hereafter referred to as riverine cores, the 1978 horizons are not readily discernable, most notably in the lack of a strong downcore increase in WBD (Figures 3.3 and B.2). Thus, based on this absence of a change in WBD, it is possible that these cores from IT6 and IT9, despite being the longest of the entire set, did not capture the entire thickness of post-dam deposits. It is also likely that the corer was stopped by denser pre-dam sed-
iment or soil layers, in which case the majority of post-dam sediments were retrieved. At all stations, dividing the thickness of the post-dam sediment section by the elapsed time period between coring and dam closure, and multiplying by the dry bulk density, yielded mean sediment accumulation rates for the individual coring sites that range from 420 to 4,900 g m\(^{-2}\) yr\(^{-1}\) (Table 3.1). The maximum value may be an underestimate due to the potentially incomplete cores at IT6 and IT9.

At lacustrine stations, post-dam sediments had significantly higher mean concentrations of OC, TP and TN and significantly lower C:N and \(\delta^{13}\)C values compared to pre-dam sediments (t-tests on individual core datasets, \(p < 0.001\)). This difference is consistent with a shift to a lake-like sedimentation regime resulting in the accumulation of autochthonous OM that is characterized by relatively low C:N and \(\delta^{13}\)C values (Kunz et al., 2011; Meyers and Teranes, 2002). Although there was substantial variation of OC, TN, TP, \(\delta^{13}\)C and C:N in the post-dam sections of these cores (Figures 3.3 and B.2), no systematic down-core trends were identified that would have suggested temporal changes in internal cycling or trophic state of the system. Moreover, mean composition of post-dam sections did not vary substantially between individual cores (Figures 3.3 and B.2, and Table 3.1).

Sediment accumulation rates were highest near the Kafue River mouth and decreased exponentially towards the dam (Figure 3.4). Along the transect extending from the dam toward the Musa River mouth, sediment accumulation rates (\(S_{\text{acc}}\)) remained almost constant, comparable to those measured at the dam. To estimate sediment loading, ITT’s surface was divided into 16 subsectors (Figure 3.1) and an appropriate sediment accumulation rate was applied to each area (see auxiliary material in Section 3.8.3 for a detailed description of this approach). The sediment load to ITT summed to \(330 \pm 87 \times 10^3\) t yr\(^{-1}\), which is equivalent to an area-averaged sediment accumulation rate of \(900 \pm 240\) g m\(^{-2}\) yr\(^{-1}\). Multiplying the \(S_{\text{acc}}\) for each sedimentation sector with mean OC, TN and TP concentrations in post-dam sections of their respective cores (Table 3.1) resulted in OC, N, and P accumulation rates (\(C_{\text{acc}}, N_{\text{acc}},\) and \(P_{\text{acc}},\) respectively), which varied similarly to \(S_{\text{acc}}\) with distance from the dam (Figure 3.4). The integrated net sediment loadings of OC, N, and P amounted to \(\sim 16,000 \pm 5,500, 1,500 \pm 520\) and \(200 \pm 67\) t yr\(^{-1}\), respectively.

The mean settling particle flux estimated from three sets of sediment trap deployments positioned near the dam (IT1) between May 2008 and June 2009 was \(790 \pm 230\) g m\(^{-2}\) yr\(^{-1}\) (Table 3.2). There was no systematic variation in the collected masses between the three deployment periods or between the individual traps installed at three different depths (Table 3.2). There were also only small variations in the mean \(\delta^{13}\)C and C:N values (\(-25.8 \pm 0.5\%_\text{o}, 9.7 \pm 0.5,\) respectively). Mean concentrations were combined with particle fluxes to yield C, N, and P settling fluxes (Table 3.2), which were larger than their re-
Table 3.1: Mean sediment core data of ITT deposits

<table>
<thead>
<tr>
<th>Station*</th>
<th>Collection</th>
<th>(z_{trans})(^b)</th>
<th>SR(^c)</th>
<th>Dry bulk density</th>
<th>(S_{acc})(^d)</th>
<th>OC</th>
<th>TN</th>
<th>TP</th>
<th>(\delta^{13}C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(cm)</td>
<td>(cm yr(^{-1}))</td>
<td>(g cm(^{-3})) (±1σ)</td>
<td>(g m(^{-2}) yr(^{-1})) (±1σ)</td>
<td>(mg g(^{-1})) (±1σ)</td>
<td>(mg g(^{-1})) (±1σ)</td>
<td>(mg g(^{-1})) (±1σ)</td>
<td>(‰) (±1σ)</td>
</tr>
<tr>
<td><strong>Dam–Kafue River</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT1</td>
<td>Jul-07</td>
<td>24.2</td>
<td>0.8</td>
<td>NA</td>
<td>970(^e)</td>
<td>54</td>
<td>18</td>
<td>5.1</td>
<td>2.0</td>
</tr>
<tr>
<td>IT1</td>
<td>May-08</td>
<td>27.5</td>
<td>0.9</td>
<td>0.12</td>
<td>1,100</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>IT7</td>
<td>May-08</td>
<td>25.5</td>
<td>0.9</td>
<td>NA</td>
<td>1,000(^f)</td>
<td>47</td>
<td>8</td>
<td>4.6</td>
<td>0.5</td>
</tr>
<tr>
<td>IT11</td>
<td>May-08</td>
<td>30.5</td>
<td>1.0</td>
<td>0.13</td>
<td>1,300</td>
<td>41</td>
<td>6</td>
<td>3.9</td>
<td>0.5</td>
</tr>
<tr>
<td>IT10</td>
<td>May-08</td>
<td>34.0</td>
<td>1.1</td>
<td>0.21</td>
<td>2,400</td>
<td>40</td>
<td>3</td>
<td>4.1</td>
<td>0.3</td>
</tr>
<tr>
<td>IT6</td>
<td>May-08</td>
<td>57.1(^g)</td>
<td>1.9</td>
<td>NA</td>
<td>4,900</td>
<td>49</td>
<td>3</td>
<td>4.5</td>
<td>0.3</td>
</tr>
<tr>
<td>IT9</td>
<td>May-08</td>
<td>48.8(^h)</td>
<td>1.6</td>
<td>0.30</td>
<td>4,900(^h)</td>
<td>49</td>
<td>3</td>
<td>4.5</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Dam–Musa river</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT2</td>
<td>May-08</td>
<td>15.3</td>
<td>0.5</td>
<td>0.10</td>
<td>510</td>
<td>63</td>
<td>8</td>
<td>6.4</td>
<td>1.0</td>
</tr>
<tr>
<td>IT4</td>
<td>May-08</td>
<td>12.4(^i)</td>
<td>0.4</td>
<td>NA</td>
<td>420</td>
<td>31</td>
<td>4</td>
<td>3.1</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td></td>
<td>26.2</td>
<td>1.0</td>
<td>0.17</td>
<td>2,000</td>
<td>47</td>
<td>10</td>
<td>4.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Station locations are illustrated in Figure 3.1

\(^b\) Refers to the transition from the pre-dam to the lacustrine sedimentation regime after the dam closure in 1978

\(^c\) Sedimentation rate

\(^d\) Sediment accumulation rate

\(^e\) Estimated by using the dry bulk density from the 2008 core collected at IT1

\(^f\) Estimated by using the mean dry bulk density from the adjacent cores (IT1 and IT11)

\(^g\) Entire core length (see text for explanation)

\(^h\) Estimated by using the dry bulk density from core collected at IT9.
Figure 3.3: Depth profiles of two representative cores from riverine (IT9, left column) and lacustrine-type (IT11, right column) sedimentation zones illustrating downcore and reservoir-wide variation in WBD, C:N, δ¹³C, OC, TN, and TP. The horizontal dotted line indicates the transition to post-dam sediment regime; below are values of pre-dam sediments.

Spective accumulations in sediment cores at IT1 by a factor of ~2 (Table 3.1). The lower C:N and δ¹³C of the sediment trap samples compared to sediment cores from the same
3.4. Results

![Graph showing sediment (S_{acc}), C (C_{acc}), N (N_{acc}), and P (P_{acc}) accumulation rates increase exponentially with distance from the dam (IT1), peaking near the Kafue River mouth (IT9), whereas those rates stay constant towards the Musa River mouth (IT4). The grey shaded area reflects therefore deposition of autochthonous OM (see text).](image)

Figure 3.4: Sediment (S_{acc}), C (C_{acc}), N (N_{acc}), and P (P_{acc}) accumulation rates increase exponentially with distance from the dam (IT1), peaking near the Kafue River mouth (IT9), whereas those rates stay constant towards the Musa River mouth (IT4). The grey shaded area reflects therefore deposition of autochthonous OM (see text).

area (Table 3.1) indicate that they contained a higher contribution of autochthonous OM (Meyers and Teranes, 2002).

3.4.2 Spillway outputs and river inputs

Having quantified C, N, and P losses via removal to ITT’s sediments, we next estimate export to downstream systems as well as riverine loading to ITT. The output loads of TN, DIN, TP, and SRP were estimated using measured water column concentrations in the depth zone of 0 to 10 m at IT1 (Figure 3.5) and daily discharge records at the spill gates (Figure 3.2). TN consisted primarily of organic N and only a few % of DIN (Figure 3.5). Thus, DIN export (210 ± 110 t N yr\(^{-1}\)) constituted only a small fraction of TN export from ITT (4,000 ± 1,000 t N yr\(^{-1}\)). For these and subsequent calculated loads, the uncertainty estimates are based on the standard deviations of the mean concentrations and an assumed uncertainty of 20% for discharge. Measured concentrations of TP and SRP in surface waters were comparable (0.013 ± 0.006 mg l\(^{-1}\), 0.009 ± 0.1 mg l\(^{-1}\), respectively), indicating that the majority of P was present as SRP and organic P or mineral phases.
### Table 3.2: Summary of sediment trap data for 2008/2009

<table>
<thead>
<tr>
<th>Deployment Depth</th>
<th>May 08–Oct 08</th>
<th>Oct 08–Feb 09</th>
<th>Feb 09–Jun 09</th>
<th>Mean ± 1σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>(m)</td>
<td>(m)</td>
<td>(m)</td>
<td>(m)</td>
</tr>
<tr>
<td>Mass S (g m⁻² yr⁻¹)</td>
<td>160</td>
<td>125</td>
<td>101</td>
<td>92.0 ± 16.8</td>
</tr>
<tr>
<td>OC (mg g⁻¹)</td>
<td>13</td>
<td>15</td>
<td>13</td>
<td>14 ± 2.0</td>
</tr>
<tr>
<td>TN (g m⁻² yr⁻¹)</td>
<td>580</td>
<td>650</td>
<td>980</td>
<td>790 ± 70</td>
</tr>
<tr>
<td>TP (mg g⁻¹)</td>
<td>120</td>
<td>61</td>
<td>100</td>
<td>92 ± 7.0</td>
</tr>
<tr>
<td>C:N</td>
<td>71</td>
<td>39</td>
<td>72</td>
<td>73 ± 4.6</td>
</tr>
<tr>
<td>δ¹³C (mol l⁻¹)</td>
<td>1.7 ± 0.5</td>
<td>1.5 ± 0.4</td>
<td>2.4 ± 0.5</td>
<td>1.8 ± 0.4</td>
</tr>
<tr>
<td>δ¹⁵N (h⁻¹)</td>
<td>14 ± 2.0</td>
<td>12 ± 2.0</td>
<td>16 ± 2.0</td>
<td>15 ± 2.0</td>
</tr>
</tbody>
</table>

- Mass S refers to the mass of sediment traps used at each deployment depth.
- OC denotes organic carbon.
- TN denotes total nitrogen.
- TP denotes total phosphorus.
- C:N denotes the ratio of carbon to nitrogen.
- δ¹³C and δ¹⁵N refer to carbon and nitrogen stable isotope ratios, respectively.

*Referring to maximum lake level (1030 masl)*
3.4. Results

were of minor importance. Export loads of TP and SRP from ITT were $140 \pm 76 \text{ t P yr}^{-1}$ and $99 \pm 32 \text{ t P yr}^{-1}$, respectively. Mass loads calculated from concentrations measured at station K1 immediately downstream of the dam (Wamulume et al., 2011) are consistent with the above estimates ($\text{TN}: 3,900 \pm 150 \text{ t P yr}^{-1}$, TP: 150 t P yr$^{-1}$, SRP: 68 t P yr$^{-1}$).

TOC and dissolved OC (DOC) export were estimated from measurements at K1 ($8.5 \pm 4.5 \text{ mg TOC l}^{-1}$, and $3.1 \pm 0.27 \text{ mg DOC l}^{-1}$; Wamulume et al., 2011), because OC concentrations were not available for multiple dates for the ITT water column. The resulting export load of TOC amounted to $110,000 \pm 63,000 \text{ t C yr}^{-1}$, of which $40,000 \pm 8,800 \text{ t C yr}^{-1}$ was DOC.

Similar to losses at the outflow, riverine inputs were estimated using the total inflow of 10.4 km$^3$ for the August 2008 to July 2009 period (Figure 3.2), measured at Hook Bridge (Figure 3.1) on a daily basis by dam operators, and mean concentrations determined from samples collected at that station (Wamulume et al., 2011). Mean concentrations were used because there was no correlation between concentrations and flow rates, and because of limited data availability. Concentrations at Hook Bridge were of the same order of magnitude as in the outflow for TOC ($10 \pm 8.0 \text{ mg C l}^{-1}$), DOC ($3.1 \pm 0.90 \text{ mg C l}^{-1}$), TN ($0.36 \pm 0.18 \text{ mg N l}^{-1}$), DIN ($0.013 \pm 0.007 \text{ mg N l}^{-1}$), TP ($0.010 \pm 0.005 \text{ mg P l}^{-1}$), and SRP ($0.009 \pm 0.005 \text{ mg P l}^{-1}$; Wamulume et al., 2011). As a consequence of sparse data the input loads were not well constrained: $100,000 \pm 86,000 \text{ t TOC-C yr}^{-1}$, $32,000 \pm 11,000 \text{ t DOC-C}^{-1}$, $3,800 \pm 2,000 \text{ t TN-N yr}^{-1}$, $140 \pm 79 \text{ t DIN-N yr}^{-1}$, $110 \pm 53 \text{ t TP-P yr}^{-1}$, and $91 \pm 23 \text{ t SRP-P yr}^{-1}$.

3.4.3 Internal cycling

Profiles of temperature and DO, as well as thermistor temperature records from station IT1, show consistently that there was a short period of deep convection between late July and early August, followed by re-stratification by mid-August (Figure 3.6). After the onset of stratification, oxygen concentrations decreased steadily in the hypolimnion, with anoxic conditions developing by December. Profiles at IT1 were representative for entire ITT, as evidenced by only minor horizontal heterogeneity observed on several dates in profiles along transects toward the Kafue and Musa River inlets (Figures B.3, B.5, B.4, and B.6; dates and locations are given in Table B.1).

Nutrient concentrations were low in the epilimnion throughout the year, while hypolimnentic concentrations of NH$_4^+$ and SRP increased over the course of the stratified period (Figure 3.5). During the period of gradual DO depletion in the hypolimnion from August to December, only minor increases occurred in the concentrations of the mineralization
Figure 3.5: Depth profiles of measured (symbols, dotted lines) and simulated (solid lines) temperature (column 1), dissolved oxygen (column 2), total nitrogen (column 3), nitrate (column 4), ammonium (column 5), and phosphate (column 6) for the eight sampling dates (indicated to the right) during the simulation period (rows 1 to 8, see Table B.1). Circles relate to measurements on water samples that were collected at stations illustrated in Figure 3.1.
products NO$_3^-$, NH$_4^+$, and SRP. From mid-December 2008 to early June 2009, substantial increases in hypolimnetic concentrations of NH$_4^+$ and SRP were observed. These increases coincided with the onset of anoxia in the hypolimnion, but also with a pronounced increase in discharge to ITT (Figure 3.2) and its accompanying suspended sediment load. The release of DIN to the hypolimnetic water column during this period had only a minor effect on overall TN concentrations, since particulate and dissolved organic forms dominated TN (Figure 3.5). A marginal (10%) increase in the mass of total TN was observed in the hypolimnion during the stratified period, mainly caused by the increase of NH$_4^+$. On the other hand, the hypolimnetic storage of SRP and TP (SRP $\approx$ TP, data not shown) increased by a factor of $\sim$4 during the stratified period.

We estimated the mineralization rate in the hypolimnion (depth < 1010 masl) as the areal hypolimnetic mineralization rate (AHM), which is calculated from the rate of change of the equivalent DO content, and considers both aerobic and anaerobic mineralization. Neglecting a few minor processes (oxidation of Fe$^{2+}$, Mn$^{2+}$, and NO$_2^-$) the concentration of DO equivalents was calculated as

$$[\text{DO}_{\text{equiv}}] = [\text{DO}] - 2 \cdot [\text{NH}_4^+] - 2 \cdot [S(-\text{II})] - 2 \cdot [\text{CH}_4]$$

(Matzinger et al., 2010). Using this definition, as well as measured DO, NH$_4^+$, and CH$_4$ concentrations, and calculating the AHM as the temporal derivative of accumulated DO$_{\text{equiv}}$ yielded $0.38 \pm 0.05$ g DO$_{\text{equiv}}$ m$^{-2}$ d$^{-1}$ (Figure 3.7). After the onset of anoxia, CH$_4$ (concentrations up to 77 $\mu$M; data not shown) formed the largest portion of DO$_{\text{equiv}}$ ($\sim$70%), while NH$_4^+$ contributed the remaining $\sim$30%. The last two data points of the measurement period (i.e., May and June 2009) were not included in this calculation, because gradual erosion and deepening of the thermocline had mixed oxygen-rich surface waters into the upper hypolimnion (Figures 3.6b and 3.7) and had already caused oxidation of reduced substances. S(-II) was not included in the calculation of AHM due to a lack of data. S(-II) was clearly present in some anoxic hypolimnetic water samples, as its odor was detected during sampling. An upper bound for possible S(-II) concentrations is 200 $\mu$M, based on mean SO$_4^{2-}$ concentration in the water column during the study period (data not shown). Using this upper bound S(-II) level, the AHM would increase by < 10%. Hence, the error introduced by neglecting S(-II) is expected to be minor (Matzinger et al., 2010).

### 3.4.4 Biogeochemical modeling: current management rules

Profiles resulting from model simulations illustrate that RES1 accurately reproduced mixing and stratification, as well as DO (Figure 3.5). Water temperatures closely followed the measured profiles, indicating that the downward mixing of heat, based on adjusted
diffusivities in the epi-, meta-, and hypolimnion, were adequately estimated. The biogeochemical processes in RES1 (e.g., primary and secondary production, mineralization of dead OM) captured the observed oxygen depletion and the build-up of nutrients (SRP, NH$_4^+$) in the hypolimnion during the stratified period (Figure 3.5).

Modeled output loads of inorganic N and P via spillways agreed reasonably well with the measurement-based estimates. RES1 underestimated outputs of DIN by $< 1\%$ (210 versus 210 t N yr$^{-1}$), of SRP by 30$\%$ (71 versus 99 t P yr$^{-1}$), and of TP by 6$\%$ (130 versus 140 t P yr$^{-1}$). Modeled OC outputs accounted for only 7$\%$ of the OC export based on
3.5 Discussion

3.5.1 Sources and fates of OM, carbon and nutrients

OM provenance and removal rates

Impounding the Kafue River at Itezhi-Tezhi altered physical and biogeochemical processes along the Kafue River such that a fraction of the allochthonous OM from upstream systems is retained or mineralized in ITT, while new autochthonous OM is produced through measured concentrations (8,000 versus 110,000 t C yr⁻¹). This difference resulted from the fact that allochthonous DOC and fine, non-settling particulate OC were not included as variables in RES1.

Figure 3.7: Storage of DO (triangles), DO equivalents (DO_{equiv}, circles) in the hypolimnion (below 1010 masl) with time. The linear fit through DO_{equiv} (dashed line) yielded the areal hypolimnetic mineralization (Matzinger et al., 2010) of 0.38 ± 0.05 g DO_{equiv} m⁻² d⁻¹. Note that we did not include the measurements in May and June (filled circles) because of down mixing of epilimnetic DO causing oxidation of the reduced species CH₄ and NH₄⁺ and therefore increasing DO_{equiv}.
primary production. In the absence of the dam, the allochthonous OM was transported to downstream systems, whereas most of the autochthonous OM would not have been produced. To assess the effects of ITT on the riverine transport of sediment, and C, N, and P cycling, it is necessary to quantify both the trapping and mineralization of OM in the reservoir, and the relative contributions of autochthonous and allochthonous material to mineralization and burial.

The relative importance of allochthonous and autochthonous OM sources for sedimentation was estimated based on the elemental composition of sediment trap material. The settling particles were assumed to be a mixture of solids having two end-member compositions, one that was primarily allochthonous material (using the composition of core IT9, OC $\approx 50$ mg g$^{-1}$; Table 3.1) and a second that was primarily autochthonous OM (assuming Redfield composition, OC $= 360$ mg g$^{-1}$). Based on these values, the OM in the sediment traps (OC $\approx 92$ mg g$^{-1}$; Table 3.2) consisted of 14% autochthonous OM. Combining these estimates of autochthonous contribution with the sediment trap flux yielded autochthonous OM sediment accumulation rates of 5.5 g C m$^{-2}$ yr$^{-1}$, 0.45 g N m$^{-2}$ yr$^{-1}$, and 0.07 g P m$^{-2}$ yr$^{-1}$ in the vicinity of IT1. If primary production (and associated sedimentation) can be reasonably considered to occur at a similar rate over the entire reservoir surface (Kimmel et al., 1990), these accumulation rates, extrapolated to the total sediment area, result in autochthonous loads per year of 2,000 t C, 170 t N, and 27 t P. The estimated C, N, and P autochthonous settling fluxes and loads represent gross sedimentation, prior to any mineralization. Alternatively, applying the same mixing approach to estimate the autochthonous fraction but this time using the C:N ratios in core IT9 ($\sim 13$), sediment traps ($\sim 9.7$) and the Redfield ratio (6.6) results in an estimated autochthonous contribution of 55%, and in accumulation rates of 21 g C m$^{-2}$ yr$^{-1}$, 1.7 g N m$^{-2}$ yr$^{-1}$, and 0.27 g P m$^{-2}$ yr$^{-1}$, respectively. However, since these rates are comparable to the total estimates in the Dam-Musa reach ($-40$ to $0$ km distance from the dam, Figure 3.4), and since 0% allochthonous contribution in this reach is unrealistic, we expect the autochthonous ratio of 14% to be the better estimate.

Mineralization and internal nutrient loading

OM undergoes mineralization while settling through the water column and mineralization continues after it is deposited in the sediments. RES1 predicted maximum hypolimnetic mineralization rates during March to May, due to peak inputs of allochthonous OM (higher discharge, Figure 3.2) and a peak in primary production (Figure B.7), and subsequent mineralization of allochthonous and autochthonous OM. As a result, the annual-averaged rate of total mineralization in RES1 was 50% greater than the measurement-based estimate
of the AHM \((0.67 \pm 0.33 \text{ versus } 0.38 \pm 0.05 \text{ g DO}_{\text{equiv}} \text{ m}^{-2} \text{ d}^{-1})\), although this difference may be within the uncertainty of the estimates. Other studies have shown that anaerobic mineralization rates in sediments can indeed be higher than aerobic mineralization rates, depending on the availability of labile OM (Maerki et al., 2009). Overall, since ITT is heavily influenced by seasonally varying allochthonous inputs, its AHM may actually be highest during the anoxic period, in contrast to other, more autochthonous OM driven systems with rather constant mineralization rates throughout oxic and anoxic periods (Matzinger et al., 2010).

Comparing the estimates for AHM with \(C_{\text{acc}}\), the burial efficiency \((BE)\) of OC can be calculated to evaluate the role of ITT in removing OC by sediment burial and mineralization. Modeled and measured AHM translate to Redfield-equivalent OC mineralization rates, \(C_{\text{miner}}\), of 70 and 40 g C m\(^{-2}\) yr\(^{-1}\), respectively. With a mean reservoir-wide \(C_{\text{acc}}\) of 43 g C m\(^{-2}\) yr\(^{-1}\) and \(BE = C_{\text{acc}}/(C_{\text{acc}} + C_{\text{miner}})\), the \(BE\) ranges between 38 and 52%. We expect a BE of 38\% to be the best estimate for the mineralization rate of OM in ITT’s hypolimnion, as it accounts both for the spatial variability of the reservoir-wide \(C_{\text{acc}}\), and the temporal variability of AHM and \(C_{\text{miner}}\).

During mineralization, DIN and SRP are released, either directly to the water column by settling material, or by diffusion from the sediments. Generally, however, the observed rate of accumulation of these mineralization products is not in direct proportion to the rate of mineralization. For instance, Caraco et al. (1990) reported a mean release of 0.003 g P (g C\(^{-1}\)) across a range of lakes, which was substantially lower than a Redfield-derived estimate of 0.02 g P (g C\(^{-1}\)). In ITT, the observed increases of SRP (29 t P; 0.01 g P (g C\(^{-1}\))) and DIN (100 t N; 0.10 g N (g C\(^{-1}\))) in the hypolimnion during the stratified period (Figure 3.5) also correspond to release rates that are substantially lower than would be expected based on the estimated AHM (0.38 ± 0.05 g DO\(_{\text{equiv}}\) m\(^{-2}\) d\(^{-1}\)) and an assumption of Redfield stoichiometry. Given the importance of allochthonous OM loading to this system, the higher C:N and C:P for allochthonous material would tend to result in lower releases of N and P per unit OM mineralized. The seemingly inefficient release of P during mineralization may also be explained by settling particles scavenging SRP (e.g., hydrous ferric oxides; Hupfer and Lewandowski, 2008). The lower than expected DIN accumulation may be due to coupled nitrification-denitrification during oxic periods (Harrison et al., 2009; Maerki et al., 2009; Seitzinger et al., 2008), and anammox during anoxic periods (Schubert et al., 2006). Hence, the difference between the maximum estimate for the seasonal N release (2,100 t N, inferred from AHM-equivalents) and the observed accumulation of N in the water column (100 t N, measured concentrations) may be considered as an upper bound estimate for denitrification in the hypolimnion (= 2,000 t N; Figure 3.8).
From August to December, measured accumulation of DIN and SRP remained low, although DO concentrations were decreasing steadily in the hypolimnion (Figure 3.5 and 3.6b). Since nutrient release and mineralization are dynamically coupled in RES1, it was not possible to capture both the observed DO depletion and the low nutrient releases if mineralization of autochthonous or allochthonous OM were the primary reductants, each having defined C:N:P. A similar issue was encountered in field measurements and measurement derived AHM, with the relatively low releases of DIN and SRP per unit OC mineralized (discussed above). Within RES1, the best way to address this issue was by invoking a background mineralization process that consumed DO (Section 3.3.3) but...
3.5. Discussion

released no nutrients. On average, the background mineralization contributed \( \sim 50\% \) to the total mineralization.

From a conceptual standpoint, the background mineralization accounts for the oxidation of reduced substances originating from the ongoing mineralization of slowly degrading OM that may continue for years to decades after deposition in the sediments (Berner, 1980; Matzinger et al., 2010; Westrich and Berner, 1984). The oxidation of methane, usually the most important end product of anaerobic mineralization, was shown to consume \( \sim 50\% \) of the DO flux into the sediments in other systems (Maerki et al., 2009). The near-zero release of N and P during this mineralization process might be explained in terms of the slowly degrading pools of OM being poor quality substrate that have high C:N:P, and that a high proportion of any liberated N and P is recycled and utilized by the sediment microbial community. It is also possible that the need to invoke such a process to explain \( \sim 50\% \) of total mineralization indicates that some aspects of the complex cycling of nutrients (e.g., coupled nitrification-denitrification, scavenging of SRP by settling particles), which RES1 does not sufficiently address, are quite important in dictating net release of N and P to the water column.

Assimilation of carbon and nitrogen

RES1 predicted a pronounced peak of phytoplankton abundance during the rainy season of the simulation period (Figure B.7). This peak corresponds reasonably well with the temporal pattern of chlorophyll-a concentrations measured between 1983 and 1985 with the exception of June and July measurements (Obrdlik et al., 1989). The phytoplankton bloom is most likely due to the relatively high availability of nutrients after the onset of the flood period and the associated input of allochthonous nutrients.

Primary production in ITT and the associated assimilation of atmospheric C and N were estimated using the phytoplankton production predicted by RES1. The growth of modeled phytoplankton (Figure B.7) translated to an annual average areal primary production rate of 280 g C m\(^{-2}\) yr\(^{-1}\). This characterizes ITT as a mesotrophic reservoir according to the range of 95 to 340 g C m\(^{-2}\) yr\(^{-1}\) given by Wetzel (2001).

The low riverine DIN input leads to a low availability of N for phytoplankton growth in the trophogenic zone of ITT (Figure 3.5). The low DIN concentrations resulted in substantial N fixation in RES1, with fixed N being used for \( \sim 30\% \) of primary production (97 g C m\(^{-2}\) yr\(^{-1}\)). The related assimilatory flux amounted to 12 g N m\(^{-2}\) yr\(^{-1}\) (\( = 6,500 \text{ t N yr}^{-1} \)), exceeding river inputs of bioavailable DIN by a factor of 50. Such a large relative importance of N fixation is typical for eutrophic rather than mesotrophic
systems, for which fixation of atmospheric N can account for even higher portions (> 80%) of total N inputs in case of severe N deficiency (Wetzel, 2001). If N fixation is in reality as important in ITT as indicated by RES1 simulations, then it suggests that the vast majority of the large organic N pool is refractory (measured TN:TP = 78, measured DIN:SRP = 3.3; Figure 3.8), and not utilized by phytoplankton for growth.

Relevance of Itezhi-Tezhi reservoir for riverine transport to the downstream wetland

The quantified mass loads were incorporated into OC, N and P mass balances as illustrated in Figure 3.8 and, together with modeling results, used to evaluate the role of ITT in altering the riverine transport of these species by removal and internal cycling. The measurement-based mass balances are used to estimate overall N and P removal efficiencies. Modeling results allowed estimating the extent to which reservoir-internal biogeochemical cycling, in particular primary production, affected spillway output loads to the Kafue Flats.

For OC, TN, and TP, the summed loads from sediment accumulation and discharge through the outflow substantially exceeded Kafue River input loads. The differences, which amount to ∼25,000 t C yr\(^{-1}\) (24% of riverine inputs), ∼3,700 t N yr\(^{-1}\) (99% of riverine inputs), and ∼240 t P yr\(^{-1}\) (200% of riverine inputs), must owe to underestimated Kafue River inputs or unaccounted for sources. It is not surprising that there would be some underestimation of the inputs to ITT given the limited data available and the pronounced seasonality in the Kafue River discharge. Dissolved and particulate inputs during flood pulses are generally difficult to quantify and easily underestimated (Cuffney and Wallace, 1988). Moreover, even when more frequent sampling is applied, relative errors of input loadings typically reach ∼50% (Moosmann et al., 2006).

Having quantified inputs and sinks of N and P, the removal efficiency \(f_{rem} = \frac{\text{sinks}}{\text{inputs}}\) of these elements was estimated. N is either lost to the sediment by burial or to the atmosphere through denitrification, adding up to total sinks of ∼3,500 t N yr\(^{-1}\) (Figure 3.8). Dividing this number by the total inputs of ∼7,500 t N yr\(^{-1}\) yielded an N removal efficiency \(f_{rem}\) of 46%. This value is in the middle of the global estimated range of 0.04% to 70% for reservoirs (Harrison et al., 2009). Using the same approach for P, total sinks, total inputs and \(f_{rem}\) account for 200 t P yr\(^{-1}\), 340 t P yr\(^{-1}\), and 59%, respectively (Figure 3.8). Both estimates for \(f_{rem}\) of N and P in ITT are lower than recent estimates by our group for Lake Kariba, also located in the ZRB (70% and 90%, respectively; Kunz et al., 2011). The difference in removal efficiencies between these two reservoirs is not surprising
given that the hydraulic residence time of Lake Kariba (3 yr) is 4 times greater than that of ITT.

The relatively high modeled amount of C and N fixation (92,000 t OC yr$^{-1}$ and 16,000 t N yr$^{-1}$) compared to loads illustrated in Figure 3.8 illustrate the potential importance of internal cycling and assimilation to the overall C and N budgets of ITT. It also raises the question of the contribution of C and N fixed within ITT to the output loads. The importance of autochthonous OM to the export load of N and C from ITT depends on the balance between its fates, i.e., either internal losses (mineralization and burial) or loss through the outflow. In RES1, the losses of autochthonous OM (i.e., the sum of phytoplankton, zooplankton, and dead autochthonous OM) through the outflow summed to 5,800 t C yr$^{-1}$, or only 5% of the measured output load (Figure 3.8). The magnitude of this outflow loss is considerably uncertain, owing to the uncertainties associated with the biological sub-model. Nonetheless, either the primary production rate or its fractional export would have to be much higher (e.g., factor of 5) before export of autochthonous OM begins to play a substantial role. Combining RES1 results with the measurement-derived mass budget, it appears as though the largest part of the discharged OC is of allochthonous origin, and that it is efficiently flushed through ITT without entering internal biogeochemical cycling.

The relatively low contribution of autochthonous OC to TOC outputs from ITT also implies efficient internal recycling of autochthonous OM and associated nutrients. We assessed nutrient recycling in ITT by calculating the N and P recycling factors, $\rho$ = assimilation/losses, where losses are the sum of net sediment accumulation, outflow losses, and, for N, denitrification losses (Essington and Carpenter, 2000). Integrated modeled phytoplankton growth resulted in a total uptake of 19,000 t N yr$^{-1}$ and 2,100 t P yr$^{-1}$; loss loads are given in Figure 3.8. Denitrification losses of autochthonous N are unknown; however, lower and upper bound estimates for $\rho_N$ can be calculated by using the total denitrification losses (Figure 3.8) and by setting denitrification = 0, respectively. Using this approach, $\rho_N$ ranged between 9 and 5. In the case of P, a value for $\rho_P$ of 9 was estimated. These ratios illustrate the highly efficient internal nutrient recycling in ITT, as expected for tropical lakes and reservoirs (Kilham and Kilham, 1990). An order of magnitude higher N assimilation compared to riverine inputs was also found in other tropical systems (Gardner et al., 1998).

On a percentage basis, the unaccounted for P inputs were substantially larger than for C and N (Figure 3.8). Dry and wet deposition may play an important role in P loading, as these pathways have been shown to deliver significant amounts of nutrients to the African Great Lakes (Bootsma and Hecky, 1993). Hao and Liu (1994) stated that burning of
biomass in the tropics transports nutrient rich particles to the atmosphere, and predicted Savannah fires as a large source in Southern Africa. Extrapolating the sum of wet and dry deposition rates of TP from Lake Malawi (Bootsma et al., 1999) to ITT results in a load of 190 t P yr$^{-1}$. This load is comparable to our missing 240 t P yr$^{-1}$. Extrapolating wet and dry deposition rates of TP from Lake Kivu (Muvundja et al., 2009), the atmospheric load would be in the same order of magnitude (800 t P yr$^{-1}$). Assuming a mass N:P ratio of 4 in atmospheric deposits (Lewis, 1981), the estimated TP deposition translate to 330 to 1,500 t N yr$^{-1}$ for ITT, which is well within the error range of N inputs.

3.5.2 Future scenarios

In a next step, we used RES1 to simulate changes in the output loads of OC, N, and P, if a maximum of 306 m$^3$ s$^{-1}$ of discharge are diverted through turbines, as suggested for ITT in the near future (Figure 3.2). Model runs incorporating these additional hypolimnetic water releases predict substantial changes in the outflow loads (Figure 3.9). For the simulation period 2008/2009, spillage would only occur between February and June, whereas the entire discharge would be turbinated during the remaining months (Figure 3.2). As $\sim$60% of the annual outflow is discharged through turbines in this scenario, the downstream water quality is determined to a great extent by the characteristics of hypolimnetic water. Riverine DO levels downstream of the dam will therefore be determined by the decreasing concentrations in the hypolimnion (Figure 3.6b). Model runs indicate that DO concentrations of $<1$ mg l$^{-1}$ may persist during several weeks prior to the opening of the spillways in February (Figure 3.2). In terms of autochthonous OC, whose suspended fraction is predominantly present in the trophogenic zone, the proportions of output loads relative

![Figure 3.9: Simulated outputs of OC, DIN and SRP in the current situation (left) and in future with Itezhi-Tezhi dam releasing bottom water through the turbines (right).](image-url)
3.6 Conclusions

Our observations in Itezhi-Tezhi reservoir (ITT) illustrate the potential of this moderate-sized reservoir (hydraulic residence time $\sim0.7$ yr) to substantially influence the transport of sediment, carbon (C) and nutrients from land to ocean by removing particulate matter and modifying biogeochemical cycles. ITT removed $\sim60\%$ of phosphorus and $\sim50\%$ of fixed nitrogen from riverine mass transport to the downstream Kafue Flats floodplain.

The biogeochemical model, RES1, provided important insights into reservoir-internal cycling. Simulation results suggest that the formation of ITT has substantially increased primary production, fixing large amounts of C (comparable to allochthonous inputs) and incorporating nutrients into autochthonous organic matter (OM). Since the availability of nutrients is generally low, N fixation was an important process, needed to explain $\sim30\%$ of total primary production. Model results suggest that internal turnover of autochthonous OM is fast, and therefore only a small proportion of autochthonous OM was lost through the outflow ($<20\%)$. Hence, $>80\%$ of autochthonous OM in ITT was buried in the sediment, or mineralized yielding CO$_2$ and CH$_4$, and N$_2$ by denitrification. Consequently, OC and TN that exit ITT may be primarily allochthonous OC and ON that were flushed through the system without undergoing substantial processing within the reservoir. Future investigations in (sub)tropical reservoirs should focus on the composition of OM entering and leaving the system, and assess the extent to which different OM pools (e.g., dissolved versus particulate, and labile versus refractory) are processed within the reservoir or augmented by autochthonous OM.

Simulation results of the effect of future operating rules at ITT, namely bottom water withdrawal through turbines at Itezhi-Tezhi Dam replacing surface water spillage, suggest that there will be substantial changes in the quality of discharged water. Low-DO levels will occur in discharge water over prolonged periods. In addition, 4- and 2-fold higher output loads of DIN and SRP and 27% lower loads of OC are predicted. Hence, substan-
tially altered downstream water quality, which may have negative effects on vulnerable ecosystems, has to be taken into account in general when evaluating changes in the dam management strategy.

3.7 Acknowledgements

Funding for this project was provided by the Competence Center Environment and Sustainability (CCES) for the ADAPT project and by Eawag. We thank the staff of the Zambia Electricity Supply Company (ZESCO) Elenestina Mwelwa and Collins Nzovu at Lusaka and Moses Mbuta and Moses Mulambe at Itezhi-Tezhi for logistical assistance, Imasiku Nyambe (UNZA) for supporting ADAPT in general and A. Wüest during his sabbatical, and the Eawag staff Christian Dinkel, Roland Zurbrügg, Jason Wamulume, Jeremias Fellmann, Ruth Stierli, Adrian Vollenweider, Silvan Thüring, Daniel Ineichen, Leticia Stojkovski, Gijs Nobbe, and Alois Zwyssig for field and laboratory assistance. We also thank Martin Schmid for modeling support.
3.8 Appendix

3.8.1 Supplementary figures

Figure B.1: Photographs of collected sediment cores from stations IT4 (Musa River) to IT1 (Itezhi-Tezhi Dam) and IT9 (Kafue River; Figure 3.1). The red dotted lines illustrate the transition depth in lacustrine cores dividing pre- (right) and post-dam (left) sediment regimes. Pictures were taken within one hour after core opening to prevent oxidation of the sediment surfaces. Note that the wet sediment surfaces caused reflections.
Figure B.2: Depth profiles of all cores illustrating downcore and lake-wide variation in WBD, C:N, δ^{13}C, OC, TN and TP.
Figure B.3: Transect of temperature profiles from the dam site (IT1) to the Musa River inflow (IT29; by row) recorded in October 2008.

Figure B.4: Transect of dissolved oxygen profiles from the dam site (IT1) to the Musa River inflow (IT29; by row) recorded in October 2008.
Figure B.5: Transect of temperature profiles from the dam site (IT1) to the Kafue River inflow (IT38; by row) recorded in November 2008.

Figure B.6: Transect of dissolved oxygen profiles from the dam site (IT1) to the Kafue River inflow (IT38; by row) recorded in November 2008.
3.8. Appendix

![Phytoplankton and Chl-a Concentration](image)

Figure B.7: Simulated phytoplankton concentration (at 2 m depth) illustrating a phytoplankton bloom in the rainy season (November to March). Phytoplankton concentration follows the temporal pattern of chlorophyll-a concentration measured by Obrdlik et al. (1989) in 1983 to 1985 with the exception of June and July data points.

### 3.8.2 Supplementary table

<table>
<thead>
<tr>
<th>Field campaign</th>
<th>Stations measured and sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water column</td>
</tr>
<tr>
<td>Feb 2007</td>
<td>IT1, IT8</td>
</tr>
<tr>
<td>Jul 2007</td>
<td>IT1, IT20</td>
</tr>
<tr>
<td>Apr 2008</td>
<td>HB(^b), K1(^c)</td>
</tr>
<tr>
<td>May 2008</td>
<td>IT1, IT2, IT4, IT6, IT7, IT8, IT11, HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Jun 2008</td>
<td>IT1, HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Aug 2008</td>
<td>HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Sep 2008</td>
<td>K1(^c)</td>
</tr>
<tr>
<td>Oct 2008</td>
<td>IT1, HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Nov 2008</td>
<td>IT1</td>
</tr>
<tr>
<td>Dec 2008</td>
<td>IT1, HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Jan 2009</td>
<td>IT1</td>
</tr>
<tr>
<td>Feb 2009</td>
<td>IT1, IT2, IT4, IT6, IT7, IT8, HB(^b), K1(^c)</td>
</tr>
<tr>
<td>Jun 2009</td>
<td>IT1, IT7, IT12</td>
</tr>
</tbody>
</table>

\(^a\) Names of sampling sites refer to the stations mapped in Figure 3.1

\(^b\) Kafue River at Hook Bridge

\(^c\) Kafue River below Itezhi-Tezhi dam.
3.8.3 Extended methods: Sedimentation model

The exponential increase of sediment accumulation rates \( S_{\text{acc}} \) from Itezhi-Tezhi Dam to the Kafue River mouth and the almost constant sediment accumulation rates from the dam to the Musa River mouth were used to estimate total particle loading to Itezhi-Tezhi reservoir’s (ITT) sediment (Figure 3.4). Assuming lower accumulation rates in shallower and littoral areas, we allowed \( S_{\text{acc}} \) to vary as a function of depth within each sector: for depths \( > 20 \text{ m} \) (base of epilimnion), \( S_{\text{acc}} \) was set to the value obtained from sediment core(s) within each sector. Over the depth range 0 to 20 m, \( S_{\text{acc}} \) increased linearly with depth, from 0 at depth = 0 m up to the core-based \( S_{\text{acc}} \). Based on these two assumptions, \( S_{\text{acc}} \) varying with distance from the dam and with depth was integrated discretely over the 16 areal sectors that were defined based on locations of sediment cores and the bathymetry (Figure 3.1).

3.8.4 Biogeochemical model

Physical model

The numerical model used in the present study is based on the model developed by Omlin et al. (2001a). Similar to the original model, the lake is conceptually separated into epi-, meta- and hypolimnion characterized by different vertical diffusion coefficients \((K_z)\). The seasonally varying depth and thickness of the metalimnion was adapted from measured temperature (T) profiles (Figure 3.5). A typical high \( K_z \) is assigned to the epilimnion for the entire simulation period \((200 \text{ m}^2 \text{ d}^{-1})\). During the stratified period, a small \( K_z \) was assigned for the metalimnion \((0.11 \text{ m}^2 \text{ d}^{-1})\). The \( K_z \) of the hypolimnion \((1.44 \text{ m}^2 \text{ d}^{-1})\) was determined with the help of the heat-budget method. The mixing period between mid-June and mid-July was defined based on available thermistor data (Figure 3.6c), during which the epilimnetic \( K_z \) is assigned to the entire water column. T is modeled by adopting the measured epilimnion T, whereas T below is simulated based on the \( K_z \)s in the different layers.

Other physical processes, such as gas exchange with the atmosphere, particle settling, and light extinction are according to Omlin et al. (2001a). For light extinction, the solar radiation at surface was averaged from long-term measurements from Lusaka airport (World Radiation Data Centre (WRDC), http://wrdc-mgo.nrel.gov/). Finally, inflows and outflows were based on measurements by ZESCO (unpublished data, 2009).
Biogeochemical model

As in Mieleitner and Reichert (2006), our model incorporates phytoplankton and zooplankton growth, respiration and death, aerobic, anoxic (i.e., nitrate (NO$_3^-$) reduction), and anaerobic (i.e., summarizing other electron acceptors than oxygen and NO$_3^-$) mineralization of organic material, nitrification, and phosphate (HPO$_4^{2-}$) removal by adsorption to organic particles (Tables B.2–B.5). The assumption of NO$_3^-$ becoming never limiting for phytoplankton growth does not hold true for ITT, being a generally nutrient poor system. This has two important implications: (i) phytoplankton growth on ammonium (NH$_4^+$) cannot be favored over growth of NO$_3^-$, since the lack of a monod-type process limitation dependent of the NO$_3^-$ concentration leads to negative NO$_3^-$ concentrations in the model when NO$_3^- < NH_4^+$ (see Mieleitner and Reichert, 2006). We therefore kept the two related process rates uncoupled (Table B.3). (ii) Nitrogen (N) fixation is likely to become important under N limiting conditions. We also adopted the simple process described by Kiirikki et al. (2001) that simulates atmospheric N$_2$ fixation by allowing phytoplankton growth independent of an N input (Table B.3).

In order to meet our goal to evaluate the fate and effect of both autochthonous and allochthonous OM, and due to the high inputs of allochthonous OM to ITT reservoir with presumably different composition, these two species were modeled as separate state variables (Table B.2). Consequently, their transformation in the lake had to be implemented in individual processes (Table B.3). In contrast to autochthonous OM, whose P content varied between 0.0014 and 0.0087 g P (g DM)$^{-1}$ depending on P availability, the P content of allochthonous OM was kept constant at 0.0087 g P (g DM)$^{-1}$ (Table B.4). This parameter, as well as the 0.017 g N (g DM)$^{-1}$ for both allochthonous and autochthonous OM, determined the release of NH$_4^+$ and HPO$_4^{2-}$ during mineralization in the water column and at the sediment water interface (Tables B.3 and B.4).

Following the approach by Matzinger et al. (2007b), we excluded an explicit sediment compartment as described by Omlin et al. (2001a), and limited mineralization processes to the sediment-water interface. To account for burial, we applied constant ratios for organic matter (OM) becoming inert. In the case of autochthonous OM, this ratio was estimated from sediment core and trap data resulting in a burial efficiency (BE) of 55% ($= 1 - \alpha_{miner,auto}$, Table B.4). For allochthonous OM, which is likely to be more refractory than autochthonous OM, we assumed a BE of 92% to match estimated allochthonous sediment accumulation ($= 1 - \alpha_{miner,allo}$, Table B.4). Based on this BE, together with the estimated inflow concentration of allochthonous OM, the net allochthonous OM sedimentation in the model matched estimated loads to the sediment.
Table B.2: State variables in the model adopted from Omlin et al. (2001a)

<table>
<thead>
<tr>
<th>State variable</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved species</td>
<td></td>
</tr>
<tr>
<td>$S_{NH_4}$</td>
<td>g N m$^{-3}$</td>
<td>Ammonium-N</td>
</tr>
<tr>
<td>$S_{NO_3}$</td>
<td>g N m$^{-3}$</td>
<td>Nitrate-N</td>
</tr>
<tr>
<td>$S_{HPO_4}$</td>
<td>g P m$^{-3}$</td>
<td>Phosphate-P</td>
</tr>
<tr>
<td>$S_{O_2}$</td>
<td>g O m$^{-3}$</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td></td>
<td>Particulate species</td>
<td></td>
</tr>
<tr>
<td>$X_{ALG}$</td>
<td>g DM m$^{-3}$</td>
<td>Algae (excluding algal P)</td>
</tr>
<tr>
<td>$X_{P,ALG}$</td>
<td>g P m$^{-3}$</td>
<td>Organic P in algae</td>
</tr>
<tr>
<td>$X_{ZO0}$</td>
<td>g DM m$^{-3}$</td>
<td>Zooplankton</td>
</tr>
<tr>
<td>$X_S$</td>
<td>g DM m$^{-3}$</td>
<td>Biodegradable dead OM</td>
</tr>
<tr>
<td>$X_I$</td>
<td>g DM m$^{-3}$</td>
<td>Inert dead OM</td>
</tr>
<tr>
<td>$X_{P,S}$</td>
<td>g P m$^{-3}$</td>
<td>Organic P in biodegradable dead OM</td>
</tr>
<tr>
<td>$X_{P,I,S}$</td>
<td>g P m$^{-3}$</td>
<td>Organic P in inert dead OM</td>
</tr>
<tr>
<td>$X_{P,I}$</td>
<td>g P m$^{-3}$</td>
<td>Phosphate adsorbed to $X_S$</td>
</tr>
<tr>
<td>$X_{S,allo}^a$</td>
<td>g DM m$^{-3}$</td>
<td>Allochthonous, biodegradable dead OM</td>
</tr>
</tbody>
</table>

$^a$ not included in the original model by Omlin et al. (2001a).

Initial model runs revealed that mineralization of allochthonous and autochthonous OM could not account for the observed dissolved oxygen (DO) depletion. This mismatch could not be resolved by increasing the respective mineralization rates or the input concentrations, as this would have led to too high concentrations of dissolved nutrients ($NH_4^+$, $NO_3^-$, $HPO_4^{2-}$) in the hypolimnion. Consequently, we assumed that the observed DO demand originates from reduced substances (i.e., $NH_4^+$, $CH_4$, $S(-II)$, and reduced metals). These substances most likely result from mineralization of older deposits of OM (either relatively refractory allochthonous OM, or buried autochthonous OM). This concept is in line with the multi-G model for the varying susceptibility of OM to degradation (Berner, 1980; Westrich and Berner, 1984). In the present model, the process “background mineralization” simulates the oxidation of reduced substances by consuming oxygen (Tables B.3 and B.5). Hence, the reduced substances are modeled indirectly by their exerted DO demand.

We assumed that relatively refractory allochthonous OM contributed to the greatest extent to background mineralization. Since these contributions are likely to be larger in the more shallow zones of the reservoirs (e.g., in deltas close to inflows), we expected the mineralization rate to vary with depth. We assumed a maximum background mineralization near the surface, and a minimum at the bottom. Multiplication of the areal background mineralization rate with the ratio of the incremental depth-dependent sediment surface...
to the incremental water volume resulted in the volumetric process rate ($k_{\text{miner}, \text{bg}}$, Table B.5).

Model calibration

The model was calibrated iteratively by systematically changing parameter values. We adjusted the model in the following hierarchical order: vertical mixing, DO depletion, dissolved nutrient release, net sediment accumulation, outflow losses, and mineralization rates. Hence, we first adjusted the epilimnetic and metalimnetic $K_z$, before adjusting parameters affecting biogeochemical processes (see Table B.6).
Table D.3: Biochemical processes with stoichiometric coefficients for all state variables

Not included in the original model by Quillan et al. (2001a)

Allochthonous algae = allochthonous algae = autotrophic algae. ALT = autochthonous, ALG = autotrophic. N, H, = water column, sed = sediment water surface, miner = background mineralization.

<table>
<thead>
<tr>
<th>Process</th>
<th>P,red</th>
<th>P,S</th>
<th>N,red</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anoxic P,red</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anoxic Mineralization of autochthonous OM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anoxic Respiration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anoxic Death</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anoxic ALG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P,red Mineralization of autochthonous OM</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P,red Respiration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P,red Death</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P,red ALG</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Not included in the original model by Quillan et al. (2001a)
Table B.4: Stoichiometric coefficients of biogeochemical processes (Table B.3; adopted from Omlin et al., 2001a)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Expression, value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_N$</td>
<td>0.063</td>
<td>g N (g DM)$^{-1}$</td>
<td>Ratio of organic N in OM (Redfield)</td>
</tr>
<tr>
<td>$a_{N,\min}$</td>
<td>0.017$^a$</td>
<td>g N (g DM)$^{-1}$</td>
<td>Ratio of organic N released by mineralization</td>
</tr>
<tr>
<td>$a_{P,\text{red}}$</td>
<td>0.0087</td>
<td>g P (g DM)$^{-1}$</td>
<td>Ratio of organic P in OM (Redfield)</td>
</tr>
<tr>
<td>$a_{P,\text{ALG}}$</td>
<td>$X_{P,\text{ALG}} \cdot (X_{\text{ALG}})^{-1}$</td>
<td>g P (g DM)$^{-1}$</td>
<td>Ratio of organic P in algae</td>
</tr>
<tr>
<td>$a_{P,S}$</td>
<td>$X_{P,S} \cdot (X_{S})^{-1}$</td>
<td>g P (g DM)$^{-1}$</td>
<td>Ratio of organic P in degradable dead OM</td>
</tr>
<tr>
<td>$a_{P,I}$</td>
<td>$X_{P,I} \cdot (X_{I})^{-1}$</td>
<td>g P (g DM)$^{-1}$</td>
<td>Ratio of organic P in inert dead OM</td>
</tr>
<tr>
<td>$b_P$</td>
<td>$b_{P,\text{min}} + \frac{b_{P,\text{max}} - b_{P,\text{min}}}{2} \cdot \tanh \left( \frac{S_{\text{HPO}<em>4} - S</em>{\text{HPO}<em>4,\text{crit}}}{\Delta S</em>{\text{HPO}_4}} \right)$</td>
<td>g P (g DM)$^{-1}$</td>
<td>P uptake by algae</td>
</tr>
<tr>
<td>$b_{P,\text{min}}$</td>
<td>0.0014</td>
<td>g P (g DM)$^{-1}$</td>
<td>Minimum P uptake by algae</td>
</tr>
<tr>
<td>$b_{P,\text{max}}$</td>
<td>0.0087</td>
<td>g P (g DM)$^{-1}$</td>
<td>Maximum P uptake by algae</td>
</tr>
<tr>
<td>$S_{\text{HPO}_4,\text{crit}}$</td>
<td>0.0042</td>
<td>g P m$^{-3}$</td>
<td>Threshold for reduced-P production</td>
</tr>
<tr>
<td>$\Delta S_{\text{HPO}_4}$</td>
<td>0.00125</td>
<td>g P m$^{-3}$</td>
<td>Parameter for reduced-P production</td>
</tr>
<tr>
<td>$f_P$</td>
<td>0.1</td>
<td>–</td>
<td>Fraction of organisms becoming inert during death</td>
</tr>
<tr>
<td>$Y_{\text{ZOO}}$</td>
<td>$Y_{\text{ZOO, \max}} \cdot \min \left( 1, \frac{a_{P,\text{ALG}}}{a_{P,\text{red}}} \right)$</td>
<td>–</td>
<td>Yield during zooplankton growth</td>
</tr>
<tr>
<td>$Y_{\text{ZOO, \max}}$</td>
<td>0.5</td>
<td>–</td>
<td>Maximum yield during zooplankton growth</td>
</tr>
<tr>
<td>$f_e$</td>
<td>$c_e (1 - Y_{\text{ZOO}})$</td>
<td>–</td>
<td>Fraction of unused food during zooplankton growth</td>
</tr>
<tr>
<td>$c_e$</td>
<td>0.7</td>
<td>–</td>
<td>Fraction of unused food during zooplankton growth</td>
</tr>
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<td>$\nu_{\text{ZOO}, N}$</td>
<td>$a_N \left( \frac{1 - Y_{\text{ZOO}}}{Y_{\text{ZOO}} - 1} \right)$</td>
<td>g N (g DM)$^{-1}$</td>
<td>Stoichiometric coefficient of N in zooplankton</td>
</tr>
<tr>
<td>$\nu_{\text{ZOO}, P}$</td>
<td>$a_{P,\text{ALG}} - a_{P,\text{red}}$</td>
<td>g P (g DM)$^{-1}$</td>
<td>Stoichiometric coefficient of P in zooplankton</td>
</tr>
<tr>
<td>$\nu_{\text{ZOO}, O}$</td>
<td>0.93 $\left( \frac{1 - f_e}{Y_{\text{ZOO}} - 1} \right)$</td>
<td>g O (g DM)$^{-1}$</td>
<td>Stoichiometric coefficient of O in zooplankton</td>
</tr>
</tbody>
</table>

$^a$ not included in the original model by Omlin et al. (2001a).
Table B.5: Rates of biogeochemical processes (Table B.3; adopted from Omlin et al., 2001a)

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Growth</strong></td>
<td></td>
</tr>
<tr>
<td>ALG&lt;sub&gt;NO3&lt;/sub&gt;</td>
<td>( k_{\text{groe}, \text{ALG}, 20} \cdot \exp (\beta_{\text{ALG}} (T - T_0)) \cdot X_{\text{ALG}} \cdot \min (\frac{\text{NO3, ALG} + \text{NO3}}{\text{NO3}}, \frac{\text{NH4, ALG} + \text{NH4}}{\text{NH4}}) \cdot X_{\text{ALG}} )</td>
</tr>
<tr>
<td>ALG&lt;sub&gt;NH4&lt;/sub&gt;</td>
<td>( k_{\text{groe}, \text{ALG}, 20} \cdot \exp (\beta_{\text{ALG}} (T - T_0)) \cdot X_{\text{ALG}} \cdot \min (\frac{\text{NH4, ALG} + \text{NH4}}{\text{NH4}}) \cdot X_{\text{ALG}} )</td>
</tr>
<tr>
<td>ALG&lt;sub&gt;N2&lt;/sub&gt;</td>
<td>( k_{\text{groe}, \text{ALG}, 20} \cdot \exp (\beta_{\text{ALG}} (T - T_0)) \cdot X_{\text{ALG}} \cdot \min (\frac{\text{N2, ALG} + \text{N2}}{\text{N2}}) \cdot X_{\text{ALG}} )</td>
</tr>
<tr>
<td>ZOO</td>
<td>( k_{\text{groe}, \text{ZOO}, 20} \cdot \exp (\beta_{\text{ZOO}} (T - T_0)) \cdot X_{\text{ZOO}} \cdot \min (\frac{\text{N2, ALG} + \text{N2}}{\text{N2}}) \cdot X_{\text{ZOO}} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Respiration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ALG</td>
<td>( k_{\text{resp}, \text{ALG}, 20} \cdot \exp (\beta_{\text{ALG}} (T - T_0)) \cdot X_{\text{ALG}} )</td>
</tr>
<tr>
<td>ZOO</td>
<td>( k_{\text{resp}, \text{ZOO}, 20} \cdot \exp (\beta_{\text{ZOO}} (T - T_0)) \cdot X_{\text{ZOO}} )</td>
</tr>
</tbody>
</table>

| Death | |
| ALG | \( k_{\text{death}, \text{ALG}, 20} \cdot \exp (\beta_{\text{ALG}} (T - T_0)) \cdot X_{\text{ALG}} \) |
| ZOO | \( k_{\text{death}, \text{ZOO}, 20} \cdot \exp (\beta_{\text{ZOO}} (T - T_0)) \cdot X_{\text{ZOO}} \) |

**Mineralization of autochthonous OM**

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerowat</td>
<td>( k_{\text{miner, aerowat}} \cdot \exp (\beta_{\text{aerowat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
<tr>
<td>Anoxwat</td>
<td>( k_{\text{miner, anoxwat}} \cdot \exp (\beta_{\text{anoxwat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
<tr>
<td>Anaerwat</td>
<td>( k_{\text{miner, anaerwat}} \cdot \exp (\beta_{\text{anaerwat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
<tr>
<td>Aeroc集团公司</td>
<td>( k_{\text{miner, aeroc集团公司}} \cdot \exp (\beta_{\text{aeroc集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
<tr>
<td>Anox集团公司</td>
<td>( k_{\text{miner, anox集团公司}} \cdot \exp (\beta_{\text{anox集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
<tr>
<td>Anaer集团公司</td>
<td>( k_{\text{miner, anaer集团公司}} \cdot \exp (\beta_{\text{anaer集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, autowat}} )</td>
</tr>
</tbody>
</table>

**Mineralization of allochthonous OM**

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerowat</td>
<td>( k_{\text{miner, aerowat}} \cdot \exp (\beta_{\text{aerowat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Anoxwat</td>
<td>( k_{\text{miner, anoxwat}} \cdot \exp (\beta_{\text{anoxwat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Anaerwat</td>
<td>( k_{\text{miner, anaerwat}} \cdot \exp (\beta_{\text{anaerwat}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Aeroc集团公司</td>
<td>( k_{\text{miner, aeroc集团公司}} \cdot \exp (\beta_{\text{aeroc集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Anox集团公司</td>
<td>( k_{\text{miner, anox集团公司}} \cdot \exp (\beta_{\text{anox集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Anaer集团公司</td>
<td>( k_{\text{miner, anaer集团公司}} \cdot \exp (\beta_{\text{anaer集团公司}} (T - T_0)) \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
</tbody>
</table>

**Miscellaneous**

<table>
<thead>
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<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miner&lt;sub&gt;bg&lt;/sub&gt;</td>
<td>( k_{\text{miner, bg}} \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
<tr>
<td>Nitrification</td>
<td>( k_{\text{nitrification}} \cdot \exp (\beta_{\text{nitrification}} (T - T_0)) \cdot \min (\frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}}) )</td>
</tr>
<tr>
<td>P-uptake</td>
<td>( k_{\text{uptake}} \cdot \frac{\text{S}_2}{\text{O}_2} \cdot \frac{\text{NO3, miner} + \text{NO3}}{\text{NO3}} \cdot \frac{1}{\text{S}_2/\text{O}<em>2} \cdot X</em>{\text{miner, allop}} )</td>
</tr>
</tbody>
</table>

---

<sup>a</sup> Abbreviations: allo = allochthonous, auto = autochthonous, ALG = algae, ZOO = zooplankton, Aero = aerobic, Anox = anoxic, Anaer = anaerobic, wat = water column, sed = sediment water surface, Miner<sub>bg</sub> = background mineralization

<sup>b</sup> Light intensity with depth (see Omlin et al., 2001a)

<sup>c</sup> from Matzinger et al. (2007b)

<sup>d</sup> not included in the original model by Omlin et al. (2001a).
### Table B.6: Physical and kinetic parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{\text{miner,allo}}$</td>
<td>0.08</td>
<td>–</td>
<td>Fraction of allochthonous OM becoming mineralized</td>
</tr>
<tr>
<td>$a_{\text{miner,auto}}$</td>
<td>0.55</td>
<td>–</td>
<td>Fraction of autochthonous OM becoming mineralized</td>
</tr>
<tr>
<td>$\beta_{\text{ALG}}$</td>
<td>0.05</td>
<td>°C⁻¹</td>
<td>Temperature dependency of algae</td>
</tr>
<tr>
<td>$\beta_{\text{BAC}}$</td>
<td>0.05</td>
<td>°C⁻¹</td>
<td>Temperature dependency of mineralizing bacteria</td>
</tr>
<tr>
<td>$\beta_{\text{ZOO}}$</td>
<td>0.08</td>
<td>°C⁻¹</td>
<td>Temperature dependency of zooplankton</td>
</tr>
<tr>
<td>$k_{\text{death,ALG,20}}$</td>
<td>0.01</td>
<td>d⁻¹</td>
<td>Rate constant at 20°C</td>
</tr>
<tr>
<td>$k_{\text{death,ZOO,20}}$</td>
<td>0.1</td>
<td>d⁻¹</td>
<td>Rate constant at 20°C</td>
</tr>
<tr>
<td>$k_{\text{growth,ALG,20}}$</td>
<td>1.1</td>
<td>d⁻¹</td>
<td>Growth rate constant of algae at 20°C</td>
</tr>
<tr>
<td>$k_{\text{growth,ZOO,20}}$</td>
<td>0.25</td>
<td>d⁻¹</td>
<td>Growth rate constant of N fixers at 20°C</td>
</tr>
<tr>
<td>$k_{\text{miner,aero,20}}$</td>
<td>0.1</td>
<td>d⁻¹</td>
<td>Aerobic mineralization rate at 20°C</td>
</tr>
<tr>
<td>$k_{\text{miner,anox,20}}$</td>
<td>0.01</td>
<td>d⁻¹</td>
<td>Anoxic mineralization rate at 20°C</td>
</tr>
<tr>
<td>$k_{\text{miner,anae,20}}$</td>
<td>0.001</td>
<td>d⁻¹</td>
<td>Anaerobic mineralization rate at 20°C</td>
</tr>
<tr>
<td>$k_{\text{resp,ALG,20}}$</td>
<td>0.05</td>
<td>d⁻¹</td>
<td>Respiration rate of algae at 20°C</td>
</tr>
<tr>
<td>$k_{\text{resp,ZOO,20}}$</td>
<td>0.003</td>
<td>d⁻¹</td>
<td>Respiration rate of zooplankton at 20°C</td>
</tr>
<tr>
<td>$K_{\text{HPO4,ALG}}$</td>
<td>0.002</td>
<td>g P m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{NO3,ALG}}$</td>
<td>0.04</td>
<td>g N m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{ALG}}$</td>
<td>34.32</td>
<td>W m⁻²</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{NH4,nitri}}$</td>
<td>1</td>
<td>g N m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{O2,nitri}}$</td>
<td>1</td>
<td>g O m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{NO3,miner}}$</td>
<td>0.1</td>
<td>g N m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{O2,miner}}$</td>
<td>0.05</td>
<td>g O m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{O2,resp}}$</td>
<td>0.5</td>
<td>g O m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$K_{\text{O2,upt}}$</td>
<td>0.5</td>
<td>g O m⁻³</td>
<td>Half saturation concentration</td>
</tr>
<tr>
<td>$v_{\text{sed,ALG}}$</td>
<td>0.2</td>
<td>m d⁻¹</td>
<td>Settling velocity of algae</td>
</tr>
<tr>
<td>$v_{\text{sed,ORG}}$</td>
<td>10</td>
<td>m d⁻¹</td>
<td>Settling velocity of OM</td>
</tr>
</tbody>
</table>

---

*a* Abbreviations: allo = allochthonous, auto = autochthonous, ALG = algae, ZOO = zooplankton, Aero = aerobic, Anox = anoxic, Anae = anaerobic

*b* altered from initial values by Omlin et al. (2001a).
Chapter 4

Spatial heterogeneity of methane ebullition in a large tropical reservoir

Tonya DelSontro, Manuel J. Kunz, Tim Kempter, Alfred Wüest,
Bernhard Wehrli, David B. Senn
submitted to Environmental Science and Technology, under revision
Abstract

Tropical reservoirs have been identified as important methane (CH$_4$) sources to the atmosphere, primarily through turbine and downstream degassing. However, the importance of ebullition (gas bubbling) remains unclear. We hypothesized that ebullition is a disproportionately large CH$_4$ source from reservoirs with dendritic littoral zones because of ebullition hot spots occurring where rivers supply allochthonous organic material. We explored this hypothesis in Lake Kariba (Zambia/Zimbabwe; surface area $>$ 5,000 km$^2$) by surveying ebullition in bays with and without river inputs using an echosounder and traditional surface chambers. The two techniques yielded similar results, and revealed substantially higher fluxes in river deltas ($\sim$10$^3$ mg CH$_4$ m$^{-2}$ d$^{-1}$) compared to non-river bays (< 100 mg CH$_4$ m$^{-2}$ d$^{-1}$). Hydroacoustic measurements resolved at 5-m intervals showed that flux events varied over several orders of magnitude (up to 10$^5$ mg CH$_4$ m$^{-2}$ d$^{-1}$), and also identified strong differences in ebullition frequency. Both factors contributed to emission differences between all sites. A CH$_4$ mass balance for the deepest basin of Lake Kariba indicated that hot spot ebullition was the largest atmospheric emission pathway, suggesting that future greenhouse gas budgets for tropical reservoirs should include a spatially well-resolved analysis of ebullition hot spots.

Keywords Bubble plumes, methane emission, methane mass balance, greenhouse gas, echosounder

4.1 Introduction

Inland waters are quantitatively important biogeochemical reactors that store, transform, and emit carbon as it travels from terrestrial ecosystems to the ocean (Cole et al., 2007). The construction of > 800,000 dams over the past century has reduced sediment loads to the oceans by $\sim$50% (Vörösmarty et al., 2003), and consequently retained and transformed substantial amounts of organic carbon that would have previously reached the ocean (Syvitski et al., 2005; Tranvik et al., 2009). In the anoxic, organic-rich, and sulfate-poor sediments of both lakes and reservoirs, 10 to 50% of organic carbon mineralization occurs via production of the potent greenhouse gas, methane (CH$_4$) (Bastviken et al., 2008). Recent estimates suggest that lakes, a previously underappreciated source of CH$_4$, account for 10 to 15% of natural CH$_4$ emissions to the atmosphere (Bastviken et al., 2004). Reservoirs have been suggested to be a substantial anthropogenic emission source (St. Louis et al., 2000) although more attention is needed to establish pre-dam emissions...
and assess the net increases in CH$_4$ emissions (dos Santos et al., 2006). Improving our understanding of CH$_4$ emissions from tropical reservoirs is particularly important since estimates based on limited data indicate that their contribution may dominate global reservoir emissions (St. Louis et al., 2000). Methane produced in anoxic layers of lake and reservoir sediments can experience multiple potential fates, beginning with oxidation of a portion of the upward diffusing CH$_4$ at the sediment oxic-anoxic interface (Frenzel et al., 1990). When sediments are overlain by anoxic bottom waters in stratified basins, CH$_4$ diffuses freely from the sediments into the water column, typically accumulating to concentrations in the µM range (Guérin et al., 2007). During seasonal deep mixing of stratified lakes, CH$_4$ stored in the anoxic hypolimnion may undergo oxidation during the gradual deepening of the thermocline (Schubert et al., 2010). Alternatively, CH$_4$ may mix into the epilimnion, where it can undergo oxidation or diffusive exchange to the atmosphere across the air-water interface (Bastviken et al., 2008; Guérin and Abril, 2007; Schubert et al., 2010). Ebullition, the efflux of CH$_4$-rich bubbles from sediment porewaters supersaturated with CH$_4$, results in the rapid release of CH$_4$ from sediments. As these bubbles rise, some CH$_4$ dissolves into the water column, the fraction of which is determined by the depth of bubble release, initial bubble size, temperature, and gaseous concentrations in ambient water (McGinnis et al., 2006). If the bubble reaches the surface, the remaining gaseous CH$_4$ will cross the air-water interface. Under certain conditions (e.g., strongly reducing sediments, shallow water column), ebullition can be an efficient and potentially dominant CH$_4$ source to the atmosphere.

CH$_4$ ebullition in lakes and reservoirs has recently received much attention (McGinnis et al., 2006; Ostrovsky, 2003); however, the episodic and stochastic nature of CH$_4$ ebullition complicates the analysis of fluxes (Soumis et al., 2005). Measuring ebullition in lakes has traditionally been a matter of capturing bubbles by deploying relatively small (< 1 m$^2$) surface floating chambers or funnels (Bastviken et al., 2004; DelSontro et al., 2010). This approach provides a coarse estimate of ebullition flux derived from a small measured area, and typically provides only limited depth-related information regarding the spatial variability of ebullition. As a result, the spatial distribution of ebullition has not been systematically studied, but has been generalized as a mostly depth-dependent phenomenon (Bastviken et al., 2004; Gunkel, 2009). Recent studies have demonstrated the use of hydroacoustic (sonar) techniques for the precise identification of ebullition zones in water bodies (Vagle et al., 2010). After calibration against bubbles of known size, and combined with data on CH$_4$ concentration in bubbles, hydroacoustic measurements can also be used to quantify real-time ebullition volume and flux (Ostrovsky et al., 2008).

The high loadings and rapid burial of organic matter that occur in river deltas may foster high rates of CH$_4$ production (DelSontro et al., 2010; Kelly and Chynoweth, 1981). The
relatively shallow depth and lower hydrostatic pressure in these areas facilitate the forma-
tion and release of bubbles from sediments, and the shorter travel path to the atmosphere
limits bubble dissolution. Therefore, we hypothesized that deltaic zones in reservoirs or
lakes could act as important hot spots for CH$_4$ ebullition. Exploring this issue in tropical
reservoirs is of particular importance given the lack of knowledge regarding this emission
pathway and the fact that they are considered the major CH$_4$ emitter among global im-
poundments (Soumis et al., 2005). The continued push for more hydropower development
in areas such as Sub-Saharan Africa (Bartle, 2002) and growing recognition that environ-
mental impacts of new reservoirs should be better mitigated (World Commission on Dams,
2000) further support the need for more information regarding CH$_4$ dynamics in existing
reservoirs.

We explored the “deltaic-zone” hypothesis by performing hydroacoustic and floating
chamber surveys in shallow embayments with and without river inlets in one of Africa’s
largest reservoirs, Lake Kariba (Figure C.1, available as auxiliary material in Section 4.5.1).
We quantified various CH$_4$ emission pathways with a particular focus on ebullition and
its spatial distribution, and compared results from the traditional chamber technique and
hydroacoustic surveys. We also used the high spatial resolution afforded by hydroacoustic
measurements to examine the characteristics of ebullition that contribute to the average
differences seen between study sites. Additionally, we compared the relative importance of
bubble emissions to the atmosphere with other pathways and, finally, placed Lake Kariba
emissions in context with other large tropical reservoirs.

4.2 Experimental

4.2.1 Study site

Lake Kariba, located along the border of Zambia and Zimbabwe (Figure C.1), is one of
the largest reservoirs worldwide (Coche, 1974) with a surface area of 5,400 km$^2$, volume
of 160 km$^3$, and maximum depth of 97 m. The highly dendritic shoreline consists of 66%
unexposed bays and river inflows (Coche, 1974). While the Zambezi River is the main
inflow of Lake Kariba, dozens of smaller rivers contribute $\sim$20% of the total inflow and
the Sanyati River alone represents $\sim$8% (Marshall, 1988). Despite their low share on total
inflow, secondary rivers contribute substantially to the overall input of organic matter and
nutrients to Lake Kariba and are therefore an important factor in determining its produc-
tivity (Coche, 1974). Although a high initial productivity was reported in Lake Kariba
(Coche, 1974), it is now considered quite oligotrophic (Marshall, 1988), and stratifies for at
least 10 months per year with turnover occurring in late July or August each year (Coche, 1974).

Fieldwork focused on Lake Kariba’s subbasin IV, the reservoir’s largest subbasin by area and volume, located adjacent to the Kariba Dam (Figure C.1; Kunz et al., 2011). Five isolated littoral zones in subbasin IV were examined. The sites named “Lufua River” (LR), “Gache Gache River” (GR), and “Charara River” (CR) had significant river inflows and will be referred to as ‘river deltas’. The sites called “Gache Gache Bay” (GB) and “Charara Bay” (CB) were relatively unaffected by inflows and called ‘non-river bays’.

4.2.2 Sampling methods

Sample collection, processing, and analysis are described briefly here with additional details in the extended methods section in Section 4.5.3 and DelSontro et al. (2010). Detailed surveys for dissolved CH$_4$, as well as sediment and surface CH$_4$ emissions were conducted in the five bays in June 2009, while open water CH$_4$ profiles were taken during campaigns in July 2007, May 2008, February and June 2009 (Figures C.1 and C.2). Depth profiles of conductivity, temperature, and dissolved oxygen were taken at most open water stations and at least once in each bay (Figure C.3). Dissolved CH$_4$ was sampled with a Niskin bottle, transferred to and poisoned in gas-tight serum bottles, and subsequently analyzed by gas chromatography (Agilent 6890N) and a flame-ion detector (GC/FID). Sediment cores were collected in each bay and diffusion was calculated using the CH$_4$ gradient measured in the porewaters via GC/FID (Table 4.1). Gross surface CH$_4$ emissions (ebullition plus diffusion) were measured in each bay (except CB) using drifting chambers and analyzed via GC/FID. Surface diffusion was estimated using measured surface water CH$_4$ concentrations and wind speed.

4.2.3 Hydroacoustic surveys

The methodology of analyzing ebullition hydroacoustically with an echosounder is similar to the process of measuring fish biomass (Ostrovsky et al., 2008; Simmonds and MacLennan, 2005). Hydroacoustic surveys of ebullition were conducted with a down-looking Simrad split-beam echosounder (EK60, 7° beam angle) with a 120 kHz transducer pinging at 5 s$^{-1}$ and a lower threshold of $-120$ dB. Bubbles could be readily distinguished from fish based on their travel path as rising bubbles appear as inclined tracks whereas fish appear as nearly horizontal tracks (Figure C.4a; Ostrovsky, 2003). After filtering out fish and noise, bubble density, $N$ (\#m$^{-3}$), can be calculated for the water volume covered by the
Table 4.1: Drifting chamber and hydroacoustic results from subbasin IV bays

<table>
<thead>
<tr>
<th>Study sites</th>
<th>Drifting chambers: Surface emission</th>
<th>Hydroacoustics: Surface ebullition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bay name (Abbr.)</td>
<td>Mean depth (m)</td>
<td>Flux (mg m$^{-2}$ d$^{-1}$)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Lufua River (LR)</td>
<td>18</td>
<td>2,100 ± 1,200</td>
</tr>
<tr>
<td>Gache Gache River (GR)</td>
<td>9</td>
<td>400 ± 300</td>
</tr>
<tr>
<td>Charara River (CR)</td>
<td>7</td>
<td>70 ± 90</td>
</tr>
<tr>
<td>Gache Gache Bay (GB)</td>
<td>8</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>Charara Bay (CB)</td>
<td>4</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(a\) LR, GR, and CR are river deltas; GB and CB are non-river bays  
\(b\) Average flux from all chamber transects ± one standard deviation  
\(c\) This is the average (± one standard deviation) of the transect sediment ebullition fluxes corrected for average CH$_4$ bubble content, for pressure/volume change at surface, and for bubble dissolution  
\(d\) No chambers were deployed in CB.

sonar beam. This was calculated by dividing the total acoustic backscatter of the analyzed water volume, \(s_v\) (m$^{-1}$), by the mean acoustic signature, called the backscattering cross-section, \(\sigma_{bs}\) (m$^2$), of all identified bubbles. For a calibrated relationship between \(\sigma_{bs}\) and bubble volume, bubble density can be converted to gas volume density, \(V_{\Sigma b}\) (ml m$^{-3}$). For this study we used the bubble volume calibration conducted by Ostrovsky et al. (2008). The volumetric density was converted to bubble gas flux (mg m$^{-2}$ d$^{-1}$) by adjusting for the pressure at the analyzed depth and multiplication by the bubble rise velocity (m s$^{-1}$), as measured by the echosounder. Lastly, CH$_4$ flux was scaled by the average bubble CH$_4$ concentration, as measured in submerged gas traps (see appendix in Section 4.5.3). Data was post-processed using Sonar 5 Pro (Lindem Acquisition, Norway). For more details, see appendix in Section 4.5.3 and Ostrovsky et al. (2008).

4.3 Results and Discussion

4.3.1 Methane concentrations and emissions in the littoral zone

Dissolved CH$_4$ concentrations in the five sampled bays varied considerably, but always exceeded saturation levels (Table C.1 and Figure C.1). LR and CR had CH$_4$ concentrations up to 5 and 2µM, respectively, while the dissolved concentrations in GR and the two non-river bays were less than 1µM (Figure C.2). Surface water CH$_4$ concentrations were highly variable within individual bays and tended to decrease in the offshore direction. The surface concentrations in the river deltas were up to an order of magnitude higher than those from the open water stations (Figure C.1), illustrating the local importance of littoral
4.3. Results and Discussion

sources. The concentration variability between bays most likely reflects the variability of \( \text{CH}_4 \) sources in the littoral zone, which can be diffusion from sediments or dissolution of rising bubbles (DelSontro et al., 2010). Sediment diffusion estimates, calculated using porewater \( \text{CH}_4 \) profiles from various regions of Lake Kariba (Figure C.2), fell within one order of magnitude of each other (Figure 4.1d, Table C.1) and were comparable with estimates from other systems (Adams, 2005). Dissolution from rising bubbles will be discussed later.

Figure 4.1: Whisker boxplots of \( \text{CH}_4 \) fluxes (mg m\(^{-2}\) d\(^{-1}\)) during June 2009 sampling of \( \text{CH}_4 \) pathways from Lufua River (LR), Gache Gache River (GR), Charara River (CR), Gache Gache Bay (GB), Charara Bay (CB), and open water stations of subbasin IV (BIV). Box represents the 25th and 75th percentile. Middle line is the median. Whiskers are the maximum and minimum values. Crosses are outliers. Number of samples used for (a) and (b) are the number of transects in Table 4.1. Number of samples for (c) and (d) are number of stations in Table C.1. (a) Surface chamber emission estimates include gas directly captured at the surface from diffusion and, if present, ebullition using drifting chambers. (b) Surface ebullition is \( \text{CH}_4 \) bubble escape to the atmosphere based on the transect averages of hydroacoustic sediment ebullition flux near the lake bottom and corrected for bubble dissolution upon ascent. (c) Surface diffusion is calculated from measured dissolved \( \text{CH}_4 \) concentrations in surface water and average daily wind speed. (d) Sediment diffusion is calculated using the \( \text{CH}_4 \) gradient measured in porewater cores.
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Surface chamber emissions, which included ebullitive and diffusive emissions, varied greatly between bays (range 3 to 2,100 mg CH$_4$ m$^{-2}$ d$^{-1}$). The differences in chamber emission magnitudes demonstrated that the three river deltas emitted substantially more CH$_4$ than the non-river bays (Figure 4.1a, Table 4.1). Surface diffusion fluxes calculated from surface water CH$_4$ concentrations were much lower than the chamber-captured emissions and only slightly higher than open water surface gas exchange (Figure 4.1c); thus the measured surface emissions could not be dominated by diffusion. Ultimately, since surface and sediment diffusion were low compared to chamber emissions and relatively constant across various regions of Lake Kariba, the variability in chamber emissions and dissolved CH$_4$ profiles within and between bays must be due to another CH$_4$ release pathway. Differences in ebullition fluxes between bays, and subsequent partial dissolution of CH$_4$ bubbles during their ascent, was therefore a potential mechanism regulating both water-air fluxes and the dissolved CH$_4$ concentrations in the littoral zone.

4.3.2 Hydroacoustic estimates of ebullition

Hydroacoustic data were used to further explore ebullition in the five study sites. The hydroacoustic method provided a very rich dataset, resulting in > 70,000 individual observations at some sites. To evaluate the data, observations were pooled into 5-m distance bins along each transect. The sediment gas flux for each bin was calculated in the bottom 3 m layer of the water column, and corrected for CH$_4$ composition of bubbles captured at each site (59 to 66% CH$_4$ by volume; see appendix in Section 4.5.3 for details). Binning yielded up to 3,000 distance- and bubble plume-integrated flux measurements (from here on called “bin flux”) per site, with each bin flux having a well-defined depth (±2 m). A bin flux could consist of a few single bubbles, one or more distinct bubble plumes, or no bubbles at all (Figure C.4b), and thus incorporated all active ebullition areas and non-bubbling areas within that 5 m distance.

The observed bin fluxes spanned 5 orders of magnitude, and fluxes having substantial magnitude were detected at high frequency even down to 40 m depth (Figure 4.2). At LR and GR, the magnitude of non-zero bin fluxes were log-normally distributed with means of ~10$^3$ mg CH$_4$ m$^{-2}$ d$^{-1}$, while at other sites the mean fluxes were clearly lower (Figure 4.2b). Extreme fluxes of > 10$^4$ mg m$^{-2}$ d were observed at LR and GR, and although these values seem quite large, they resulted from episodic releases of gas that were clearly visible in echograms (Figure C.4b). Ramos et al. (2006) also observed intermittent extreme fluxes up to $2 \times 10^4$ mg CH$_4$ m$^{-2}$ d$^{-1}$ while measuring CH$_4$ flux at 5 minutes resolution on a reservoir surface with stationary dynamic chambers.
Figure 4.2: a) Frequency of sediment ebullition found in bins according to depth for Lufua River delta (LR), Gache Gache River delta (GR), Charara River delta (CR), Gache Gache Bay (GB), and Charara Bay (CB). b) Magnitude of sediment ebullition bin fluxes according to depth (left) and overall distribution of measured fluxes (right) in each surveyed bay. Note different x-axis scales between panels. Non-zero fluxes shown on log scale. Red line is 1-m average including zero flux values.
To compare hydroacoustic estimates with drifting chamber measurements for each bay, average surface ebullition fluxes for the hydroacoustic transects were calculated (Figure 4.1b). Hydroacoustic transect averages were found by first calculating the mean of the bin fluxes (including zero fluxes) along each of the multiple transects within each bay, then by correcting for actual bubble CH$_4$ content and for bubble dissolution during ascent using a discreet bubble model (McGinnis et al., 2006; see appendix in Section 4.5.3). The mean surface fluxes from hydroacoustic surveys and drifting chambers agreed reasonably well (same order of magnitude; Figures 4.1a and b, Table 4.1) at LR and GR. The agreement with chamber measurements at CR and GB was not as strong as at the other sites, and some of the difference between hydroacoustic and chamber estimates at any site likely arises from differences in transect locations and coverage (Figure C.2, Table 4.1).

The hydroacoustic measurements corroborate the findings from chamber measurements that CH$_4$ fluxes across the air-water interface in river deltas were 1 to 3 orders of magnitude higher than in non-river bays. While both methods identified river deltas as ebullition hot spots, the distinction was even more apparent in the hydroacoustic data (Figure 4.1), where flux estimates from GR and CR were more similar to LR. Although the mean hydroacoustic fluxes of GR and CR were 2- to 4-fold lower than LR (Table 4.1), all river delta ebullition fluxes were at least an order of magnitude greater than that of the non-river bays.

In contrast to their considerable qualitative agreement, the two methods differed dramatically in their effectiveness. The hydroacoustic transects covered an order of magnitude more area than the chambers and were acquired in less than half the time (Table 4.1). Moreover, while both techniques yielded mean flux estimates, only the hydroacoustic method provides more precise information about how ebullition varies over finer spatial scales. For example, the 5 m hydroacoustic bin fluxes document the heterogeneity of ebullition along a single transect (Figure 4.3), which would be averaged out in a drifting chamber measurement. This heterogeneity, specifically differences in ebullition frequency and ebullition magnitudes, also contribute to the variability in average fluxes observed between the surveyed sites (Figure 4.2). For example, the magnitudes of the non-zero bin fluxes (Figure 4.2b) were substantially higher in LR and GR (mean, 4,600 and 4,200 mg CH$_4$ m$^{-2}$ d$^{-1}$, respectively) than in the non-river bays (mean, 1,800 and 30 mg CH$_4$m$^{-2}$ d$^{-1}$ for GB and CB, respectively). However, the mean sediment ebullition magnitude in the CR delta (1,900 mg CH$_4$ m$^{-2}$ d$^{-1}$) and the non-river GB were almost the same (Figure 4.2b); thus the factor of 7 difference in transect averages between these two sites was due to the frequency of ebullition (i.e., 37% of the surveyed area of CR was bubbling, while only 5% in GB; Figure 4.2a). Overall, ebullition frequency was higher in the river deltas than the non-river bays (Figure 4.2a).
Figure 4.3: Hydroacoustic sediment ebullition bin fluxes in Lufua River delta. A constant of 0.1 was added to all fluxes to allow plotting of the zero fluxes on a log scale. Bathymetry contours (labelled by numbers 4 to 20) are at 2 m. River inflow is indicated with an arrow. A low ebullition flux zone is apparent along the shallow northern shelf and a high ebullition zone in the deep part of the former river channel.

The differences in ebullition magnitude and frequency amongst the river delta sites are also noteworthy as they indicate the extreme variability of ebullition within an ebullition hot spot. While LR had an average transect flux that was 2-fold higher than that of GR (Table 4.1), they had similar non-zero flux distributions (Figure 4.2b). Therefore, the higher transect flux from LR was primarily due to the higher frequency of ebullition (67% versus 37%) rather than the magnitude of the non-zero fluxes. On the other hand, the difference between the transect averages for LR and CR appears to have been a function of both the magnitude of the non-zero fluxes (mean, 4,600 versus 1,900 mg CH₄ m⁻² d⁻¹) as well as ebullition frequency (67% versus 37%; Figure 4.2).

The hydroacoustic data was also used to explore the extent to which water column depth influences sediment ebullition flux. CH₄ surface emissions
from ebullition have been shown elsewhere to be negatively correlated with depth (Gunkel, 2009; and references therein). Those studies, which relied on surface chambers, attributed the depth dependency of emissions to increased bubble dissolution with height of bubble rise. It has also been suggested that the sediment ebullition flux could decrease with depth due to increasing hydrostatic pressure (Bastviken et al., 2004; Ostrovsky et al., 2008). Although there was considerable variability, over a depth range of 5 to 40 m in LR we observed an order of magnitude decrease in the average bin flux (including zero fluxes) as a function of depth (red line, Figure 4.2b), and a similar decrease in the mean of the non-zero bin fluxes.

These variations of ebullition magnitude and frequency with depth at LR were likely more related to the geomorphology and sedimentation dynamics of this site rather than with depth itself. For example, depth may serve as a proxy for distance from the river mouth (Figure 4.2), and the decrease in average ebullition flux with depth may reflect decreased organic matter input to sediments further (up to 40 m depth) from the river mouth, and a resulting decrease in CH$_4$ production. The lower frequency of ebullition in shallow regions of LR (< 10 m), which was not necessarily expected, may also be an artifact of the bay’s geomorphology. The bay into which the Lufua River empties has a deep (∼20 m) submerged channel. The shallower sides of the bay may receive less sediment loading than the submerged river channel, potentially resulting in less CH$_4$ production and less ebullition. This appears to indeed be a plausible explanation based on the spatial variability of bin fluxes in LR (Figure 4.3). Ebullition was quite low along the shallow northern part of the bay (blue zone, Figure 4.3), while higher fluxes were found in the deep channel (red zone, Figure 4.3). The higher ebullition fluxes at depth could also be a result of increased bubble release due to higher velocities at the sediment-water interface due to currents (Keller and Stallard, 1994). Whatever the cause, the 10-fold decrease in sediment ebullition flux with depth observed in LR is greater than the 5-fold decrease in surface flux that would result from additional bubble dissolution (assuming average LR conditions: 9 mm diameter bubble with 59% CH$_4$ by volume at 24°C). Thus, systematic spatial variations in sediment ebullition flux can be quantitatively more important than dissolution-related decreases in surface ebullition.

A depth-flux relationship was not observed in GR or CR (Figure 4.2b); however, the surveys did not extend as deeply into those bays as in LR. Interestingly, the majority of observations made in the shallow region of GR were found to have no ebullition (Figure 4.2a). This may also be partly due to the geomorphology of the bay for the same reason as in LR (i.e., shallow sides disconnected from main channel), and also because observations essentially began in the river itself (Figure 4.2). It is also important to note that at most sites flux estimates were not made for the shallowest regions (< 2 to 3 m) due to interference
from submerged vegetation or the near-field limitation of echosounding (Simmonds and MacLennan, 2005). Ebullition dynamics in these shallow regions could potentially alter the overall average ebullition estimates for each site and any observed depth relationships, but the results discussed here for the depth ranges that were well-covered by hydroacoustic surveying remain valid.

4.3.3 Subbasin IV methane sources and fate

A basic box model approach was used to assess the relative importance of the main processes governing CH$_4$ dynamics in subbasin IV over a full year (Figure 4.4), which typically includes 10 months of stratification (Figures C.6 and C.7).

Methane loading to the epilimnion was calculated by considering both diffusion and dissolution from bubbles. For the diffusion loading estimate, an average diffusive flux from sediment core data of the bays (40 ± 20 mg m$^{-2}$ d; Table C.1) was applied to the

![Diagram](image_url)

Figure 4.4: Subbasin IV CH$_4$ mass balance just before seasonal mixing (end of stratification period) when accumulation is at its maximum in the hypolimnion. Arrows show annual CH$_4$ emissions in t yr$^{-1}$ for sediment diffusion to the hypolimnion and epilimnion, diffusion at the lake surface, discharge through the dam, ebullition dissolution into the epilimnion, and atmospheric methane release from bubbles. Locations of CH$_4$ oxidation are labeled.
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epilimnetic sediment area (depth < 30 m; Figure C.3) and resulted in \( \sim 17,000 \text{ t CH}_4\text{yr}^{-1} \) entering the epilimnion. However, the actual amount of diffusing CH\(_4\) that reached the water column may have been substantially less due to CH\(_4\) oxidation at the sediment-water interface and the fact that the diffusion rate estimate was calculated from CH\(_4\)-rich cores taken in the bubbling bays. Ebullition was assumed to occur only in the subbasin IV bays with river inputs since negligible amounts of ebullition emission were found from bays with no river input. Therefore, total ebullition was estimated in the three surveyed river deltas plus three river deltas that were not surveyed but have substantial catchment areas and flows (Figure C.1a, Table C.2). The average acoustic ebullition flux for each surveyed delta (Table 4.1) was applied to that bay’s area. The areas of the three deltas not surveyed were scaled by the average flux of LR, GR, and CR (870 mg m\(^{-2}\) d\(^{-1}\)). Recognizing that methane production rate may vary seasonally due to differences in organic matter loading (e.g., wet versus dry seasons, which are dynamic in this system), we conservatively estimated that ebullition occurs in the subbasin IV deltas for only half the year (Karenge and Kolding, 1995). Water level changes also can significantly influence ebullition rates (Ostrovsky et al., 2008). This dataset did not allow for such an effect to be quantified; however, water levels before and during fieldwork were high and constant, so our flux estimate may be considered a minimum. The overall estimate for ebullition emission to the atmosphere from the six deltas in subbasin IV was 16,000 t CH\(_4\) yr\(^{-1}\) (Figure 4.4). To calculate this estimate, average bubble parameters from the hydroacoustic data of the three surveyed deltas (bubble diameter of 9 mm containing 62% CH\(_4\)) were assumed, and an average depth of 15 m was used to determine that \( \sim 35\% \) of the CH\(_4\) from rising bubbles dissolved into the water column, equating to 9,000 t CH\(_4\) yr\(^{-1}\).

If the total CH\(_4\) mass that entered the epilimnion from bubble dissolution and diffusion (26,000 t) had been mixed over the entire epilimnetic volume via horizontal mixing it would have yielded a concentration of \( \sim 32 \mu\text{M} \), which is three orders of magnitude greater than the measured concentration in the surface waters of the lacustrine part of the lake (< 0.1 \mu M; Figure C.1b). Thus, CH\(_4\) released from littoral sediments did not accumulate in the water column, but must have been oxidized (either in the oxic surface layer of the sediments or the water column), as has previously been suggested (Guérin and Abril, 2007; Kankaala et al., 2007). The required oxidation rate in the water column to offset this accumulation (90 nmol l\(^{-1}\) d\(^{-1}\)) is consistent with aerobic oxidation rates observed elsewhere (Bastviken et al., 2002).

The atmospheric releases considered in this analysis included diffusive flux across the air-water interface, export of CH\(_4\) via turbines, and ebullition. Gas exchange at the air-water interface, calculated using the average surface water CH\(_4\) concentrations of open water and bays as well as monthly mean wind speeds (Mungwena, 2002), amounted to
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∼180 t CH$_4$ yr$^{-1}$. Methane export through the turbines over a year was approximated by estimating the zone of influence of the turbine intakes and seasonal variations in CH$_4$ profiles (Figures C.1b, C.6, C.7 and appendix in Section 4.5.3). This approach resulted in ∼170 t CH$_4$ yr$^{-1}$ released via the turbines (Figure 4.4). Ebulbition, however, was the dominant atmospheric release pathway of CH$_4$ with 16,000 t escaping directly to the atmosphere (Figure 4.4).

Accumulation of CH$_4$ in the basin’s hypolimnion was quantified using dissolved CH$_4$ concentration profiles at several stations sampled during different stages of stratification across multiple years (Figures C.1, C.5 and appendix in Section 4.5.3). Methane accumulation set in after the onset of anoxia, and on the order of ∼11,000 t CH$_4$ accumulated in the hypolimnion over ten months of stratification. The total flux from the hypolimnetic sediment area required to support this accumulation (23 mg m$^{-2}$ d$^{-1}$) was comparable to the estimated sediment diffusion flux from hypolimnetic sediments (30 mg m$^{-2}$ d$^{-1}$, calculated from a lacustrine subbasin IV core). Other potential sources to the hypolimnion, such as deep ebullition, are therefore not needed to explain the CH$_4$ accumulation.

The fate of the 11,000 t of CH$_4$ stored in the basin’s anoxic hypolimnion during stratification must be assessed indirectly. In the completely mixed water column sampled in July 2007 storage was only 30 t of CH$_4$ (Figure 4.4). Temperature data from subbasin IV during our years of observation (data not shown) indicate that the thermocline deepened and was gradually eroded over the course of May to July until the water column was fully mixed, which was consistent with past observations (Coche, 1974). During this period, export of CH$_4$ via diffusion across the air-water interface plus export through the turbines can explain < 1% of the decrease in CH$_4$ storage. Thus, almost all of the stored CH$_4$ must have been oxidized by methanotrophic microbes during the gradual deepening of the thermocline and oxycline, as has been observed elsewhere (Schubert et al., 2010).

Overall, the dominant fates of CH$_4$ in Lake Kariba were oxidation (total = 37,000 t) and export of CH$_4$-rich bubbles across the air-water interface (16,000 t). Ebulbition export, which we conservatively assumed to occur only in river deltas with reasonable spatial and temporal considerations, exceeded the estimates for surface diffusion and CH$_4$ export through the turbines by two orders of magnitude (Figure 4.4), thus making ebullition the dominant CH$_4$ emission pathway in Lake Kariba’s largest basin.

4.3.4 Implications for tropical reservoir emissions

Estimating CH$_4$ emission from the entire reservoir is of interest given the size of Lake Kariba and that the subbasin IV results suggest that ebullition is quite important to
the lake’s overall CH\textsubscript{4} budget. Recognizing the considerable uncertainty in extrapolating the ebullition emission rates from three river deltas to the entire lake, such as other studies have done with much less spatial coverage, a conservative approach for upscaling the estimates from this study was taken. Our goal with such a rough estimate of total ebullition emission was to allow an order of magnitude comparison between the different CH\textsubscript{4} fates and pathways within the lake, and in comparison to other tropical reservoirs.

The CH\textsubscript{4} flux via turbine/downstream degassing remains unchanged. Using surface concentrations from open water stations of subbasin IV (Figure C.1) and the other basins (data not shown), a diffusion estimate of \(~540\text{ t CH}_{4}\text{ yr}^{-1}\) was calculated for the surface of Lake Kariba. The ebullition flux can be extrapolated in various ways; for example, with the method employed by other published studies where a limited number of chamber or gas trap measurements were used to extrapolate ebullition to the rest of the unmeasured littoral area (e.g., see dos Santos et al., 2006). Along these lines (albeit without the depth-integration used in other studies because our drifting chamber measurements already average flux over depth) a surface ebullition estimate could be calculated by multiplying the average chamber measurement of \(640\text{ mg CH}_{4}\text{ m}^{-2}\text{ d}^{-1}\) to the \(2,000\text{ km}^{2}\) littoral zone of the lake (depth < 20 m) to obtain an estimated annual flux of \(>4 \times 10^{5}\text{ t yr}^{-1}\).

However, our observations of the spatial heterogeneity of ebullition in Lake Kariba indicate that this approach is not adequate and, with no ebullition data for the other subbasins, the following estimate is the closest approximation that can be made with the available data. We employed the same spatially and temporally conservative method as described above for subbasin IV, assuming ebullition only occurs in the deltas of substantial rivers (roughly 4% of total lake area) during half of the year (Table C.2). This approach resulted in an order of magnitude lower estimate of \(3.9 \times 10^{5}\text{ t yr}^{-1}\) (Table C.2) that remains two orders of magnitude greater than the other atmospheric emission pathways combined. Thus, ebullition flux from river deltas, a previously undocumented CH\textsubscript{4} source from large reservoirs, has the potential to be the dominant atmospheric CH\textsubscript{4} source from Lake Kariba despite being a minimal fraction of the total lake area. When all our potential sediment CH\textsubscript{4} release estimates (diffusion and ebullition) are summed and converted to carbon release units, the value (\(88,000\text{ t C-CH}_{4}\text{ yr}^{-1}\)) is generally consistent with a recent study that estimated OC loading and burial efficiency in Lake Kariba sediments (see appendix in Section 4.5.3; Kunz et al., 2011). We are therefore confident in the order of magnitude of our estimates for all CH\textsubscript{4} emission pathways in this system, which indicate that ebullition is most likely the dominant emission pathway in Lake Kariba.

The substantial contribution of ebullition to total CH\textsubscript{4} emissions in Lake Kariba contrasts strongly with observations in other large tropical reservoirs where dominant CH\textsubscript{4}
emissions were at the turbines (Table C.3 and references therein). This disparity results in part from the vertical placement of water intake levels in Lake Kariba, which lead mostly surface waters rich in oxygen and poor in CH$_4$ to the turbines (Figures C.6 and C.7; Anderson et al., 1960). Other well-studied tropical reservoirs have turbine inlets that withdraw anoxic hypolimnetic water or a mixture of hypolimnetic and epilimnetic water (Table C.3). Therefore, an important design strategy for reducing greenhouse gas emissions from reservoirs is the placement of turbine intakes in order to avoid the release of anoxic deepwater.

Although we used a conservative approach to estimate CH$_4$ ebullition in the dendritic littoral zone of Lake Kariba, ebullition export of CH$_4$ from this 60-year-old hydropower scheme turned out to be the highest among the well-studied tropical reservoirs (Table C.3). Total areal emission from Lake Kariba, however, was the lowest, potentially due to the advanced age of the Kariba Dam (Abril et al., 2005; Soumis et al., 2005). It could then be inferred that the high ebullition emission measured in river deltas reflects the most recent carbon input from the catchment and thus the deltas have no relation to the reservoir age. Ultimately, a direct quantitative comparison of the CH$_4$ emission pathways in Lake Kariba with those from other tropical reservoirs is difficult because the idea of potential ebullition hot spots or littoral heterogeneity were not considered in most of those studies. Such hot spots could easily be missed in large systems, and therefore more detailed (re)analysis of CH$_4$ fluxes at terrestrial-aquatic linkages with better integrating technologies, such as eddy covariance (Eugster and Plüss, 2010), or spatially explicit methods like hydroacoustics is warranted.

### 4.4 Acknowledgments

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4.5 Appendix

4.5.1 Supplementary figures

Figure C.1: a) Lake Kariba with open water stations and five study bays labeled. Arrows point to river inflows with modeled discharge (m$^3$s$^{-1}$; Landert, 2009). b) Methane profiles for open water stations in subbasin IV. Each panel is a different sampling campaign labeled with the month and year. Note that the upper left panel is only up to 1μM scale, while the others are up to 80μM.
Figure C.2: Top: Sampling in bays. Legend refers to all maps. CB1 is only station in Charara Bay. Images from Google Earth. Bottom: Methane profiles in bays. Legend refers to all four panels (i.e., station 1 is red in every panel). Station numbers refer to above map. Charara Bay had only the single red profile in the lower right panel and the other three are from Gache Gache Bay.
Figure C.3: Temperature and oxygen profiles at each surveyed bay and subbasin IV station B99. River deltas are LR (Lufua River), GR (Gache Gache River), and CR (Charara River). Non-river bays are GB (Gache Gache Bay) and CB (Charara Bay). Station numbers as shown in the legend title correspond with Figure C.2.
Figure C.4: a) Example of a Lufua River delta echogram showing the sediment bottom, bubbles, and fish. b) Example of 5 m distance bins in 3 m layer above bottom in Lufua River delta. Bin fluxes calculated for each bin vary from zero (1#1) to > 10,000 mg CH$_4$ m$^{-2}$d$^{-1}$ (*). In both panels, Z is depth in meters. Colors are target strength (TS) of echoes in dB and x-axis is time in hh:mm:ss.
Figure C.5: Standing CH$_4$ stocks per month in subbasin IV. Months based on measured data shown in red. The remaining months were calculated using the exponential regression shown that represents the accumulation based on measured data.

\[ y = 15.851e^{0.5707x} \]
Figure C.6: Methane dynamics and dam outflow typical of January, March, and May in Lake Kariba. Dashed line is location of oxycline separating CH$_4$-rich hypolimnion (concentrations in pink) from the CH$_4$-poor epilimnion (concentrations in blue). The complicated flow regime through the two turbines on the south bank and the one on the north bank (heights of turbines shown in masl) was estimated using an adapted slot orifice equation (see Section 4.5.3 and Fan, 2008). Stratified flow results are illustrated by the black lines labeled with an elevation (in masl) showing the water layer thickness that flowed through each turbine. The percentage of epi- and hypolimnion percentage of the water flowing through each turbine is shown and was used to calculate CH$_4$ discharge through the dam.
Figure C.7: Methane dynamics and dam outflow typical of July, September, and November in Lake Kariba. Dashed line is location of oxycline separating CH$_4$-rich hypolimnion (concentrations in pink) from the CH$_4$-poor epilimnion (concentrations in blue). The complicated flow regime through the two turbines on the south bank and the one on the north bank (heights of turbines shown in masl) was estimated using an adapted slot orifice equation (see Section 4.5.3 and Fan, 2008). Stratified flow results are illustrated by the black lines labeled with an elevation (in masl) showing the water layer thickness that flowed through each turbine. The percentage of epi- and hypolimnion percentage of the water flowing through each turbine is shown and was used to calculate CH$_4$ discharge through the dam.
### 4.5.2 Supplementary tables

Table C.1: Dissolved CH$_4$ profiles and porewater cores measured in bays of subbasin IV

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</tr>
<tr>
<td>Lufua River (LR)</td>
<td>2 ± 2 (10)</td>
<td>50 ± 20 (3)</td>
</tr>
<tr>
<td>Gache Gache River (GR)</td>
<td>0.4 ± 0.4 (9)</td>
<td>70 ± 40 (3)</td>
</tr>
<tr>
<td>Charara River (CR)</td>
<td>0.9 ± 0.7 (7)</td>
<td>30 ± 20 (2)</td>
</tr>
<tr>
<td>Gache Gache Bay (GB)</td>
<td>0.1 ± 0.4 (3)</td>
<td>40 ± 40 (1)</td>
</tr>
<tr>
<td>Charara Bay (CB)</td>
<td>0.4 ± 0.01 (1)</td>
<td>4 ± 3 (1)</td>
</tr>
</tbody>
</table>

$^a$ RD = river delta; NB = non-river bay

$^b$ Average of surface water CH$_4$ concentrations at each station (usually two measurements within every 5 m) ± one standard deviation

$^c$ Average flux ± one standard deviation (duplicate core taken at each station).
### Table C.2: All potential ebullition hot spots (river deltas) in Lake Kariba (see Figure C.1a)

<table>
<thead>
<tr>
<th>River delta</th>
<th>Subbasin number</th>
<th>Area (km²)</th>
<th>Q (m³ s⁻¹)</th>
<th>Surface ebullition (mg CH₄ m⁻² d⁻²)</th>
<th>Total emission (t CH₄ yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lufua IV</td>
<td>IV</td>
<td>17.9</td>
<td>8</td>
<td>1,450</td>
<td>4,665</td>
</tr>
<tr>
<td>Gache Gache IV</td>
<td>IV</td>
<td>13.5</td>
<td>1.7</td>
<td>770</td>
<td>1,865</td>
</tr>
<tr>
<td>Charara IV</td>
<td>IV</td>
<td>3.9</td>
<td>2.2</td>
<td>400</td>
<td>281</td>
</tr>
<tr>
<td>Ume IV</td>
<td>IV</td>
<td>30.3</td>
<td>35.1</td>
<td>873</td>
<td>4,765</td>
</tr>
<tr>
<td>Sanyati IV</td>
<td>IV</td>
<td>2.8</td>
<td>153.4</td>
<td>873</td>
<td>434</td>
</tr>
<tr>
<td>Nyaoodzi IV</td>
<td>IV</td>
<td>27.6</td>
<td>6.2</td>
<td>873</td>
<td>4,335</td>
</tr>
<tr>
<td>Chipepo III</td>
<td>III</td>
<td>16.2</td>
<td>1.2</td>
<td>873</td>
<td>2,541</td>
</tr>
<tr>
<td>Chezya III</td>
<td>III</td>
<td>56.5</td>
<td>2.2</td>
<td>873</td>
<td>2,358</td>
</tr>
<tr>
<td>No name III</td>
<td>III</td>
<td>21.5</td>
<td>1.1</td>
<td>873</td>
<td>3,388</td>
</tr>
<tr>
<td>No name III</td>
<td>III</td>
<td>3.0</td>
<td>0.7</td>
<td>873</td>
<td>479</td>
</tr>
<tr>
<td>Zongwe III</td>
<td>III</td>
<td>11.7</td>
<td>3.9</td>
<td>873</td>
<td>1,839</td>
</tr>
<tr>
<td>Maze III</td>
<td>III</td>
<td>10.1</td>
<td>4.4</td>
<td>873</td>
<td>1,588</td>
</tr>
<tr>
<td>Masumu III</td>
<td>III</td>
<td>9.0</td>
<td>1.1</td>
<td>873</td>
<td>1,417</td>
</tr>
<tr>
<td>Sengwa III</td>
<td>III</td>
<td>21.2</td>
<td>6.1</td>
<td>873</td>
<td>3,335</td>
</tr>
<tr>
<td>Nagandu II</td>
<td>II</td>
<td>1.2</td>
<td>1</td>
<td>873</td>
<td>190</td>
</tr>
<tr>
<td>No name II</td>
<td>II</td>
<td>1.3</td>
<td>0.7</td>
<td>873</td>
<td>204</td>
</tr>
<tr>
<td>No name II</td>
<td>II</td>
<td>1.6</td>
<td>0.8</td>
<td>873</td>
<td>248</td>
</tr>
<tr>
<td>Lokola II</td>
<td>II</td>
<td>15.5</td>
<td>5.2</td>
<td>873</td>
<td>2,435</td>
</tr>
<tr>
<td>Zambezi I</td>
<td>I</td>
<td>9.5</td>
<td>1,100</td>
<td>873</td>
<td>1,498</td>
</tr>
<tr>
<td>Namazanda</td>
<td>I</td>
<td>4.7</td>
<td>5.7</td>
<td>873</td>
<td>734</td>
</tr>
</tbody>
</table>

| Total                |                 | 237        |            | 38,600                              |

*Boundary of delta area extended to either the 30 m depth contour or the visual extent of the bay, whichever came first

*Flow rates modeled using a physical-based model (SWAT) and catchment area (see Landert, 2009)

*Surface ebullition is the mean flux from each measured delta or the average of the measured deltas (Lufua, Gache Gache, and Charara) for all unmeasured bays

*Total emission based on 6 months of active ebullition due to the wet and dry season variability.
### Table C.3: Tropical reservoir surface CH$_4$ emission comparison$^a$

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>$z$ (m)</th>
<th>Surf (km$^2$)</th>
<th>Diff (kt yr$^{-1}$)</th>
<th>Ebull</th>
<th>Degas (kt yr$^{-1}$)</th>
<th>Total emission (t km$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petit Saut, French Guiana$^b$</td>
<td>35</td>
<td>300</td>
<td>1</td>
<td>0.4</td>
<td>5</td>
<td>6.4</td>
</tr>
<tr>
<td>Balbina, Brazil$^c$</td>
<td>35</td>
<td>1,770</td>
<td>30</td>
<td>40</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Serra da Mesa, Brazil$^d$</td>
<td>146</td>
<td>1,784</td>
<td>60</td>
<td>20</td>
<td>200</td>
<td>280</td>
</tr>
<tr>
<td>Tucurui, Brazil$^d$</td>
<td>90</td>
<td>2,430</td>
<td>90</td>
<td>7</td>
<td>2,000</td>
<td>2,097</td>
</tr>
<tr>
<td>Kariba, Zambia/Zimbabwe$^e$</td>
<td>97</td>
<td>5,364</td>
<td>0.5</td>
<td>38.6</td>
<td>0.2</td>
<td>40</td>
</tr>
</tbody>
</table>

$^a$ Abbreviations: Surf = Surface area; $Z =$ maximum depth; Diff = diffusion; Ebull = ebullition; Degas = dissolved CH$_4$ degassing through turbines and/or downstream

$^b$ Source: Abril et al. (2005)

$^c$ Source: Kemenes et al. (2007)

$^d$ Diffusion and ebullition from Bambace et al. (2007), degassing from dos Santos et al. (2006)

$^e$ this study.

### 4.5.3 Extended methods

#### Dissolved CH$_4$ concentrations

Water samples for dissolved CH$_4$ were taken using a Niskin bottle and flushed through 125 ml serum bottles before being poisoned with CuCl and closed air free with a stopper and aluminum cap. For analysis, the headspace method was used (McAllufie, 1971). Thus, a N$_2$ headspace was added through the stopper with a second, open needle expelling the displaced water. Samples were then shaken vigorously and placed in a sonic bath for 30 minutes to allow for equilibration before the headspace was analyzed with gas chromatography and flame ionization detection (GC/FID).

#### Sediment emissions

Methane diffusion from the sediment was calculated from the porewater concentration gradient assuming a Fickian diffusive process with diffusivities derived by Furrer and Wehrli (1996) and as described in DelSontro et al. (2010). The CH$_4$ gradient was measured using a sediment corer and tubes with pre-drilled holes at 1-cm resolution for porewater sampling with a small syringe. The wet sediment was transferred to a serum bottle and conserved with a CuCl solution to prevent CH$_4$ oxidation before closing it with a stopper and aluminum cap. As air was acting as the headspace gas, control samples were also taken to know the atmospheric CH$_4$ content at the time. Samples were stored upside
down and then shaken thoroughly before analysis to allow equilibration of the dissolved CH$_4$ within the headspace (McAllufie, 1971). Methane concentrations were measured via GC/FID and the control concentration was subtracted from all porewater results.

**Surface emissions**

Surface gas exchange was calculated using the boundary layer equation along with measured surface water CH$_4$ concentrations and wind speed (e.g., Duchemin et al., 1999). Drifting chambers were unanchored floating diffusion chambers that consisted of a buoyed bucket (surface area 0.086 m$^2$, volume 221) to collect gas diffused at the air-water interface and surfacing bubbles (see DelSontro et al., 2010; for more details). Chambers were released upwind in the area of interest and allowed to drift. Airtight tubing was secured to a hole at the top of the chamber with a three-way stopcock for sampling the collected gas. The gas volume of the tubing was flushed before sampling, then the actual gas sample was preserved by injecting it into a serum bottle pre-filled with a saturated NaCl solution and pre-closed airtight with a stopper and aluminum cap. The solution replaced by the gas was discarded via an open needle and samples were stored upside down until analysis. Methane flux over the deployment period was calculated from the concentration increase, which was measured via GC/FID.

As the drifting chambers collected both diffusion and ebullition, we also calculated diffusion at the lake surface using the boundary layer equation (e.g., DelSontro et al., 2010). The piston velocity was calculated according to equations 3 and 5 of Crusius and Wanninkhof (2003) although actual wind speed data was scarce. Wind speeds were constructed from the few readings available at the Kariba airport during sampling (NOAA, USA) and long-term daily means and diurnal differences compiled by Mungwena (2002) and Coche (1974). Specifically, for the calculation of surface diffusion in the bays, all measured surface methane concentrations were used along with the piston velocity based on either the available daytime wind speed for July (Mungwena, 2002) or the actual wind speed.

**Hydroacoustic surveys**

Surveys of ebullition were conducted with a vertically-down oriented Simrad split-beam echosounder (EK60, 7° beam angle) with a 120 kHz transducer operating at a ping rate of 5 s$^{-1}$ and a lower threshold of $-120$ dB. The echosounder was mounted $\sim$30 cm below the water surface and calibrated with a $\sim$23 mm diameter standard copper target (Foote et al., 1987). The surveys consisted of either grid or zigzag transects depending on the
shape of the bay (red lines, Figure C.2). Data was processed with the Sonar 5 Pro software (Lindem Acquisition, Norway) after conversion with a time-varied gain (TVG) of $40 \times \log_{10} R$, where $R$ is range or depth of target, for a more accurate measurement of acoustic strength of a target called the backscatter cross-section, $\sigma_{bs}$ ($m^2$). Target strength ($TS$) is the common log representation of $\sigma_{bs}$, calculated as $10 \times \log_{10} \sigma_{bs}$ in units of dB (Simmonds and MacLennan, 2005). For a more accurate TS measurement, only single echoes holding to the following single echo criteria were accepted during conversion: (1) pulse lengths within 0.8 and 1.20 relative to the transmission pulse, (2) maximum angle standard deviation of 0.30 degrees, and (3) maximum gain compensation of $\pm 3$ dB.

In order to determine bubble density, $N$ (# m$^{-3}$), the echo-integration method of Sonar 5 Pro called TS-sv scaling was used. The acoustic energy in the desired volume of water, $s_v$ (m$^{-1}$), was divided by the average $TS$ of the targets in question (in this case, bubbles), thus yielding $N$. Bubble density was calculated for the bottom 3 m water strata starting from a 0.5 m buffer line above the lake bottom reflection as to avoid disturbance from sediments, plants, or fish lying on or near the bottom. Another buffer line was placed 1 m from the echosounder depth to avoid shallow locations where the bottom approached the near field zone (Simmonds and MacLennan, 2005). A cross-filter detector (Balk and Lindem, 2000) was applied to the file for more reliable bubble tracking, which is needed to determine the TS distribution of bubbles. Bubbles were tracked in the bottom 3 m water layer of each transect. Bubbles and non-bubble signals (i.e., fish or plankton) were distinguished based on their rise velocity. Rising bubbles have angled tracks when recorded from a moving boat ($0.15 \text{ m s}^{-1} < V_z < 0.5 \text{ m s}^{-1}$), while other signals tend to have horizontal tracks in echograms with almost no vertical velocity ($V_z < 0.1 \text{ m s}^{-1}$; Figure C.4; Ostrovsky, 2003. Finally, $N$ was calculated after cleaning all non-bubbles from the echograms with a working threshold of $-70$ dB.

In order to convert $N$ to gas volume density, the bubble volume associated with the mean $TS$ of the tracked bubbles was used. Bubble volume was calculated using the $TS$-bubble volume relationship in equation 4 from the echosounder calibration of Ostrovsky et al. (2008). Gas volume density found for each bin was converted to mass density using the Ideal Gas Law for the depth at which the bin was located. Finally, hydroacoustic sediment CH$_4$ flux was calculated using the average rise velocity of all tracked bubbles and the bubble CH$_4$ composition, which was found via GC/FID analysis of gas bubbles collected with traditional gas traps. As CH$_4$ bubbles dissolve partially during their ascent in the water column, a discreet bubble model (McGinnis et al., 2006) was used to estimate surface emission flux from the hydroacoustic sediment flux. Bubble dissolution heavily depends on initial bubble size and release depth as well as composition of the bubble and the ambient water.
Gas traps

The custom-made gas traps, which are inverted funnels with an opening of \( \sim 0.280 \text{ m}^2 \) surface area, were placed at \( \sim 1 \text{ m} \) height above the lake bed (see DelSontro et al., 2010; for more details). Collected gas volume was measured after retrieval at the lake surface in an attached cylinder and the flux was calculated in \( \text{ml m}^{-2} \text{s}^{-1} \). In addition, collected gas was sampled via an air-tight glass syringe through a septum at the top of the cylinder and delivered to a sterile serum bottle pre-filled with \( \text{N}_2 \) and closed airtight with a stopper and an aluminum cap. Samples were analyzed for \( \text{CH}_4 \) by GC/FID.

Subbasin IV hypolimnion \( \text{CH}_4 \) accumulation

The monthly \( \text{CH}_4 \) stock in subbasin IV was extrapolated from all \( \text{CH}_4 \) profiles measured in this basin (Figure C.1), thus values for February, May, June, and July were calculated. The average concentration of sampled depths from all profiles measured was applied to their corresponding depths. Concentrations between two sampling points of a profile were assumed to change linearly. The concentration profile was then multiplied by the volume of each depth strata to find \( \text{CH}_4 \) mass per strata, which were then summed to find total \( \text{CH}_4 \) stock for the basin. The \( \text{CH}_4 \) stock for the four sampled months nicely represented the major transitions in the annual hydrological cycle of subbasin IV and revealed that an exponential increase in \( \text{CH}_4 \) accumulation was likely over the course of one year (Figure C.5). Therefore, the \( \text{CH}_4 \) stock likely during the remaining 8 months of the year that were not sampled were calculated using the exponential regression best representing the hydrologic conditions illustrated by the four measured stocks (\( \text{CH}_4 \) stock = 15.851 \( e^{0.5707x} \), where \( x \) is month, \( R^2 > 0.99, n = 4; \) Figure C.5).

Dam discharge estimation

The degassing flux (\( J_{\text{deg}} \)) was approximated using an approach similar to that used by Soumis et al. (2004) and Galy-Lacaux et al. (1997),

\[
J_{\text{deg}} = (C_{w,u} - C_{w,d}) \times Q
\]

where \( C_{w,u} \) is the \( \text{CH}_4 \) concentration in water upstream of the dam, \( C_{w,d} \) is the methane concentration in water leaving the dam, and \( Q \) is dam discharge.

Concentrations at B99, the station closest to the dam (Figure C.1), were used for determining the \( \text{CH}_4 \) concentration of waters passing through the dam. The four samplings at B99 and an exponential regression were used to extrapolate concentrations to the eight
months not sampled. The oxycline level progression throughout one year was determined using temperature and dissolved oxygen data from 2007 until 2009 (data not shown) and was corrected for changing water levels.

Kariba dam has two turbine intakes on the south bank and one on the north bank; therefore, a mixture of water from different heights passes through to the downstream river. Based on the capacities of the turbines, it was estimated that 47% of total discharge passes through the one intake to the north bank turbines, 36% enters the higher intake, and 17% leaves through the lower intake on the south bank. In 2009, no water passed through the spillgates.

Finally, to determine the stratified flow through the turbine intakes and the withdrawal layer thickness, $D$ (m), a slot orifice equation adapted from Fan (2008) was used:

$$D = 2.0 \left( Q \ w^{-1} \ N^{-1} \right)^{0.5}$$

where $Q$ is discharge, $w$ is the width of the basin arm next to the intakes, and $N$ is the buoyancy frequency (strength of density stratification) that was determined based on conductivity, temperature and depth profiles. Figures C.6 and C.7 show bi-monthly results of stratified flow through Kariba Dam, including the migrating boundary between the CH$_4$-poor epilimnion and CH$_4$-rich hypolimnion.

**Whole lake emission upscaling and carbon loading comparison**

For the comparison with the carbon loading to the system, diffusion from sediments in the other subbasins must be calculated along with the total ebullition emissions. Subbasin IV diffusion plus the diffusion from the other subbasins (assuming 30 mg CH$_4$ m$^{-2}$ d$^{-1}$ calculated in a subbasin IV core) is equivalent to 43,900 t C yr$^{-1}$ (58,500 t CH$_4$ yr$^{-1}$). Ebullition emissions from the entire lake were extrapolated assuming only river deltas were active emitting regions for half of the year. The active ebullition area of the river deltas was assumed to be directly in front of the river and only up to where the bay met the open water or 20 m, whichever came first. Thus, surface ebullition from Lake Kariba deltas resulted in 38,600 t CH$_4$ yr$^{-1}$ in atmospheric emissions. Assuming a bubble dissolution rate of 35% allows us to calculate that a total of 44,500 t C yr$^{-1}$ (59,400 t CH$_4$ yr$^{-1}$) is released from the sediments via ebullition. Therefore, via diffusion and ebullition a total of 88,400 t C yr$^{-1}$ is possibly released from Lake Kariba sediments in the form of CH$_4$. Kunz et al. (2011) calculated a net carbon accumulation of 120,000 t C yr$^{-1}$ based on profundal core data as well as that from the deltas of the two major inflows. A burial efficiency of 41% was also found (Kunz et al., 2011). If we assume that 50% of the carbon remineralization results in CH$_4$ (Bastviken et al., 2008), then an emission of $\sim$86,000 t C yr$^{-1}$ is possible based on the
Kunz et al. (2011) estimate. Any differences between the carbon release estimates would arise from the fact that Kunz et al. (2011) did not account for all deltaic zones in Lake Kariba, and while the burial efficiency in deltas tends to be higher than in the lacustrine, the organic loading and sedimentation rates tend to also be higher in these areas (Sobek et al., 2009).
Chapter 5

Conclusion and Outlook
5.1 Conclusion

5.1.1 Effects of large dams in the Zambezi River Basin

This work was based on the primary hypothesis that, large dams in general, and specifically those in the Zambezi River Basin (ZRB), disrupt the riverine transport of sediment, carbon, and nutrients by both physical removal and by changing biogeochemical cycles. Our investigation of two major reservoirs in the ZRB, Lake Kariba and Itezhi-Tezhi (ITT), proved this hypothesis by showing that large reservoirs are important regulators of sediment, carbon (C), nitrogen (N) and phosphorus (P) transport, and of cycling of these substances by sediment removal and reservoir-internal processing.

By examining sediment records of Lake Kariba and ITT we demonstrated that both reservoirs are important sinks of river transported sediment, organic C (OC), N and P. A suite of sediment cores was used to describe and quantify the sedimentation regime in the two reservoirs. Due to the pronounced seasonality and interannual variability of sediment delivery by the tributaries, allochthonous sediment contributions are deposited as distinct flood layers of varying thickness over time. In addition to temporal variability, sediment accumulation was shown to vary spatially, both quantitatively and qualitatively. The variation in sediment quality was described based on geochemical signatures of the various organic matter (OM) sources. Associated with sediment retention was the removal of OC and nutrients, the latter accounting for up to 90% of inputs to the reservoirs (P removal efficiency in Lake Kariba). This high efficiency illustrates the importance of this sink function of the reservoirs for the ZRB, although, in comparison to global means for reservoirs, areal accumulation rates are relatively low for Lake Kariba and ITT. Nevertheless, the resulting decrease in riverine transport of sediment, C and nutrients most likely causes negative effects in downstream ecosystems, such as erosion and nutrient deficits. Nutrient removal by reservoirs may be considered as a positive effect in rivers receiving high anthropogenic nutrient loadings, e.g., as in developed regions. Here, in contrast, low-nutrient conditions of the relatively pristine rivers in the ZRB may be aggravated by the sink function of reservoirs.

In addition to the regulation of riverine transport, Lake Kariba and ITT were shown to act as efficient biogeochemical reactors. Primary production in the reservoir, which is larger relative to riverine systems, produces autochthonous OM, which is mineralized or buried within the reservoir or transported downstream. Autochthonous OM constitutes a relatively high fraction of total OM deposits in lacustrine sediments (> 45% in Lake Kariba) compared to global means (< 12%). For ITT, the assimilated load of C from primary production is in the same order of magnitude as riverine inputs; however, efficient
Internal recycling, mineralization and burial results in a low fraction of autochthonous OM in the outflow.

Mineralization of autochthonous OM, together with allochthonous OM, results in a net release of CO$_2$ and CH$_4$, which constitute an anthropogenic source of these greenhouse gases. Although historic data are not available, the overall greenhouse gas potential of these emissions is likely to be higher than in the pre-dam state, due to (i) mineralization of the additional autochthonous production, and (ii) anaerobic mineralization of allochthonous OM yielding the more potent greenhouse gas CH$_4$, which partly replaces pre-dam aerobic mineralization yielding CO$_2$. Our quantification of CH$_4$ emissions from Lake Kariba through different pathways revealed the dominance of CH$_4$ ebullition in littoral zones that receive lateral inflows. This finding is in contrast to other tropical reservoirs, where typically turbine outflow contribute a large portion to gross emissions. However, high ebullition rates from such littoral emission hot spots covering a relatively low portion of the reservoir surface indicate the importance of a detailed analysis of this emission pathway for the quantification of overall CH$_4$ emissions from reservoirs, and may indicate that ebullition has been underestimated in earlier studies of tropical reservoirs. In summary, despite the high emissions from ebullition hot spot areas and thanks to the low losses through the outflow of Lake Kariba, a conservative estimate of the reservoir-wide CH$_4$ emissions resulted in a 3 to 100 times lower total areal emission rate compared to other tropical reservoirs.

In terms of N cycling, modeling results illustrate the importance of N fixation as a N source for ITT, due to a generally low availability of bioavailable N. On the other hand, N is lost to the atmosphere via denitrification. Denitrification was shown to be a substantial N sink in both reservoirs (~50% of all N losses).

The results of our analysis of the biogeochemical effects in reservoirs illustrate the substantial changes of river damming on elemental cycles and transport. As a consequence, future dam development needs to take these effects into account as part of their environmental impact assessment.

### 5.1.2 Comparison of Lake Kariba and Itezhi-Tezhi reservoir

The most obvious difference between Lake Kariba and ITT is their size (Table 1.1). Consequently, ITT is flushed in a shorter period of time, resulting in a less pronounced effect of dam-induced transformation on the river transported constituents. In particular, a higher portion of sediment and associated C and nutrient inputs are retained in Lake Kariba. However, the sedimentation rate is smaller in Kariba (mean of lacustrine cores
Chapter 5. Conclusion and Outlook

∼0.2 cm yr$^{-1}$) compared to ITT (∼1 cm yr$^{-1}$), since Kariba’s sediment input load is smaller relative to the surface area.

Lake Kariba is influenced by numerous small tributaries, whereas ITT is largely dependent on its major inflow, the Kafue River. Kariba’s small tributaries are expected to transport substantial loads of OM and nutrients to the reservoir, creating the above mentioned hot spots of methanogenesis and CH$_4$ ebullition. Since such small tributaries are missing in ITT, we expect lower CH$_4$ emissions rates through ebullition, similar to littoral areas in Lake Kariba that are unaffected by small tributaries. Nevertheless, high ebullition rates may exist in the Kafue delta. Concerning downstream CH$_4$ outgassing, we do not expect high emissions from ITT, as only surface water is spilled. This setting may however change with the onset of power production (see below).

5.1.3 The potential for dam management optimization

Our analysis of Lake Kariba and ITT highlighted the importance of discharge structures in dams for the downstream water quality. If available, such structures allow for adjusting the intake levels for turbinated and spilled water. These levels correspond to water column depths, and therefore, since the reservoirs stratify, to different concentrations of dissolved and particulate constituents through most of the year.

With ITT’s current configuration, only surface water is discharged (with the rare exception of bottom water being spilled during extremely low water levels). In the near future, power production will depend on bottom water withdrawal through available discharge structures. Owing to this change in the outflow regime, our modeling results suggest low dissolved oxygen (DO) concentration and even anoxic conditions in the outflow during several weeks, as well as an increase in the output loads of dissolved inorganic N and P by a factor of 4 and 2, respectively. On the one hand, anoxic conditions, together with higher concentrations of potentially toxic reduced substances (Friedl and Wiest, 2002), are not desirable. On the other hand, higher N and P outputs may be beneficial for the downstream ecosystems if they have low nutrient availability. The respective increases in N and P loads, however, are relatively small. Overall, there is a trade-off for managing downstream water quality by discharging epilimnetic or hypolimnetic water. Moreover, it is important to note that this argumentation only holds true for annual mass balances, as the seasonal dynamic is not taken into account. Yet, this dynamic is important for approximating natural conditions and ultimately for nutrient availability in the downstream ecosystems. Therefore, the planning of artificial flood pulses from the dam mimicking nat-
ural flooding conditions should also consider water quality aspects in addition to timing and amount of water being released.

In contrast to Itezhi-Tezhi Dam, at Kariba both turbine intakes and spillway outlets are located in the approximate depth zone of the thermocline. As a consequence, a mixture of epilimnetic and hypolimnetic water is discharged from the dam. In terms of methane (CH$_4$), this setting is favorable, as CH$_4$ accumulating in the hypolimnion gets oxidized within the reservoir water body. Consequently, relatively low concentrations of CH$_4$ are found in the outflow, thus limiting the outgassing of CH$_4$ in the downstream river reaches. This emission pathway would be more important for overall emissions if predominantly hypolimnetic and CH$_4$-rich water would be turbinated. It has been shown for South American reservoirs that downstream outgassing may dominate total emissions, resulting in much larger CH$_4$ fluxes to the atmosphere than estimated in our study (e.g., dos Santos et al., 2006). Such a scenario may apply to ITT, when mainly hypolimnetic water will be turbinated in future. In fact, water column profiles of CH$_4$ concentrations measured near Itezhi-Tezhi Dam showed that CH$_4$ accumulates in the hypolimnion during the stratified period (data not shown), similar to Lake Kariba.

Similar to CH$_4$, concentration differences of C and nutrients between epilimnetic and hypolimnetic water may be cancelled out in the outflow of Lake Kariba. Although not specifically addressed in this study, the in-reservoir removal of these substances may be partly compensated for, as some hypolimnetic water, which is relatively enriched in dissolved N and P, is discharged through turbines and/or spillways. In terms of DO, mixing of epilimnetic and hypolimnetic water prevents anoxia in the outflow.

In summary, there is optimization potential in the management of dam discharge regarding downstream water quality. However, the existing discharge structures at both dams may be insufficient to address this task. To our knowledge, there are no structures planned that would allow adjusting the levels for the turbine intakes, neither at Kariba, nor at Itezhi-Tezhi Dam. Today, such structures enabling selective withdrawal are commonly used in dams (Morris and Fan, 1998). As an alternative or in addition to intake structures, oxygen poor discharge can be oxygenated by applying turbine venting (e.g., Hopping et al., 1997), by installing aeration weirs (e.g., Hauser et al., 1993) or by aerating the reservoir in front of the intakes (Singleton and Little, 2006).

In contrast to the above listed optimization potentials for the dam management, other dam-related effects are much more difficult to address with technical measures. These processes include fundamental changes associated with damming of rivers, particularly sediment and particle-bound nutrient removal. For the former effect, different mitigation strategies for relatively small dams exist. Morris and Fan (1998) describe the applicability
of flood bypasses that allow diverting sediment loads to downstream river reaches and prevent reservoir siltation. Naturally, these structures are not applicable to large reservoirs like Lake Kariba and ITT. In reservoirs with a residence time $\ll 1$ yr – typically run-of-the-river reservoirs – bottom water releases can be used for flushing accumulated sediments during storm events (Morris and Fan, 1998). While Kariba Dam lacks respective structures and has a too long residence time, ITT’s diversion tunnels near the bottom might be suitable for this purpose when density currents reach the dam (De Cesare et al., 2001).

5.2 Outlook

5.2.1 Net sedimentation

Examining sediment cores proved to be a powerful tool in quantifying the sink function of reservoir sediments. In the absence of long-term data series, sediment records helped in estimating the historic development of biogeochemical cycling in reservoirs. In addition to this temporally integrated signal, sediment cores also provide spatially integrated information, which is especially useful for studying large lakes featuring large spatial heterogeneity such as Lake Kariba. Moreover, the geochemical signature of sediment deposits reliably indicates the relative contributions of different sediment sources.

Our extrapolation of single core data to the entire reservoir sediments is based on relatively crude assumptions. To improve the representativeness of core data, we suggest the following adjustments in the sampling strategy. (i) In addition to longitudinal coring transects, lateral transects of a few additional cores would greatly improve the understanding of the depth dependency of sediment accumulation rates and of littoral sedimentation. (ii) Since it is difficult to constrain sediment accumulation rates in river deltas using simple coring devices as well as using classical sediment age models, more sophisticated methods would be required to increase the precision of overall sedimentation estimates. By using longer core liners, one may be able to ensure that the base of reservoir deposits is captured in the cores. If done at multiple locations, the extent of the delta region may become better outlined. Alternatively, if logistically feasible, seismic surveying systems could be used to generate sediment transects giving more accurate imagery of the magnitude and extent of deposits.

Sampling aiming at sectioning of pure lithotypic sediment in the cores of Lake Kariba and ITT is extremely difficult because of the fine layering at mm-scale. However, such samples would be required to describe the history and the interannual variability of the reservoirs in more detail. Depth resolution of geochemical sediment data could substan-
tially be increased by measuring the elemental composition directly on the split-surface of cores. E.g., XRF core scans may be used. Statistical analysis (e.g., PCA) of the resulting data may then yield a detailed stratigraphic description of the sediment records. This would be interesting for further exploring the flooding history and the related extent of allochthonous inputs to the reservoirs.

### 5.2.2 Gross sedimentation

Lakes are often described based on data collected at the deepest site in the centre of the lake. In turn, reservoirs are difficult to describe by a single, representative sampling site due to longitudinal gradients (Thornton et al., 1996). Moreover, reservoirs have their maximum depth usually in front of the dam. Hence, placing sediment traps at this location unlikely results in gross sedimentation rate estimates valid for the entire reservoir. It is particularly difficult to discern the significance of allochthonous OM contributions to the collected matter in the trap. Therefore, it would be desirable to moor several sediment traps along the longitudinal axis of reservoirs to resolve the longitudinal gradients in gross sedimentation.

For the quantification of the relative contribution of allochthonous and autochthonous OM sources we applied a quality-based approach that assumed certain sediment end member composition. To better constrain our results, measurements of the elemental composition of the source material, e.g., lacustrine phytoplankton and riverine OM, would yield a more precise mixing prediction.

A second limitation of sediment traps originates from artifacts introduced by mineralization of the collected trap material during deployment. Bloesch and Burns (1980) therefore suggest biweekly sampling intervals to minimize mineralization effects, in favor of addition of preservatives. This approach, however, is costly as it would require a lot of personnel for the regular samplings.

Since primary productivity and allochthonous inputs may vary interannually, gross sedimentation rates inferred from sediment traps samples may also be subject to interannual variations. This may result in substantially over- or underestimated gross sedimentation rates. For instance, Pasche et al. (2010) found that during a two-year deployment period of sediment traps the resulting gross sedimentation rate was only 50% of the long-term average. As longer deployment periods are often not feasible, independent estimates of gross sedimentation, e.g., from estimates of internal loadings, would be beneficial (Pasche et al., 2010).
5.2.3 Mass balances

While our mass balances for Lake Kariba and ITT were based on relatively solid estimates on net sedimentation and output loads, estimates of input loads were associated with large uncertainties. Major reasons to this are the lack of historic data series on water quality and our limited time in the field for own measurements. It is essential for future studies that the existing river discharge monitoring is maintained sustainably by the local authorities (e.g., the Zambian Department of Water Affairs, DWA, or the Zambezi River Authority, ZRA). Additionally, it would be ideal if this program included a minimum suite of water quality parameters. Sampling may be optimized by aiming at a better representation of the high-flow periods, when river loads are expected to be at maximum.

5.2.4 Biogeochemical modeling

Model architecture. Based on the limited data availability from ITT, we chose a relatively simple model approach (i.e., one-dimensional, adoption of existing models instead of creating a new model from scratch). One of the fundamental drawbacks of the present model implemented in AQUASIM is the boundary condition of a constant lake volume. Hence, the model levels out any imbalances between inflow and outflow. Although our model simulations did not show different outcomes depending on the lake volume, the system would be more realistically represented, if the model allowed for the seasonal volume changes accounting for up to 60% of the maximum. According to P. Reichert (personal communication), this issue may be solved by limiting the lake compartment to the minimum volume. On top of this compartment, a mixed-reactor compartment with variable volume would represent the mixed epilimnion. The two compartment types can be linked in AQUASIM, allowing for unhindered exchange of energy and substances across the interface.

A potential alternative would be choosing a different model platform. For instance, the two-dimensional model CE-QUAL-W2 (Cole and Wells, 2002) would allow for incorporating water level fluctuations and for simulation of the longitudinal variability in the reservoir. However, in contrast to the bi-monthly sampling intervals at the dam site, data from distant sampling stations is only available from one to three individual dates, making calibration of a two-dimensional model difficult.

Data availability. In general, there was a lack of data for a thorough model calibration. Most importantly, no data on the biological activity was available for the study period. Moreover, as atmospheric deposition may be a significant source of nutrients for ITT, data
on dry and wet deposition of N and P may help to better constrain primary production. Finally, as pointed out above, river inputs were poorly constrained from the available measurements. Of prime interest would be the significance of ITT’s internal processes for the fractionation between bioavailable and refractory C, N, and P species.

**Future model applications.** Given the efforts for dam management optimization at ITT in relation to its downstream effects for the Kafue Flats (McCartney and Houghton-Carr, 1998; Schelle and Pittock, 2005; Scott Wilson Piésold, 2003a,b; Sinyangwe and Stephenson, 2005), the present model may be used to quantify the effects of different management options on the biogeochemistry of ITT and the water quality in its outflow and the downstream Kafue Flats. In a second step, the model may serve as a scientific decision tool. Moreover, coupling of the present model to biogeochemical and hydrological models developed for Kafue Flats (Meier et al., 2011) may allow for an integral assessment of dam-related downstream impacts.

### 5.2.5 Methane emissions

Data collected from Lake Kariba shows the importance of CH$_4$ emissions by ebullition in the littoral zones affected by tributary inflows. Surprisingly, these fluxes were high although the reservoir level was at maximum, resulting in hydrostatic pressure impeding the release of gas bubbles. However, to improve the robustness of the estimates, spatial and temporal coverage of the sampling strategy should be optimized. Hence, we suggest expanding the measurements to other times of the year, and to other potentially important emission hot spots. For instance, it would be interesting to examine if the supply of OM from secondary tributaries is sufficient to allow methanogenesis at a high rate throughout the dry season. In terms of spatial coverage, it is unclear if emissions reach high levels in littoral zones upstream of the study sites in basin IV. High emission rates in basins I, II and III seem possible at least based on our visual observation of ebullition.

At the current stage, the causality between elevated methane emissions in tributary deltas and the assumed high input of allochthonous OM from these tributaries remains undetermined. Hence, it could again be reasonable to collect additional samples as part of a larger monitoring effort. Particularly, we suggest further examining the sediments of tributary deltas in a first step. The accumulation rates of organic C may then be compared to littoral sediments that are not directly affected by tributaries.
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“Pain is inevitable. Suffering is optional.” Haruki Murakami
Bibliography


(Oreochromis niloticus and Serranochromis thumbergi), and crayfish (Cherax quadricarinatus) in Lake Itezhi-tezhi and Lake Kariba, Zambia. * Archives of Environmental Contamination and Toxicology, 59*, 291–300. doi: 10.1007/s00244-010-9483-8.


Soils Incorporated (2000). Kariba Dam case study, Input to the World Commission on Dams. World Commission on Dams, Cape Town, South Africa.


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