

DECLARATION

This thesis was written and submitted in accordance with the rules and regulations governing the award of Master of Science in Integrated Water Resources Management of the University of Zambia. I further declare that the thesis has neither in part nor in whole been presented as substance for award of any degree, either to this or any other University. Where other people’s work has been drawn upon, acknowledgement has been made.

Signature of Author:

Date:

APPROVAL

This dissertation of Frank Chisoni Nyoni is approved as fulfilling the requirements of the Degree of Master of Science in Integrated Water Resources Management of the University of Zambia.

Signature: Chairperson:

1st Examiner:

2nd Examiner:

External Examiner:

ABSTRACT

This study focuses on the spatial and temporal variability of various carbon fractions and fluxes in relation to major biogeochemical parameters in the Zambezi River in Zambia and its major tributary, the Kafue River. Concentrations and composition of stable isotopes of dissolved organic carbon, particulate organic carbon and dissolved inorganic carbon were measured for a range of biogeochemical characteristics. Physico-chemical parameters, aquatic metabolism and partial pressure of CO₂ (pCO₂) were measured using multi-meters and headspace technique to determine the dynamics of carbon. To determine factors influencing the two river systems, stable isotope compositions were also used. Results indicate that pH decreased (7.4 to 6.9 on average) whereas dissolved organic carbon (DOC) increased (3.1 to 4.5 mg/L on average) over sections of the river that traverse extensive floodplains in both rivers. Weathering and dissolution of silicate elements predominated in the Zambezi whereas carbonate weathering and dissolution in the Kafue River, making dissolved inorganic carbon (DIC) twice as high (1.6 mmol/L on average) in the Kafue River compared to the Zambezi River (0.7 mmol/L on average). Heterotrophic respiration in the floodplains resulted in the depletion of dissolved oxygen (6.7 to 1.8 mg/L on average). The pCO₂ averaged 2,880 and 4,426 ppm during the wet season and 944 and 2,790 ppm during the dry season on the Zambezi and Kafue rivers, respectively. The isotopic signature for DOC ($\delta^{13}\text{C}$ -DOC) for both rivers averaged around -22.0 ‰ suggesting DOC is of mixed origin, C₃ (65%) and C₄ (35%) vegetation. Isotopic signature for POC ($\delta^{13}\text{C}$ -POC) in both rivers ranged between -29‰ and -24‰ suggesting more aquatic produced phytoplankton on reservoirs (C₃ origin) and terrestrially derived C₃ vegetation along the river channels. The variations in the isotopic signature for DIC ($\delta^{13}\text{C}$ – DIC) values (-22 to -5‰) for both rivers could largely be explained by the different relative contributions of silicate and carbonate weathering as observed in the Si/Ca ratio. The isotopic signature on the Kariba Reservoir was enriched (-4‰ to -1‰) in the ¹³C isotope. The carbon dynamics of the Zambezi and the Kafue rivers are different. Differences in geology, land-use (agriculture and mining) and hydrological regimes of the two river systems account for the majority of the differences observed in the patterns of carbon on the two river systems.

ACKNOWLEDGEMENTS

Special thanks go to Professor Imasiku A. Nyambe for believing in me and for giving me guidance during his supervision of this dissertation. Thanks also go to Dr. Cristian Teodoru for guiding me through the research and the science of this dissertation. A great heart is in Mrs. Charity Lweya Mundia, PhD student, and George Z. Ndhlovu, Provincial Water Officer in Department of Water Affairs, through whom dreams became reality. Am indebted and grateful to my dear wife, Fridah Mwelwa Nyoni, and my wonderful son, Brian Takondwa Nyoni and lovely daughter, Victoria Bupe Nyoni, for their unwavering love and support during the times I had to be away for months doing research. Special thanks to UNZA-IWRM Centre, Ms Carol Mweemba and Ms. Ingrid Mugamya for working out many logistics.

I also appreciate the financial support of the Royal Danish Embassy (DANIDA) through the Danish Embassy Lusaka for the opportunity given to receive training at University of Zambia (UNZA) and Technical University of Denmark (DTU). The financial support of the Katholieke University (K.U) of Leuven under the AFRIVAL project made it possible for me to travel around almost the whole Zambia and part of Mozambique as we followed major river systems in Zambia from source to confluence. The opportunity accorded me to learn new techniques in the Laboratories of K.U Leuven in Belgium will forever be appreciated.

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CHAPTER 1: INTRODUCTION

1.1 Background

The transfer of carbon from the land to the oceans via river systems is a key link in the global carbon cycle (Ludwig et al., 1996; Brunet et al., 2009; Richey, 2005). While accounting for only 0.3 % of total freshwater resources and covering just a small portion (~1%) of the Earth surface, inland waters process about 2.7 Petagrams of Carbon annually (Pg C/yr) of which about 0.9 Pg C/yr is estimated to reach oceans (Cole et al., 2007; Aufdenkampe et al., 2011). Riverine carbon is found in several forms. It can be Organic Carbon (OC) or Inorganic Carbon (IC), whereas these forms can be found as either Dissolved Organic Carbon (DOC) or Dissolved Inorganic Carbon (DIC). Carbon can also be found in particulate phases as Particulate Organic Carbon (POC) and/or Particulate Inorganic Carbon (PIC). PIC is only found in particular cases where CaCO_3 is oversaturated in the river. Rivers also discharge into the world's oceans approximately 0.5 Pg C/yr as DIC and about 0.4 Pg C/yr as organic C with about one-half each as POC and DOC (Probst et al., 1994). Variations in catchment slopes, vegetation, geology, climate and size account for the differences in the carbon fluxes of individual river systems (Hope et al., 1994). Globally, riverine DOC fluxes depend on drainage intensity, basin slope and to a larger extent, the amount of carbon stored in soils, whereas POC is a function of total sediment load which principally depends on drainage intensity, rainfall intensity and basin slope (Ludwig et al., 1996).

Dissolved Organic Carbon (DOC) in the river can have many different sources. Most prominent among sources are terrestrial inputs whilst in-stream biological processes (autochthonous source) and atmospheric inputs contribute to a lesser degree. Likens et al. (1983) reports values for DOC concentration ranging between 0.07 and 3.10 mg/L and POC concentration of between 0.02 and 1.83 mg/L in rainwater. Allochthonous sources in the river (which is the carbon not produced in the river itself) comprises the terrestrial and atmospheric inputs. Terrestrial inputs are mainly from vegetation through litter, leaching from live vegetation, microbial metabolism in soils, erosion of soil

organic matter and root exudation (Thurman, 1985). Other sources could also be from anthropogenic sources such as effluent and industrial discharges.

Dissolved Inorganic Carbon (DIC) is produced by weathering and dissolution of carbonate and silicate rocks. Other sources include soil respiration, aquatic respiration and atmospheric dissolution. In headwater streams, the main source of CO₂ gas is from the unsaturated zone of the soil, which is formed during respiration of live roots and by microbial decay of litter and the roots (Edwards and Harris, 1977). DIC may also be present as CO₂ generated by the decomposition of dissolved organic matter (Das et al., 2005). These processes generate the alkalinity of the river water, and also influence the pH of water, which governs the subsequent partitioning of DIC between dissolved CO₂, bicarbonate and carbonate ions. At high pH (8.2 and above) the carbonate ion (CO₃²⁻) is the dominant species, whereas between pH 6 - 8 the bicarbonate ion (HCO₃⁻) is the dominant species and at low pH the neutral H₂CO₃ (CO₂(aq)) dominates. The fraction of DIC present as dissolved CO₂ is almost always at concentrations much greater than the atmospheric concentration (Richey, 2005; Cole and Caraco, 2001) resulting in a net flux of CO₂ to the atmosphere, thereby demonstrating that rivers are a source of CO₂ to the atmosphere. The only way that dissolved CO₂ can exist at supersaturated conditions in rivers is if allochthonous sources dominate and/or the waters are net heterotrophic (i.e. gross primary production is lower than ecosystem respiration) fueled by carbon from the land (Cole and Caraco, 2001).

Tropical river systems are estimated to account for 60 and 34 % of global riverine C flux and sediment delivery, respectively, to the global oceans (Ludwig et al., 1996). Current figures based on recent data compilations suggest that globally, more than half of the carbon that enters freshwater ecosystems from the terrestrial biome is processed and emitted into the atmosphere as C gases, while less than 50% ultimately reach the ocean (Cole et al., 2007; Tranvik et al., 2009). In view of the increasingly recognized importance of freshwater ecosystems in the carbon cycle (Cole et al., 2007; Tranvik et al., 2009; Aufdenkampe et al., 2011; Raymond et al., 2013) and considering the disproportionate role tropical rivers have in global riverine C export, the

biogeochemistry of tropical rivers merits particular attention. Despite large uncertainties related to these global estimates, it is however evident that freshwater ecosystems play vital ecological and biogeochemical roles in the carbon cycle, that is however, largely disproportional to their areal extent (Cole et al., 2007). Nevertheless, their contribution to either regional or global carbon budgets remains yet unclear as inland waters are rarely incorporated into terrestrial C models. Quantifying the role of freshwater systems as C sinks and sources, understanding the link between terrestrial and aquatic environment and the underlying biogeochemical processes are therefore fundamental for reliable assessments of land use-related changes in carbon dynamics and for improving the balance approach of ecosystem carbon budgets (Cole et al., 2007).

This research is a part of a large interdisciplinary project (“African river basins: catchment-scale carbon fluxes and transformations”) hosted at the Department of Earth and Environmental Sciences (K.U. Leuven) and the Chemical Oceanography Unit (Université de Liège), which explores the role of large tropical river systems in carbon cycling at the catchment scale. The present study focus is on the spatial and temporal variability of various carbon fractions and fluxes in relation to major biogeochemical parameters in the Zambezi River in Zambia in comparison with the Kafue River, its major tributary. Based on detailed survey of spatial distribution and temporal variability of a range of physico-chemical and biological parameters extended over two years period, this Zambian component of the research attempted to quantify and compare C fluxes of the Zambezi and Kafue rivers, and explore how distinct local and regional factors (land-use, geology, vegetation patterns, hydrological and anthropogenic activities, etc.) influence the behaviour of the Zambezi and Kafue rivers.

1.2 Study Area

The Zambezi River rises in northwest Zambia from a small spring on the gentle upland of the Southern Equatorial Divide - the watershed that separates the river from north-west-flowing tributaries of the Congo. For some 30 km, the Zambezi headwaters flow to the north, towards the Congo, but then the course swings to the south-west, around a low ridge of Karoo Sandstone known as Kalene Hills (Moore et al., 2007). This direction is

maintained for a further 200 km into Angola before the river finally turns south-eastwards into Zambia on its way to the Indian Ocean. It is with such indecision that southern Africa's largest river commences its course (Moore et al., 2007). From its headwaters to the delta in Mozambique, the Zambezi River runs over 2,600 km and connects eight African nations that share different portions of its 1.4 Mio km² drainage basin: Angola (18.3%), Namibia (1.2%), Botswana (2.8%), Zambia (40.7%), Zimbabwe (15.9%), Malawi (7.7%), Tanzania (2.0%) and Mozambique (11.4%) (Davies, 1986). A little above the confluence with the west bank Lungwebungu Tributary, which rises in the Angolan highlands, the Upper Zambezi widens into the Barotse Floodplains. This is a very low gradient stretch of shallow, languid water, some 180 km in length and 30 km in maximum width during periods of peak flood, which extends to just above Ngonye Falls. A second geomorphologically distinct section of the river, designated the Middle Zambezi commences immediately below the Victoria Falls. It is characterized by a markedly steeper gradient than the section above the Victoria Falls. Downstream of the Chicoa Basin, the river flows through one last gorge - the Cahora Bassa, before entering an indolent stretch of the river known as the Lower Zambezi, which traverses the Cretaceous and Tertiary Sedimentary cover of the low-lying (0–400m) Mozambique Coastal Plain (Moore et al., 2007). Several large dams have been constructed on the Zambezi and tributaries (e.g. Kariba, Cahora-Bassa, Itzhi Tezhi) and others are under construction making the Zambezi River the most dammed river in Africa (Figure 1.1).

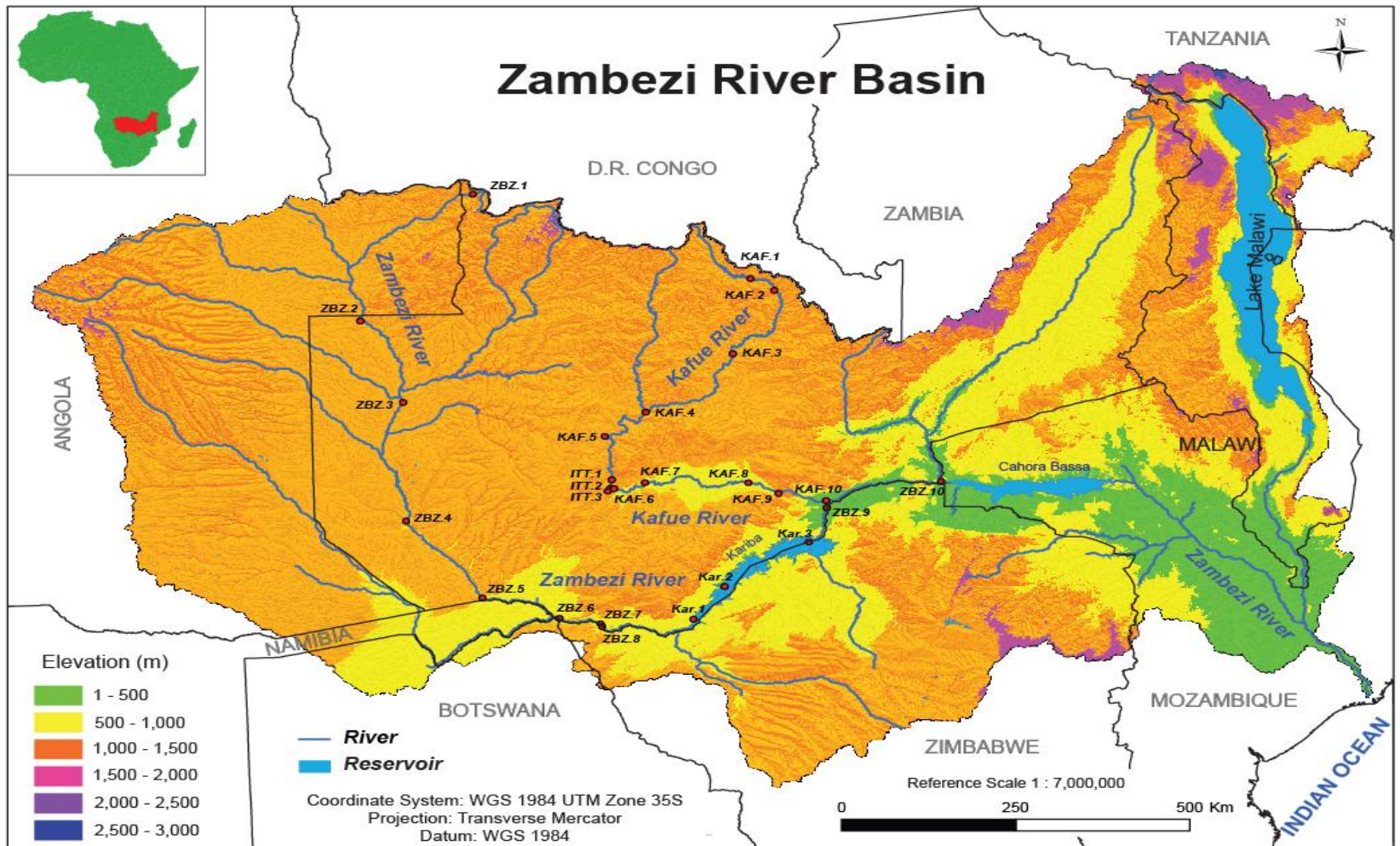


Figure 1.1: Map showing the elevation gradient within the catchment, the major hydrographic network and the distribution of sampling sites (modified after C.R. Teodoru, unpublished data)

The Kafue River Basin is a major sub-catchment of the Zambezi River Basin and lies entirely within Zambia. The basin covers only around 20 % of the total land area of Zambia (152,000 km²) but it is home to almost half of the country's population of about 13 million people (CSO, 2010). Given its large concentration of mining, industrial and agricultural activities, the Kafue River Basin plays a central role in the economy of the country. The Kafue River originates in northwestern Zambia, from where it flows south to the Itezhi Tezhi Storage Dam. At Itezhi Tezhi the river turns east and passes through the Kafue Flats. Further downstream, the river drops steeply into the Kafue Gorge, after which the Kafue joins the Zambezi River approximately 100 km upstream from the Mozambican Border. The river is 1,500 km in length (up to the confluence with the Zambezi). Its drainage basin can be sub-divided into three sub-basins (a) the upper basin in the wetter northern part of Zambia, roughly north of Itezhi Tezhi Dam, an area mostly impacted by mining activities; (b) the middle area referred to as the Kafue Flats from Itezhi Tezhi to the Kafue Gorge and (c) the lower part of the river from the Kafue Gorge down to the confluence with the Zambezi River where the river drops steeply from the plateau to the level of the Zambezi River (Wamulume, 2011). The Kafue River Basin is the most studied and developed of Zambia's river basins (JICA-MEWD, 1995).

1.2.1 Climate

The Zambezi River lies within the tropics. The upper and middle course of the river is on an upland plateau and traverses much of the Western Province of Zambia which has an average temperature of 22.1 °C (JICA-MEWD, 1995). The winter months (June to August) are cool and dry, with temperatures averaging 20 °C. Between August and October there is a considerable rise in average temperatures, particularly in the river valley itself; just before the rains begin in October. The annual rainfall ranges from 700 mm in the extreme southwest to 1,400 mm in the north and is 1,001 mm on average (JICA-MEWD, 1995). During this time, the Upper Zambezi receives nearly all its total rainfall and this accounts for the great variation in the flow of the river throughout the year. Studies have suggested that a microclimate in the area of Kariba Reservoir has created a rise in precipitation, possibly as a result of a lake breeze blocked by the escarpment that produces thunderstorms (The World Bank, 2010).

The Kafue River Basin has the same tropical climate with two distinct seasons, a wet season between November and March and a dry season between April and October. Mean temperature varies from 13 °C to 20 °C in July and 21 °C to 30 °C in November (JICA-MEWD, 1995).

Annual mean climatic conditions described in the Water Resources Master Plan (JICA-MEWD, 1995) are an annual mean temperature of 21.3 °C, average annual rainfall of 1,001 mm and an average annual pan-evaporation of 2,061 mm.

1.2.2 Hydrology

Rainfall and runoff in the Kafue River Basin are comparatively high, averages around 1,050 mm and 12,913 km³ per year, respectively (The World Bank, 2010). The highest flows occur in March and are estimated to be 9,715 km³. The Kafue Gorge Upper (KGU) hydropower station is located at Kafue Gorge, where this gauging station is located. Releases from the Itzhi Tezhi Dam (ITT) regulate power generation. Between the ITT and KGU lies the ecologically important floodplain called the Kafue Flats which has gentle river gradient and high evaporation losses. Therefore, releases from the ITT may not reach the KGU for up to 2 months, which attenuates flows considerably (The World Bank, 2010). The monitoring station on the Kafue River is located about 60 km downstream the Kafue Gorge, which receives the flow as at the Kafue Gorge because there are no contributors in between these two points. Below the Gorge, flow is almost constant throughout the year except for short pulses which are as a result of flow regulation (Figure 1.2) (ZESCO, 2013). However, the unregulated flow measured at the Hook Bridge on the Kafue River shows very regular and clear cycles annually. Sampling for the wet season campaign (February to March, 2012 and January to March, 2013) and dry season campaign (October to November, 2013) are indicated by yellow bars in Figure 1.2.

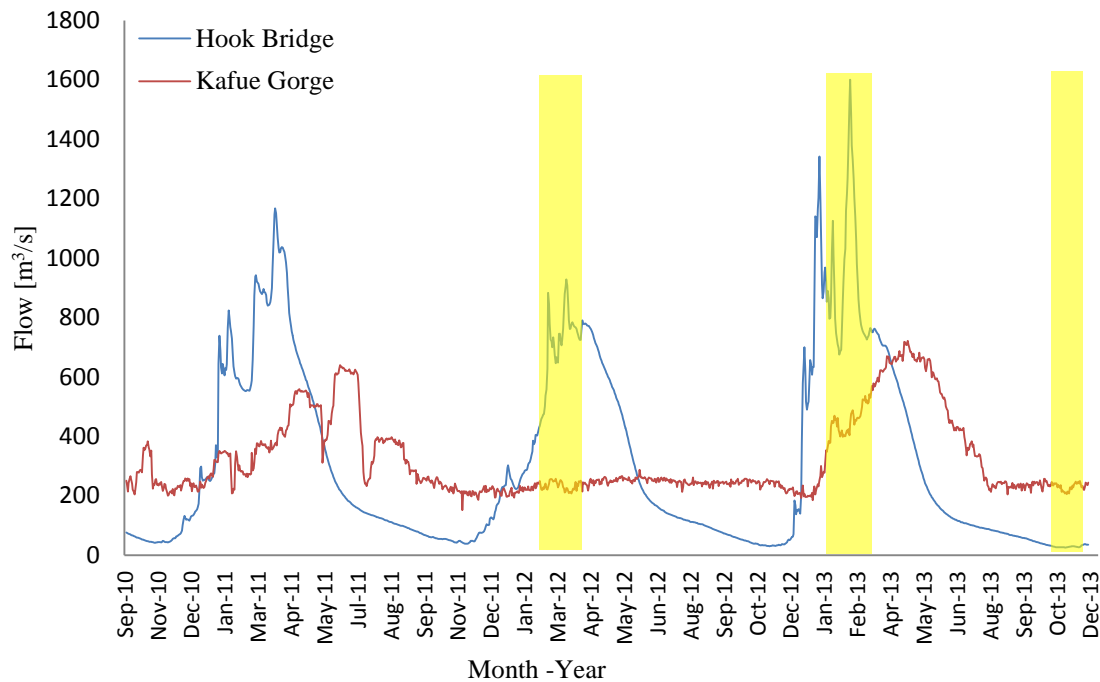


Figure 1.2: Hydrograph showing unregulated flow at Hook Bridge and regulated flow at Kafue Gorge, Zambia. Yellow bars show times of sampling in 2012 and 2013 campaigns (After Zambia Electricity Supply Corporation, 2013)

The Kariba Dam, located at the border of Zambia and Zimbabwe, creates the Kariba Reservoir which is the second largest man-made lake in Africa after Lake Volta. This sub-basin has a mean annual precipitation of 700 mm/year but nevertheless contributes an estimated $8,400 \text{ km}^3/\text{year}$ to overall flow in the basin (The World Bank, 2010). The hydropower station generates 30% of the hydropower capacity for Zambia. This gauging station is located approximately 75 km from our monitoring station on the Zambezi River. Since the monitoring station is downstream, it receives the regulated flow at Kariba Dam. Below the Kariba Dam, flow is almost constant throughout the year except for short pulses (flow regulation). The flow at the Victoria Falls shows very clear and regular annual cyclicality (Figure 1.3). Sampling for the wet season campaign (February to March, 2012 and January to March, 2013) and dry season campaign (October to November, 2013) are indicated by yellow bars in Figure 1.3.

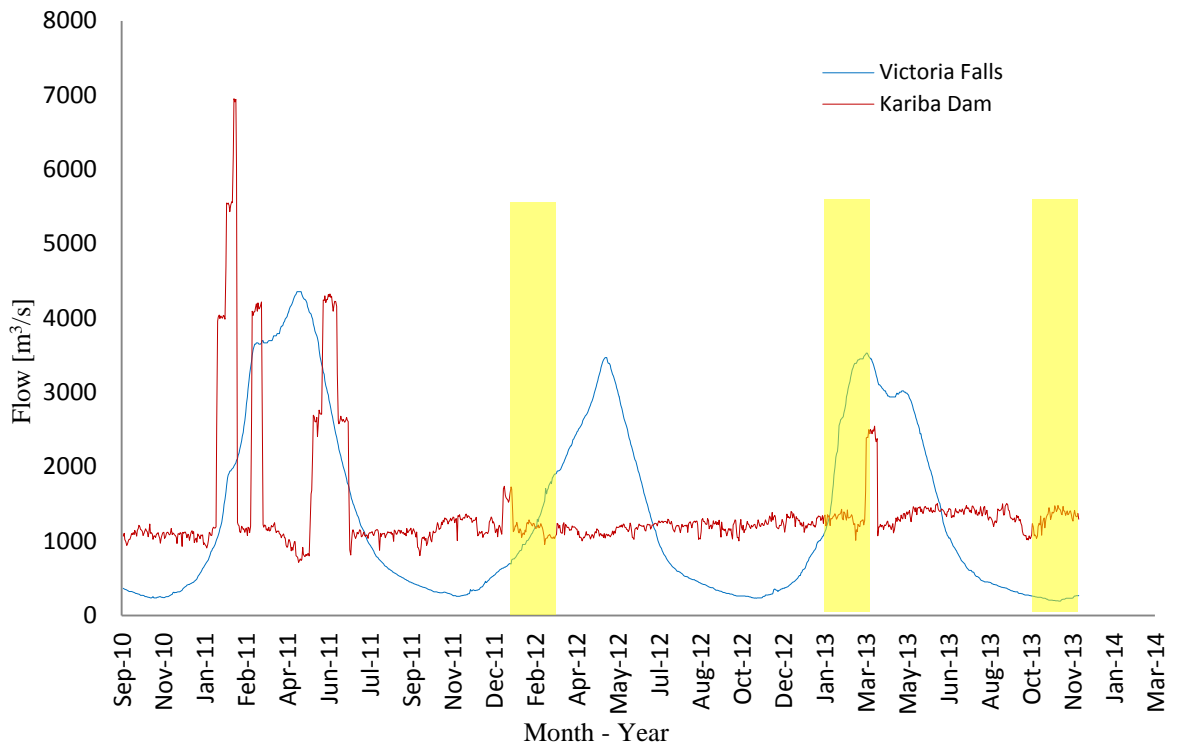


Figure 1.3: Hydrograph showing unregulated flow at Victoria Falls and regulated flow at Kariba Dam, Zambia. Yellow bars show times of sampling in the 2012 and 2013 campaigns (After Zambezi River Authority, 2013)

1.2.3 Geology

The geology of Zambia comprises various rock formations and layers consisting of igneous, sedimentary and metamorphic rocks from Precambrian to Recent times (Figure 1.4).

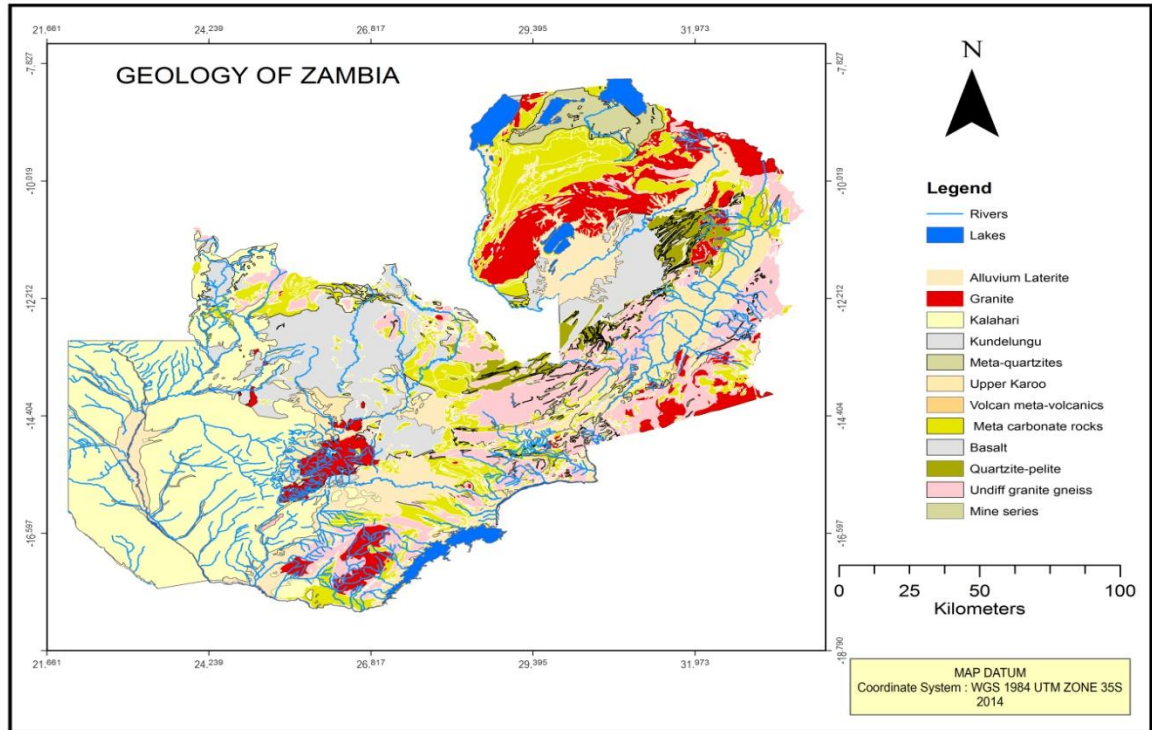


Figure 1.4: Geology of Zambia (modified after Armstrong, 2009)

The Cenozoic and Mesozoic supergroups have particular attention in this study because much of the Zambezi River traverses them. The Katanga Supergroup is also important because it characterizes much of the Copperbelt and Central regions of Zambia where the Kafue River passes. The geological age from Cenozoic to Precambrian Era are briefly summarized in Table 1.1.

Brief descriptions of the Supergroups are given as follows:

(i) Basement Complex

The complex is the oldest sequence in Zambia that consists of highly deformed gneisses, schists, conglomerates, quartzites, crystalline limestone, migmatites and granites. The outcrops are mainly in the east and south-eastern parts of Zambia (JICA-MEWD, 1995).

Table 1.1: Table showing the stratigraphy of Zambia (modified after Armstrong, 2009)

Geological Age		Supergroup	Groups or Formation	Rocks and Sediments
Cenozoic Era	Quaternary	Cenozoic	Alluvium	Alluvium sands, Gravel with clay
	Tertiary		Kalahari Group	
Mesozoic Era	Cretaceous	Mesozoic	Lower Cretaceous Formation	Fine sand, Sandstone with clay
				Mudstones, Siltstones
Palaeozoic Era	Jurassic Carboniferous	Karoo	Upper Karoo Group	Basalt, Interbedded sandstones, Sandstones, Mudstones, Siltstones
			Lower Karoo Group	Mudstones with coal measure, Siltstones, Sandstones, Conglomerates
	Silurian Ordovician	Lower Palaeozoic		Quartzites, Shales, Sandstones
	Early Palaeozoic Precambrian	Katanga	Kundelungu Group	Carbonate rocks with shales, Shales, Siltstones
Upper Roan Group			Dolomites, Argillites	
Lower Roan Group			Quartzites, Argillites, Dolomites, Conglomerate, Mine series shales	
Precambrian Era	Basement and Muva	Muva Group	Shales, Mudstones, Sandstones	
		Basement Complex	Basement gneisses, Migmatites, Schists	
Various age mainly older Precambrian		Intrusive and Metamorphic Rocks		Basic-igneous rocks, Meta-igneous rocks, Amphibolites, Metasediments

(ii) Katanga Supergroup

The Katanga Supergroup comprises shale, sandstone, quartzites, limestones, conglomerates and dolomite layers that range from Precambrian to Cambrian in age. It occurs in the northern and central parts of Zambia (JICA-MEWD, 1995). The Kafue River traverses much of the Katanga Supergroup on the Copperbelt.

(iii) Lower Palaeozoic Supergroup

The supergroup comprises shales, quartzites and arkose sandstones. Lower Palaeozoic Supergroup is extremely limited and its existence is only evident in the mid-Zambezi Valley and western parts of Zambia, where it overlies the Katanga Supergroup (JICA-MEWD, 1995).

(iv) Karoo Supergroup

The supergroup occurs along the Luangwa River, mid-Zambezi Valley and western part of Zambia (JICA-MEWD, 1995). Tillites of fluvio-glacial origin, mudstones coal measure, marls, conglomerates and basalts corresponding to the Carboniferous to Jurassic Period compose the Karoo Supergroup.

(v) Mesozoic Supergroup

The supergroup occurs along the Zambezi River and to the west of Zambia, overlying the basalt of the Karoo Supergroup (JICA-MEWD, 1995). The supergroup has an estimated thickness of 100 m of mudstones judged to be Cretaceous in age based on the discovery of certain fossils.

(vi) Cenozoic Supergroup

The supergroup comprises Tertiary Sandstone, Quaternary consolidated sand layers (duricrusts) and clay layers. In a larger part of the extreme west of Zambia (Barotse Basin), Cenozoic Supergroup overlies the Mesozoic Supergroup (JICA-MEWD, 1995).

(vii) Intrusive Rocks

These are of varying age and type, which mainly intrude the Precambrian rocks and the majority are granites. The remainder are gabbros, dolerites, syenites and others (JICA-MEWD, 1995).

1.3 Problem Statement

There is paucity of data on the biogeochemistry of river systems in Zambia. Zambezi River is the 4th largest river in Africa (and the largest flowing into the Indian Ocean from the African continent), yet its biogeochemistry has seldom been studied. Similarly, its tributary the Kafue River only has a handful of existing studies (e.g. Wamulume et al., 2011; Zurbrügg, 2012; Zurbrügg et. al., 2013). This does not demonstrate their equal importance in regional C cycles, and therefore suggest that further research is needed in order to effectively incorporate these aquatic ecosystems into whole-landscape perspectives. Moreover, given immanent climate and land-use change, population rise and ongoing economic development, understanding the interaction between terrestrial and aquatic ecosystems is therefore vital for ecosystem carbon budgets and balancing approaches as those changes will exert further pressure on these aquatic environments. It is in this regard that this study is undertaken to determine and compare the carbon dynamics of the Zambezi and Kafue rivers and also determine and compare how distinct local and regional factors are influencing the behaviour of these two river systems.

1.4 Research Objectives and Research Questions

This section outlines the objectives of this study and the research questions it attempts to answer. These are to determine and compare:

- (i) Carbon dynamics of the Zambezi and the Kafue rivers; and
- (ii) How distinct local and regional factors (land-use, vegetation patterns, geology, hydrological and anthropogenic activities) are influencing the behaviour of the Zambezi and Kafue rivers.

By quantifying and comparing C dynamics of the Zambezi and Kafue rivers, this comprehensive study intends to answer the following research questions:

- (i) Which particular sites (headwaters, reservoirs and floodplains) are the primary hotspots for CO₂ evasion?
- (ii) How much of the C fractions are undergoing downstream export in these two river systems?
- (iii) What is the influence of floodplains and reservoirs on river biogeochemistry?
- (iv) What is the influence of catchment land-use and vegetation patterns on the inputs, origin and biogeochemical processing of organic matter in aquatic systems?

1.5 Significance of the Study and Scientific Contribution

The rising population in Zambia has changed land uses and has increased water usage (e.g. new dams, more water use for agriculture) and the increasing economic and industrial development have also accelerated pollution of aquatic systems. These anthropogenic activities are thus changing the biogeochemistry of river systems. Results of this study are of a great importance for the management of natural water resources in Zambia as they will highlight the role of freshwaters in the cycling of carbon which in turn plays a vital role in the emissions of carbon dioxide from river systems, a potent heat trapping gas which has influence on the global warming and climate change/variability affecting humans today. Knowledge of impacts of reservoirs and floodplains on river biogeochemistry is also of great significance to companies such as ZESCO who would manage bottom water releases in reservoirs which affects downstream ecosystem functioning and productivity (e.g. fisheries). This study would also benefit ZESCO with the knowledge of whether there is CO₂ release or uptake at Kariba Reservoir because producing energy with no or low carbon footprint could earn the company monetary benefit on the Carbon Credits Market. This being the first comprehensive study at basin scale to explore the role of large tropical river systems on carbon cycling makes significant scientific contribution to under-represented scientific literature on biogeochemistry in Zambia.

CHAPTER 2: LITERATURE REVIEW

This chapter reviews literature that relates to this study. The global carbon budget, carbon pools and the role of fresh water in the global carbon cycle are reviewed in literature. River water parameters that are cardinal to this study are reviewed and the knowledge gap that this study fills is identified.

2.1 The Global Carbon Budget

Carbon is part of the building block of life. All living things are made of elements, the most abundant of which are oxygen, carbon, hydrogen, nitrogen, calcium and phosphorous. Of these, carbon easily bonds with other elements to form compounds necessary for life such as sugars, starches, fats and proteins. The total carbon pool on Earth is estimated at about 10^{23} g C (Schlesinger, 1997). The carbon that is part of the global carbon cycle is called the active pool of carbon and is approximately 4×10^{19} g C (Schlesinger, 1997).

Carbon is also present in the Earth's atmosphere, soils, oceans and crust. When viewing the Earth as a system, the atmosphere, soils, oceans and the earth's crust can be referred to as carbon *pools* (sometimes also called *stocks* or *reservoirs*) because they act as storage houses for large amounts of carbon (Figure 2.1) (NASA Earth Science Enterprises, 2010).

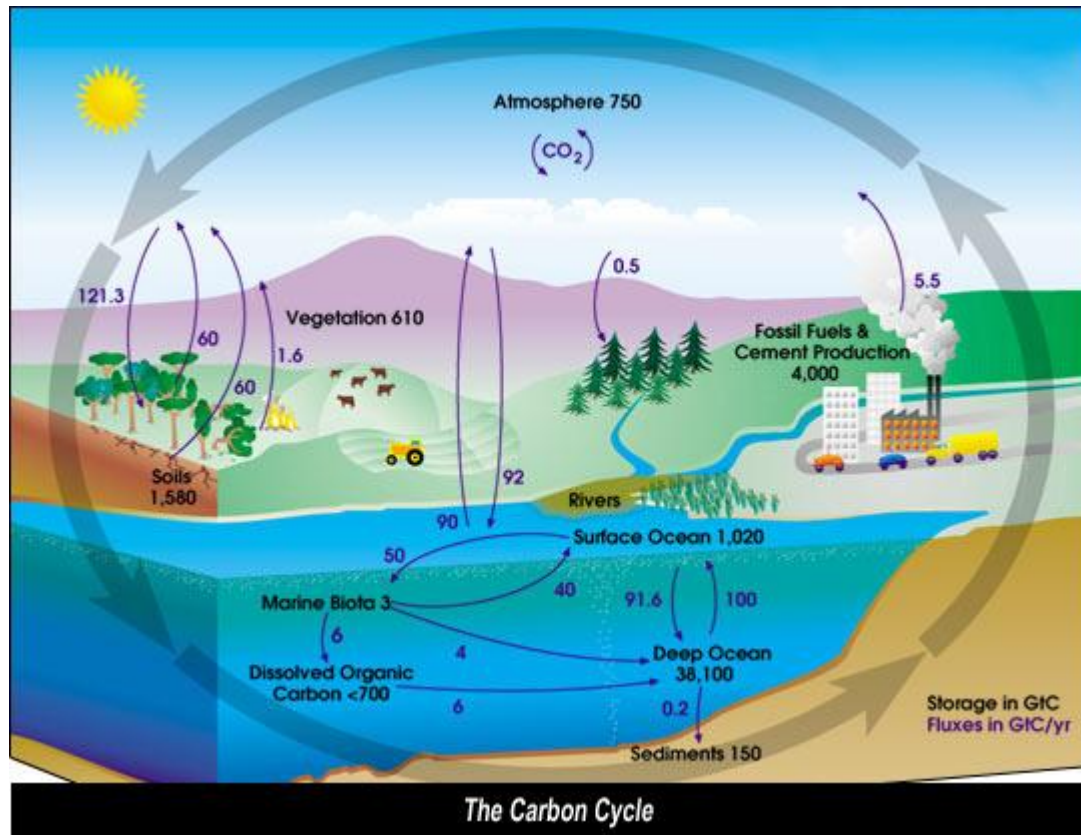


Figure 2.1: Global Carbon Cycle. Units for pools (black) are 10^{15} C and fluxes (blue) in 10^{15} C/yr. (NASA Earth Science Enterprises, 2010)

2.2 Carbon Pools

This section describes the different carbon pools which act as storage houses for large amounts of carbon.

2.2.1 The Earth's Crust

The majority of the carbon is buried in sedimentary rocks within the Earth's crust with approximately 6.5×10^{22} g C as carbonates (Schlesinger, 1997) and about 1.6×10^{22} g C in organic compounds (Des Marais et al., 1992). These are rocks produced either by the hardening of mud (containing organic matter) into shale over geological time or by the collection of calcium carbonate particles from the shells and skeletons of marine organisms into limestone and other carbon containing sedimentary rocks. About 4,000 Petagrams of Carbon (Pg C) is stored in the Earth's crust as hydrocarbons formed over

millions of years from ancient living organisms under intense temperature and pressure. These hydrocarbons are commonly known as fossil fuels (Des Marais et al., 1992).

2.2.2 The Oceans

The Earth's oceans contain 38,100 Pg C (Figure 2.1), most of which is in the form of dissolved inorganic carbon. A much smaller amount of carbon, approximately 1,000 Pg, is located near the ocean surface making the oceans the largest near surface carbon pool. This carbon is exchanged rapidly with the atmosphere through both physical processes such as CO₂ gas dissolving into the water and biological processes such as the growth, death and decay of plankton. Therefore, changes in the atmospheric carbon dioxide concentration can be buffered by the oceans because at equilibrium, the ocean contains about 56 times as much carbon as the atmosphere (Schlesinger, 1997).

2.2.3 The Atmosphere

The atmosphere contains approximately 750 Pg C (Schimel et al., 1995), most of which is in the form of carbon dioxide with much smaller amounts as methane (CH₄) and various other compounds. Although this carbon is considerably less than that contained in the oceans or crust, carbon in the atmosphere is of vital importance because of its influence on the greenhouse effect and climate. The relatively small size of the atmospheric C pool also makes it more sensitive to disruptions caused by an increase in sources (volcanic eruption, anthropogenic pollution) or sinks of C from the Earth's other pools. National Oceanic and Atmospheric Administration (NOAA) is a United States Federal Agency focused on the conditions of the ocean and the atmosphere. NOAA operates the station Mauna Loa in Hawaii, known to be the oldest continuous carbon dioxide (CO₂) measurement station in the world and as such it has become the primary global benchmark site for monitoring the increase of this potent heat-trapping gas. On 9th May, 2013, the daily mean concentration of carbon dioxide in the atmosphere at Mauna Loa surpassed 400 parts per million (ppm) for the first time since measurements began in 1958 (Figure 2.2).

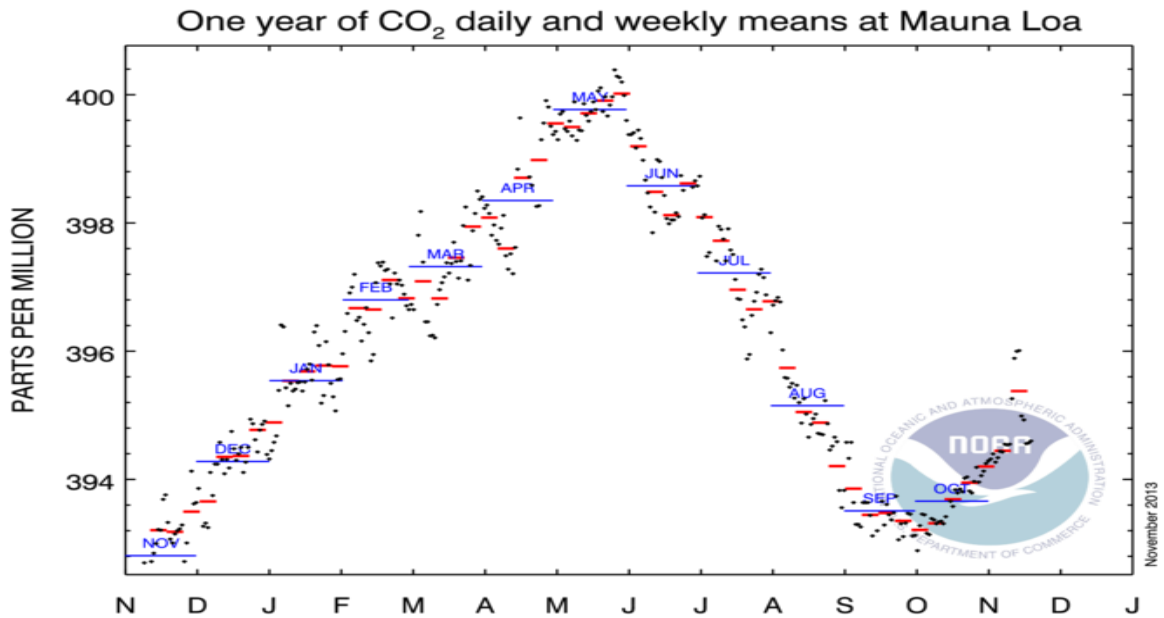


Figure 2.2: Weekly (red line), monthly (blue line) and daily (black points) averages at Mauna Loa for the year 2013 (NOAA website)

The increase of atmospheric CO₂ levels that has occurred in the past several centuries is the combined result of increased C emissions to the atmosphere due to increased consumption of fossil fuels and from terrestrial ecosystems via deforestation and other forms of land clearing. Human impact is the most important contributor to this increase in CO₂ emissions to the atmosphere. Rising CO₂ concentration is the main driver of present climate variability/change and global warming (IPCC, 2007).

2.2.4 Terrestrial Ecosystems

Terrestrial (land) ecosystems are a natural unit consisting of all plants, animals and micro-organisms in an area functioning together with all the non-living physical factors of the environment such as water, rocks, light and temperature. These ecosystems contain carbon in the form of plants, animals, soils and microorganisms (bacteria and fungi). Of these, plants and soils are by far the largest contributor. Unlike the Earth's crust and oceans, most of the carbon in terrestrial ecosystems existed in organic form in most upland ecosystems and was likely to have been fairly constant before widespread human disturbance of soils (Schlesinger, 1997). In this context, the term "organic" refers to compounds produced by living organisms, including leaves, wood, roots, dead plant

material and the brown organic matter in soils (which is the decomposed remains of formerly living tissues). Plants exchange carbon with the atmosphere relatively rapidly through photosynthesis, in which CO₂ is absorbed (Gross Primary Production, GPP) and converted into new plant tissues and Ecosystem Respiration (ER), where some fraction of the previously captured CO₂ is released back to the atmosphere as a product of metabolism by plants (Autotrophic Respiration, AR) or by animals, bacteria and fungi (Heterotrophic Respiration, HR) (Cole and Caraco, 2001). Collectively, the Earth's plants store approximately 610 Pg C (Figure 2.1). The total amount of carbon in the world's soils is estimated to be 1,580 Pg C (Figure 2.1) most of which enters the soils in the form of dead plant matter that is broken down by microorganisms during decay. The decay process also releases carbon back to the atmosphere because the metabolism of these microorganisms eventually breaks most of the organic matter all the way down to CO₂ (Cole et al., 2007). Ecosystems that emit more of this CO₂ to the atmosphere have an ER greater than GPP. This difference between GPP and ER is called Net Ecosystem Production (NEP). A positive NEP represents a net autotrophic ecosystem and a negative NEP represents a net heterotrophic ecosystem (Olson et al., 1983).

2.3 Fresh Water Systems in the Global Carbon Budget

Inland (fresh) waters were previously described to be passive conduits (Figure 2.3) but rivers act not only as vectors from land to ocean but also as significant sources of CO₂ to the atmosphere. The amount of carbon that leaves the terrestrial biosphere through inland waters is much larger than the amount that ultimately reaches the ocean (Cole et al., 2007).



Figure 2.3: Figure illustrating inland waters as passive conduits of carbon

More recent studies indicate a different scenario (Cole et al., 2007; Richey et al., 2002; Aufdenkampe et al., 2011). According to Meybeck (2006), the scientific community

developed interest in carbon species in the river systems in the 1980s. From then on, it is increasingly becoming recognized that freshwater ecosystems are capable of processing large quantities of carbon, thereby becoming active components of global carbon cycling. Current figures based on recent data compilations suggest that more than half of the carbon that enters freshwater ecosystems from the terrestrial biome may be processed and emitted into the atmosphere as C gases whereas less than 50% ultimately reach the ocean (Cole et al., 2007; Tranvik et al., 2009). According to Aufdenkampe et al. (2011), rivers receive, transport and process carbon that is equivalent to the net terrestrial ecosystem production in their watersheds. This therefore, makes river systems critical in determining the quantity and composition of carbon that finally reaches the coastal zone. Carbon enters the river systems via soil respiration, chemical weathering, physical erosion and leaching. Aufdenkampe et al. (2011) suggests that only a fraction of this carbon that enters the river systems finally reaches the ocean. Cole et al. (2007) estimates that the amount of carbon that enters freshwater ecosystems from the terrestrial ecosystems is about 1.9 Pg C/yr. From this amount only 0.9 Pg C/yr reaches the ocean. What remains of this carbon is either out-gassed as inorganic carbon to the atmosphere or is buried mainly as organic carbon in soil sediments. Aufdenkampe et al. (2011) suggests that carbon received by the river systems from the terrestrial ecosystem amounts to 2.7 Pg C/yr and only one third of the carbon finally reaches the ocean (0.9 Pg C/yr). These findings are summarised in Figure 2.4;

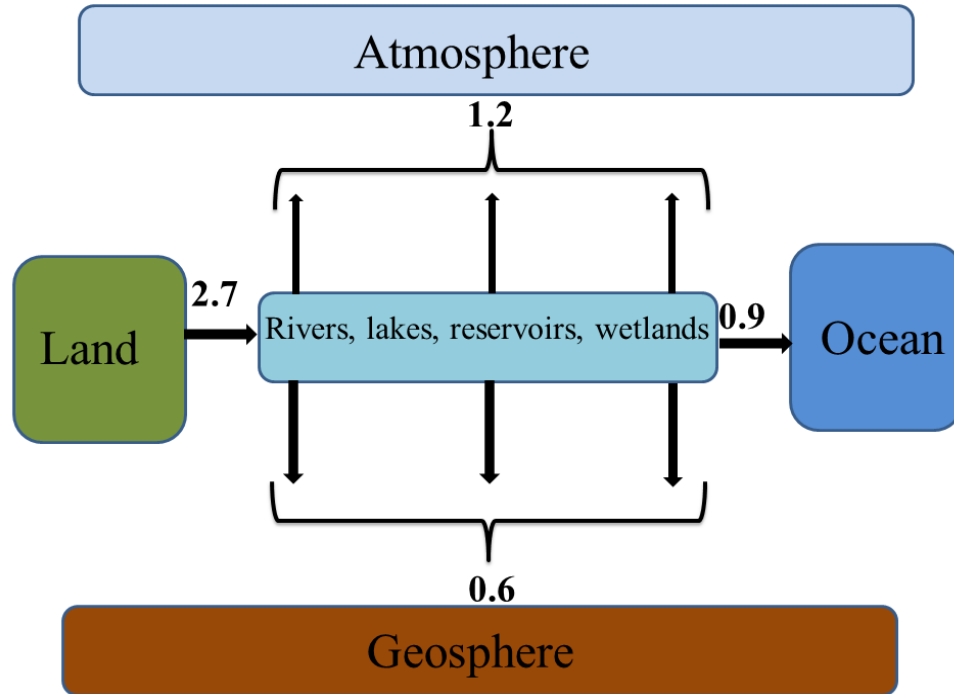


Figure 2.4: Estimates of carbon fluxes by Aufdenkampe et al. (2011). Wetlands are not included in these estimates. All numbers are in Petagrams C/yr

Rivers and lakes are almost always found to be super-saturated with CO₂ compared to atmospheric conditions and therefore a source of CO₂ to the atmosphere (Aufdenkampe et al., 2011). Aufdenkampe et al. (2011) estimated this contribution to be 1.2 Pg C/yr (Figure 2.4). Anthropogenic activities are also known to contribute importantly to atmospheric CO₂ pool. Canadell et al. (2007) estimated that anthropogenic activities reached 9.1 Pg C/yr. When compared with the emissions from the river systems, it becomes apparent that the amount of CO₂ emitted to the atmosphere by freshwater ecosystems cannot be ignored. The calculations of river emissions did not include CO₂ coming from wetlands, which was however approximated to be 2.08 Pg C/yr (Aufdenkampe et al., 2011). Rivers can also be a sink of carbon (0.6 Pg C/yr) that is buried in sediments. Raymond et al. (2013) reports that rivers emit about five times more CO₂ to the atmosphere than all lakes and reservoirs put together. The authors' spatial analysis reveals a flux of this greenhouse gas that is larger than previously estimated and dominated by hotspot regions in the tropics. The CO₂ emissions predicted by Raymond and co-workers' analysis are largely from tropical rivers and lakes in

Southeast Asia and Amazonia. This global analysis reveals an annual CO₂ flux of 1.8 Pg C from rivers to the atmosphere, and 0.32 Pg C from lakes and reservoirs. The study excluded wetlands for which coarser estimates such as those of Aufdenkampe et al. (2011) are available (2.08 Pg C/yr). The resulting carbon transfer from terrestrial systems to inland waters amounts to 5.7 Pg C/yr, substantially higher than the 2.7 Pg/yr previously estimated (Raymond et al., 2013).

2.4 River Water Parameters

This section describes parameters that are important to measure in order to determine river water biogeochemistry.

2.4.1 Dissolved Organic Carbon (DOC)

According to Kolka et al. (2008), Dissolved Organic Carbon (DOC) is defined as organic C molecules that pass through a 0.45 µm pore-size filter and occurs as the result of decomposition of plant or animal material. This is usually the major form of carbon transported with soil solution and in streams. Most significant is the transport from the forest floor to the mineral soil. The internal fluxes of DOC within the ecosystem are in general higher than the net loss of DOC to groundwater and surface waters and concentrations in rain water are generally very low but increases as the water passes through the canopy and forest floor (Moore, 1989; Kolka et al., 2008). Colour in water, especially a straw or tea colour, comes from the leaching of humic substances from plant and soil organic matter. Humic substances (=humic acids + fulvic acids) dominate the DOC accounting for 30 - 50% of total DOC (Thurman, 1985). Humic substances can contribute 50 to 90% of the DOC in coloured waters. They are also responsible for the colour observed in many rivers particularly the humic acids (Visser, 1984). According to Meybeck (2006), DOC concentrations range from less than 1 to 40 mg/L, depending on environmental conditions with a global average of 5 mg/L. DOC concentration in river water is positively correlated with river discharge and the rising limb of a hydrograph, which contains higher DOC concentrations than the falling limb at similar discharges. Hope et al. (1994) explains that this resulting relationship is because of the 'flushing

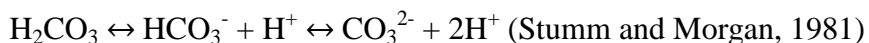
effect' caused by the transmission of 'old soil water' stored in the subsoil and the inundation of previously bare or stagnant areas of the stream channel with increasing catchment precipitation.

2.4.2 Total and Dissolved Inorganic Carbon (TIC, DIC)

Total and Dissolved Inorganic Carbon (TIC, DIC) is produced by weathering and dissolution of carbonate and silicate rocks, although may also be present as dissolved CO₂ generated by the decomposition of dissolved organic matter (Das et al., 2005). These processes generate the alkalinity of the river water and also influence the pH of water, which governs the subsequent partitioning of DIC between dissolved CO₂, bicarbonate and carbonate ions. The fraction of DIC present in waters as dissolved CO₂ is almost always at concentrations much greater than the atmosphere (Kempe, 1982; Cole and Caraco, 2001), making rivers a net source of CO₂ to the atmosphere. The dissolved inorganic carbon (DIC) is the sum of the following carbon species:

$$\text{DIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

with [H₂CO₃*] representing the sum of dissolved CO₂ and carbonic acid concentrations: [CO₂(aq)] + [H₂CO₃], which is mainly composed of CO₂(aq) (Stumm and Morgan, 1981). The different species of DIC are in equilibrium with one another through the following reactions:



This equilibrium highly depends on the pH of the water (Figure 2.5). At high pH the carbonate ion (CO₃²⁻) is the dominant species, whereas between pH 6 - 8 the bicarbonate ion (HCO₃⁻) is the dominant species, and at low pH the neutral H₂CO₃ (CO₂(aq)) dominates.

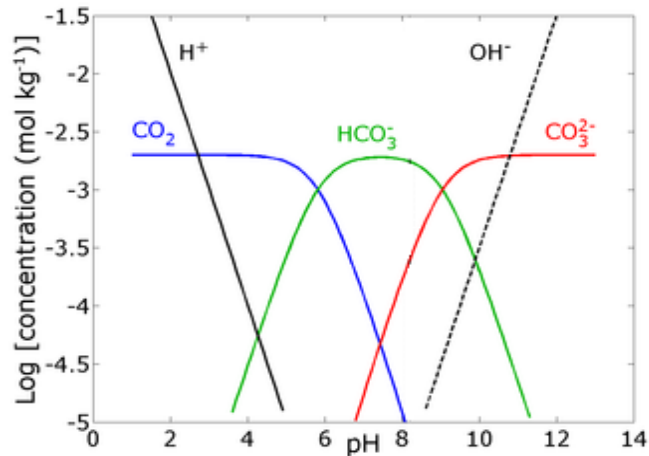
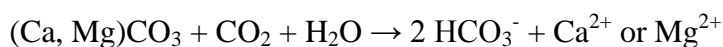


Figure 2.5: Carbonate equilibrium of DIC components (After Zeebe, 2009)

Sources of DIC include atmospheric dissolution, aquatic respiration, soil respiration and chemical weathering. The major source of CO₂ in headwater stream is CO₂ gas from the unsaturated zone of the soil, which is formed during respiration of live roots and by microbial decay of roots and litter (Edwards and Harris, 1977).

Weathering reactions can be seen as weak acid (mostly carbonic acid) slowly dissolving basic minerals. River waters containing large quantities of weathered minerals are characterized by higher concentrations of calcium, magnesium and bicarbonate ions (Richey, 2005). For DIC, especially the bicarbonate ion (HCO₃⁻), chemical weathering of carbonate rock is very important. Half of the HCO₃⁻ is coming from the carbonate rock and the other half is coming from atmospheric and soil CO₂ (Meybeck and Vorosmarty, 1999), according to the weathering reaction stoichiometry:



If the weathered minerals are noncarbonated minerals then all of the DIC originates from atmospheric and soil CO₂ (Meybeck and Vorosmarty, 1999):

Noncarbonated minerals + CO₂ + H₂O → HCO₃⁻ + cations + weathered minerals + dissolved silica.

2.4.3 Particulate Organic Carbon (POC)

Particulate Organic Carbon (POC) represents one of the main pools of organic carbon observed in the ocean. It is composed by living (phytoplankton, zooplankton and bacteria) as well as non-living materials (aggregates, pellets and detritus) and is an important parameter of the global carbon cycle (Richey, 2005). POC is the main form by which organic carbon synthesized through photosynthesis in the upper layer is transferred to the deep ocean. There it can be sequestered over geological time-scales. Conversely to DOC, particulate organic carbon (POC) is the carbon fraction that is larger than 0.7 μm and is collected on filters (Richey, 2005).

It should also be noted that besides the allochthonous (carbon not produced in the river itself) organic matter inputs, there are also autochthonous (in-stream biological processes) organic matter sources in rivers such as organic matter produced by autotrophic organisms, including phytoplankton and aquatic macrophytes. Thus, a part of the particulate organic carbon comes from in-stream production (Mayorga, 2004).

The process of sorption between minerals (clay and silt) and organic matter is the primary pathway for fine particulate organic matter formation. It is likely that this adsorption already forms within the soils prior to erosion into the rivers (Richey, 2005). A world average concentration of POC is estimated at 3.45 mg/L, of which 1.30 mg/L comes from rock erosion and weathering and 2.35 mg/L is carbon derived from the soil and atmosphere (Meybeck, 2006).

2.4.4 Stable Isotopic Signatures

Isotopes are atoms of the same element that differ in atomic mass due to differences in the number of neutrons contained in the atoms' nuclei (Clayton, 2003). For example, isotopes of carbon are ^{12}C , which contains 6 protons, 6 electrons and 6 neutrons; ^{13}C which also has 6 protons and electrons, but has 7 neutrons; and ^{14}C which also contains 6 protons and electrons, but has 8 neutrons. Having too few or too many neutrons compared to protons causes instability such as ^{14}C . These unstable 'radioisotopes' will decay to stable products. Other isotopes such as ^{12}C and ^{13}C do not decay, because their

particular combinations of neutrons and protons are stable (Clayton, 2003). These are referred to as stable isotopes.

Stable isotope abundances are expressed as the ratio of the two most abundant isotopes in the sample compared to the same ratio in an international standard using the 'delta' (δ) notation. Because the differences in ratios between the sample and standard are very small, they are expressed as parts per thousand or 'per mil' (‰) deviation from the standard (Mckinney et al. 1950 as cited by Sharp, 2007). For example, for carbon:

$$\delta^{13}\text{C}_{\text{sample}} = \left\{ \left(\frac{^{13}\text{C}/^{12}\text{C} \text{ sample}}{^{13}\text{C}/^{12}\text{C} \text{ standard}} \right) - 1 \right\} \times 1000$$

The standard is defined as 0 ‰. For carbon, the international standard is Pee Dee Belemnite (PDB), a carbonate formation, whose generally accepted absolute ratio of $^{13}\text{C}/^{12}\text{C}$ is 0.011180 (Fry, 2006). Materials with ratios of $^{13}\text{C}/^{12}\text{C} > 0.011180$ have positive delta values and those with ratios of $^{13}\text{C}/^{12}\text{C} < 0.011180$ have negative delta values (Figure 2.6).

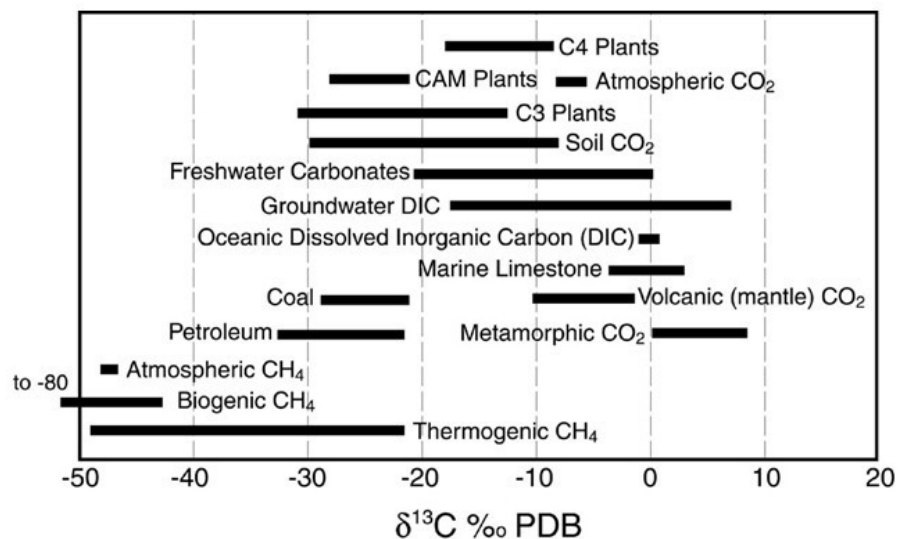


Figure 2.6: Typical ranges observed for carbon stable isotope signatures for a variety of organic and inorganic C species (After Wittke, 2009)

a) Plant Species

Stable isotope techniques are applied to constrain different sources of organic carbon in river water. This is because organic carbon can be either of autochthonous or allochthonous origin. For plant species, C stable isotope signatures ($\delta^{13}\text{C}$) are dependent on the photosynthetic pathways of C3 plants and C4 plants. The names C3 and C4 come from the first product of carbon fixation in these plants; i.e. in C4 plants the first product of the carbon fixation has 4-carbon atoms in contrast to the 3-carbon atoms product in C3 plants. All trees, shrubs and temperate grasses belong to the group of the C3 plants. Most tropical grasses belong to the group of the C4 plants, which are more adapted to arid conditions compared to C3 vegetation and they have advantages under low water availability. $\delta^{13}\text{C}$ values thus differ substantially between terrestrial C3 plants (and C3 plant-dominated soils) and C4 plants (or C4 plant dominated soils), which have typical $\delta^{13}\text{C}$ values of about -28 and -13 ‰, respectively (Still and Powell, 2010; Kohn, 2010).

b) River Water Carbon Isotopic Signatures

The isotopic signatures to be considered are $\delta^{13}\text{C}$ - DIC, $\delta^{13}\text{C}$ - DOC and $\delta^{13}\text{C}$ - POC. Dissolved Inorganic Carbon (DIC), Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) in river water have various sources. As such the composition of isotopic signatures of carbon in river water helps constrain their sources (Figure 2.7) (Brunet et al., 2009).

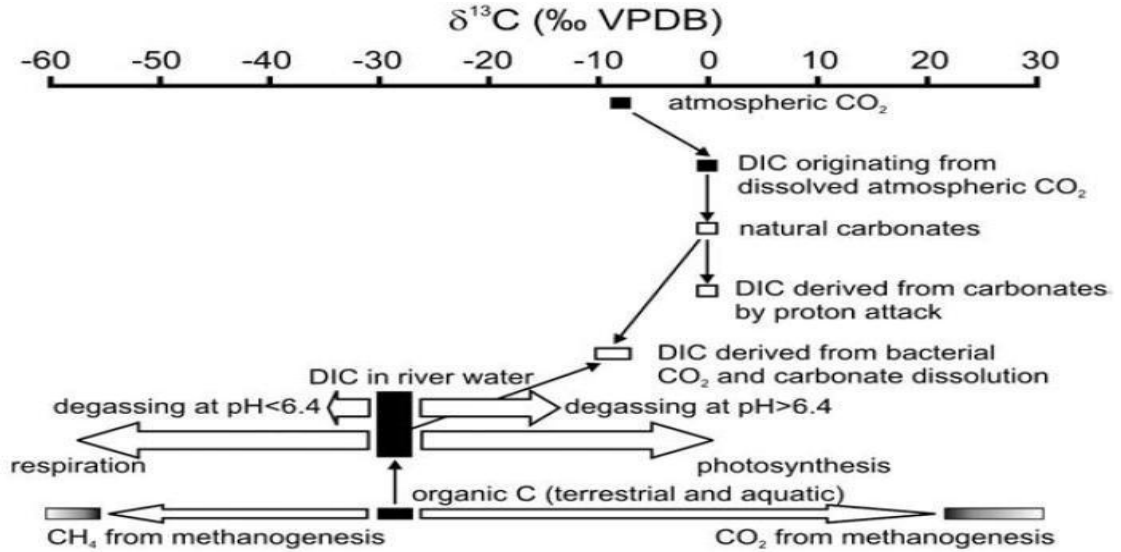


Figure 2.7: Carbon isotope signature of various components of the carbon cycle in rivers. The effects of biochemical processes on $\delta^{13}\text{C}$ are shown with arrows (After Brunet et al., 2009)

Fractionation of atmospheric CO_2 as it dissolves in river water is around 7 ‰. This gives the range of between -1 ‰ to -8 ‰ (Zhang et al., 1995). Brunet et al. (2009) postulates that if carbonates participating in dissolution are from the fossils (marine type), then the DIC resulting from carbonate dissolution by proton attack will average around 0 ‰ for $\delta^{13}\text{C}$ - DIC. It is very often that weathering of carbonates is done by soil CO_2 . In such instances, the $\delta^{13}\text{C}$ - DIC will vary between 0 ‰ and -24 ‰ since $\delta^{13}\text{C}$ of soil water in a C_3 dominated system will average around the latter value. The lighter isotope evades rather easily from a pool, so the process of degassing will result in a heavier DIC pool unless water has pH lower than 6.4 (Brunet et al., 2009).

2.4.5 pH and Total Alkalinity

The pH of natural waters is an important variable controlling many important geochemical reactions such as the solubility of carbonates. In turn, the pH is buffered mostly by the content of inorganic carbon species (Richey, 2005). The measure for the size of this buffering against pH is alkalinity. A stream that has large inputs of acid is well buffered against decreases in pH if it has high alkalinity. Total Alkalinity is formally defined as the equivalent sum of the bases that are titratable with strong acid

(Stumm and Morgan, 1981). The listing of ions shown in Drever (1988) was " $m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{B(OH)}_4^-} + m_{\text{H}_3(\text{SiO})_4^-} + m_{\text{HS}^-} + m_{\text{organic anions}} + m_{\text{OH}^-} - m_{\text{H}^+}$ ". Total Alkalinity is measured by adding a strong acid until all the anions listed above are converted to uncharged species. The Total Alkalinity is not affected by temperature, pressure or pH, though the values of individual constituents are, mostly being conversions between HCO_3^- and CO_3^{2-} (Stumm and Morgan, 1981).

2.4.6 Dissolved Oxygen and Conductivity

Oxygen saturation or dissolved oxygen (DO) is a relative measure of the amount of oxygen that is dissolved or carried in a given medium. It can be measured with a dissolved oxygen probe such as the Professional Optical Dissolved Oxygen (Pro-ODO) meter in liquid media usually water. The standard unit is milligrams per litre (mg/l) or % oxygen per litre (Swanson and Baldwin, 1965).

Electrical conductivity is a measure of water's ability to conduct electricity, and therefore a measure of the water's ionic activity and content. The higher the concentration of ionic dissolved constituents, the higher the conductivity. Conductivity of the same water changes substantially as its temperature changes. This can have a confounding effect on attempts to compare this feature across different waters or seasonal changes in this parameter for a particular body of water. The use of specific conductance (SpC: conductivity normalized to temperature of 25°C) eliminates this complication and allows valuable comparisons to be made (Swanson and Baldwin, 1965). SpC is generally found to be a good measure of the concentration of total dissolved solids (TDS) and salinity. Values of SpC can differ greatly from system to system because the composition of inflowing tributaries reflects the geology of their watersheds and non-point source pollution, for example, agricultural run-off and industrial inputs (Swanson and Baldwin, 1965). Units of microSiemens per centimeter (μScm^{-1}) or milliSiemens per centimeter (mScm^{-1}) can be used in SpC measurements.

2.5 Gap Analysis for this Study

There is paucity of data on biogeochemistry of river systems in Zambia. Wamulume (2011) and Wamulume et al. (2011) studied the hydrology and biogeochemistry of the dam-impacted Kafue River and Kafue Flats (Zambia). The objectives were to (i) characterize the spatial and temporal variability in the relative importance of different water inputs (riverine input, direct precipitation, lateral inputs) and river – floodplain exchange in the Kafue Flats, and (ii) characterize the temporal and spatial variability of nitrogen, carbon, and phosphorus concentration, speciation and loads over an annual cycle, in the Kafue River as it flows through the Kafue Flats. Further studies at doctoral level were by Zurbrügg (2012) who studied the biogeochemistry of a large tropical floodplain system (Kafue Flats, Zambia): River-floodplain exchange and dam impacts and another by Kunz et al. (2011) who looked at sediment accumulation and carbon, nitrogen and phosphorus deposition in the Kariba Reservoir with a specific objective to quantify the current and historic impact of Kariba Reservoir on downstream transport and cycling of particles, organic carbon, nitrogen and phosphorus. These studies only concentrated on the Kafue Flats and Kariba Reservoir whereas the current study covered the entire stretch of the Zambezi and Kafue rivers in Zambia. For example, Zurbrügg et al. (2013) studied isotopic compositions of DOC and POC in the Kafue Flats in relation to organic carbon and nitrogen export from the Kafue Flats whereas this study determined isotopic compositions of DIC, DOC and POC for the entire Zambezi and Kafue rivers and the Kariba and Itezhi Tezhi reservoirs in relation to carbon dioxide emissions. This study determined partial pressure of carbon dioxide in the rivers and reservoirs to bring in perspective the role of inland waters in carbon dioxide emissions, since increasing carbon dioxide emissions are influencing climate change/variability and global warming which are negatively impacting on humans, hence the need to generate more knowledge in this area.

CHAPTER 3: STUDY METHODS

This chapter introduces sampling and analytical techniques used during the course of the wet and dry sampling periods of this study. Some parameters were measured on site whereas others were analysed in the Laboratory. Laboratory methods which were used for analysis are also described in this chapter.

3.1 Sampling and Analytical Techniques

Sampling for spatial variability of biogeochemical characteristics was conducted during the wet season of 2012 (February to April) and 2013 (January to March) and the dry season of 2013 (October to November). Both rivers (Zambezi and Kafue) were sampled at between 100 – 150 km intervals. Reservoirs (Kariba and Itezhi Tezhi) and floodplains (Barotse and the Kafue Flats) were also sampled. A total of 10 sites were sampled on each river (Zambezi and Kafue) and 3 on each reservoir (Kariba and Itezhi Tezhi). The Zambezi River was sampled at Kalene Hills (ZBZ.ST.1), Chavuma (ZBZ.ST.2), Lukulu (ZBZ.ST.3), Kalongola (ZBZ.ST.4), Sesheke (ZBZ.ST.5) and Kazungula (ZBZ.ST.6). In Livingstone, the Victoria Falls was sampled just before the Fall (ZBZ.ST.7) and Just after the Fall (ZBZ.ST.8). The next sampling point along the river stretch was at Chirundu (ZBZ.ST.9) and the last point was in Luangwa (ZBZ.ST.10). Kariba reservoir was sampled at its start (Kar.1), midway the reservoir (Kar.2) and towards the end of the reservoir (Kar.3). The Kafue River was sampled at Chingola (KAF.ST.1), Mfulira (KAF.ST.2), Mpongwe (KAF.ST.3), just before confluence with Lunga River in Kasempa (KAF.ST.4), Hook Bridge (KAF.ST.5), just below the Itezhi Tezhi Dam (KAF.ST.6), Namwala (KAF.ST.7), Nakambala Sugar Estates in Mazabuka (KAF.ST.8), at the bridge in Kafue Town (KAF.ST.9) and the last point was in Chirundu (KAF.ST.10). Itezhi Tezhi Reservoir was sampled at its start (ITT.1), midway the reservoir (ITT.2) and towards the end of the reservoir (ITT.3). The data from the sampling campaigns is given in Appendix 1. The sampling points are shown in Figure 3.1.

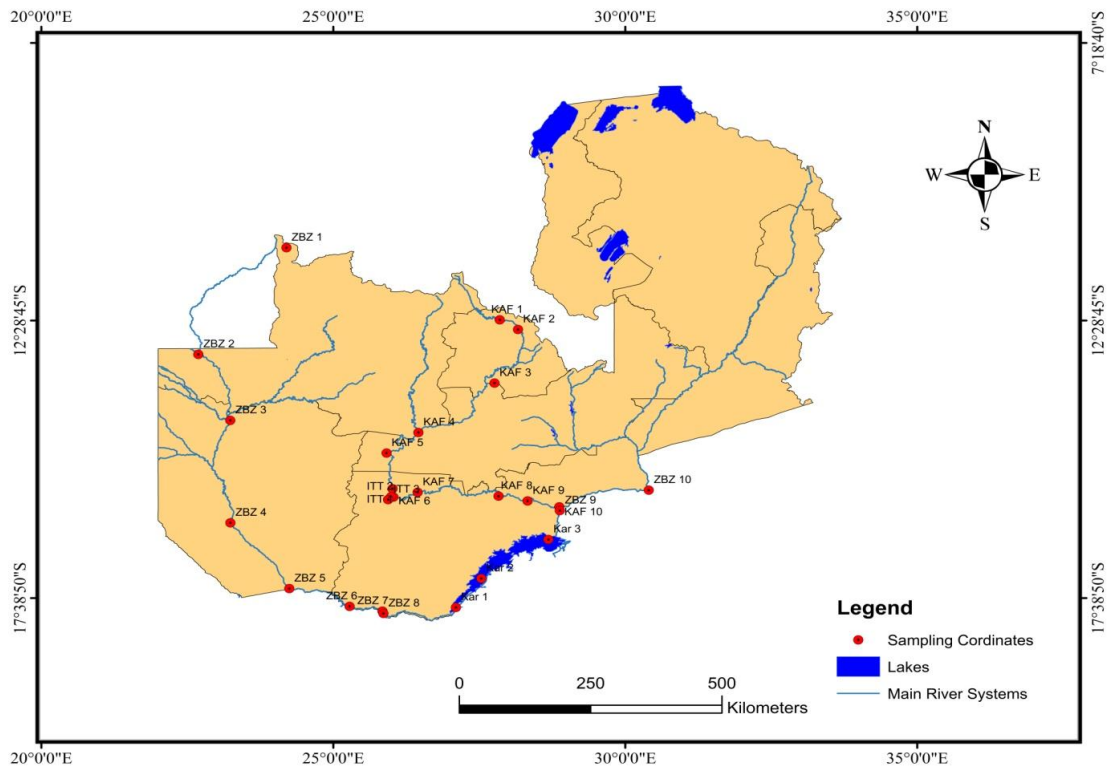


Figure 3.1: Map showing sampling sites for this study on the Zambezi, Kafue rivers and Kariba, Itzhi Tezhi reservoirs in Zambia

Additionally, two high frequency (bi-weekly) monitoring stations were set up in 2012, one on the Zambezi River in Chirundu District (ZBZ.ST.9), approximately 12 km upstream the confluence with the Kafue River and one on the Kafue River (KAF.ST.10), approximately 6 km upstream its confluence with the Zambezi River. In-situ measurements and water sampling was performed generally in the middle of the river channel from a boat. Some sampling sites were set in sections of the river which had a pontoon or a bridge in order to facilitate sampling in the middle of the river channel and eliminate potential contamination which may be introduced by sampling from the shoreline. The coordinates and sampling frequency of all sampling sites are shown in Table 3.1.

Table 3.1: Table showing codes, coordinates and sampling frequency for all sampling sites. Mark “X” indicates sampling was done during that campaign

CODE	LAT (DD)	LONG (DD)	SAMPLING FREQUENCY			
			2012		2013	
			WET	DRY	WET	DRY
ZBZ.ST.1	-11.12198	24.19863	X		X	X
ZBZ.ST.2	-13.10773	22.68901	X		X	X
ZBZ.ST.3	-14.33721	23.23592	X		X	X
ZBZ.ST.4	-16.24473	23.23882	X		X	X
ZBZ.ST.5	-17.46661	24.24698	X		X	X
ZBZ.ST.6	-17.79853	25.28073	X		X	
ZBZ.ST.7	-17.88741	25.84259	X		X	X
ZBZ.ST.8	-17.93106	25.85963	X		X	
Kar.1	-17.81893	27.10094	X			
Kar.2	-17.278970	27.534780	X		X	
Kar.3	-16.520270	28.683660	X		X	X
ZBZ.ST.9	-16.01624	28.87979	X		X	X
ZBZ.ST.10	-15.63554	30.40335	X		X	X
KAF.ST.1	-12.46425	27.85076	X		X	X
KAF.ST.2	-12.64500	28.16470	X		X	
KAF.ST.3	-13.64231	27.61623	X		X	
KAF.ST.4	-14.56243	26.45772	X		X	X
KAF.ST.5	-14.94511	25.91404	X		X	X
ITT.1	-15.61025	26.01468	X		X	
ITT.2	-15.76020	25.98881	X		X	X
ITT.3	-15.81248	25.93894	X		X	
KAF.ST.6	-15.76383	26.03033	X		X	X
KAF.ST.7	-15.67564	26.44536	X			
KAF.ST.8	-15.74914	27.82954	X		X	X
KAF.ST.9	-15.83655	28.23771	X		X	X
KAF.ST.10	-15.95120	28.860240	X		X	X

3.1.1 Global Positioning System Coordinates

At every sampling site, the coordinates (Latitude and Longitude) were recorded with a Global Positioning System (GPS). The date, time and data of each particular sampling site were recorded (Appendix 1).

3.1.2 Dissolved Oxygen, Temperature and Barometric pressure

These three parameters were measured with the Professional Optical Dissolved Oxygen (Pro ODO) instrument. This instrument consists of an electrical device connected with a cable to a combined oxygen and temperature probe. The instrument reads temperature (at 0.1 °C accuracy), atmospheric air pressure (at 0.1 mmHg accuracy), dissolved oxygen (at 0.01 mg/l accuracy) and percentage oxygen saturation (at 0.1 % accuracy).

The oxygen probe was calibrated before each sampling schedule. This was done by putting a rubber cap over the probe with a wet sponge inside. Water saturated air should read an oxygen saturation of 100% and initial values recorded. To gather valid readings, the probe was submerged under the water surface for a few minutes until readings stabilized.

3.1.3 Conductivity and pH

Conductivity and pH were measured using the Professional Plus (Pro Plus, Quattro cable bulkhead) instrument. This probe was calibrated before taking any measurements at each site. The pH calibration was done by submerging the probe in NBS (US National Bureau of Standards) buffer solutions of 4 and 7, prepared in advance before going for field sampling. Calibration for conductivity was performed on a single occasion before fieldwork with YSI 3167 conductivity calibration solution (1000 $\mu\text{S cm}^{-1}$ at 25 °C, KCl). In order to get correct readings, the probe was submerged under the water surface for a few minutes until readings stabilized. The pH was measured in mV (at 0.1 mV accuracy) and in normal pH units (at 0.01 accuracy). Both conductivity and specific conductivity (i.e. conductivity normalized to a temperature of 25 °C) were measured *in-situ* (at 0.1 $\mu\text{S/cm}$ accuracy).

3.1.4 DIC, CO₂ and $\delta^{13}\text{C}$ – DIC

The Niskin-bottle was used to collect river water at about 0.5 m below the water surface. Two 40 mL glass headspace vials were over-filled with river water from the Niskin-bottle for Dissolved Inorganic Carbon (DIC) and one 60 mL glass headspace vial was also over-filled with river water from Niskin-bottle for CO₂. All glass vials containing samples were spiked with 200 μL of saturated HgCl₂ solution to inhibit any biological activity. The bottles were then gently crimped without any bubbles inside and wrapped

in tissue. Same river water from the Niskin-bottle was also stored (over-filled) in one 12 mL glass headspace vial (exetainer) for $\delta^{13}\text{C}$ - DIC. After the addition of 20 μL of saturated HgCl_2 solution and the careful closing without the introduction of any air bubbles, all samples were stored at ambient temperature in readiness for shipment to Belgium for analysis in the Laboratories of Katholieke University (KU) in Leuven.

3.1.5 Total Suspended Matter

Total Suspended Matter (TSM) was measured using a specific filtration set (Figure 3.2). River water was taken with a plastic bottle from about 0.5m below the surface of the water. Using river water, the inside of the set was rinsed out to make sure that particles from the previous site were all removed. Using gloves and tweezers, a pre-combusted and pre-weighed 0.7 μm , 47 mm glass fibre filter (GFF) was placed into position on the filtration set. In order to create a homogenous sample, the bottle containing the sample was shaken up and swirled before pouring in the graduated cylinder. A manual vacuum pump was used to create a partial vacuum to suck the water through the filter.



Figure 3.2: Filtration set for Total Suspended Matter (TSM) used during sampling on the Kafue and Zambezi rivers, Zambia

Once all the water had been completely filtered (between 1000 mL to 2000 mL, lesser for more turbid water), the filter was taken out carefully and placed in a plastic tray to dry. The filtrate was kept for further use in other parameters described hereunder.

3.1.6 Total Alkalinity

The leftover water from TSM filtration was re-filtered using a 0.2 μm Minisart high flow single use syringe filter (hereafter called Acrodisc filter) for Total alkalinity (TA). The water was stored in a 100 mL High Density Polyethylene (HDPE) vial without addition of any preservative, sealed and stored in a cooler box in readiness for shipment to KU Leuven for laboratory analysis.

3.1.7 Major elements

Filtrate from the TSM filter set (Figure 3.2 above) was re-filtered using an Acrodisc filter. The water was put in a 20 mL plastic HDPE vials (elements vial). No preservative

was added to the elements vial. Samples were stored in a cooler box in readiness for shipment to Belgium for laboratory analysis at KU Leuven.

3.1.8 Dissolved Organic Carbon (DOC)

Similar to major elements, filtered water from the TSM filter set (Figure 3.2 above) was re-filtered using an Acrodisc filter to be used for DOC analysis. The water was put in a 40 mL glass vial (Supelco, with teflon-lined septa) for DOC. Using a micropipette, 50 μL of 50 % Phosphoric acid (H_3PO_4) was added to the DOC vials to evacuate any DIC contained in the bottle. The DOC vials were stored at ambient temperature until analysis for DOC was carried out in the laboratories of Katholieke University in Leuven, Belgium.

3.1.9 Particulate Organic Carbon (POC)

A specific filtration set was used for POC. The inside of the set was rinsed out with river water to make sure that no particles were left from the previous site. With gloves and tweezers, a pre-combusted 0.7 μm , 25 mm Glass Fibre Filter (GFF) was placed into position. River water was taken from about 0.5 m below the water surface using a 2 L plastic bottle. Before pouring in the graduated cylinder the water was shaken up to make sure a homogeneous sample was taken. A manual vacuum pump was used to create a partial vacuum to suck the water through the filter. Once all the water had run through (between 300 mL to 500 mL, lesser for more turbid water), the filter was taken out and placed in a plastic tray to dry. Dried filters were packed and shipped to Belgium for further analysis in the KU Leuven laboratories.

3.1.10 Primary production (PP)

For the determination of primary production rates, two incubation polycarbonate, 500 mL bottles were rinsed and filled with 400 mL of river water drawn from about 0.5 m below the water surface. Using a micropipette, 500 μL of the ^{13}C -spike solution ($\text{NaH}^{13}\text{CO}_3$, ± 40 mg dissolved in 12 mL exetainer with surface water) was added to each bottle and shaken for good mixing. One exetainer for each incubation bottle was filled with incubated water (without air bubbles) in order to measure the degree of ^{13}C labeling in the DIC pool and 20 μL of saturated HgCl_2 was added for conservation. The incubation bottles were then affixed to a rope and left afloat on the water surface for

minimally 2 hours under ambient light conditions. After this incubation period, the water was filtered using the same procedure for POC, and filters dried and stored in plastic trays for further analysis in the laboratories in Belgium. The exact time between the addition of the spike and the filtration was noted for the calculation of the primary production rates. At every 6 to 8 sites, the same procedure was followed with blacked out bottles (with black tape). The purpose of this was for correction for the production of POC and changes in the ^{13}C signature other than primary production.

3.1.11 Respiration rate

Bacterial respiration was measured in-situ from the decrease in O_2 concentration after dark incubation. A set of eight glass (air-tight) bottles were filled up (overflowed) with water samples from the Niskin bottle and sealed without any air bubbles inside. Initial conditions (dissolved oxygen concentration, % oxygen saturation, barometric pressure and temperature) were determined using Pro-ODO probe in three of the glass bottles and five bottles were incubated for 24 hours in dark (to prevent photosynthesis), at in-situ temperature (in an isothermal box filled up with river water). After about 24 hours, the dissolved oxygen concentration, % oxygen saturation, barometric pressure and temperature were measured again and the exact incubation time recorded (Figure 3.3).



Figure 3.3: Setup for measurement of respiration in aquatic systems of the Zambezi, Kafue rivers and Kariba, Itzhi Tezhi reservoirs, Zambia

Bacterial respiration was done following Kragh et al. (2008), who were among the first to use this approach to measure respiration in natural water samples. It was calculated using;

$$RR = (DO_r - DO_i)/t$$

Where: DO_r is the dissolved oxygen concentration of the river water, DO_i is the dissolved oxygen concentration after incubation and t is the incubation time. Respiration rate was thus expressed as the amount of oxygen consumed per unit of volume and time.

3.1.12 pCO₂ and Fluxes

In-situ measurements of partial pressure CO₂ (pCO₂) concentrations in water were determined using the headspace technique (Figure 3.4).

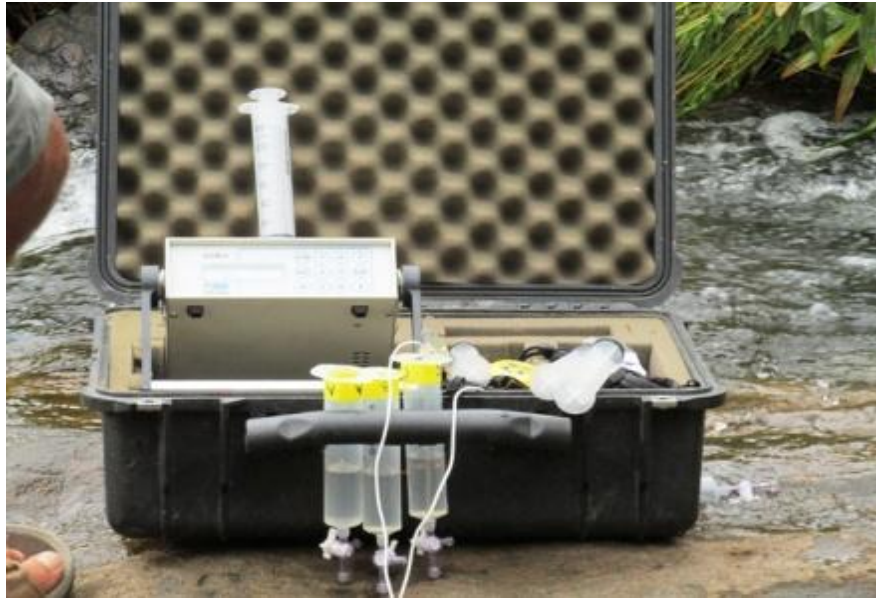


Figure 3.4: Headspace Technique for pCO₂ measurement used in the Zambezi, Kafue rivers and Kariba, Itezhi Tezhi reservoirs, Zambia

A volume of 30 mL water sample collected in 60 mL polypropylene syringes was mixed with 30 mL air (of known CO₂ concentration) and gently shaken for 5 minutes to equilibrate the gases in the water and air. The headspace volume (30 mL) was then transferred into a new syringe and gently injected into a non-dispersive infrared instrument (PP-System EGM-4) for CO₂ determination. Aqueous pCO₂ was then calculated from the ratio between the headspace and sample volumes using the gas solubility at sampling temperature (Weiss, 1974). Ambient air pCO₂ concentration at each location was measured directly by injecting air samples into the EGM-4 analyzer.

Carbon dioxide gas (CO₂) fluxes to the atmosphere were measured using custom designed floating chambers consisting of a one-piece PVC cylinder with surface area of 0.1134 m² and total volume of 17 liters. Starting at ambient atmospheric concentration, the air inside the chamber is circulated in the closed loop and analyzed for CO₂ with a non-dispersive infrared instrument (PP-System, model EGM-4, accuracy 1%) with readings every 30 seconds over 30 minutes period. Temperature inside the chamber was monitored continuously and taken into consideration for the flux calculation. Readings

were collected for both drifting and static modes unless the river conditions or logistics did not allow. The static and drift modes are shown in Figure 3.5.



(a) Static mode on Kafue River



(b) Drift mode on Zambezi River

Figure 3.5: Floating Chamber Technique for measuring carbon fluxes with (a) showing static mode on the Kafue River and (b) showing drift mode on the Zambezi River in Zambia

The rate of accumulation for both gases (slope in $\mu\text{atm}/\text{min}$) was calculated from measured concentrations plotted on a graph as function of time and the fluxes were estimated in accordance with methods described in Marchand et al. (2009):

$$F_{\text{FC}} = [(s \times V) / (mV \times S)] \times f$$

where: F_{FC} is the flux measured with the floating chamber in $\mu\text{mol m}^{-2} \text{d}^{-1}$; s is the slope of the change in concentration in $\mu\text{atm min}^{-1}$; V is the volume of the chamber in litres (L); mV (molar volume) is the volume of one mole of gas in L atm mol^{-1} ; S is the surface area of the floating chamber over the water in m^2 and f is the conversion factor from minute (min) to day (d) ($1\text{d} = 1440 \text{min}$).

Before and after each chamber measurement, data on average wind speed, air temperature, humidity, barometric pressure and wave height were also measured for correction of gas exchange at water surface. Flux chamber measurements were

preferentially performed on drift-mode in order to avoid potential overestimation of fluxes due to enhanced gas exchange velocity induced by local turbulence (water rushing against chamber) created by the chamber walls. For chamber measurements performed on a static position, water velocity relative to the chamber was recorded and a correction factor function of water velocity was applied to those fluxes.

All samples (water, filters, sediment) were transported to KU Leuven in Belgium for further laboratory analysis.

3.2 Laboratory Analysis

Some parameters which could not be measured in the field were subjected to further analysis in the Laboratory. The field and laboratory data as used in this study are given in Appendix 1. Procedures for analysis are described hereunder.

3.2.1 $\delta^{13}\text{C}$ – DIC

The method of analysis for $\delta^{13}\text{C}$ – DIC is based on the procedure described in Gillikin and Bouillon (2007). A headspace was created inside the exetainers of about 2.2 to 2.5 mL using a syringe and needle through a rubber septum (Figure 3.6). Helium was injected using a second needle into the exetainers simultaneously with the water removal. After that, 12 drops of warm phosphoric acid (H_3PO_4 , 99%) were added to the exetainers to convert the DIC into CO_2 , which equilibrated between the liquid phase and the gaseous headspace. In order to reduce the possibility of exchange with atmospheric CO_2 , the samples were left upside down so that there is no contact between headspace and septum. The samples were left to equilibrate overnight at room temperature.

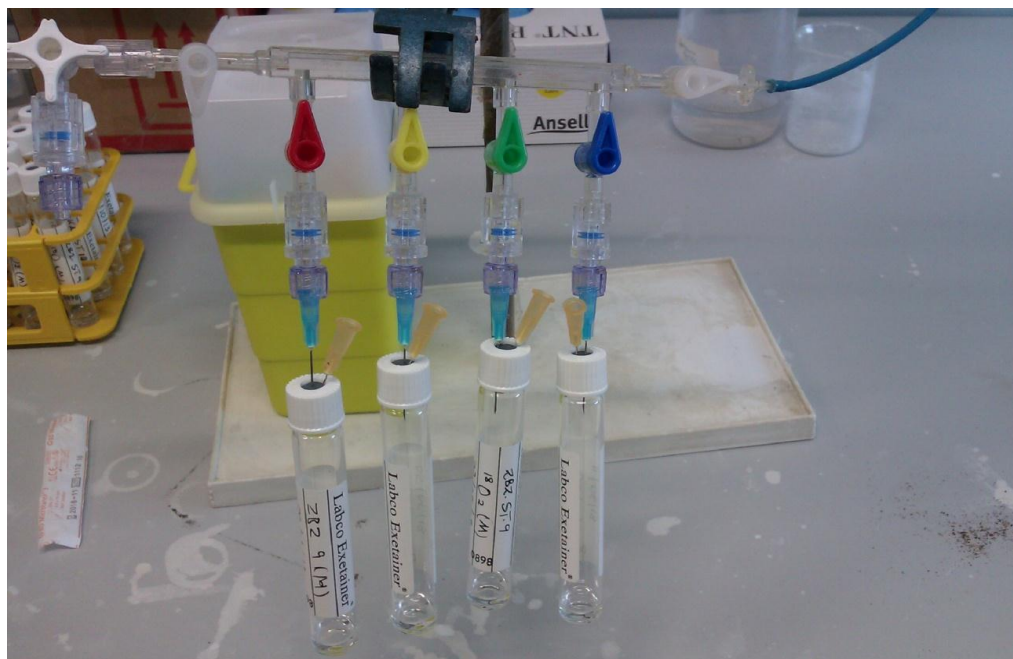
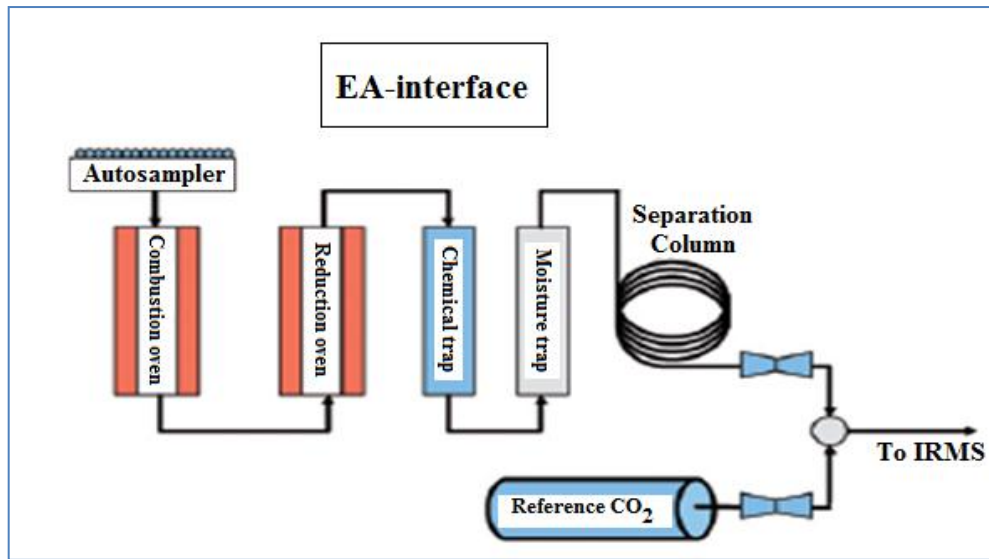
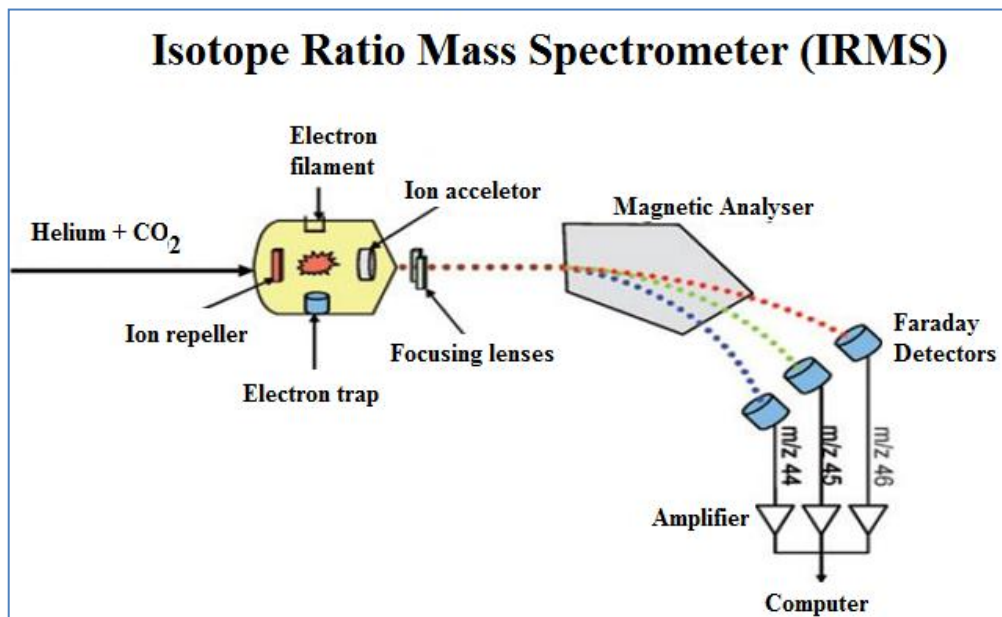


Figure 3.6: $\delta^{13}\text{C}$ – DIC exetainers injected with inert helium gas for the analysis of $\delta^{13}\text{C}$ – DIC in Leuven, Belgium

$\delta^{13}\text{C}$ – DIC was measured with a Thermo Flash EA/HT connected to a ConFloIV and Thermo DeltaV Advantage Continuous Flow (CF)-Isotope Ratio Mass Spectrometer (IRMS) (Figure 3.7). Isodat software was used in the analysis procedure (Gillikin and Bouillon, 2007).



(a)



(b)

Figure 3.7: Representation of (a) Elemental Analyzer (EA) interface and (b) Isotope Ratio Mass Spectrometer (IRMS) used for measuring $\delta^{13}\text{C}$ – DIC and $\delta^{13}\text{C}$ – POC. For the analysis of ^{13}C the chemical trap was not used. Separation column was held at 50°C. The helium flow was set at 90 mL/min (Modified after Muccio and Jackson, 2009)

Before any injection was done, an airtight syringe was first flushed with Helium gas three times. Then the syringe was flushed three times with sample from headspace and then 1 mL of the headspace sample was injected into the port after three CO₂ reference peaks had completed their run. After a complete run of all the samples, one more CO₂ reference peak was auto-injected for 20 seconds at the end to correct for any drifts on the sample peaks. The standards used were IAEA-CO-1 (Marble) - δ¹³C: + 2.492 ‰; δ¹⁸O: -2.4 ‰) and LSVEC (Lithium carbonate of known δ¹³C value). To correct for the partitioning of CO₂ between headspace and the water phase and to calculate the δ¹³C of the total DIC, the equation of Miyajima et al. (1995) was applied:

$$\delta^{13}C_{DIC} = \frac{Volume_{headspace} * \delta^{13}C_{measured} + (Volume_{bottle} - Volume_{headspace}) * \beta * (\delta^{13}C_{measured} + \epsilon_g^a)}{Volume_{headspace} + (Volume_{bottle} - Volume_{headspace}) * \beta}$$

Where β = 0.872 at 23 °C (Ostwald solubility coefficient)

ε_g^a is calculated from e = -373/T + 0.19 thus ε = -1.07 at 23 °C

V_{bottle} = internal volume of the sampling vial

Spreadsheets already inserted with formulas were used for calculations and correction of δ¹³C and DIC concentrations (Paul et al., 2007).

3.2.2 δ¹³C - POC and POC

For analysis of POC and δ¹³C - POC signature, filters were acidified with HCl (37 %) for 4 hours in order to get rid of all inorganic carbon. The filters were subsequently dried at 60 °C overnight. The filters were then placed in small silver capsules, which had been pre-combusted at 450 °C for at least four hours to remove any contaminants. Capsules were closed and compressed to make sure they did not contain any air (Figure 3.8).

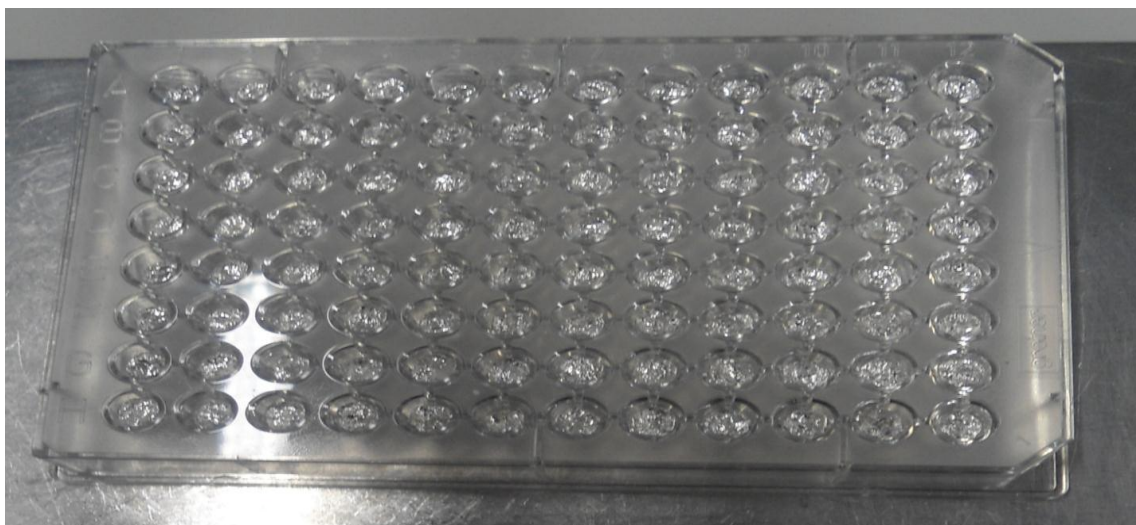


Figure 3.8: Pre-combusted silver capsules compressed and placed in a tray before analysis of the samples collected from the Zambezi, Kafue rivers and Kariba, Itezhi Tezhi reservoirs in Zambia

Bulk carbon content and the $\delta^{13}\text{C}$ - POC signature were measured with the same apparatus as $\delta^{13}\text{C}$ - DIC. The silver capsules with sample were subjected successively to: combustion, reduction, water trap and separation by gas chromatography. Inert helium gas was used as carrier gas. The sample was inserted in the Elemental Analyzer (EA) (Figure 3.7a) through an auto - sampler. The combustion took place after injection of O_2 at a temperature of 1,070 °C. The column is filled with ash trap. It has chromium oxide necessary for burning and quartz to avoid blowing of column. The combustion products are all N forms in NO_x , CO_2 , SO_2 and H_2O . The excess of O_2 was absorbed in the copper (Cu) reduction column at a temperature of 640 °C. This metallic Cu is thus oxidized to Cu^{2+} , with a colour change of the column from orange-brown to grey-blue. O_2 was reduced to form H_2O and retained in the moisture trap. NO_x was also reduced to N_2 . Thermal Conductivity Detector (TCD) was the detector used. The method consisted of 3 reference CO_2 pulses followed by the sample peak and one more CO_2 reference pulse at the end. These reference pulses serve to correct for drift of the Isotope Ratio Mass Spectrometer (IRMS). The standards used for $\delta^{13}\text{C}$ -signature and bulk carbon standardization, were Acetanilide (at 0.15, 0.3, 0.45 and 0.6) and IAEA C6 (at 0.15, 0.3, 0.45 and 0.65). The calibration was a two point linear normalization described by Paul et

al. (2007). The two standards used had isotopic compositions far away from each other in order to provide sufficient range on the graph for the sample being measured. The standard was analyzed simultaneously with the sample. For blank corrections, empty silver capsules were combusted. The sample peak was integrated with the software (Isodat 3.0) and along with the standards the amount of bulk carbon could be determined. This amount was divided by the volume of water filtered in the field to give the POC concentration (Paul et al., 2007).

3.2.3 $\delta^{13}\text{C}$ - DOC and DOC

Samples for DOC analysis were prepared from the field through filtering of river water using an Acrodisc and evacuation of DIC with 50 μL H_3PO_4 . A Total Organic Carbon (TOC) Analyser (Aurora) was used to analyse DOC concentration in the Laboratory (Figure 3.9). The machine automatically adds HCl and bubbles out CO_2 . It heats up the sample and adds persulphate. The detector used was the Non Dispersive Infra Red (NDIR) (Bouillon et al., 2006).

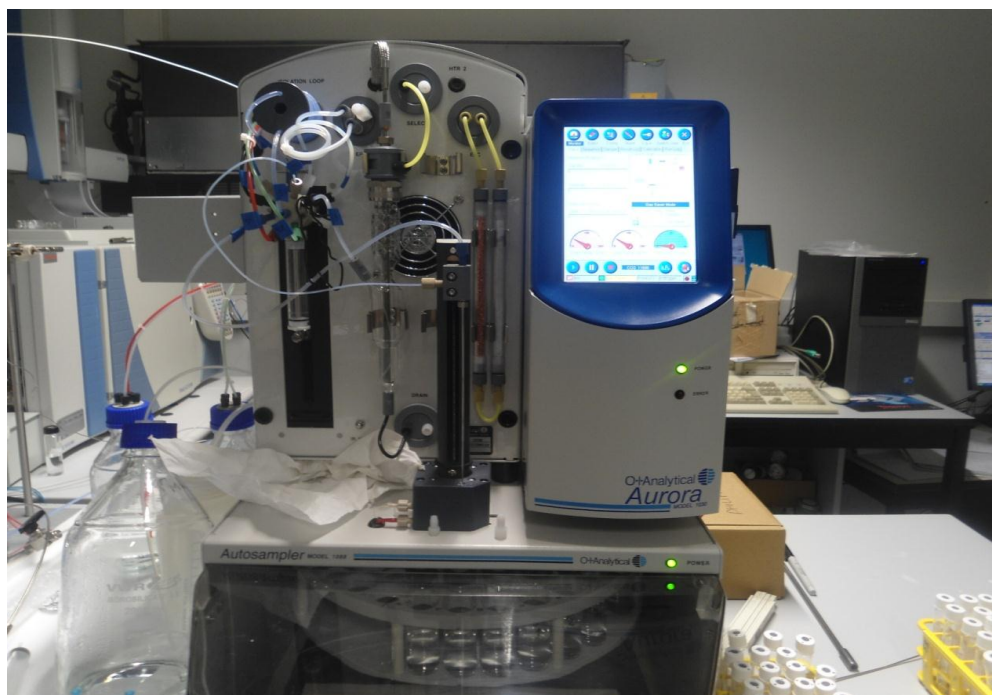


Figure 3.9: TOC Analyser for analysis of DOC in the Zambezi, Kafue rivers and Kariba, Itezhi Tezhi reservoirs in Zambia. It is interconnected with EA, Conflo IV and IRMS (Bouillon et al., 2006)

In order to measure concentrations and isotopes, the machine is interconnected to the EA then goes to the ConfloIV and ends up in the Isotope Ratio Mass Spectrometer (IRMS). In the Elemental Analyzer, only the Cu column is used to trap oxides at 640 °C. For purposes of controlling the uniform flow of CO₂ into the IRMS, a cryotrap is fitted in the sequence for this purpose. Isodat software is used to determine the isotopic signatures of DOC (Bouillon et al., 2006).

3.2.4 Total Suspended Matter

Total Suspended Matter (TSM) filters were dried overnight at 60 °C and weighed. The difference between the initial weight and final weight was determined, and along with the known water volume filtered, TSM concentrations (mg L⁻¹) were calculated.

3.2.5 Total Alkalinity

These analyses were carried out by the Chemical Oceanography Unit, University of Liège (ULG), as a collaborating partner in the research. The results were provided to this research.

3.2.6 Primary production rates

The filters for primary production were analysed in the same way as the filters to quantify POC concentrations and ¹³C - POC signature. The exetainers were analysed in the same way as the analysis of the ¹³C - DIC. To calculate primary production rate, the following equation was used (Hama et al., 1983):

$$PP = \frac{POC_f \times (\%^{13}POC_f - \%^{13}POC_i)}{t \times (\%^{13}DIC - \%^{13}POC_i)}$$

with t the incubation time, $\%^{13}DIC$ the percentage ¹³C of the DIC after the bottles had been spiked, POC_f the particulate organic carbon after incubation, $\%^{13}POC_i$ and $\%^{13}POC_f$ the initial (i.e. *in-situ* ¹³C-signature of the POC) and final (i.e. after incubation) percentage ¹³C of the POC, respectively.

3.2.7 DIC and pCO₂

Using pH, Total Alkalinity and Temperature values, DIC and pCO₂ were computed using thermodynamic constants of Millero (1979) as implicated in CO₂SYS (Lewis and

Wallace, 1998). Before inserting into the software, Total Alkalinity was changed in units from mmol to μmol by multiplying with a 1000. If all data is correctly inserted and all empty rows eliminated, the software outputs values for DIC and pCO_2 .

CHAPTER 4: DATA ANALYSIS AND RESULTS

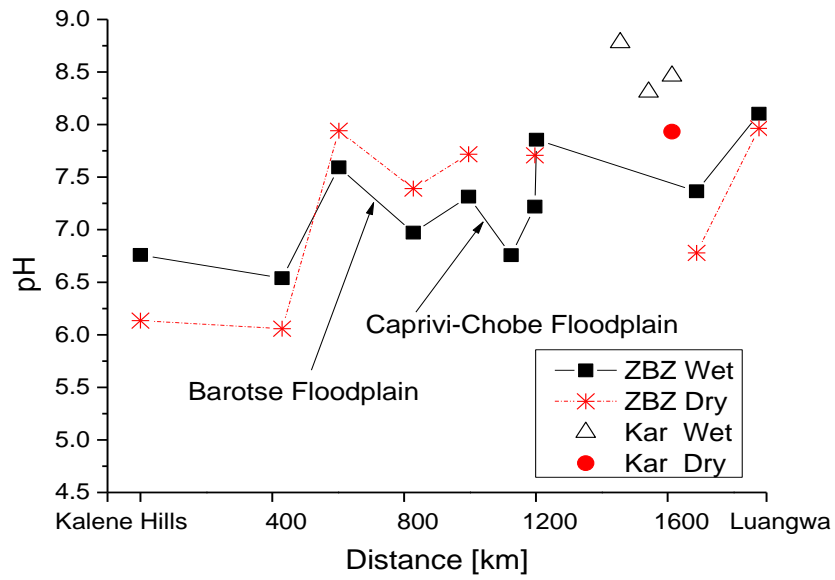
This chapter presents the results of this study and analysis of the data without detailed discussion of the results. Detailed discussions of these results are in Chapter Five. Explanations to the variations, patterns or trends are included in this chapter together with graphical representations of the results. Results of this study were generated from the sampling points that are shown in Figure 3.1 above.

4.1 River Water pH

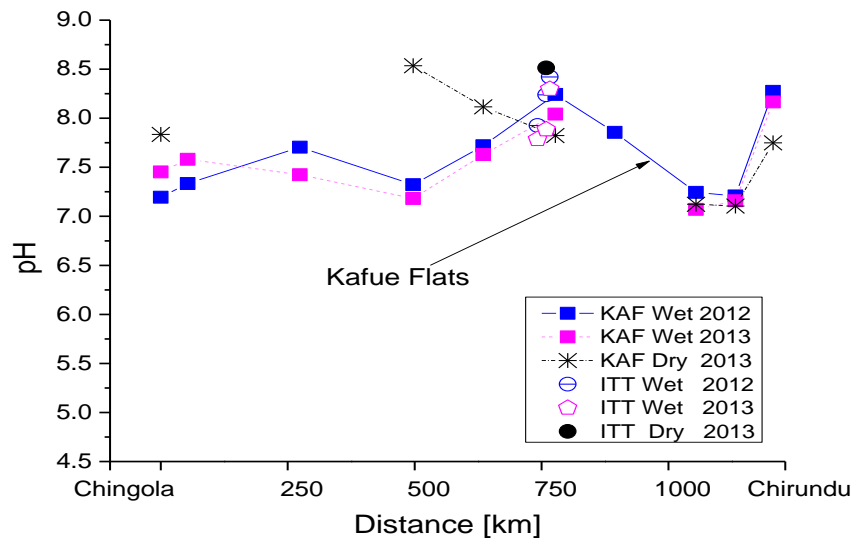
The Zambezi River was measured for pH from Kalene Hills to Luangwa at the selected sampling points (Figure 4.1a). The pH varied between 6.5 and 8.1 during the 2012 wet season and between 6.1 and 8.0 during the 2013 dry season along this stretch. Only 2012 pH values were analyzed for the Zambezi River because the pH probe malfunctioned during the 2013 wet season campaign and therefore only 3 points out of the 13 points were measured. The Kariba Reservoir was also measured and recorded high pH values averaging 8.5 during the 2012 wet season and 7.9 during the 2013 dry season campaigns.

The Kafue River was measured for pH from Chingola to Chirundu at the selected sampling points (Figure 4.1b). The pH varied between 7.2 and 8.3 during the 2012 wet season and between 7.1 and 8.2 during the 2013 wet season campaigns. Dry season values varied between 7.1 and 8.5 during the 2013 campaign along this stretch, with the station just before the confluence with Lunga River in Kasempa (KAF.ST.4) recording the maximum value of 8.5 during the dry season campaign. Similar to the Kariba Reservoir, the Itezhi Tezhi Reservoir also recorded high pH values averaging 8.1 and 7.9 during the 2012 and 2013 wet season campaign, respectively. The Itezhi Tezhi Reservoir averaged 8.5 during the 2013 dry season.

A similar pattern of decreasing pH over sections of the river that traverse extensive floodplains was observed during both the wet and dry season campaigns because respiration of organic matter leads to pH decrease (cf. Wamulume, 2011).



(a)



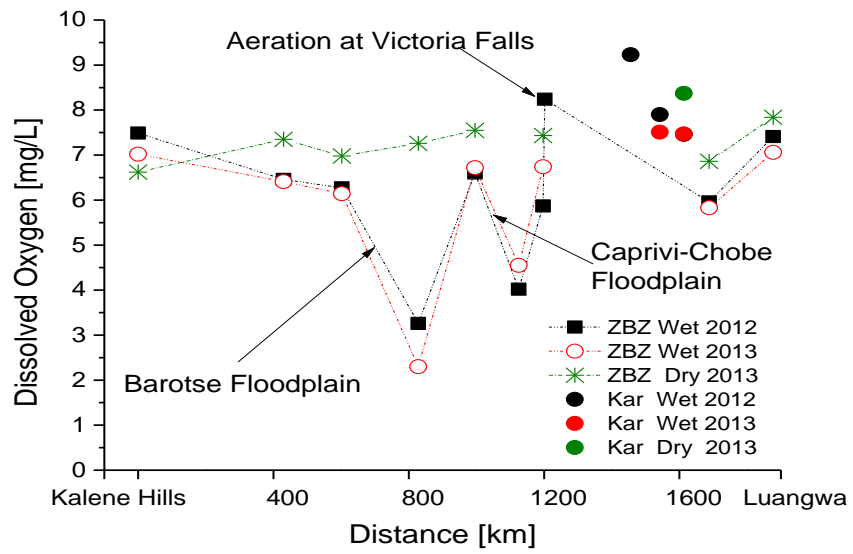
(b)

Figure 4.1: pH values for the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

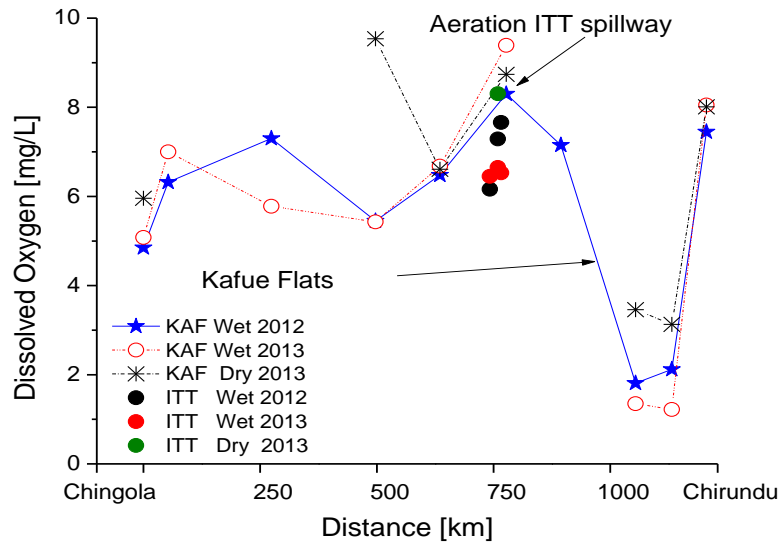
4.2 Dissolved Oxygen (DO)

The Zambezi River was measured for Dissolved Oxygen (DO) from Kalene Hills to Luangwa at the selected sampling points (Figure 4.2a). The river recorded DO values at a minimum of 3.3 and 2.3 mg/L for the Feb-March, 2012 and Jan-Feb, 2013 wet season campaigns, respectively, recorded along the river channel where the Barotse floodplains are located. Highest DO value of 8.2 mg/L was recorded just below the Victoria Falls (ZBZ.ST.8) during the 2012 wet season campaign, attributed to re-aeration process as the water plunges down the fall. During the dry season campaign, minimum value of 6.6 mg/L was recorded at the source of the Zambezi River. Decrease in DO over the Barotse Floodplain was observed only during the wet season compared to the dry season when the river had receded from the floodplains and thus had reduced the residence time over this section of the river that traverses the floodplain. During the same sampling periods, DO values of 9.2 and 7.5 mg/L for the 2012 and 2013 wet season campaigns, respectively, were recorded at the Kariba Reservoir. During the dry season campaign, the DO of the reservoir only went as high as 8.3 mg/L.

The Kafue River was measured for DO from Chingola to Chirundu at the selected sampling points (Figure 4.2b). DO was at a minimum of 1.8 mg/L in the Mazabuka Sugar Plantation (KAF.ST.8) which is towards the end of the Kafue Flats for the Feb-March, 2012 and 1.4 mg/L for the Jan-Feb, 2013 wet season campaigns. Maximum DO values were 8.3 and 9.4 mg/L for the 2012 and 2013 campaigns, respectively, recorded at KAF.ST.6 station just below the Itzhi Tezhi (ITT) Reservoir. As DO values here were higher than in the epilimnetic waters of the reservoir, this rise in DO could be explained by similar re-aeration processes observed at the Victoria Falls. An increase in DO is seen after the Kafue Gorge going towards the monitoring point at KAF.ST.10, just before the confluence with the Zambezi River. During the dry season campaign, the Kafue River recorded minimum DO value of 3.1 mg/L at KAF.ST.9 station and a maximum value of 9.5 mg/L at KAF.ST.4 station. DO values of 7.6 and 6.6 mg/L for the 2012 and 2013 campaigns, respectively, were recorded at the ITT Reservoir. During the dry season campaign, the ITT Reservoir recorded 8.3 mg/L DO.



(a)



(b)

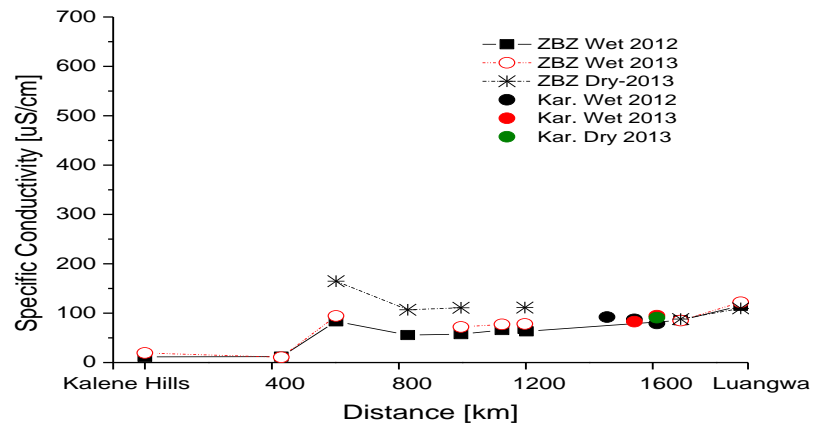
Figure 4.2: Dissolved Oxygen in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itzhi Tezhi Reservoir in Zambia

4.3 Specific Conductivity

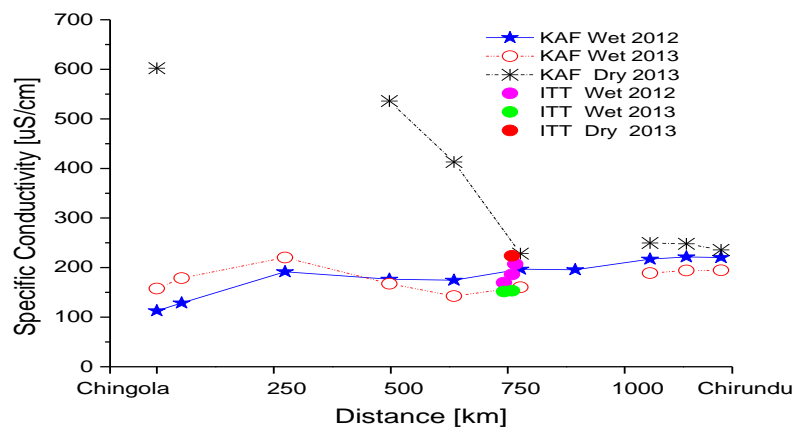
Specific conductivity (SpC) for the Zambezi River was measured from Kalene Hills to Luangwa at the selected sampling points (Figure 4.3a). SpC values were at a minimum of 11.6 $\mu\text{S}/\text{cm}$ at the source of the Zambezi River (ZBZ.ST.1) for the Feb-March, 2012 and 10.8 $\mu\text{S}/\text{cm}$ at Chavuma (ZBZ.ST.2) for the Jan-Feb, 2013 wet season sampling campaigns. During the same sampling periods, maximum specific conductivity values were 115.1 $\mu\text{S}/\text{cm}$ and 122.1 $\mu\text{S}/\text{cm}$ for the 2012 and 2013 campaigns, respectively, both recorded at Luangwa (ZBZ.ST.10), just before the confluence with the Luangwa River. Although the first two stations that recorded lowest specific conductivity values were not measured during the dry season, the values measured at other stations still indicated that the dry season had relatively higher specific conductivity values, averaging 115.3 $\mu\text{S}/\text{cm}$ compared to an average of 65.4 $\mu\text{S}/\text{cm}$ during the wet season. Reduced water volume and dissolved mineral elements coming from land-use related activities such as mining and agriculture could account for higher dry season specific conductivity values compared to the wet season where dilution has an effect on specific conductivity.

Kafue River specific conductivity was measured from Chingola to Chirundu at the selected sampling points (Figure 4.3b). Specific conductivity was minimum at the first sampling point in Chingola (KAF.ST.1) at 112.7 $\mu\text{S}/\text{cm}$ for the Feb-March, 2012 and 142.5 $\mu\text{S}/\text{cm}$ at Hook Bridge (KAF.ST.5) for the Jan-Feb, 2013 sampling campaigns. During the same sampling periods, maximum specific conductivity values were 220.4 $\mu\text{S}/\text{cm}$ and 194.5 $\mu\text{S}/\text{cm}$ for the 2012 and 2013 campaigns, respectively, both recorded just before the confluence with the Zambezi River in Chirundu (KAF.ST.10). Dry season values for the Kafue River were much higher (averaging 359.0 $\mu\text{S}/\text{cm}$) compared to an average of 181.0 $\mu\text{S}/\text{cm}$ during wet season campaigns. It was observed that values became moderated after the Itezhi Tezhi Reservoir, reaching 235.6 $\mu\text{S}/\text{cm}$ at the last sampling point in Chirundu (KAF.ST.10). Overall, while the conductivity of the Kafue increases downstream during both wet season campaigns, an opposite trend (decrease downstream) is observed during the dry season, when headwaters reached up to an order of magnitude higher values.

The Kafue River had on average higher SpC values (181.0 $\mu\text{S}/\text{cm}$) compared to the Zambezi River (65.4 $\mu\text{S}/\text{cm}$) during the wet season and an average of 359.0 $\mu\text{S}/\text{cm}$ compared to the Zambezi River (115.3 $\mu\text{S}/\text{cm}$) during the dry season. The higher dissolved solutes in the Kafue River could be linked to the larger concentration of mining, industrial and agricultural activities in the Basin, similar to what has been described in section 1.2 above.



(a)

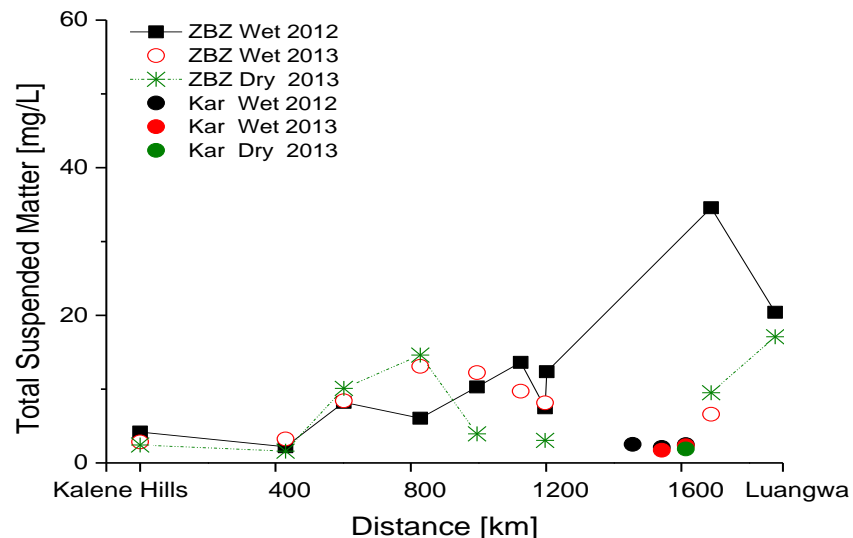


(b)

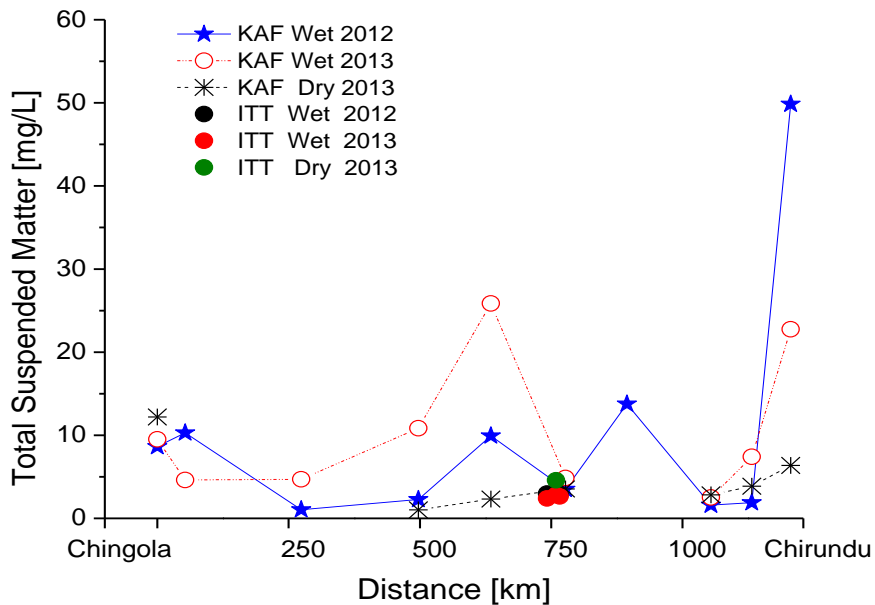
Figure 4.3: Specific conductivity values for the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.4 Total Suspended Matter

Total Suspended Matter (TSM) along the Zambezi mainstream, sampled at selected sampling points from Kalene Hills to Luangwa, varied between 2.2 and 34.6 mg/L and 2.8 and 93.4 mg/L during the Feb-March, 2012 and Jan-Feb, 2013 wet season campaigns, respectively (Figure 4.4a). The dry season had relatively lower values with 1.6 mg/L at Chavuma (ZBZ.ST.2) and 17.0 mg/L at the end of the river stretch (ZBZ.ST.10). The Kafue mainstream was sampled at the selected sampling points from Chingola to Chirundu and ranged between 1.0 and 49.9 mg/L and 2.5 and 22.8 mg/L in Feb-March, 2012 and Jan-Feb, 2013 campaigns, respectively (Figure 4.4b). The last sampling point along the river, KAF.ST10, recorded the maximum values. The dry season campaign had relatively lower values with the highest record of 12.0 mg/L at the first station (KAF.ST.1). All the other stations ranged between 1.0 mg/L and 12.0 mg/L. In all campaigns, both ITT and Kariba reservoirs were on the lower end of the TSM concentrations since low flow and longer residence time allow the settling of the suspended matter. TSM levels are higher during periods of high water flow, when tropical rivers generally exhibit the highest particulate matter load due to runoff and high erosion rates (cf. Coynel et al., 2005; Hung and Huang, 2005).



(a)



(b)

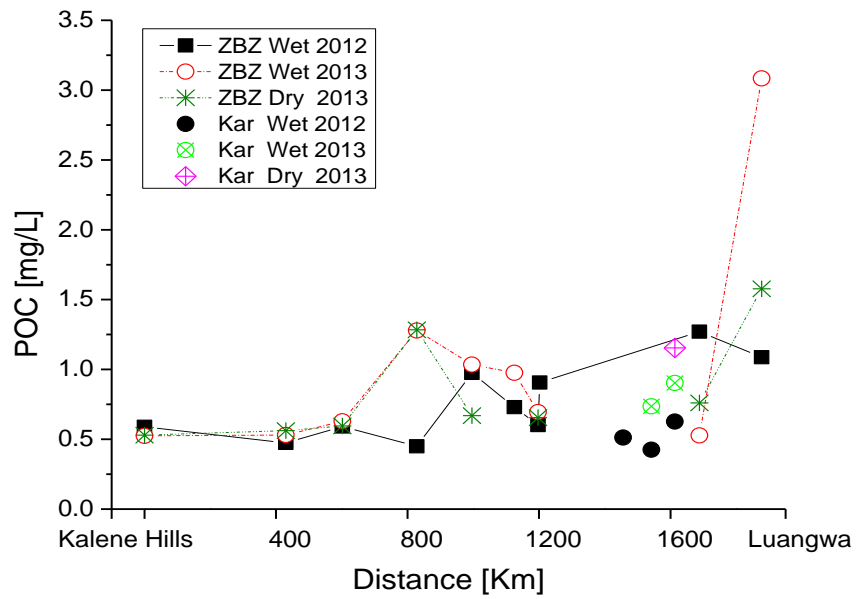
Figure 4.4: Total Suspended Matter in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.5 Particulate Organic Carbon (POC)

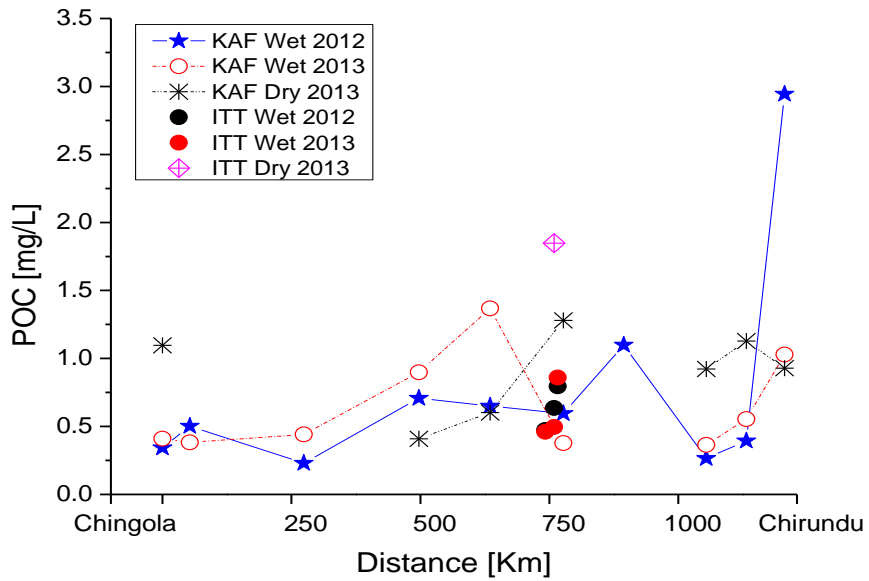
Particulate Organic Carbon (POC) along the Zambezi mainstream was sampled at the selected sampling points from Kalene Hills to Luangwa and varied from 0.4 to 1.3 mg/L and from 0.5 to 3.1 mg/L during the Feb-March, 2012 and Jan-Feb, 2013 wet season campaigns, respectively (Figure 4.5a). The dry season campaign recorded a very similar pattern to that of the 2013 wet season campaign. Kalongola (ZBZ.ST.4) which is located where the river traverses extensive floodplains recorded a surprisingly low value (0.4 mg/L) in the 2012 wet season campaign but consistently recorded higher values (1.27 and 1.28 mg/L) during the 2013 wet and dry seasons, respectively. The last sampling point in Luangwa (ZBZ.ST.10) consistently recorded high POC values of 1.1, 3.1 and 1.6 mg/L for the 2012 wet season, 2013 wet and dry seasons, respectively. Besides the allochthonous organic matter inputs, there are also autochthonous organic matter sources

in rivers such as organic matter produced by autotrophic organisms, including phytoplankton and aquatic macrophytes (Mayorga, 2004). Thus, a part of the particulate organic carbon comes from in-stream production. In lentic waters, such as lakes, reservoirs and during floodplain inundation, fine suspended matter drops out thus enriching such waters with lighter particulate organic matter (cf. Mayorga, 2004). Therefore, Kariba Reservoir had low TSM values but recorded high POC of 1.2 mg/L in the dry season campaign and ranged between 0.4 and 0.9 mg/L during the 2012 and 2013 wet season campaigns. The ITT showed a similar pattern to that of the Kariba and recorded high POC of 1.8 mg/L in the dry season campaign and ranged between 0.5 and 0.9 mg/L during the 2012 and 2013 wet season campaigns.

The POC in the Kafue mainstream at the selected sampling points from Chingola to Chirundu varied between 0.3 and 2.9 mg/L and 0.4 and 1.4 mg/L in Feb-March, 2012 and Jan-Feb, 2013 wet season campaigns, respectively. The dry season campaign had relatively higher values between stations compared to the wet season campaigns but still ranged between 0.4 and 1.3 mg/L. In a similar pattern to the Zambezi River, the last sampling point (KAF.ST.10) also consistently recorded high POC values of 2.9, 1.0 and 0.9 mg/L for the 2012 wet season, 2013 wet and dry seasons, respectively (Figure 4.5b). Allochthonous organic matter inputs contribute largely to high POC values that are associated with high TSM as observed on the lasting sampling stations (KAF.ST.10 and ZBZ.ST.10) similar to what has been described in section 2.4.3 above.



(a)

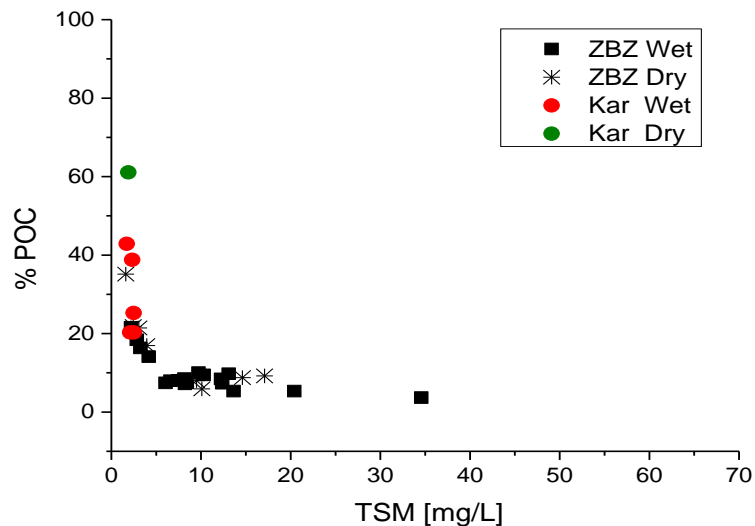


(b)

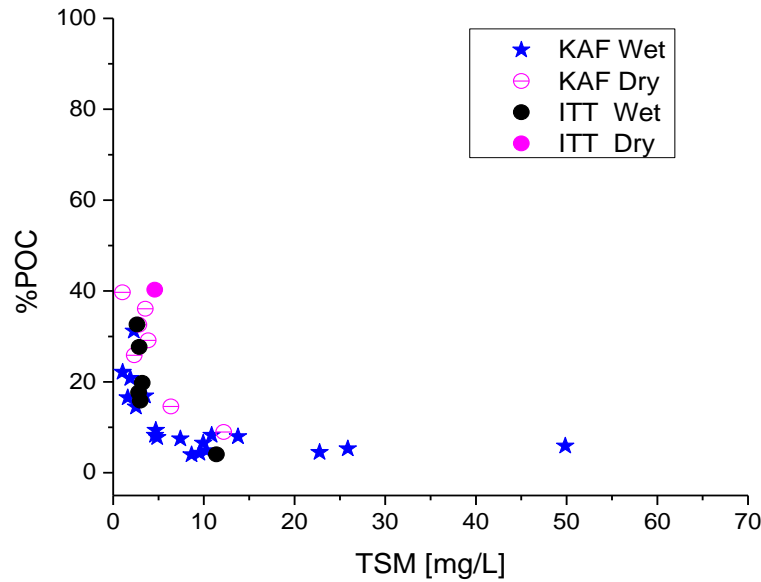
Figure 4.5: Particulate Organic Carbon in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itzhi Tezhi Reservoir in Zambia

A consistent inverse relationship between TSM and percent POC (%POC) (i.e. POC concentration divided by the total suspended matter concentration (TSM) and expressed in %, (thus x 100), was found for both rivers (Figures 4.6a and b). The highest %POC value of 42.9 % during the wet season and 61.1 % during the dry season campaign were recorded on the Kariba Reservoir. Since TSM levels are higher during periods of high water flow (Coynel et al., 2005), particulate matter load due to runoff and high erosion rates reduces during the dry season and this explains why the dry season recorded a higher %POC as compared to the wet season.

It is interesting how reservoirs differ from river systems because even when TSM is lowest in reservoirs, the relative contribution of the organic fraction (%POC) is high. High %POC values were also recorded at the Itezhi Tezhi Reservoir during both the wet and dry season campaigns (32.6 and 40.3 % POC, respectively). This is also attributed to lentic waters dropping out much of the fine suspended matter on reservoirs and floodplains, leaving the lighter organic matter suspended and thus recording high POC in low TSM conditions (cf. Mayorga, 2004) and increased phytoplankton production in low flow conditions (cf. Bouillon et al., 2012).



(a)



(b)

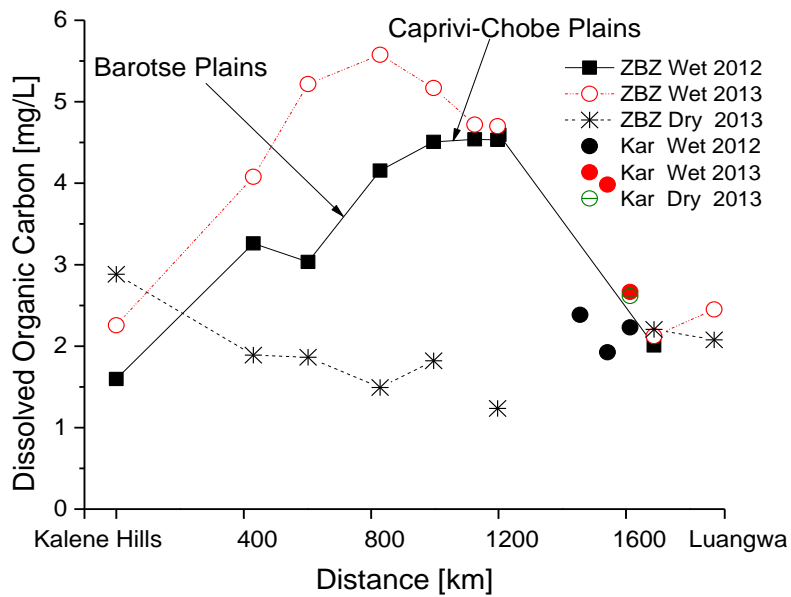
Figure 4.6: Total Suspended Matter (TSM) and %Particulate Organic Carbon (POC) in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.6 Dissolved Organic Carbon (DOC)

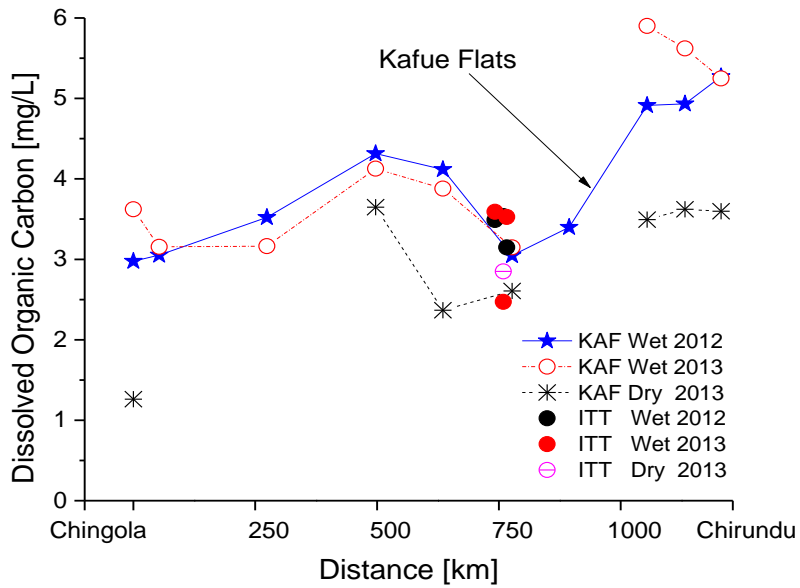
The Zambezi River was measured for Dissolved Organic Carbon (DOC) from Kalene Hills to Luangwa at the selected sampling points (Figure 4.7a). The source of the Zambezi (ZBZ.ST.1) recorded 1.6 mg/L which was a minimum value for the Feb-March, 2012 and 2.3 mg/L for Jan-Feb, 2013 wet season sampling campaigns. DOC along the Zambezi River increased in sections of the river that traversed extensive floodplains with Kalongola (ZBZ.ST.4) recording 4.2 mg/L during the Feb-March, 2012 campaign and a maximum value of 5.6 mg/L for the Jan-Feb, 2013 wet season campaign, showing the relative significance of floodplains in DOC contribution to river channels. DOC and DIC are the most dominant fractions of the aquatic carbon pool in floodplains but DOC is the most significant pool of reduced carbon in aquatic systems (Volka et al., 1997), being responsible for significant lateral fluxes (Cole et al., 2007; Bass et al., 2011). Inundation of bare grounds in sections of the river that traverse

extensive floodplains increase terrestrial contribution to the DOC pool and thus account for this proportional increase in DOC (cf. Hope et al., 1994). DOC values decreased during the dry season campaign with ZBZ.ST.7 station recording the lowest at 1.2 mg/L and the highest was recorded at Kalene Hills (ZBZ.ST.1) at 2.9 mg/L. The decrease during the dry season is because the floodplains recede and as such terrestrial contribution to the DOC pool reduces.

The Kafue River was measured for DOC from Chingola to Chirundu at the selected sampling points (Figure 4.7b). Minimum DOC values were at the first sampling point in Chingola (KAF.ST.1) at 3.0 mg/L in the Feb – March, 2012 and 3.1 mg/L at KAF.ST.6 for the Jan-Feb, 2013 wet season campaigns. During the same sampling periods, DOC values of 4.9 and 5.9 mg/L were recorded in the Nakambala Sugar Estates (KAF.ST.8) for the 2012 and 2013 campaigns, respectively. Similar processes as described above for the floodplains on the Zambezi River account for this increase in DOC as well since KAF.ST.8 station lies within the Kafue Flats. DOC did not have a very wide variance (1.2 to 5.9 mg/L) during both wet season campaigns and in both rivers. During the dry season, DOC in the Kafue River ranged between 1.3 and 3.7 mg/L. Both the Kariba and ITT reservoirs were well within the value ranges of the rivers. The Kariba recorded maximum of 2.4 and 4.0 mg/L during the 2012 and 2013 wet season campaigns, respectively. The ITT recorded maximum DOC values of 3.5 and 3.6 mg/L during the 2012 and 2013 wet season campaigns, respectively. Dry season values were 2.6 and 2.8 mg/L for the Kariba and the ITT reservoirs, respectively.



(a)



(b)

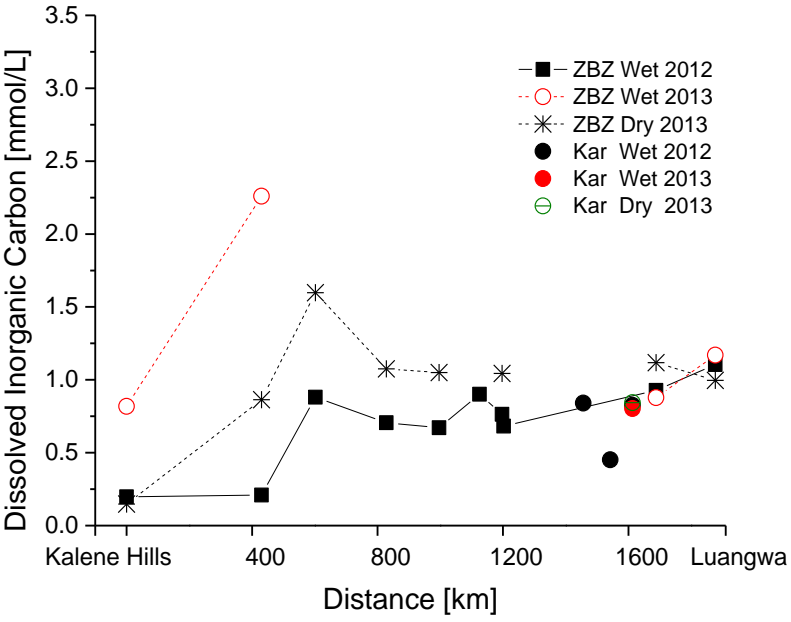
Figure 4.7: Dissolved Organic Carbon in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.7 Dissolved Inorganic Carbon (DIC)

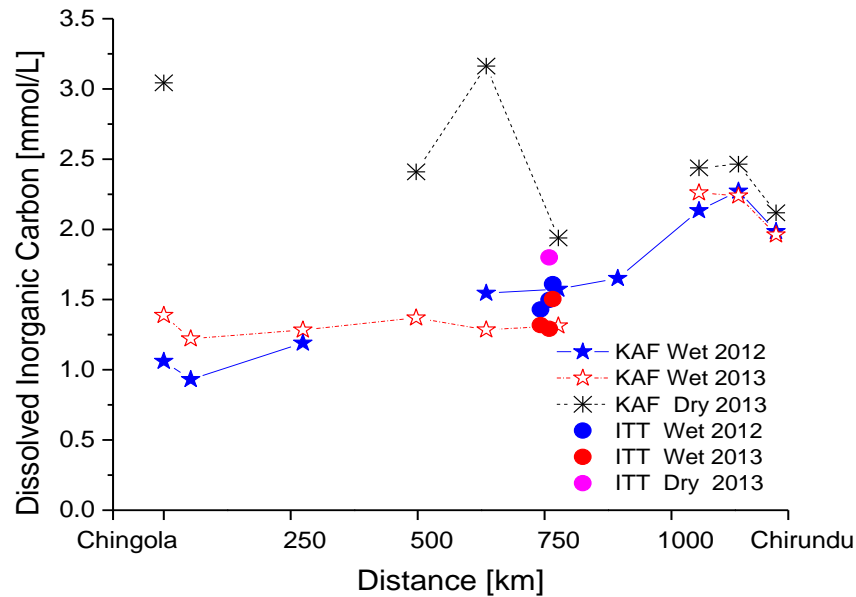
The Zambezi mainstream was measured for Dissolved Inorganic Carbon (DIC) from Kalene Hills to Luangwa at the selected sampling points (Figure 4.8a). Minimum DIC value of 0.2 mmol/L was recorded at the source of the Zambezi in Kalene Hills (ZBZ.ST.1) and had an increasing trend going to a maximum value of 1.1 mmol/L in Luangwa (ZBZ.ST.10) for the Feb-March, 2012 campaign. The 2013 wet season campaign followed a similar pattern as in 2012 and started at 0.8 mmol/L at the source and increased to 1.2 mmol/L in Luangwa. According to Das et al. (2005), DIC is produced by weathering and dissolution of carbonate and silicate rocks, although may also be present as dissolved CO₂ generated by the decomposition of dissolved organic matter as described in section 2.4.2 above. The downstream increase of DIC could be attributed to the continuous weathering and dissolution of silicate elements as the Zambezi River flowed downstream through the silicate-carbonate rich Katanga Supergroup and Basement Complex rocks of north-western Zambia and Kalahari sands of Western and Southern Zambia (Nyambe, 2014 – Personal communication). The dry season DIC values were relatively higher with all stations from ZBZ.ST.2 to ZBZ.ST.10 ranging between 1.0 and 1.6 mmol/L. The dry season campaign recorded an increase in DIC values possibly due to evaporation to concentrate the dissolved mineral elements in the river waters.

The Kafue mainstream was measured for DIC from Chingola to Chirundu at the selected sampling points (Figure 4.8b). The Kafue River had minimum DIC value of 1.0 mmol/L at Mufulira (KAF.ST.2) station and recorded a maximum value of 2.3 mmol/L at the bridge in Kafue Town (KAF.ST.9) station in the Feb – March, 2012 wet season campaign. During the Jan-Feb, 2013 wet season campaign, DIC varied between 1.2 and 2.3 mmol/L from Mufulira (KAF.ST.2) to Mazabuka (KAF.ST.8) station. Dry season values for the Kafue River also increased ranging between 2.0 and 3.1 mmol/L from Chingola to Chirundu. What was very clear from the results was that the DIC values for the Kafue were on average (1.6 mmol/L) twice as high (0.7mmol/L) as those of the Zambezi River and this could be attributed to carbonate weathering and dissolution which was predominant on the Kafue River whereas weathering and dissolution of

silicate elements in the Zambezi River (Figure 4.10d). Both the Kariba and ITT reservoirs were well within the river DIC values since the respective contributing river channels could have influenced reservoir DIC values. The Kariba recorded maximum of 0.8 and 0.8 mmol/L during the 2012 and 2013 wet season campaigns, respectively. The ITT recorded maximum DIC values of 1.6 and 1.5 mmol/L during the 2012 and 2013 wet season campaigns, respectively. Dry season values were 0.8 and 1.8 mmol/L for the Kariba and the ITT reservoirs, respectively.



(a)

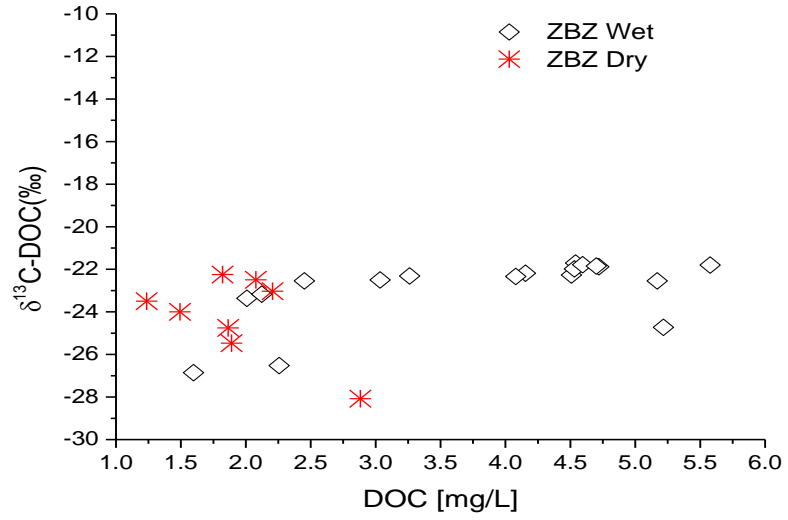


(b)

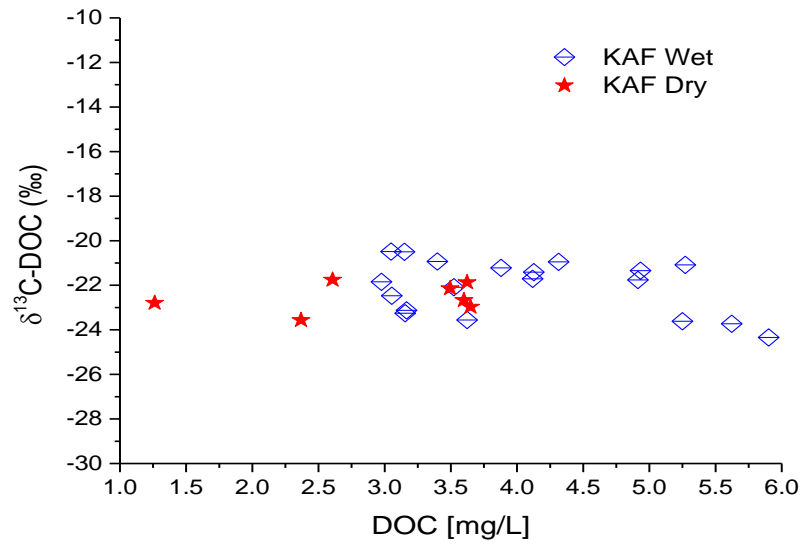
Figure 4.8: Dissolved Inorganic Carbon in the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.8 $\delta^{13}\text{C}$ - DOC and DOC

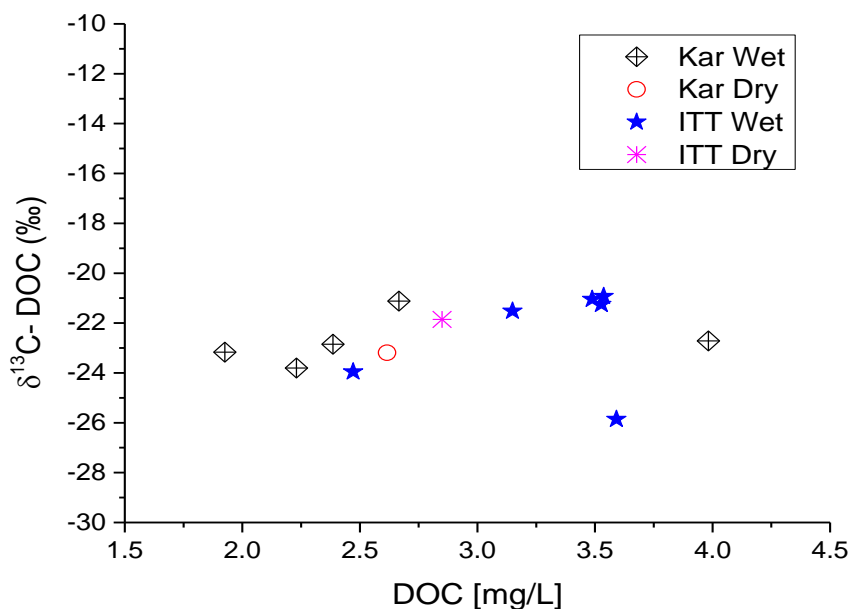
The $\delta^{13}\text{C}$ - DOC values for the Zambezi River measured from Kalene Hills to Luangwa at selected sampling points ranged between -26.9 and -21.7 ‰ during the 2012 wet season campaign and also between -26.5 and -21.8 ‰ during the 2013 wet season campaign (Figure 4.9a). The dry season campaign recorded a range of -28.1 to -22.2 ‰. The Kafue River was measured at the selected sampling points from Chingola to Chirundu and had a narrower range of between -22.4 and -20.5 ‰ during the 2012 wet season campaign and between -24.3 and -20.5 ‰ during the 2013 wet season campaign (Figure 4.9b). The dry season ranged from -23.6 to -21.8 ‰. Both the Zambezi and the Kafue rivers averaged around -22.0 ‰ over both the wet and the dry seasons. The two reservoirs, Kariba and Itezhi Tezhi, also fell within the same ranges as the river values (Figure 4.9c). The plots of $\delta^{13}\text{C}$ - DOC and DOC concentrations show that there is no correlation between these two parameters since data points follow a horizontal pattern to the x-axis (Figures 4.9a, b and c).



(a)



(b)



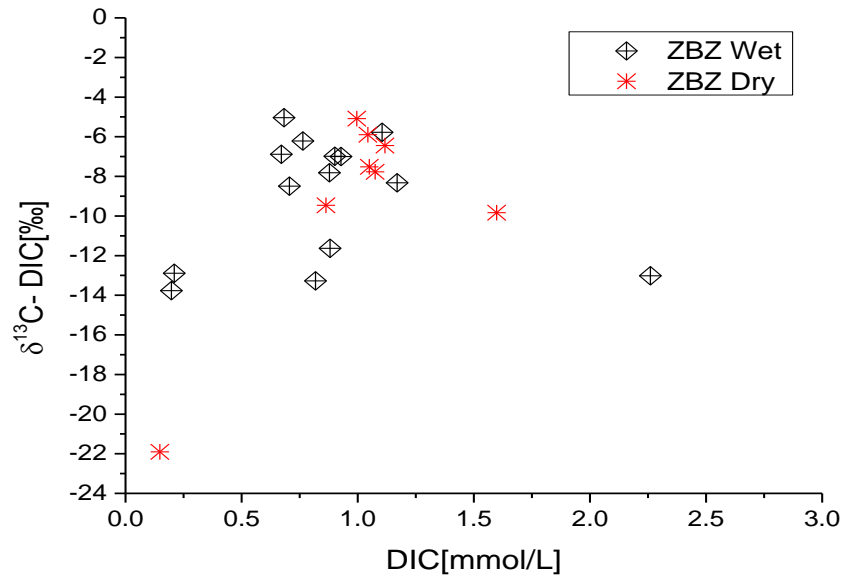
(c)

Figure 4.9: $\delta^{13}\text{C}$ - DOC isotopic signature for the wet and dry seasons on the (a) Zambezi River (b) Kafue River and (c) Kariba and Itezhi Tezhi reservoirs in Zambia

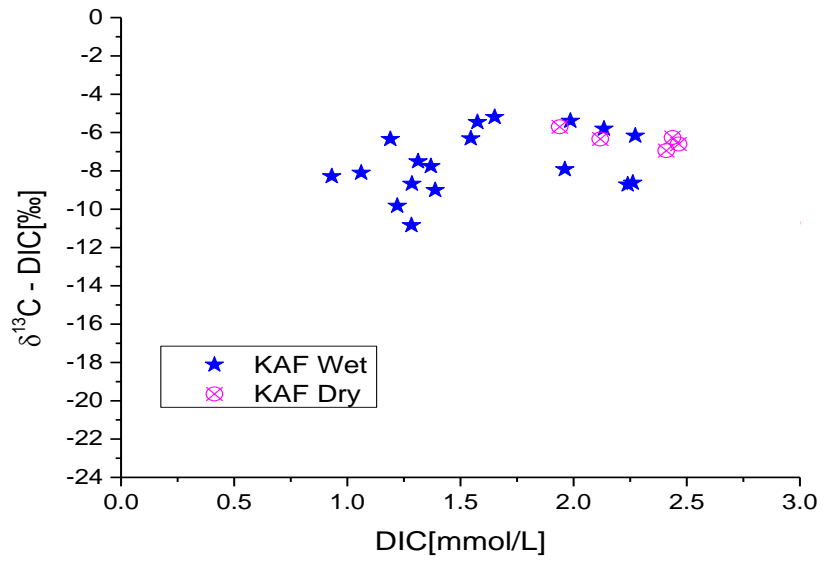
4.9 $\delta^{13}\text{C}$ - DIC and DIC

The Zambezi mainstream was measured for $\delta^{13}\text{C}$ - DIC from Kalene Hills to Luangwa at the selected sampling points (Figure 4.10a). $\delta^{13}\text{C}$ - DIC for the Zambezi River during the 2012 wet season campaign was between -13.8 and -5.0 ‰ at ZBZ.ST 1 and ZBZ.ST.8 stations, respectively. During the 2013 wet season campaign, $\delta^{13}\text{C}$ - DIC values ranged between -13.3 and -6.1 ‰ recorded at the source (ZBZ.ST.1) and Kalongola (ZBZ.ST.4) stations, respectively. The dry season campaign recorded values between -22.0 ‰ at ZBZ.ST.1 and -5.1 ‰ at ZBZ.ST.10 stations. The Kafue River was also measured for $\delta^{13}\text{C}$ - DIC from Chingola to Chirundu at the selected sampling points (Figure 4.10b). During the 2012 wet season campaign, the Kafue River recorded values between -8.3 and -5.2 ‰ at KAF.ST.2 and KAF.ST.7, respectively. In the 2013 wet season campaign, values ranged between -10.8 and -7.5 ‰ recorded at KAF.ST.3 and

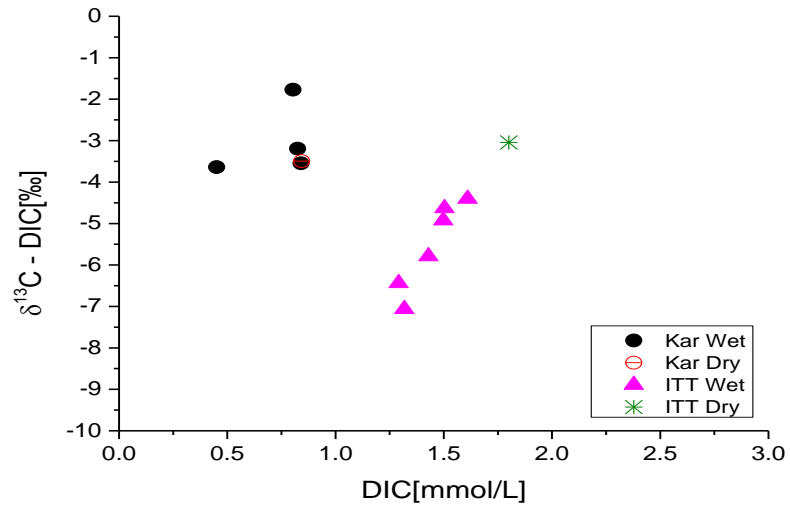
KAF.ST.6, respectively. The dry season recorded -10.7 ‰ at KAF.ST.1 and -5.7 ‰ at KAF.ST.6. The Kafue River had a narrower range (-5.2 to -10.8 ‰) in the $\delta^{13}\text{C}$ - DIC values compared to the Zambezi River (-5.0 to -22.0 ‰) for both wet and dry seasons. The Kariba Reservoir ranged between -4.0 and -1.0 ‰ whereas values in the ITT Reservoir varied between -7.0 and -4.0 ‰. The $\delta^{13}\text{C}$ - DIC had a positive correlation with DIC concentration in the ITT Reservoir ($r^2 = 0.89$) but the Kariba Reservoir and the rivers did not exhibit any such correlations (Figure 4.10c). Initial sampling points of river systems recorded lowest values of $\delta^{13}\text{C}$ - DIC (averaging -16.3 ‰) at Kalene Hills (ZBZ ST.1) and averaging -9.0 ‰ between Chingola (KAF.ST.1) and Mpongwe (KAF.ST.3). Stations located at points where the rivers traverse extensive areas of floodplains recorded higher values (averaging -6.8 ‰) at Kalongola (ZBZ.ST.4) and before the Victoria Falls, coming from Caprivi-Chobe (ZBZ.ST.7) and an average of -6.0 ‰ at beginning of Kafue Flats (KAF.ST.6) and Namwala (KAF.ST.7). DIC in the reservoirs was more enriched in the ^{13}C isotope compared to rivers. The reservoirs, especially the Kariba, were enriched in the ^{13}C isotope possibly due to the preferential use of the 'lighter' CO_2 by phytoplankton during primary production. Figure 4.10d showed that the Zambezi River and the Kariba Reservoir had Si/Ca ratios close to 1. Exceptions are observed for higher values between 2 and 5 and an extreme one (circled in Figure 4.10d) which had a ratio value of 15 at the source of the Zambezi, indicating very high relative amounts of Si, suggesting that weathering and dissolution of silicates dominates. The Kafue River and the Itezhi Tezhi Reservoir had Si/Ca ratios close to 0.5 during the wet season. This ratio suggests that weathering and dissolution of carbonates dominated along the Kafue River and on the Itezhi Tezhi Reservoir. During the dry season, the values (circled in Figure 4.10d) moved further towards 0.2, most likely as a result of carbonate weathering and dissolution in the limestone geology the Kafue River passes through (Armstrong, 2009).



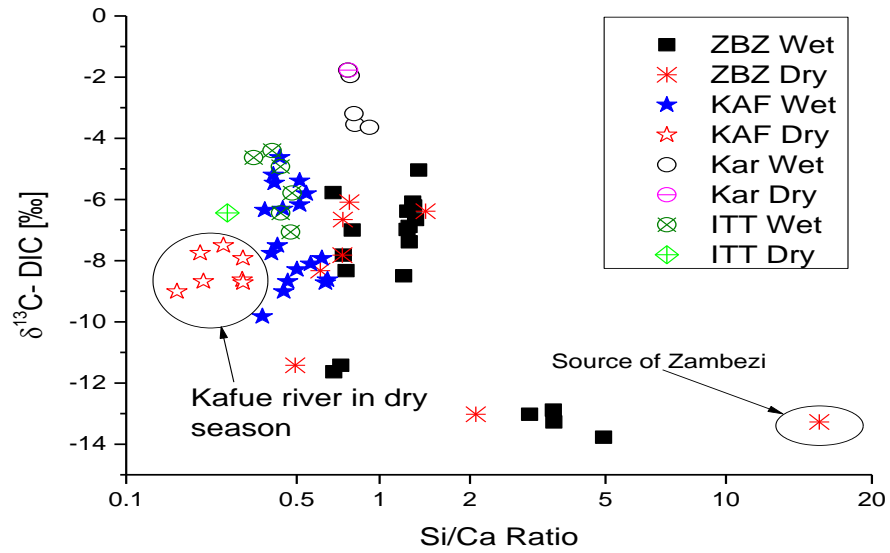
(a)



(b)



(c)

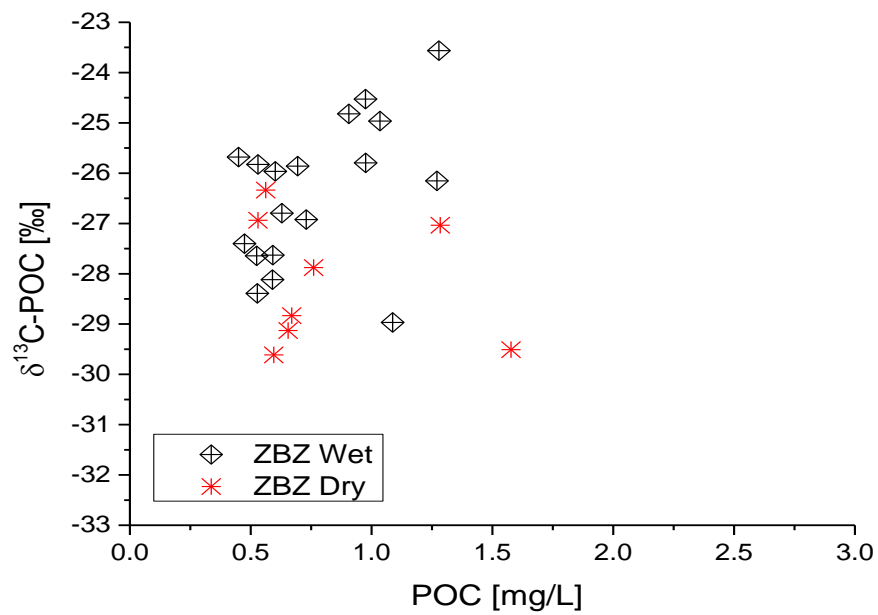


(d)

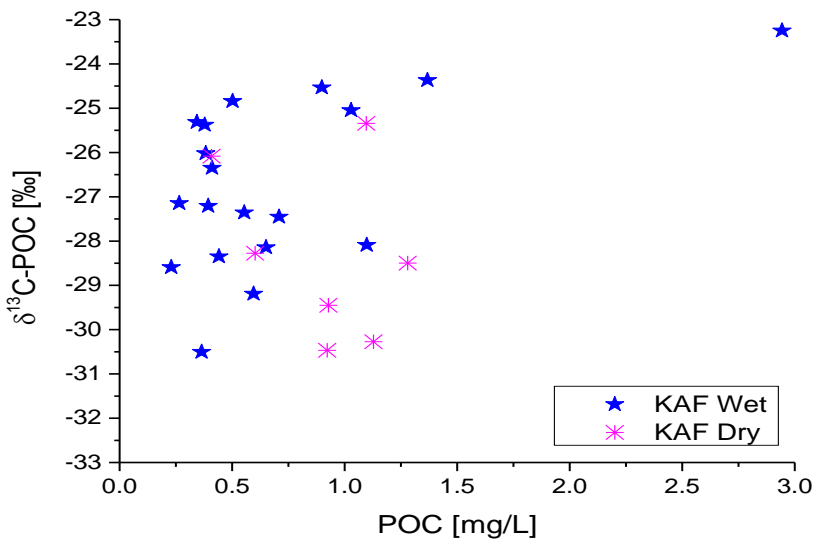
Figure 4.10: Plot of $\delta^{13}\text{C} - \text{DIC}$ versus DIC for the wet and dry seasons on the (a) Zambezi River (b) Kafue River (c) Kariba and Itezhi Tezhi reservoirs and (d) $\delta^{13}\text{C} - \text{DIC}$ isotopic signature plotted with Si/Ca ratio for the Zambezi, Kafue rivers and the Kariba, Itezhi Tezhi reservoirs, Zambia

4.10 $\delta^{13}\text{C}$ - POC and POC

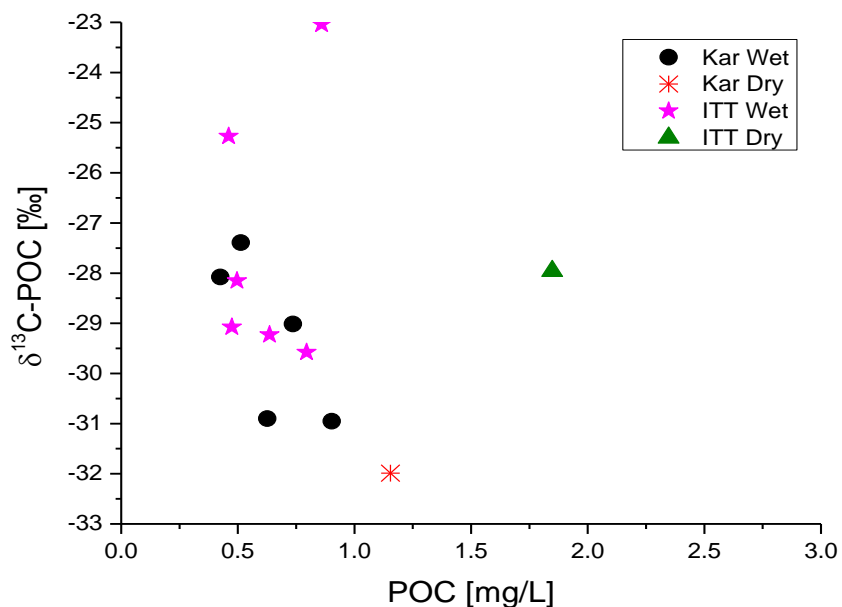
$\delta^{13}\text{C}$ - POC for the Zambezi River at the selected sampling points from Kalene Hills to Luangwa during the 2012 wet season campaign was between -29.0 and -24.5 ‰, recorded at the source of the Zambezi (ZBZ.ST 1) and Sesheke (ZBZ.ST.5) stations, respectively (Figure 4.11a). During the 2013 wet season campaign, $\delta^{13}\text{C}$ - POC ranged between -28.4 and -23.1 ‰, recorded at Chirundu (ZBZ.ST.9) and Luangwa (ZBZ.ST.10), respectively. The dry season campaign recorded values of -29.6 ‰ at ZBZ.ST.3 and -26.3 ‰ at ZBZ.ST.2 stations. During the 2012 wet season campaign, the Kafue River was measured at the selected sampling points from Chingola to Chirundu and recorded $\delta^{13}\text{C}$ - POC values between -29.2 and -23.2 ‰, recorded at below Itezhi Tezhi (KAF.ST.6) and Chirundu (KAF.ST.10) stations, respectively. In the 2013 wet season campaign, values ranged from -30.5 to -24.4 ‰ at KAF.ST.8 and KAF.ST.5 stations, respectively. The dry season recorded -30.4 ‰ at KAF.ST.8 and -25.3 ‰ at KAF.ST.1 stations (Figure 4.11b). The Kariba Reservoir values ranged between -32.0 and -29.0 ‰ whereas values in the ITT Reservoir varied between -29.5 and -25.3 ‰ (Figure 4.11c). POC in the reservoirs was more depleted in the ^{13}C isotope, in particular Kariba Reservoir compared to the rivers and these values are within the range of values reported for typical terrestrial C3-plants (Peterson and Fry, 1987). Therefore, this range of values could suggest a higher C3 contribution to POC than to DOC in the reservoirs. In the reservoirs, there is also a significant contribution of phytoplankton to POC as observed in the %POC values found (Figures 4.6a and b). The Itezhi Tezhi Reservoir was within the same $\delta^{13}\text{C}$ - POC value range as the Kafue River in both the wet and dry seasons. There is no correlation observed between $\delta^{13}\text{C}$ - POC and POC both in the reservoirs and the main river channels (Figures 4.11a, b and c).



(a)



(b)



(c)

Figure 4.11: $\delta^{13}\text{C}$ - POC isotopic signature for the wet and dry seasons on the (a) Zambezi River (b) Kafue River and (c) Kariba and Itezhi Tezhi reservoirs in Zambia

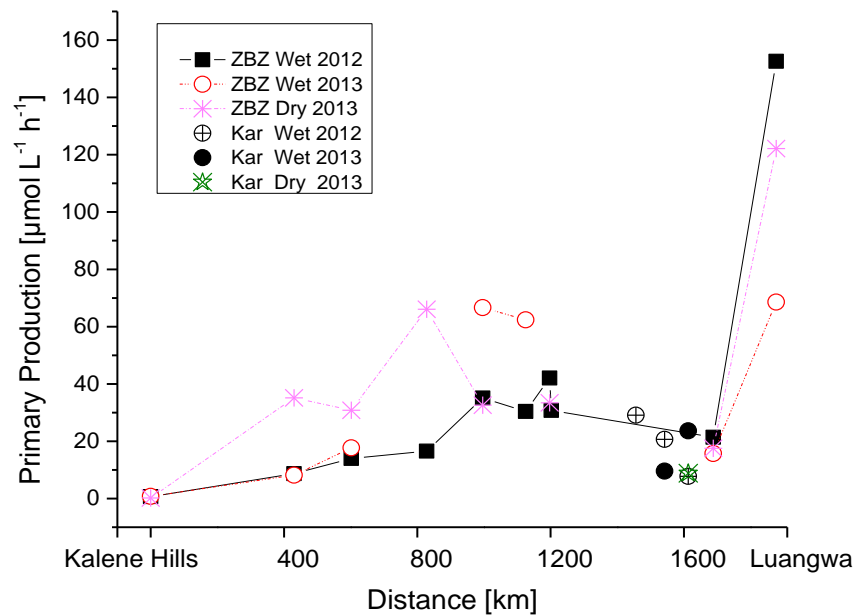
4.11 Primary Production Rates

Primary production rates for the Zambezi River were measured from Kalene Hills to Luangwa at the selected sampling points (Figure 4.12a). Primary production rates fluctuated along the river stretch but were lowest at the source of the Zambezi (ZBZ.ST.1) and highest at the last sampling point in Luangwa (ZBZ.ST.10) with 0.7 and 152.6 $\mu\text{mol L}^{-1} \text{h}^{-1}$, respectively, in the 2012 wet season campaign. This similar pattern of downstream increase was also followed in the 2013 wet season and dry season campaigns. In the 2013 wet season, primary production rates measured were 0.8 and 68.0 $\mu\text{mol L}^{-1} \text{h}^{-1}$ at the source in Kalene Hills and last sampling point in Luangwa (ZBZ.ST.10), respectively. Primary production during the dry season ranged between 0.2 and 122.1 $\mu\text{mol L}^{-1} \text{h}^{-1}$ recorded at the source and last sampling point in Luangwa, respectively. The Kariba Reservoir fell within the same range of values as the Zambezi

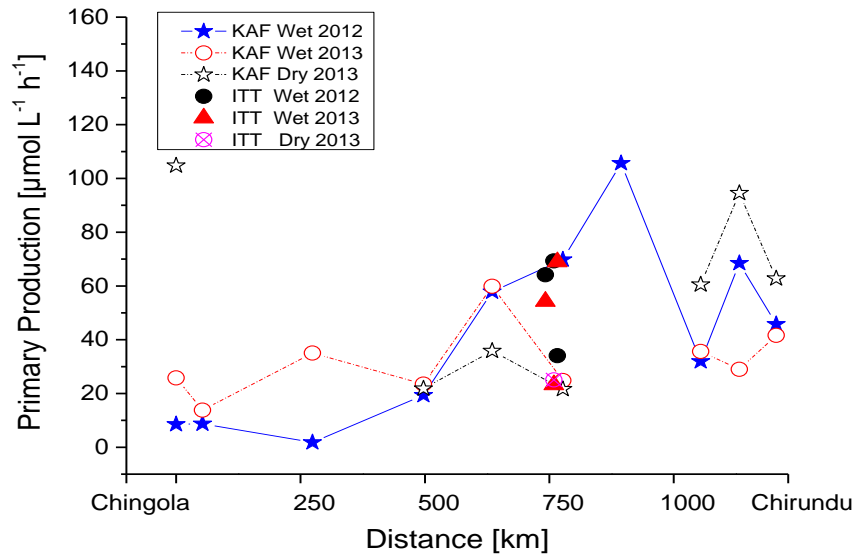
River recording averages of 19.2, 16.6 and 8.8 $\mu\text{mol L}^{-1} \text{h}^{-1}$ during the 2012 wet season and 2013 wet and dry seasons, respectively. Light availability is the major controlling factor for primary productivity of rivers (Bonetto, 1986). Thus, turbidity reduces the amount of light available for photosynthetic reactions. According to Bonetto (1986), lower rates of phytoplankton production are often observed in periods of high discharge because Total Suspended Matter (TSM) concentrations would have reduced light penetration. However, paired t-tests done at 0.05 significance level showed that there was no significant difference in the primary production rates between 2012 and 2013 ($p=0.83$), 2012 and dry season ($p=0.52$) and 2013 and dry season ($p=0.43$). During the dry season, lower TSM concentrations are expected as described in section 4.4 above, thus higher primary production rates are expected. Another factor determining riverine primary productivity is nutrient concentrations (Davies et al., 2008) because photosynthesis depends partly on the availability of inorganic nutrients. Primary production rates in the Kariba Reservoir (averages of 19.2, 16.6 and 8.8 $\mu\text{mol L}^{-1} \text{h}^{-1}$) falling within the same range of values as the Zambezi River (0.2 to 152.6 $\mu\text{mol L}^{-1} \text{h}^{-1}$) could probably be explained by these factors.

Primary production rates for the Kafue River were measured from Chingola to Chirundu at the selected sampling points (Figure 4.12b). The Kafue River primary production rates had the same increase pattern along the river stretch as observed in the Zambezi River. In the 2012 wet season campaign, the lowest rate of 8.5 $\mu\text{mol L}^{-1} \text{h}^{-1}$ was measured at the first sampling point in Chingola (KAF.ST.1) and highest rate of 105.6 $\mu\text{mol L}^{-1} \text{h}^{-1}$ was measured at Namwala (KAF.ST.7) which is within the Kafue Flats. The 2013 wet season campaign followed a similar pattern with lowest rate of 13.8 $\mu\text{mol L}^{-1} \text{h}^{-1}$ recorded at Mufulira (KAF.ST.2) station and highest rate of 59.9 $\mu\text{mol L}^{-1} \text{h}^{-1}$ recorded at the Hook Bridge (KAF.ST.5). The dry season recorded the highest rate of 104.8 $\mu\text{mol L}^{-1} \text{h}^{-1}$ in Chingola (KAF.ST.1) and then fluctuated, the lowest rate of 21.6 $\mu\text{mol L}^{-1} \text{h}^{-1}$ recorded at KAF.ST.6 right below the ITT Reservoir. The Itezhi Tezhi did not show any peculiar pattern but had all values falling well within those of the main river, averaging 55.8, 48.8 and 25.1 $\mu\text{mol L}^{-1} \text{h}^{-1}$ during the 2012 wet season, 2013 wet and dry seasons, respectively. Paired t-tests done showed that there was no significant

difference in the primary production rates between 2012 and 2013 wet seasons ($p=0.76$), 2012 wet season and dry season ($p=0.43$) and 2013 wet and dry seasons ($p=0.15$) at 0.05 significance level. Not all sites were measured at the same time of day and therefore sites showing higher primary productivity such as KAF.ST.5 in the 2013 wet season and KAF.ST.1 in the dry season could be a result of increased light intensity during the measurement period and may not be representative of the average daily primary production at that site. No correlations were drawn between primary production and incoming light intensity in either the Zambezi or the Kafue rivers because this parameter was not measured and nutrient levels of the two rivers was not included in the scope of this study.



(a)



(b)

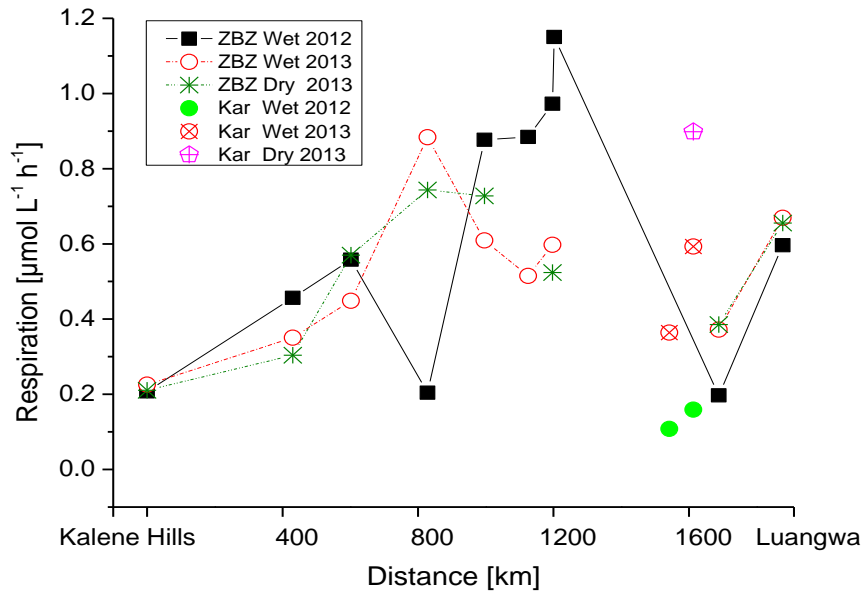
Figure 4.12: Primary Production rates for the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.12 Bacterial Respiration rates

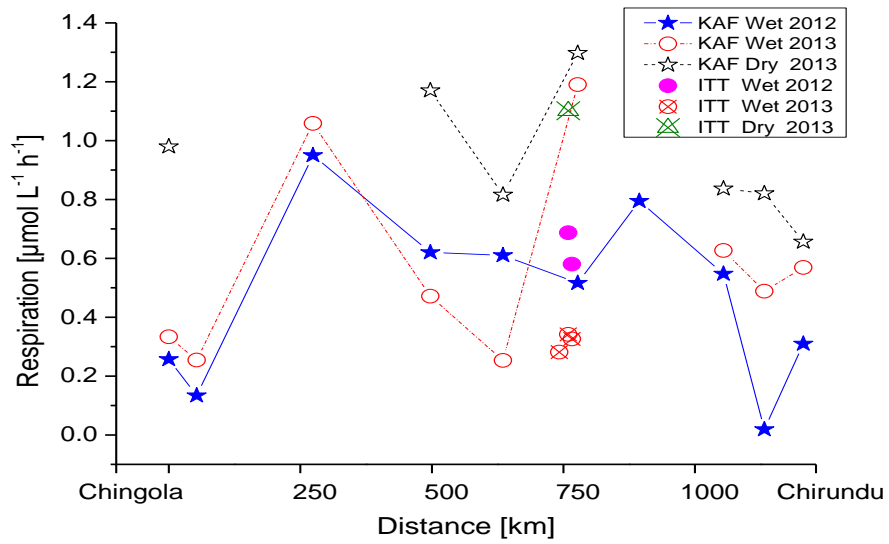
Bacterial respiration rates in the Zambezi River varied along the river stretch at the selected sampling points from Kalene Hills to Luangwa (Figure 4.13a). Respiration rate was lowest at Chirundu (ZBZ.ST.9) at $0.2 \mu\text{mol L}^{-1} \text{h}^{-1}$ and highest in Livingstone (ZBZ.ST.8) at $1.2 \mu\text{mol L}^{-1} \text{h}^{-1}$ during the wet season of 2012. During the 2013 wet season, the rate of bacterial respiration was lowest at the source of the Zambezi in Kalene Hills recording $0.2 \mu\text{mol L}^{-1} \text{h}^{-1}$ and was highest at Kalongola (ZBZ.ST.4) station which recorded $0.9 \mu\text{mol L}^{-1} \text{h}^{-1}$. Kalongola (ZBZ.ST.4) is towards the end of the section of the river that traverses extensive floodplains in the Barotse floodplains. During the dry season, bacterial respiration rate was lowest at the source of the river at $0.2 \mu\text{mol L}^{-1} \text{h}^{-1}$ and the highest was again at Kalongola (ZBZ.ST.4) at $0.7 \mu\text{mol L}^{-1} \text{h}^{-1}$. This trend shows that organic matter respiration is high in sections of the river that traverse extensive floodplains because of high organic matter available for respiring organisms (Davies et al., 2008). Carbon coming from autochthonous primary production in sections

of the river that traverse extensive floodplains is more labile to bacterial respiration, though not abundant compared to allochthonous sources (Thorp and Delong, 2002). Paired t-tests done at 0.05 significance level showed that there was no significant difference in the bacterial respiration rates between 2012 and 2013 wet seasons ($p=0.78$), 2012 wet and 2013 dry season ($p=0.95$) and 2013 wet and dry seasons ($p=0.89$). The Kariba Reservoir values were within the range of those of the main river channel, averaging 0.8 , 0.5 and $0.9 \mu\text{mol L}^{-1} \text{h}^{-1}$ during the 2012 wet season and 2013 wet and dry seasons, respectively.

Bacterial respiration rates in the Kafue River varied along the river stretch at the selected sampling points from Chingola to Chirundu (Figure 4.13b). The values did not follow any particular pattern and recorded the lowest rate of $0.02 \mu\text{mol L}^{-1} \text{h}^{-1}$ at Kafue Town (KAF.ST.9) station and recorded the highest rate of $0.8 \mu\text{mol L}^{-1} \text{h}^{-1}$ at Namwala (KAF.ST.7) during the 2012 wet season campaign. Namwala (KAF.ST.7) is located within the Kafue Flats. During the 2013 wet season campaign, the lowest rate of $0.3 \mu\text{mol L}^{-1} \text{h}^{-1}$ was recorded at Hook Bridge (KAF.ST.5) and KAF.ST.6 recorded the highest rate of $1.2 \mu\text{mol L}^{-1} \text{h}^{-1}$. During the dry season, the lowest rate of $0.7 \mu\text{mol L}^{-1} \text{h}^{-1}$ was recorded at Chirundu (KAF.ST.10) and the highest rate of $1.3 \mu\text{mol L}^{-1} \text{h}^{-1}$ was recorded at KAF.ST.6. This station sits just below the Itezhi Tezhi spillway and is at the onset of the Kafue Flats. KAF.ST.7 station which consistently recorded high respiration rates was not measured during the dry season campaign. The Itezhi Tezhi Reservoir recorded a high rate of respiration giving $1.1 \mu\text{mol L}^{-1} \text{h}^{-1}$. This compared very well with the high values recorded at the station just below the reservoir at KAF.ST.6. Paired t-tests showed that there was no significant difference in respiration rates recorded during the 2012 and 2013 wet season campaigns ($p=0.20$) at 0.05 significance level. However, both the 2012 and 2013 wet season respiration rates were much lower compared to the dry season rates ($p=0.001$ and 0.008). Light intensity is a major factor determining the composition of the algal community (Hill, 1996). Higher respiration rates during the dry season compared to the wet season could also be linked to increased water temperatures for aquatic metabolism (Gudasz et al., 2010).



(a)



(b)

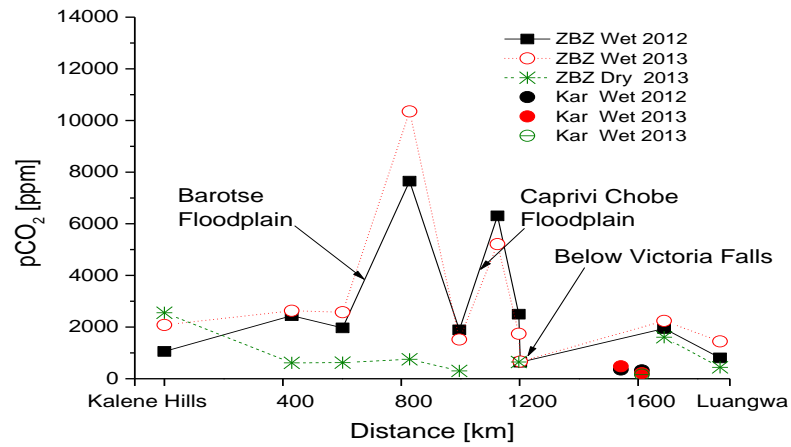
Figure 4.13: Bacterial respiration rates for the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

4.13 Partial Pressure of Carbon Dioxide (pCO₂)

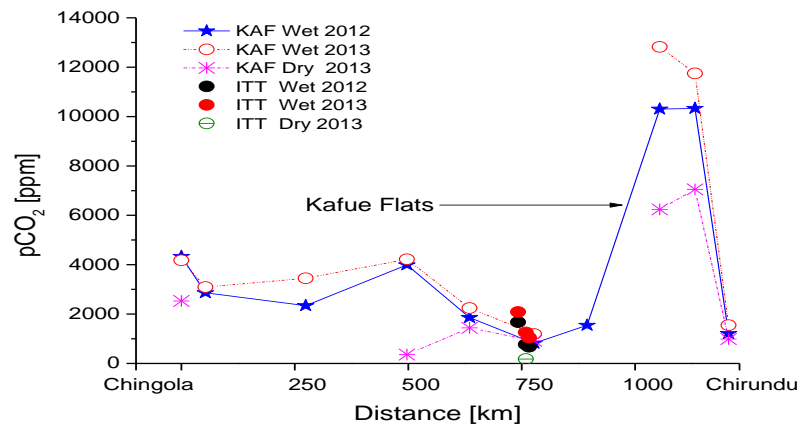
The Zambezi mainstream was measured for partial pressure of carbon dioxide (pCO₂) from Kalene Hills to Luangwa at the selected sampling points (Figure 4.14a). The river recorded lowest partial pressure of carbon dioxide (pCO₂) values of 642 and 663 ppm just below the Victoria Falls for the Feb-March, 2012 and Jan-Feb, 2013 sampling campaigns, respectively. During the same sampling periods, high pCO₂ of 7,650 and 10,351 ppm for the 2012 and 2013 wet season campaigns, respectively, were recorded at the end of the section of the river that traverses extensive floodplains at Kalongola (ZBZ.ST.4). Relatively high pCO₂ values of 6,307 and 5,210 ppm for the 2012 and 2013 wet season campaigns, respectively, were recorded at ZBZ.ST.6 station, which is also located immediately downstream an extensive floodplain (Caprivi-Chobe floodplains). During the dry season, floodplains recede and do not impact greatly on pCO₂. The Zambezi River ranged between 304 and 2,555 ppm, recorded at ZBZ.ST.5 and ZBZ.ST.1 stations, respectively. The Kariba Reservoir had much lower pCO₂ values of 324 and 217 ppm for the 2012 and 2013 wet season campaigns, respectively, well below atmospheric CO₂. The dry season campaign recorded 157 ppm at Kariba Reservoir. This CO₂ sink can earn ZESCO monetary benefit on the Carbon Credits Market.

The Kafue mainstream was measured for partial pressure of carbon dioxide (pCO₂) from Chingola to Chirundu at the selected sampling points (Figure 4.14b). The Kafue River recorded lowest pCO₂ values of 820 and 1,191 ppm at KAF.ST.6 station (just below the ITT Reservoir) for the Feb-March, 2012 and Jan-Feb, 2013 wet season sampling campaigns, respectively. The station at Nakambala Sugar Estate in Mazabuka (KAF.ST.8) which is within the Kafue Flats recorded high values of 10,331 and 12,819 ppm for the Feb-March, 2012 and Jan-Feb, 2013 wet season campaigns, respectively. During the dry season campaign, pCO₂ values reduced along the river stretch with the lowest value of 360 ppm recorded at KAF.ST.4 and the highest value of 7,051 ppm recorded at the end of the Kafue Flats (KAF.ST.9). The Itezhi Tezhi Reservoir, unlike the Kariba Reservoir on the Zambezi, recorded pCO₂ values that were well within the values of the main river channel due to the influence of the Kafue River, recording lowest values of 675 and 1,049 ppm for the 2012 and 2013 campaigns, respectively.

It is observed that sections of the river that traverse extensive floodplains (ZBZ.ST.4, ZBZ.ST.6 and KAF.ST.8) recorded highest $p\text{CO}_2$ values because floodplains are among the most productive ecosystems on Earth and have been considered atmospheric CO_2 sources in inland water budgets (Abril et al., 2013).



(a)



(b)

Figure 4.14: Partial pressure of carbon dioxide for the (a) Zambezi River and Kariba Reservoir (b) Kafue River and Itezhi Tezhi Reservoir in Zambia

CHAPTER 5: DISCUSSION

This chapter discusses the results presented in Chapter Four following the objectives of this study. It starts with the spatial and temporal variability of biogeochemical parameters and then discusses the influence of floodplains on biogeochemical parameters. It also highlights the impact of reservoirs on river biogeochemistry. The last section discusses the temporal evolution of discharge at the two monitoring stations (ZBZ.ST.9 and KAF.ST.10) as it relates to Dissolved Organic Carbon (DOC), Particulate Organic Carbon (POC) and Total Suspended Matter (TSM).

5.1 Spatial and temporal variability of biogeochemical parameters

The pH was increasing along both river stretches in both the wet and dry season campaigns and generally ranged between 6.0 and 8.5 in both rivers (Figures 4.1a and b above). There was, however, an observable pH decrease (7.4 to 6.9 on average) over sections of the river that traverse extensive floodplains such as Barotse, Caprivi-Chobe and the Kafue Flats. According to Wamulume (2011), respiration of organic matter leads to pH decrease and this was observed on the Barotse, Caprivi-Chobe and the Kafue Flats. Despite this trend, paired sample t-tests done on the dry and wet season campaigns found that pH values recorded in the dry season were not significantly different from those of the wet season in both 2012 ($p = 0.1$) and 2013 ($p = 0.09$) at 0.05 significance level, for both the Zambezi and the Kafue rivers.

The Kafue River had on average higher SpC values (181.0 $\mu\text{S}/\text{cm}$) compared to the Zambezi River (65.4 $\mu\text{S}/\text{cm}$) during the wet season and an average of 359.0 $\mu\text{S}/\text{cm}$ compared to the Zambezi River (115.3 $\mu\text{S}/\text{cm}$) during the dry season. Seasonal variations on the Kafue River indicated that specific conductivity was significantly lower during the 2013 wet season ($p=0.027$) compared to the dry season campaign. The wet season of 2012 ($p=0.058$) was not significantly different from the dry season. The wet seasons were not significantly different in specific conductivity values in 2012 and 2013 ($p=0.74$). The high conductivity values in the Kafue River as compared to the Zambezi River are indicative that the Kafue River carries more dissolved solutes which

increase along the river stretch since the trend showed a downstream increase. The geology and land-use (mining, agriculture) of this sub-catchment could be largely influencing this pattern. The very high specific conductivity values (averaging 359.0 $\mu\text{S}/\text{cm}$) during the dry season can be attributed to reduced water volume (opposite effect to dilution), dissolution of mineral elements and anthropogenic activities along the river stretch. Wamulume (2011) found similar specific conductivity values in the Kafue Flats in 2008 with 451 $\mu\text{S}/\text{cm}$ as the highest observed value during the dry season at a station in proximity of our KAF.ST.5 station at the Hook Bridge. During the dry season of this study, the Hook Bridge (KAF.ST.5) recorded 413.1 $\mu\text{S}/\text{cm}$. In the stretch where the Kafue River flows through the Kafue Flats, the highest observed value was 225 $\mu\text{S}/\text{cm}$ Upstream Sable Farms (K4) (Wamulume, 2011), a station in proximity of our Nakambala Sugar Estate station (KAF.ST.8) for this study which recorded 249.7 $\mu\text{S}/\text{cm}$ during the dry season. Salter (1985) conducted a water quality study in the Kafue River between June 1978 and May 1979, with two sampling stations close to our KAF.ST.8. The study found that the average conductivity was 172 $\mu\text{S}/\text{cm}$ with a range of 110 $\mu\text{S}/\text{cm}$ to 260 $\mu\text{S}/\text{cm}$. Salter (1985) also observed that the seasonal variation of conductivity presented two peaks, one between August and October (230 $\mu\text{S}/\text{cm}$) and the other between January and June (260 $\mu\text{S}/\text{cm}$). Salter (1985) attributed the elevated conductivity in dry season to greater evaporation. These observations were similar and consistent with this study.

Dissolved Organic Carbon (DOC) is derived from various sources including atmospheric inputs, in-stream production (degradation of organic matter) and terrestrial origin (C3 or C4 vegetation contribution). DOC dominated the total organic C pool (TOC) particularly in low TSM conditions (Barotse, Caprivi-Chobe and the Kafue Flats) and POC dominated the TOC pool when TSM concentrations were higher. Results of POC concentration for both the Zambezi and the Kafue Rivers (Figures 4.5a and b above) show KAF.ST.10 and ZBZ.ST.9 with consistently high POC values of 1.1, 3.1 and 1.6 mg/L and 2.9, 1.0 and 0.9 mg/L, respectively, due to high TSM concentrations during the 2012 wet season and 2013 wet and dry season campaigns. Such relationships are normally observed in other river systems (Bouillon et al., 2009). With less suspended particles for the organic matter to adsorb to, more organic matter remains in the

dissolved state and during low flow periods or in lakes, reservoirs and floodplains, fine suspended matter drops out and lighter, more organic components remain suspended (Mayorga, 2004). This is observed in the POC values (1.2 and 1.8 mg/L) for the Kariba and ITT during the dry season campaign (Figures 4.5a and b above) which were relatively high despite low TSM conditions. DOC concentrations will range between <1 to 40 mg/L, with a global average being found to be 5 mg/L (Meybeck, 2006). DOC averages for the Zambezi River were 3.6 and 4.2 mg/L for 2012 and 2013 campaigns respectively whereas the Kafue River shows averages for DOC of 3.8 and 4.1 mg/L for the 2012 and 2013 campaigns, respectively. The dry season DOC averages were 1.9 mg/L on the Zambezi River and 2.9 mg/L on the Kafue River, which were all lower than the global average.

Data on $\delta^{13}\text{C}$ - DOC for African river systems are scarce. Spencer et al. (2012) provides values of -29.2 ‰ for the lower Congo River and -27.9 ‰ for the Luilu River (Southern Savannah of the DR Congo) and Brunet et al. (2009) report a remarkably stable signature (-29.0 ± 0.04 ‰) for DOC samples collected at various locations over 2 years in the Nyong River Basin (Cameroon). In the Tana River Basin (Kenya), which contains significant areas of C4 vegetation, Bouillon et al. (2009) found dry season $\delta^{13}\text{C}$ - DOC signatures to be relatively stable throughout the catchment, averaging -23.9 ± 0.3 ‰. These studies are consistent in showing terrestrial C3 vegetation as the predominant source of DOC in these systems. For this study, the $\delta^{13}\text{C}$ - DOC values for both the Zambezi and the Kafue rivers averaged around -22 ‰. This range suggests that DOC is of mixed origin, the stronger signal being of C3 origin (65%) and about 35% coming from the contribution of C4 vegetation, also consistent with the above previous studies. Zurbrügg et al. (2013) found $\delta^{13}\text{C}$ - DOC values for the Kafue River and Kafue Flats of -25.5 ± 0.4 ‰. Both the values for this study and those of Zurbrügg et al. (2013) for $\delta^{13}\text{C}$ - DOC and DOC are given in Appendix 2. The $\delta^{13}\text{C}$ - DOC and DOC values for this study and that of Zurbrügg et al. (2013) were similar and consistent (Figure 5.1).

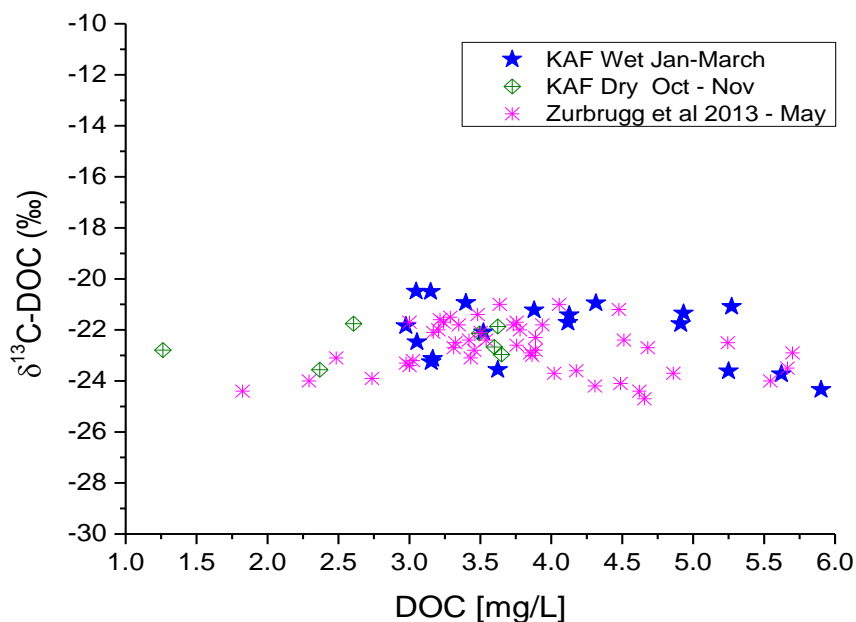


Figure 5.1: $\delta^{13}\text{C}$ - DOC versus DOC for this study and that of Zurbrugg et al. (2013)

Wamulume (2011) found TOC (POC + DOC) around 3 - 8 mg C/L during Feb, 2009 and 12 - 23 mg C/L in June, 2008 and May, 2008 and 2009 for the Kafue Flats. The findings of Wamulume (2011) are consistent with our wet season campaigns data. This could be because terrestrial inputs during wet seasons become more pronounced as the bare grounds become inundated. Seasonal variations for POC on the Zambezi River (Figure 4.5a above) showed that there were no significant differences in the POC recorded during the 2012 and 2013 wet season campaigns ($p=0.3$) and between both wet season campaigns and that of the 2013 dry season campaign ($p=0.6$ and 0.3) at 0.05 significance level. The results for the Kafue River indicate a similar pattern (Figure 4.5b above). The values for the 2012 and 2013 wet season campaigns were not significantly different ($p=0.7$) and both wet season campaigns recorded figures that were no different from those of the dry season ($p=0.8$ and 0.4). Seasonal variations for DOC on the Zambezi River between the 2012 and 2013 wet season campaigns indicate that DOC was significantly different ($p=0.01$) at 0.05 significance level. The values for DOC were also significantly different ($p=0.01$) between the 2013 wet and dry season campaigns.

They were, however, not significantly different between the 2012 wet season campaign and the 2013 dry season. DOC of the Kafue River was not significantly different ($p=0.25$) between the wet seasons of 2012 and 2013. However, the values of both the 2012 and 2013 wet season campaigns were significantly different ($p=0.0006$ and 0.001) from the 2013 dry season values. This is expected because contributions of DOC from terrestrial ecosystems are greatly reduced during the dry season (Hope et al., 1994).

The $\delta^{13}\text{C}$ - POC isotopic signatures in both rivers ranged between -30.4‰ and -23.1‰ . POC in the reservoirs was more depleted in the ^{13}C isotope, in particular in the Kariba Reservoir, with $\delta^{13}\text{C}$ - POC values as low as -32‰ . The ITT Reservoir was within the same value range (-29.5 and -25.3‰) as the Kafue River (-30.4 and -23.2‰). These values suggest more aquatic produced phytoplankton on reservoirs (C_3 origin) and terrestrially derived C_3 vegetation along the river channels. A high phytoplankton contribution is consistent with the low $p\text{CO}_2$ values recorded during low discharge conditions, including some values below atmospheric equilibrium (e.g. Kariba Reservoir) suggesting the drawdown of CO_2 by photosynthesis (cf. Bouillon et al., 2012).

Both the values for this study and those of Zurbrügg et al. (2013) for $\delta^{13}\text{C}$ - POC and POC are given in Appendix 2 and compared in Figure 5.2. This study sampled the Kafue River and the Kafue Flats between January and March during the wet season campaigns and between October and November during the dry season whereas Zurbrügg et al. (2013) sampled the Kafue Flats in May, 2009 and 2010 (Figure 5.2).

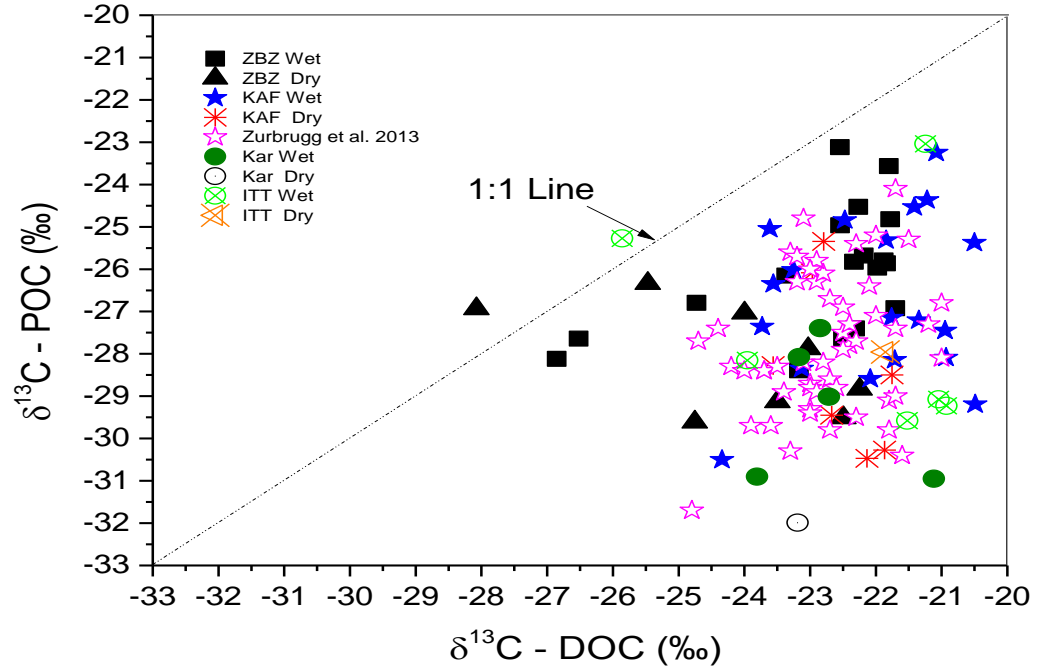


Figure 5.2: Plot of $\delta^{13}\text{C} - \text{POC}$ and $\delta^{13}\text{C} - \text{DOC}$ on a 1:1 Line graph for Zambezi, Kafue rivers, Kariba, Itzhi Tezhi reservoirs and findings of Zurbrugg et al. (2013)

Since all $\delta^{13}\text{C} - \text{POC}$ values are falling within the same range (-30.4 ‰ and -23.1‰), this could suggest that this is the typical value range for $\delta^{13}\text{C} - \text{POC}$ along this river segment. Figure 5.2 shows that $\delta^{13}\text{C} - \text{DOC}$ is consistently higher than $\delta^{13}\text{C} - \text{POC}$. The global average $\delta^{13}\text{C}$ value of C3 vegetation is about -28.5‰ (Kohn, 2010). Thus the $\delta^{13}\text{C} - \text{DOC}$ values averaging -22 ‰ suggests a mixture of C3 vegetation (about 65%) and C4 vegetation (about 35%) (Still and Powell, 2010). For POC, values in the region of -29‰ suggest a higher C3 contribution to POC than in DOC. In the reservoirs, there is also a significant contribution of phytoplankton to POC as could be observed that %POC during the dry season campaign on the Kariba Reservoir was as high as 61% (Figure 4.6a above).

Dissolved Inorganic Carbon (DIC) has many sources including atmospheric dissolution, aquatic respiration, soil respiration and chemical weathering. The major source,

especially in headwater streams, is known to be soil CO₂ (Edward and Harris, 1977). The Kafue River has been observed to contain twice as high DIC as the Zambezi River. The Kafue River DIC could be influenced by chemical weathering and dissolution of carbonate rocks coming from the limestone geology (Katanga supergroup) that characterizes much of the Copperbelt (Table 1.1 above) and Central regions (Figure 1.4 above). The plot of δ¹³C - DIC with the silica and calcium (Figure 4.10d above) showed the dominance of calcium (coming from calcium carbonates) in the limestone geology of Kafue River. The Si/Ca became even more pronounced during the dry season as it moved more towards the ratio value of 0.2. The Zambezi River on the other hand was observed to transport more silicate elements compared to the Kafue River, also attributed to the geological formations of Cenozoic and Mesozoic supergroups which it traverses (Table 1.1 above). The source of the Zambezi during the dry season campaign gave a ratio value of 15 (Figure 4.10d above), denoting very high relative concentrations of silicate elements.

The δ¹³C - DIC values (-22 to -5 ‰) for both rivers could be linked to the chemical dissolution observed in the Si/Ca ratio. The isotopic signature on the Kariba Reservoir (-4‰ to -1‰) was more enriched in the ¹³C isotope. As atmospheric CO₂ dissolves into the river water it fractionates by about 7 ‰; i.e from -8 ‰ to -1 ‰ (Zhang et al., 1995; Mook, 2000). Atmospheric dissolution could be the major driving factor at Kariba since pCO₂ values were well below CO₂ atmospheric concentration (CO₂ uptake). The ITT ranged between -7 ‰ to -4 ‰. The ITT, because of the influence of the main river channel was releasing CO₂ and not uptaking.

5.2 Influence of Floodplains on biogeochemical parameters

Floodplains are among the most productive ecosystems on Earth and can behave both as carbon sinks or sources. The efficient storage of carbon in waterlogged soils and enhanced sedimentation during flooding can lead to a substantial sink of C; yet they can also provide a source of dissolved organic carbon to rivers, and have been considered atmospheric CO₂ sources in inland water budgets (Abril et al., 2013). Friedl and Wuest (2002) affirm that wetland vegetation can support the outgassing of CO₂ in the

surrounding water through two mechanisms. Firstly, litterfall and root exudation release labile organic carbon to the water where the organic carbon is further decomposed; in this organic carbon pathway, heterotrophic metabolism and outgassing occur concomitantly in the open waters. Secondly, submerged roots and microbial respiration in wetland soils release CO₂ to the water; this CO₂ is then transported to open areas, where outgassing occurs. This further consolidates wetlands as sources of CO₂. The functioning of floodplains strongly depends on alternating water levels that cause water flows from the river to the floodplain and back. This hydrological river-floodplain exchange is a key process for deposition and mobilization of organic matter and nutrients (Wamulume, 2011). Heterotrophic respiration in the floodplains results in the depletion of dissolved oxygen. Floodplains under discussion here are the Barotse and Caprivi-Chobe floodplains along the Zambezi River and the Kafue Flats along the Kafue River. Dissolved Oxygen (DO) was found to have minimum values in the Mazabuka Sugar Plantation sampling point (end of the Kafue Flats) at 1.8 mg/L and 1.4 mg/L for the Feb-March, 2012 and Jan-Feb, 2013 sampling campaigns, respectively (Figure 4.2b above). These findings are consistent with the African Large Dams Project (ADAPT) research on the Kafue Flats that found minimum value of 1.1 mg/L upstream of Sable Farms which is in the proximity of our KAF.ST.8 station during February, 2009 (Wamulume, 2011). According to Wamulume (2011), this station where minimum DO was consistently observed, is a zone of the Kafue River where discharge is consistently higher than other upstream stations within the Flats, as such the increase in flow at this station resulted in low-oxygen water entering the main river channel from the Flats leading to persistent low oxygen levels. Very low DO values such as these below 2.0 mg/L induce hypoxic conditions in rivers. Research has shown that these levels have an adverse impact on ecosystem functioning, including fisheries productivity (Mitsch and Gosselink, 2007).

The pH followed the pattern of DO (Figures 4.1a and b and Figures 4.2a and b above) with minimum values being recorded where the river traverses areas with extensive floodplains. Therefore, similar processes that influence a decrease in dissolved oxygen also result in a pH decrease (cf. Wamulume, 2011).

High pCO₂ values were predominantly found in areas where the river traverses areas with extensive floodplains. This trend was observed only during the wet season campaign in the Zambezi River and both in the wet and dry season campaigns in the Kafue River. The major difference is that the hydrology of the Kafue Flats (where pCO₂ was also high during the dry season) is regulated by the ITT Dam operation and results generally in extensive flooding even during dry season periods. These higher pCO₂ values are consistent with the decrease in O₂ concentrations and pH, and can likely be ascribed to the mineralization of organic matter within the floodplains, and the concentration of CO₂-enriched waters to the main river channel (Abril et al., 2013). It is important to note here that this effect of mineralization is not necessarily due to increased community respiration rates in the water column (the community respiration do not show any evidence of this), but likely due to the strong sediment/soil-water interactions, whereby soil respiration increases the CO₂ content of the overlying floodplain waters (Abril et al., 2013). On the other hand, the higher nutrient loads (Davies et al., 2008) and low suspended matter concentrations due to the sedimentation taking place in the floodplains allow for higher light penetration thus enhancing primary production rates (Bonetto, 1986). During the 2013 wet season campaign, ZBZ.ST.4 station, which is located in the section of the river which traverses the Barotse floodplains recorded pCO₂ of 10,351 ppm compared to 751 ppm at the same station during the dry season campaign. However, KAF.ST.7 which is located in the Kafue Flats recorded pCO₂ of 11,749 ppm during the 2013 wet season campaign and recorded 7,051 ppm during the dry season at this same station (Figures 4.14a and b above). The highest primary production rate of 105.6 μmol L⁻¹ h⁻¹ was measured in the Kafue Flats. The Kafue Flats influence the biogeochemistry of the Kafue River more than does the Barotse floodplain on the Zambezi River because of their different hydrological regimes. The Barotse floodplains get dry in the dry season whereas the Kafue Flats never gets dry even in the dry season because it is being consistently supplied with water stored in the Itezhi Tezhi Reservoir. The Barotse floodplains do not have an upstream reservoir to buffer the downstream flow.

Dissolved Organic Carbon (DOC) concentrations showed an increasing trend in all floodplains (Figures 4.7a and b above), suggesting the high productivity of the

floodplains. Wetlands can export substantial amounts of dissolved organic carbon to the river channels compared to POC. DOC is the most significant pool of reduced carbon in aquatic systems and is a significant source of energy to aquatic food webs (Maurice and Leff, 2002). These floodplains under discussion could therefore be sources of riverine POC and DOC, large sources of CO₂ to the atmosphere and sinks to riverine sediment (Abril et al., 2013).

5.3 Impact of reservoirs on river biogeochemistry

According to Friedl and Wuest (2002), dams impact the hydrological, chemical, physical and biological characteristics of a water body when changing it from a riverine to lacustric conditions. Construction of reservoirs further interrupts the flow of organic carbon, changes the nutrient balance and alters oxygen and thermal conditions. Other changes include increases in residence time, temperature, stratification and reduction in turbulence, most often a decrease in particles and turbidity, and sometimes an increase of autochthonous primary production. A further potential consequence of the transition from a river to a reservoir is the depletion of oxygen in the deep water and the onset of hypoxia (Friedl and Wuest, 2002). The upstream part of the reservoir receives the easily degradable organic matter transported by the river, which settles at the bottom and is mineralized. In the reservoir, *in-situ* produced particles (e.g. algae) settling to the bottom consume oxygen. Thermal stratification reduces the exchange between surface and deep water, eventually leading to anoxic conditions. Oxygen is produced in the epilimnion but the presence of a thermocline during this seasonal stratification does not allow the top water to mix with the bottom water (hypolimnion) (Figure 5.3). The bottom water therefore becomes hypoxic after depleting all the oxygen through production of CO₂ and CH₄ during mineralization of the organic matter (Friedl and Wuest, 2002). Therefore, stratification and oxygen depletion of the bottom waters is a serious impact of reservoirs on river biogeochemistry because when these waters are released, the hypoxic conditions cause problems to downstream ecosystems (Mitsch and Gosselink, 2007).

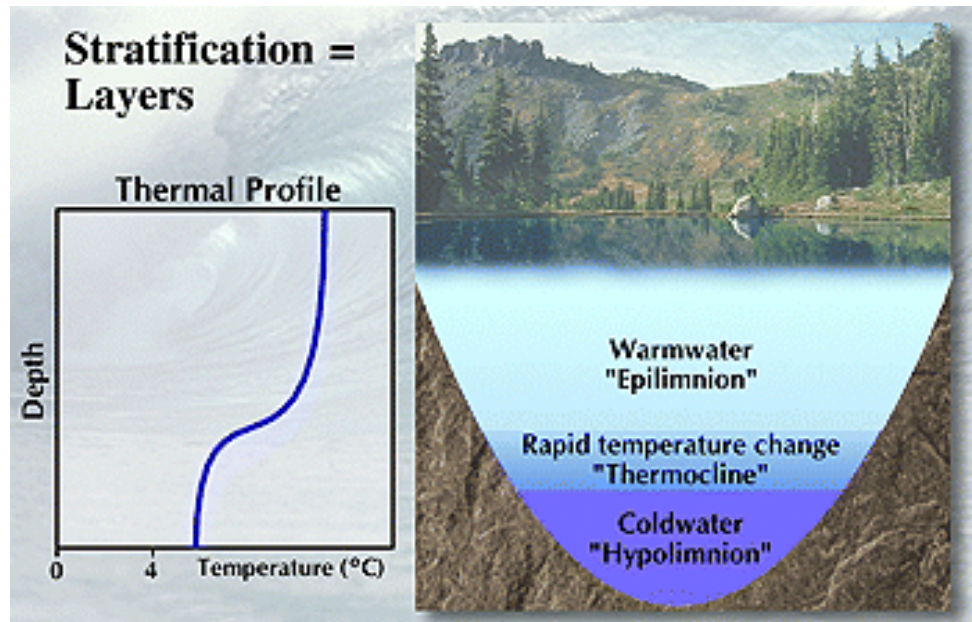


Figure 5.3: Illustration of seasonal stratification which probably occurs on the Kariba and Itzhi Tezhi reservoirs, Zambia (Modified after Alsa Allaby and Micheal Allaby, 2004)

When the water just below the dam wall was measured in the 2013 dry season campaign, a very high $p\text{CO}_2$ value (2,600 ppm) and low DO (5.63 ppm) was found, confirming that the dam wall releases bottom water from the reservoir which is rich in CO_2 and CH_4 . In countries such as the USA, discharged water from reservoirs has to meet certain water quality standards. For example, many US Federal Energy Regulatory Commission licenses now include minimum dissolved oxygen levels typically ranging from 5 to 6 ppm in the released water (Mobley, 1997 as cited by Friedl and Wuest, 2002). If reservoirs are used for drinking water supply, the quality standards are even higher. As a consequence, drinking water suppliers and hydropower generators must frequently add large quantities of (often pure) oxygen to the stored water prior to or during release to mitigate this environmental impact. Another impact is the cold water pollution of the river systems through the release of reservoir bottom waters (Sherman, 2000). This type of pollution has potential to impact on downstream ecosystems (algae, fish etc) (Sherman, 2000). TSM and POC which comes with the river (mostly terrestrial) settles in the reservoir where POC is mineralized and converted into CO_2 , CH_4 and what

the reservoir exports downstream is aquatic produced (an increase of autochthonous primary production from allochthonous sources is as a result of reservoirs) (Friedl and Wuest, 2002). DOC was higher (4.6 and 4.7 mg/L) at the river inflow (ZBZ.ST.7) into the reservoir during wet season campaigns and twice as low below the dam (2.2 and 2.7 mg/L) suggesting a reduction in export. The opposite happened during dry season which had low DOC (1.2 mg/L) at inflow and relatively higher (2.5 mg/L) at outflow suggesting an increase in export. The inflow (KAF.ST.5) on the Kafue River also had higher DOC (3.9 and 4.3 mg/L) and relatively lower DOC below the ITT Dam (3.0 – 3.1 mg/L) during the wet seasons. During the dry season, the trend was reserved and DOC was lower at inflow (2.3 mg/L) and higher at outflow (2.6 mg/L) just like on the Zambezi River. DIC was higher below the dam during 2012 wet and 2013 dry campaigns (1.0 and 1.3 mmol/L) compared to 0.7 and 1.0 mmol/L at the inflow (ZBZ.ST.7) suggesting that Kariba exports DIC downstream. The inflow (1.5 and 3.2 mmol/L) and outflow (1.5 and 1.9 mmol/L) at ITT did not show export of DIC during both the 2012 wet season and 2013 dry season campaigns.

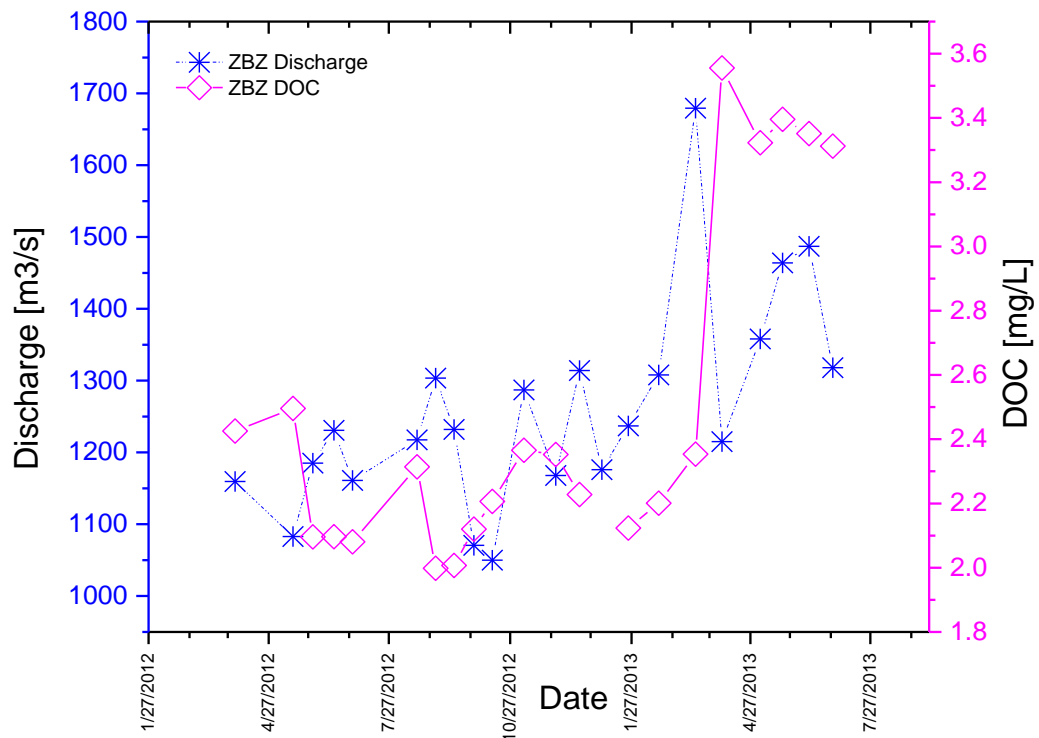
The $\delta^{13}\text{C}$ - DIC value found at the Kariba Reservoir showed that the ^{13}C isotope was enriched (Figure 4.10c above) due to atmospheric dissolution and possibly primary production. Phytoplankton preferentially uses 'light' CO_2 so the remaining CO_2 (DIC) becomes more enriched in the ^{13}C isotope. Repeated measurements have shown that Kariba Reservoir does not emit CO_2 . Further studies on this could put the Zambia Electricity Supply Cooperation (ZESCO) on the Carbon Credits Market and have monetary benefit from producing energy with no or low carbon footprint. However, continuous spatially and seasonally resolved data and fluxes of other greenhouse gases such as CH_4 and N_2O would be required to further substantiate this assertion.

5.4 DOC, POC and TSM with regulated Discharge at monitoring stations (ZBZ.ST.9 and KAF. ST. 10)

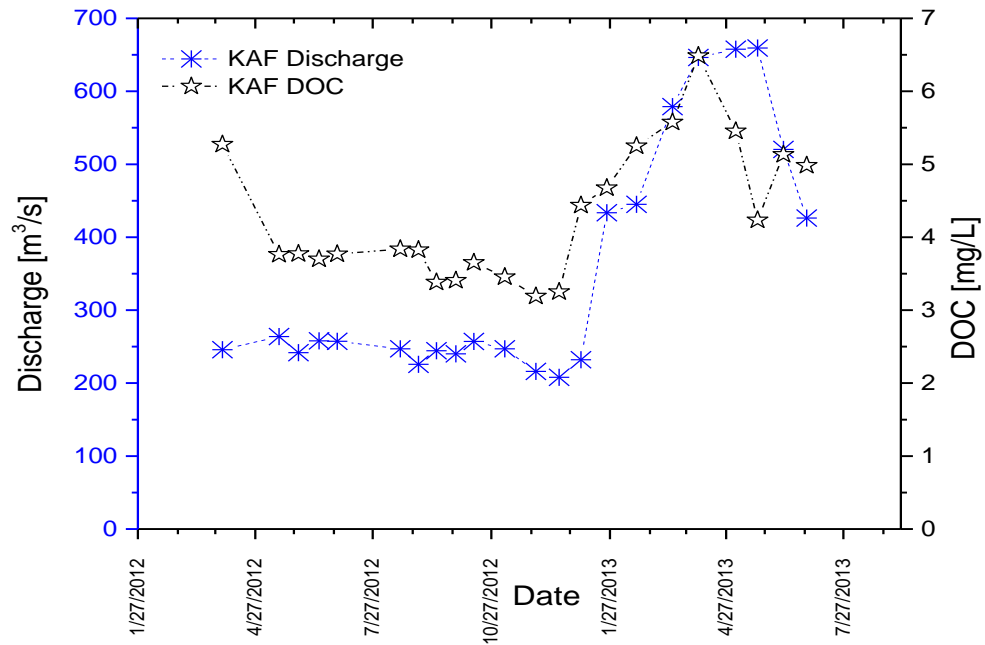
The regulation of flow at the Kafue Gorge on the Kafue River and the Kariba Dam on the Zambezi River (Figures 1.2 and 1.3) due to the construction of reservoirs along the river channels impacts on river biogeochemistry especially DOC, POC and TSM. The monitoring station on the Kafue River (KAF.ST.10) is about 60 km from the Kafue Gorge, and there are no major contributors in between these two points. Therefore, the discharge at the monitoring station could be within acceptable approximations to that at the Gorge. The monitoring station on the Zambezi River (ZBZ.ST.9) is about 75 km from the Kariba Dam. The contribution of the Lusitu River (tributary) to the flow regime at this monitoring station could be considered insignificant because it is a small river. Therefore, the flow at this monitoring could also be approximated to be well within that at the Kariba Dam.

Temporal evolution of discharge and DOC at ZBZ.ST.9 station (Figure 5.4a) shows the Zambezi River to be following a similar pattern for DOC and discharge. DOC concentration on the Zambezi River linearly rises with rising discharge but rises later (delayed) as the river begins to approach peak discharge. The DOC concentration is seen to continue to rise even after peak discharge. KAF.ST.10 station (Figure 5.4b) showed that in the Kafue River, the concentration of DOC in the water is positively correlated with river discharge, similar to the Zambezi River. DOC is seen to increase linearly when the limb of the hydrograph is rising but falls sharply at peak discharge. Evolution of DOC concentrations at KAF.ST.10 on the Kafue River follows a hysteresis loop (i.e. lower concentrations at similar discharge during the falling limb of the hydrograph compared to the rising limb), with lower DOC concentrations during the falling stages of the hydrograph. This loop was also noted by Bouillon et al. (2012) in their study of the Oubangui River in the Central Africa Republic. Inundation of bare grounds with increase in precipitation (peak discharge) explains the proportional rise in DOC because the contribution of terrestrial ecosystem to DOC becomes greater in both river systems. Hope et al.(1994) attributes this relationship to the ‘flushing effect’ caused by the transmission of ‘old soil water’ stored in the subsoil and the inundation of previously

bare or stagnant areas of the stream channel with increasing catchment precipitation. The occurrence of hysteresis loops for DOC and other solutes in general has sometimes been interpreted as a “flushing” effect, whereby baseflow values are considered reflective of a predominant groundwater signature, and changes in concentrations are the result of event water flushing DOC from soils (Boyer et al., 1996 as cited by Bouillon et al., 2012).



(a)



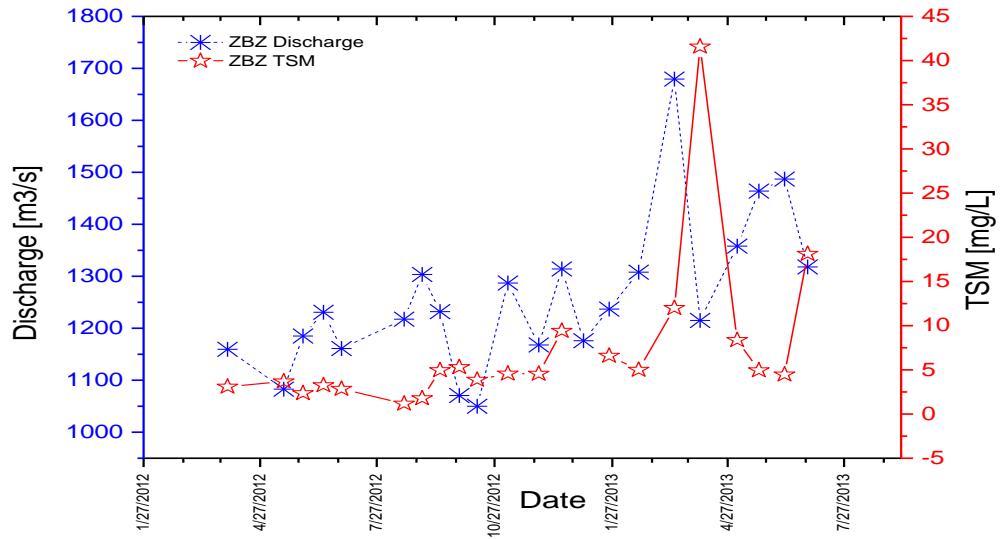
(b)

Figure 5.4: Temporal evolution of Discharge and DOC concentrations at (a) ZBZ.ST.9 station, Zambezi River and (b) KAF.ST.10 station, Kafue River between 02/04/2012 and 29/06/2013, Zambia

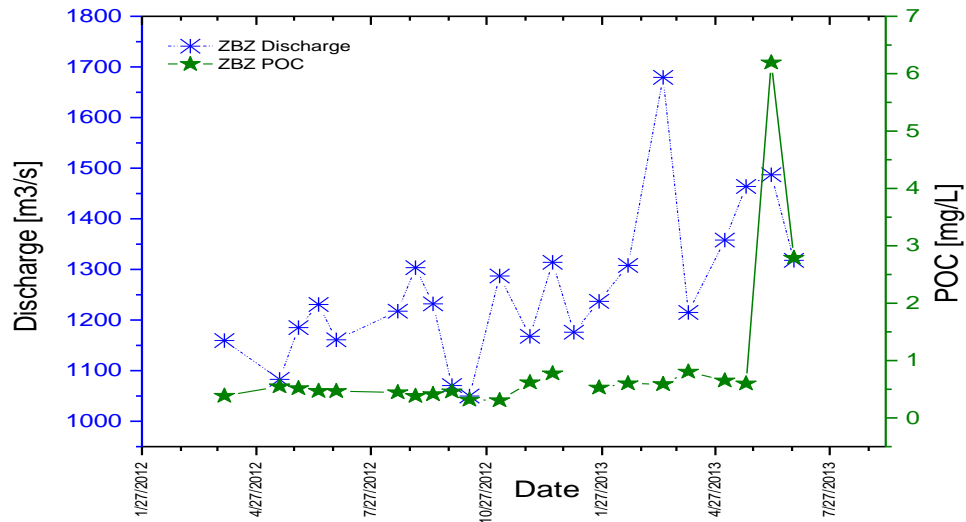
Temporal evolution of discharge with TSM and POC at ZBZ.ST.9 station shows that TSM and POC follow the same pattern on the Zambezi River (Figures 5.5a and b). Similarly, temporal evolution of discharge with TSM and POC at KAF.ST.10 station shows that TSM and POC follow the same pattern on the Kafue River (Figures 5.5c and d). POC and TSM on the Zambezi River rises after the discharge has approached the peak whereas on the Kafue River, POC and TSM rises as the rising limb of the hydrograph rises but falls before the peak discharge. A clear hysteresis loop is shown on the Kafue River.

The ZBZ.ST 9 and KAF.ST.10 stations are influenced by the Kariba and the Itezhi Tezhi reservoirs, respectively. Reservoirs have low TSM values and thus the Total Organic Carbon pool (DOC and POC) dominates. As the water from these reservoirs begins to flow into the river channels, sediment and suspended matter begins to build. This results

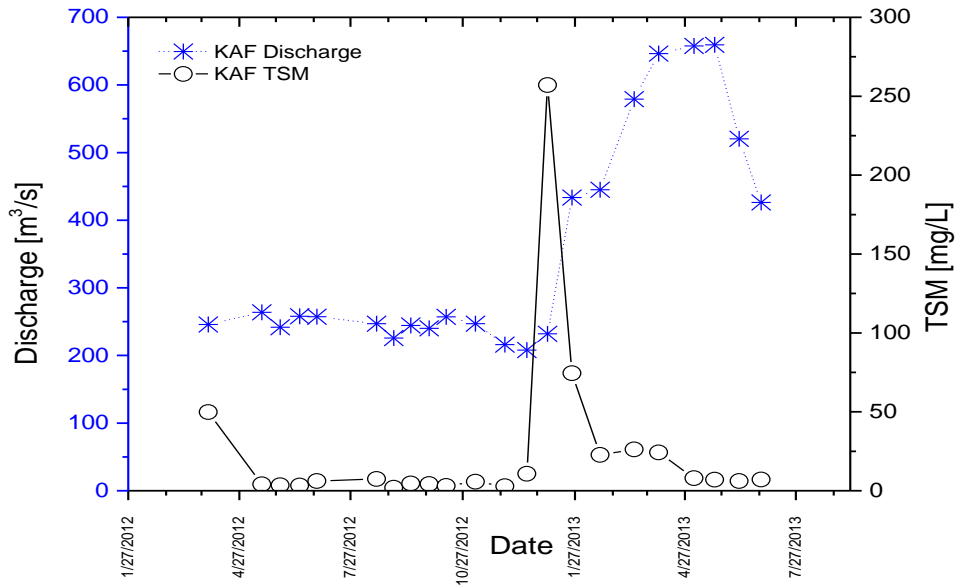
in the rise of DOC, TSM and POC. For DOC (Figures 5.4a and b) and TSM, POC (Figures 5.5a, b, c and d) concentrations markedly increase with increasing discharge and hence, the majority of the transport fluxes occur during the wet season (Bouillon et al., 2012). POC is a function of total sediment load which principally depends on drainage intensity, rainfall intensity and basin slope (Ludwig et al., 1996).



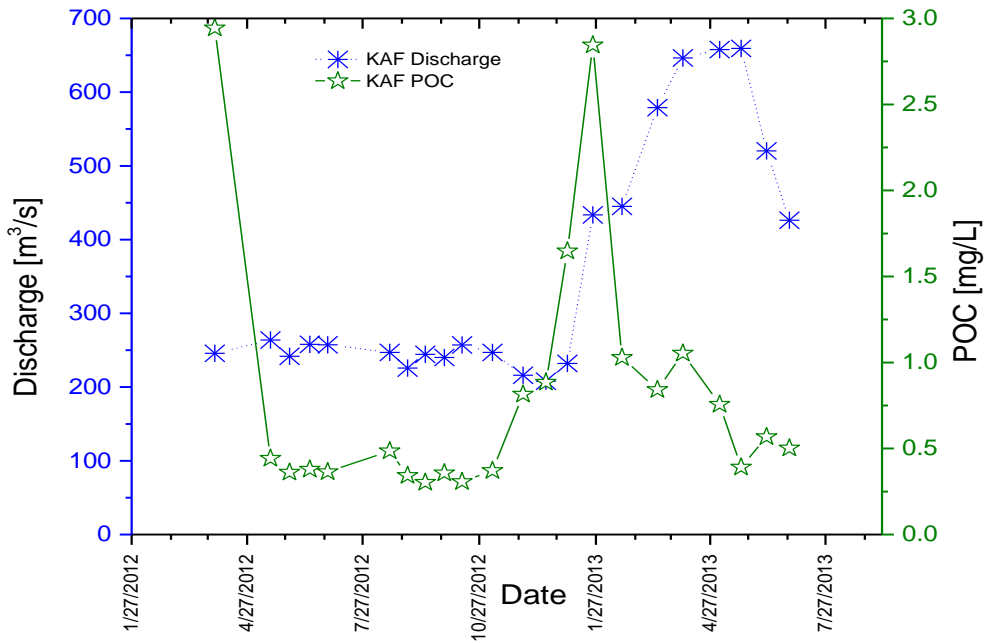
(a)



(b)



(c)



(d)

Figure 5.5: Temporal evolution of Discharge and TSM, POC concentrations at (a) and (b) ZBZ.ST.9 station, Zambezi River and (c) and (d) KAF.ST.10 station, Kafue River between 02/04/2012 and 29/06/2013, Zambia

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

This chapter concludes on the major findings of this study and proposes recommendations to the government, institutions such as the Zambia Electricity Supply Corporation (ZESCO), The University of Zambia Integrated Water Resources Management (UNZA-IWRM) and others.

6.1 Conclusions

The carbon dynamics of the Zambezi and the Kafue rivers are different. Differences in geology, land-use (agriculture and mining) and hydrological regimes of the two river systems account for the majority of the differences observed in the patterns of carbon on the two river systems. Therefore, the conclusions of this study relate to these factors as itemized below:

- (i) Geology: Weathering and dissolution of silicate elements was predominant in the Zambezi River, largely influenced by the geological formations of the Cenozoic and Mesozoic Supergroups on which much of the Zambezi River traverses. Carbonate weathering and dissolution had higher dominance in the Kafue River, largely influenced by the geological formations of the Katanga Supergroup on which much of the river traverses, making DIC twice as high (1.6 mmol/L) in the Kafue River compared to the Zambezi (0.7 mmol/L).
- (ii) Land-use: The Kafue River had on average higher SpC values (181.0 $\mu\text{S}/\text{cm}$) compared to the Zambezi River (65.4 $\mu\text{S}/\text{cm}$) during the wet season and an average of 359.0 $\mu\text{S}/\text{cm}$ compared to the Zambezi River (115.3 $\mu\text{S}/\text{cm}$) during the dry season because the Kafue River carried higher amounts of dissolved solutes linked to the larger concentration of mining, industrial and agricultural activities in the Basin. The higher dry season SpC values could mainly be attributed to reduced water volume (opposite effect to dilution) compared to the wet season where dilution has an effect on SpC. Dissolved mineral elements are probably coming from mining and agriculture, among other anthropogenic activities along the river stretch.

- (iii) Hydrology: Sections of the river that traverse extensive floodplains (Baroste) on the Zambezi River observed high $p\text{CO}_2$ values (averaging 9,000 ppm) during the wet season and relatively low $p\text{CO}_2$ (averaging 751 ppm) during the dry season. Sections of the river that traverse extensive floodplains (Kafue Flats) on the Kafue River observed high $p\text{CO}_2$ values (averaging 11,560 ppm) during the wet season and still relatively high $p\text{CO}_2$ (averaging 6,241 ppm) during the dry season. The major difference is due to the hydrology of the Kafue Flats that is regulated by the ITT Dam operation and resulting generally in extensive flooding even during dry season periods because it is being consistently supplied with water stored in the Itezhi Tezhi Reservoir. The Barotse Floodplains on the other hand, get dry in the dry season because they do not have an upstream reservoir to buffer the downstream flow.
- (iv) pH: generally fell within the same range (6.0 to 8.5) in both rivers. The reservoirs on both rivers, Kariba and ITT on the Zambezi and the Kafue, respectively, recorded higher pH (average of 8.5 on Kariba and 8.1 for ITT during 2012 wet season) compared to the river channels providing the inflows (averaging 7.2 on Zambezi and 7.4 on Kafue in 2012 wet season). pH for both rivers was observed to be decreasing (from 7.4 to 6.9 on average) during both the wet and dry season campaigns over sections of the river that traversed extensive floodplains. Paired sample t-tests done on the dry and wet season campaigns found that pH values recorded in the dry season were not significantly different from those of the wet season in both 2012 ($p = 0.1$) and 2013 ($p = 0.09$) at 0.05 significance level, for both the Zambezi and the Kafue rivers.
- (v) DO: Decrease in DO was observed in sections of the rivers that traversed floodplains (6.3 to 2.3 mg/L over the Barotse and 7.1 to 1.4 mg/L over the Kafue Flats) in both the wet and the dry season campaigns due to the mineralization of organic matter. This also made floodplains to be “hotspots” for CO_2 evasion. This decrease of DO in bottom waters was observed to be one of the impacts of reservoirs on both the Zambezi and the Kafue Rivers.

The bottom water becomes hypoxic after depleting all the oxygen through production of CO₂ and CH₄ during mineralization of the organic matter, affecting functioning of downstream ecosystems including fisheries and productivity.

- (vi) DOC and $\delta^{13}\text{C}$ – DOC: DOC did not have a wide variance (1.2 to 5.9 mg/L) in both rivers during the wet and dry season campaigns. The relative increase of DOC during the 2012 and 2013 wet season (average 3.6 and 4.2 mg/L for Zambezi and 3.8 and 4.1 mg/L for the Kafue) compared to the 2013 dry season (averaging 1.9 mg/L for Zambezi and 2.9 mg/L for Kafue) can be attributed to terrestrial inputs becoming more during the wet season as the bare grounds become inundated. Floodplains showed their relative significance in DOC contribution to river channels by showing a consistent increase in DOC values (averaging 3.1 to 4.5 mg/L) over sections of the river that traversed extensive floodplains. The $\delta^{13}\text{C}$ - DOC value (-22 ‰) suggested vegetation contribution to DOC in the Zambezi and the Kafue rivers is of mixed origin, C3 (65%) and C4 (35%).
- (vii) POC and $\delta^{13}\text{C}$ – POC: Reservoirs, especially the Kariba, were more depleted in the ¹³C isotope. The $\delta^{13}\text{C}$ - POC values (between -32.0 and -29.0 ‰) showed the dominance of aquatic produced phytoplankton of C3 origin on both reservoirs and terrestrially derived C3 vegetation along the river channel. $\delta^{13}\text{C}$ - DOC and $\delta^{13}\text{C}$ - POC values for both rivers (between -30.4 ‰ and -23.1‰) show that contribution of the terrestrial ecosystem to DOC and POC was a dominating factor.
- (viii) DIC and $\delta^{13}\text{C}$ – DIC: Initial sampling points of river systems recorded lowest values of $\delta^{13}\text{C}$ - DIC (averaging -16.3 ‰) at Kalene Hills (ZBZ ST. 1) and averaging -9.0 ‰ between Chingola (KAF.ST.1) and Mpongwe (KAF.ST.3). Stations located at points where the rivers traverse extensive areas of floodplains recorded higher values (averaging -6.8 ‰) at Kalongolo (ZBZ.ST.4) and before the Falls (ZBZ.ST.7) and an average of -6.0 ‰ at beginning of the Kafue Flats (KAF.ST.6) and Namwala (KAF.ST.7). $\delta^{13}\text{C}$ -

DIC (-22 to -5 ‰) and Si/Ca ratio in both rivers (0.2 to 0.5 on Kafue and 1.0 to 15.0 on Zambezi) show that chemical weathering and dissolution could be linked as a contributor to river DIC and atmospheric dissolution (-4 to -1‰) as a dominant process on the reservoirs as pCO₂ values (324 , 217 and 157 ppm for the 2012 wet and 2013 wet and dry seasons) at the Kariba Reservoir were below atmospheric CO₂ concentration. The reservoirs, especially the Kariba, were enriched (-4 to -1‰) in the ¹³C isotope possibly due to the preferential use of the ‘lighter’ CO₂ by phytoplankton during primary production. The reservoirs were also observed to export DIC downstream though primary production on the reservoirs was within value ranges of the river channels.

6.2 Recommendations

The study recommends that:

- (i) ZESCO supports UNZA - IWRM Centre and other researchers to undertake this research task further because CO₂ uptake at Kariba, if substantiated with spatially and seasonally resolved data on fluxes and other greenhouse gases, could earn ZESCO monetary benefit on the Carbon Credit Market for producing energy with no or low carbon footprint at the Kariba Dam;
- (ii) The Climate Change and Mitigation Unit in the Ministry of Lands, Natural Resources and Environmental Protection includes river biogeochemistry on their research agenda with a view to scale it up to other river systems not covered in this research; and
- (iii) The University of Zambia, particularly the Integrated Water Resources Management Centre (IWRM), includes biogeochemical studies in both their curriculum and research aspects in order to generate new knowledge and make the findings public so that awareness on the importance of river biogeochemistry in water resources management is enhanced.

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APPENDICES

Appendix 1: Data for the Zambezi, Kafue rivers and Kariba, Itezhi Tezhi reservoirs for the 2012 wet and 2013 wet and dry seasons campaigns for this study

2012 WET SEASON

No.	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO ₂ (ppm)
1	ZBZ.ST.1	2/5/2012 11:00	11.6	7.49	6.76	0.21	0.68	4.2	0.59	-28.8	14.1	1.6	-26.9	-13.8	0.20	1056.3
2	ZBZ.ST.2	2/7/2012 8:00	12	6.46	6.54	0.46	8.69	2.2	0.47	-27.4	21.6	3.3	-22.3	-12.9	0.21	2443.7
3	ZBZ.ST.3	2/8/2012 7:45	83.4	6.27	7.59	5.58	13.98	8.2	0.59	-27.6	7.2	3.0	-22.5	-11.6	0.88	1968.5
4	ZBZ.ST.4	2/10/2012 8:10	55.7	3.26	6.97	0.20	16.57	6.1	0.45	-25.7	7.4	4.2	-22.2	-8.5	0.71	7650.3
5	ZBZ.ST.5	2/11/2012 8:50	57.5	6.6	7.31	0.88	35.10	10.3	0.98	-24.5	9.5	4.5	-22.3	-6.9	0.67	1889.7
6	ZBZ.ST.6	2/11/2012 15:30	65.9	4.02	6.76	0.88	30.40	13.6	0.73	-26.9	5.4	4.5	-21.7	-7.0	0.90	6307.3
7	ZBZ.ST.7	2/12/2012 9:00	68.2	5.87	7.22	0.97	42.09	7.5	0.60	-26.0	8.1	4.5	-22.0	-6.2	0.76	2500.4
8	ZBZ.ST.8	2/14/2012 9:45	63.1	8.24	7.86	1.15	30.78	12.4	0.91	-24.8	7.3	4.6	-21.8	-5.0	0.68	641.6
9	ZBZ.ST.9	2/19/2012 13:05	85.6	5.96	7.37	0.20	21.41	34.6	1.27	-26.8	3.7	2.0	-23.4	-7.0	0.93	1942.5
10	ZBZ.ST.10	2/24/2012 9:05	115.1	7.41	8.10	0.60	152.62	20.4	1.09	-27.9	5.3			-5.8	1.11	805.6
11	KAF.ST.1	3/23/2012 8:45	112.7	4.85	7.19	0.26	8.53	8.6	0.34	-25.3	3.98	2.98	-21.84	-8.10	1.06	4338.0
12	KAF.ST.2	3/24/2012 7:55	128.5	6.32	7.33	0.13	8.75	10.3	0.50	-24.8	4.89	3.05	-22.47	-8.29	0.93	2863.1
13	KAF.ST.3	3/24/2012 17:35	191.6	7.3	7.71	0.95	1.81	1.0	0.23	-28.6	22.17	3.52	-22.09	-6.34	1.19	2339.8
14	KAF.ST.4	3/26/2012 17:00	176.6	5.45	7.32	0.62	19.38	2.3	0.71	-27.5	31.20	4.31	-20.95	-5.62		3992.2
15	KAF.ST.5	3/27/2012 10:35	174.5	6.48	7.72	0.61	57.86	9.9	0.65	-28.1	6.55	4.12	-21.71	-6.31	1.55	1858.0
16	KAF.ST.6	3/28/2012 13:45	196.8	8.3	8.24	0.52	69.83	3.5	0.60	-29.2	16.94	3.05	-20.49	-5.46	1.58	819.9
17	KAF.ST.7	3/30/2012 11:15	195.6	7.15	7.86	0.79	105.66	13.8	1.10	-28.1	7.98	3.40	-20.93	-5.19	1.65	1546.3

No.	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO ₂ (ppm)
18	KAF.ST.8	3/31/2012 13:25	217.1	1.81	7.24	0.55	31.93	1.6	0.27	-27.1	16.54	4.91	-21.76	-5.80	2.13	10301.1
19	KAF.ST.9	4/1/2012 9:25	221.5	2.12	7.21	0.02	68.49	1.9	0.39	-27.2	20.80	4.93	-21.35	-6.17	2.27	10331.3
20	KAF.ST.10	4/2/2012 8:15	220.4	7.45	8.27	0.31	45.77	49.8	2.94	-23.2	5.91	5.27	-21.08	-5.39	1.99	1211.9
21	ITT.1	3/29/2012 9:55	169.7	6.16	7.93	0.09	64.16	3.0	0.47	-29.1	15.88	3.49	-21.05	-5.79	1.43	1673.0
22	ITT.2	3/29/2012 12:30	186	7.29	8.24	0.69	69.31	3.2	0.64	-29.2	19.79	3.54	-20.93	-4.93	1.50	769.8
23	ITT.3	3/29/2012 15:45	207.2	7.66	8.42	0.58	34.05	2.9	0.79	-29.5	27.68	3.15	-21.52	-4.40	1.61	674.7
24	Kar.1	2/15/2012 15:45	92.1	9.23	8.78	1.31	29.10	2.5	0.51	-29.4	20.3	2.4	-22.8	-3.5	0.84	
25	Kar.2	2/16/2012 10:00	87.4	7.9	8.31	0.11	20.68	2.1	0.43	-28.9	20.3	1.9	-23.2	-3.6	0.45	355.8
26	Kar.3	2/18/2012 11:00	79.2	7.46	8.46	0.16	7.76	2.5	0.63	-30.9	25.3	2.2	-23.8	-3.2	0.83	324.0

**2013 WET
SEASON**

No	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO ₂ (ppm)
1	ZBZ.ST.1	1/13/2013 10:30	19.50	7.02	5.91	0.23	0.78	2.85	0.52	-27.64	18.42	2.3	-26.52	-13.27	0.82	2082.3
2	ZBZ.ST.2	1/14/2013 15:37	10.80	6.41		0.35	8.18	3.24	0.53	-25.83	16.36	4.1	-22.33	-13.02	2.26	2630.4
3	ZBZ.ST.3	1/16/2013 10:22	94.30	6.14		0.45	17.70	8.42	0.63	-26.80	7.46	5.2	-24.73	-11.42		2575.7
4	ZBZ.ST.4	1/17/2013 12:05		2.30		0.88		13.09	1.28	-23.56	9.77	5.6	-21.80	-6.09		10351.2
5	ZBZ.ST.5	1/18/2013 8:53	72.00	6.72		0.61	66.63	12.24	1.03	-24.96	8.45	5.2	-22.55	-6.66		1519.7
6	ZBZ.ST.6	1/19/2013 10:35	77.40	4.55		0.51	62.35	9.72	0.98	-25.79	10.04	4.7	-21.88	-7.38		5210.1
7	ZBZ.ST.7	1/21/2013 10:22	78.20	6.74		0.60		8.14	0.69	-25.86	8.53	4.7	-21.84	-6.38		1740.6
8	ZBZ.ST.8															662.8
9	ZBZ.ST.9	1/25/2013 10:16	85.10	5.83	7.42	0.37	15.73	6.60	0.53	-28.39	7.99	2.1	-23.17	-7.82	0.88	2238.5
10	ZBZ.ST.10	1/29/2013 10:40	122.10	7.06	7.76	0.67	68.58	93.40	3.08	-23.12	3.30	2.5	-22.55	-8.33	1.17	1447.0
11	KAF.ST.1	2/8/2013 10:56	157.70	5.08	7.45	0.33	25.78	9.51	0.41	-26.35	4.31	3.6	-23.56	-9.01	1.39	4179.6

No.	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO_2 (ppm)
12	KAF.ST.2	2/7/2013 15:05	178.80	7.00	7.58	0.25	13.82	4.62	0.38	-26.02	8.28	3.2	-23.25	-9.82	1.22	3093.3
13	KAF.ST.3	2/3/2013 9:02	220.40	5.78	7.42	1.06	35.06	4.71	0.44	-28.35	9.38	3.2	-23.13	-10.84	1.28	3452.3
14	KAF.ST.4	2/10/2013 16:08	167.40	5.43	7.18	0.47	23.49	10.85	0.90	-24.53	8.28	4.1	-21.41	-7.75	1.37	4221.8
15	KAF.ST.5	2/11/2013 10:24	142.50	6.68	7.63	0.25	59.86	25.87	1.37	-24.37	5.29	3.9	-21.22	-8.68	1.29	2245.3
16	KAF.ST.6	2/13/2013 15:12	160.40	9.39	8.04	1.19	24.82	4.85	0.38	-25.38	7.79	3.1	-20.50	-7.50	1.31	1190.6
17	KAF.ST.7															
18	KAF.ST.8	2/15/2013 10:48	189.00	1.35	7.07	0.63	35.63	2.51	0.36	-30.40	14.49	5.9	-24.34	-8.62	2.26	12819.9
19	KAF.ST.9	2/16/2013 9:12	194.20	1.22	7.16	0.49	29.01	7.40	0.55	-27.35	7.48	5.6	-23.73	-8.72	2.24	11749.4
20	KAF.ST.10	2/17/2013 13:00	194.50	8.05	8.17	0.57	41.64	22.75	1.03	-25.04	4.52	5.2	-23.61	-7.92	1.96	1551.9
21	ITT.1	2/12/2013 11:15	151.60	6.45	7.79	0.28	54.27	11.39	0.46	-25.27	4.04	3.6	-25.86	-7.06	1.32	2085.3
22	ITT.2	2/12/2013 14:49	153.30	6.65	7.89	0.34	23.25	2.81	0.50	-28.15	17.65	2.5	-23.95	-6.44	1.29	1253.6
23	ITT.3	2/13/2013 9:33		6.53	8.30	0.33	68.95	2.63	0.86	-25.34	32.63	3.5	-21.24	-4.63	1.50	1049.3
24	Kar.1															
25	Kar.2	1/22/2013 14:31	82.80	7.51		0.36	9.59	1.72	0.74	-29.01	42.87	4.0	-22.71	-1.95		480.4
26	Kar.3	1/24/2013 9:50	94.88	7.47	8.47	0.59	23.62	2.33	0.90	-30.95	38.80	2.7	-21.12	-1.04	0.80	216.6

**2013 DRY
SEASON**

No	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO_2 (ppm)
1	ZBZ.ST.1	10/19/2013 13:30		6.62	6.14	0.21	0.189	2.4	0.53	-26.9	21.8	2.9	-28.1	-21.9	0.15	2555
2	ZBZ.ST.2	10/20/2013 11:20		7.35	6.06	0.30	35.121	1.6	0.56	-26.3	35.2	1.9	-25.5	-9.5	0.86	617
3	ZBZ.ST.3	10/21/2013 09:15	164.80	6.98	7.94	0.57	30.81	10.1	0.59	-29.6	5.9	1.9	-24.8	-9.8	1.60	624
4	ZBZ.ST.4	10/22/2013 10:50	106.90	7.26	7.39	0.74	66.08	14.6	1.28	-27.0	8.8	1.5	-24.0	-7.8	1.07	752
5	ZBZ.ST.5	10/24/2013 10:00	110.90	7.55	7.72	0.73	32.60	3.9	0.67	-28.8	17.0	1.8	-22.2	-7.5	1.05	304

No.	Code	Date/ Time	Sp. Con ($\mu\text{S/cm}$)	DO (mg/L)	pH	Bacterial Respiration ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Primary Production ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	TSM (mg L^{-1})	POC (mg L^{-1})	$\delta^{13}\text{C}$ - POC (‰)	%PO C (%)	DOC (mg L^{-1})	$\delta^{13}\text{C}$ - DOC (‰)	$\delta^{13}\text{C}$ - DIC (‰)	DIC (mmol L^{-1})	pCO_2 (ppm)
6	ZBZ.ST.7	10/25/2013 09:50	111.40	7.44	7.71	0.52	33.44	3.1	0.66	-29.1	21.4	1.2	-23.5	-5.9	1.04	650
7	ZBZ.ST.9	10/27/2013 08:30	88.10	6.86	6.78	0.39	17.57	9.5	0.76	-27.9	8.0	2.2	-23.0	-6.4	1.12	1608
8	ZBZ.ST.10	11/10/2013 12:57	109.70	7.84	7.96	0.66	122.13	17.1	1.58	-29.5	9.2	2.1	-22.5	-5.1	1.00	441
9	Kar.3	10/29/2013 11:00	90.95	8.37	7.93	0.90	8.85	1.9	1.15	-32.0	61.1	2.6	-23.2	-3.5	0.84	157
10	KAF.ST.1	11/14/2013 11:00	602.20	5.96	7.84	0.98	104.77	12.2	1.10	-25.34	9.0	1.26	-22.79	-10.7	3.04	2529
11	KAF.ST.4	11/15/2013 12:20	536.00	9.54	8.54	1.17	21.83	1.0	0.41	-26.08	39.7	3.65	-22.97	-6.9	2.41	360
12	KAF.ST.5	11/16/2013 09:35	413.10	6.61	8.12	0.82	35.82	2.3	0.60	-28.28	25.9	2.37	-23.56	-7.9	3.16	1441
13	KAF.ST.6	11/17/2013 12:20	228.20	8.74	7.82	1.30	21.61	3.5	1.28	-28.50	36.1	2.61	-21.75	-5.7	1.94	916
14	KAF.ST.8	11/20/2013 10:00	249.65	3.46	7.12	0.84	60.52	2.8	0.92	-30.44	32.6	3.49	-22.14	-6.3	2.44	6242
15	KAF.ST.9	11/21/2013 10:00	247.95	3.13	7.10	0.82	94.56	3.9	1.13	-30.27	29.1	3.62	-21.87	-6.6	2.46	7051
16	KAF.ST.10	10/28/2013 09:30	235.60	8.01	7.75	0.66	62.78	6.4	0.93	-29.45	14.6	3.60	-22.67	-6.3	2.12	988
17	ITT.2	11/18/2013 11:45	223.65	8.31	8.51	1.10	25.07	4.6	1.85	-27.96	40.3	2.85	-21.86	-3.7	1.80	177

Appendix 2: Data from Zurbrugg et al. (2013) used for comparison with this study in Figure 5.1 and Figure 5.2

River/Floodplain	Date		POC (mg/L)		$\delta^{13}\text{C-POC}$ (‰)		DOC (mg/L)		$\delta^{13}\text{C-DOC}$ (‰)	
	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013
Kafue River	23/03/2012	01/05/2010	0.34	0.45	-25.3	-29.7	2.9	2.7	-21.8	-23.9
Kafue River	24/03/2012	01/05/2010	0.50	0.52	-24.8	-28.9	3.1	3.0	-22.5	-23.4
Kafue River	24/03/2012	01/05/2010	0.23	0.41	-28.6	-28.2	3.5	2.5	-22.1	-23.1
Kafue River	26/03/2012	01/05/2010	0.71	0.35	-27.5	-27.4	4.3	3.0	-21.0	-21.7
Kafue River	27/03/2012	01/05/2010	0.65	0.33	-28.1	-27.5	4.1	3.3	-21.7	-22.5
Kafue River	28/03/2012	01/05/2010	0.60	0.47	-29.2	-27.1	3.1	3.2	-20.5	-22.0
Kafue River	29/03/2012	01/05/2010								
Kafue River	29/03/2012	01/05/2010		0.32		-28.2	3.5	3.5		-22.8
Kafue River	29/03/2012	01/05/2010						3.5		-22.1
Kafue River	30/03/2012	01/05/2010	1.10	0.20	-28.1	-27.8		3.5	-20.9	-22.4
Kafue River	31/03/2012	01/05/2010	0.27	0.15	-27.1	-29.3	4.9	3.9	-21.8	-23.0
Kafue River	01/04/2012	01/05/2010	0.39	0.20	-27.2	-28.4	4.9	4.0	-21.4	-23.7
Kafue River	02/04/2012	01/05/2010	2.94	0.20	-23.2	-29.7	5.3	4.2	-21.1	-23.6
Kafue River	03/02/2013	01/05/2010	0.41	0.28		-28.3	3.6	4.3	-23.6	-24.2
Kafue River	07/02/2013	01/05/2010	0.38				3.2	4.5	-23.3	-24.1
Kafue River	08/02/2013	01/05/2010	0.44	0.26	-26.4	-27.7	3.2	4.7	-23.1	-24.7
Kafue River	10/02/2013	01/05/2010	0.90	0.26	-26.0	-28.4	4.1	4.9	-21.4	-23.7
Kafue River	11/02/2013	01/05/2010	1.37	0.49	-28.4	-27.4	3.9	4.6	-21.2	-24.4
Kafue Floodplain	13/02/2013	01/05/2010	0.38	0.32	-25.4	-26.7	3.1	4.1	-20.5	-22.7
Kafue Floodplain	15/02/2013	01/05/2010		0.25		-28.7		4.0		-23.0
Kafue Floodplain	16/02/2013	01/05/2010	0.36		-30.5		5.9	5.1	-24.3	-22.3
Kafue River	28/10/2013	01/05/2009	0.55	0.42	-27.4	-31.3	5.6	2.7	-23.7	

River/Floodplain	Date		POC (mg/L)		$\delta^{13}\text{C-POC}$ (‰)		DOC (mg/L)		$\delta^{13}\text{C-DOC}$ (‰)	
	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013	This study	Zurbrugg et al., 2013
Kafue River	08/11/2013	01/05/2009	1.03	0.50	-25.0	-30.4	5.2	3.2	-23.6	-21.6
Kafue River	14/11/2013	01/05/2009	1.10	0.50	-25.3	-29.8	1.3	3.7	-22.8	-21.8
Kafue River	15/11/2013	01/05/2009	0.41	0.72	-26.1	-28.1	3.7	3.6	-23.0	-21.0
Kafue River	16/11/2013	01/05/2009	0.60	0.61	-28.3	-29.1	2.4	3.3	-23.6	-21.8
Kafue River	17/11/2013	01/05/2009	1.28	0.28	-28.5	-29.1	2.6	3.9	-21.8	-21.8
Kafue River	18/11/2013	01/05/2009	0.92	0.32	-30.5	-27.0	3.5	3.3	-22.1	
Kafue River	20/11/2013	01/05/2009	1.13	0.22	-30.3	-26.8	3.6	4.1	-21.9	-21.0
Kafue River	21/11/2013	01/05/2009	0.93	0.18	-29.5	-27.3	3.6	4.5	-22.7	-21.2
Kafue River	24/11/2013	01/05/2009		0.23		-28.6		4.7		-22.7
Kafue River		01/05/2009		0.31		-28.4		5.5		-24.0
Kafue River		01/05/2009		0.26		-27.7		4.6		
Kafue River		01/05/2009		0.27		-28.9		5.7		-22.9
Kafue River		01/05/2009		0.29		-27.9		5.2		-22.5
Kafue River		01/05/2009		0.33		-28.3		5.7		-23.5
Kafue River		01/05/2009		0.36		-28.2		4.8		