Hydrol. Earth Syst. Sci. Discuss., 7, 4371–4409, 2010
www.hydrol-earth-syst-sci-discuss.net/7/4371/2010/
doi:10.5194/hessd-7-4371-2010

Hydrology and
Earth System
Sciences
Discussions

Hydrochemistry (major and trace elements) of Lake Malawi (Nyasa), Tanzanian Northern Basin: local versus global considerations

P. Branchu[1], **L. Bergonzini**[2], **J.-P. Ambrosi**[3], **D. Cardinal**[4], **M. Delalande**[2,*], **E. Pons-Branchu**[5], **and M. Benedetti**[6]

[1]Laboratoire Régional de l'Ouest Parisien, 12 rue Teisserenc de Bort, 78190 Trappes, France
[2]UMR-CNRS 8148 IDES, Bât. 504, Université Paris-Sud, 91405 Orsay Cedex, France
[3]CEREGE – UMR 6635 – Europôle Méditerranéen de l'Arbois, BP 80, 13545 Aix En Provence cedex 04, France
[4]Royal Museum for Central Africa, Dept. of Geology and Mineralogy, 3080 Tervuren, Belgium
[5]LSCE – UMR 1572, Orme des Merisiers Bât. 701, Centre CEA de Saclay, 91191 Gif sur Yvette Cédex, France
[6]UMR 7154 – IPGP, Université Paris 7, Case postale 7052, 75205 Paris Cedex 13, France

*present address: UMR7517 Laboratoire d'Hydrologie et de Géochimie de Strasbourg, 1 rue Blessig – 67084 Strasbourg Cédex, France

Received: 8 June 2010 – Accepted: 14 June 2010 – Published: 7 July 2010

Correspondence to: P. Branchu (philippe.branchu@developpement-durable.gouv.fr)

Abstract

This paper presents the first inventory of dissolved minor and trace element (F, Al, Fe, Mn, Ba, Cd, Cr, Cu, Pb, Mo, Bi, Sr, Zn) concentrations in Lake Malawi, the second largest African lake. Sampling was carried out during 1993 dry season in the northern part of the lake. Trace metal concentrations were measured, together with Ca, Mg, Na, K, Cl, SO_4, Alkalinity and Si, along three profiles in the lake northern extremity, in five tributaries and two on-land hydrothermal springs. Water profiles show similar elemental distributions and concentrations that are influenced by lake physical-chemical stratification. Stratification, assessed using temperature, conductivity, Si and Mn profiles, is characterised by two boundaries: the thermocline (70–90 m) and the oxicline (150–190 m). Elemental water concentrations are discussed using simple covariance analyse. Epilimnetic concentrations and distribution are also influenced by atmospheric deposition and river diving. Comparison of dissolved concentrations for potentially polluting elements with World Health Organisation Guidelines and those reported for other East African lakes shows that this reservoir is uncontaminated despite an increasing human stress. Major element behaviour is assessed through a 3 boxes model. In this model Cl and K are conservative elements whereas Si is removed from the solution by diatom productivity and sedimentation. Ca, Na, Mg and alkalinity show low reactivity. Evaporation is one of the controlling factors of lake element concentration that superimposes on the watershed control. Hydrothermal activity, not evidenced in the lake, controls the chemistry of one of the main northern tributary. Chemical comparison between Northern rivers and other tributaries characterises the geographical and geological specificity of studied northern watershed. Moreover the lake annual chemical budget shows that northern watershed generates the main elemental input to the lake, illustrating the dual importance of this area in terms of water and ionic recharge to the lake.

1 Introduction

Tropical lakes are of fundamental importance for regional economies and biodiversity conservation, but they experience large limnological changes that greatly affect their productivity, ecology, physico-chemistry and their water level at the time scale of human life. The mechanisms behind these fluctuations are not fully understood. For example, Tanganyika's falling productivity over the past century has been recently linked to increased water temperature and then higher stratification (Verburg et al., 2003; O'Reilly et al., 2003). The unprecedented rates of sedimentation increase since the early 1960's in the Lake Tanganyika basin suggests strong disturbances, which involves a combination of climatic and anthropogenic causes (e.g. heavy rainfall and deforestation; Cohen et al., 2005). Lake Victoria eutrophication (Machiwa, 2003) and metals-metalloids contamination of its waters and sediments (Ikingura et al., 2006; Kishe and Machiwa, 2003; Ramlal et al., 2003) have been linked to human threats expressed through fishing pressure, land use changes, urbanisation, industry, mining and new species introduction. Indeed, in the East African Great Lakes region, the high annual growth of population (about 2.5% according to the Population Reference Bureau, 2009) is responsible for large watershed pressure and for water stress that can lead to contamination and/or overexploitation of both water and fish resources (Cohen et al., 1996). Consequences of such human activities could be drastic, as these reservoirs constitute an important provider of freshwater and fish protein. Researches on anthropogenic disturbances in East African Great Lakes focus particularly on the possible eutrophication that is a regional scale problem (UNEP/IETC, 2000) and on sedimentary inputs to lakes (Hecky et al., 2003; Machiwa, 2003). On Lake Malawi, studies were focused on organic-pollutants in water and sediments, trace elements in sediments and mercury food web contamination (Karlson et al., 2000; Kidd et al., 1999, 2003). According to these characterisations and other reports on the pollution of East African Great Lakes (Cohen et al., 1996), Lake Malawi appears to be relatively preserved besides a water warming during last century (Branchu et al., 2005a; Vollmer et al., 2005) and increase of deforestation, along with runoff, since 1967 (Calder et al., 1995) changing the lake water balance; Furthermore it has been shown that potential changes in water compositions of the tributaries could induce important changes in the Lake Malawi water quality (Branchu et al., 2005b). The goals of this study are 1) to characterise the inorganic water geochemistry of northern part of Lake Malawi, 2) to determine its origin 3) to discuss the specificity of the northern watershed.

Lake Malawi (Fig. 1), 570 km long (9°30′–14°40′ S; 34° E), 700 m of maximum depth and a volume of 7790 km^3 (Vollmer et al., 2002), is the second largest surface water reservoir on the African continent and represents about 6% of the world surface free freshwaters. The lake presents at its south a surface outlet, the Shire River (Fig. 1). Overall, its catchment (126 500 km^2) is affected by a tropical climate and is mainly located on the western coast drained by the Songwe, North and South Rukuru, Dwanga, Bua and Linthipe Rivers (Fig. 1). The eastern shore is mainly drained by the Ruhuhu River and the northern one by the Kiwira, Mbaka, Lufirio and Lumbila Rivers (Fig. 1). This northern basin is characterised by the Poroto-Rungwe and Livingstone mountains, volcanic rocks and has the highest specific water flow compared to the rest of the catchment (Bergonzini, 1998). The lake is meromictic with a permanent thermo-haline stratification (Halfman, 1993), which limits mixing and oxygen penetration at depths where biological degradation of settling organic matter is predominant, leading to anoxia between 170 and 300 m (Halfman, 1993; Vollmer et al., 2002). This hydrodynamic scheme is somewhat simple since spatio-temporal variations occur due to internal waves and upwelling (Eccles, 1974; Hamblin et al., 2003). According to classification based on nutrient budget concentration it would be considered as oligotrophic but due to its high plankton production rates it is rather considered as mesotrophic (Bootsma et al., 2003). Its water composition belongs to the "common" East African waters (Kilham and Hecky, 1973), resulting from a water-rock interaction dominance (Kilham, 1990; Gibbs, 1970), mostly controlled by the weathering of Precambrian granitic and metamorphic rocks of its watershed with little influence of the Rungwe volcanic rocks (Hecky and Bugenyi, 1992). The present study focuses on the northern part of the lake and its watershed (Fig. 1) that expresses singular features, with tectonic, seismic, volcanic and hydrothermal activities compared with the rest of the catchment and a relatively high heat flows at the lake's bottom (Branchu et al., 2005a). It is based on major, minor and trace element (Alkalinity, Cl, F, SO_4, K, Ca, Na, Mg, Si, Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, Sr, Mo, Cd, Ba and Pb) analyses performed on water column and tributaries.

2 Material and methods

2.1 Sample collection and processing

During the framework of the CASIMIR (Comparative Analysis of Sedimentary Infill Mechanisms in Rifts) Belgian project, and especially during the fieldwork of October 1993, different types of waters from the north basin (Tanzanian part of Livingstone basin) were sampled on land and on-board of the *Nyanja* vessel. Three lake water profiles (P1, P2 and P3, Fig. 1), corresponding to epilimnetic (0–105 m) and metalimnetic (105–220 m) waters, were sampled using a 5 L PVC Hydro-Bios® bottle. On land, five rivers and two hydrothermal springs were also sampled (Fig. 1). 500 mL polypropylene (PP) flasks were flushed and filled with sampled water, flask cap was then sealed using Parafilm® and stored at temperature <4 °C until processing. Water samples were then processed in a closed place on a clean surface: 240 mL were filtered using a frontal filtration unit (Sartorius®, 47 mm type) through 0.45 µm cellulose nitrate membranes (Sartorius® type). Two PP flasks were filled with this filtered sample, only one (200 mL) being acidified at pH∼1 (with Suprapur 65% HNO_3). Non-acidified samples were devoted to anion analyses and acidified ones to cation, Si and trace element analysis. For alkalinity determination, one PP flask (60 mL) was fully filled by non-filtered water. All PP flasks and filters were previously washed using acidified (Suprapur 65% HNO_3) MilliQ water and rinsed with MilliQ water. All the reagents are analytical grade. The filtration unit was rinsed before each operation with MilliQ water and then sample's aliquot is flushed. All samples were stored at temperature <4 °C and sealed using Parafilm®. Non-refrigerated transport was restricted to a few days, water samples were stored at 4 °C at the CEREGE (Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement, Aix-en-Provence) prior to analysis.

2.2 Analytical methods

Dissolved concentrations of major anions (Cl, F and SO_4) and cations (K, Ca, Na and Mg) were measured using capillary electrophoresis (CIA from Waters®). Calibrations ranged from 0.1 to 20 ppm for anions and 0.2 to 20 ppm for cations. Electrolyte was Chromate-OFM, pH 8, for anions and UV Cat2, pH 6, for cations. Alkalinity was determined by potentiometric HCl titration with calculation of equivalent volume by the Gran method. Al and Fe concentrations were measured using Graphite Furnace Atomic Absorption Spectrometry (GFAAS: Z8200 Hitachi®). Calibrations ranged from 2 to 40 ppb for Al and 1 to 40 ppb for Fe. Si was measured with Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES: JY 38 type III) in the 1–10 ppm range. All these analyses were performed at CEREGE. Concentrations of Cr (mass: 52), Mn (55), Ni (60), Cu (65), Zn (66), Sr (88), Mo (95), Cd (111), Ba (138) and Pb (208) were measured in the 0.05–20 ppb range by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on a Fisons Instrument® Plasma Quad $PQ2^+$ at the Royal Museum for Central Africa (Tervuren, Belgium). An internal standard (In) was added to samples before analysis to correct for sensitivity drift. Analytical standard deviations and, for ICP-MS, calculated detection limits and reproducibility (in the lower part of the calibration range) are reported in Table 1. To consider potential metal contamination during sampling and field processing, Hydrobios bottle blank analysis using MilliQ water has been performed at laboratory (Table 1). However, hydrobios bottle blank trace element analyses reveal potential contamination in Zn and Pb but in a lower range than measured concentrations.

CTD casts were performed in the north basin prior to sampling with a Sea-Bird SBE 25 logger. Only temperature and electrical conductivity (expressed as reference conductivity, K_{25}) are presented, dissolevd oxygen concentration was unfortunately not measured due to probe problems.

Thermodynamic computations discussed below were performed using MINTEQA2 equilibration speciation model and data set presented in Tables 2 and 3.

3 Results and interpretations

Water column and on land (rivers and hydrothermal springs) data are presented in Tables 2 and 3 for major and trace elements, respectively. Lake Malawi major ions and general physical-chemical features are presented with reference to previous limnological characterisations. To our knowledge this work provides the first minor and trace elements data set relative to Lake Malawi whereas previous contaminants studies were mainly focussed on organic pollutants in water and on metals in fish and sediments (Karlson et al., 2000; Kidd et al., 1999, 2003).

3.1 Lake water column data

Temperature decreases from surface (25.4 °C) to 240 m (22.8 °C) with a main gradient between 70 and 90 m (Fig. 2a), whereas conductivity increases from 256.7 $\mu S\,cm^{-1}$ at the surface to 263.5 $\mu S\,cm^{-1}$ at 240 m with three main gradients at about 50–60 m, 70–90 m and 190–210 m (Fig. 2b). Cl, Ca, Na, K, Mg and alkalinity concentrations (Table 2) are similar for the three profiles and display no significant changes with depth according to standard deviations SO_4 values are highly variable without clear depth-related trend. Si concentrations exhibit the same behaviour in the three profiles and increase sharply below 70 m (Table 2, Fig. 2c). Ionic budget indicates that no significant ion is missing as the imbalance percentage is in the range of analytical standard deviation (Table 2). From these data an average weight salinity of 0.203±0.003‰ is calculated;

main contributors being carbonates (72%), Na (10%) followed by Mg (6%), Ca (6%), K (3%) and Cl (2%).

Presented temperature and conductivity data match well with seasonal pattern defined by Eccles (1974) and Gonfiantini et al. (1979) (Table 4) and, except for SO_4; major ion concentrations are comparable for the same depth range with the ones reported previously (Tables 4 and 5). Decrease in chloride concentrations between 1976 (Gonfiantini et al., 1979), 1980–81 (Hecky, unpublished) are discussed elsewhere (Branchu et al., 2010). Surface temperature is colder at the end of the dry season (September–October) than at its beginning (June) and warmer during the raining one (January). Metalimnetic waters express also seasonality but mixing processes play an important role, mainly at the end of the dry season. The present salinity value for surface waters computed from major ion concentration (0–25 m) 0.203‰ matches well the 0.208‰, computed from Gonfiantini et al. data (1979). Similarity between 1976 and 1993 ionic characterisations can illustrate a relative steady state for major elements. Other published data (e.g., Talling and Talling, 1965) are not included in our comparison as they concern mainly surface waters and do not allow ionic balance computation.

At the three stations several trace elements as Mn, Fe, Al, Ni, Pb, Cd, Ba and Sr are enriched in surface water (0–10 m; Fig. 2d–f, Table 3). Deeper, Mn concentrations (Fig. 2d) are homogeneous, and then increase below 150–190 m whereas Fe (Fig. 2e), Ni and Pb profiles are homogeneous in the first 200 m and only increase for deepest samples (197 and 240 m, for P2 and P3, respectively). Other elements as F, Cr, Cu and Mo are characterised by relatively homogeneous profiles. Data relative to minor and trace elements of surface point (10 m) in P1 station and relative to F at 5 m depth in P3 station are outliers that are not considered in average and standard deviation computations (Table 3).

3.2 River water and hydrothermal spring data

There is no previous published data on the chemistry of Lake Malawi tributaries except for Si (Bootsma et al., 2003).

Lumbila River that drains the Livingstone fault top is much colder (19.5 °C) than other rivers (27< T °C< 30) and also than epilimnetic waters. Rivers are diluted compared to lake waters except for Kiwira River. Their chemistry (Table 2) is dominated by carbonates and by Na (Kiwira and Mbaka Rivers), Na and Ca (Lufirio and Songwe Rivers) and Na, Ca and K (Lumbila River). Dissolved concentrations are scattered (i.e. standard deviation >30%, largely above the analytical variability) for all major components, whereas dissolved Cr, Ni, Cu and Pb concentrations are similar (i.e. standard deviation <15%, Tables 2 and 3). The high K, Na, Si, Cl, SO_4, F, Mo and Cd concentrations in the Kiwira River explain most of this scattering. Highest Sr concentration occurs in the Lufirio River. Cd and F concentrations are below the detection limit except for Kiwira River.

Both hydrothermal spring waters have neutral pH, temperatures of about 60 °C and homogenous major element concentrations (Tables 2 and 3) with high Na and HCO_3 contents. Ni and Cd concentrations are below the detection limit. In Giggenbach (1991) triangular diagrams, these waters lie in the carbonate corner and are considered immature (no chemical equilibrium). Major element chemistry matches well with previous characterisations (Harkin, 1960; Makundi and Kifua, 1985) whereas no data on trace elements were previously published.

Kiwira River singularity is associated to a hydrothermal influence (see hot springs chemistry in Tables 2 and 3). Hydrothermal springs are indeed present in its watershed with a flow that could reach about $1\,m^3\,s^{-1}$ (James, 1959). Their contribution to the lake chemistry is significant as the Kiwira River represents about 5% of the total river contributio to the lake (Bergonzini, 1998). Thermodynamic computation predicts a Ca, Mg, Sr and Ba carbonate precipitation from the spring that accounts for their low contribution to the Kiwira River. Such prediction is confirmed by occurrence of carbonate crusts in some hydrothermal fields (Pisarskii et al., 1998; Branchu et al., 2005b). Moreover Kiwira waters are in equilibrium with dolomite according to computations. The rich Na-HCO_3 hot springs (Table 2) could be associated to the presence of a magma chamber at depth (Pisarskii et al., 1998; Branchu et al., 2005b).

3.3 Indirect evidences of redox gradients

In absence of dissolved oxygen (DO) concentration measurements, serveral indirect evidences were used to propose a qualitative redox profile:

- an empirical mid column (150–250 m) relation, between the occurrence of a conductivity increase just at the zero DO concentration is defined using data from Gonfiantini et al. (1979), Halfman (1993) and Vollmer et al. (2002). Such a relation is common in meromictic systems (Taillefert et al., 2000). From this consideration P3 waters should be anoxic below 190 m depth (Fig 2b).
- In such meromictic lakes, redox disturbance during sampling and processing should also be raised as they were performed under oxic conditions. Indeed for redox sensitive elements (such as Mn), with solubility depending of the oxidation state important artefacts may occur. At Lake Malawi pH (7.5–8.5), Mn(II) oxidation reaction and rate are complex and variable leading to half-life values spanning a large range (Wehrli, 1990; Davison, 1993). Due to rapid sample processing (few hours after sampling) Mn profiles may be used as qualitative data for the deeper, reductive layer. Then, the increase of dissolved Mn, below 190 m (Fig. 2d) illustrates the occurrence of a redox decrease.

Both indirect evidences, are in aggreement and allow to locate oxicline between 150 and 190 m where waters become anoxic. This is depth is similar to the DO depth measuerd by Vollmer et al. (2002): 190 m.

3.4 Water column physico-chemical structure

From the above results, a schematic view of bio-physico-chemical distribution with depth corresponding to the end of the dry season is proposed using temperature, conductivity, dissolved Si and Mn concentration profiles (Fig. 3). Correlated Si and conductivity profiles (r=0.97 in the whole water column, Fig. 3) partly result from the interaction between mixing (or stratification), biological (photosynthesis, remineralisation) processes (Bootsma et al., 2003). Others processes such as sinking of diluted river waters (Hecky et al., 2003) or record of past evaporative conditions in deep waters (Gonfiantini et al., 1979; Branchu et al., 2010) influence also Si and conductivity profiles (cf. latter). As diatom primary production removes Si from the water in the euphotic zone, the mixing seems effective above 75 m. Below this limit, corresponding to the thermocline and to a conductivity and density shift, slow mixing processes and biological degradation predominate, releasing Si and others nutrients and increasing conductivity. In a relative poor ventilated system these processes theoretically lead to anoxia in depth. From qualitative considerations reported above oxycline coulb be located between 150 m and 190 m where anoxy occure.

In Lake Malawi, the sequence of oxidants used during organic matter degradation was previously reported, for O_2 and NO_3, (Bootsma and Hecky, 1993), the above schematic view complete this sequence with Mn. This sequence may be related to a Eh decrease with increasing depth from the top of the oxicline.

In this physico-chemical structure, the dissolved concentrations of Ca and Mg are correlated (r=0.73) illustrating a solubility control by a carbonate phase as epilimnetic waters are slightly oversaturated with respect to calcite, dolomite and aragonite, whereas metalimnetic ones become undersaturated.

3.5 Trace element covariance

All these biological-physical-chemical and hydrodynamical processes control water column trace element profiles. Element similarity matrixes are usually used to identify trace element carrier-phases and their reactivity (e.g., Balistrieri et al., 1994). Applied to the whole water column of Lake Malawi (using Pearson's correlation coefficient, n=23), dissolved Al concentrations are correlated with Ni, Cd and Pb (r=0.72; 0.79; 0.74, respectively), suggesting their association in a particulate (or colloidal) phase solubility control in the lake and/or in the watershed. Al is also correlated with Fe (r=0.64). Dissolved Al/Fe ratio in the water column, except for P2 and P3 deepest points, is the same than suspended matter (SM) Al/Fe measured in river Kiwira, Songwe, Mbaka and Lumbila (Branchu, 2001) seems to be controlled by a particulate (or colloidal) Al-Fe phase. Consistent with a Al/Fe>=1, the SM from tributaries are mainly clay minerals: kaolinite, illite and vermiculite types (Branchu et al., 2005a) that have high adsorption capacity (Drever, 1988). Submicron size clay minerals can be found in water samples even after filtration and are natural carrier of trace elements (Allard et al., 2002). Fe oxi-hydroxides should be associated as coatings with these clay minerals. The release of Fe under reducing conditions corresponds to an increase of Pb and Ni suggesting their association with Fe oxi-hydroxides as previously observed in aquatic systems (Benoit et al., 1994; Balistrieri et al., 1994).

Several elements show correlation but without depth related gradient. Sr and Ba are well correlated (r=0.92) suggesting their control by a same phase. Cu, Cr and Ni covary (r=1 and 0.75, between Cr and Cu and Cr and Ni, respectively) and their averaged relative ratio is the same in the water column (0–200 m) and in the tributaries, suggesting a direct watershed control. Due to redox This implies for metals having affinity with Mn and mainly Fe oxi-hydroxides a possible scavenging by these freshly reactive surfaces (Sigg et al., 1987; Trivedi and Axe, 2001).

From this covariance analyse some phase associations are proposed but trace metal behaviour is not assessed through the present data set. In future works a particular attention should be paid to suspensed matter characterization and to deeper water column sampling followed by sample processing in anoxic conditions.

3.6 Local processes

Local processes are superimposed over this general pattern. At P3, temperature and conductivity show indeed gradients within surface water (0–70 m): the upper layer (0–20 m) is warmer and with higher conductivity than the thermocline bound layer (Fig. 2a,b). Relative to the surface water the higher density (lower conductivity and temperature) of Lumbila River enables it to sink in the water column down to the thermocline (Branchu et al., 2005b). A similar layer was identified during 1992 rainy season in the southern part of Livingstone Basin near the Ruhuhu River mouth (Halfman and Scholz, 1993). Lake surface waters (0–10 m) are also characterised by a metal enrichment (Mn, Fe, Al, Ni, Pb, Cd, Ba and Sr) at all stations. As tributaries water concetrations are lower for these elements than surface lake water one's, they cannot contribute significantly to this level except by interaction with their particulate load (clay minerals and other particles). Such enrichment can be associated, as for oceanic or other lakes, to atmospheric deposition and then to the elemental scavenging by settling particles (Stumm and Morgan, 1996). In tropical regions potential sources of such depositions are denuded soils and biomass burning from local or long-range area. In lakes Malawi and Tanganyika watersheds, biomass burning mainly occurs during the dry season and has been proposed to partly explain N, S and P rain concentrations (Bootsma et al., 1996; Langenberg et al., 2003). However soil and wind influence also Ca, Mg rain contents (Bootsma et al., 1996). In addition to this rainy influence, it is likely that biomass burning and wind over eroded soils should also influence dry depositions, which is probably responsible of the lake surface enrichment. The homogeneity between and along the three profiles indicates comparable effects of the predominant processes that occur in North Lake Malawi.

3.7 Water quality assessment

Finally, our data (lake and rivers) allow, for elements of health significance in drinking water (Cr, Ni, Cu, Mo, Cd, Pb, F and Mn) a water quality evaluation based on comparison with World Health Organisation guidelines (WHO, 2004) and comparison with other East African lake data (Kilham and Hecky, 1973; Bugenyi, 1982; Cohen et al., 1996; Challe, 2002; Table 6). Globally, Lake Malawi and northern river concentrations are below WHO guidelines and the ones measured in regional lakes classified as contaminated (Cohen et al., 1996). However, Cu concentrations are high, in the same range than those measured in Lakes Edward and George contaminated by copper mines (Bugenyi, 1982). Lead in Lake Malawi is the only exception with extreme values exceeding the guidelines (Table 6). Kiwira river fluoride concentration is higher than the WHO guideline resulting from the influence of hydrothermal springs in its watershed (Branchu et al., 2005a). Presented data characterise an uncontaminated system (lake and northern rivers) but enriched compared to the World Average River (Martin and Windom, 1991). In accordance with previously published data on heavy metals in aquatic food web and sediments (Kidd et al., 1999, 2003), Lake Malawi is an uncontaminated system from dissolved trace metal consideration whereas potentially polluting human activities are present in Malawi watershed. The sole anthropogenic process with visible impact evidenced from this study is the atmospheric inputs partly due to biomass burning and to soil erosion.

4 Lake Malawi water and chemical budgets

Lake Malawi chemical budget was firstly published by Hecky and Bugenyi (1992). Northern tributaries that have specific features (geological, hydrological, relief, ...) have however been understimated in this budget. Recently we published an original water budget for Lake Malawi based on monthly data (recorded over several years) of tributary and outlet flows, evaporation and precipitation over water surface and on lake-level records (Branchu et al., 2010; Table 7). This northern area, including Songwe, Kiwira, Mbaka, Lumbila and Lufirio watersheds, covers about 9% of the total catchment area and drains the Rungwe volcanoes that culminate at about 3000 m a.s.l.. The high relief, responsible of the highest precipitation rates of the whole catchment (more than 2000 mm y^{-1} in the northern area compared to 1350 mm y^{-1} for mean lake watershed), generates about 20% of total river inflow. In this budget, computed for steady state conditions, inputs to the lake are equally distributed between direct precipitation and river inputs whereas outputs are dominated, at 83%, by direct evaporation. Water residence time is 99 years for the whole lake and 5 years for the epilimnion illustrating the relative isolation of deep waters.

Hydrochemical budget is computed using this water budget and chemical data from Bootsma et al. (1996, 2003) for rain and our water column data set completed for depth

>250 m by Gonfiantini et al. (1976). Global River inflow to the Lake is computed using present chemical data set completed with Hecky and Bugenyi (1992) river data set (additional 15% of lake global runoff and about 35% of the whole catchment) including rivers Linthipie, Bua, Dwangwa, Luweya, N. Rukuru, N. Rumphi and S. Rukuru. The 65% remaining river inflow, corresponding to about 35% of the catchment, that are not characterised from a physico-chemical consideration are globally associated to steep area. An average composition, computed from similar characterised area, has then been attributed to this remaining catchment. Chemical steady state assumption is required to compute this budget and constant chemical composition of waters are required. From Table 5, we can estimate a temporal (seasonal and interannual) variability (expressed as coefficient of variation) of water column (0–250 m) composition lower than 10% with higest variability for potassium and magnesium.

Seasonal and inter annual variations of river chemistry have also been considered as Hecky and Bugenyi data correspond to the end of the rainy season whereas the present data characterise the end of the dry season. The importance of chemical and flow variability has been demonstrated in such environments but affects differently major elements (Vandelannoote et al., 1999; Hecky et al., 2003; Langenberg et al., 2003). For major elements (Ca, Na, Mg, K, Cl) the seasonal to interannual variability was assessed for Mbaka and Kiwira rivers by comparing data from October 1993, November 2001 and March 2005 (Delalande, 2008). A mean temporal coefficient of variation of 22% is computed. For Si (in its soluble reactive phase) it has been shown that concentrations are stable throughout the year, a mean temporal coefficient of variation of 19% was computed (Bootsma et al., 2003).

For all elements the main input to the lake is from rivers (>75%). For all elements, except Si and Cl, the lake residence time (average ca. 520 years) about 5 times higher than for water, illustrates the relatively slow vertical excanges between surface and deep waters. The long Cl residence time (ca. 1000 years) is linked to the high hypolimnetic Cl content of deep waters that was associated to record of past different climatic conditions (Gonfiantini et al., 1979). The whole lake higher residence time of alkalinity

(Table 8) can be related to photosynthesic activity in epilimnetic waters and degradation in deep waters. Moreover, the hypolimnetic alkalinity increase (Gonfiantini et al., 1979) is partly due to nutrient remineralisation associated with anaerobic degradation of organic matter. Other contribution for example for Si can be associated to sinking of river waters (Bootsma et al., 2003)

5 Lake Malawi mean tributary concentration

In order to determine the mean tributary concentration two approaches are followed. In the first one, this concentration is directly computed from data used in the dydrochemical budget, using following Eq. (1)

$$[R]_i = 1/Q \cdot \sum (Q_j \cdot [R_j]_i) \tag{1}$$

with: element i concentration (mol L^{-1}) in: global catchment average tributary $[R]$, individual tributaries $[R_j]$, water fluxes (L y^{-1}): from tributaries Q, from individual tributaries Q_j ($Q{=}\sum Q_j$). $[R]_i$ concentrations are presented for Ca, Na, Mg, Cl, Alk, K and Si in Table 8.

The second approach for assessing global tributray concentration is based on an epilimnetic hydrochemical budget in steady state conditions (Eq. 2).

$$\mathrm{d[Ep]}_i/\mathrm{d}t = 0. \tag{2}$$

This allows computing the dissolved chemistry of the global Catchment Average Tributary (CAT), following Eq. (3) and assuming that for each element Lake chemical inputs are equal to Lake chemical outputs and that epilimnetic concentration is equal to outflow concentration.

$$[\mathrm{CAT}]_i = 1/Q \times (Q_{\mathrm{em}} \cdot ([\mathrm{Ep}]_i - [\mathrm{Met}]_i) + Q_{\mathrm{ex}} \times [\mathrm{Ep}]_i - P \times [P]_i) \tag{3}$$

with: element i concentration (mol L^{-1}) in: global catchment average tributary $[\mathrm{CAT}]_i$, epilimnion $[\mathrm{Ep}]_i$, metalimnion $[\mathrm{Met}]_i$ and precipitations $[\mathrm{P}]_i$, water fluxes (L y^{-1}): from tributaries Q, from precipitations P, exchanged between epi- and metalimnion Q_{em} and to outlet Q_{ex}.

Data used (in Eq. 2) are from i) Lake water budget and Lake vertical water fluxes (Table 7, from Bergonzini, 1998; Vollmer et al., 2002), ii) rain chemistry (Bootsma et al., 1996, 2003) and iii) present water column chemistry. This equation only considers dissolved fluxes but dissolved element fluxes induced by precipitation/dissolution of particulate phases (in the water column and in sediments) are also included in this computation. Groundwater fluxes are not identified in this equation but are expressed through Q and [CAT]. Evaporative process that concentrates ions in the surface is also integrated in this computation. Then comparison between R and CAT can be used to illustrate elemental behaviour (reactive or conservative) in eplimnetic water. Only siking of river water from steep catchments is not taken into account. Differences are then interprated in terms of reactivity of a disolevd element in epilimnetic waters.

R and CAT values plotted in a Gibb's diagram (Gibbs, 1970; Kilham, 1990) fall in the central part of the boomerang shape (not shown) illustrating their control by rock weathering. Comparison between R and CAT is presented for major elements (Fig. 4). For Cl and K, similitude between computed concentrations (Eqs. 1 and 2) reinforces the steady state assumption and demonstrate the boxes model accuracy and data set validity. For Ca, Na and Mg CAT slightly underestimates (about 19%) the concentration whereas for alkalinity it overestimates it slightly (21%). This variability is likely due to variability in data (flow and chemistry, see above). However Ca, Na and Mg have been previously involved in diagenetic processes (Hecky and Bugenyi, 1992) that could remove then from the lake and store them in the sedimentary pool. Moreover a thermodynamic computation suggests occurrence of a Ca, Mg carbonate controlling phase (cf. above). Occurrence of such phase in the water column is also consistent with the modern sediments of the lake where authigenic and biological calcites are present even if they have a low contribution to the total particle fluxes (Pilskaln, 2004). As expected, Si is particular as R (Eq. 1) is 123 times higher than CAT (Eq. 2). Differences between both computations are explained by the biological cycle. Si is largely removed from the euphotic zone in the epilimnion during diatom productivity and then from the lake by sedimentation, whereas dissolution occurs in the meta- and hypo-limnion (Bootsma et al., 2003; Pilskaln, 2004).

Major element (Si excepted) epilimnetic residence time is similar to the water one (about 4 years). Ca, Na, Mg, Cl, K and alkalinity epilimnetic waters are about 3.0 more concentrated than average input (R and CAT) which can be explained mainly by evaporation that concentrates inputs. Si is a nutrient with a high recycling rate, a short residence time and an input concentration 5.7 times more concentrated than eplimnetic one.

Computation of a trace metal annual budget is unrealistic as inputs are only partly known for the northern tributaries and therefore remain poorly constrained. Steady state computation (Eq. 2) of the CAT gives for all elements (except Mn) a concentration about 3 times higher than the epilimnetic measured one. The computation neglects the uncharacterised atmospheric input even if for some elements such fluxes may be important (see above). Mn is the only trace element showing a concentration gradient between epi- and meta-limnion. Input of dissolved Mn from the metalimnion, where sinking particulate Mn is dissolved trough reduction, can explain the negative Mn concentration computed for the average tributary (Eq. 2).

6 Lake chemistry control: the northern area specificity

The northern area is responsible of 57% of the total Na input by runoff to the lake and at least of 48% for Cl, 35% for alkalinity and from 28 to 31% for other major elements illustrating the importance of this zone.

Northern tributary composition (Table 2) is compared to R. Specificity of the Kiwira River presented above is illustrated here with high Cl and Na contents and low Ca and Mg contents. For major elements, except Cl that is in low concentration in sampled rivers, average concentration of northern river, Kiwira River excluded, exceeds by a factor 2 R_i. General accordance between major element CAT and R (Fig. 4) allow to be confident on CAT computations to assess trace element tributary input to the Lake. Trace elements, except Al and Fe that are about 10 times more concentrated, are in average 2 more concentrated in the average northern river than in CAT.

Both approaches (Eqs. 1 and 2) are consistent and allow to characterise the global river concentration that is globally lower, particularly for K, alkalinity, Al, Fe, Cu, Pb, Cr and Ni, than in the northern rivers. The most likely explanation for this enrichment factor is the peculiarity of the northern watershed (Branchu et al., 2005b). All the features (high relief, high precipitation rates) of this northern area, including a higher mineral charge of northern rivers, characterise high weathering rates. The enrichments of local rocks relative to the "average" watershed (Precambrian granitic and metamorphic rocks) is assessed by comparing their major element composition (e.g., Harkin, 1960) to the upper continental crust composition (UCC; Wedepohl, 1995) and for trace elements a basaltic composition (Drever, 1988) has been compared to the UCC. Weathering of basic rocks could explain the relatively high alkalinity: rocks of the trachyte-phonolite series accounting for the high K concentrations and the basalts for the enrichment in Cu, Cr, and Ni. The chemistry of the northern tributaries is then controlled by the high weathering rates of rocks of the Rungwe volcanic center; in addition for the Kiwira River the hydrothermal signal superimposes on this bedrock signature.

7 Summary and conclusions

This is the first published report on minor and trace element water chemistry in Lake Malawi and one of the rare dealing with major element chemistry. Regional geology, weathering processes, evaporation, biological processes and hydrothermal activity mainly control Lake Malawi major, minor and trace element concentrations. In this context, the Rungwe volcanic rocks are an important source of element to the lake. Whereas sub-lacustrine hydrothermal input has not been observed, the influence of on-land spring is noticeable through the Kiwira River. We found no evidence of anthropogenic contamination except some dry atmospheric deposition, probably linked to biomass burning and soil erosion, that influences the surface layer concentrations for several trace metals (Mn, Fe, Al, Ni, Zn, Pb, Cd, Ba, Sr). The water column physicochemistry presents the usual features reported for stratified lakes: a Si and conductivity increase below the thermocline and a Mn enrichment in the suboxic-anoxic waters. Biological scheme of organic matter production-degradation and slow mixing processes dominate these features. At local scale temperature and conductivity in surface layer are also influenced by river inputs. Behaviour of trace metal is not discussed but covariance between elements could be indicative of phase association. Carbonates could indeed control Ca and Mg concentrations. Some trace elements (Zn, Pb, Ni) could be associated to Fe and Mn hydroxides whereas most of them do not show particular trend with depth. This study is a new contribution to the knowledge of this unique ecosystem and large reservoir of freshwater and food. Nevertheless the complete comprehension and modelling of such aquatic system require more data.

A detailed investigation of the water column around thermocline will permit to precise spatial extension of sinking river layer; in the same way a detailed investigation around oxicline would allow to precise i) oxidant sequence linked to organic matter degradation, ii) nature of the “turbid layer” occurring at or just above the depth of DO disappearance.

Future work should include the effect of spatial and temporal variability on the geochemical parameters, an exhaustive characterisation of the inputs into the lake system (rivers, wet and dry depositions), a characterisation of the dissolved and particulate phases. While Lake Malawi in regard to analysed elements, is a non contaminated water body, this status is relative as it was recently shown that due to inertia of the hydrochemical system, the present-day non-contamination of lake waters does not imply a systematic non-pollution of tributaries (Bootsma and Hecky, 1993; Branchu et al., 2005a). Computations of chronic contamination response, using simple 3-boxes model, indicate that once pollution is detected, it will be persistent for a long time depending on the element reactivity. This reactivity linked to liquid-solid reactions is associated to biological and physico-chemical processes described here. A global watershed monitoring program should then be organised in the near future. Monitored parameters should be relevant with metallic and organic pollutants and also euthrophication.

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Table 1. Analytical characteristics for water analysis.

Elements	Relative standard deviation (%)[1]	Reproductibility (ICP-MS) %[2]	Detection limit (ICP-MS)[3]	Hydrobios Bottle Blank
tmmol L^{-1}				
Cl	1			
SO4				
K	5			
Na	1			
Ca	2			
Mg	2			
µmol L^{-1}				
F	5			
Al	5			
Si	2			
Sr	2	1	0.0008	<DL
Ba	1	4	0.0014	<DL
nmol L^{-1}				
Fe	2			
Cu	3	8	3.2	<DL
Zn	2	3	7.6	25.8
Cr	4	9	1	<DL
Mn	4	9	1.3	<DL
Ni	3	6	1.7	<DL
Mo	3	12	1.2	<DL
Cd	6	18	0.4	<DL
Pb	2	18	0.2	0.4

<DL: concentration lower than detection limit

[1] Mean value computed using all analyses performed 3 times in repeatability conditions

[2] Computed using two analyses performed in reproducibility conditions in the lower concentration range

[3] Detection limit=3σ blank value. σ calculated with 15 blank determinations

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Table 2. Major ion concentrations (µmol L^{-1}, except alkalinity in µeq L^{-1}).

Sample/ depth	Ca	Na	Mg	K	Cl	SO$_4$	Alkalimity	F	Si	Ionic balance (%)
P1 station (water depth: ca. 215 m)										
10	455	922	322	151	152	5.7	n.a.	<[*]	15.7	–
50	458	860	295	154	105	1.1	n.a.	22.2	12.8	–
100	483	902	312	162	106	<	n.a.	18.1	51.6	–
150	486	902	306	160	119	1.6	n.a.	20.0	67.6	–
190	490	948	312	190	97	<	n.a.	16.5	87.9	–
P2 station (water depth: ca. 200 m)										
0	450	861	294	151	125	4.7	2333.9	22.0	14.6	0.2
10	452	880	295	140	128	2.7	n.a.	19.9	18.9	–
20	458	885	305	152	136	11.1	2368.2	18.9	19.6	0.2
30	470	880	313	161	140	38.3	2397.8	21.4	18.9	0.2
50	451	880	294	156	95	<	n.a.	20.8	18.2	–
75	459	887	298	165	153	3.8	n.a.	20.0	19.2	–
100	446	859	292	153	55	<	n.a.	17.0	50.2	–
125	463	886	300	166	104	7.8	2461.3	17.0	58.7	0.6
150	464	888	292	161	75	<	n.a.	16.7	66.9	–
197	453	854	260	164	114	7.0	2400.7	14.3	103.2	2.1
P3 station (water depth: ca. 245 m)										
5	508	923	314	166	104	<	n.a.	<[*]	17.8	–
10	494	910	315	167	85	<	n.a.	19.5	18.5	–
25	492	902	305	176	106	<	n.a.	19.6	18.9	–
50	484	906	304	182	79	7.0	n.a.	15.6	17.1	–
75	482	895	301	173	133	11.4	n.a.	16.5	17.4	–
100	483	916	314	171	171	6.8	n.a.	21.9	49.1	–
150	501	940	313	182	141	5.4	n.a.	22.5	78.7	–
200	499	897	317	170	142	2.9	2407.3	20.2	104.3	5.8
240	496	906	309	164	99	1.6	2402.3	21.8	133.89	6.5
Average	474	895	303	164	115	<5.3	2395.9	19.2	45.0	–
SD (%)	4.1	2.7	4.2	7.0	24.1	>146	1.6	12.5	78.8	–
Tributaries										
Songwe	317.4	504.1	206.9	146.1	<	<	1267.9	<	355.3	14.5
Kiwira	179.7	2659.8	203.7	346.6	1037.2	72.2	2294.4	79.6	4247.1	3
Mbaka	237.5	867.9	177.7	184.1	24.1	<	1751.4	<	544.7	2.9
Lumbila	221.6	209.6	99.5	56.6	<	<	815.1	<	296.2	5.4
Lufirio	490.7	683.1	232.4	108.1	<	<	2120.0	<	297.6	2.7
Average	289.4	984.9	184.0	168.3	–	–	1649.8	–	1148.2	–
SD (%)	42.5	98.2	27.8859	65.5	–	–	37.0	–	151.1	–
Hydrothermal springs										
Mapulo	950	53 210	910	1750	7120	3120	50[a]	50.5	1780	–
Kasimulo	1130	58 230	930	1890	6270	3890	45[a]	41.3	1520	–
Average	1040	55 720	920	1820	6695	3505	47.5	45.9	1650	–

n.a.: Not analysed

<: Below calibration limit, in this case average is computed using the first calibration point

[a] Values calculated from the difference of meq cations minus meq anions

[*] Not considered for average and SD computations (see text)

Table 3. Trace element concentrations (nmol L^{-1}).

Sample/ depth	Fe	Al	Ti	Cr	Mn	Ni	Cu	Zn	Sr
P1 Station (water depth: ca. 215 m)									
10	n.a.	770.0*	8.8*	82.9*	23.4*	12.1*	54.8*	161.9*	2377.5*
50	334.1	1223.1	10.1	40.2	25.9	37.2	2311.9	335.9	1354.6
100	277.5	1179.0	16.9	36.7	30.8	37.4	2105.9	360.4	1571.8
150	286.1	1323.9	14.7	38.8	71.3	46.3	2179.1	831.4	1589.1
190	230.8	723.8	9.5	31.3	122.6	29.7	1914.4	283.9	1577.0
P2 station (water depth: ca. 200 m)									
0	521.1	2036.6	14.9	32.7	187.0	35.9	1909.3	541.7	1571.5
10	714.8	1114.5	10.3	28.2	118.6	23.2	1774.9	248.7	1500.5
20	221.9	872.8	7.3	34.3	20.1	26.3	1979.4	279.9	1585.3
30	211.8	800.2	7.5	30.8	16.0	26.8	1864.2	239.6	1509.9
50	265.0	1005.9	10.1	35.2	20.5	27.8	1984.7	281.7	1577.1
75	198.0	743.8	7.5	31.0	13.7	28.0	1922.7	250.5	1526.8
100	188.7	659.3	7.5	29.3	13.7	21.6	1778.9	246.6	1578.3
125	296.0	844.7	9.2	29.0	14.1	26.1	1798.6	291.8	1510.7
150	222.6	1078.9	9.0	33.4	25.9	30.2	1950.3	270.3	1605.0
197	428.7	1691.3	11.8	79.3	1076.8	82.7	3847.5	567.2	1567.4
P3 station (water depth: ca. 245 m)									
5	698.7	3129.7	24.1	39.9	77.0	87.5	2204.6	979.2	1620.8
10	399.8	1595.8	11.1	35.5	22.9	34.6	1989.6	312.5	1552.8
25	258.6	1213.7	8.3	42.7	36.3	41.2	2426.2	307.5	1532.0
50	194.6	1269.9	9.4	38.7	19.1	39.0	2279.5	307.7	1554.9
75	282.2	1298.0	9.8	44.4	19.6	39.4	2437.2	333.8	1594.1
100	n.a.	1483.4	7.8	38.1	24.5	39.6	2126.2	326.5	1520.0
150	224.9	713.6	9.3	39.2	17.4	40.9	2266.9	305.1	1643.4
200	208.6	1955.4	9.3	38.5	859.0	32.3	2179.1	302.4	1573.7
240	417.2	1151.9	9.4	41.7	1873.3	43.4	2338.5	370.0	1573.5
Average	321.9	1265.6	10.6	37.8	204.6	38.1	2155.2	372.8	1556.1
SD (%)	47.3	44.0	36.1	26.9	221.7	42.8	19.6	50.4	3.6
Tributaries									
Songwe	637.1	1186.5	20.9	32.2	192.5	25.2	1816.0	227.2	925.6
Kiwira	1487.2	3856.1	210.2	30.1	435.3	28.6	1729.5	263.5	601.9
Mbaka	366.0	6674.1	16.7	28.8	24.6	22.8	1759.0	207.2	932.4
Lumbila	1213.2	2113.5	23.3	32.2	95.4	27.8	1874.1	246.7	660.5
Lufirio	1505.1	<	14.3	31.8	252.0	32.8	1854.9	236.0	1736.4
Average	1041.7	<2780.9	57.1	31.0	200.0	27.4	1806.7	236.1	971.3
SD (%)	49.5	>92.8	150.1	4.9	79.0	13.8	3.4	8.9	46.7
Hydrothermal springs									
Mapulo	1414	482	105	23	268	<	1845	242	30 229
Kasimulo	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a.: Not analysed

<: Below detection limit or calibration limit for Al. In this case average is computed using the first calibration point or the detection limit.

* Not considered for average and SD computations (see text)

Table 3. Continued.

Sample/ Depth	Mo	Cd	Ba	Pb
P1 station				
10	12.5*	1.9*	940.8*	0.9*
50	7.5	0.8	411.7	41.5
100	8.5	1.0	500.9	39.3
150	8.4	2.7	511.4	38.1
190	8.3	0.7	494.5	34.2
P2 station				
0	8.6	2.4	531.0	51.1
10	8.1	0.6	470.1	32.9
20	9.7	1.0	513.4	34.5
30	8.3	0.7	473.6	32.6
50	8.7	0.9	505.9	36.5
75	8.6	0.3	474.6	33.2
100	8.6	0.4	511.2	30.3
125	8.2	1.0	478.8	34.3
150	9.7	5.3	515.7	34.2
197	11.3	1.8	510.8	79.4
P3 station				
5	10.2	3.1	561.1	86.9
10	10.3	1.4	502.2	39.2
25	11.2	1.0	484.5	40.7
50	10.0	1.0	490.3	37.7
75	9.8	1.1	504.2	46.6
100	8.9	1.7	478.1	38.4
150	9.4	0.8	524.8	45.6
200	8.6	1.0	513.0	36.8
240	8.5	0.9	515.7	55.4
Average	9.1	1.4	499.0	42.6
SD (%)	11.1	81.1	5.7	33.4
Tributaries				
Songwe	9.4	<	198.2	37.2
Kiwira	92.6	2.2	118.4	36.9
Mbaka	26.0	<	154.6	34.9
Lumbila	3.0	<	83.3	38.0
Lufirio	6.6	<	258.1	35.4
Average	27.5	< 0.6	162.5	36.5
SD (%)	136.1	–	42.1	3.5
Hydrothermal springs				
Mapulo	98	<	781	36
Kasimulo	n.a.	n.a.	n.a.	n.a.

n.a.: Not analysed

<: Below detection limit. In this case average is computed using detection limit.

* Not considered for average and SD computations (see text)

Table 4. Comparison with previous temperature, conductivity and dissolved silicon data.

Ref./date	Depth range	Temperature (°C)	Conductivity (µS cm^{-1})	Si (µmol L^{-1})	Ref
Central Basin: Jun 1976	0–80	25.61	248.5		Gonfiantini et al. (1979)
	80–200	23.07	258.2		
Central and south. Basins Jan 1992	0–80	26.15	257.6		Halfman (1993)
	80–200	23.21	(K25) 261.2		
North. Basin: Oct 1993	0–80	24.86	(K25) 256.1	17.5	This study
	80–200	23.19	259.1	71.8	
Whole lake: Sep 1996–Sep 98	0–105			20.7±3.1	Bootsma et al. (2003)
	105–220			76.7±10.0	
North. Basin: Sep 1997	0–80	24.48	(K25) 255.5		Vollmer et al. (2002)
	80–200	23.16	257.3		

Table 5. Major element mean epilimnetic concentrations (and standard deviation in %): comparison with previous studies.

		Ca	Mg	Na	K	Cl	Alk.	Ionic balance
				µmol L^{-1}			µeq L^{-1}	(%)
Gonfiantini et al. (1979)	0–250 m[1]	470	311	894	164	140	2379	0.6
–Jun 1976		(3.7)	(1.3)	(1.7)	(3.2)		(1.7)	
Hecky (unpublished)	0–250 m[2]							
–Nov 1980		451	258	960	136	140		
		(3.0)	(27.7)	(3.4)	(7.6)	(6.3)		
May 1981		442	278	873	160	137		
		(3.0)	(1.9)	(1.8)	(1.6)	(4.2)		
This work	0–240 m	474	303	895	164	115	2396	1.8
(Oct 1993)		(4.1)	(4.2)	(2.7)	(7.0)	(24.1)	(1.6)	
Variability (coefficient of variation in %)		3.3	9.5	5	9.9	1.3	0.5	

[1] Data are available for one 640 m deep water column.

[2] Data are available for one 600 m deep water column.

Table 6. Comparison between ranges of concentrations (µg/L) for Cr, Ni, Cu, Zn, Mo, Cd, Pb, F and Mn, i) analysed in Lake Malawi, ii) published for other East African lakes (Bugenyi, 1982; Cohen et al., 1996; Challe, 2002) and iii) from the WHO guidelines (2004).

Concentration (µg/L)	Malawi	Tanganyika[1]	Victoria[2]	Edward[3]	George[3]	WHO (2004)
Cr	1.5–4.1					50^{P}
Ni	1.3–5.1					20^{P}
Cu	112.8–244.5	<6	5–57.6	15–130	90–110	2000
Zn	15.7–64.0	<1	25–125			5000^{*}
Mo	0.7–1.1					70
Cd	<0.1–0.6	<10	2–8	9–11	5–6	3
Pb	6.3–18.0	0.007–0.12	7–94	1.1	6	10
Mn	0.8–102.9	10	50–3280			400^{C}
F	271.7–427.5	1060				1500

[1] Challe (2002) except F (Kilham and Hecky, 1973)

[2] Compilation from Cohen et al. (1996)

[3] From Bugenyi (1982)

[P] Constituents for which there is some evidence of a hazard but the available information on health effects is limited.

[*] From WHO guidelines, 2nd edn. (1998)

[C] Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water.

(Grey filled cases correspond to excess values relative to WHO guidelines)

Table 7. Annual water budget in Lake Malawi (Branchu et al., 2010.)

Volume (km^3)[a]	
Lake	7790
Epilimnion	2760
Metalimnion	2310
Hypolimnion	2720
Input (km^3 y^{-1})[b]	
Rivers	40.2
Rain	38.5
Total	78.7
Output (km^3 y^{-1})[b]	
Outflow	13.5
Evaporation	65.2
Total	78.7
Vertical exchange time (y)[a]	
Epi-metalimnetic	4
Meta-hypolimnectic	18
Residence time (y)[c]	
Lake	99
Epilimnion	5

[a] From Vollmer et al. (2002)
[b] Adapted from Bergonzini (1998)
[c] Residence time computation assumes steady state conditions. Residence time=volume/input

Table 8. Chemical budget of Lake Malawi.

	Ca	Na	Mg	Cl	Alk	K	Si
Mass (Gmol)							
Lake	3786	6893	2486	1610	18 707	1324	772
Epilimnion	1292	2456	905	386	6431	469	46
Input (Gmol y^{-1})	7.5	15.2	4.6	1.7	25.5	2.3	7.9
Riverine Input (%)	96	96	98	88	75	93	84
Input $[R]_i$ (µmol L^{-1})	94.7	193.3	58.4	21.1	324.4	29.0	100.1
Output (Gmol y^{-1})	6.2	10.6	3.6	2.0	29.0	2.3	0.3
Residence time (y)[a]							
Lake	508	459	540	966	733	580	98
Epilimnion	4	4	4	3	4	4	0.7

[a] Residence time computation assumes steady state conditions. Residence time=mass/input

Computed from hydrological data of Table 7, and chemical data of rain (Bootsma et al., 1996, 2003), river (this study completed by Hecky and Bugenyi, 1992) and water column (this study, completed for depth >250 m by Gonfiantini et al., 1976).

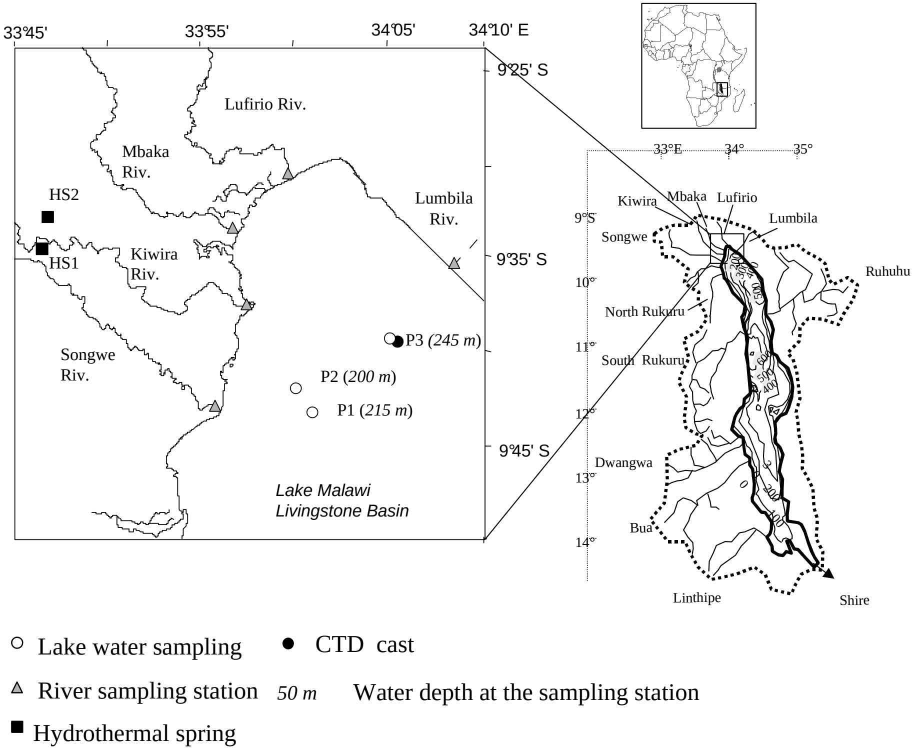

Fig. 1. Schematic bathymetric and hydrographic map of Lake Malawi and locations of water sampling stations in the Livingstone Basin and its catchment. Inset box shows location of Lake Malawi in Africa.

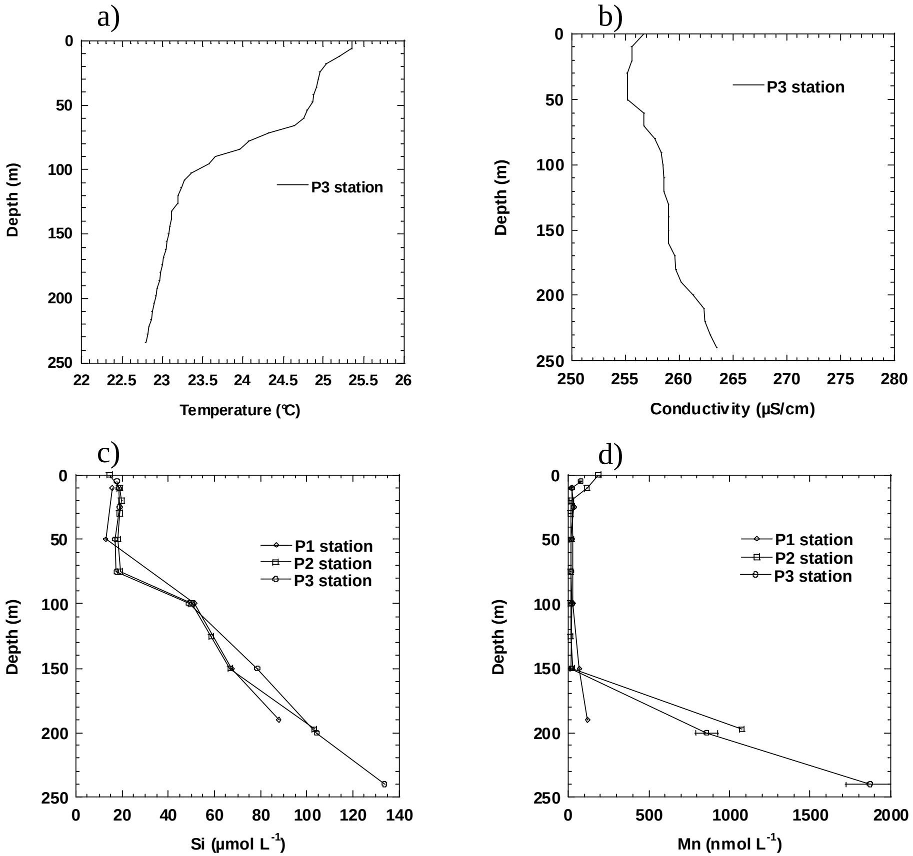

Fig. 2. Depth profiles of **(a)** temperature, **(b)** conductivity and dissolved (0.01 µm filtrates) **(c)** Si and **(d)** Mn. Error bars (only reported for P3 station due to clarity considerations) correspond to 2×Table 1 standard deviation.

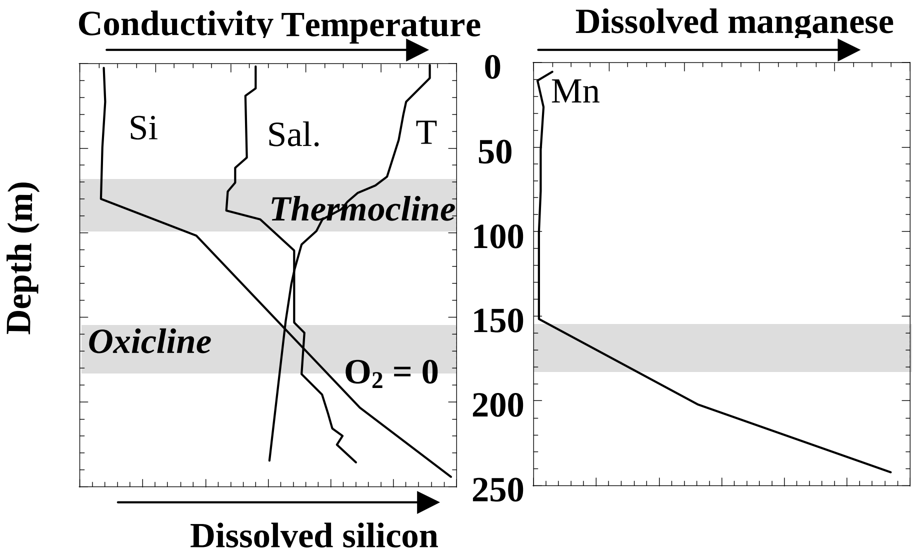

Fig. 3. Physical-chemical and hydrodynamic features of the water column Concentration/Temperature/Conductivity scales are relative.

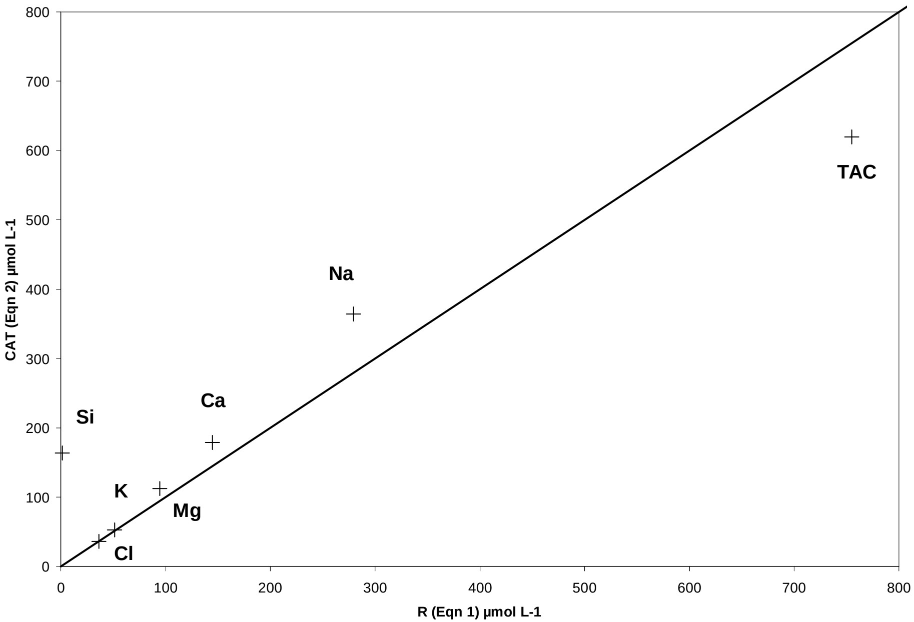

Fig. 4. Major elements (Na, Ca, Mg, K, Si and alkalinity) comparison between R and CAT.