Lake Victoria - Carbon, Nitrogen, Phosphorus and Stable Isotope ($\delta^{13}C$) comparison between lake and catchment sediments

LAXMI GAYATRI DEVI BASAPURAM

MSc Thesis (30 ECTS credits)
Science for Sustainable development
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1. Abstract:

Lake Victoria situated in East Africa faces an acute problem with eutrophication. Many reasons like agricultural production, industrialization, anthropogenic processes, the introduction of species, and economic activities have caused a stress to the overall well-being of the lake. Excess carbon, nitrogen, and phosphorus drive an increase in productivity which affects eutrophication. Previous studies on sediments and nutrient concentrations in the lake have concluded that nutrient concentrations increase due to release from the catchment. This study focuses on catchment sediments collected from four different sites and compares the results with sediments from two additional sites in the lake. The sediment core from Siaya indicates the highest concentrations of TOC (180 g/kg), TN (13 g/kg) and TP (17000 µg/L). It is a rural site and poor agricultural practices such as the burn and slash, use of too many fertilizers, clearance of land, atmospheric deposition and precipitation increase elemental concentrations in the sediments compared to the more urban sites. In the lake sediments, the BILL core had higher concentrations of TP (430 g/kg) and TN (16 g/kg) compared to the other site (LV-95) which is located far away from the margins of the lake. This core, however, had high TOC levels (180 g/kg). The increase of nutrient levels in lake sediments is thought to be due to non-point sources from the catchment. Analyses of stable carbon isotope were used to infer the different organic matter source in the sediments. Based on the range of values for δ¹³C vs. C/N it is inferred that aquatic algal production and C4 vascular plants are the dominant sources for the organic matter input. The chemical characterization of catchment and lake sediments provides a qualitative link to nutrient influx and eutrophication in the lake.

Keywords: Nutrients, Stable isotope (δ¹³C), Agriculture, Industrialization, Eutrophication.
2. Introduction:

Eutrophication is an environmental change that is caused by the increase of nutrient content in water bodies. This increase, triggers the growth of toxic blue-green algae, making the water bodies unfit for consumption or use. Lake Victoria has been facing eutrophication problem several times throughout history. The Lake Victoria basin contributes towards agriculture, food production, transportation, shelter, drinking water, energy and also as a pathway for draining wastes. It is these activities, that pose threat to the water body. Today, almost 30 million people live in its catchment. The population started to increase around the lake in the 1900s when the railroad to Kisumu and Kampala was built. Commercial fishing led to the introduction of tilapia and Nile perch which targeted the native cichlids and quickly reduced their numbers in the lake by 1970. The change in fish communities affects the response of algal communities in a lake ecosystem, this change is termed a top-down controversy (Hecky 1993; Hecky et al. 2010; Hecky et al 2006; Kayombo and Jorgensen 2003; World Bank 1996).

The change in temperature, nutrients and oxygen levels in the lake, is in contrast to the change in phytoplankton population. The temperature and stratification of the lake changed from 1960 to 1990, due to climatic conditions. For example, high temperature during summer and a long rainy season characterized the years 1962 to 1964. This increase was observed after the mixing season extending from June to August. The change in lake’s stratification brought down the oxygen levels rapidly-with the outbreak of stratification in the lake. The deeper levels of the lake have been anoxic since 1990-1991. Almost half of the lake is affected by this change and is one of the main causes that facilitate the accumulation of phosphorus. The chlorophyll concentrations have increased 10 fold, creating a pelagic zone in the upper 20m of the lake, due to saturation in oxygen levels. This increase of photosynthetic activity has therefore reduced phosphorus deposition by 10 fold since the 1960s (Hecky 1993; Hecky et al. 2010; Hecky et al. 2006).

The reduced oxygen levels at the bottom of the lake, throughout the stratified season, has strengthened the process of denitrification. The oxi-anoxic conditions in the lake, maintaining a turbulent diffusion system, supply electrons that stimulate denitrification. This build-up of denitrification lowers the ratios of dissolved phosphorus to fixed nitrogen, therefore, such low ratios of N:P favors the growth of blue-green cyanobacteria, the dominant phytoplankton species in these waters (Hecky 1993; Kayombo and Jorgensen 2003).

Another threat that has changed the conditions in the lake system is the growth of water hyacinth. It is a flowering plant that grows in nutrient-rich water bodies and its first reported occurrence in Lake Victoria was during the late 1980’s. The plant spread quickly, onto the entire lake, blocking the waterways, areas near bays and landings in less than a decade. It has created a great stress on the lake by reducing the oxygen supply that killed fishes, acting as a physical barrier for transportation, fishing, water supply, breeding a different variety of vector mosquito species and a home for snakes (Kayombo and Jorgensen 2003; World Bank 1996).

These effects mentioned above are occurring in the lake waters. Meanwhile, in the lake’s catchment, a lot of other stresses are happening that play a major role in eutrophication of the lake. The main threat is the need for agricultural land due to population increase, leading to deforestation conjoined with poor agricultural practices. The farmers used fire to clear the land and the burnt ash was used as a nutrient for plant growth. The ash is rich in phosphorus, with low concentrations of sulfur, iron, potassium, and nitrogen that are usually transported into the lakes through rain, soil erosion or atmospheric deposition. The other contaminants or pollutant
runoff is due to the use of pesticides in agricultural practices, urban wastewater inputs, industrial activities around the lake such as gold mining and textile industries, have contaminated the lake with nutrients since the 1950s (Kayombo and Jorgensen 2003; World Bank 1996; Hecky et al. 2006).

All these changes have increased algal growth in the lake five-fold and reduced the water quality. Lakes are considered to be the receiving systems that work as a natural and effective sink for nutrients, therefore whichever material enters Lake Victoria stays in it. This is due to the poor flushing system of the lake (Hecky et al. 2006; Kayombo and Jorgensen 2003; World Bank 1996; Hecky 1993; Hecky et al. 2010).

3. Background:

a. General description:

Lake Victoria is the world’s second largest freshwater lake, its surface area is 68,000 km² and a catchment that extends up to 193,000 km². It is located in between latitudes 0° 30’N to 3° 12’S stretching to 412 km (almost reaches the equator) and longitudes 31° 37’ to 34° 53’E, stretching 355 km from west to east. The capacity of this shallow, tectonic lake is 2,760 km³, with an average depth of 40 m. It is situated at an altitude of 1,100 m above sea level and with a predicted shoreline of 3,500 km. The shoreline has many shallow bays and convoluted inlets, most of which are swamps and wetlands. The water residence time in the lake is 23 years and the flushing time (volume/average outflow) is 138 years. It is because of low flushing and long residence times, that any material entering the lake takes a long time to leave (Kayombo and Jorgensen 2003; World Bank 1996).

The lake is surrounded by five countries, three of which share most of the catchment (Uganda, Tanzania, and Kenya) and two share the lake’s drainage basin (Rwanda and Burundi). These countries contribute to 18% of input to the lake through riverine discharge. From the Tanzanian area there are seven rivers (Mara, Kagera, Grumeti, Mbalageti, Mirongo, Mori, and Simiyu), four rivers from Uganda (Bukora, Katonga, Kagera and Sio) and a total of ten rivers flow from Kenya (Nyando, Sio, Nzoia, Kibos, Kuja, Migori, Riaria, Sindumiriu, Yala and Mawa). Out of all these rivers, Kagera is the largest that also drains from Rwanda and Burundi. The rest of the input (86%) is through rainfall (precipitation), which is almost similar to the evaporation rates (76%) from the lake. Discharge into River Nile is the only outlet from the lake. The minimum discharge per year is 23.4 km³, which accounts for 24% of the outlet capacity- more than the input. These Nile waters provide hydroelectricity, for the people living around the lake, at the Owen Falls (Kayombo and Jorgensen 2003; World Bank 1996).
b. The fate of C, N, and P in Wetlands:

There are three major nutrients that play a crucial role in contributing towards eutrophication. The increased input of these nutrients into the water body results in eutrophication. The study of each of these nutrients and their fate in a wetland is described as follows:

i. Carbon:

Carbon is an important nutrient for living organisms. It is a source for algal photosynthesis, a vital component in cell structure and a source for electron supply for microbial processes. Carbon dioxide is available through the atmosphere, respiratory activity of living organisms and from carbonate alkalinity (which is not a limiting factor in natural water) (King 1970; DeLaune and Reddy 2008).

The transfer of atmospheric carbon dioxide to aquatic systems is a slow process hence, the plants adapt to the carbonate alkalinity of the waters, as their source of carbon dioxide. The alkalinity in any water body is due to excess amounts of free carbon dioxide released through a continuous reduction of bicarbonates and other forms of inorganic carbon. This available free carbon dioxide is taken up by the plants for photosynthesis. The photosynthetic activity depends on the abundance of oxygen, carbon dioxide, and light. The transfer rates of carbon dioxide uptake, for photosynthetic activity in algae, depends upon the concentration of free carbon in the aquatic systems (King 1970; DeLaune and Reddy 2008).

The Carbon cycle in aquatic systems or wetlands serves as a source or a sink. The stages of carbon absorption till decomposition are as follows:

- **Plant biomass carbon**: The inorganic carbon that is taken up by the aquatic plants or algae is converted to organic carbon, this is known as primary production. The production in wetlands is usually higher when compared to terrestrial ecosystems and are a reservoir for 68% of land-based carbon emissions. When there is an increased intake of nutrients from river floods and ground waters, the production increases.

- **Particulate organic matter**: Organic debris from plants, litterfall from forested wetlands undergo decomposition which is a major source of detritus to the soil. Organic carbon is stored in both living substances like algae, microbial biomass, and vegetation, along with non-living substances like dead plant debris, humic and nonhumic substances in soil organic matter, which are more in wetlands. This type of organic matter provides energy and organic carbon is slowly mineralized through microbial catabolic activities as inorganic forms of carbon.

- **Microbial biomass carbon**: The decomposition of detritus into small fragments, is done through heterotrophic microflora present in the soil. The microbes in the soil have an important role in balancing the energy in the ecosystem, through regulating the nutrient availability for primary production and decomposition.

- **Dissolved organic matter (DOM)**: The composition of organic matter that is dissolved in water represents dissolved organic carbon in that particular aquatic system. The DOM is less than 1% of the total soil organic matter but accounts for 90% of the surface waters as total organic carbon (TOC).

- **Gaseous forms of Carbon**: Carbon dioxide and methane are the end products released after the decomposition of the organic matter under aerobic and anaerobic conditions respectively. The pH of water is responsible to maintain the balance between dissolved and inorganic gaseous carbon. The decomposed organic matter releases carbon dioxide that is fixed during photosynthesis, whereas the organic matter which is undecomposed retains in the soil through humification (long-term storage of nutrients and contaminants) (DeLaune and Reddy 2008).
ii. Nitrogen:

The productivity in ecosystems is regulated by a limiting nutrient - nitrogen. Nitrogen exists in both organic form as nucleic acids, amino acids, proteins and urea, and in inorganic form as dinitrogen, ammonia/ ammonium N, nitric oxide, nitrous oxide, nitrate, and nitrite. The nitrogen reactions in the biosphere are responsible for the productivity and functioning of the ecosystem. The sources of nitrogen into wetlands are of two types, point and nonpoint. Point sources are wastewaters from municipalities, industries, construction sites, sanitary sewers, mines and oil fields. Nonpoint sources are runoff from agriculture, urban runoff, atmospheric deposition and biological nitrogen fixation (DeLaune and Reddy 2008).

The nitrogen cycle is almost similar to the carbon cycle, where the fate of Nitrogen is discussed below and the components are known as reservoirs of nitrogen:

**Plant biomass nitrogen**: The essential nutrient for the productivity of algae and macrophytes in aquatic systems is nitrogen. Their sources are biological fixation, mineralization of organic nitrogen in soil and water. In plants, it is responsible for the process of photosynthesis and lower concentrations would slow down the enzyme activities in roots, leaves, and tissues for the production of proteins.

**Particulate organic nitrogen**: Soil organic matter is the largest storage unit of nitrogen, which includes living forms of organic matter such as microbial biomass, vegetation- submerged and emerged and nonliving forms such as dead plant matter and peat. Soil organic matter that accumulates over time, is not readily bioavailable. Other factors that influence the bioavailability of nitrogen are hydrological fluctuations, electron acceptor availability, temperature, microbial activity and water depth.

**Microbial biomass nitrogen**: The nitrogen in the microbial biomass is the most active and key component of the cycle and helps in regulating the quantity of bioavailable nitrogen. The microbes use both organic and inorganic forms of nitrogen for the growth of cells.

**Dissolved organic nitrogen (DON)**: In a detrital layer, the dissolved organic nitrogen is produced via leaching of the materials from dead organic matter. Some amounts of DON is remineralized based on the characteristics of the source material.

**Inorganic forms of nitrogen**: Ammonium, nitrate, and nitrite are the general inorganic forms found in wetlands and are unstable.

**Gaseous end products**: Ammonium volatilization and denitrification, are the two procedures that export ammonia, nitrous oxide, and nitrogen respectively from soil and water to the atmosphere (DeLaune and Reddy 2008).

iii. Phosphorus:

There has been much research to study the fate of phosphorus in wetlands since the past five decades. Phosphorus is the important nutrient for the development of vegetation in terrestrial as well as aquatic ecosystems. The large-scale inputs of phosphorus in any ecosystem is through atmospheric deposition and natural mineral weathering. The transfer of phosphorus from uplands to aquatic systems is rapid and had increased during the urbanization and green revolution, with the onset of using fertilizers in agricultural fields. The capacity to retain phosphorus in wetlands has decreased, due to development of new technologies, to meet the food needs of the elevated population (DeLaune and Reddy 2008; Reddy et al. 1999; Heathwaite et al. 1996).
Phosphorus entering the aquatic systems occurs in both inorganic and organic forms. The relative distribution of these forms depends upon the type of land use in the catchment, soil conditions, and type of vegetation. Inorganic phosphorus is the most bioavailable form of phosphorus, whereas organic P has to be converted to inorganic to be available. The cycle is effective and includes the exchange or interaction between abiotic and biotic pools. The biotic processes of storage of phosphorus are assimilation by vegetation, plankton and microorganisms and the abiotic processes would be sedimentation, adsorption to soils, precipitation and exchange between soil and water. The phosphorus cycle is strongly related to sediment cycle and takes a long time for the transformation process (Reddy et al. 1999; Heathwaite et al. 1996). The following steps are included in the phosphorus cycle:

1. The process of weathering, which is hydrolysis or chelation of rock minerals, release phosphorus into soils.
2. From the soil, through assimilation (enzyme synthesis), P is taken up by the plant biota. Through dissimilation (bacterial decomposition), P is deposited back into the soil.
3. Either through soil erosion or through assimilation and dissimilation, P is transferred to water bodies, where they occur as soluble reactive forms (orthophosphate).
4. The P in water is then adsorbed to the underlying sediments and are known as hydrospheric sediments when absorbed by terrestrial sediments they are known as atmospheric sediments. Although these sediments can undergo desorption and released back into the water bodies or atmosphere respectively.
5. The last step, the rocks are formed after a continuous deposition of the sediments.

Within the series, the phosphorus does not undergo redox reaction and geochemical flow depends upon the transport of suspended sediments in water and emission of dust into the atmosphere (Heathwaite et al. 1996).

4. Objectives:

Most of the investigations till today have focused on the deterioration of the lake and its water quality. There is very little information available on the lake sediments and those from the catchment area. The aim of this project is to study the distribution of total C, N, and P, in lake sediments and compare this with the catchment sediments. The analysis was done in the first 100 cm of sediment samples, collected from different locations in the catchment and the lake itself. This comparison of elemental concentrations and the carbon isotope analyses in same samples will help to understand the flow of nutrients, the changes in nutrient cycle and the possible reasons for eutrophication of the lake.
The study provides an idea about, the rate of nutrient loading into the lake, from different areas with distinctive features. This is the first survey, that compares the lake and catchment sediments in the Lake Victoria basin to understand the reasons for rapid eutrophication process in the lake.

a. Research questions:

1. What are the concentrations of C, N, and P in the catchment and the lake sediments?
2. What changes are observed in the nutrient cycle and what are the reasons for these changes?
3. What can be inferred from the results about the causes for eutrophication in Lake Victoria?
b. Site description:

The chosen sites in Lake Victoria catchment represents different landscape features and are wetlands. The lake basin is shallow compared to other rift lakes. A total of six sites have been cored from the catchment area and two from the lake, but this study focuses on four sites from the catchment and the two lake sediment cores. Each site has different geological conditions, land-use practices, and urban development. The map below shows sampling locations, followed by their geographical position (Odhiambo 2016) (Njagi 2017).

![Map of sampling locations](image)

**Figure 1:** Sampling locations in and around Lake Victoria.

<table>
<thead>
<tr>
<th>Sampling Area</th>
<th>Sample core code</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kisumu</td>
<td>DK</td>
<td>0°7'59.94&quot; S</td>
<td>34°44'57.24&quot; E</td>
</tr>
<tr>
<td>Homa Bay</td>
<td>HK</td>
<td>0°31'37.32&quot; S</td>
<td>34°26'37.56&quot; E</td>
</tr>
<tr>
<td>Siaya</td>
<td>KK</td>
<td>0°4'7.50&quot; N</td>
<td>34°7'43.98&quot; E</td>
</tr>
<tr>
<td>Busia</td>
<td>SPK</td>
<td>0°10'32.74&quot; N</td>
<td>34°0'23.80&quot; E</td>
</tr>
<tr>
<td>Buvuma</td>
<td>BILL</td>
<td>0°20' N</td>
<td>33°16' E</td>
</tr>
<tr>
<td>Lake Victoria</td>
<td>LV95-2P</td>
<td>00°27.70&quot; S</td>
<td>33°21.10&quot; E</td>
</tr>
</tbody>
</table>

**Table 1:** Geographical Coordinates of the sampling points.
Kisumu (DK) (Urban site):
It is a port city in Kisumu county. The country has a population of about 1 million, 40% of which live in the main Kisumu city. The common economic practices are fishing and agriculture, which are supported by the lake. Various industries are located within the country eg: fishing, agriculture, and textile processing. The climatic conditions are warm and humid since the average rainfall ranges from 1,200 to 1,300 mm annually. Temperatures in such areas range between 20 and 35 °C (Njagi 2017).

Homa Bay (HK) (Urban site):
It is the capital town of Homa Bay County. The people here practice fishing, which has lately been affected by the growth of water hyacinth. They also practice small-scale farming of crops like sugar cane, potatoes, and maize. The geological characteristics of this area are volcanic rock types and formation of grey medium-grained tuffs. They experience two types of rainy seasons- long (March-May) and short (September-November), with an average rainfall of 1,100 mm annually. Temperatures ranges are 26 to 34 °C. January to March are the hottest months and April to November are the coolest (Njagi 2017).

Siaya (KK) (Rural site):
Both DK and HK sites are situated at an elevation lower than KK and SPK. Siaya is a rural area, with a good potential for irrigation, livestock, and agriculture. This is because they are situated at higher altitude. Ferralsols, basalts, rhyolites, and dacites constitute the basic geology in the area. The county experiences rainfall a pattern almost similar to Homa Bay, long rainfall (March- June) and short rainfall (September- December). The highlands of Siaya receive on an average 800-2000 mm of rainfall annually, whereas the lowlands receive 800-1600 mm of rainfall annually. Temperature ranges from 27 to 28.8 °C (Abura et al 2017).

Busia (SPK) (Rural site):
This county lies at the entrance to Kenya and has a population of about 1 million and their main economic activities are farming, fishing, and trade. The tropical humid climate in this area is under the influence of Lake Victoria. The mean rainfall in Busia is between 900 mm and 1500 mm annually. Long rainfall is experienced during March- June and short rainfall between September- October. Average temperature ranges between 24°C and 26 °C (Kenya Information Guide 2015).

Buvuma island (BILL- Bavuma channel):
A group of 50 islands around Lake Victoria in Uganda is the Bavuma islands. Nearly 20,000 people are residents here. The popular economic activity in Buvuma islands is fishing. Few agricultural lands and forests have been cut down to burn charcoal. The climatic conditions of these islands are unclear (World Gospel Mission).
5. Methods:

a. Preparation Work:

Sediment cores HK, DK, SPK, and KK were collected using a Vibra corer, BILL using UWITEC™ gravity corer (Stager et al. 2009) and LV-95 were collected using piston core from a depth of 68 m (Talbot and Lærdal 2000). The cores were packed in long PVC pipes and stored at -18°C, the lake cores were sealed and stored at 4°C. For the laboratory analysis, the catchment cores were sliced into 1-cm samples and labeled. They were freeze-dried at -55 °C; the wet and dry weights were noted, before and after the process of freeze-drying to calculate the bulk density. The freeze-dried samples were homogenized and used for the different geochemical analysis (for the first 100 cm in all the cores).

b. Geochemical Proxies:

i) The concentration of the elements (C and N) and δ¹³C stable isotope analysis:

The samples at 5 cm intervals were weighed (200 mg each interval) and transferred into centrifuge tubes. For accurate determination of the elemental concentrations or stable C isotope analyses of organic matter, the sample must be decarbonated (Ramnarine 2011). Therefore, the samples were treated with few drops of 1N HCl. The procedure is explained in a stepwise manner in Appendix 1.

The decarbonated dried samples are transferred into Eppendorf tubes and shipped to the Stable Isotope Mass Spectrometry Laboratory, University of Florida, for CN and isotope analysis. In the lab, the samples were loaded into tin capsules and arranged, in an automated Zero Blank sample carousel with 50 position capacity, on a Carlo Erba NA 1500 CNS elemental analyzer. The samples are completely and spontaneously, oxidized by flash combustion at 1020°C, in an oxygen-rich atmosphere inside a quartz column. This combustion process converts all the inorganic and organic substances into combustion products. The sample gas is passed through a reduction furnace, at 650°C using Helium as a carrier.

The furnace consists of elemental copper that removes excess oxygen from the samples. The resulting stream is passed through a chemical trap, made of magnesium perchlorate to remove water and then swept through a 0.8-m gas chromatographic column, where nitrogen and carbon dioxide are separated by the thermal conductivity signal at 115°C. The signal is proportional to the concentration of carbon and nitrogen elements. The sample gas is then individually passed into a ConFlo 2 preparation system and into a Thermo Electron Delta 5 Advantage isotope ratio mass spectrometer. The flow mode of sample gases was continuous and was measured relative to the laboratory reference for both the gases. The carbon isotope results are expressed in standard delta notation relative to V-PDB (Vienna – Pee dee Belmenite).

ii) Phosphorus analysis:

The procedure for determining the concentration of phosphorus and its forms, in the sediment samples, is divided into two parts: 1) sequential extraction procedure (Standards, Measurements, and Testing extraction) and 2) spectrophotometry detection method (Blue Method).
The sequential extraction procedure or the SMT extraction is based on the Williams method and the final modification was done by Ruban. The extraction aims fractionation of phosphorus, this involves the leaching of three forms- inorganic phosphorus (IP), organic phosphorus (OP) and total phosphorus (TP) in calcareous sediments. The procedure can be used on siliceous and organic-rich sediments as well. The method is reliable and easy to handle and can be used to calculate the releasable phosphorus stocks from lake sediments (Wang et al. 2013; Pardo et al. 2004). The protocol for the extractions is described in Appendix 2 (Ruban et al. 1999).

The ‘blue method’ is a procedure, in which the production and degradation of phosphomolybdic acid take place, due to the presence of acidic molybdate solution with ascorbic acid. The blue color is due to the formation of a molybdenum complex that is measured at 882 nm, after the addition of potassium antimonyl tartarate solution. This reaction is stable for long periods (maximum of 30 minutes) and the blue color develops rapidly. The detailed protocol, along with the reagents required is explained in Appendix 2 (Murphy and Riley 1962).

6. Results:

   a. Total Carbon (TOC):

The total organic carbon graphs in Figure 2. is divided into two parts Zone A and B (0-50 cm and 50-100 cm respectively) for convenience in understanding the accumulation trend along the length of the core. Zone A is assumed as accumulation in recent years up to the last 300 years and Zone B follows deposition from 300 years to almost a thousand years.

In Kisumu (core DK), zone B shows continuous accumulation with a slight and very slow increase until 50 cm, whereas in zone A, drastic changes with two low concentration levels was recorded at around 100 years (23 g/kg at 36 cm) and around 30 years (13 g/kg at 16 cm). The highest amounts in the entire length of the core were observed in recent years (12 cm- 45 g/kg). In Busia (core SPK), zone B indicates consistent and steady accumulation whereas in zone A there is a steady core upward increase until the highest value (36 g/kg) concentration occurs at 6 cm.

In Homa Bay (core HK), zone A shows uniform concentrations. In Zone B the highest value (48 g/kg) occurs at 56 cm and then declines to the level as seen in zone A. In Siaya (KK core), TOC concentration in zone B maintains a patterned trend but indicates a rapid and continuous increase in accumulations core upwards in zone A. The highest value 180 g/kg concentration occurs in recent years around 20 cm.
Figure 2: TOC concentrations (g/kg) vs depth in sediment cores retrieved from the catchment in Lake Victoria.
b. Total Nitrogen (TN):

Figure 3: TN concentrations in (g/kg) vs depth in sediment cores retrieved from the catchment in Lake Victoria.

At all catchment sites, similar trends as for the TOC concentrations are observed for the TN concentrations. Just like the TOC trends in Siaya, the highest TN concentration (13 g/kg) in zone A at 20 cm, zone B follows the same trend as TOC in KK. In Kisumu zone, A has two inflection points for TN in the core upwards trend of 1.7 g/kg at 36 cm and 1.1 g/kg 16 cm. Furthermore, a sharp increase occurs in recent years 3.4 g/kg at 12 cm, zone B follows the same
trend as TOC. In Busia, a gradual increase in TN accumulation from zone B extending to zone A, with the highest concentration of 3.6 g/kg occurring at 3 cm. The total nitrogen concentrations in HK core is similar to the TOC distribution in the same core, concentration in zone A do not vary much and the maximum 4.6 g/kg value occurs around 56 cm in zone B.

c. C/N ratio:

The C/N trend for each of the cores is different from each other. A slight increase is observed in Kisumu in zone B at 100 cm (11.5) to 52 cm (12.4) till zone A at 48 cm (12.3) to 28 cm (13.8). A similar decrease in trend is observed in Busia and Homa Bay in zone A around 40 cm. KK has a rapid increase in zone A, with the maximum concentration (15.9) at 30 cm.

Figure 4: C/N ratio vs depth in sediment cores retrieved from the catchment in Lake Victoria.
d. $\delta^{13}$C- stable carbon isotope:

Stable isotope $\delta^{13}$C‰ values were observed to be decreasing from zone B to zone A in both Busia and Siaya. In Kisumu and Homa Bay, the trends show a steady gradual decrease core upwards followed by an increase of values in zone B.
e. Phosphorus: Phosphorus concentrations occur in three separate fractions - inorganic (IP), organic (OP) and total phosphorus (TP).

Figure 6: Phosphorus fractions vs depth in DK core (Kisumu) retrieved from the catchment.

Figure 7: Phosphorus fractions vs depth in SPK core (Busia) retrieved from the catchment.

Figure 8: Phosphorus fractions vs depth in HK core (Homa Bay) retrieved from the catchment.
Figure 9: Phosphorus fractions vs depth in KK core (Siaya) retrieved from the catchment.

In Kisumu (Fig. 6), the phosphorus concentration levels are mostly low (zone B) for the deeper sediment. In Zone A - the P fractions mostly show an increasing trend. The TP concentration is the highest 8900 mg/kg at 71 cm in zone B. This trend is same and low in zone A, followed by the next highest 3100 mg/kg at 24 cm inorganic phosphorus level in zone A. Organic phosphorus levels appear to be slightly high in zone A of Kisumu.

In Busia (Fig. 7), the TP and IP levels are almost. In both cases, the high values are observed in zone A, but the maximum TP concentration of 3300 mg/kg occur at 14 cm recorded in recent years. Inorganic phosphorus is mostly steady in zone A of SPK core. In contrast, a gradual increase is seen in OP levels in zone A.

In Homa Bay (HK Fig. 8), all the three fractions are observed to have a continuous steady trend, except for OP in zone A which indicates the sample at 12 cm to be high (6900 µg/l). Similarly, in Siaya (Fig. 9), OP and TP show consistent values in zone A, but a slight increase occurs in both concentrations recorded in recent years. Inorganic phosphorus shows the maximum value at 12 cm (5700 µg/l) among all three components.

f. Lake Victoria sediments (BILL and LV-95):

Although the values of TOC are high in both cores, they show a small variation in the accumulation pattern in zone A recorded in recent years. Total nitrogen concentration in BILL core, shows increase in zone B and that increase is maintained throughout zone A. A gradual decrease in the TN values are observed in Lake Victoria core, from zone B to zone A. C/N ratio was high in zone B, but there is a decrease in zone A. In LV-95 core, the highest 17.5 at 4 cm value occurs in zone A, which is the maximum compared to other values in the core.

δ¹³C values in BILL core (Fig. 11), steadily decrease from zone B to zone A and reaches the lowest value -20.87 ‰ at 6 cm. For the LV-95 core, the values are from a study by Talbot and Lærdal (2000). This trend is almost like the BILL core, showing a decrease in recent years.
Figure 10: TOC, TN and C/N ratio of the two lake sediments (BILL- Uganda and LV-95 Kenya) vs depth.
Phosphorus fractional concentrations for BILL (Buvuma Channel core)
Phosphorus fractional concentrations for Lake Victoria (LV-95).

Figure 11: $\delta^{13}$C and phosphorus fractional concentrations vs depth in sediment cores retrieved from Lake Victoria.

Phosphorus concentrations increase in the BILL core. All the three fractions show an increase in zone A (recent years) with the highest (230 mg/kg) IP values at 4 cm, OP at 5 cm (330 mg/kg) and TP at 8 cm (790 mg/kg). These values are considerably higher than the other concentration levels in the core. There is a sudden decrease in OP and TP near 40 cm in zone A, but the decrease did not last long. In LV-95, there is not much increase or decrease in IP and OP concentrations in zone A and zone B, except for the sudden decrease in IP near 80 cm. TP shows the maximum (330 mg/kg) value at 11 cm which decreases to 240 mg/kg, recorded in zone A.
7. Discussion:

a. Nutrient cycle and Eutrophication:

The terrestrial ecosystems work on large biogeochemical cycles with input and output systems. The input to the cycles is through three major sources - geological, meteorological and biological. Geological inputs are the depositions of nutrients through mass wasting or erosion and dissolved ions in discharge water (surface and groundwater). Aerial input is through atmospheric deposition of gaseous materials, dust, and precipitation. These fractions are fixed to the soil through biological fixation, which is then considered as meteorological input. Biological input is the results from activities of living substances, where the depositional material is generated elsewhere. Chemicals in form of dissolved state and particulate state moving in water are known as geological output, gaseous form diffusion through wind is known as meteorological output and transport through living organism activity is known as biological output (Bormann and Likens 1967).

Nutrients are present in four compartments of the ecosystem: 1) the atmosphere where molecules or atoms are present in gaseous form or bound to particles, 2) the soils of the catchment that contain ions adsorbed or dissolved in soil solutions, 3) organic debris, i.e., dead remains of living organisms, 4) in soil and rock minerals. The interaction of the terrestrial nutrient cycle with the aquatic hydrological cycle is related to the amount of water that enter or leave in an ecosystem through leaching and flushing respectively. This interaction is mainly brought by humans and their activities. This supply of nutrient into the water bodies influences the growth of algae and vascular plants in the water ecosystems. A large amount released from this supply would make the freshwater or marine ecosystems eutrophic. The external supply of these nutrients can be divided depending upon the sources as point and non-point sources. Point sources are usually easy to monitor and control, whereas non-point sources are difficult to regulate, and the source characteristics are extremely biased (Smith et al. 1999).

b. Total Organic Carbon, Total Nitrogen, and its accumulation:

In a lake ecosystem, if primary production is more than the rate of decomposition, it results in net accumulation. This accumulation is regulated by decomposers like benthic invertebrates, bacteria, and fungi. At the end of the decomposition process, the organic matter undergoes burial due to constant accumulation. At this point, the decomposition rates are slow and reduced since there a shift from aerobic to anaerobic conditions. This results in a stratified build up of partially decomposed matter in the sediments (DeLaune and Reddy 2008).

TOC and TN are geological proxies, that are used to study the changes in deposition and preservation in a lacustrine environment. Changes in TOC reflects the disappearance of organic matter due to remineralization. This shows the different sources of organic matter entering into a wetland ecosystem. The values are influenced by the presence of other elements in the sediments since they have been represented as mass ratios. The increase of TOC in sediments is due to the urbanization, deforestation and atmospheric deposition. TOC accumulation is also affected by the grain size variations, the concentration increases with the increase in fine-grained soil particles (Routh et al. 2007; Das et al. 2008).

The dramatic increase in TOC and TN concentrations in the sites KK, DK and SPK in Fig. 2 and 3, is a result of reduced decomposition of organic matter and atmospheric deposition. KK and SPK are rural sites, therefore, agriculture production dominates on these sites and also
rainfall pattern is higher at the two urban sites HK and DK. Since the agricultural production is dominant, the use of fertilizers is also high at both sites. The increase in carbon and nitrogen concentrations in DK are due to the industrial and human activities since it is an urban site with increasing population. Overgrowth of water hyacinth on the lake water has diverted several people to focus on industrialization. The decrease in concentrations in HK at the initial depths (50-100 cm) could be terrestrial runoff due to siltation or during rainfall. Although HK, does not show a considerable change in accumulation above 50 cm, the highest accumulation is due to the effect of urbanization after the construction of the railroad.

The accumulation in lake sediments BILL and LV-95 from Fig. 10, has numerous reasons such as disposal of urban waste like sewage, industrial waste, agricultural wastes from fertilizers and irrigation methods, through soil erosion- either through rivers or through rainfall and lastly due to an atmospheric deposition that introduces the nutrients into the lakes. Buvuma shows higher concentration levels compared to the other sites. Rainfall and atmospheric deposition are two major sources of input of carbon and nitrogen into the lakes. The increase in accumulation of these nutrients depicts an increase in primary production- in the BILL core. A gradual decrease in accumulation levels in LV-95 could possibly be because of mixing due to wind currents (Talbot and Lærdal 2000; Stager 2009; Odhiambo 2016).

c. C: N in sediments:

Carbon to nitrogen ratio is used as a proxy to understand and characterize the different sources of sedimentary organic matter. In some studies, this ratio is used to infer the amount of nitrogen available to utilize it for decomposition processes. This is because nitrogen is assumed to be the limiting nutrient for the phytoplankton production in lakes. When the ratio is less than 8.3, nitrogen- phytoplankton growth occurs. If the value is between 8.3 and 14.6, a moderate supply of nitrogen is available for the growth and if the ratio is >14.6 it indicates lack of nitrogen. For the analysis in lake sediments, the scale values are added by 5 because C/N generally increases by 5 units during the sediment burial (first few centimeters) depending upon the lake’s residence time and stabilizes later. Therefore, the scale values are < 13.6, 13.6- 19.6 and > 19.6.

In catchment sediments, C/N values are characterized by protein and cellulose contents. Algae and phytoplankton are rich in proteins, but low in cellulose, whereas terrestrial plants are rich in cellulose and low in protein levels. Phytoplankton derived sediment is believed to have a C/N <10-12, C/N between 10 and 20 indicates a mixture of both phytoplankton and terrestrial organic matter and >20 indicates a chiefly vascular plant origin.

The consistent increase in C/N values in DK and HK in Fig. 4, reveals that there were high rates of deforestation, turning vascular plants into organic mass. As mentioned above the two urban sites are industrialized and therefore, land clearance was required for development. Sometimes the C/N values range from between 10-20, indicating algal inputs from the lake. In case of SPK and KK, for the same reasons, an effect of deforestation is inferred. Consistent with this there is evidence like wooden bits, twigs and root debris observed while slicing the cores. The low values may also be due to extensive exposure of organic matter to oxidation and microbial degradation after deforestation. In lake sediments, BILL core has a value less than 13.6, which indicates growth of algae or phytoplankton due to the supply of nitrogen. Similarly, in LV-95, the values ranged between 13.6 and 19.6, which implies algal growth under moderate availability of nitrogen (Routh et al. 2007; Das et al. 2008; Talbot and Lærdal 2000; Meyers 1994).
d. Stable carbon isotope:

The Stable isotope analysis is used to study the difference between aquatic and terrestrial plant sources for organic matter and primary productivity changes in lake ecosystems. Plants use two types of pathways to utilize the available atmospheric carbon, C3 Calvin pathway is one method in which $^{13}$C is chemically differentiated to produce a $\delta^{13}$C shift of -20‰. The C4 Hatch-Slack Pathway is another method where dispersal isotopic shift of -7‰ is observed. Land plants that follow the Calvin pathway using atmospheric CO$_2$ that has an isotopic value equal to -27‰ (or between -25 and -35‰). In contrast, plants using the Hatch-Slack Pathway the values are equal to -14‰ (or between -10 and -16‰). Algae in freshwater ecosystems use the dissolved carbon dioxide which is in isotopic equilibrium with atmospheric carbon dioxide. The $\delta^{13}$C values for aquatic organic matter range between -22 and -20‰, this -7‰ difference between algal and terrestrial C$_3$ plants is used to understand the sources and organic matter distribution in lake sediments. Sometimes the isotopic signals from the sources become difficult to interpret because the sediment organic matter has contributions from both C$_3$ and C$_4$ vascular plants as well as algae. Hence to overcome this situation, C/N ratios are plotted vs. the isotopic values which help in the better differentiation of organic matter (Das et al. 2008; Talbot and Lærdal 2000; Meyers 1994).

The sites Kisumu and Homa Bay show $\delta^{13}$C signals between -20 and -14‰. Combining the C/N values of these sites along with this range, it is inferred that the source for organic matter is partially algal production and partially terrestrial C$_4$ vascular plants. The sudden change in the isotope levels in HK at around 50-60 cm is when the railroad stressed on clearing lands using fire for the development and caused nutrient input. Carbon isotope values in addition to the C/N values of KK site, reveals that the distribution of organic matter is by primary production terrestrial C$_4$-plants. The source in these sites was distributed due to the need for clear lands and use for agriculture. It is known that grasslands and forest lands were cleared using fire and deforestation. Similarly, SPK having $\delta^{13}$C values ranging between -17 and -10‰, implies that the source producers are C$_3$- and C$_4$-terrestrial plants. In BILL and LV-95 as observed in Fig. 11, the values extending between -20 and -21‰ and -20 and -22‰, respectively. Here, the distribution of organic matter indicates primary production in aquatic algae. When C/N ratio of these sites are compared, it is noted that the production took place when there were high concentrations of nitrogen in BILL and moderate levels in LV-95.

e. Phosphorus and its fractions:

To understand the transformation and transport of phosphorus the separation of P into different pools is helpful. Inorganic phosphorus is associated with crystalline and amorphous forms of other elements such as aluminum, iron, magnesium, and calcium and it accounts for 50 – 60% in total phosphorus. It is also known that this form of phosphorus is bioavailable and terrestrial plants and aquatic algae readily take if dissolved for primary production. On the other hand, OP accounting for the rest of the TP pool is associated with different organisms and organic matter. IP is loosely bound to facilitate the uptake by plants or algae and/or adsorption into soil particles for long-term storage. The role of OP and its cycling is a complicated pathway and its exact characteristics are not completely known (Wang et al. 2013; DeLaune and Reddy 2008).

Sediments in lakes and catchments often contain high amounts of organic matter content, therefore, the factors responsible for the decomposition and break-down of organic matter regulates the continued storage of nutrients. Due to low mineral and high organic matter in sediments, phosphorus is readily stored. Most studies focus on the IP since it is biologically available. The slow decomposition rates of organic phosphorus under anaerobic conditions
makes this pool less available for microbial degradation. OP plays a major role in the pool of bioavailability because IP is released into the water or sediments after OP mineralization (Reddy et al. 1999).

In Kisumu, the concentrations of IP has increased (Fig. 6), from which it can be inferred that its availability to aquatic plants has increased. This could be due to increase in population and anthropogenic activities in recent times. Atmospheric deposition and mining activities play a major role in the difference in concentrations, due to which the decomposition and accumulations of OP have increased in this site.

In Homa Bay, both the IP and OP concentrations have increased in recent times (Fig. 8). The reason for this increase is similar to Kisumu since both sites have been rapidly urbanized in recent decades. Organic phosphorus increase is due to high decomposition rates after land clearances for development.

Busia and Siaya are rural areas. There is a gradual increase in OP in SPK due to increased rates of decomposition through bad farming practices. IP increase in KK is most likely due to using fertilizers and atmospheric deposition (Fig. 7 and 9).

Lake sediments BILL and LV-95, Fig. 11- the high levels of IP and OP prove the continuous accumulation of organic agricultural and urban runoff, atmospheric deposition is the main causes for this change in concentrations.

f. Comparision and Causes for Eutrophication:

Nutrient concentrations increased in the upper few centimeters at almost all the sites, which is clearly a result of urbanization, improper agricultural practices and effect of high rainfall in recent times. Few sites that showed the difference in concentrations in zone B, that is further down the core are the result of changes in the lake and its catchment in the past such as railroad construction, urbanization, intensive agricultural practices, and deforestation, etc. The increase in the primary production inferred from the concentrations of nutrients match the growth of population and agricultural activities around the lake. The use of TOC, TN, TP, C/N ratio and stable isotope values as proxies, justifies the study and determine the causes for eutrophication as soil disturbance and its resultant effect on the lake. Completion of the railroad, has increased settlement and commercial fish marketing, agricultural production and industrialization (Verschuren et al. 2001).

The total organic carbon and total nitrogen concentrations are high in lake sediments when compared to all the catchment sites, this is a general condition since it is known that the increase is due to rainfall and soil erosion, urban and agricultural runoffs. Out of all the catchment sites, KK had high values of TOC and TN, which implies high primary production and accumulation into the soils (comparing results in Figs. 2 and 3 with Fig. 10). The stable isotope signals and C/N values indicate the organic matter sources in the sediments. In lake sediments, the source of organic matter was mostly algal species, which is clearly due to high concentrations of carbon, nitrogen, and phosphorus and aquatic C₃ plants. In catchment sediments, C₃, C₄, and algal communities were involved (comparing data in Figs. 4 and 5 with Fig. 10 and 11). The decline in primary production is due to deforestation and forest fires. Total phosphorus accumulation in catchment sediments is mostly due to atmospheric deposition, decomposition of dead plant and algal biomass and use of fertilizers. The lake, in general, receives input from the catchment (comparing concentrations in Figs. 6, 7, 8, 9 with Fig. 11) helps us understand the eutrophication pathway of the lake:
8. Conclusion:

The analyses of complementary geochemical proxies in Lake Victoria indicates eutrophication that is driven by anthropogenic activities and climatic conditions in and around the lake basin. Variations in nutrient concentrations indicate that there is a high rate of primary production. Distribution of different sources and input to the lake and its catchment is identified by the combination of P, C/N, and stable carbon isotope values. It is inferred that organic matter in the lake and in the basin is mostly derived from algae. The three nutrients carbon, nitrogen, and phosphorus are important for plant growth as well as algal production. It is the excess amounts that would cause the irreversible impacts to the lake and the catchment, considering the excess amounts is through the non-point sources. Our research with the use of geochemical proxies has provided further insight to identify these sources.
9. References:


Biological and Chemical Oceanography Data and Management Office (BCO-DMO) 2018, Funded by the U.S. National Science Foundation. https://www.bco-dmo.org/instrument/506239


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World Gospel Mission, Africa Gospel Church, Buvuma Islands Ministry http://www.buvuma.org/about
10. Appendix:

1: Decarbonization protocol:

Add 1N HCl to 200 mg of soil sample in a centrifuge tube. The mixture should make a slurry.

Centrifuge at 3000 g for 15 minutes.

Discard the supernatant and wash the sediments with deionised water (12 ml), shake it for 5 minutes.

Centrifuge again at the same speed and time. Discard the liquid.

Repeat step 3 and 4, then dry the samples at 60°C for overnight.

Figure 13: Step-wise decarbonization procedure.

2: Phosphorus analysis:
Sequential extraction: (Ruban et al. 1999).

Things to do before the start of the procedure:

1) All the reagents used must be of high purity (99.5% minimum).
2) All glassware and plasticware are cleaned in phosphate-free detergent, soaked for 24 h in 1.2 mol L⁻¹ HCl and air-dried before use.
3) A blank sample should be carried out through the entire extraction procedure.
4) The calibrant solutions should be prepared on the day of analysis. Solutions prepared earlier than a week should not be used, and the spectrophotometer should be on for 30 minutes before using it.
5) The extraction should be carried out at a temperature of 21±1°C.
6) In case of contamination, the solutions or samples must be prepared again.
7) The work area should always be clean and dry.
Procedure:

A. Concentrated HCl-extractable P
1. Weigh 200 mg of dry sediment in a porcelain crucible.
2. Calcinate at 450°C for 3 h.
3. Pour the cool ash into a centrifuge tube.
4. Add 20 ml of 3.5 mol L⁻¹ HCl with a pipette. HCl is added directly to the crucible to ease the transfer of the ash.
5. Cover the tube and stir overnight (16 h).
6. Centrifuge at 2000 g for 15 min.
7. Collect the extract in a test-tube for the analysis of concentrated HCl-P.

B. IP (inorganic phosphorus) and OP (organic phosphorus)

a. IP.
1. Weigh 200 mg of dry sediment in a centrifuge tube.
2. Add with a pipette 20 ml of 1 mol L⁻¹ HCl.
3. Cover the tube and stir overnight (16 h).
4. Centrifuge at 2000 g for 15 min.
5. Collect the extract in a test-tube for IP analysis.

b. OP
1. Add 12 ml of demineralized water to wash the residue. Stir for 5 min.
2. Centrifuge at 2000 g for 15 min and discard the supernatant.
3. Repeat a.1 and a.2 once.
4. Allow the residue to dry (in the tubes) in a ventilated drying cupboard at 80 °C. Put the tubes in an ultrasonic bath for 10 s and transfer to a porcelain crucible.
5. Calcinate at 450°C for 3 h.
6. Pour the cooled ash into the centrifuge tube.
7. Add 20 ml of 1 mol L⁻¹ HCl with a pipette. HCl can be added directly to the crucible to ease the transfer of the ash.
8. Cover the tube and stir overnight (16 h).
9. Centrifuge at 2000 g for 15 min.
10. Collect the extract in a test-tube for OP analysis.

The extracted samples were marked and stored in dry test tubes. Reagents used in this procedure are 1 mol L⁻¹ HCl and 3.5 mol L⁻¹ HCl. 1.2 mol L⁻¹ HCl is used for washing the glassware.

Absorption method (Blue method): (Murphy and Riley 1967)

Materials required:

1) Sulphuric acid (2.5 M): 35 ml of Concentrated H2SO4 diluted to 250 ml using milli-Q water.
2) Ammonium molybdate (4%): Transfer 4 g (NH4)₆Mo₇O₂₄*4H₂O is diluted in a 100 ml volumetric flask with Milli-Q water.
3) Ascorbic acid (0.1 M): Dissolve 1.75 g ascorbic acid in 100 ml of Milli-Q water. If stored in a refrigerator, the solution will last up to a month.
4) Potassium antimony (III) tartrate hydrate (1 mg Sb/ml) (KSb solution): Dissolve 0.685 g of K (SbO) C₄H₂O₆. 0.5 H₂O in Milli-Q water and make it up to 250 ml. Store in a dark bottle in a refrigerator.

5) Phosphate stock solution (100 mg PO₄): 0.439 g of KH₂PO₄ is measured after heating the salt at 105 °C for 2 hours. To 1000 ml of Milli-Q water, the weighed salt is added and stored in refrigerated at a cool temperature. This solution can be used for one month.

6) Phosphate calibration standard solution (1000 µg PO₄): Dilute the stock solution 100 times. Add 1 ml of the standard stock solution to 100 ml of Milli-Q water. Store for no more than about 1 week.

Reagent Blend solution:
Sulphuric acid- 250 ml, Ammonium Molybdate solution- 75 ml and KSb-solution- 25 ml are mixed together to form a cocktail solution. The mixture should be done after sulphuric acid cools down. To 175 ml of the cocktail solution, 75 ml of Ascorbic acid is mixed (solution B) which is pale yellow in color, this solution B is to be made the same day as the analysis.

Four standards of concentrations 0 (blank), 40, 80 and 120 µg/L should be prepared for generating the calibration curve. 0, 2, 4 and 6 ml of phosphate calibration standard solution is added in four 50 ml flasks. To this, add 8 ml of Reagent blend solution B (yellow color) and make the volume up to 50 ml with Milli-Q water. After 15- 30 minutes, blue color at different intensities are observed. No color should be seen in the blank, if there is any contamination it should be prepared again. The intensities are calibrated in a spectrophotometer at 882 nm wavelength.

Sample preparation: Few amounts of the extracted sample (<500 µL) must be used to avoid wrong calibrations. The acidity in the samples affect the calibration values. Hence, the sample amount should be calculated accordingly. Here is a flowchart for the sample preparations:

![Flowchart](image)

Figure 14: Blue Method sample preparation.
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