Surficial sediment phosphorus fractions along a biogeochemical gradient in Nyanza (Winam) Gulf, northeastern Lake Victoria and their possible role in phosphorus recycling and internal loading

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Abstract Different phosphorus fractions and metal element composition of surficial sediments were measured on three occasions in 2005 and 2006 along a transect between Nyanza Gulf and offshore Lake Victoria, in order to assess the potential for sediments to contribute to the water column P concentrations in Lake Victoria. Total phosphorus (TP), apatite phosphorus (AP), inorganic phosphorus (IP) and organic phosphorus (OP) increased in sediments along the gulf towards the main lake while the non-apatite inorganic phosphorus (NAIP) increases were less defined. The longitudinal gradient of sediment TP and its fractions in Nyanza Gulf is a result of high rates of terrigenous input and resuspension and transport of the light, phosphorus rich inorganic and organic matter towards the main lake. TP in the sediment ranged from 812.7 to 1,738 mg/kg dry weight (DW) and was highest in the Rusinga Channel, the exchange zone between the gulf and the main lake. AP was the most important TP fraction, contributing between 35 and 57.3% of TP. Ca content in the sediment was strongly associated with TP and AP in the sediment ($r^2 = 0.92$ and 0.98, respectively) in the gulf and the channel, indicating the importance of apatite in controlling P availability in these zones. In the gulf and the Rusinga Channel, the less bioavailable apatite phosphorus dominated, whereas in the deeper main lake OP was the major fraction illustrating the importance of anaerobic release of P from sediments and acceleration of internal P loading in the main lake.

Keywords Nyanza Gulf · Phosphorus fractions · Phosphorus recycling · Surficial sediments

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Introduction

Phosphorus is an essential element in the functioning of aquatic ecosystems as it is one of the major nutrients (together with carbon and nitrogen) that is required by primary producers and is often the nutrient in shortest supply relative to demand by algae (Hecky and Kilham 1988). Phosphorus entering aqueous environments is usually in different forms, including: crystalline, occluded, adsorbed, particulate organic, soluble organic and soluble inorganic phosphorus (Schaffer and Oglesby 1978). In the water column phosphorus may be recycled between particulate and soluble phases through physical, chemical or biological



processes (Kleiner and Stabel 1989; Shafer and Armstrong 1994; Suzumura et al. 2004). The particulate form can settle from the water column or can be solubilized into the water column through microbial activity and physical or chemical dissolution. In sediments, phosphorus can be transformed and redistributed among the various chemical fractions according to biological activity, redox conditions, and pH (Holtan et al. 1988). Its remobilization from sediments is dependent on the chemical fractions present and the other physical and chemical properties of the sediment (Boström et al. 1988a; Pettersson 1998; Kalff 2002).

Of the soluble phosphorus fraction, only orthophosphate (PO_4^{3-}) is directly biologically utilizable, and its biogeochemical transformation has elicited much interest from both limnologists and water resources managers. Under aerobic conditions, PO₄³⁻ interacts with many cations (e.g., Fe³⁺ and Ca²⁺) to form relatively insoluble compounds that precipitate out of the water column to the sediment (Spivakov et al. 1999; Wetzel 2001). According to the classical model first proposed by Mortimer (1941), PO₄³⁻ is strongly sorbed to iron oxyhydroxide (FeOOH) or precipitated as FePO₄ under aerobic conditions. PO₄³⁻ can also coprecipitate, with CaCO3 in alkaline water bodies (Golterman 1995). However, under reduced redox conditions (E_7 of about 200 mV), during the development of anoxia in the hypolimnion and in the sediment, Fe³⁺ in the aggregates is reduced to the soluble Fe²⁺ leading to dissolution of FeOOHPO4 aggregates and therefore releasing PO₄³⁻ and Fe²⁺ to the hypolimnia (Caraco et al. 1993; Wetzel 2001; Kalff 2002). This internal cycling of phosphorus can be a significant source of phosphorus for phytoplankton photosynthesis depending on a lake trophic status and during seasons of low external phosphorus input (Caraco et al. 1993; Wetzel 2001; Kalff 2002). In eutrophic and hypereutrophic lakes sediment phosphorus release can delay lake restoration even after reduction of external input (Pettersson 1998); and therefore, understanding of the forms of sediment phosphorus and the potential for release or loss of biologically available phosphorus in the water body is essential in lake management because P is often limiting algal biomass and growth.

Study of phosphorus biogeochemistry in sediment of aquatic environments normally involves partition of the phosphorus pool into its labile and refractory components in order to determine its bioavailability (Boström et al. 1988b; Levy and Schlesinger 1999). A

number of sequential fractionation procedures have been developed (e.g., Williams et al. 1976; Hieltjes and Lijklema 1980; Hedley et al. 1982; Ruttenburg 1992; Ruban et al. 2001) and used to characterize phosphorus in soil and sediment. The most widely used method (or its modification) is the Williams method (Williams et al. 1971, 1976), a modification of which has been developed and adopted by the European Union laboratories as a harmonized protocol for the determination of extractable contents of phosphorus in freshwater sediments (Ruban and Demare 1998; Pardo et al. 2003). This method, which has been used in this study, uses NaOH and HCl to sequentially extract different phosphorus fractions, namely: the HCl-extractable phosphorus fraction (apatite phosphorus, AP), which consists of orthophosphate present in highly insoluble crystal lattices of apatite grains and is normally considered unavailable for biological use; the NaOHextractable phosphorus fraction (non-apatite inorganic phosphorus, NAIP), which is associated with oxides and oxyhydroxides of Al, Mn and Fe and is considered potentially available; and the organic phosphorus which consist of all phosphorus associated with carbon atoms via C-O-P or C-P bonds, and can become available for reuptake through enzymatic degradation of the organic bonds. As a result of the high reactivity of P with these inorganic and organic compounds, P concentrations are generally kept very low in aquatic systems and frequently become limiting for photosynthetic organism and the productivity of aquatic systems.

Spatial variability in the concentration of surficial sediment phosphorus and its fractions can be influenced by the nature of geologic sources as well as diagenetic and hydrodynamic processes. Phosphorus associated with dense minerals and refractory terrigenous sediments will normally settle nearshore whereas the P in solution and P fractions associated with lighter organic and colloidal matter can be transported to the more offshore areas through water movement. Resuspension and entrainment of bottom sediment can lead to winnowing and focusing of phosphorus associated with lighter particulate matter from more physically active near shore areas to the deeper offshore lake zones (e.g., Johnson and McCave 2008). Diagenetic processes in the sediments lead to transformation and release of labile P fractions and retention and burial of the refractory fraction (Penn et al. 1995). Sediment diagenesis can



occur at different rates under different conditions in different areas in a lake due to varying physical, chemical and morphological conditions therefore resulting in spatial variability in concentration of phosphorus and its fractions in bottom sediments.

Most past studies in Lake Victoria have mainly focused on phosphorus concentration in the lake water column and possible relationship with external input (Talling 1966; Kilham and Kilham 1990; Guildford and Hecky 2000, Lung'ayia et al. 2001; Guildford et al. 2003; Gikuma-Njuru and Hecky 2005; Tamatamah et al. 2005). However, the dramatic ecosystem changes, including increased eutrophication (Hecky 1993) and deoxygenation of the hypolimnion (Hecky et al. 1994) that have taken place in Lake Victoria in the past five decades has lead to increased interest in sedimentation processes and possible role of bottom sediments in nutrient recycling in the lake (Hecky 1993; Hecky et al. 1996; Holtzman and Lehman 1998; Verschuren et al. 1998, 2002). Analysis of phosphorus in sediment cores retrieved from an offshore station has shown evidence of increased phosphorus sedimentation in Lake Victoria in the past four decades (Hecky 1993; Hecky, unpublished data). The reported high phosphorus concentration in the open waters of Lake Victoria (Hecky 1993) has been associated with increased chemical weathering of eroded particulates due to land use changes in the lake catchment over the last century (Holtzman and Lehman 1998). However, the physical and geochemical state of phosphorus associated with terrigenous matter from the catchment is yet to be fully understood. In this study spatial variability in the concentration of different phosphorus fractions in the surficial sediments along a biogeochemical gradient in northeastern Lake Victoria was analyzed in relation to other elements in the sediment and water column phosphorus fractions, in order to assess the potential role of sediment phosphorus in contributing to the increasing P concentrations in Lake Victoria.

Methods and materials

Study area

Lake Victoria is the world second largest freshwater body by surface area (68,800 km²) and has a mean depth of 40 m. The lake is bounded by Kenya, Tanzania and Uganda and has a shoreline length of 3,440 km, most of which is very irregular with shallow bays and gulfs (Akiyama et al. 1977). The lake contributes significantly to the economies of the riparian countries through its fishery (with annual catch of 800,000–1,000,000 metric tones valued at USD 350–400 million; Lake Victoria Fisheries Organization (LVFO) 2009) and is an important source of drinking water to the riparian communities. In the past half century the lake has undergone major dramatic water quality and biological changes associated with increased nutrient input, introduction of exotic fish species and climate change (Ogutu-Ohywayo 1990; Hecky 1993; Kling et al. 2001).

The study was carried out in the northeastern Lake Victoria between 34° 08.85′ and 34° 55.30′E and between 0° 18.50' and 0° 20.81'S at 1,143 m a.s.l. (Fig. 1). The area has three morphologically distinctive areas, namely the main lake (mean depth 40 m); the shallow, wide and elongated Nyanza gulf (surface area 1,300 km², mean depth 10 m, maximum width 30 km and length 50 km); and the narrow and deep Rusinga Channel (minimum width 5 km, depth between 12 and 39 m), which connects the gulf and the main lake and is a zone of dynamic exchange between the gulf and the main lake. Several rivers drain into the Nyanza Gulf from the southeast, with an annual discharge of 2.4 km³ and carry high loads of suspended sediments and nutrients from their highly intensive agricultural catchments as well as industrial and municipal sources (Lung'ayia et al. 2001; Calamari et al. 1995; Lake Victoria Environmental Management Project (LVEMP) 2005a). The hydrological and morphometric characteristics of Lake Victoria and Nyanza Gulf are presented in detail in Crul (1995), Bootsma and Hecky (1993) and Gikuma-Njuru and Hecky (2005).

Field sampling and laboratory analysis

Six stations, located along a transect between the eastern end of the gulf and the main lake (Fig. 1) were sampled on three different occasions: June and September 2005 and February 2006. Sediment samples were collected using an Ekman Dredge sampler and the top (about 2 cm) sediment was taken and transported to the laboratory, where it was dried in an air circulating oven at 105°C for 24 h. The dried



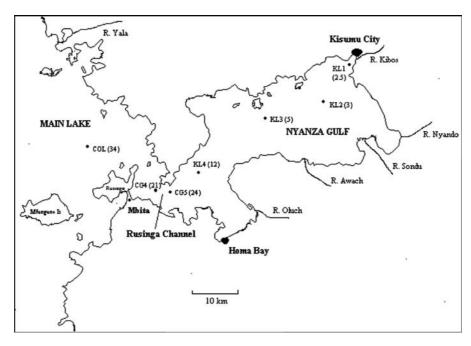


Fig. 1 Map of northeastern Lake Victoria showing the location of the sampling stations and depth (in parenthesis), river tributaries sampled and major towns

sediment was ground and preserved in airtight glass vials during transportation to the University of Waterloo laboratories for analysis. Sequential extraction of different phosphorus fractions was carried out using the method described by Ruban et al. (2001) and Pardo et al. (2003), which separates sedimentary associated phosphorus into four categories, namely the non-apatite inorganic phosphorus (NAIP), the apatite phosphorus (AP), inorganic phosphorus (IP), organic phosphorus (OP) and total phosphorus (TP). A detailed description of the procedure is given in Ruban et al. (2001) and Pardo et al. (2003) and only a general outline will be described here. The extraction is done in three separate steps, each involving sequential extractions to separate different fractions from a 0.2 g sediment sample as follows:

(1) To extract NAIP and AP fractions, the sample is extracted with 20 ml 1 M NaOH with shaking for 16 h at room temperature. After centrifuging for 15 min at 1,200g, the supernatant is separated from the residue and 4 ml of 3.5 M HCl is added to 10 ml of supernatant and allowed to settle for 16 h and after centrifuging NAIP is analyzed in the resultant supernatant. The residue from the first step is extracted using 20 ml 1 M HCl,

- shaking for 16 h and after centrifuging AP is analyzed in the supernatant. The main difference between this protocol and that used by Williams et al. (1976) is that only one extraction for NAIP is done whereas in the Williams method the fraction is extracted in two different steps and it is therefore likely that the EU protocol may underestimate NAIP while overestimating AP fractions (Pardo et al. 2003).
- (2) In the second extraction, the sample is extracted using 20 ml, 1 M HCl shaking for 16 h and after centrifuging IP is analyzed in the supernatant. The residue is calcinated for 1 h at 450°C and then extracted with 20 ml, 1 M HCl shaking for 16 h and after centrifuging OP is analyzed in the extract.
- (3) TP in the sample is extracted directly from the sample after calcination for 3 h at 450°C using 20 ml, 3.5 M HCl, shaking for 16 h at room temperature.

Although operationally by this scheme NAIP is hydroxide extractable P we will refer to it as NAIP as is commonly done in the literature. Similarly AP by this scheme is an acid soluble precipitate remaining after hydroxide extraction which could include P bound to/in



carbonate compounds. However subsequent analysis to be presented below confirmed that this fraction is most likely apatite.

Analysis of phosphate in the extracts was done according to American Public Health Association (APHA 1995) using the ascorbic acid method after necessary dilutions. All the samples required a 20–40 times dilution and therefore pH adjustment was not necessary. Total organic carbon and nitrogen in sediment was analyzed using a Carbon–Nitrogen Analyzer, Model CE 440 Elemental Analyzer (Exeter Analytical, Inc.) after acid treatment. Metal ions in the NAIP extract were analyzed using atomic absorption spectroscopy.

Elemental composition in the sediment was analyzed using ITRAX micro-X-ray fluorescence (XRF) core scanner (Cox Analytical System). Samples were packed in cuvettes and arranged on a piece of wood in a way to resemble a sediment core, since the scanner normally analyzes whole sediment cores, and the data for each sample was delineated using the X-ray scan characteristics of cuvette walls. The X-ray scanner gives relative element content and therefore pre-analyzed standards were included and used to calculate absolute concentration of the ions.

Lake water samples were collected near the surface (approximately 1 Secchi depth) using a 5-L van Dorn sampler for the analysis of phosphorus fractions (Total phosphorus, TPw; soluble reactive phosphorus, SRP (orthophosphate, PO_4^{-3}); and particulate phosphorus, PP), particulate carbon and particulate nitrogen (PC, PN) and total suspended sediment (TSS). Known sample volumes were immediately filtered, in the field, through pre-combusted, pre-weighed GFF filters for the analysis of particulate fractions (PP, PN, PC) and TSS. The filter and water samples were stored in an ice cooler during transportation to the Kisumu laboratory where analysis was done within 24 h. The filters were dried in an air circulating oven at 105°C for 24 h; and after weighing to obtain a measure of TSS, analysis of particulate nutrients was done. Phosphate in PP was extracted using persulfate method (APHA 1995) after combusting the filter with content at 550°C. Loss on ignition (LOI) was calculated from the weight difference after combusting filter and content at 550°C for 30 min. For analysis of TP_w (subscript 'w' differentiates water column TP from sediment TP), a known volume of the water sample was digested using ammonium persulfate in an autoclave for 30 min at 137 kPa. The concentration of phosphorus in PP and TPw digests was analyzed using the ascorbic acid method as described in APHA (1995). PC and PN were analyzed using Carbon-Nitrogen Analyzer, Model CE 440 Elemental Analyzer (Exeter Analytical, Inc.) after packing the filters into aluminum cups. Water samples were collected near the mouths of inflowing rivers (Fig. 1), and TSS, PP, PN and PC in the river water were analyzed together with the lake water samples. Suspended particulate phosphorus concentration per unit dry weight (SP) in the lake and river water was calculated using PP and TSS values and was used to compare water column PP with the sediment P content. Temperature, dissolved oxygen (DO) and pH in the water column were measured using a multiprobe, Hydrolab® Sonde with a Surveyor 2a® meter readout.

Sediments from station CG5 (Fig. 1) could not be sampled because the bottom consisted only of rocks and pebbles and therefore no sediment results will be reported but the station will be referred to in the discussion section.

Results

Water column properties

Lake water properties varied horizontally along the study transect and vertically in the water column (Fig. 2). Temperature ranged from 24.40 to 28.21°C with KL1 having the highest average temperature (Fig. 2a). Dissolved oxygen ranged from 0.71 to 10.98 mg/l and anoxic conditions were observed below the thermocline (18 m) at COL in the main lake in September, when strong thermal stratification was occurring. The mid-gulf stations KL3 and KL4 had DO oversaturation whereas KL1 and CG4 had relatively lower average % DO saturation (76, 83%) compared to other stations (Fig. 2a). Water column pH were generally high (> 8.5) ranging from 7.79 to 10.27 with relatively lower values observed at the Rusinga Channel station, CG4, compared to the other stations. The concentration of total phosphorus in the water column (TP_w) ranged from 86.3 to 242.7 μg/l and was highest in the eastern gulf station KL1 nearest the City of Kisumu (Fig. 2b). SRP concentrations were high and ranged from 15.3 µg/l in KL3



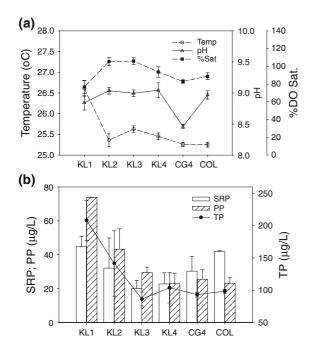


Fig. 2 Mean and standard errors of water quality parameters (a) Temperature, pH and percentage of dissolved oxygen (DO) saturation (b) Soluble reactive phosphorus (SRP), particulate phosphorus (PP) and total phosphorus (TP)

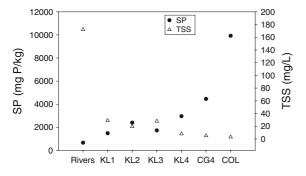
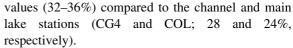


Fig. 3 Concentrations of suspended sediment phosphorus (SP) and total suspended sediment (TSS) in the inflowing rivers and in the lake in January 2006. The SP concentration was calculated from TSS and PP concentrations

to 41.9 μ g/l in the main lake. Particulate phosphorus (PP) concentration decreased monotonically along the study transect to a lowest average value of 23.2 μ g/l in the main lake (Fig. 2b). The contribution of SRP to TP_w varied between 20 and 43% with COL having the highest percentage contribution and KL2 having the lowest percentage contribution. PP accounted for between 24 and 36% of TP_w with the eastern gulf stations (KL1–KL3) having higher



The concentration of phosphorus in suspended sediment per dry weight (SP) increased along the gulf-main-lake transect from 1,487.6 mg/kg DW in KL1 to 9,924.8 mg/kg DW in COL (Fig. 3). In contrast, total suspended sediment (TSS) decreased along the transect, from 29 mg/l in KL1 to 3.1 mg/l in COL. The river tributaries had relatively lower SP concentration (668 mg/kg DW) compared to the lake water column (Fig. 3). River Sondu, which contributes about 60% of water input, had the lowest SP concentration (Table 1). Particulate carbon (PC) in the water column ranged from 1.1 to 6.9 mg/l and followed the same trend as PP (Fig. 2). The eastern gulf station KL1, located near Kisumu City (population of 0.5 million and without treatment of sewage) and the Kibos River (Fig. 1), had relatively higher average TPw, PP and PC concentrations than the other stations (222.5 μ g/l, 79.5 μ g/l and 6.9 mg/l, respectively).

Surficial sediment fractions

TP in sediments increased from $812.7 \pm 48.9SD$ (standard deviation) to 1,738 \pm 11.8SD mg/kg DW between KL1 and CG4 but then decreased to $1,330.5 \pm 10.6$ SD mg/kg in the main lake (Fig. 4). AP followed the same trend as TP, increasing more 3-fold between KL1 and CG4, 299.1 ± 19.8 SD to 947.6 ± 16.5 SD mg/kg DW, before declining to 593.3 \pm 37.4 mg/kg at the open lake station. In contrast, OP increased continuously towards the main lake from $267.2 \pm 19.8SD$ to 467.6 ± 37.4 SD mg/kg and NAIP varied along the transect but with less defined trend. LOI, an estimate of organic content in the sediment, increased towards main lake from $153.3 \pm 9.4SD$ the 268.5 ± 10.6 SD mg/kg (Fig. 4f), similar to the trend observed for OP.

Trends were observed in the contribution of different P fractions (OP, AP and NAIP) to the TP in the sediment (Fig. 5). NAIP contributed between 18.2 and 31.2% of TP and AP contributed between 35.0 and 57.3% of TP and both fractions (NAIP and AP) varied with opposite trends along the study transect, with percentage of AP increasing towards the main lake while the relative contribution of NAIP



Table 1 Concentration of total suspended sediments (TSS) and particulate phosphorus, nitrogen and carbon in the river inflows

	Discharge (m³/s)	TSS (mg/l)	PP (mg/l)	PN (mg/l)	PC (mg/l)
R. Nyando	18.3	291.4	0.3	0.6	5.0
R. Sondu	43.0	165.0	0.03	0.1	0.9
R. Kibos	1.6	368.3	0.25	1.1	8.7
R. Awach	3.3	1,465	0.42	3.2	27.3
R. Oluch	2.1	66.0	0.5	0.3	2.4

decreased. The contribution of OP to TP varied between 24.2 and 39.6% but showed no monotonic trend. The channel station CG4, near the outlet of Nyanza Gulf, had the lowest contribution of OP and highest contribution of AP to TP (24.2 and 57.3%, respectively).

TP constituted between 0.08 and 0.18% of the sediment dry weight (DW), with a higher contribution observed in the channel compared to the gulf and main lake zones (0.08–0.13 and 0.13%, respectively). This relative enrichment at CG4 was mostly due to higher AP content. Organic carbon content constituted between 5 and 15% of the sediment DW and nitrogen contributed between 0.6 and 1.4%. The sediment carbon to phosphorus molar ratios were higher than the Redfield value of 106 often considered typical of plankton (Redfield et al. 1963),

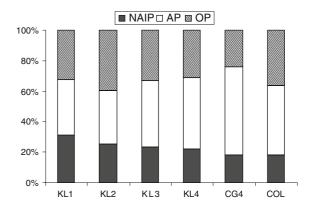


Fig. 5 Relative percentage contribution of different phosphorus fractions to TP in the sediment along the gulf-main-lake transect

ranging from $122.5 \pm 18.8 \mathrm{SD}$ to $279 \pm 10.0 \mathrm{SD}$; but the nitrogen to phosphorus ratios were close to the Redfield ratio (16) except in the main lake where a higher value of 23.7 ± 1.1 was recorded (Table 2). The channel station (CG4) had relatively lower C and N to P ratios (122.5 $\pm 1.1 \mathrm{SD}$ and $11.9 \pm 1.2 \mathrm{SD}$, respectively) compared to other stations indicating enhanced P enrichment of bottom sediment in the channel outlet largely because of the AP enrichment.

The Pearson correlation between different sediment and water column fractions showed both positive and negative correlation between some P fractions (Table 3). AP was strongly correlated with IP and TP in the sediment, indicating the strong contribution of AP to these other P fractions in the

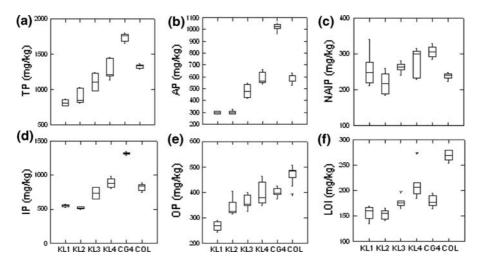


Fig. 4 Box plots of different sedimentary phosphorus fractions and loss on ignition (LOI) in the gulf (KL1-KL4), channel (CG4) and in the main lake (COL)



	KL1	KL2	KL3	KL4	CG4	COL
C (g/kg)	66.6	52.8 (3.4)	72.4 (0.2)	92.5 (6.2)	82.1 (10.1)	143.7 (14.2)
N (g/kg)	6.6	6.4 (0.6)	8.8 (0.04)	10.8 (0.6)	9.3 (0.6)	14.2 (0.3)
P (mg/kg)	813	896 (102)	1,107 (144)	1,275 (136)	1,737 (57)	1,331 (31)
C:P	212.3	152.9 (9.1)	171.4 (28.0)	189.9 (32.9)	122.5 (18.8)	279.3 (10.0)
N:P	18.0	16.0 (0.5)	17.8 (2.8)	18.9 (3.1)	11.9 (1.2)	23.7 (1.1)
C:N	11.8	9.5 (0.3)	9.6 (0.0)	10.0 (0.1)	10.3 (0.63)	11.8 (0.13)

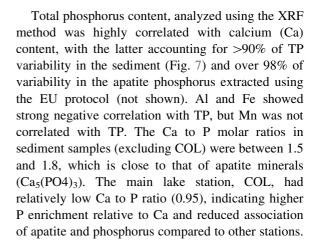
Table 2 Sedimentary carbon (C), nitrogen (N) and phosphorus (P) concentrations and molar ratios of P to N and C and C to N

Values in the parenthesis are the standard deviations

lake sediment (Fig. 5). Suspended sediment phosphorus as a proportion of dry weight (SP) was strongly correlated with AP, TP and organic N fractions in the sediment and station depth was significantly correlated with all sediment fractions except NAIP. Unlike AP which showed strong correlation with some sediment and water column fractions NAIP had no strong correlation with any fraction. There was no significant correlation between the water column P fractions TP_w and SRP and the sedimentary P fractions, except TP_w and sediment OP which were significantly correlated. Total phosphorus in the water column had strong negative correlation with water column organic C and N.

Elemental composition and phosphorus association

The spatial variation in concentration of total phosphorus and metal elements (Fe, Mn and Al), analysed using XRF are presented in Fig. 6. Phosphorus content followed the same spatial trend as TP analysed using the extractions method (Fig. 3), with the highest value in the channel. Total metal elements (except Mn) followed a general decreasing trend towards the main lake after KL1. KL1 had relatively lower Fe and Mn values compared to the other eastern gulf stations (KL2 and KL3) but had highest Al concentration. The concentration of metal ions in the NAIP fraction extract was negligible compared to the total content (Fig. 6; Table 4) but within comparable magnitude with the NAIP fraction (Fig. 3). The concentration of Al and Fe ions in the NAIP extract varied between stations but with no defined pattern. In contrast, extracted Mn concentration increased continuously from 2.07 to 4.72 mg/kg between KL1 and COL.



Discussion

The content of total phosphorus and its fractions in the surficial bottom sediments vary between different lakes according to productivity, prevailing catchment geology and anthropogenic input. According to Holtan et al. (1988), concentration of total phosphorus in natural lake sediments varies from approximately 10 mg/kg DW in sandy coastal sediment to about 10,000 mg/kg DW in iron and carbonate-rich gyttja. The concentration range observed along the current study transect (770-1,796 mg/kg DW) is in the lower range of Holtan but is within the range reported for other large lakes. Williams et al. (1976) reported TP concentrations ranging from 188 to 2,863 mg/kg in both offshore and highly eutrophied inshore stations in Lake Erie. OP concentrations in Lake Victoria (250 to 500 mg/kg) were higher than values Williams et al. reported for Lake Erie (0–286 mg/kg), consistent with higher phytoplankton biomass in Lake Victoria compared to Lake Erie



Table 3 Pearson correlation coefficients (r-critical = 0.708, 99% CI; n = 12) between different phosphorus fractions in the water column and in the sediments and station depth

	SRP*	$TP_{\rm w}*$	SP*	SN*	SC*	NAIP	AP	TP	OP	IP	C	N
TP _w *	0.736											
SP*	-0.128	-0.576										
SN*	-0.462	-0.786	0.621									
SC*	-0.481	-0.764	0.482	0.977								
NAIP	-0.045	-0.031	0.356	0.021	-0.066							
AP	-0.208	-0.567	0.708	0.366	0.254	0.471						
TP	-0.258	-0.539	0.747	0.414	0.296	0.643	0.946					
OP	-0.151	-0.516	0.824	0.547	0.492	0.408	0.632	0.717				
IP	-0.223	-0.474	0.648	0.298	0.168	0.632	0.958	0.971	0.553			
C	0.042	-0.353	0.632	0.301	0.246	0.055	0.658	0.545	0.628	0.5		
N	-0.085	-0.472	0.718	0.358	0.3	0.169	0.734	0.648	0.768	0.578	0.961	
Depth	0.133	-0.351	0.856	0.418	0.308	0.306	0.69	0.689	0.779	0.611	0.85	0.845

Correlation was done after log-transformation. Bold values are those with significant correlation (P < 0.01). SP, SN and SC are suspended particulate phosphorus, nitrogen and carbon per unit dry weight (SP, SN and SC)

^{*} Water column fractions

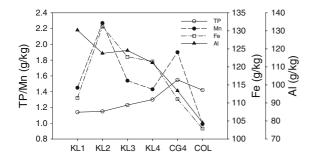


Fig. 6 Total phosphorus and metal element content in the surficial sediments, measured using Scanning X-ray fluorescence (XRF) scanner. Samples are for February 2006

Table 4 Metal ion concentrations in the NAIP fraction extract

	Al (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
KL1	259.0	45.3	2.1
KL2	257.0	38.5	2.9
KL3	251.5	46.3	2.4
KL4	275.0	52.4	3.1
CG4	215.0	39.4	3.7
COL	295.5	53.8	4.7

(6.9–21.1 and 3.9–5.3 μg Chl *al*l, respectively; Gikuma-Njuru et al. 2006; Smith et al. 2005) and the much higher TP concentrations in Lake Victoria. Lake Victoria is unique among the African and world great lakes due to its high nutrient concentrations,

relatively shallow depth and associated high algal productivity and biomass (Hecky and Bugenyi 1992; Bootsma and Hecky 1993; Hecky 2000). The relatively high algal biomass in Lake Victoria is reflected in the observed high seston phosphorus (PP) in the lake (Fig. 2b). This high PP concentration in Lake Victoria will result in high P sedimentation and consequent P enrichment of the bottom sediments (Hecky 1993). The sedimented phosphorus may be permanently buried or may undergo biological and chemical transformation to the bio-available SRP which is recycled back into the water column (Reynolds and Davies 2001) and allowing lake sediments to act as an internal source of P and to potentially sustain P concentrations in overlying waters.

Spatial gradients of phosphorus fractions

Phosphorus in surficial sediments showed a well defined gradient along the study transect with TP, OP and AP concentrations increasing along the gulf into the main lake (Fig. 5). A similar increasing trend of TP in the gulf sediments was reported by LVEMP (2005b), with TP increasing from 784 to 1,407 mg/kg between KL1 and KL4. Higher TP values, 1,980–2,773 mg/kg DW (Hecky, unpublished data) were measured in the surficial sediments from a core



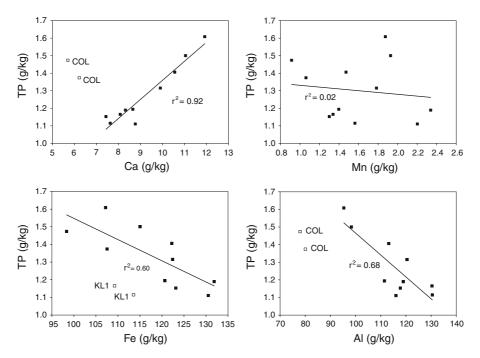


Fig. 7 Relationship between total phosphorus (TP) and metal element (Ca, Mn, Fe, Al) concentrations in the sediment analyzed using XRF scanner. Data points indicated with *open*

squares and stations identifiers were considered outliers and not included in the regression. Data are for September 2005 and February 2005 samples

retrieved from a more offshore station in Lake Victoria (V-96-5; see Vershuren et al. 2002 for location), located about 60 km from nearest shoreline and 68 m deep, an indication that the observed increasing trend of TP in sediments continues into the deep offshore areas. NAIP and AP fractions measured by Hecky (unpublished), using methods of Williams et al. (1976) accounted for about 10% of TP each whereas OP accounted for 80% of TP in the offshore core which contrasts with the shallower, more nearshore stations in the current study where AP dominated (Fig. 5). With increasing depth and distance from the lake shore the organic autochthonous sediments will increasingly dominate as seen for OP in station V-96-5.

The observed onshore to offshore increase of sedimentary phosphorus fractions and total concentration is likely influenced by physical processes which act to resuspend and transport lighter colloidal and organic matter from shallow areas to deeper offshore areas. Our transect samples along a depth gradient and depth was well correlated with TP and other P fractions. Nõges and Kisand (1999) found twice as much TP in the depositional central and southern parts of Lake Võrtsjärv, a shallow eutrophic

lake in Estonia, compared to northern erosional parts. Rusinga Channel, the exchange zone between the Nyanza Gulf and the main Lake Victoria is characterized with high water currents (20–40 cm/s: Njuru 2001; Romero et al. 2005), which act to transport bottom sediments and associated phosphorus from the gulf into the deeper areas in the channel and the main lake. These higher velocities explain the absence of sediments at CG5 despite its depth.

The highest observed TP and AP values on our transect, observed in CG4 (deepest of the station within Nyanza Gulf) may result from sediment focusing into this area from the eastern zones. The relatively high AP and low OP contribution to TP in this area (CG4; Fig. 6) may be associated with continued winnowing by resuspension and transport of lighter organic sediments away from the higher energy narrow channel area, leaving behind denser AP associated inorganic sediments. Sediment samples from CG4 also had lower C and N relative to P compared to other stations (Table 2) consistent with the hypothesized winnowing action. Resuspension and entrainment of light sediment fractions has been observed in deeper more offshore parts of the lake. Verschuren et al. (1998) observed discontinuities in



Holocene deposits in sediment cores retrieved in lake areas at depth shallower than 50 m, which they attributed to wind-driven turbulence and entrainment of organic matter and clay-sized mineral particles to the deeper mid-lake areas.

The trend of increasing P concentrations towards the deeper offshore areas may also be attributed to reduced mineralization of the settled organic sediments due to reduced biological activity associated with prolonged hypolimnetic anoxic conditions in the main lake (Hecky 1993; Hecky et al. 1994). Mineralization of organic matter in the sediment proceeds at a lower rate under anoxic conditions (Holtan et al. 1988; Moore et al. 1992), leading to accumulation of particulate organic matter and soluble organic substances in the sediment (Gale et al. 1992). Although anoxic conditions enhance release of phosphorus associated with metal oxides and oxyhydroxides (Wetzel 2001; Kalff 2002), release of organic matter bound P can be decreased under anoxic conditions and organic P will accumulate at higher rates than less stable fractions such as NAIP (Gale et al. 1992).

Influence of terrigenous sediment input

The low P concentrations in the eastern gulf area can be associated with the quality of the minerogenic allochthonous sediment input from the rivers, which enter the gulf near this area (Fig. 1). The TP concentration in the riverine suspended sediments (668 mg/kg DW) is much lower than the concentrations of bottom sediments in KL1 and KL2 (1,128.8 and 1,352.0 mg/kg, respectively; Fig. 4), located in the gulf area directly influenced by the river inflows, implying that the incoming riverine sediments have a diluting effect on the P concentrations in bottom sediments as has been observed elsewhere (Holtan et al. 1988). The riverine suspended sediments have coarser grain sizes and are mainly denser mineral particles that preferentially settle to the bottom while the finer more P rich fractions, including organic particles, remain in suspension. In addition, algal productivity will also produce relatively P rich particulate organic matter. Gikuma-Njuru and Hecky (2005) found a gradient in water transparency along the gulf that would allow high rates of primary productivity towards the main lake as inorganic turbidity increasingly settles to the lake bottom and light conditions improve. Consequently, along the gulf-main-lake transect, both TP and OP concentrations in deposited sediments would be expected to increase with distance and depth from the turbid, riverine source areas. The observed high correlation between station depth and sediment OP is consistent with the observed increasing trend of P concentration along the gulf-main-lake transect (Fig. 4) where depth increases from 2 to 34 m (Fig. 1).

Apatite-phosphorus association and P availability

Apatite phosphorus (AP) was the most important P fraction, contributing between 35 and 57.3% of TP (Fig. 6). Nõges and Kisand (1999) found that AP contributed up to 85% of TP in a shallow eutrophic Lake Võrtsjärv, Estonia and Williams et al. (1976) reported values between 20 and 100% of AP in TP in Lake Erie. In the two lakes (Erie and Võrtsjärv), the highest percentage AP contribution to TP was in the near-shore areas where allochthonous input was high and denser apatite grains would settle.

Apatite phosphorus (AP) consists of orthophosphate present in the crystal lattice of the mineral apatite and is a detrital product of chemical weathering (Bostan et al. 2000); and, therefore the source for the AP would be the rivers entering in the eastern gulf area. However, the size of the apatite grains may allow them to be carried in suspension from the river mouths along the gulf until depths are great enough to reduce resuspension. Williams et al. (1976) observed both silt-sized and clay-sized apatite in Lake Erie together with the normal sand and other course fractions. However, the source of apatite in Lake Erie was erosion of glacially formed clay and sand deposits (primarily physical weathering) while in Lake Victoria the source would be highly chemically weathered tropical soils where individual apatite grains are released during erosion. Although apatite rich volcanic rock occurs in the Lake Victoria basin (Holtzman and Lehman 1998), there is no literature on apatite fractions in the soils of the gulf catchment and therefore the origin of apatite P in the lake sediment remains uncertain. In addition to allochthonous sources AP can be produced in the water column during high primary production in hard waters as a result of calcite formation and phosphorus co-precipitation and by hydroxyapatite precipitation, but in Lake Victoria this is unlikely to occur due to



relatively soft waters and particularly the low calcium concentration (5.6 mg/l; Hecky and Bugenyi 1992).

The observed strong relationship between TP and Ca in the sediment (Fig. 7) indicate that in the Nyanza Gulf and Rusinga Channel, phosphorus is mainly in the highly insoluble apatite form which is generally considered to be unavailable to microbes and therefore not readily available for release to the water column (Williams et al. 1976). The TP in the main lake sediment does not fit in this AP–TP model because autochthonous organic sediment dominate sedimentation and therefore OP is the dominant P form. Organic P is formed from biological uptake and by definition can be available depending on the ability of microbes to breakdown the organic compounds and remobilize the OP (Montigny and Prairie 1993).

Role of bottom sediment in internal P loading

Bottom sediment can act both as a source or sink of phosphorus to the water column through release of phosphorus from the sediment or through permanent burial of sedimented particulate phosphorus (Holtan et al. 1988; Hecky et al. 1996). If burial exceeds release there is a net loss of P from the water column whereas, if release is higher than burial, sediments act as net source of P to the water column (Katsev et al. 2007). The available historical data for Lake Victoria shows high P sedimentation rates compared to sediment P release rates: Kamp-Nielsen et al. (1981) reported a TPP sedimentation rate of 30 and 8 mg/m²/day in Nyanza Gulf and in a offshore station in northern Lake Victoria, respectively, and Lake Victoria Environmental Management (LVEMP 2005b) reported a P release rate of 1.73 mg/m²/day in the gulf, indicating that in the gulf sediments may be a net P sink. However, although no release data is available for the main lake it can be assumed that the persistent hypolimnetic hypoxia in the main lake results in higher P release rates from NAIP compared to the well oxygenated gulf and channel. Hypolimnetic P release from surficial sediments in the main Lake Victoria has been invoked as one of the main causes of the observed relatively high SRP concentration in the main lake compared to the inshore areas (Hecky et al. 1996; Gikuma-Njuru and Hecky 2005). However, more studies are required in order to confirm this hypothesis.

There was no significant correlation (P > 0.05) between water column SRP and TP_w and sediment P fractions (Table 3) when all sampling locations are included, indicating that the lake sediment may not be an important source of P to the lake water column compared to external sources and P cycling in the water column. It is however important to note that only one station was sampled in the main lake and therefore these relationships between water column and sediment P fractions maybe only valid for the gulf and the channel and especially given that the main lake has different water column oxygen conditions compared to the gulf and the channel (Gikuma-Njuru and Hecky 2005).

Conclusions

Terrigenous sediment input from the river inflows and effluents from the City of Kisumu at the eastern end of Nyanza Gulf acted in concert with physical processes to produce a longitudinal gradient of TP and its fractions in the surficial sediments along the axis of the Gulf. The river tributaries had a diluting effect on phosphorus associated with the lake bottom sediment, since they bring in suspended sediment (mainly inorganic) with lower P concentrations compared to the surficial bottom sediments within the gulf. Along the gradient, the coarser grained inorganic allochthonous suspended matter is replaced by more AP rich fine suspended sediments due to winnowing from shallower depths as well as more P rich autochthonous organic suspended particulate matter, which on sedimentation result in P enrichment of bottom sediments as depth increases along the axis of the gulf.

In the Nyanza Gulf and the Rusinga Channel, the less bioavailable apatitic phosphorus dominated in bottom sediments, whereas in the main lake the potentially available OP became more abundant making internal P loading from sediments potentially more important in the main lake compared to the gulf. Increased internal P loading (especially from hypoxic/anoxic deep waters, Hecky et al. 1994) together with atmospheric input of readily available P directly to the enormous surface of Lake Victoria (Tamatamah et al. 2005) may account for the



observed high SRP concentration in the main lake water column compared to the gulf (Hecky et al. 1996; Gikuma-Njuru and Hecky 2005). The resultant low proportion of potentially available sediment P in the gulf and the generally declining P content of gulf sediments from west to east suggest the gulf is efficiently retaining much of the TP entering from its catchment as concluded by Gikuma-Njuru and Hecky (2005). In order to restore Lake Victoria ecosystem and forestall further degradation, management of phosphorus input from point and non-point sources in the catchment should be undertaken. This can be achieved through implementation of good land-use practices and treatment of municipal and industrial effluents. Restoration of riparian wetlands should also be done in order to enhance pollutant filtering capacity of the lake.

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