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Phosphorus sorption characteristics of sediment in the Simiyu and Kagera River basins: implications for phosphorus loading into Lake Victoria

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As part of a larger study to assess the influence of land use on riverine and atmospheric phosphorus (P) loading to Lake Victoria, P sorption characteristics of eight composite bottom sediment samples from the Simiyu and Kagera rivers were determined using the Langmuir equation. The samples had low to medium Langmuir adsorption maxima (Γ_m), ranging from 107 to 201µg g^{-1}. Langmuir binding energy co-efficient (*K*) ranged from 60 to 181µg l^{-1} and the equilibrium P concentration at zero sorption (EPC_0) from 0.1 to 2.75µg g^{-1}. By using Langmuir co-efficients derived from P sorption experiments and soluble reactive phosphorus (SRP) concentrations measured in rivers as well as the in-shore waters of Lake Victoria, it was possible to determine the potential release of SRP into the lake by sediment from the two catchments. For the 2000 water-year, it was estimated that about 28.65 ± 0.89 (mean ± SD) and 66 ± 6.76 tons of SRP were released into Lake Victoria by sediment deposited by the Simiyu and Kagera rivers, respectively. The implications of these results to future management of cultural eutrophication in Lake Victoria are also discussed.

Keywords: Langmuir equation, phosphorus loading, phosphorus transport model, river sediment, SRP, water quality

Introduction

The agricultural and environmental importance of phosphorus has led to extensive research effort directed towards understanding its behaviour in soils and water (Logan 1982, Froelich 1988, Sharpley *et al*. 1992). Composite water samples examined in these studies have shown that about 75% of non-point P measured in rivers draining agricultural watershed is in association with sediments (i.e. particulate P) and is not immediately available for algal growth. However, once transported into the lake, these sediment particles may either continue to retain P already bound onto their surfaces or release sorbed P in reactive form, which is in turn linked to the process of eutrophication of lakes and reservoirs.

The partitioning between solid and solution phase P is controlled by a variety of interrelated physical, chemical and biological processes. One of these processes is a reversible sorption process, which is controlled by sediment grain size (De Pinto *et al.* 1981, Stone and Mudroch 1989), pH and redox potential (Nürnberg 1984, Sallade and Sims 1997), temperature (Mack and Barber 1960), bacterial activity, competitor ions (Hue 1991) and by sediment mineral composition. The knowledge of the capacity of the fluvial sediment to bind P and the mechanism by which this 'inert' solid-phase P is released into solution under a wide variety of environmental conditions is important for predicting water quality impacts of surface waters sensitive to eutrophication.

Several rivers in the Lake Victoria watershed drain predominantly subsistence agricultural land in which erosion by run-off significantly increases the rate of delivery of sediment from the watershed to streams and the lake. Although information is available on the dissolved/reactive and particulate P loading from several rivers draining into the lake, little is known about P sorption characteristics of sediment brought into the lake by rivers and their potential for releasing P into the lake water. This information is particularly important as a preliminary step toward developing models that predict lake response to phosphate release from the loading generated by river sediment, and to refine existing lake phosphate budgets (e.g. Mugidde *et al*. 2003).

The objectives of the present work were twofold: 1) to determine the P sorption characteristics of sediments in the Simiyu and Kagera rivers, and 2) to estimate the amount of reactive P (SRP) released into Lake Victoria by sediments originating from the Simiyu and Kagera rivers.

Materials and methods

Sample collection, treatment and analyses

The present study was conducted in the Simiyu and Kagera catchments located in the south and south-western parts of Lake Victoria in Tanzania (Figure 1). Twenty-four sediment samples were collected once during November 2000 at representative locations in the two catchments (Figure 2). Since this work was part of a larger study to assess the influence of land use on riverine and atmospheric P loading to the Lake Victoria, bottom sediments were sampled at sites where other water quality parameters were routinely meas-

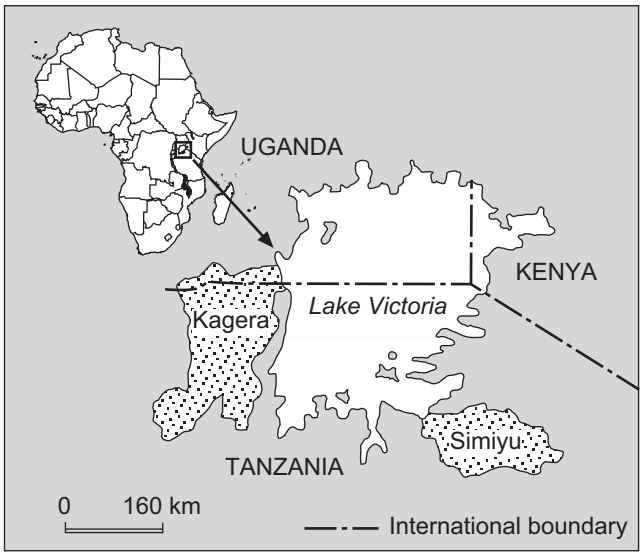


Figure 1: Map of Lake Victoria showing the study basins of Simiyu and Kagera

ured during the 18 months of field research in the catchments. Samples were collected with a grab sediment sampler at three equidistant locations across the stream. At each transect, samples were taken at approximately a 10cm depth, immediately placed on ice and transported to the water quality laboratory at Mwanza where they were composited by mixing 500g of the three sub-samples from each sampling location, air-dried, ground and sieved to 2mm mesh. The top sediment (10cm depth) was used because it is easier to collect and is in direct contact with overlying waters, hence more likely to have a larger and more direct impact on P concentration in the river water. Both air-dried and sieved sediment samples were packed in airtight plastic bags and transported to the laboratory at the Soil Science Department of the Sokoine University of Agriculture in Morogoro, Tanzania, where P sorption characteristics were determined.

The P sorption experiments were conducted by adding 3g of air-dried sediment in 50ml centrifuge tubes containing 30ml of a series of equilibrating SRP concentrations (0, 100, 200, 300, 400, 500 and 600µg P l^{-1}) (Fox and Kamprath 1970). These equilibrating P concentrations were selected to reflect a wide range of mean SRP concentrations: 500, 100 and 10µg P l^{-1} measured in the Simiyu, Kagera and in-shore waters of Lake Victoria, respectively. The equilibrations were performed in triplicate and to reduce the effect of unequal ionic concentrations, 0.5ml of 0.01M $CaCl_2$ was added to each centrifuge tube. Two drops of toluene were also added to each tube to minimise potential bacterial uptake of P during the equilibration period. The bottles were sealed, placed in a reciprocal platform shaker and shaken for a 30-minute period twice daily for six days at room temperature (27 ± 2°C). At the end of the equilibration period the samples were centrifuged for five minutes at 3 000rpm and then filtered through a pre-combusted Whatman GF/C filter (~0.45µm). The filtrates were colorimetrically analysed for P at 882nm using the ascorbic acid method (Parsons *et al*. 1984).

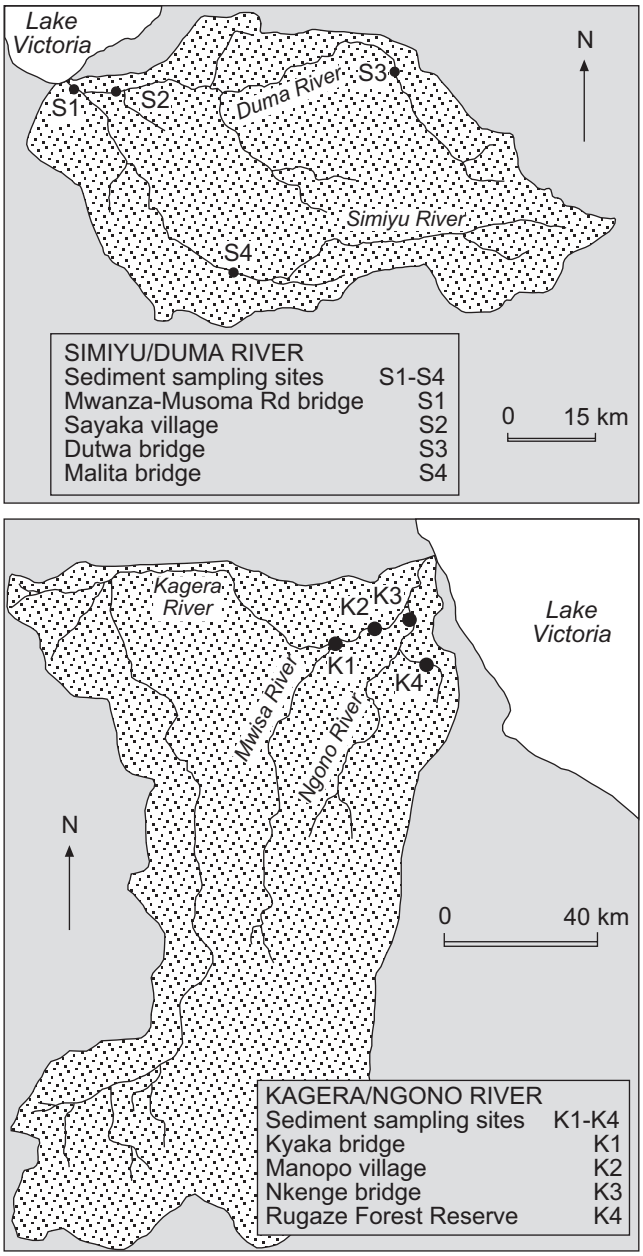


Figure 2: Sediment sampling sites in the Simiyu and Kagera drainage basins

P sorption was calculated as the difference between the amount of P initially added to each sediment-containing tube and that in solution at equilibrium. Sorption values greater than zero were interpreted as inorganic P adsorbed from solution onto the sediment, while values less that zero indicated inorganic P released from the sediment into solution. The data obtained were expressed as P adsorbed/desorbed per unit weight of sediment (µg P g^{-1}) at solution P concentration (µg P l^{-1}).

The non-linear form of the Langmuir adsorption equation was used to evaluate P adsorption characteristics of sediments from the two rivers. The Langmuir equation relates the amount of species adsorbed (Γ) to its concentration (C)

in solution:

$$\Gamma = \alpha + \frac{\Gamma_m C}{K + C}$$

where α is the y-intercept, and Γ_m and K are constants. Γ_m is the P sorption maxima for a given initial P range, and K is the equilibrium constant related to the free energy of adsorption (ΔG) (Stumm and Morgan 1981) defined as:

$$K = \exp\left[\frac{-\Delta G}{RT}\right]$$

where R is the gas constant (8.314J mol^{-1} K^{-1}) and T is the absolute temperature. Using the three parameters (α, Γ_m and K) obtained by fitting the sorption data to the non-linear Langmuir equation, it was also possible to calculate equilibrium phosphate concentration at zero sorption (EPC_0), defined as the point at which sorption of P from the interstitial water to the sediments and desorption from the sediments to the interstitial water are equal (Taylor and Kunishi 1971). EPC_0 was determined as an intercept value at zero P sorption.

In this study the maximum sorption (Γ_m), binding energy-related constant of sorption reaction (K), and equilibrium phosphate concentration at zero sorption (EPC_0) were used to characterise P sorption in sediment samples. The fitness test of the P sorption data to the Langmuir adsorption equation was performed using the non-linear regression procedure of SYSTAT. SYSTAT estimated the Langmuir co-efficients (α, Γ_m, and K) by least squares method using a modified Gauss-Newton algorithm. The difference in P sorption-desorption parameters among different sediment samples were also tested with the general linear model of SYSTAT.

Results and discussion

Phosphate sorption characteristics of sediments

The results of phosphate sorption experiments with individual sediment samples are shown in Figure 3. At lower solution P concentrations (<200µg P l^{-1}), P sorption increased with increasing P concentration. The increase then became less in the solution P concentration range of 200 to 400µg P l^{-1}. For sediments in the Kagera Basin the near maximum sorption was attained at 400, but not in the Simiyu Basin where maximum sorption was not attained even at equilibrium concentration of 600µg P l^{-1}.

The ability to accurately predict P sorption characteristics of the adsorbent materials is dependent upon the conformity of the data to an adsorption equation (Ratkowsky, 1986). In this study, phosphate sorption by sediment was well described by the Langmuir equation with fitting co-efficients (r^2) ranging from 0.91 to 0.99 (Table 1). Theoretically, Γ_m values represent the maximum amount of P that a soil or sediment can sorb, which is an indication of the total number of P sorption sites that exist in a sediment/soil. By using the estimate model of SYSTAT, the analysis of variance (ANOVA) showed that there were significant differences in adsorption capacities between sediments in the two catchments ($P < 0.04$). However, no significant differences were found between the means of adsorption energy (K) ($P < 0.15$) and EPC_0 ($P < 0.46$) for sediment samples within each catchment.

Phosphate sorption and release of sediment-bound P to Lake Victoria

At EPC_0 phosphate is neither adsorbed from solution to the sediment nor desorbed from sediment to solution and is often interpreted as the equilibrium condition for natural systems (Taylor and Kunishi 1971). However, in a system as complex as the river and the lake, such equilibrium conditions for sorption of P by sediment are rarely attained. Under non-equilibrium conditions fluvial sediment tend to sorb or desorb P depending on the existing physico-chemical conditions. For example, when SRP concentration in rivers and the lake are generally much higher than sediment EPC_0 values, the sediments will be more likely to sorb than to desorb

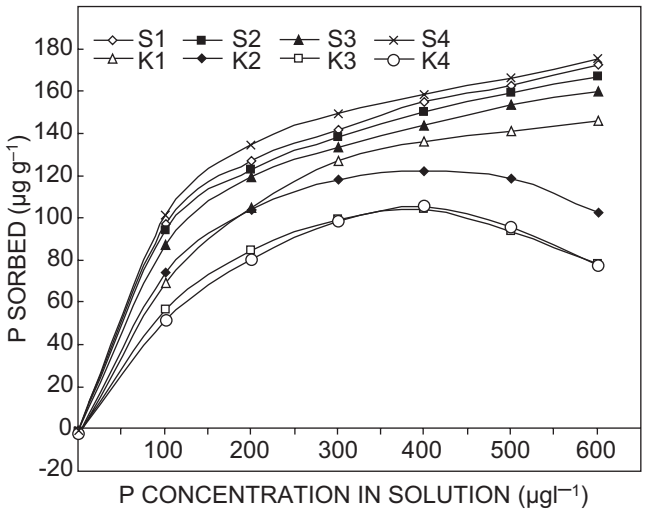


Figure 3: Phosphorus sorption isotherms for sediment samples in the (S) Simiyu and (K) Kagera basins

Table 1: Estimates of Langmuir co-efficients (α, Γ_m, and K), EPC_0, and fitting co-efficient (r^2) of sorption data to Langmuir equation

Langmuir co-efficient	Simiyu River				Kagera River			
	S1	S2	S3	S4	K1	K2	K3	K4
α (µg g^{-1})	0.45	0.21	0.06	0.75	–3.00	–2.68	–2.62	–2.21
Γ_m (µg g^{-1})	197.75	195.41	189.07	201.74	197.62	132.58	108.82	107.64
K (µg l^{-1})	106.89	115.03	117.89	105.65	181.26	66.90	67.81	60.23
EPC_0 (µg l^{-1})	0.24	0.12	0.04	0.39	2.79	1.38	1.67	1.26
r^2	0.99	0.99	0.99	0.99	0.99	0.93	0.92	0.91

P, and *vice versa*. Therefore, the quantity of phosphate adsorbed on solids at concentrations greater than the sediment EPC_0 is a measure of the mass of reactive phosphate per unit weight of solids that is potentially available for release to solution (Froelich 1988).

Based on this theory, empirical models that make use of river sediment loading data, SRP concentrations in streams and the receiving lake and Langmuir adsorption co-efficients from sorption experiments on river sediment have been described and used to simulate the transport and potential release of sediment-bound P to lakes (e.g. Stone *et al*. 1991). These models were developed with the assumption that the maximum theoretical transport of sediment-bound P through a river system (P_{sed}) is a function of the phosphate adsorption characteristics of individual sediment particles (described by Langmuir co-efficients from sorption experiments) in a given period of river sediment transport. In the present study the period of transport is considered as one year (to coincide with measurements of SRP concentration and sediment loading in the Simiyu and Kagera rivers during agricultural non-point source modelling studies in 1999 and 2000 (Tamatamah 2002) (Table 2). An additional assumption for the models is that the Langmuir adsorption maximum (Γ_m) derived from laboratory experiments approximates the maximum adsorption behaviour of sediment in nature. The factors influencing P adsorption and desorption in soils and sediments have been discussed in more detail elsewhere (Syers *et al.* 1973, Sanyal and De Datta 1991).

The model proposed for this study, which also takes into account the reversible kinetic control of phosphate by fluvial sediment and the range of SRP concentrations found in river systems can be expressed by the following equation:

$$P_{sed\ max} = \left[\alpha + \frac{\Gamma_m * SRP}{K + SRP} * Wt_{sed} \right]$$

where $P_{sed\ max}$ is maximum adsorbed phosphate transported (tons P yr^{-1}), SRP is soluble reactive phosphorus concentration in water (µg l^{-1}), and wt_{sed} is the weight of sediment transported (tons yr^{-1}).

At normal to high discharge conditions SRP concentrations in the Simiyu River exceed sediment EPC_0 (Table 2). The lower sediment EPC_0 would increase the adsorption of P by riverine sediment. However, when such tributary sediment reaches the in-shore waters of Lake Victoria, where SRP concentrations range from undetectable to 20 (mean =10) µg l^{-1} (Mugidde 2001), much of the sediment-bound P is released into solution, thus increasing a pool of dissolved inorganic P in the lake.

Therefore, by comparing maximum theoretical P adsorption capacity of sediments over a range of SRP concentrations measured in rivers and the lake, the transport and potential release of phosphate from tributary sediment to Lake Victoria can be simulated using the equation shown above. In the results of model simulations presented in Table 3, the amount of SRP potentially released from tributary sediment to Lake Victoria is determined by subtracting the maximum sediment-bound P load simulated at 10µg l^{-1}, the ambient SRP concentration in the in-shore waters of the lake, from total load simulated at mean SRP concentrations observed in the rivers (100µg L^{-1} for Kagera and 500µg l^{-1} in the Simiyu; Table 2).

The results suggest that on an annual basis and at normal riverine SRP concentrations approximately 29 (std. dev. 1) and 66 (std. dev. 7) tons of SRP are potentially released into Lake Victoria from sediment originating from the Simiyu and Kagera rivers, respectively (Table 3). Of course, these estimates would only be valid if: (1) SRP concentrations in the Simiyu and Kagera rivers were within the mean values used in the model simulation, (2) all sediments in the rivers were transported into Lake Victoria, and (3) SRP concentrations in the in-shore waters of Lake Victoria remained around 10µg l^{-1}.

In comparison with the observed SRP load in the Kagera and Simiyu rivers during the 2000 water-year (Table 2), the

Table 2: Observed SRP and sediment loading to Lake Victoria from the Simiyu and Kagera River in the year 2000 (from Tamatamah, 2002)

Parameter	Simiyu River	Kagera River
SRP concentration (µg l^{-1})	40–1 430	10–120
(Mean ± std error)	(500 ± 44.14)	(99.6 ± 13.99)
SRP load (tons yr^{-1})	29	161
Sediment load (tons yr^{-1})	198 918	1 177 366

Table 3: Model simulation of transport and potential release of sediment-bound phosphate to Lake Victoria

River	Sediment load (tons yr^{-1})	α	Γ_m	K	Simulation of fluvial transport and potential release of sediment-bound P (tons yr^{-1}) SRP concentration in water (µg l^{-1})			Estimate of SRP released to L. Victoria (tons yr^{-1})
					10	100	500	
Simiyu	198 918							
S1		0.45	197.75	106.89	3.4		32.4	**29.0**
S2		0.21	195.41	115.03	3.1		31.6	**28.5**
S3		0.06	189.07	117.89	2.9		30.4	**27.5**
S4		0.75	201.74	105.65	3.5		33.1	**29.6**
Kagera	1 177 366							
K1		-3.00	197.62	181.26	12.2	82.7		**70.5**
K2		-2.68	132.58	66.90	20.3	93.5		**73.3**
K3		-2.62	108.82	67.81	16.5	76.3		**59.8**
K4		-2.21	107.64	60.23	18.1	79.1		**61.0**

model simulation results indicate that sediment provides a large reservoir of SRP loading to the lake. For example, about 50% of the total annual SRP load derived from the Simiyu River is associated with riverine sediment. The work of Nürnberg (1984) has shown that once deposited into the lake, sediments can release their sorbed P on a timescale ranging from a few hours to months, depending on a wide range of other physico-chemical and biological factors controlling P sorption. Due to watershed management control programs currently instituted by the Lake Victoria Environment Management Project (LVEMP), there could perhaps be a decrease in the P loading to Lake Victoria in the coming years. However, if this LVEMP mandate is met, lake SRP concentrations will be expected to fall further below the sediment EPC_0. Under these conditions, increased release of phosphate from fluvial sediment may result, thus creating a lag effect on the effort to lower lake dissolved P concentrations and the ongoing process of eutrophication. In Lake Victoria, this problem will further be complicated by the recent prolonged anoxic conditions reported in deeper waters (Ochumba and Kibaara 1989, Hecky *et al*. 1994), which tend to further reduce sediment Al and Fe affinity for sorbed P.

The lack of long-term sediment sampling for sorption experiments in the two catchments is a major limitation of this study. The particle size composition of sediment samples used in this study represents actual distribution of sediment in transport only at the time of sampling, thus samples collected once during November 2000 may possibly not be representative of the actual distribution of sediment in these rivers. Furthermore, it is the suspended sediment (material <63µm) rather than bottom sediment that is generally considered to be the most geo-chemically active and important for P transport in fluvial systems (Stone and Mudroch 1989, Sharpley and Gburek 1998). Suspended sediment mainly consists of materials eroded from terrestrial surfaces within the drainage basin rather than being mobilised directly from the channel bed. In this regard, estimates determined in this study should be viewed as a first-order approximation of the actual SRP load potentially released into Lake Victoria from Simiyu and Kagera sediments (29 and 66 tons yr^{-1}, respectively), and may represent conservative values.

Conclusion

Models of water quality management require information about the source, fate and effects of sediment and associated nutrients, such as P. This study provides field data on how the knowledge of sorption characteristics of sediment and soluble P concentration in rivers and the receiving lake can be used to identify the varying potential of fluvial sediments as a source of soluble P to lakes and reservoirs. Quantification of the biological availability of particulate P to algae and other aquatic organisms in water is an important step towards predicting the potential water quality impacts of materials transported from catchments to the waters of Lake Victoria, which are sensitive to eutrophication.

Furthermore, the investigation points to the need for additional research on sediment sorption chemistry in the catchments in order to validate the present results, not only with additional and more rigorous sampling involving suspended sediments, but also under different sampling seasons and environmental conditions.

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