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Phosphorus transport and retention in a channel draining an urban, tropical catchment with informal settlements

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Abstract. Urban catchments in sub-Saharan Africa (SSA) are increasingly becoming a major source of phosphorus (P) to downstream ecosystems. This is primarily due to large inputs of untreated wastewater to urban drainage channels, especially in informal settlements (or slums). However, the processes governing the fate of P in these catchments are largely unknown. In this study, these processes are investigated. During high runoff events and a period of base flow, we collected hourly water samples (over 24 h) from a primary channel draining a 28 km² slum-dominated catchment in Kampala, Uganda, and from a tertiary channel draining one of the contributing slum areas (0.54 km^2) . The samples were analysed for orthophosphate (PO₄-P), particulate P (PP), total P (TP), suspended solids (SS) and hydrochemistry. We also collected channel bed and suspended sediments to determine their geo-available metals, sorption characteristics and the dominant phosphorus forms. Our results showed that the catchment exported high fluxes of P ($0.3 \text{ kg km}^2 \text{ d}^{-1}$) for PO₄-P and 0.95 for TP), which were several orders of magnitude higher than values normally reported in literature. A large proportion of P exported was particulate (56% of TP) and we inferred that most of it was retained along the channel bed. The retained sediment P was predominantly inorganic (> 63 % of total sediment P) and consisted of mostly Ca and Fe-bound P, which were present in almost equal proportions. Ca-bound sediment P was attributed to the adsorption of P to calcite because surface water was near saturation with respect to calcite in all the events sampled. Fe-bound sediment P was attributed to the adsorption of P to iron oxides in suspended sediment during runoff events given that surface water was undersaturated with respect to iron phosphates. We also found that the bed sediments were P-saturated and showed a tendency to release P by mineralisation and desorption. During rain events, there was a flushing of PP which we attributed to the resuspension of P-rich bed sediment that accumulated in the channel during low flows. However, firstflush effects were not observed. Our findings provide useful insights into the processes governing the fate and transport of P in urban slum catchments in SSA.

1 Introduction

Phosphorus (P) derived from urban catchments in sub-Saharan Africa (SSA) is increasingly becoming a major cause of eutrophication of urban fresh water bodies (Nhapi et al., 2002; Nyenje et al., 2010). This is primarily attributed to the increasing release of untreated or partially treated wastewater into the environment especially in the informal settlements or slums. The number of informal settlements in most cities in SSA is growing rapidly following rapid urbanisation and population growth. Furthermore, these areas often lack sewerage systems for collecting and treating wastewater while at the same time the existing on-site sanitation systems are usually poor. Consequently, most wastewater generated from these types of catchments is discharged untreated or partially treated into urban streams/channels resulting in the introduction of high concentrations of nutrients (nitrogen, N, and phosphorus, P) to downstream fresh water bodies (NWSC, 2008; Kulabako et al., 2010; Isunju et al., 2011; Bere, 2007; Nhapi and Tirivarombo, 2004; Nhapi et al., 2002; Foppen and Kansiime, 2009; Katukiza et al., 2010). This has led to deterioration in the water quality of most urban fresh water bodies in SSA due to eutrophication. Phosphorus is considered to be the limiting nutrient for eutrophication (Reddy et al., 1999). However, current literature shows there is limited research on P transport in urban catchments dominated with informal settlements especially in SSA.

A large number of studies in recent years have focused on understanding the dynamics of P transport during highand base-flow periods (e.g. Stutter et al., 2008; Zhang et al., 2007; Blanco et al., 2010; Peters and Donohue, 2001; Jordan et al., 2005). It is often realised that high flows exhibit higher P concentrations predominantly in particulate form compared to base flows (or low flows). This is largely attributed to the flushing of pollutants and sediments from the catchment by the increased flow. The first-flush effect is also usually reported and it occurs when the first part of the storm runoff has substantially higher concentrations of pollutants than later parts (Deletic, 1998). A view therefore exists that during the rising limb of the hydrograph, there is an initial flushing of P-rich sediments generated from either terrestrial catchment runoff or from the resuspension of channel bed sediments (e.g. Zhang et al., 2007; Rodríguez-Blanco et al., 2013; Blanco et al., 2010; Evans et al., 2004; Stutter et al., 2008). First-flush effects are, however, not widely reported for dissolved nutrients such as NO3 and PO4 because other mechanisms such as dilution and discharge from base flows tend to be dominant (Zhang et al., 2007; Blanco et al., 2010; Evans et al., 2004; Chua et al., 2009; Jordan et al., 2005).

There is also a large number of studies focusing on understanding the chemical processes that influence the transport and fate of phosphorus in streams and rivers (e.g. Froelich, 1988; Evans et al., 2004; Bedore et al., 2008; Olli et al., 2009). These processes generally include precipitation and dissolution, adsorption to soils and sediments and redox reactions. The precipitation of P minerals usually occurs with Fe, Al, Ca and Mn ions and this normally leads to retention of P in sediments (Evans et al., 2004; Bedore et al., 2008; Golterman and Meyer, 1985; Reddy et al., 1999). In hard and alkaline fresh waters, most P is often retained by precipitating as hydroxyapatite (Olli et al., 2009; Golterman, 1995). The adsorption of P to iron, aluminium or manganese oxides and hydroxides in sediments or soils is also another important process that contributes to the retention of P to bed sediments in river systems (Froelich, 1988; Golterman, 1995). In Ca-rich waters, P is also widely reported to adsorb and coprecipitate with calcite precipitates (e.g. Bedore et al., 2008; Olli et al., 2009; Golterman, 1995). Phosphorus retained in the bed sediments can also be released back into discharging waters by a number of processes, which generally include (e.g. Fox et al., 1986; Søndergaard et al., 1999; Boers and de Bles, 1991) (1) the mineralisation of organic phosphorus in the bed sediment, (2) increased solubility of phosphate minerals or desorption when external P loads are low and (3) the release of Fe-bound P following the reductive dissolution of Fe^{3+} to Fe^{2+} in anoxic conditions.

Whereas a lot of research has been done on P transport in surface water, little has been done in urban informal settlements especially in SSA. Most research is carried out in agricultural and forested watersheds and in temperate systems (e.g. Evans et al., 2004; Rodríguez-Blanco et al., 2013; Blanco et al., 2010), with very few studies in tropical, urban informal systems. However, these two systems could have contrasting mechanisms controlling P transport due to differences in climate, land use and geology. Hence, the fate of P in urban tropical catchments with informal settlements remains unknown (Nyenje et al., 2010). Chua et al. (2009) presented a case study of P transport in a tropical environment but they only focused on P transport dynamics during high and low flows without providing insights into the chemical processes regulating P transport. Informal catchments are rapidly evolving in urban areas in SSA and so is the amount of wastewater and P discharged in the environment. There is therefore a strong need to understand and manage the transport of P in these catchments.

Hence, the main objective of this paper was to contribute to the understanding of processes influencing the transport and fate of P in drainage channels in a slum-dominated tropical catchment in Kampala, Uganda. More specifically, our objectives were to (i) determine the concentrations of the various forms of P discharged from the urban slum catchment during high- and low-flow conditions, (ii) identify the effect of rainfall runoff on the discharge of P, and (iii) identify the dominant geochemical mechanisms that are likely controlling the fate of P in these channels.

2 Catchment description

The upper Lubigi catchment (28 km²) is located Northwest of Kampala, the capital city of Uganda, with the outlet at latitude 0°21' N and longitude 32°33' E (Fig. 1). The catchment is largely urbanised with a number of illegal informal settlements (or slums) such as Bwaise, Mulago, and Kamwokya, located in low-lying areas (Fig. 1). Bwaise slum is located at the outlet of the catchment. The underlying geology of the catchment is characterised by Precambrian basement rocks consisting of predominantly granite gneiss overlain by deeply weathered lateritic regolith soils (about 30 m thick) (Taylor and Howard, 1999). The saturated regolith is an important aquifer containing shallow groundwater flow systems that usually discharge as springs in the valleys of the catchment (Flynn et al., 2012; Taylor and Howard, 1998). These springs generally form the upper reaches or headwaters of the secondary channels or streams (Nyenje et al., 2013a). The mineralogy of the weathered regolith is dominated by noncalcareous kaolinite and quartz minerals with minor amounts



Fig. 1. Location of the study area (upper Lubigi catchment) in Kampala, the capital city of Uganda.

of crystalline iron oxides (Flynn et al., 2012). The mean annual rainfall measured at the Makerere University weather station (see location in Fig. 1) is 1450 mm a^{-1} with two rain seasons (March–May and September–November). During heavy storms, low-lying areas experience a lot of flooding because the catchment is highly urbanised. In slum areas like Bwaise (Fig. 1), flooding is even worse because of heavy siltation and blockage of drainage pipes owing to poor solid waste disposal (Kulabako et al., 2010).

The catchment is unsewered (not provided with a sewer). In fact, most parts in the city of Kampala (> 90%) as well as other urban areas in SSA (> 70%) are largely unsewered (Nyenje et al., 2010) implying that most people living in these areas rely on on-site sanitation for wastewater disposal. However, due to poor on-site sanitation systems especially in slum areas (Kulabako et al., 2007; Nyenje et al., 2013a; Isunju et al., 2011; Katukiza et al., 2010), most wastewater generated in the catchment ends up into the drainage system hence introducing a number of pollutants and nutrients to downstream ecosystems. The drainage system consists of small open drains or tertiary channels located between buildings, which convey a combination of runoff and wastewater (primarily grey water: Katukiza et al., 2010,

2014) into a system of larger channels, or secondary channels. The secondary channels then discharge into the primary Nsooba channel (about 3 m wide), which eventually discharges through the Bwaise slum into the Lubigi swamp (not shown in Fig. 1). The Lubigi swamp is one of the largest wetlands in the city of Kampala and, like many other wetlands in Uganda, it performs a number of important functions such as the retention of the nutrients derived from urban catchments via drainage channels (e.g. Natumanya et al., 2010; Okiror et al., 2009). Most wetlands in Uganda are, however, being degraded due to extensive encroachment for agricultural activities and infrastructure development. This has hampered their ability to retain nutrients, resulting in deterioration of adjacent water bodies such as Lake Victoria due to eutrophication (Kansiime et al., 2005; Kansiime and Nalubega, 1999; Kelderman et al., 2007; Kyambadde et al., 2005; Mugisha et al., 2007).

3 Methodology

3.1 Discharge monitoring and precipitation

Stream gauges, each equipped with a Mini-Diver data logger (Schlumberger water services, Delft, the Netherlands), were installed in Nsooba channel at the outlet of the catchment (B1) and at two upstream locations B5 and B6 to monitor discharge along the Nsooba primary channel (Fig. 1). The divers continuously recorded water levels at 20 min intervals. The water levels were compensated for atmospheric pressure using a Baro-Diver (Schlumberger water services, Delft, the Netherlands) installed near the stream gauges. The compensated water levels, H (cm) were converted to discharge, Q (m³ s⁻¹) using rating curves $(Q = 0.0006 H^2 - 0.0076 H : r^2 = 0.99)$, n = 13 for B1, $Q = 0.0039 H^{1.4152}$: $r^2 = 0.89 n = 7$ for B5 and $Q = 0.0021 H^{1.54}$: $r^2 = 0.86$, n = 4 for B6), that were developed from a series of discharge measurements carried out. These discharges were measured during different hydrological situations using the salt dilution method (Moore, 2004). It was not possible to perform discharge measurements in the tertiary channel in Bwaise slum (Fig. 1). Long-term daily precipitation data, which were used to estimate the annual average precipitation, were provided by the Uganda meteorological department whose nearest weather station is located in Makerere University, about 2 km from the outlet of the catchment (Fig. 1). During storms, rainfall data at 5 min intervals and 0.2 mm resolution were obtained from the CREEC project (the Centre for Research in Energy and Energy Conservation; http://creec.or.ug/) located next to the College of Engineering, Design, Art and Technology, Makerere University, about 2 km from the catchment outlet.

3.2 Water quality sampling and analysis

We initially collected water samples at intervals of 1–2 h for 24 h during a low flow period on 26 May 2010 (depicting base-flow conditions) and during two rainfall events on 28 June and 28 July 2010. The samples were collected in clean 1 L plastic bottles from the primary channel (Nsooba) at the catchment outlet (B1) and in one of the tertiary channels (B4) in the Bwaise III slum (Fig. 1). Tertiary channels are considered to be the primary source of P into the primary channel due to sewage effluents especially in slum areas (Nyenje et al., 2013b; Katukiza et al., 2010). To account for spatial and temporal variability of our data, we collected two more rainfall events on 18 September 2012 and on 8 November 2012 at two upstream locations (B5 and B6) along the Nsooba primary channel (Fig. 1).

All water samples were first analysed on-site for electrical conductivity (EC), temperature, pH, dissolved oxygen (DO) and alkalinity (HCO₃) immediately after sampling. EC and temperature were measured with an EC electrode (Tetra-Con 325, WTW) connected to an EC meter (WTW 3310), pH with a pH electrode (SenTix 21, WTW) connected to pH meter (WTW 3310) and DO with a DO sensor (CellOx 325, WTW) connected to a DO meter (WTW 3310). The meters were calibrated before taking measurements. HCO3 was determined by titrating with 0.2 M sulfuric acid. After onsite measurements, the water samples were kept in a cool box at 4°C and transported to Makerere University Public Health and Environmental Engineering (PH & EE) Laboratory. Here, the samples were analysed for total phosphorus (TP), orthophosphate (PO4-P) and total dissolved phosphorus (TDP), ammonium (NH₃-N), nitrate (NO₃-N), total solids (TS) and total suspended solids (SS) in less than 24 h after collecting the samples. TP was determined on unfiltered samples using the Ascorbic acid method after digestion with persulfate (APHA/AWWA/WEF, 2005), TDP on filtered samples using the same method as TP and PO₄-P determined on filtered samples using the ascorbic acid method (Murphy and Riley, 1962). Particulate phosphorus (PP) was calculated as the difference between concentrations of TP and TDP. Nitrate (NO₃-N) and ammonium (NH₃-N) were determined on filtered samples using the cadmium reduction method and the Nessler method, respectively. All filtered samples were passed through 0.45 um Whatman membrane filters. Final readings were carried out on a HACH DR/4000 U spectrophotometer (USA). Suspended solids (SS) were calculated as the difference between TS and TDS. Total solids (TS) were determined by evaporating an unfiltered sample in an oven at 105 °C for 24 h, and then determining the mass of the dry residue per litre of sample, whereas TDS were determined using the same method as TS but on samples filtered using Whatman GF/C filters (APHA/AWWA/WEF, 2005). Samples collected at locations B1 and B4 were very turbid and frequently clogged the filter papers. For these samples, SS were calculated as the difference between TS and the TDS estimated from EC as recommended in APHA/AWWA/WEF (2005) in such situations. Here, TDS were estimated from EC using a conversion factor of 0.56, which was computed from a series of TDS and EC values measured during our initial samplings. The factor we used was within acceptable limits (0.55-0.7;APHA/AWWA/WEF, 2005). Cations and anions were measured on filtered samples at the UNESCO-IHE laboratory in the Netherlands only for the samples collected at locations B1 and B4: cations (Ca, K, Mg, Na, Mn and Fe) using an inductively coupled plasma spectrophotometer (ICP - Perkin Elmer Optima 3000) and anions (Cl and SO₄) by ion chromatography (IC - Dionex ICS-1000). These samples were filtered on-site using 0.45 µm Whatman membrane filters and kept cool at 4 °C prior to analysis. Cation samples were preserved by adding 2 drops to concentrated nitric acid.

3.3 Mineral saturation indices

We used the PHREEQC model code (version 2, Parkhurst and Appelo, 1999) to calculate the saturation indices of the most important phosphate minerals including calcite (CaCO₃), hydroxyapatite (Ca₅(PO₄)₃(OH)) and vivianite (Fe₃(PO₄)₂ · 8 H₂O) (Stumm and Morgan, 1981). These minerals can regulate P either by precipitation/dissolution (for hydroxyapatite and vivianite) or by co-precipitation (for calcite). Strengite (FePO₄ · 2 H₂O) was not considered because surface water was anoxic and alkaline (as shown in results), and under these conditions the strengite forming Fe³⁺ is expected to be insoluble (Appelo and Postma, 2007). Moreover, Fe³⁺ is insoluble in the pH range of 5–8. We also determined the saturation indices of rhodochrosite (MnCO₃) and siderite (FeCO₃) because these metal carbonates can also regulate the concentrations of P by co-precipitation or by precipitation/dissolution reactions.

3.4 Sediment sampling and analysis

We collected both surface and deep layer bed sediments at locations B1, B7 and B4 (see Fig. 1). The surface layer sediment (herein called shallow sediment) is where most P interactions between the water column and bed sediment occur (Hooda et al., 2000), whereas deep layer sediments represent older deposits that can give insights into earlier interactions that took place. Shallow sediment was loose and was sampled at depths of 0-30 cm using a 1m long multisampler with a 40 cm internal diameter (Eijkelkamp, the Netherlands). Deep layer sediments were more consolidated and were sampled at depths of 30-60 cm using a hand auger. In the tertiary channel (B4, Fig. 1), only the shallow sediment was sampled because the channel was lined and the sediment layer was thin (< 10 cm). Due to logistic reasons, suspended sediments were only collected from location B1 during the first rainfall event. This was done by settling and decanting water samples collected in 20L jerry cans. At the Public Health and Environmental Engineering Laboratory, Makerere University, Uganda, the sediments were air-dried for two weeks. All samples were then sieved using a 2 mm sieve, kept in plastic bags and then transported to the UNESCO-IHE, the Netherlands, for analysis. For suspended sediment, only the sample collected during the peak flow at 11:30 LT (event 1) was analysed because the other samples did not contain enough useable sediment for the soil experiments. Sediments were analysed for geo-available metals (Fe, Ca, Mg and K), pH, organic matter (OM), organic carbon (OC), available phosphorus and grain size distribution. Geo-available metals were extracted with 0.43 M HNO₃ (Rauret, 1998; Novozamsky et al., 1993) and analysed using an ICP spectrophotometer (Perkin Elmer Optima 3000). Al and Si were not determined due to analytical limitations. Available phosphorus was extracted using the Bray 2 method (Bray and Kurtz, 1945) and analysed by spectrophotometry using the ascorbic acid method. Grain size distribution was determined at the VU University Amsterdam, the Netherlands, by laser diffraction technique using the Helos/KR Sympatec instrument (Konert and Vandenberghe, 1997). The pH was measured on a 2.5:1 water to soil suspension. Soil OC was determined using the Walkley–Black method (Walkley and Black, 1934). Soil OM was estimated from OC using a conversion factor of 1.722 based on the assumption that OM contains 58% carbon (Kerven et al., 2000). All measurements were carried out in duplicate and the results averaged.

3.5 Sequential extraction of phosphorus species from selected sediments

To determine the different forms of phosphorus in the stream sediments, we used a sequential extraction technique described by Ruban et al. (2001). The technique was slightly modified to adapt to the equipment available at the laboratory whereby the sediment-solution ratio of $10:1 \text{ (mg mL}^{-1}\text{)}$ was maintained, but the amount of soil used was 500 instead of 200 mg. The following forms of P were extracted: P bound to iron, aluminium and manganese oxides and hydroxides (Fe/Al/Mn-bound P), P associated with Ca (Ca-bound P), inorganic P (IP), organic P (OP) and total P. Before analysis, the sediment was first oven dried at 60 °C for 2 h. For each form of P. extractions then were carried out by adding 50 mL of extracting solution to 500 mg of sediment (or the residue of a previous extraction) and the mixture stirred for 16h. The samples were centrifuged at 4000 rpm for 15 min and the P in the extract determined by spectrophotometry using the ascorbic acid method. Fe/Al/Mn-bound P was extracted from 500 mg of dry sediment using 1 M NaOH (also referred to as NaOH-P). The residue from this extraction was used for the extraction of Ca-bound P using 1 M HCl (also referred to as HCl-P). Total P was extracted from 500 mg of dry sediment using 3.5 M HCl. IP was extracted from 500 mg of dry sediment using 1 M HCl. The residue of the IP extraction was washed with distilled water and calcinated at 450 °C for 3 h and then the ash used for extraction of OP using 1M HCl. All extractions were carried out in duplicate and the results averaged.

3.6 Phosphorus sorption experiments on selected sediments

Sorption experiments were carried out using duplicate batch experiments. Thereto, 25 mg of sediment samples were accurately weighed and mixed with 500 mL of 0.01 M CaCl₂ solution of varying initial P concentrations of 0, 20, 40, 80, 100 and 250 mg L⁻¹ (i.e. a soil-solution ratio of 0.05). The CaCl₂ solution minimises the competition for sorption sites between phosphate ions and other ions (Froelich, 1988). The phosphorus solutions were prepared using anhydrous KH₂PO₄. The P concentrations used were much higher than those present in the channel (\cong 0.5 mg PL⁻¹) in order to establish the maximum adsorption capacity of the sediments. The mixtures were gently shaken on an orbital shaker at 100 rpm to equilibrate. After 24 h equilibrium time,

the final P concentrations in the solutions were measured by spectrophotometry using the ascorbic acid method. The amount of phosphate sorbed was calculated as

$$C_{\rm ads} = \frac{\left(C_o - C_{\rm eqm}\right) \times V}{m} \times 1000,\tag{1}$$

where C_{ads} is the sorbed amount of P (mg kg⁻¹), C_o is the initial P concentration in solution (mg L⁻¹), C_{eqm} is the measured P concentration in solution after equilibrium (mg L⁻¹), V is the volume of the sample in litres (0.5 L in this experiment) and m is the mass of the dried soil sample (kg).

To establish which sorption isotherm provided the best fit, the Langmuir (Eq. 2) and Freundlich (Eq. 3) equations were fitted to the data. These two equations are often employed to describe adsorption processes (Appelo and Postma, 2007; Golterman, 1995):

$$C_{\rm ads} = \frac{S_{\rm max} \, C_{\rm eqm}}{K_L + C_{\rm eqm}},\tag{2}$$

$$C_{\rm ads} = K_F \cdot C_{\rm eqm},\tag{3}$$

where S_{max} is the maximum adsorbed amount possible (mg kg^{-1}) and K_L , K_F and n are adjustable constants (-).

4 Results

4.1 The hydrochemistry of drainage channels

Table 1 presents the hydrochemistry of surface water based on the samples collected at the catchment outlet and in the tertiary channel during base-flow conditions. Surface water in the Nsooba primary channel was primarily alkaline (pH=7.0-7.5; mean of 7.3) and had high values of EC $(471-612 \,\mu\text{S cm}^{-1})$: mean of 554 $\mu\text{S cm}^{-1}$), high concentrations of HCO₃ (181–326 mg L^{-1} : mean of 213 mg L^{-1}) and Cl (26.2–71.3 mg L^{-1} : mean of 40.8 mg L^{-1}) and relatively high concentrations of cations, primarily Na (4.1- 51 mg L^{-1} ; mean of 14.9 mg L⁻¹) and Ca (3.4–25.5 mg L⁻¹; mean of 8.2 mg L^{-1}). The tertiary channel, which drains Bwaise slum, was more alkaline (pH = 7.4-7.8; mean of 7.7) and had much higher concentrations of dissolved solutes - about 3 times higher than in the Nsooba primary channel. The mean base-flow concentration of PO₄-P in the primary channel was 0.36 mg L^{-1} (range = $0.11-0.78 \text{ mg L}^{-1}$) accounting for 30 % of TP (1.2 mg L^{-1} ; Table 1). In the tertiary channel, it was 3.3 mg L^{-1} (range = 2–4.8 mg L⁻¹) accounting for 64 % of TP (5.2 mg L^{-1} ; Table 1). Hence, PP was the dominant form of P in the primary channel during base flows whereas in the tertiary channel PO₄-P was dominant.

The channels were generally anoxic and characterised by low concentrations of dissolved oxygen (DO $< 1 \text{ mg L}^{-1}$; Table 1) in both the primary and the tertiary channel. Consequently, the concentrations of NO₃-N were

Table 1. Hydrochemistry of drainage channels during base-flow conditions at the catchment outlet and in the tertiary drain. Data are shown in concentration ranges with the average values in brackets.

Parameter	Nsooba channel (Outlet, B1)	Tertiary channel (B4)					
EC (μ S cm ⁻¹)	471-612 (554)	1511–1983 (1792)					
<i>T</i> (°C)	19.7–28.4 (24.5)	19.3–28.3 (24.2)					
pH	7.0–7.5 (7.3)	7.4–7.8 (7.7)					
$DO (mg L^{-1})$	0.03-1.87 (0.7)	0.03-0.99 (0.37)					
$Ca (mg L^{-1})$	3.4-25.5 (8.2)	7.1-46.0 (20.3)					
Mg (mg L^{-1})	0.75-6.20 (1.98)	2.3-28.3 (7.8)					
$K (mg L^{-1})$	2.8-24 (7.5)	13.5-89.3 (39.5)					
Na (mg L^{-1})	4.1-51.0 (14.9)	21.5-229.9 (77.0)					
Fe (mg L^{-1})	0-0.47 (0.12)	0.01-0.31 (0.07)					
$Mn (mg L^{-1})$	0.14-1.28 (0.40)	0.04-1.13 (0.48)					
$NH_3-N (mg L^{-1})$	6.8-12.1 (10.4)	24.5-41.0 (32.4)					
$NO_3-N (mg L^{-1})$	0.5-3.6 (1.61)	0-7.4 (1.66)					
$Cl (mg L^{-1})$	26.2-71.3 (40.8)	26.5-117.6 (78.3)					
$HCO_3 (mg L^{-1})$	181-326 (213)	522-725 (624)					
$SO_4 (mg L^{-1})$	5.7–27.5 (9.5)	3.8–28.0 (11.8)					
Phosphorus forms (mg L^{-1})							
TP	0.51-1.61 (1.15)	3.5-7.7 (5.2)					
PP	0.09-0.93 (0.64)	0.9-4.8 (2.2)					
PO ₄ -P	0.11-0.78 (0.36)	2-4.8 (3.3)					

low (< 1.6 mg L^{-1}) while NH₃-N concentrations were high (mean of 10.4 mg L^{-1} in the primary channel and 32.4 mg L^{-1} in the tertiary channel). With regard to redox sensitive elements, Fe concentrations were very low (mean < 0.12 mg L^{-1}) whereas SO₄ concentrations were high (about 10 mg L^{-1} ; Table 1). Although Mn concentrations were also low (mean of 0.4 mg L^{-1} in the primary channel and 0.48 mg L^{-1} in the tertiary channel), they were relatively higher than the Fe concentrations. Hence, the redox status of the surface water was likely Mn-reducing.

4.2 Saturation indices (SIs)

Surface water is considered to be saturated or near saturated when the saturation index (SI) of a given mineral ranges between -0.5 < SI < 0.5 (Deutsch, 1997). A range of -0.7 < SI < 0.7 is also considered in some studies (e.g. Griffioen, 2006). In the tertiary drain, most samples were saturated (-0.4 < SI < 0.4) with respect to calcite and rhodochrosite (Fig. 2b). In the primary channel, some samples were near saturation levels with respect to calcite and rhodochrosite (0 < SI < -0.7) whereas some were undersaturated (SI < -1) especially during rain events (Fig. 2a). The two minerals (calcite and rhodochrosite) therefore likely regulated P concentrations by co-precipitation (or the adsorption of P onto carbonate precipitates). The SI values of MnHPO₄ were high but relatively constant (SI ranged



Fig. 2. Saturation indices of the most important phosphate minerals during base-flow and runoff events: (a) at the outlet of the catchment and (b) in the tertiary channel draining the Bwaise III slum. The minerals vivianite and siderite are not shown here because they had high negative values of saturation indices suggesting that they were not present.

from 2 to 3) in both the tertiary and the primary channels and in all the events (Fig. 2). These high saturation levels of MnHPO₄ were likely regulated by the near saturated levels of rhodochrosite, which suggests that MnHPO₄ was not reactive. The term reactive mineral here refers to a mineral that can easily dissolve into or precipitate from the water column under certain conditions (Deutsch, 1997). The SI values of iron phosphates (vivianite) were most of the times less than -1 (undersaturated) implying that these minerals were either not present or not reactive. Surface water was supersaturated with respect to hydroxyapatite in the tertiary channel (Fig. 2b) but undersaturated in the primary channel (Fig. 2a).

4.3 Phosphorus concentrations during base flow

During base-flow conditions, high concentrations of P were measured in the Nsooba channel, with values ranging from 0.51 to 1.61 mg L^{-1} (average 1.15 mg L^{-1}) for TP, 0.09 to 0.93 mg L^{-1} (average 0.64 mg L^{-1}) for PP and 0.11 to

0.78 mg L⁻¹ (average 0.36 mg L^{-1}) for PO₄-P (Table 1, Fig. 3a). The dominant form of P was PP accounting for 56% of TP whereas PO₄-P accounted for 31%. Concentrations of P seemed to vary slightly during the day with relatively higher concentrations (> 1 mg L⁻¹ as TP) occurring between 07:00 LT and midnight, and lower concentrations occurring after midnight (< 1 mg L⁻¹ TP) (Fig. 3a). The base-flow P concentrations in the tertiary channel were much higher than in the primary Nsooba channel and ranged 3.5–7.7 mg L⁻¹ (average of 5.2 mg L⁻¹) for TP, 0.9–4.8 mg L⁻¹ (average of 3.3 mg L⁻¹) for PP and 2–4.8 mg L⁻¹ (average of 3.3 mg L⁻¹) for PO₄-P (Table 1; Fig. 6a). Here particulate P accounted for 42% of TP whereas PO₄-P accounted for 58%.

4.4 Phosphorus concentrations during rainfall events

We collected hourly data over 24 h on four rainfall events on 26 June 2010 and 28 July 2010 (at the catchment outlet, B1,





Fig. 3. Temporal trends in concentrations of phosphorus (TP, PP and PO₄-P) and SS in the Nsooba channel at location B1 (catchment outlet) during (**a**) a base-flow event, (**b**) rainfall event 1 and (**c**) rain fall event 2.

and in the tertiary channel, B4) and on 18 September 2012 and 8 November 2012 (at upstream locations B5 and B6 along the primary channel).

In all these events, there was a simultaneous increase in concentrations of TP and PP (and SS as well) with peak concentrations almost coinciding with the peak discharge of the rainfall-runoff hydrographs (Figs. 3-5). Thereafter, base-flow concentrations were restored. At the catchment outlet, B1, about 8.6 mm (intensity of 14 mm h^{-1}) fell during the first event (28-29 June 2010) producing a peak discharge of $6.7 \text{ m}^3 \text{ s}^{-1}$. Subsequently, there was an increase in concentrations of TP and PP, and concentration peaks of $4 \text{ mg } \text{L}^{-1}$ for TP and $3.66 \text{ mg } \text{L}^{-1}$ for PP (about 92%) of TP) were realised (Fig. 3b). During the second event $(28-29 \text{ July } 2010; 14.8 \text{ mm}, \text{ intensity of } 6.5 \text{ mm h}^{-1})$, two smaller peak discharges of 1.3 and 1.4 m³ s⁻¹ were produced. Consequently, two peak concentrations of TP and PP were produced (Fig. 3c). The first concentration peak had 3.0 mg L^{-1} for TP and 2.4 mg L^{-1} for PP whereas the second had 2.1 mg L^{-1} for TP and 1.5 mg L^{-1} for PP.



Fig. 4. Temporal trends in concentrations of phosphorus (TP, PP and PO_4 -P) and SS in the Nsooba channel at location B5 during (a) rainfall event 3 and (b) rainfall event 4. Note: during these events, precipitation data was not available and is therefore not presented.



Fig. 5. Temporal trends in concentrations of phosphorus (TP, PP and PO₄-P) and SS in the Nsooba channel at location B6 during (**a**) rainfall event 3 and (**b**) rainfall event 4.

In the upper locations (B5 and B6; Fig. 1), the drainage area was smaller (about 8 km^2) resulting into smaller discharges (peak of about $2 \text{ m}^3 \text{ s}^{-1}$; see Figs. 4 and 5) after a storm event. However, the peak concentrations of PP and TP at these locations after the storm events were slightly



Fig. 6. Temporal trends in concentrations of phosphorus (TP, PP and PO_4 -P) and SS in a tertiary channel discharging from the Bwaise slum during (a) a base-flow event, (b) rain event 1 and, (c) rain event 2. Discharge measurements were not possible at this site.

higher than those observed at the catchment outlet, which had a larger drainage area. For example, at location B5, about 7 mm of rain fell on 18 September 2012 (event 3) producing a peak discharge of $1.9 \text{ m}^3 \text{ s}^{-1}$. The resulting peak concentrations of TP and PP were 6.8 mg L^{-1} for TP and 5.7 mg L^{-1} for PP (about 84 % of TP) (Fig. 4a).

In the tertiary channel, the P trends following storm events were similar to those in the primary channel, except here, the concentrations were much higher (see Fig. 6b and c). For example, after the first rainfall event (28 June 2010), peak concentrations of 19.7 mg L^{-1} for TP and 14.1 mg L^{-1} for PP were realised (almost 3 times higher than corresponding peak concentrations in the primary channel) (Fig. 6b).

Rainfall events also increased the concentrations of suspended solids (SS) and we observed that the concentration peaks of SS generally coincided with those of PP and TP (see Figs. 3–6). However, the responses of PO₄-P were not readily evident as was observed for TP and PP (Figs. 3–5) except in the tertiary channel (Fig. 6b, c). In all runoff events sampled,



Fig. 7. Mean concentrations of P forms in the bed and suspended sediments. The P forms included Fe/Al-bound P, Ca-bound P, OP, total P and available P (Bray-2 extractable P). Suspended sediments were only collected at peak flow during event 1 (error bars represent standard error, n = 2).

the concentrations peaks of PP and TP were realised after the peak discharge implying a late delivery of nutrients.

4.5 Physical and chemical characteristics of sediments

Table 2 presents the results of the soil analyses. The bed sediments had very high values for sand content (63–83%) and low values for silt content (5–11%). Suspended sediments, however, had a high silt content (56%) and low sand and clay contents (< 23% each). The sediments were alkaline with pH ranging from 7.1 to 7.3. Organic matter content ranged from 1.8 to 3% and was highest in deeper sediments. Based on the 0.43 M HNO₃ extraction, Ca was the dominant cation followed by Fe and then Mn. Al was not determined due to analytical limitations. Hence Ca, Fe and Mn were most capable of interacting with P. Suspended sediments contained higher contents Ca, Fe and Mn than the bed sediments.

The results of sequential P extraction showed that the total sediment P ranged from 1375 to 1850 mg kg⁻¹. Inorganic P was the dominant form of P in the sediments accounting for over 63 % (range of 64–80 %) of the total sediment P (Fig. 7). Here Ca-bound P and Fe/Mn-bound P were present in almost equal proportions (i.e. 51-54 and 46-49% of total P, respectively). The measured IP contents (not shown) were close to the calculated values (sum of Ca-P and Fe-P) except for suspended sediments. Organic P accounted for 17-22 % of total sediment P whereas adsorbed P (i.e. Bray-2 extractable P) accounted for only 5-8% of total sediment P. Hence, P retained in sediments was probably a result of precipitation of calcium and iron phosphates or the adsorption of P to iron/manganese oxides. Suspended sediment collected during the peak of the first rain event had the highest content of phosphorus (total sediment P of 2316 mg kg^{-1}) of which Ca-bound P accounted for 43 % of the total sediment P and Fe/Mn-bound P

				Geo-a	available	metals	(mg kg	g ⁻¹)	G distril	rain siz	ze ** (%)
Location	рН (—)	OM* (%)	OC* (%)	Ca	Mg	K	Mn	Fe	Sand	Silt	Cla

173

216

375

130

292

939

Shallow sediment (< 30 cm)

Suspended sediment (Event 1 at 11:30 LT)

105

194

311

117

381

1405

387

348

767

375

379

908

3761

3269

3437

2338

2262

5755

79

77

63

84

83

23

14

16

26

11 12

56

7

7

11

5

5

21

3636

4691

8505

2729

7620

18125

Table 2. Physical and chemical properties of bed and suspended sediments in the Nsooba channel and in the tertiary channel of the Bwaise slum.

*OM, organic matter; OC, organic carbon; ** clay (< 2 µm), silt (2-50 µm) and sand (50 µm-2 mm)



B1 (outlet)

B1 (outlet)

B1 (outlet)

B4 (tertiary drain)

B7

B7

7.1

7.3

7.3

7.2

7.3

_

3.0

3.0

2.0

2.7

1.8

1.7

1.7

1.2

1.6

1.1

_

Fig. 8. Langmuir sorption isotherms for sediments sampled at locations B1 (catchment outlet), B7 (inlet of slum area) and B4 (tertiary channel).

accounted for 29 % of the total sediment P. There seemed to be no significant differences between the shallow and deep sediments.

From the P sorption experiments, the Langmuir isotherm provided the best fit of the sediment data ($r^2 = 0.85-0.98$; Fig. 8). The sediments in the tertiary channel, however, had a poor fit ($r^2 = 4.3$) probably due to the relatively low Fe content (2262 mg kg⁻¹) compared to that in the Nsooba channel (> 3400 mg kg⁻¹) (Table 2). The maximum sorption capacity (S_{max}) of the sediments ranged from 820 to 2350 mg kg⁻¹ (Fig. 8). Deeper sediments had the highest sorption capacity ($S_{max} = 2350 \text{ mg kg}^{-1}$). Shallow sediments generally had low sorption capacities ($S_{max} = 1550 \text{ mg kg}^{-1}$ in Nsooba sediment and $S_{max} = 850 \text{ mg kg}^{-1}$ in the tertiary channel). From Fig. 8, it became clear that the predicted amount of P sorbed to the sediment based on the measured PO₄-P concentrations (means of 0.36 and 3.3 mg L⁻¹; Table 1) was about 0.02 mg g⁻¹ (or 20 mg kg⁻¹), which is much less than the sum of the inorganic and the Bray-2 extractable P (1.15–1.29 mg g⁻¹; Fig. 7). Hence, the sediments were likely P saturated.

5 Discussion

5.1 Phosphorus exported from the catchment

Our results showed that the average base-flow concentrations of PO₄-P and TP at the outlet of the studied catchment were 0.36 and 1.2 mg L^{-1} , respectively (Fig. 3a; Table 1). These concentrations are about 16 times the eutrophication limit of $0.075 \text{ mg TP L}^{-1}$ proposed by Dodds et al. (1998) for streams implying that the channel was very eutrophic. For a mean base flow of $0.22 \text{ m}^3 \text{ s}^{-1}$ (Fig. 3), the fluxes of PO₄-P and TP from the studied catchment were about 0.3 and 0.95 kg km⁻² d⁻¹, respectively. These fluxes appear to be very high compared to those normally reported in published literature for agricultural, forested and other urban catchments. Jordan et al. (2007) for example reported a TP flux of $0.2 \text{ kg} \text{ km}^{-2} \text{ d}^{-1}$ for a 5 km² rural agricultural catchment in Northern Ireland. In a mixed land use catchment in Galicia, Spain, Rodríguez-Blanco et al. (2013) reported a much lower TP flux of 0.04 kg km⁻² d⁻¹. Zhang et al. (2007) found a TP flux of only $0.034 \text{ kg km}^{-2} \text{ d}^{-1}$ in nutrient runoff from forested watershed in central Japan. Nhapi et al. (2006)

showed that the TP flux for the two major river inflows to the eutrophic Lake Chievero in the city of Harare (Zimbabwe) ranged between 0.1 and 0.35 kg km⁻² d⁻¹. Although these rivers were heavily polluted by on-site sanitation and sewage overflows from treatment plants, the TP fluxes were still low when compared to those in our study. Our findings therefore suggest that phosphorus exported from urban catchments with informal settlements (or slums) poses a very serious threat to downstream surface water quality due to eutrophication.

5.2 Source of phosphorus

There are three possible sources of P the high concentrations of observed in the Nsooba channel: groundwater exfiltration, precipitation and anthropogenic sources (use of agricultural fertilisers and sewage effluents). However, groundwater and precipitation in the study area contain relatively low concentrations of P ($< 0.06 \text{ mg L}^{-1}$ as PO₄-P; Nyenje et al., 2013b). There is also limited use of fertilisers for agriculture in the study area and in most parts of Uganda. Hence, sewage effluents were the most likely sources of P in the studied channels. The lack of a sewer system and the existing poor onsite sanitation systems in the studied catchment means that most wastewater generated from households was directly discharged untreated into the drainage channels thereby introducing high levels of nutrients. The water quality of these channels was characterised by high concentrations of EC, HCO₃, NH₄, PO₄-P and cations (Table 1), which is typical of wastewater streams derived from sewage effluents. A recent study by Katukiza et al. (2014) revealed that most wastewater in these channels is composed of grey water (wastewater from bathrooms, kitchens and laundry), which is normally transported to the primary channel via small channels (or tertiary channels) between households especially in slum areas. We monitored one of the tertiary channels in the Bwaise slum and indeed it contained very high P concentrations (TP = 3.5- 7.7 mg L^{-1} and PO₄-P=2-4.8 mg L⁻¹; Table 1) similar to those found in grey water in this slum area (6–8 mg TP L^{-1} ; Katukiza et al., 2014). The influence of domestic wastewater as a source of P can also be seen from the 24 h trends of the base-flow concentrations of TP in the primary channel (Fig. 3a). From midnight onwards, the concentrations of TP in the primary channel were less than $1 \text{ mg } \text{L}^{-1}$, whereas from 07:00 to 10:00 LT they were greater than 1 mg TP L^{-1} (Fig. 3a). This suggested that P was being added to the system during the hours of the day and this was likely due to wastewater effluents from human activity. This may also explain why orthophosphates accounted for the largest proportion of P in the tertiary channel given that orthophosphate is the dominant form of P in wastewater streams (Bedore et al., 2008). We therefore concluded that sewage effluents, especially from grey water streams, were the main source of P in the studied catchment.

5.3 Effects of rainfall runoff events

Rainfall runoff events indicated a flushing of P predominantly in particulate form (e.g. 92% of TP during event 1 was particulate, Fig. 3b). This flush was characterised by a sharp increase in concentrations of TP and PP (and SS) during the rising limb of the hydrograph and a subsequent decrease during the falling limb and finally restoration of baseflow concentrations. This phenomenon was present in all the four rainfall events at the catchment outlet (B1), the upstream stations B5 and B6 and in the tertiary channel (B4). During the second event (Fig. 3c), there were two discharge peaks at B1 which resulted in two concentration peaks of TP and PP, with the later peak lower than the former probably due to flushing effects. The peak concentrations of SS during the runoff events coincided with those of TP and PP in all the four rain events (Figs. 3–6), which implied that most phosphorus transported during rain events was associated with suspended sediments. These sediments were likely mobilised from the resuspension of the P-rich bed sediments accumulated in the channel or by erosion of material stored on the urban surface. We observed that the peak concentrations of TP and PP in the primary channel during storm events were not so different at the catchment outlet and the upstream locations B5 and B6, yet discharge varied significantly because of differences in drainage areas. It is therefore unlikely that catchment runoff was the primary source of TP and PP during rain events. Instead, we think that resuspension of P-rich bed sediment played a more important role. This sediment phosphorus was likely deposited during low flows because a large amount of P (about 56%) in the primary channel was particulate during the base-flow event sampled. Our results therefore suggest that there was a flushing of TP and PP, primarily due to the resuspension of bed sediments. Flush effects were not observed for the dissolved form of P (PO₄-P) probably because other mechanisms such as precipitation/dissolution or dilution were more dominant.

First-flush effects for PP and SS have been reported in many studies investigating P transport during storm events (e.g. Stutter et al., 2008; Zhang et al., 2007). They occur when the rising limb of a hydrograph contains higher concentrations of pollutant than the falling limb (Deletic, 1998). Results from our study, however, seem to suggest that PP and TP did not exhibit first-flush effects. This is because the concentration peaks of PP and SS were most of the times realised after the peak events (see Figs. 3–6), implying that the falling limb contained higher concentrations of pollutants than the rising limb. This could have been caused by the poor on-site sanitation systems in the catchment. Here, wastewater especially from pit latrines is normally released into the drainage channels after rain events (particularly when increased flows are observed) as a cheap way of emptying the latrines (see description study area). One study by Chua et al. (2009) also investigated a tropical catchment with proportions of rural and urban land use similar to the catchment we studied, and they also observed that the first-flush effects were generally weak for TP and PP. In our study, however, our sample collection was not frequent enough during peak flows and it is therefore not possible to confirm whether the first-flush effects for PP were present or not.

5.4 Sediment-water column phosphorus interactions

5.4.1 P retention and role of overlying water

The settling of particulate matter is one of the most important mechanisms of P retention in the channel bed sediments (Reddy et al., 1999). As already mentioned above, our results showed that most P discharged at the outlet of the catchment during low flows was particulate (56% of TP) and was likely retained along the channel bed by settling. Fractionation analyses also showed that the P retained in the bed sediment was largely inorganic accounting for 64-80% of the total sediment P. Additionally, inorganic sediment P was mostly bound to Ca (HCl-P) and Fe/Mn (NaOH-P) and in almost equal proportions (51–54 and 46–49% respectively; Fig. 7). This implies that P retention processes in the bed sediment were attributed to either mineral precipitation or the adsorption of P to sediments. Therefore, sediment inorganic P that was bound to Ca (or Ca-bound P) could either be mineral precipitates of hydroxyapatite or P adsorbed to calcite. These two minerals (hydroxyapatite and calcite) are widely reported in literature to regulate P transport in river systems by precipitation and co-precipitation respectively (e.g. Reddy et al., 1999; Golterman, 1995; Griffioen, 2006; Tournoud et al., 2005). However, the nature of the rocks in our study area (Precambrian granite-gneiss rocks; see section "Catchment description") shows that there are no carbonate-bearing rocks like calcite. Hence, the likely source of calcite in sediment, if it was present, was through mineral precipitation reactions in the water column (i.e. calcite precipitates). Sediment inorganic P bound to Fe/Mn (or Fe/Mn-bound P) was likely a result of the adsorption of P to iron oxides or the precipitation of iron and manganese phosphates. Note that we were unable to determine Al in this study and therefore the role of aluminium oxides to the adsorption of P is not considered. Here, below, we try to identify the relative importance of these two processes (sorption and mineral solubility) to the retention of P in the sediment.

With regard Ca-bound P, geochemical speciation results showed that surface water was most of the times near saturation or saturated with respect to calcite in both the primary and the tertiary channels (0 < SI < 0.7; Fig. 2) implying that calcite was reactive (may equilibrate with surface water) in the studied channels. The channels were, however, undersaturated with respect to hydroxyapatite (SI generally less than -1) in the primary channel but oversaturated in the tertiary channel (SI generally greater than 1). This phenomena likely occurred due to the high concentrations of Ca ($7.1-46 \text{ mg L}^{-1}$) and phosphate ($2-4.8 \text{ mg L}^{-1}$ as PO₄-P) in the tertiary channel (Table 1) and the low concentrations in the primary channel (Ca=3.4–25.5 mg L⁻¹; PO₄ – P=0.1–0.9 mg L⁻¹) following dilution. Hence, hydroxyapatite seemed not to be reactive. Indeed some studies suggest that hydroxyapatite precipitation can only take place when the SI > 9.4 and when Ca concentrations are very high (> 100 mg L⁻¹) (e.g. Diaz et al., 1994). Given that phosphorus has strong adsorption affinity to calcite (e.g. Reddy et al., 1999) and that calcite was reactive, we conclude that Cabound P in the bed sediments was due to the adsorption of P to calcite precipitates.

With regard to Fe/Mn-bound P, the studied drains were undersaturated with respect to vivianite (SI < -3; not shown in Fig. 2) implying that vivianite was not present in the studied channels. Strengite was also likely not present because Fe^{3+} is insoluble in the pH range of 5-8 (Appelo and Postma, 2007), which was the pH range of the drainage channels studied (pH = 7.0-7.8). MnHPO₄ was consistently oversaturated (SI \cong 2–3) in both the tertiary and the primary channel, which suggests that this mineral was not reactive. It is also possible that the high SI values of MnHPO₄ were caused by the near saturated state of rhodochrosite (MnCO₃) because surface water was saturated with respect to this mineral (Fig. 2a, b). Although mineral carbonates such as calcite can regulate P by co-precipitation (e.g. Freeman and Rowell, 1981), there are currently no published reports of phosphorus scavenging by rhodochrosite (MnCO₃). Hence, P bound to the iron/manganese oxides was likely due to the adsorption of P to iron/manganese oxides. We think that iron oxides played a more important role instead of manganese oxides because of the dominance of Fe-rich laterite in the study area. The adsorption of P to iron oxides likely occurred during and after rain events when there was resuspension of bed sediment and the erosion of Fe-rich soils from urban surface.

Nutrient ratios are also often used to predict whether the deposited sediment P is produced by adsorption or precipitation reactions or both. A molar ratio of $Fe/P \cong 2$ (range = 1.5-2.5) suggests that Fe-bound P in the sediment was produced by the precipitation of iron phosphates such as vivianite and strengite whereas higher ratios (Fe / P = 3.3-9.7) suggest that it was produced by the adsorption of P to iron oxides (e.g. Cooke et al., 1992; Gunnars et al., 2002; Clark et al., 1997). For Ca, the limiting Ca: P ratio for mineral precipitation is about 1.7 (Freeman and Rowell, 1981). In our study, both the Fe: P and Ca: P molar ratios in the sediment were too high (> 3.6 for Fe : P and > 5.2 for Ca : P; Table 3) to argue that the precipitation of iron and calcium phosphates took place. Instead, these high ratios confirm that sediment inorganic P was produced by the adsorption of P to calcite and iron oxides. These revelations are in agreement with our earlier arguments from mineral saturation indices that the adsorption of P to calcite and iron oxides regulated P transport in the studied drains.

Based on the discussions above, Fig. 9 shows a schematic of the processes likely affecting P transport in the studied

	System	Fe:P* (molar)	Ca:P** (molar)	OC:OP (molar)	Remarks			
	Nsooba channel, Uganda							
	Sediment B1 – deep	leep 3.8 5.0		17	This study			
	Sediment B7 – deep	3.6	5.2	15	This study			
	Sediment B1 – shallow	3.6	12.1	9	This study			
	Sediment B7 – shallow	2.6	3.6	14	This study			
	Water column (base flow)	0.2	17.8		This study			
	Suspended sediment	14.9	4.5		This study			
	Tertiary channel, Uganda							
	Sediment B4 – shallow	2.3	9.2	9	This study			
	Water column (base flow)	0.0	4.7		This study			
	Nakivubo channel, Uganda							
	Bed sediment	1–6		68–92	Kansiime and Nalubega (1999)			
	Mozhaisk reservoir, Russia							
	Bed sediment	5.7			Martynova (2011)			
	P*, iron bound P (NaOH – P); P**, calcium bound P (HCl – P)							
Q	Storm hydrograph Additional P input Wastewater released during and after large storms events							
Evtorn	Flush of Particulate P Due to re-suspension of bed sediment							

Table 3. Nutrient and metal molar ratios of bed sediments and the water column in comparison with literature values.

Fig. 9. Schematic of the possible phosphorus transport processes during low flow and high flood events. The grey oval shapes of different sizes illustrate settling and resuspension of particulate P.

catchment. Currently, there are few published studies in urban informal settlements in SSA with which we can compare our results with regard to P transport. One study by Kansiime and Nalubega (1999), however, did try to investigate the removal of P by sediment in the Nakivubo channel/swamp, which had received wastewater from the city of Kampala (Uganda), for over 30 yr. The findings of this study, on the contrary, suggested that the precipitation of CaCO₃ was not a very important process for P retention because of the low

P discharge

Ca content (60 mg kg^{-1}) and the low Ca-bound P (10 % of TP) in the sediment. The retention of P was instead attributed to precipitation of vivianite because of the low Fe: P molar ratios (1-3). However, this study did not carry out geochemical speciation of phosphate phases in the overlying water to confirm if there was a strong likelihood for vivianite to precipitate. In our study, Fe: P ratios in the sediment were generally high (> 3.6; Table 3) and the overlying water was undersaturated with respect to iron phosphates. In addition,

Settling of particulate P

P bound to Fe-oxides

Wastewater via tertiary

Settling of particulate P

(Organic P + CaCO3- P)

Base flow

Internal P loading

(mineralization & Fe-P dissolution)

 $\land \land \land$

 \wedge Retained sediment P (primarily inorganic P

channels

 \bigtriangledown Base flow

P dischara

the sediment Ca content was very high (> 2000 mg kg⁻¹; Table 1) while at the same time Ca-bound P contributed over 50 % of total sediment P. This implies that there were indeed interactions between Ca and P in our study. These findings show that P retention processes in surface water in urban informal settlements can vary significantly depending on the location.

5.4.2 P release from sediments

Our results further indicated that the bed sediments, particularly the shallow ones, were P saturated because the total sediment P was almost equal to or more than maximum P sorption capacity, S_{max} (Figs. 7, 8). For example, the S_{max} of the shallow sediments at location B1 was 1550 mg kg⁻¹ whereas the total sediment P was 1668 mg kg^{-1} (Figs. 7, 8). In the tertiary drain, the S_{max} was 820 mg kg⁻¹ whereas total sediment P was 1840 mg kg^{-1} . The P saturation state of sediments is one of the most important factors that indicate the potential for sediments to release P (Hooda et al., 2000). Three processes are mainly responsible for the release of P from sediments: (1) mineralisation of organic matter, (2) desorption, and (3) reductive dissolution of P bound to iron oxides (e.g. Fox et al., 1986; Søndergaard et al., 1999; Boers and de Bles, 1991). Given that surface water was Mn-reducing, it is unlikely that reductive dissolution of Fe-bound P took place. Hence, if P release took place, it was by mineralisation of organic matter or by desorption.

Metal/nutrient and C/P molar ratios are also often used to indicate P release by dissolution of metal bound P and mineralisation of organic P respectively. Fe : P (and Ca : P) ratios < 2 indicate a tendency for bed sediments to release PO₄ (Jensen et al., 1992). Table 3 shows that Fe : P ratios in the water column in our study were very low (< 2) whereas Ca : P ratios were very high (up to 17) indicating that P was potentially released from Fe-bound P in the sediment by desorption. On the other hand, P release by mineralisation usually occurs when the C : P molar ratio < 200 (Stevenson, 1986). In our study, the C : P ratios of all sediments collected were less than 200 implying that there was a potential for mineralisation of P from the organic P retained in the bed sediment.

This study has provided useful insights into the processes regulating the transport of sanitation-related phosphorus in drainage channels in a typical urban slum catchment. We showed that the adsorption of P to iron oxides in the sediments and to calcite precipitates in the water column played an important role in regulating P transport to downstream areas. We have also demonstrated the presence of flush effects and the role of the channel-bed sediments to release phosphorus back into the water column. Knowledge of these processes is crucial in developing process-based water quality models, which can aid policy and decision making regarding strategies to reduce nutrients exported from urban catchments. A complete understanding of these processes, however, requires more research to be carried out in these types of catchments. Future work could focus on using onsite automated samplers and analysers in order to obtain high-resolution data, which allows for improved understanding (at a much higher scale) of the P transport processes and the trends that occur when hydrological conditions change.

6 Conclusions

In this study, we attempted to understand the processes governing the transport and retention of phosphorus (P) during high and low flows in a channel draining a 28 km^2 urban catchment with informal settlements in Kampala, Uganda. Results from our study revealed the following.

- A large amount of phosphorus was discharged from the studied catchment. The base-flow concentrations of P in the primary channel were 1.15 mg L^{-1} for total P and 0.36 mg L^{-1} for PO₄-P, which were about 16 times the minimum required to cause eutrophication. The corresponding P fluxes of $0.3 \text{ kg km}^2 \text{ d}^{-1}$ for PO₄-P and $0.95 \text{ kg km}^2 \text{ d}^{-1}$ for TP were also of several orders of magnitude higher than values normally reported in published literature for other catchments.
- By comparing the hydrochemistry and P concentrations in the primary channel and a tertiary channel draining a slum area, we were able conclude that the primary source of P in the channels was the direct discharge of untreated wastewater into the tertiary channels, primarily due to grey water effluents from informal settlements.
- In the four rain events we sampled, we observed a flushing of P mainly in particulate form. We attributed this flushing to the resuspension of the P-rich bed sediments that had accumulated in the channel during low flows. It is unlikely that the terrestrial runoff significantly contributed to the flushing of TP and PP because the concentration peaks of TP and PP during the rain events were almost similar irrespective of the sample location along the primary drain. Our results, however, seemed to suggest that first-flush effects were not present. In all the rain events sampled, the concentration peaks of TP, PP and SS were realised after the peak discharge. This was likely caused by the poor on-site sanitation practices in the catchment whereby most residents, especially in informal settlements, release untreated wastewater into drainage channels during and after storm events.
- In relation to chemical processes, our results indicated that P transport in the channels was regulated by the co-precipitation of P with calcite precipitates and by the adsorption of P to iron oxides, especially during rain events when there was resuspension of sediments.

These findings were consistent with our other findings that the retained P in the sediment was largely inorganic (64–80% of total sediment P) and was bound to Ca and iron/manganese oxides in almost equal proportions (51–54 and 46–49%, respectively). The retention of P by settling of organic matter also seemed to be important because organic-bound P in the bed sediments was also relatively high (i.e. 17–22% of the total sediment P). The sediments, however, showed potential to release P to the overlying water by mineralisation of organic matter and desorption of P bound to iron oxides/hydroxides.

Our study provides useful insights into mechanisms likely controlling P transport in a typical urban catchment with informal settlements. To have a complete understanding of the P transport processes in these catchments, we recommend that additional P transport studies be carried out in other urban informal catchments with emphasis on high-resolution nutrient monitoring during high flows.

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