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ORIGINAL ARTICLE

# Stream water nutrient and organic carbon exports from tropical headwater catchments at a soil degradation gradient

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**Abstract** Carbon and nutrient losses were quantified from four small headwater catchments in western Kenya in the year 2008. They include a forested catchment and three catchments under maize continuously cultivated for 5, 10 and 50 years following forest conversion. The C isotopic composition of dissolved organic C (DOC) in stream discharge suggested that soil organic C (SOC) derived from the original forest rather than OC from maize may have contributed to a large extent to watershed OC losses, even 50 years after the forest was removed. Flow-weighted stream water concentrations of DOC and coarse particulate OC, all N species, total P, K and Na significantly ($P < 0.05$) increased in streams after forest conversion and long-term cultivation. Solute concentrations increased despite the fact that soil contents decreased and total water flow increased indicating mobilization of C and N, P and K from soil with progressing cultivation. In contrast, Ca and Mg concentrations in stream water did not systematically change after deforestation and cultivation, and may be controlled by geochemical weathering rather than by changing water flow paths or topsoil contents. All OC and nutrient exports increased with longer cultivation over decadal time scales ($P < 0.05$) to the same or greater extent than through deforestation and the first years of cultivation. Fluvial OC and total N losses were 2 and 21 % of total SOC and total N decline, respectively, in the top 0.1 m over 50 years. Fluvial OC losses therefore played a minor role, and SOC losses were mainly a result of microbial mineralization. Resulting total N losses by stream discharge, however, were large with 31 kg $ha^{-1}$ $year^{-1}$ after 50 years of continuous cropping in comparison to fertilization of 40 kg N $ha^{-1}$ $year^{-1}$. Most (91 %) of the N losses occurred as $NO_3^-$. In contrast, P losses by stream discharge were negligible in comparison to plant uptake. Water losses should be managed to reduce soil fertility declines especially through large N export from agricultural headwater catchments. However, stream concentrations of both P (0.01–0.15 mg $L^{-1}$)

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and N (0.4–4.8 mg $L^{-1}$) were moderate or low with respect to possible consequence for human health and not responsible for eutrophication observed in Lake Victoria.

**Keywords** Carbon · Cultivation · Degradation gradient · Forest conversion · Headwater catchment · Nutrients

## Introduction

The impact of land use change on nutrient and soil organic carbon (SOC) dynamics in the tropics is particularly severe since soil degradation is more rapid than in temperate zones (Spaans et al. 1989; Malmer and Grip 1990; Grip et al. 2004; Hartemink et al. 2008). Continuous cultivation and land tillage cause rapid loss of SOC (Mann 1986; Davidson and Ackerman 1993; Tilman et al. 2002; McLauchlan 2006; Solomon et al. 2007) due to the disruption of the physical, biochemical, and chemical mechanisms of soil organic matter (SOM) stabilization. However, the reduction in SOC stocks may not be solely attributed to increased mineralization losses to $CO_2$, but could include a significant, yet poorly quantified proportion of stream water losses (Davidson and Ackerman 1993). On a basin and headwater catchment scale of forests, stream water OC losses appear to be a minor fraction of total SOC losses compared to mineralization of $CO_2$ (Richey et al. 2002; Johnson et al. 2006b). However, the importance of fluvial OC losses during the first years of conversion from forests to cultivation, which are the most important in terms of SOC losses (Davidson and Ackerman 1993) have not been well quantified. While mineralization losses typically decrease with greater period of cultivation (Kimetu et al. 2009), the stream water discharge usually increases (Williams et al. 1997; Germer et al. 2010; Recha et al. 2012), potentially increasing the importance of fluvial OC losses as cultivation progresses.

Soil organic matter decline leads to rapid nutrient release of N and P as well as reduced cation exchange capacity resulting in diminished nutrient retention of the soil (Lal 2006). However, surprisingly little information is available on how soil degradation following land use conversion affects nutrient losses from watersheds. On a plot level, information on accelerated decrease in soil nutrient contents resulting from various types of agricultural practices has been gathered in both temperate (Nair and Graetz 2004; Schipper et al. 2007) and tropical regions (Pandey et al. 2010). However, studies on nutrient losses from entire catchments have mostly been confined to forests rather than to different agricultural watersheds with increasing period of cultivation. Studies from Malaysia and the Amazon examined impacts of disturbances (Zulkifli 1990), pasture (Thomas et al. 2004) and forest clearing (Lesack 1993; Malmer 1996; Williams and Melack 1997; Williams et al. 1997). It is not clear, to what extent continuous cultivation and accompanying soil degradation over time affect fluvial nutrient losses in addition to the effects of loss of forest cover, and how these fluvial losses compare to nutrient input and crop uptake.

Not only the relationship between agricultural nutrient input and fluvial export is unclear, but also what these exports mean for pollution of waterways. Lake Victoria, the largest tropical lake in the world, is significantly contaminated with DOC and nutrients, notably P, posing a threat to people, the fish industry and biodiversity (Verschuren et al. 2002). It is widely believed that the contamination originates from landuse change induced by agriculture (Scheren et al. 2000; Hecky et al. 2010). This is a common attribution and non-point source pollution with N and P by agriculture is indeed observed in many parts of the world (Carpenter et al. 1998). Yet, fertilizer use in tropical smallholder agriculture is typically much lower than in industrialized countries where detailed assessments are available. No data are available that investigate the nutrient and OC loads of agricultural headwaters in Africa and the contribution that deforestation by burning and progressive cultivation would make.

The dynamics of nutrient and C losses over the course of the year can provide insight into the mechanism and pathways of nutrient and C in watersheds (Markewitz et al. 2004; Johnson et al. 2006a). Typically, we expect a dilution of nutrient and C concentrations during the rainy season (Likens and Bormann 1995). However, under certain circumstances of highly weathered soils, concentrations may increase during the wet season as a result of greater surficial flow paths that mobilize solutes from nutrient and C-rich topsoils (Markewitz et al. 2004). It is not clear whether forest conversion and soil cultivation may change the relationship between water and nutrient concentrations and how these dynamics

are modified in tropical soils rich in weatherable minerals (Davidson et al. 2004; Yusop et al. 2006) with high exchangeable base cation contents (Kimetu et al. 2008). The fluvial DOC losses may be a significant fraction of C losses and of total solute losses in watersheds (Selva et al. 2007). In forest ecosystems, the majority of the fluvial organic C losses occurred as DOC rather than coarser organic C fractions (Johnson et al. 2006b; Selva et al. 2007). Despite the lower importance of particulate organic C, most of the organic C was mobilized from the topsoil litter layer (Johnson et al. 2006a, b). Whether the same is true for agricultural soils, or whether subsoil organic C may gain in importance for soils depleted in SOC by long-term cultivation is not clear.

The purpose of this study was to quantify the fluvial nutrient and OC losses from headwater catchments separating the effects of soil degradation and concomitant losses of soil organic matter contents from those of forest clearing in the upper catchments of the Lake Victoria basin. It is hypothesized that (1) stream water OC losses increase in importance with length of cultivation; (2) long-term cultivation is as or more important than deforestation and short-term cultivation for increasing nutrient and OC losses; and (3) headwaters with small holder agriculture are not important sources of N and P to rivers and lakes. The effects of continuous agricultural land use on nutrients were investigated by comparing three headwater catchments following forest conversion to continuous maize production for either 5, 10, or 50 years in Western Kenya with a catchment that has remained forested.

## Methods

### The study site

The field measurements were done in Kapchorwa within Nandi County in Kenya, which is located in Eastern Africa. The site is located 60 km northeast of Lake Victoria at longitude 35°0′0″ E and latitude 0°10′0″N (Recha et al. 2012). The region belongs to the sub-humid ecological zone characterized by a bimodal rainy season with a mean annual precipitation of 2,000 mm (Awiti et al. 2008). The "long rain season" is from April to June (~1,200 mm) and the "short rain season" from August to October (~800 mm). The site has a mean elevation of 1,800 m above sea level, a maximum daily temperature of 26 °C and a minimum of 11 °C (Glenday 2006).

The Kakamega-Nandi forest in Western Kenya is the country's only remaining tropical rain forest. Massive deforestation has taken place to create land for settlement and farming. About 16 % of forest cover was lost between 1986 and 2001 (Awiti et al. 2008). The forest forms the easternmost relic of the Guinean-Congolian rainforest belt, which once spanned from East to West Africa. The area around this forest is among the most densely populated rural areas in the world. It had a population density of 778 persons per $km^2$ in 2009 compared to 73 persons per square kilometer for the entire country (Kenya National Bureau of Statistics 2010). Consequently the forest is under high anthropogenic pressure, which is mirrored by the decreasing natural forest cover and intensive cultivation (deGraffenried and Shepherd 2009; Swallow et al. 2009). Past deforestation rates in the Kakamega-Nandi forest indicated a decrease of forest area and an increase in the fragmentation of natural, old-growth forest (Lung and Schaab 2006).

Soils in the Kapchorwa catchment are kaolinitic Acrisols (FAO-UNESCO-ISRIC 1988), which are classified as Ultisols in the US soil taxonomy (Soil Survey Staff 2003). The parent material of these soils is principally granite, with some inclusions of Precambrian gneisses, which supports Luvisols (Werner et al. 2007) and other undifferentiated basement system rocks at higher elevations (Jaetzold and Schmidt 1983). Soils in the catchment have 45–49 % clay, 15–25 % silt, and 26–40 % sand (Kimetu et al. 2008).

The forest section of the Kapchorwa catchment is part of the Kakamega-Nandi forest composed of tropical rainforest species. It is largely an indigenous forest with a 30-m closed canopy dominated by evergreen hardwood species. The most common species are *Funtumia africana*, *Ficus* spp, *Croton* spp, and *Celtis* spp (Glenday 2006). Other species include *Aningeria altissima* (A. Chev.), *Milicia excelsa* (Welw.) C.C. Berg, *Antiaris toxicaria* (Lesch.) and *Chrysophyllum albidum* (G. Don), *Olea capensis* (L.) and *Croton megalocarpus* (Hutch.) (Kinyangi 2008). The above and below ground net primary production of trees in a tropical forest is estimated at 15.2 Mg $ha^{-1}$ $year^{-1}$ (Hertel et al. 2009). The agricultural catchments have maize as the sole crop, and

have been under maize cultivation since conversion from forest cover. The maize grain yields without fertilizer input in the 5-, 10- and 50-year old agricultural catchments are 6.5, 5.5 and 2.5 Mg $ha^{-1}$ $year^{-1}$, respectively (Ngoze et al. 2008).

## Hydrologic instrumentation and fieldwork

In order to identify the headwater catchments, the time when native forests were converted to agriculture was determined from historical community settlement patterns over the last century (Bleher et al. 2006; Recha et al. 2012). Specific years of conversion were verified from data available from records of the Kenyan government from the Department of Forests, the Ministry of Agriculture, as well as from interviews with officials of local institutions and from county council records. Within each site, population settlement patterns were distinct and newly acquired fields were excised from sections of the native forest for agriculture. All four headwater catchments are located within an area of 6 $km^2$ (Fig. 1) and represent a soil degradation gradient that corresponds to years under maize cultivation that has been used in several other studies (Kimetu et al. 2008, 2009; Ngoze et al. 2008; Kimetu and Lehmann 2010; Recha et al. 2012). Such chronosequences substitute time for space and have to be carefully selected to assure similar properties before the change (Huggett 1998). Also hydrological differences between catchments have to be considered (Elsenbeer, 2001; Johnson et al. 2006b) and only clear trends across the entire set of the four catchments are interpreted here.

Hydrologic instrumentation was installed in 2006 (Recha et al. 2012) and catchments monitored continuously. The boundaries of each catchment were determined using a Global Positioning System (GPS) on the landscape around each spring up to the plateau, using an average of five to eight independent assessments. The GPS data were then used to generate a Geographical Information System (GIS) output and map of the area. The sizes of the catchments were 12.8 ha for the forest, 14.4 ha for the 5-year old conversion, 9.1 ha for the 10 year conversion and 10.0 ha for the 50-year conversion. There were a total of one, six, and eleven households living in the 5-, 10-, and 50-year conversion catchments, respectively. A standard V-notch weir was constructed at each catchment outlet for determining stream discharge. Stream stage was recorded using water capacitance probes (Odyssey Dataflow Systems Pty Ltd., New Zealand) installed at the weir. The probes were programmed to give a reading of the average stream stage at 2 min. Data from these probes were downloaded biweekly. The weir ratings were determined at low and intermediate flows. The weir rating correlation coefficients were $r^2 = 0.944$, $r^2 = 0.915$, $r^2 = 0.926$, $r^2 = 0.931$ for the forest, 5-, 10- and 50-year conversions, respectively. The stream hydrographs were normalized by corresponding catchment sizes to allow comparison between responses for the 4 catchments.

Stream water sampling was done biweekly at the weir outlet, at the beginning and mid of every month. The water samples were filtered through 0.45-μm pore-size glass-fiber filter, into two separate 50-mL centrifuge vials. We added thymol into the first 50-mL centrifuge vial that was used for determination of calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), total dissolved phosphorus (TDP), nitrate nitrogen ($NO_3$–N), ammonium nitrogen ($NH_4^+$-N) and total dissolved nitrogen (TDN). We added 10 % HCl into the second 50-mL centrifuge vial that was used for determination of dissolved organic carbon (DOC) and the DOC stable isotopic ratio of $^{13}C$ to $^{12}C$. The 0.45-μm pore-size glass-fiber filter paper with sediment was air dried and kept for the determination of coarse particulate organic carbon (CPOC), the CPOC isotopic ratio of $^{13}C$ to $^{12}C$, and coarse particulate nitrogen (CPON).

Five soil samples from 0 to 0.1 m depth were collected randomly by stratifying for location within slope and plateau of each catchment, after carefully removing the litter layer (capturing only the mineral horizon). They were analyzed for SOM, SOC, total N, available P, Ca, K, Mg and Na. Similarly, four sites were randomly selected by stratifying for location within slope and plateau of each catchment and additional soil sampled at depths of 0.1–0.3, 0.3–0.9, 0.9–1.5, 1.5–2.4 m. Bulk density was determined by the soil core method; we used five soil samples from a depth of 0–0.1 m in each catchment (Campbell and Henshall 1991). Soil porosity (ø) was computed from bulk density ($\rho_b$) and particle density ($\rho_p$) using the formula $ø = 1 - (\rho_b/\rho_p)$. The use of organic and inorganic fertilizers was assessed in all studied agricultural watersheds by a full survey of all households using interviews. Farmer interviews in the watersheds confirmed information provided by the studies of Kinyangi (2008), Kimetu (2009),

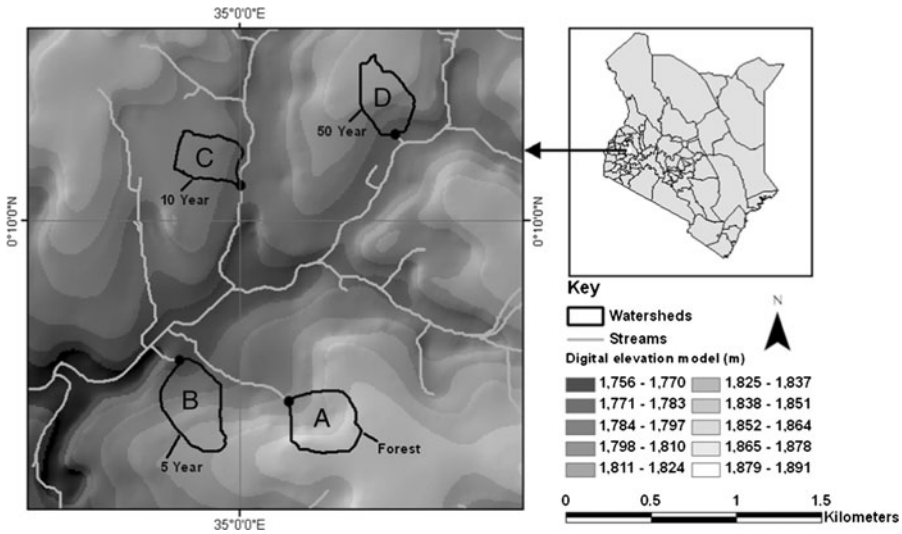


**Fig. 1** Map of the study area of the Kapchorwa headwater chronosequence of catchments in western Kenya, and its approximate location within Kenya (inset shows Kenya and its districts). The weir positions are shown by dots in each catchment. *Letters* indicate land use histories of the catchments: forested catchment (**a**), maize cultivation for 5 years (**b**), 10 years (**c**) and 50 years (**d**) following forest conversion

and Moebius-Clune et al. (2011). The soils received nil, or only very little inorganic fertilizer since forest clearing, no animal manure, and were always cropped with maize. From the interviews, only di-ammonium phosphate (DAP, N:P:K of 18:46:0) fertilizer was used at an application rate of 6 and 9 kg $ha^{-1}$ within the 10 year and 50 year watersheds, respectively, for the year 2008. The farmers in the 5 year watershed did not use any fertilizer. The N and P addition was 1.02 and 2.76 kg $ha^{-1}$, respectively, for the 10 year watershed. The addition for the 50 year watershed was 1.62 and 4.14 kg $ha^{-1}$ of N and P, respectively. Animal manure was not used in any household.

### Laboratory measurements

Soil total C was determined by dry combustion after fine grinding soil using a Mixer Mill (MM301, Retsch, Germany). Samples were analyzed for total C contents with a Europa ANCA-GSL CN analyzer (PDZ Europa Ltd., Sandbach, UK). Soil organic matter (SOM) was determined by loss on ignition (Storer 1984) and soil pH (in water) at the w/v ratio 1:2.5 using a glass electrode (Thermo Scientific, Beverly, MA, US). Filters containing CPOC were ground using a Mixer Mill (MM301, Retsch, Germany) and analyzed for total C, the isotopic ratio of $^{13}C$ to $^{12}C$, and CPON using a coupled Europa 20–20 continuous isotope ratio mass spectrometry (PDZ Europa Ltd., Sandbach, UK). The Mehlich 3 extraction procedure (Mehlich 1984) was used for the available soil P, Ca, Mg, K and Na. The Ca, Mg, K, Na and P concentrations were obtained by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, ARCOS, Germany). TDN was analyzed using Shimadzu's Total Nitrogen Module, TNM-1 that uses chemiluminescence. Dissolved organic nitrogen (DON) was computed using the formula $DON = TDN - NO_3^- + NH_4^+$. DOC analysis was carried out on a Shimadzu Total Organic Carbon-Visionary Series (TOC-$V_{CSH}$) analyzer following the procedure described by Qian and Mopper (1996). $NO_3$–N and $NH_4^+$-N were determined on a Seal AQ2-Automated Discreet Analyzer (Seal Analytical, England).

### Statistical analyses

Statistical analyses were done using JMP Version 8 (SAS Institute Inc, Cary, NC, USA) for soil properties and stream water solutes of the four catchments. A one way ANOVA was used for the soil properties, and a repeated measure analysis controlling for date of sampling was performed for the stream water solutes. Both analyses were followed with posthoc multiple comparisons using a Tukey correction for multiple comparisons when the catchment effect was significant. Comparisons were considered significant at $P < 0.05$.

## Results

### Soil properties

Within the top 0.1 m, the SOM and SOC concentrations significantly decreased by 59 % and 75 %,

**Table 1** Soil properties in the top 0.1 m

| | Forest | 5 year conversion | 10 year conversion | 50 year conversion |
|---|---|---|---|---|
| Soil organic matter (%) | 17.08a | 13.67b | 8.53c | 7.00d |
| Soil organic carbon (g $kg^{-1}$) | 108.3a | 68.8b | 36.4c | 27.5c |
| Soil organic carbon (t $ha^{-1}$) | 86.6a | 62.6b | 37.5c | 32.2c |
| Soil nitrogen (g $kg^{-1}$) | 11.2a | 6.9b | 3.4c | 2.3c |
| Soil nitrogen (t $ha^{-1}$) | 8.96a | 6.28b | 3.50c | 2.69c |
| Soil bulk density (g $cm^{-3}$) | 0.80c | 0.91b | 1.03ab | 1.17a |
| Total porosity | 0.70a | 0.66b | 0.61bc | 0.56c |
| Moisture at 0.33 bar (% v/v, field capacity) | 34.7a | 34.1a | 24.9b | 23.0b |
| pH (water, 1:2.5) | 7.39a | 6.48b | 6.23b | 5.81c |
| Available P (g $kg^{-1}$) | 0.011a | 0.007a | 0.003a | 0.006a |
| Available K (g $kg^{-1}$) | 0.69a | 0.58ab | 0.23b | 0.44ab |
| Available Ca (g $kg^{-1}$) | 6.25a | 4.98a | 1.77b | 2.91b |
| Available Mg (g $kg^{-1}$) | 0.73a | 0.45b | 0.20c | 0.33bc |
| Available Na (g $kg^{-1}$) | 0.026a | 0.020a | 0.010a | 0.011a |

Means within a row followed by the same letters are not significantly different from each other at $P < 0.05$ (n = 5)

respectively, and the soil N contents by 79 % from the forest to the 50-year old agricultural catchment (Table 1). The forest SOC and soil N were significantly ($P < 0.05$) higher than the 5-year conversion. Soils in the 10- and 50-year conversion did not differ. The SOM, SOC and N loss was very rapid in the first 10 years of conversion decreasing by 50, 66 and 70 %, respectively. Available soil P, K and Na did not change as a result of forest clearing and soil use between the studied watersheds. In contrast, extractable Ca and Mg significantly ($P < 0.05$) decreased over time (Table 1). Similarly, pH values significantly decreased from forest (7.39) to agriculture (5.81).

The soil $\rho_b$ increased rapidly by 28.8 % in the first 10 years of cultivation from 0.80 to 1.03 g $cm^{-3}$ (Table 1). Overall, the soil $\rho_b$ increased by 46.3 % from 0.8 to 1.17 within 50 years of cultivation. The rapid increase in $\rho_b$ in the first 10 years after forest conversion was followed by a 12 % drop in the total porosity from 0.69 to 0.61 in the same period.

In the 0–0.1 m depth, the soil $\delta^{13}C$ values were $-26.07 \pm 0.68$ ‰, $-25.37 \pm 0.84$ ‰, $-21.21 \pm 0.87$ ‰ and $-19.18 \pm 0.44$ ‰ for the forest, 5-, 10- and 50-year conversion catchments, respectively (Fig. 2). This indicates enrichment in the heavier isotope from the forest to the catchment under cultivation for 50 years. The $\delta^{13}C$ values at the topsoil (0–0.1 m) increased linearly over time from −26.07 to −19.18 ‰ ($r^2 = 0.95$; $P < 0.0001$), with similar trends at depth. Similarly, the $\delta^{13}C$ values became less negative deeper in the profile for all the catchments indicating a slight enrichment in the heavier isotope compared to the topsoil.

## Stream water chemistry

The $\delta^{13}C$ composition of CPOC (Table 2) did not change from the forest (−27.52 ‰) to the 10 year conversion (−27.28 ‰). The 50-year old catchment had a slightly higher $\delta^{13}C$ value compared to the other catchments. The streamwater DOC $\delta^{13}C$ composition

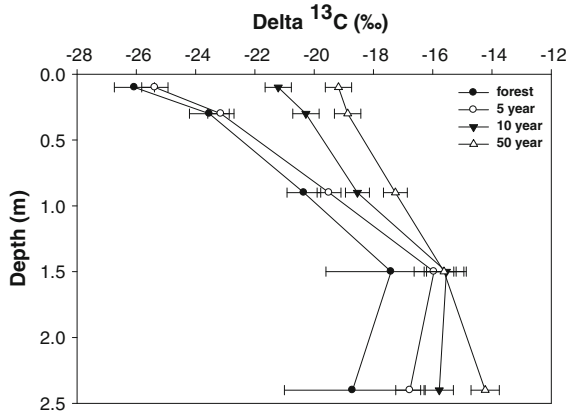


**Fig. 2** Long term shift in the isotopic composition of $\delta^{13}C$ of the soils at various depths in the watersheds. n = 4. *Bars* are ±1 standard deviation of the mean for each depth

**Table 2** The isotopic composition of $\delta^{13}C$ of the CPOC and DOC, and the flow weighted nutrient concentrations of the headwater catchments

| | Forest | 5 year conversion | 10 year conversion | 50 year conversion |
|---|---|---|---|---|
| *Sediment and filtered streamwater* | | | | |
| CPOC $\delta^{13}C$ (‰) | −27.52b | −27.29b | −27.28b | −26.40a |
| DOC $\delta^{13}C$ (‰) | −28.59c | −28.25c | −26.79b | −22.75a |
| *Streamflow concentrations* | | | | |
| DOC (mg $L^{-1}$) | 1.31a | 1.48a | 1.47a | 1.52a |
| CPOC (mg $L^{-1}$) | 1.25a | 1.43a | 1.49a | 1.65a |
| CPON (mg $L^{-1}$) | 0.12a | 0.14a | 0.15a | 0.16a |
| TDN (mg $L^{-1}$) | 0.49b | 0.67b | 4.83a | 4.64a |
| $NO_3^-$ (mg $L^{-1}$) | 0.40b | 0.58b | 4.71a | 4.52a |
| DON (mg $L^{-1}$) | 0.10a | 0.09a | 0.10a | 0.12a |
| TDP (mg $L^{-1}$) | 0.03b | 0.01b | 0.05b | 0.15a |
| K (mg $L^{-1}$) | 0.36c | 0.80b | 0.95a | 1.18a |
| Ca (mg $L^{-1}$) | 7.23a | 5.55b | 5.48b | 7.16a |
| Mg (mg $L^{-1}$) | 3.01a | 2.04c | 1.61d | 2.54b |
| Na (mg $L^{-1}$) | 2.99c | 3.70c | 4.65b | 5.61a |

Means within a row followed by the same letters are not significantly different from each other at $P < 0.05$ (n = 24 for CPOC $\delta^{13}C$, n = 4 for DOC $\delta^{13}C$, and n = 12 for all others)

followed the same trend as the sediment but with a significantly greater magnitude of enrichment in the heavier isotope from the forest and recent conversion to the 10-year old conversion. Discharge in the 50-year conversion had a significantly higher value than that of all other headwaters (−22.75 ‰). The flow-weighted average concentrations of DOC, CPOC and CPON did not change with forest conversion and duration of cultivation (Table 2). TDN concentrations in the discharge from forest and 5-year catchments did not differ, but increased with longer cultivation. $NO_3^-$ was the dominant form of dissolved N (91 %) in the Kapchorwa watershed fluvial ecosystem, followed by DON (9 %), whereas $NH_4^+$ was below our detection limit. The 10- and 50-year conversions had nine times higher TDN concentrations compared to the forest and most recent conversion. Stream TDP concentrations were at least one order of magnitude lower compared to TDN, Ca, K, and Mg. TDP concentrations of the forest, 5- and 10-year conversions were threefold lower than that of the 50-year conversion ($P < 0.05$). Stream water K and Na concentrations both increased upon forest conversion and subsequent cultivation. Overall, K concentrations increased threefold and Na concentrations twofold following 50 years of cultivation after forest conversion. In contrast to all other solutes, Ca and Mg concentrations did not show a consistent trend from forest to cultivation.

The total C exports increased after forest conversion and with subsequent cultivation (Table 3). The DOC and CPOC export doubled in the first 5 years following forest conversion. The increase continued by a further 43 and 70 % from the 5- to the 50-year conversions, respectively. Amounts of CPON, TDN and $NO_3^-$ exported were also twice the first 5 years after forest conversion. Upon longer cultivation between 5 and 10 years, CPON export increased 3.5 times, while the TDN and $NO_3^-$ export increased eightfold. Between 10 and 50 years of continuous cultivation, the amount of CPON export doubled while that of TDN and $NO_3^-$ did not increase further. The magnitude of TDP export was far less than that of C and all other nutrients. The amounts of TDP exported did not change after forest conversion (<0.03 kg $ha^{-1}$), but increased with subsequent cultivation up to the 0.98 kg $ha^{-1}$. The cations (K, Ca Mg and Na) exhibited a similar trend whereby the amounts exported increased from the forest to the 5-, 10- and 50-year conversions. Among the measured base cations, K had the lowest export while Ca had the highest.

There was not a clear separation of the hydrograph between the long rainy (April-June) and short rainy (August-October) seasons in the Kapchorwa catchment in 2008. The stream flow response to precipitation events increased with longer cultivation (Fig. 3). There were no relevant changes in the concentrations of DOC, TDN, TDP, Ca, and Mg across the whole

**Table 3** Streamwater carbon and nutrient exports (kg $ha^{-1}$ $year^{-1}$) from the Kapchorwa headwater catchments

| | Forest | 5 year conversion | 10 year conversion | 50 year conversion |
|---|---|---|---|---|
| DOC | 3.87 | 6.85 | 8.46 | 9.79 |
| CPOC | 3.94 | 6.60 | 8.57 | 10.63 |
| CPON | 0.33 | 0.64 | 0.87 | 1.03 |
| TDN | 1.45 | 3.12 | 27.76 | 29.93 |
| $NO_3^-$ | 1.18 | 2.68 | 27.09 | 29.16 |
| DON | 0.27 | 0.44 | 0.67 | 0.77 |
| TDP | 0.09 | 0.03 | 0.29 | 0.98 |
| K | 1.06 | 3.68 | 5.44 | 7.61 |
| Ca | 21.4 | 25.7 | 31.5 | 46.2 |
| Mg | 8.93 | 9.42 | 9.23 | 16.38 |
| Na | 8.86 | 17.08 | 26.70 | 36.22 |

year. The K and Na concentrations, however, decreased slightly after the long rainy season in August and remained low for the short rainy season. Overall, there was no relationship between the solute concentrations and discharge (Fig. 4).

## Discussion

### Sources of fluvial OC and nutrient losses

Even though annual fluvial OC exports increased more than three-fold (our study) and $CO_2$ evasion from SOC mineralization decreased (Kimetu and Lehmann 2010), annual DOC and CPOC losses by stream water of 22 kg $ha^{-1}$ from the highly degraded soils were still low with only 2 % mineralization losses of the 1,200 kg $ha^{-1}$ determined by direct measurements from the soil surface using static vented chambers. Similarly, cumulative fluvial organic C losses were 0.9 t $ha^{-1}$ (2 %) over the first 50 years (using linear interpolation of the sum of DOC and CPOC) compared to SOC losses of 54 t $ha^{-1}$ in the first 0.1 m (calculated from Table 1; similar SOC losses reported by Solomon et al. 2007; Kimetu and Lehmann 2010). It is possible that inorganic C and particularly dissolved $CO_2$ may significantly contribute to total fluvial C losses from watersheds as shown in the Amazon (Johnson et al. 2008). However, even with a possibly larger inorganic than organic C loss, microbial mineralization from the soil still exceeds 90 % of total SOC losses over the 50 years. The quantified fluvial C export is low compared to other studies. Moore et al. (2010) observed a fluvial total organic C removal of 12 % by a Bornean blackwater river in a peat-covered area of Indonesia. Cumulative fluvial N losses over the first 50 years (using linear interpolation of the sum of TDN and CPON) were 1.3 t $ha^{-1}$ compared to the total soil N losses of 6.3 t $ha^{-1}$ (representing 21 %) in the first 0.1 m (calculated from Table 1). Similar to fluvial C losses, watersheds at our site showed lower export than at other locations.

Both fluvial CPOC and DOC were mainly mobilized from the topsoil, as $\delta^{13}C$ values in stream discharge were lower than in the topsoil and soil values increased with depth as also reported by Krull et al. (2002) at a nearby site. Similar conclusions were drawn by Frank et al. (2000) and Raymond and Saiers (2010) who found most of the DOC losses to be derived from the topsoil in catchments in central Switzerland and eastern United States, respectively. Alternatively, the low $\delta^{13}C$ values in our study may also indicate that OC losses originated from older SOC fractions characterized by small size and association with minerals that showed lower $\delta^{13}C$ values in the same chronosequence (Kinyangi 2008). The isotopic composition of the topsoil correlated strongly with the DOC $\delta^{13}C$ ($r^2 = 0.84$; $y = 1.132x + 7.1478$) as well as with the CPOC $\delta^{13}C$ ($r^2 = 0.83$; $y = 18.25x - 49.523$), but with a low slope for CPOC.

### Nutrient losses, crop production and stream pollution

Total N (TDN + CPON) losses of 31 kg $ha^{-1}$ $year^{-1}$ in the highly degraded soils were relevant compared to crop N uptake of maize at the same sites with 90 kg N $ha^{-1}$ $year^{-1}$ (Kimetu et al. 2008). There was no fertilizer application in the recent conversion, while applications in the 10- and 50-year conversions were about 40 kg N $ha^{-1}$ (average from all farms in the studied catchments). The typical application rates to maize by most farmers in the entire region are 20 kg N $ha^{-1}$ (Ngoze 2008), less than the stream water losses reported here. Even more dramatic were the fluvial Ca and Mg losses of 46 and 16 kg $ha^{-1}$ $year^{-1}$, respectively, which were greater than uptake by a single maize crop of 20 and 10 kg $ha^{-1}$, respectively (Kimetu et al. 2008). In contrast, annual fluvial P losses of 1 kg $ha^{-1}$ were low compared to plant uptake of 10 kg $ha^{-1}$ (Kimetu et al. 2008) and

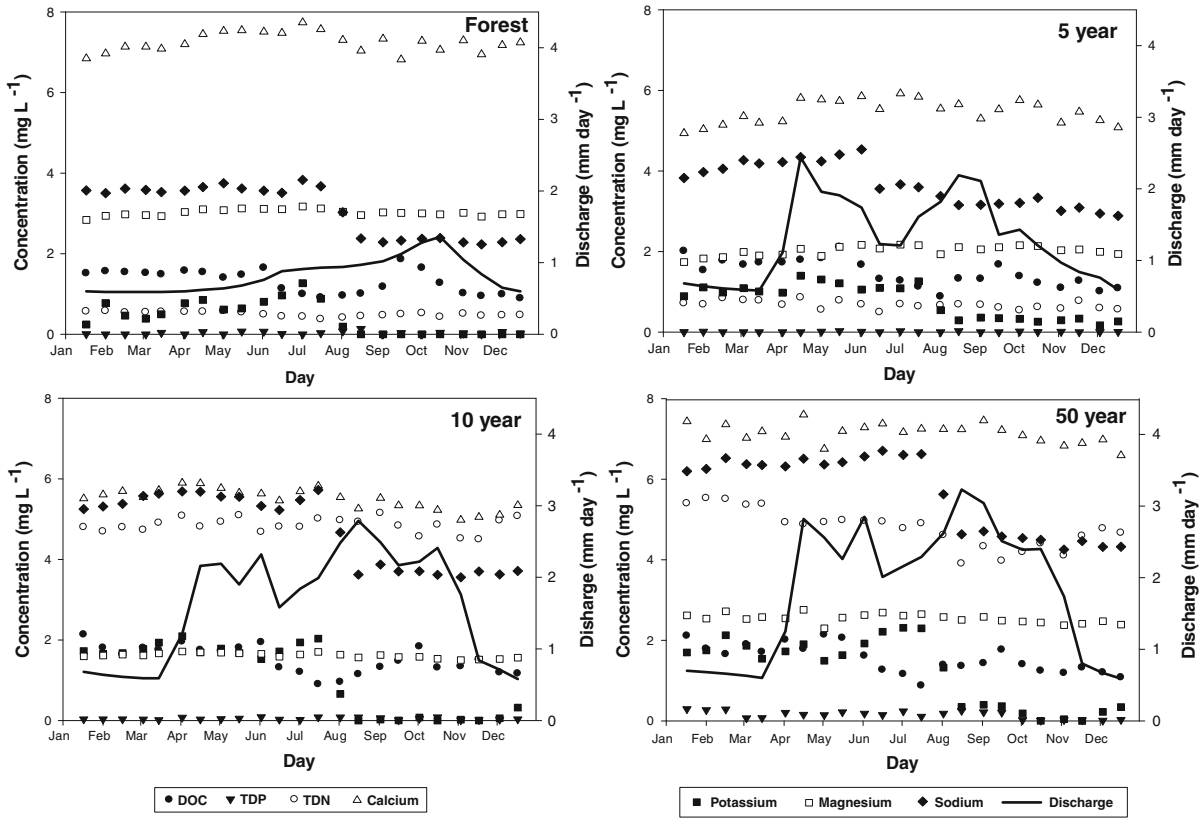


**Fig. 3** Bi-weekly discharge and concentrations of DOC, Na, Ca, K and Mg of the Kapchorwa headwater catchments

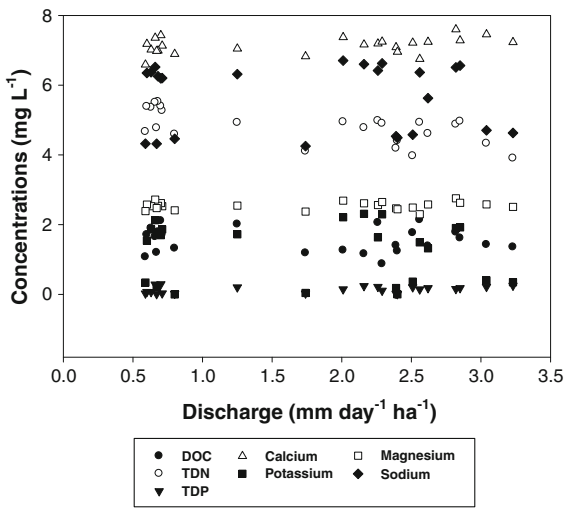


**Fig. 4** The relationship between discharge and DOC, Na and nutrient concentrations in the 50 year watershed

fertilization of about 7.5 kg P $ha^{-1}$ (sum of inorganic and organic fertilizers averaged for all farms) in the oldest conversion. However, redistribution of P within the watershed was not measured and stream water losses are only a lower boundary of actual losses of soil P. Nonetheless, both Ca and Mg as well as P losses by stream water may not be as serious as N losses because available P, Ca, and Mg in soil decreased much less than total N (Table 1; similar for the same sites reported by Ngoze et al. 2008; Kinyangi 2008), and crops were found to respond less to P than to N additions (Ngoze et al. 2008). In addition, TDN concentrations and total losses by stream discharge increased the most by forest conversion and continuous cultivation compared to any other nutrient studied here.

Despite the significant N losses from stream discharge for agricultural productivity, the observed concentrations in the studied headwater catchments are not an environmental concern for aquatic environments. Average annual N concentrations at or below 3 mg $L^{-1}$ and maximum concentrations of 6 mg $L^{-1}$ during the dry season of December to March (Fig. 2) do not pose a risk for human health

(Rubio-Arias et al. 2010) and are not expected to cause eutrophication (Hill et al. 2011; King and Balogh 2011). Similarly, P concentrations of 0.01–0.15 mg P $L^{-1}$ (Fig. 2) in the stream discharge are moderate but not a cause for significant environmental concern (Auer et al. 1986; King and Balogh 2011; Yu et al. 2011). Values up to 6.7 mg $PO_4$-P $L^{-1}$ have been found in the River Thames catchment in the UK (Young et al. 1999) and up to 10 mg $PO_4$-P $L^{-1}$ in the Spree River in Germany (Lewandowski and Nutzmann 2010). Also DOC concentrations are significantly lower in the studied headwaters than in the lower Yala and Lake Victoria (Lalah and Wandiga 2006). Therefore, the well documented contamination of the lower Yala River (Aloo 2003) and Lake Victoria with DOC, N and P which has been suspected to cause the observed eutrophication (Scheren et al. 2000; Lalah and Wandiga 2006; Hecky et al. 2010) does not seem to be caused by agriculture in the headwater catchments, but must occur further downstream.

## Carbon and nutrient losses after landuse change

Our DOC concentrations and total losses were in the same range as reported by Lesack et al. (1984) from the Gambia River in the West African savannah with a DOC concentration of 1.98 mg $L^{-1}$ and DOC export of 2.67 kg $ha^{-1}$ $year^{-1}$. Similar DOC concentrations but 2–10 times greater export were found by Cairns et al. (2009) in the forests of the Oregon Cascades and of southern Amazonia by Johnson et al. (2006b), yet values are within the range reported for a variety of watersheds elsewhere (Lesack et al. 1984; Selva et al. 2007; Stutter et al. 2008; Waldron et al. 2009). The CPOC and CPON concentrations and export were in the same order of magnitude as those of DOC and DON. This finding differs from that of Vidal-Abarca et al. (2001) who found DOC to be the most important fraction (98 %) of organic C flowing in a saline and semi-arid stream in Spain. Similarly greater proportions of DOC were also reported by Johnson et al. (2006a, b) from southern Amazonia. Therefore, particulate OC losses are greater than in other studies, but the observed fluvial OC losses from the forest seem to be representative of those found in other studies. The examined change of solute losses as a response to landuse change may therefore be indicative of losses in other regions.

The increase in streamwater concentrations of TDN, $NO_3^-$ and DON with longer duration of cultivation can be attributed to three sources. (1) Mineralization of SOM led to accumulation of mineral N and especially nitrate (as seen from stream water concentrations) which is weakly adsorbed to soil minerals and easily leached. (2) The greater number of households on older conversions presumably led to higher inputs of farm manure from the cattle kept by the farmers. The manure was shown to consist of 22 g N $kg^{-1}$ (Kimetu et al. 2008). Half of the farmers in the older conversions applied inorganic fertilizer equivalent to 40 kg N $ha^{-1}$. (3) As stated above, only farmers with fields that have been cultivated for 10 years or longer apply mineral fertilizers. Fields that have been recently cleared at the same sites are rarely fertilized due to their high N mineralization rates and their low response to mineral (Ngoze et al. 2008) and organic N applications (Kimetu et al. 2008).

The increase in fluvial K and Na concentrations with longer cultivation may be explained by lower SOC contents and the soil mineralogy being dominated by kaolinite, both resulting in low cation retention (Kimetu and Lehmann 2010). Krull et al. (2002) reported mineralogy dominated by quartz, kaolin and mica, with minor components associated with feldspars and oxides in the adjacent Kakamega part of the forest. They observed an abundance of quartz, kaolinite, muscovite and microcline with a slight increase in goethite with increasing soil depth. The observed greater proportion of surface runoff of 4–10 % of rainfall from forest compared to long-term cultivated fields (Recha et al. 2012) may also have led to a greater mobilization of K and Na near the surface. Extractable K concentrations did not decrease with forest conversion and cultivation (Table 1; compare with Kinyangi 2008). Similar to N, a greater number of households in the older conversion watersheds may have added more kitchen waste that are rich in K and Na such as ash from firewood cookstoves and farm yard manure. Kimetu et al. (2008) documented contents of 23.2 g K $kg^{-1}$ in the manure.

The lack of change or even slight decrease in Ca and Mg stream water concentrations may be a result of a dominance of weathering as the primary source of Ca and, to a certain extent, Mg. In addition, the significant decrease in extractable Ca in the topsoil (Table 1) in combination with the rather decreasing stream water

concentrations after forest conversion point at the subsoil as the primary source of Ca.

### Intra-annual dynamics of stream water solutes

None of the solute concentrations (except DOC, Na and K) changed with the strong changes in discharge between January and December 2008 (Figs. 3 and 4). No significant correlations were established between any of the solutes and stream discharge (Fig. 4) which is in contrast to other studies that typically show significant changes in DOC and nutrient concentrations throughout the year (Markewitz et al. 2001; Johnson et al. 2006b; Bucker et al. 2011). Although variations in intra-annual stream concentrations are often observed, the solutes can either be more concentrated during high flow in the rainy season due to export of mainly surficial nutrients (Markewitz et al. 2001) or less concentrated due to dilution during heavy rainfall and larger volume of stream discharge (Elsenbeer et al. 1994; Anderson et al. 1997; Tsujimura et al. 2001; Grimaldi et al. 2004). The constant concentration of N, P, Mg and Ca with varying discharge over seasonal time scales in our study may be explained by a balance between changes in water delivery and solute delivery (Salmon et al. 2001). Ca and Mg can be delivered from both organic-rich soil horizons and weathering of deeper soil (Yusop et al. 2006). During low flows, the Ca and Mg would be derived from the weathered mineral subsoil, whereas near surface storm event flow (Noguchi et al. 1997) could entrain these solutes from the organic-rich topsoil.

In contrast, the Na and K concentrations in all four catchments dropped during the month of August at the onset of the second rainy season. The sources of K as well as Na are associated with leaching and decomposition of leaves and organic matter, and thus are expected to be available at greater quantities in the upper soil profile (Proctor et al. 1989; Veneklaas 1991). Therefore, prolonged rain may have leached K and Na contained in the litter layer from the soil surface similar to what has been observed for DOC in southern Amazonia (Johnson et al. 2006b) where the litter layer disappeared towards the end of the rainy season (Selva et al. 2007).

## Conclusion

Results from this study indicate that conversion of forest catchments to continuous maize cropping had a significant effect on the hydrochemistry of headwater streams. All OC species and nutrient concentrations increased with forest conversion and cultivation except for Ca and Mg. The reason may be the proportional greater importance of geochemical weathering for Ca and Mg. Dilution of major solutes during the rainy season frequently observed elsewhere did not occur here, except for K and Na. Fluvial OC export was low compared to estimated mineralization of SOC and stream P losses were negligible, but N losses by stream water must be addressed to curtail declining crop productivity. In terms of nutrient pollution and possible contamination of water resources, the N and P levels are not of concern and agriculture in the headwaters seems to play a minor role for the observed eutrophication of the downstream Yala River system and Lake Victoria.

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