



## Distribution and origin of suspended matter and organic carbon pools in the Tana River Basin, Kenya

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**Abstract.** We studied patterns in organic carbon pools and their origin in the Tana River Basin (Kenya), in February 2008 (dry season), September–November 2009 (wet season), and June–July 2010 (end of wet season), covering the full continuum from headwater streams to lowland mainstream sites. A consistent downstream increase in total suspended matter (TSM, 0.6 to 7058 mg l<sup>−1</sup>) and particulate organic carbon (POC, 0.23 to 119.8 mg l<sup>−1</sup>) was observed during all three sampling campaigns, particularly pronounced below 1000 m above sea level, indicating that most particulate matter exported towards the coastal zone originated from the mid and low altitude zones rather than from headwater regions. This indicates that the cascade of hydroelectrical reservoirs act as an extremely efficient particle trap. Although <sup>7</sup>Be/<sup>210</sup>Pb<sub>xs</sub> ratios/age of suspended sediment do not show clear seasonal variation, the gradual downstream increase of suspended matter during end of wet season suggests its origin is caused by inputs of older sediments from bank erosion and/or river sediment resuspension. During wet season, higher TSM concentrations correspond with relatively young suspended matter, suggesting a contribution from recently eroded material. With the exception of reservoir waters, POC was predominantly of terrestrial origin as indicated by generally high POC : chlorophyll *a* (POC : Chl *a*) ratios (up to ~41 000). Stable isotope signatures of POC ( $\delta^{13}\text{C}_{\text{POC}}$ ) ranged between −32 and −20 ‰ and increased downstream,

reflecting an increasing contribution of C4-derived carbon in combination with an expected shift in  $\delta^{13}\text{C}$  for C3 vegetation towards the more semi-arid lowlands.  $\delta^{13}\text{C}$  values in sediments from the main reservoir (−19.5 to −15.7 ‰) were higher than those found in any of the riverine samples, indicating selective retention of particles associated with C4 fraction. Dissolved organic carbon (DOC) concentrations were highest during the end of wet season (2.1 to 6.9 mg l<sup>−1</sup>), with stable isotope signatures generally between −28 and −22 ‰. A consistent downstream decrease in % organic carbon (% OC) was observed for soils, riverine sediments, and suspended matter. This was likely due to better preservation of the organic fraction in colder high altitude regions, with loss of carbon during downstream spiraling.  $\delta^{13}\text{C}$  values for soil and sediment did not exhibit clear altitudinal patterns, but values reflect the full spectrum from C3-dominated to C4-dominated sites. Very low ratios of organic carbon to mineral surface area (OC : SA) were found in reservoir sediments and suspended matter in the lower Tana River, indicating that these are stable OC pools which have undergone extensive degradation. Overall, our study demonstrates that substantial differences occur in both the quantities and origin of suspended sediments and organic carbon along the river profile in this tropical river basin, as well as seasonal differences in the mechanisms causing such variations.

## 1 Introduction

Rivers play an important role in the global carbon (C) cycle, and process  $\sim 2.7 \text{ Pg C annually}$ , of which  $\sim 0.9 \text{ Pg C yr}^{-1}$  is estimated to reach oceans (Cole et al., 2007; Aufdenkampe et al., 2011). Rivers do not merely transport C from the terrestrial biome to the oceanic environment, but also bury and process organic matter, generally acting as a source of  $\text{CO}_2$  to the atmosphere (Cole and Caraco, 2001; Mayorga et al., 2005; Cole et al., 2007). Although the riverine C flux may be small compared to the gross global fluxes between ocean-atmosphere ( $90 \text{ Pg C yr}^{-1}$ ) and terrestrial-atmosphere ( $120 \text{ Pg C yr}^{-1}$ ) interfaces (Schlünz and Schneider, 2000; Prentice et al., 2001; Houghton, 2004; Sabine et al., 2004), the fluvial C flux transport is of the same order as the respective net ecosystem production ( $2.2 \text{ Pg C yr}^{-1}$ ) (Cole and Caraco, 2001; Cole et al., 2007; Battin et al., 2008; Aufdenkampe et al., 2011).

Riverine systems transport C mainly as DOC, POC and dissolved inorganic C (DIC). Globally, rivers discharge into the world's oceans approximately  $0.5 \text{ Pg C yr}^{-1}$  as DIC and about  $0.4 \text{ Pg C yr}^{-1}$  as organic C (OC), with about one-half each as POC and DOC (Meybeck, 1993; Probst et al., 1994; Ludwig et al., 1996; Ludwig and Probst, 1998; Schlünz and Schneider, 2000). Fluvial C fluxes may differ strongly among individual rivers due to the large variation in variables such as catchment slopes, vegetation, geology, climate and size (Hope et al., 1994). The global sediment yield of rivers is estimated at  $160\text{--}180 \text{ t km}^{-2} \text{ yr}^{-1}$  in pre-dammed conditions (Vörösmarty et al., 2003). However, most current C flux estimates do not account for human impact such as retention of material in reservoirs; hence, actual sediment load and POC transport to the oceans may be lower because of increased damming of rivers (Vörösmarty et al., 2003; Syvitski et al., 2005).

Riverine POC is mainly derived from soils, litterfall and primary production while DOC arises from degradation of organic matter in the soil, leaching of plant litter and, to a lesser degree, from the contribution of autochthonous biological processes occurring in the stream (Meybeck, 1993; Ludwig et al., 1996; Finlay and Kendall, 2007). Globally, riverine DOC fluxes are dependent on drainage intensity, basin slope and to a larger extent, the amount of C stored in soils, while POC on the other hand is a function of TSM fluxes which principally depend on drainage intensity, rainfall intensity and basin slope (Ludwig et al., 1996). In the majority of rivers, the POC content of TSM ranges between 1 and 20 %, but it can exceptionally reach 0.5 % for highly turbid rivers, or values greater than 20 % for lowland rivers draining swamps (Meybeck, 1982, 1993; Ittekkot, 1988; Ludwig et al., 1996; Mayorga et al., 2010).

The origin of riverine organic C is commonly categorized as either allochthonous-derived from terrestrial organic matter or autochthonous-derived from in-situ biological production (Hope et al., 1994; Finlay and Kendall, 2007). According

to the river continuum concept (Vannote et al., 1980), the relative contribution of different sources to total OC varies with stream size, where allochthonous C is expected to be important in first order streams, giving way to autochthonous production downstream as the stream size increases. As turbidity increases in large or disturbed rivers, light limits autotrophic production again, and hence allochthonous forms of C are expected to dominate energy flow (Vannote et al., 1980). Besides the river continuum concept (Vannote et al., 1980), the serial discontinuity concept (Ward and Stanford, 1983) accounts for disturbances in river flow such as congestion by dams, while the flood pulse concept (Junk et al., 1989) accounts for the exchange of material with surrounding flooded plains. Tropical rivers account for 60 % of estimated C flux and 34 % of the sediment delivery to the global oceans (Ludwig et al., 1996; Schlünz and Schneider, 2000). In view of the increasingly recognized importance of freshwater ecosystems in the C cycle (Cole et al., 2007; Battin et al., 2008; Tranvik et al., 2009; Aufdenkampe et al., 2011), and considering the disproportionate role tropical rivers have in global riverine C export, the biogeochemistry of tropical rivers merits particular attention. Given the relative scarcity of data, this requires both a better quantification of material (export) fluxes, as well as multi-proxy studies on the origin and processing of organic matter. The quantification of bulk concentrations of TSM, POC, DOC, allow the quantification of export fluxes, while stable isotopes and radioisotopes provide information on sources and time-scales of processing, respectively.

Carbon stable isotope signatures ( $\delta^{13}\text{C}$ ) are dependent on the photosynthetic pathway, and thus differ substantially between terrestrial  $\text{C}_3$  plants (and  $\text{C}_3$  plant-dominated soils) and  $\text{C}_4$  plants (or  $\text{C}_4$  plant-dominated soils), which have typical  $\delta^{13}\text{C}$  value of about  $-28$  and  $-13$  ‰, respectively (Still and Powell, 2010; Kohn, 2010). Freshwater autotrophs such as phytoplankton can have a wide range of  $\delta^{13}\text{C}$  signatures ( $-42$  to  $-19$  ‰ according to Finlay and Kendall, 2007), depending e.g. on the  $\delta^{13}\text{C}$  values of DIC.

Thus, stable isotopes have frequently been used, in combination with other proxies such as elemental ratios (POC : PN) and/or POC : Chl *a* ratios, to constrain the relative contribution of different organic matter sources (autochthonous vs. allochthonous), and to understand C fluxes and the fate of terrigenous C in river systems (Kendall et al., 2001; Finlay and Kendall, 2007). Radionuclides, particularly  $^7\text{Be}$ ,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ , have recently been applied as tracers to identify source regions of sediments, quantify residence and settling times of particles within a given river basin, as well as understanding aspects of fluvial sediment erosion, transport, deposition and resuspension (Matisoff et al., 2002, 2005). Both  $^7\text{Be}$  ( $t_{1/2} = 53.3 \text{ d}$ ) and  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3 \text{ yr}$ ) are delivered to the Earth surface through wet and dry fallout and both elements sorb strongly to particles, hence, qualifying as tracers of sediment origin (Bonniwell et al., 1999; Matisoff et al., 2002; Saari et al., 2010). The ratio of  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  in suspended

matter reflects the age of sediment (i.e. the time since the sediment received both  $^7\text{Be}$  and  $^{210}\text{Pb}_{\text{xs}}$  from atmospheric deposition) and can be used to quantify the proportion of resuspended bottom material in the water column (Olsen et al., 1986). Thus, a decrease in the  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratio reflects an increase in the time since the sediment was “tagged” with atmospherically derived  $^7\text{Be}$  and  $^{210}\text{Pb}_{\text{xs}}$ , since  $^7\text{Be}$  has a much shorter half-life than  $^{210}\text{Pb}$ . Alternatively, a decrease in this ratio may reflect dilution of  $^7\text{Be}$ -rich sediment with  $^7\text{Be}$ -deficient old sediment (Matisoff et al., 2005).

The present study focuses on the distribution and origin of OC pools in the Tana River, Kenya, as regulated by reservoirs and along a longitudinal gradient. It is based on four sampling campaigns which include three basin-wide surveys covering different seasons (dry season – February 2008, wet season – September–November 2009, and end of wet season – June–July 2010) and one follow-up campaign in September 2011. These data provide one of the most complete studies quantifying and characterising riverine OC at the scale of an entire tropical river catchment.

## 2 Materials and methods

### 2.1 Study area

The Tana River is the longest river in Kenya ( $\sim 1100$  km), with a total catchment area of  $\sim 96\,000$  km<sup>2</sup> (Fig. 1a). The basin experiences a bimodal hydrological cycle, with long rains between March and May, and short rains between October and December (Fig. 2). The river system can be separated into two main parts, here referred to as the “Tana headwaters” and the “lower main Tana” (Fig. 1b). The Tana headwaters encompass a set of small mountainous streams that form the perennial source of the Tana River, and which originate from the Aberdares Range in the central highlands of Kenya, the highlands around Mount Kenya, and the Nyambene Hills in eastern Kenya (Fig. 1a). The lower main Tana encompasses the section downstream of the Nyambene Hills, where the river continues for about 700 km through semi-arid plains. Along this stretch, tributaries only discharge in short pulses during the wet season. As a result, the lower main Tana forms a single transport channel during the dry season, delivering material to the Indian Ocean (Maingi and Marsh, 2002). Along the lower main Tana, extensive floodplains are found between the towns of Garissa and Garsen (Fig. 1a). Yet, flooding has been irregular in recent decades, as the river flow is regulated by five hydro-electric dams upstream (Maingi and Marsh, 2002). The associated reservoirs have a combined surface area of 150 km<sup>2</sup>, and a substantial amount of sediment is trapped behind these dams (Dunne and Ongweny, 1976; Brown and Schneider, 1998). The basin experiences variable rainfall patterns, decreasing from the headwaters ( $> 3050$  m, annual precipitation  $\sim 1800$  mm yr<sup>-1</sup>), upper highlands (2450–3050 m,

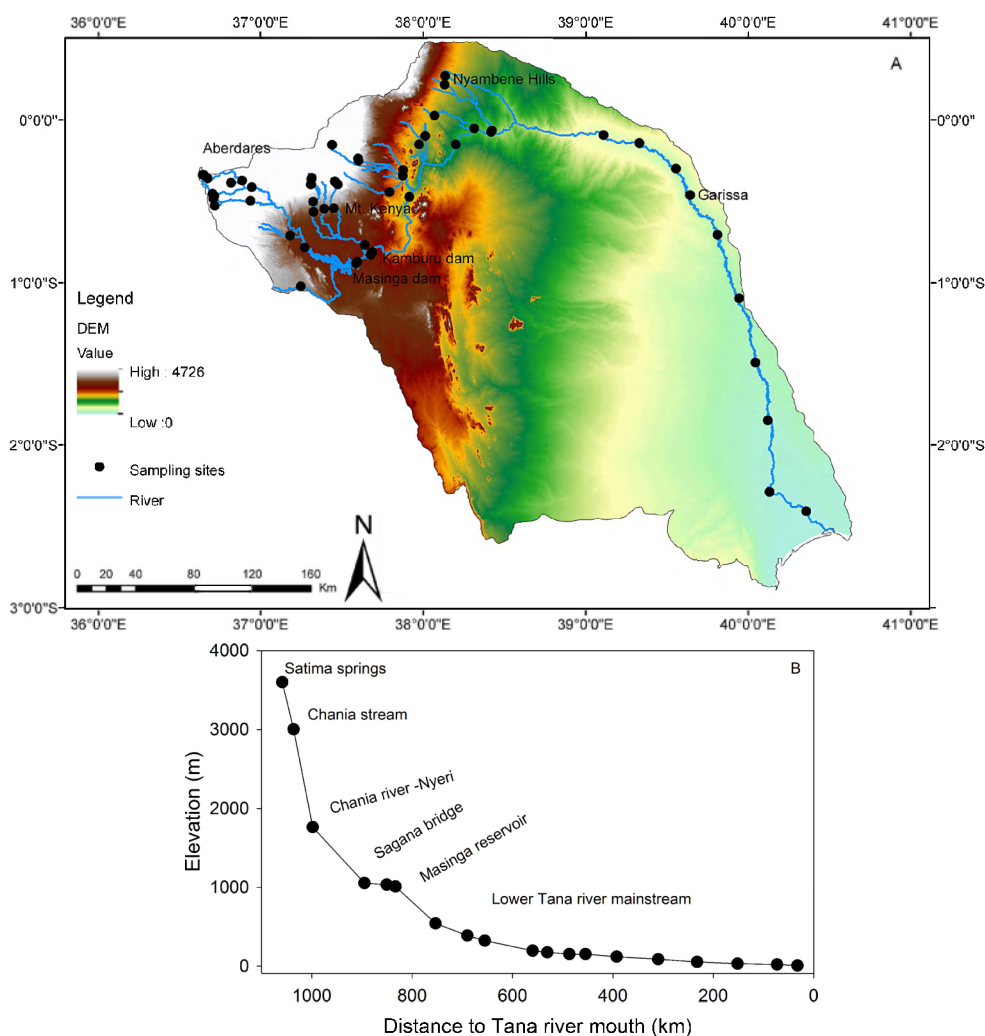
annual precipitation  $\sim 2200$  mm yr<sup>-1</sup>), mid-altitude catchment (1850–900 m, annual precipitation between 900 and 2000 mm yr<sup>-1</sup>), to the lower semi-arid Tana catchment (900–10 m) which receives 450–900 mm yr<sup>-1</sup> (Brown and Schneider, 1998). The mean annual river discharge is 156 m<sup>3</sup> s<sup>-1</sup> as measured at Garissa gauging station (data from the Global River Discharge Database, available on <http://daac.ornl.gov/RIVDIS/rivdis.shtml>). The average river discharge measured at Garissa station during the wet season (208.5 m<sup>3</sup> s<sup>-1</sup>; October and November 2009) was 1.7 and 1.4 times higher than during the dry season (122.9 m<sup>3</sup> s<sup>-1</sup>; February 2008) and end-of-wet-season (145.2 m<sup>3</sup> s<sup>-1</sup>; June and July 2010), respectively (Fig. 2). The high-altitude headwaters (Aberdares, Mt. Kenya) are characterized by montane forest vegetation and moorlands at the highest elevations, giving way to more intense agricultural activities in mid altitude regions. The semi-arid lower Tana is dominated by open to wooded savannah grassland, with some riverine gallery forests along the Tana River.

### 2.2 Sampling and analytical techniques

Water, sediment and soil sampling was carried out during three campaigns in February 2008 (dry season), September–November 2009 (wet season), and June–July 2010 (end of wet season) (Fig. 2), with additional sampling of riverbank sediments in September 2011. Samples were taken throughout the river basin (Fig. 1 – Supplement Table 1), and sampling sites included a subset of small streams in the headwater regions, an approximately equidistant set of locations along the main lower Tana, and two of the five hydro-electric reservoirs (Masinga and Kamburu). The first field survey in February 2008 only covered a subset of these field sites, for which the water column data have already been presented in Bouillon et al. (2009), and only the data on soils and riverine sediments are further detailed here. In both the 2009 and 2010 campaigns, an extensive basin-wide survey was carried out. During the follow-up fieldtrip in September 2011, depth profiles of riverbank soils were collected at several sites along the lower Tana River.

Water samples were taken with a Niskin bottle at  $\sim 0.5$  m below the water surface, or using a bucket when sampling from bridges along the main river. Samples for TSM were taken by filtration of a known volume of surface water on 47 mm GF/F filters (nominal porosity = 0.7  $\mu\text{m}$ ), which were pre-weighed and pre-combusted (4 h at 450 °C), and then dried and re-weighed after filtration. Samples for POC, particulate nitrogen (PN), and  $\delta^{13}\text{C}_{\text{POC}}$  were obtained in a similar way by filtering a known volume of surface water on pre-combusted 25 mm GF/F filters (0.7  $\mu\text{m}$ ) and drying. In the laboratory, these filters were exposed to HCl fumes for 4 h to remove inorganic C, re-dried and packed in Ag cups.

Topsoil samples (surface 0–5 cm layer) were collected at all sampling sites (except the Masinga and Kamburu reservoirs), slightly upstream from the water sampling location

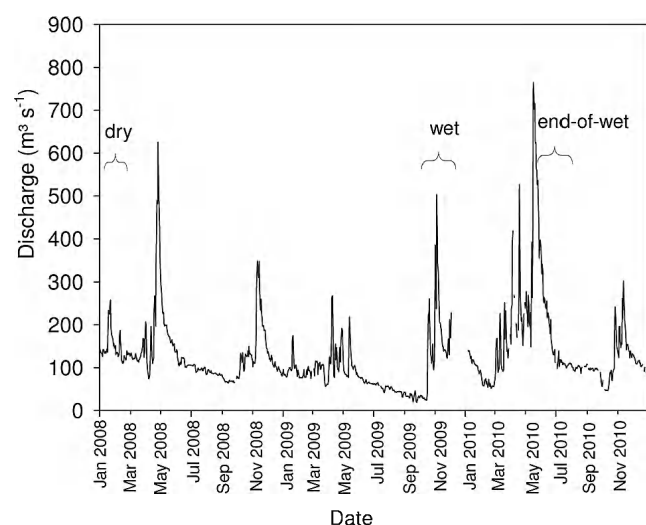


**Fig. 1.** (A) Digital Elevation Model (DEM) of the Tana River Basin, which consists of two main geographical units, the Tana headwaters and the main lower Tana. The 57 sampling sites are indicated by black dots. (B) Profile of the Tana River from headwaters to Tana mouth. Sampling stations for the lower Tana River are indicated, as well as a selected number of headwater sampling sites to show their overall position.

and  $\sim 10$  m from the riverbank. Along the main Tana River, riverbed sediments were sampled with a Van Veen grab, while in the shallow headwater streams, sediment was directly collected into sample tubes. An unusually dry period preceded the fieldwork in September–October 2009 and led to historically low water levels in the Masinga reservoir. This enabled easy access to the reservoir bottom. Three short sediment cores (up to 30 cm) were taken at the lowest sites accessible, and within the zone where clear, thick sediment deposits were present. In the same campaign, the Van Veen grab was used to retrieve surface sediment from the Kamburu reservoir. All soil and sediment samples were stored in liquid  $N_2$  during transport, and upon return to the laboratory, they were preserved at  $-20^\circ\text{C}$  until further analysis. In the laboratory, sediment and soil samples were dried, ground and homogenized using a mortar and pestle. A weighed subsam-

ple was transferred into a Ag cup to which a 10 % HCl solution was added to remove all carbonates. The samples were then dried at  $60^\circ\text{C}$  for 24 h, and if necessary, the procedure was repeated.

POC, PN, and  $\delta^{13}\text{C}_{\text{POC}}$  from filters, soil and sediment samples were determined on a Thermo elemental analyzer–isotope ratio mass spectrometer (EA-IRMS) system (various configurations, either Flash1112, FlashHT with Delta+XL or DeltaV Advantage), using the thermal conductivity detector (TCD) signal of the elemental analyzer (EA) to quantify POC and PN, and by monitoring 44, 45, and 46  $m/z$  signal on the isotope-ratio mass spectrometer (IRMS). Quantification and calibration of  $\delta^{13}\text{C}$  data were performed with IAEA-C6 and acetanilide which was internally calibrated vs. international standards. Reproducibility of  $\delta^{13}\text{C}_{\text{POC}}$  measurements was typically better than  $\pm 0.2\%$ , while relative standard



**Fig. 2.** Discharge measurements for the Tana River (2008–2010) as recorded at Garissa station (data source: Water Resource Management Authority). Brace brackets indicate the duration of the three field investigations.

deviations for calibration standards for POC and PN measurements were typically < 2 % and always < 5 %. POC : PN ratios are presented on a weight : weight basis.

Samples for DOC and  $\delta^{13}\text{C}_{\text{DOC}}$  were obtained by pre-filtering surface water through pre-combusted GF/F filters (0.7  $\mu\text{m}$ ), with further filtration through 0.2  $\mu\text{m}$  syringe filters, and were preserved with  $\text{H}_3\text{PO}_4$  in glass vials with teflon-coated screw caps. DOC and  $\delta^{13}\text{C}_{\text{DOC}}$  were measured with either a customized Thermo HiperTOC coupled to a Delta+XL IRMS (Bouillon et al., 2006), or by manual injection in a Thermo IsoLink HPLC-IRMS (similar to the method described in Albéric, 2011). Samples for pigment analysis were obtained by filtering a known volume of surface water on pre-combusted 47 mm GF/F filters, which were immediately packed in cryotubes and stored in liquid  $\text{N}_2$ . Upon return to the laboratory, these were stored at  $-20^\circ\text{C}$  until further analysis. Pigments were extracted in 10 ml acetone : water mixture (90 : 10), and a subsample was separated by HPLC on a C18 reverse phase column (Bouillon et al., 2009). Calibration was performed with working standards prepared from commercially available pure compounds.

Surface area (SA) measurements were made on 200–600 mg freeze-dried and homogenized samples of soils, sediments and TSM using multi-point Brunauer-Emmet-Teller adsorption isotherms (Brunauer et al., 1938). Measurements were made using a 25 Quantachrome NOVA 3000 SA analyzer, and verified with BCR-173 (Institute for Reference Materials and Measurements).

Samples for radionuclide analysis were obtained by filtering a known volume of surface water on 102 mm polycarbonate membrane filters. The activities of  $^7\text{Be}$ ,  $^{210}\text{Pb}$  and

$^{226}\text{Ra}$  were determined on the dried suspended matter using a low background-high efficiency well type  $\gamma$ -counter placed in a lead shield and protected from cosmic rays using an anti-cosmic shielding made of plastic scintillators (Schmidt et al., 2009). Standards used for calibration of the  $\gamma$ -detector were IAEA standards (RGU-1; RGTh-1; IAEA-314).  $^7\text{Be}$  values were corrected for radioactive decay that occurred between sample collection and counting. Excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) was calculated by subtracting the activity supported by parent isotope  $^{226}\text{Ra}$  from the total activity measured in particles. The  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  AR can be used to calculate the age of the sediments or the fraction of new sediments (Matisoff et al., 2005):

$$\text{Age} = \frac{1}{(\lambda_{^7\text{Be}} - \lambda_{^{210}\text{Pb}})} \ln(\text{AR}_0/\text{AR}) \quad (1)$$

$$\% \text{ new sediment} = (\text{AR}/\text{AR}_0) \times 100, \quad (2)$$

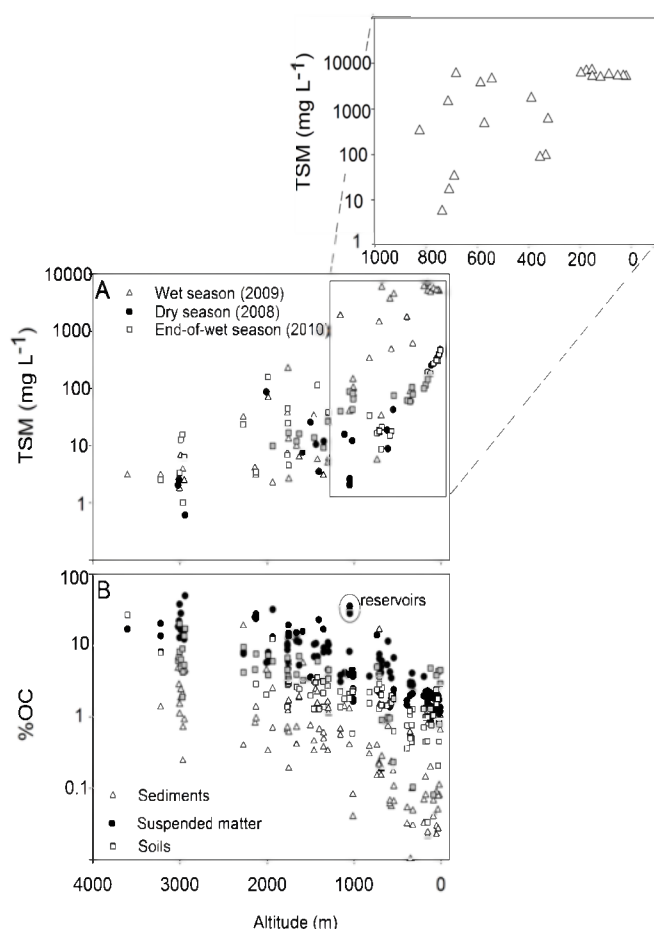
where  $\lambda_{^7\text{Be}}$  and  $\lambda_{^{210}\text{Pb}}$  are the decay constants of  $^7\text{Be}$  ( $0.013 \text{ d}^{-1}$ ) and  $^{210}\text{Pb}$  ( $8.509 \times 10^{-5} \text{ d}^{-1}$ ). AR and  $\text{AR}_0$  are the  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  AR of suspended particles and of the atmospheric fallout, respectively. In the absence of direct measurements in the study area, we estimated a  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratio of 12 for atmospheric fallout, based on literature data (Liu et al., 2001; Saari et al., 2010). While this places an uncertainty on the absolute estimates of the sediment age or % new sediment, it does not affect relative variations in these estimates.

### 3 Results

#### 3.1 Total suspended matter and particulate organic carbon

The full dataset is available as Supplement Tables 1–6. The TSM concentrations recorded during the dry season in 2008 (0.6 to  $483 \text{ mg l}^{-1}$ ) showed a similar range as during the end of wet season conditions in 2010 (1 to  $471 \text{ mg l}^{-1}$ ), while the range during the wet season was one order of magnitude larger (2 to  $7058 \text{ mg l}^{-1}$ ), with the highest values obtained in the lower main Tana. Paired t-tests confirm that TSM values were similar during dry season and end of wet season datasets ( $p > 0.05$ ), but significantly higher during the wet season campaign. In the dry season campaign of 2008, there is consistent increase in TSM in the lower main Tana, and this pattern is basically replicated in 2010. In the wet season campaign of 2009, TSM concentrations are an order of magnitude higher, and show no trend along the lower Tana River axis (Pearson correlation,  $p > 0.05$ ; Fig. 3a). In the headwater regions, TSM shows strong variability between streams in all campaigns with exceptionally high values in selected tributaries (Muringato, Thanandu, Mathioya, Mutonga and Maara) during the wet season (Supplement Table 1; Fig. 3a).

Concentrations of POC during the wet season ( $0.23$  to  $119.8 \text{ mg l}^{-1}$ ) were much higher than during the dry season



**Fig. 3.** Altitudinal profiles of **(A)** total suspended matter concentrations, and **(B)** % OC in suspended matter, soils and sediments along Tana River Basin during three sampling seasons. For panel **(B)**, data from the different sampling seasons were combined.

(0.3 to 5.8 mg l<sup>-1</sup>) and end of wet-season (0.4 to 12.6 mg l<sup>-1</sup>) (Supplement Table 1). POC concentrations show a similar pattern with altitude as TSM, i.e. a consistent downstream increase during all sampling campaigns (Pearson correlation,  $p < 0.01$ ).

The organic C content (% OC) of the suspended matter ranged from 1.1 to 49.8 %, 0.9 to 32.1 % and 1.2 to 37.9 % for dry season, wet season and end of wet season campaigns, respectively (Supplement Table 1), and the organic C content decreased downstream (Fig. 3b). TSM and % OC showed an inverse relationship during the three seasons (Pearson correlation,  $p < 0.01$ ). POC : PN ratios (weight : weight) were significantly lower ( $p < 0.05$ ) during the wet season ( $9.6 \pm 2.5$ ) as compared to end of wet season ( $11.3 \pm 3.0$ ) and dry-season ( $10.5 \pm 2.6$ ) datasets (Supplement Table 1).

The  $\delta^{13}\text{C}_{\text{POC}}$  values ranged from  $-26.5$  to  $-21.2$  ‰,  $-31.8$  to  $-19.9$  ‰, and  $-27.1$  to  $-21.4$  ‰ with means of  $-23.8 \pm 1.6$  ‰,  $-24.7 \pm 2.8$  ‰ and  $-24.3 \pm 1.6$  ‰ during dry season, wet season and end of wet season campaigns, respec-

tively (Supplement Table 1; Fig. 4a). The values for different seasons were not significantly different (paired t-test,  $p > 0.05$ ). Generally, the  $\delta^{13}\text{C}_{\text{POC}}$  values increased downstream during all the three sampling campaigns (Pearson correlation,  $p < 0.01$ ; Fig. 4a). Overall, the  $\delta^{13}\text{C}_{\text{POC}}$  values during the three seasons were not significantly different for headwaters and so were the values for the lower main Tana (paired t-test,  $p > 0.05$ ). However, values for most sites above 2950 m in Aberdares and Mt. Kenya headwaters were more  $^{13}\text{C}$ -enriched. Overall, Mt. Kenya tributaries were the most depleted ( $-26.3 \pm 2.0$  ‰), Aberdares and Nyambene Hills intermediate ( $-24.6 \pm 1.0$  and  $-24.0 \pm 1.8$  ‰, respectively) and Tana River mainstream the most enriched ( $-22.5 \pm 1.0$  ‰). POC : Chl *a* ratios were generally high (75 to 40781) with remarkably low values recorded in reservoirs (Supplement Table 1; Fig. 4b).

### 3.2 Dissolved organic carbon and $\delta^{13}\text{C}_{\text{DOC}}$

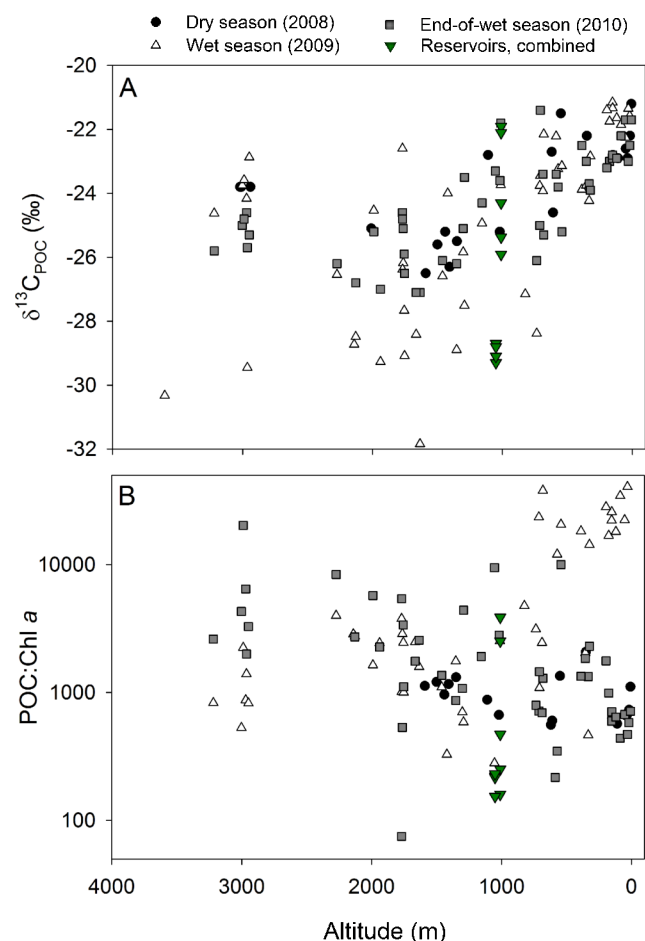
Concentrations of DOC during the dry season (0.3 to 2.5 mg l<sup>-1</sup>) were significantly lower (paired t-test,  $p < 0.01$ ) compared to wet season (0.2 to 6.4 mg l<sup>-1</sup>) and end of wet season (2.1 to 6.9 mg l<sup>-1</sup>) (Supplement Table 1; Fig. 5a). Overall, DOC values for Aberdares, Mt. Kenya tributaries and Tana River mainstream showed seasonal differences ( $p < 0.01$ ) but values for Nyambene Hills tributaries were similar during the three seasons ( $p > 0.05$ ). DOC concentration increased downstream during wet season (Pearson correlation,  $p < 0.01$ ; Fig. 5a).

The  $\delta^{13}\text{C}_{\text{DOC}}$  values ranged from  $-27.7$  to  $-21.8$  ‰,  $-26.9$  to  $-21.4$  ‰ and  $-26.9$  ‰ to  $-20.9$  ‰, with means of  $-23.8 \pm 1.1$  ‰,  $-24.4 \pm 1.3$  ‰ and  $-24.0 \pm 1.1$  ‰ for dry season, wet season and end of wet season campaigns, respectively (Supplementary Table 1; Fig. 5b). The values were similar during all the three campaigns (paired t-test,  $p > 0.05$ ). The mean values were  $-24.2 \pm 1.0$  ‰,  $-24.6 \pm 1.3$  ‰,  $-24.2 \pm 1.7$  ‰ and  $-23.7 \pm 0.9$  ‰ for Aberdares (1763 to 3600 m), Mt. Kenya (572 to 2964 m), Nyambene Hills (333 to 736 m) tributaries and Tana mainstream (8 to 1054 m), respectively.  $\delta^{13}\text{C}_{\text{DOC}}$  and  $\delta^{13}\text{C}_{\text{POC}}$  were significantly correlated during the wet season only (Pearson correlation,  $r^2 = 0.55$ ;  $p < 0.01$ ; Fig. 6a). The ratio of dissolved to particulate organic C (DOC : POC) ranged from 0.02 to 16.4 for the entire dataset over the three campaigns. The means were  $0.95 \pm 0.59$ ,  $1.52 \pm 2.50$  and  $2.26 \pm 2.01$  for dry season, wet season and end of wet season campaigns, respectively. DOC : POC ratios showed a decreasing trend with TSM, and hence generally decreased downstream during all the three seasons (Pearson correlation,  $p < 0.01$ ; Fig. 7).

### 3.3 Soil and sediment carbon pools

Data on % OC of soils and riverine sediments were combined for the three sampling campaigns. The soil % OC ranged between 0.03 to 20.2 % (Supplement Table 2), with a mean

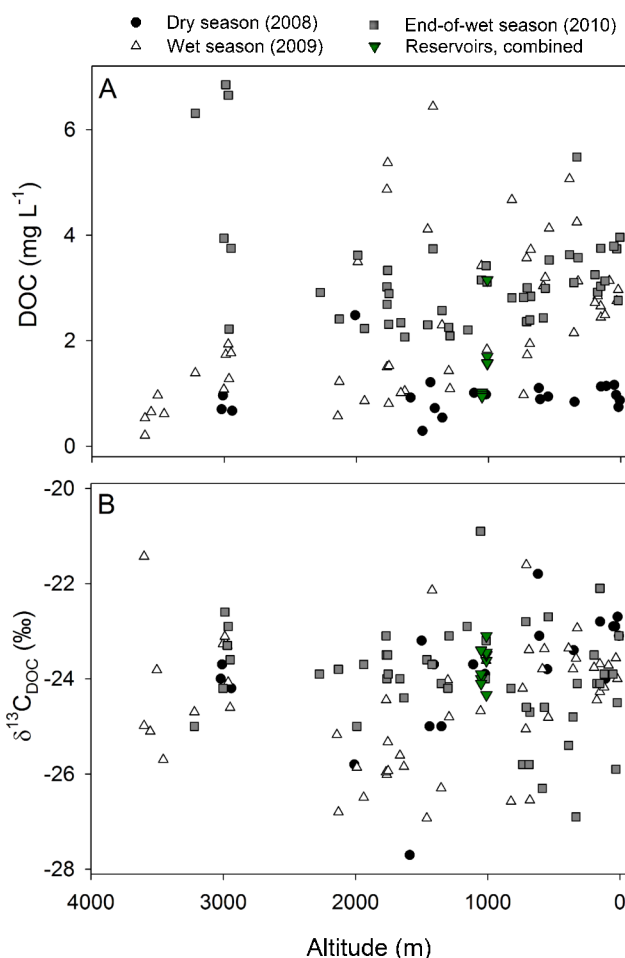




**Fig. 4.** Altitudinal profile of (A)  $\delta^{13}\text{C}_{\text{POC}}$  and (B) POC:Chl *a* ratios along Tana River Basin during three sampling seasons. Data from the reservoirs are from all sampling campaigns combined and include those from Bouillon et al. (2009).

basin-wide value of  $3.5 \pm 3.9$ . Similarly, the % OC of riverine sediment ranged from 0.01 to 5.7 % with a basin-wide mean of  $1.3 \pm 2.6$  (Supplement Table 2). Both the soil and sediment % OC decreased consistently downstream (Pearson correlation,  $p < 0.01$ ; Fig. 3b). Soil and sediment values were significantly different (paired t-test,  $p < 0.05$ ). The  $\delta^{13}\text{C}$  values of the soil show a weak positive correlation with altitude (Pearson correlation,  $r^2 = 0.23$ ;  $p < 0.05$ ), and an overall range between  $-28.5$  and  $-13.2$ ‰ (Supplement Table 2). The  $\delta^{13}\text{C}$  data of the riverine sediment showed a slightly smaller range (between  $-27.8$  and  $-16.2$ ‰ – Supplement Table 2) and did not show a systematic pattern with altitude (Pearson correlation,  $p > 0.05$ ).

Overall, % OC from riverbank soil depth profiles ranged between 0.05 to 1.7 % whereas  $\delta^{13}\text{C}$  values ranged between  $-26.1$  and  $-11.9$ ‰ (Supplement Table 3). The % OC decreased with depth while  $\delta^{13}\text{C}$  values generally increased with depth at Tana Primate and Garsen sites (Pearson correla-



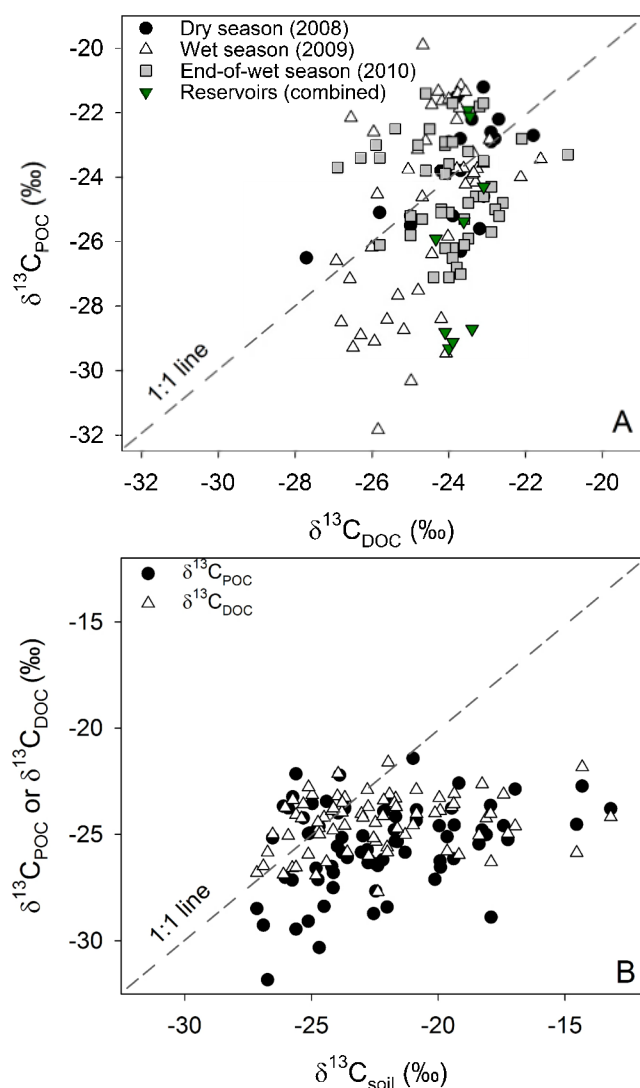
**Fig. 5.** Altitudinal profile of (A) DOC concentration, and (B)  $\delta^{13}\text{C}_{\text{DOC}}$  along Tana River Basin during three sampling seasons.

tion,  $p < 0.05$ ) but no systematic patterns could be discerned at the Garissa and Hola sites (Pearson correlation,  $p > 0.05$ ; Supplement Table 3).

Sediment % OC on cores from Masinga Reservoir ranged from 1.1 to 1.9 % (Supplement Table 4), and although concentrations differed between the cores, they generally decreased with depth (Fig. 8a); while that of sediments in Kamurur Dam was 1.84 % (Supplement Table 2). The  $\delta^{13}\text{C}$  values from Masinga cores ranged between  $-19.6$  and  $-15.7$ ‰ (Supplement Table 4), and increased consistently with depth (Fig. 8b) whereas the single sample from Kamurur dam sediment was  $-20.7$ ‰.

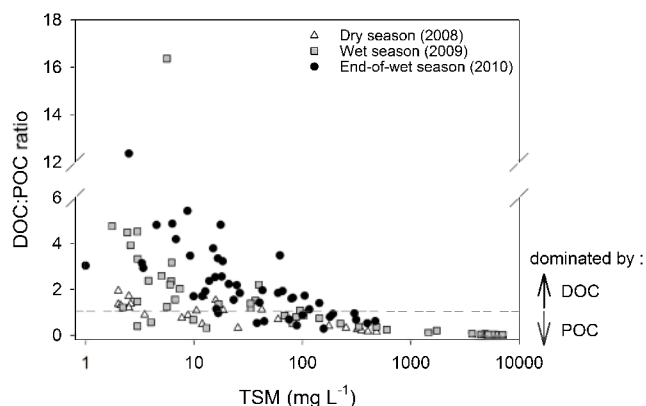
### 3.4 Specific surface areas

Specific SA ranged between  $2.4$  to  $98.2 \text{ m}^2 \text{ g}^{-1}$ ,  $0.9$  to  $105 \text{ m}^2 \text{ g}^{-1}$  and  $39.9$  to  $82.3 \text{ m}^2 \text{ g}^{-1}$  for soil, riverine sediment and suspended matter, respectively (Supplement Table 5). The SA for soils and riverine sediments decreased consistently downstream (Pearson correlation,  $p < 0.01$ ;

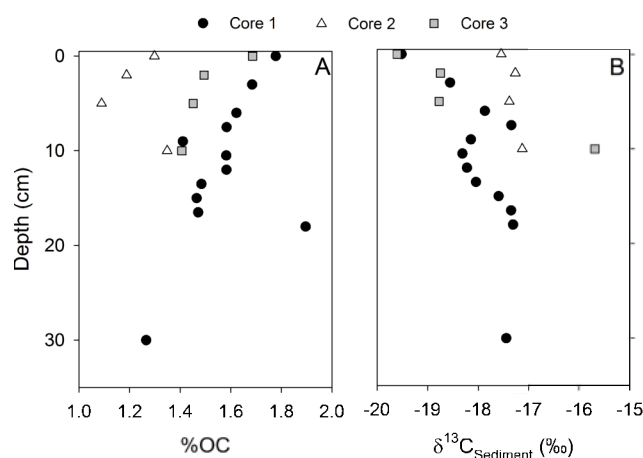


**Fig. 6.** Plots of (A)  $\delta^{13}\text{C}_{\text{POC}}$  vs.  $\delta^{13}\text{C}_{\text{DOC}}$  throughout the Tana River Basin, (B)  $\delta^{13}\text{C}_{\text{soil}}$  vs.  $\delta^{13}\text{C}_{\text{POC}}$  and  $\delta^{13}\text{C}_{\text{DOC}}$  for tributaries along Tana River Basin (i.e. mainstream data not included in panel B).

Fig. 9a) while those of suspended matter increased downstream. Riverine sediment % OC and SA were positively correlated (Pearson correlation,  $p < 0.01$ ; Fig. 9b) but soil and suspended matter were not correlated ( $p > 0.05$ ). The SA values from the Masinga (Supplement Table 4) and Kamururu (Supplement Table 5) reservoirs sediments were notably high, and ranged between  $59.8$  to  $93.8 \text{ mg OC m}^{-2}$ . The OC : SA ratios ranged between  $0.1$  to  $14.6 \text{ mg OC m}^{-2}$ ,  $0.1$  to  $7.1 \text{ mg OC m}^{-2}$  and  $0.2$  to  $0.5 \text{ mg OC m}^{-2}$  for soil, sediment and suspended matter, respectively (Supplement Table 5). Generally, soil OC : SA ratios were significantly higher than riverine sediments ( $p < 0.01$ ). However, OC : SA ratios did not show a systematic pattern with altitude. The OC : SA ratios from Masinga and Kamururu dams sediment cores ranged



**Fig. 7.** Relation between DOC : POC ratio vs. TSM along Tana River Basin, (B) % OC vs.  $\delta^{13}\text{C}_{\text{OC}}$  for tributaries upstream of Masinga reservoir. Horizontal line in panel (A) indicates a DOC : POC ratio of 1.



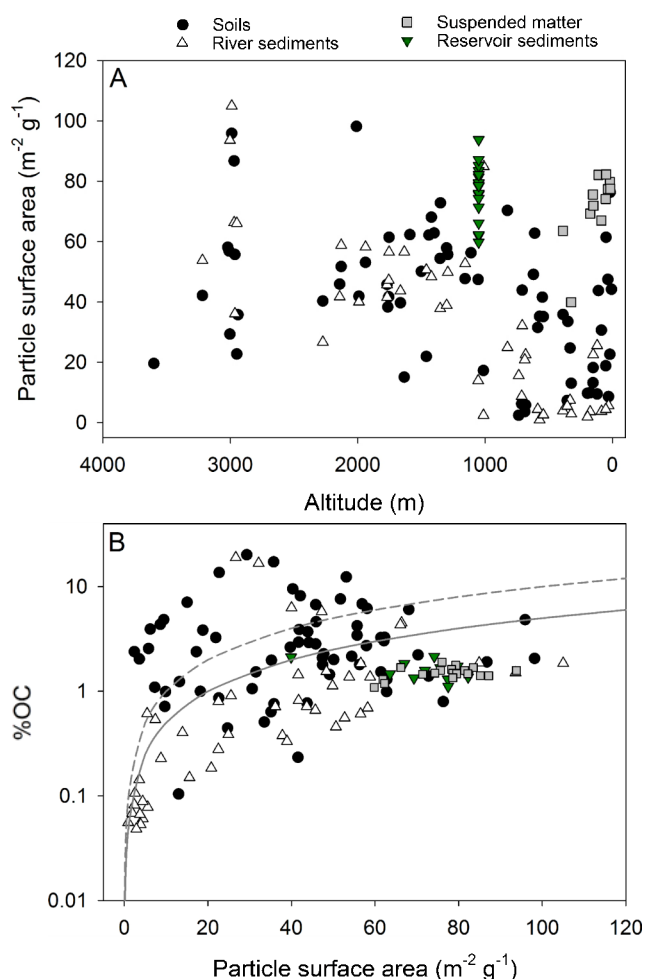
**Fig. 8.** Plots of (A) sediment core depth vs. sediment % OC (B) sediment core depth vs.  $\delta^{13}\text{C}_{\text{sediment}}$  at Masinga Reservoir.

between  $0.16$  to  $0.25 \text{ mg OC m}^{-2}$ . However, neither SA nor the OC : SA ratio exhibited a systematic pattern with core depth.

### 3.5 Activities of radionuclides

The particulate activity ratios of  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ( $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  AR) ranged between  $0.5$  and  $2.4$  during wet season and increased consistently downstream (Pearson correlation,  $p < 0.05$ ;  $R^2 = 0.76$ ; Fig. 10a), while during the end of wet season campaign, values showed greater variability, and ranged between  $0.02$  and  $4.5$  (Supplement Table 6; Fig. 10a). The age of suspended sediment ranged from  $124$  to  $244$  days and  $75$  to  $478$  days during wet and end of wet season, respectively (Fig. 10b).





**Fig. 9.** Profile of (A) altitude vs. SA, (B) SA vs. %OC of soil, sediment and suspended matter along Tana River Basin during three sampling seasons. Dashed lines bound the monolayer equivalent lines; region of organic carbon to surface area ratios (OC : SA) of 0.5–1.0 mg OC m<sup>-2</sup> SA.

## 4 Discussion

### 4.1 Sediment dynamics along the Tana River flow-path

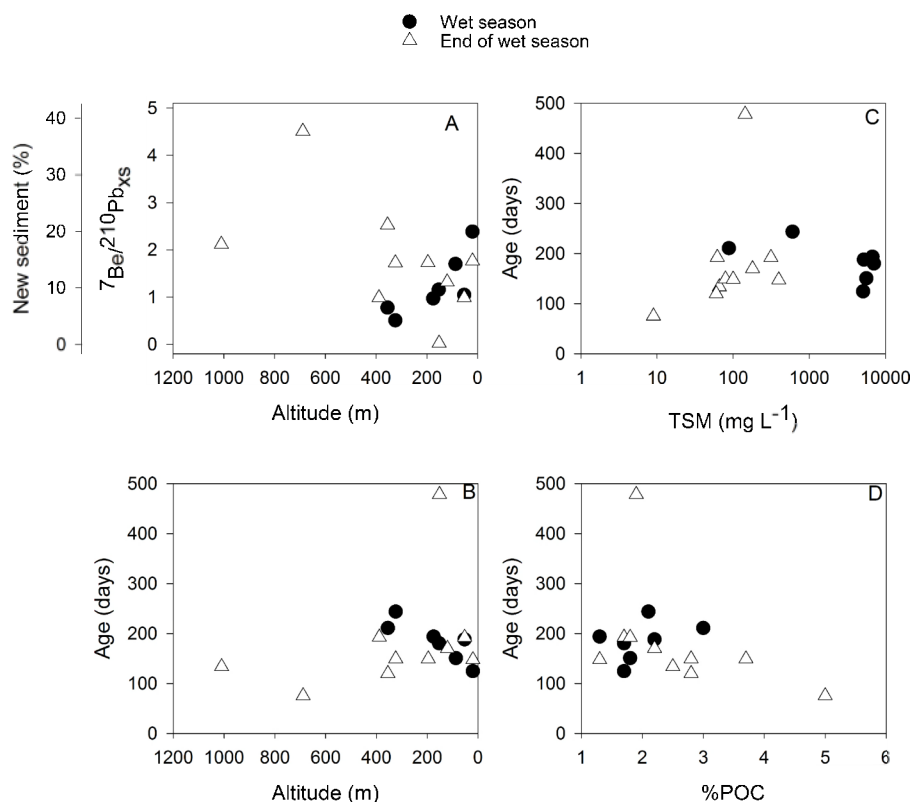
As expected (Dunne and Ongweny, 1976; Kitheka et al., 2005), TSM concentrations were highest during high-flow conditions of the wet season, in particular for the lower main Tana River. TSM profiles during all seasons studied show that, with few exceptions, high-altitude streams have relatively low TSM concentrations. Considering that the Tana River sustains several reservoirs along its channel, a substantial amount of sediment is trapped, with Masinga and Kamburu dam alone estimated to retain ~6.0 and 3.0 million t yr<sup>-1</sup>, respectively (Dunne and Ongweny, 1976; Brown and Schneider, 1998 and references therein). Despite the presence of these reservoirs, high TSM values were recorded beyond the reservoirs in the lower main Tana. The TSM pro-

file is much more variable during the wet season, with several minima and maxima along the lower river course (see Fig. 3a, note the log scale on the y-axis). Sediment inputs could be expected from the ephemeral streams (lagas) during flash floods. Monthly sampling conducted by Kitheka et al. (2005) for two years between 2000 to 2003 recorded TSM concentrations in the range of 530 to 1930 mg l<sup>-1</sup> at Garsen (see Fig. 1 for location). The maximum of this range is much lower than the value we recorded during our wet season campaign at the same site (5098 mg l<sup>-1</sup>). Compared to many other African river systems (e.g. Martins, 1983; Lesack et al., 1984; Seyler et al., 1995; Bird et al., 1998; Coynel et al., 2005; 1.7 to 135 mg l<sup>-1</sup>), the TSM concentrations encountered in the lower main Tana during the wet season were exceptionally high.

In the dry and end of wet season, TSM concentration data are lower than in the wet season, but still high at Masinga bridge located ~2 km downstream of Masinga reservoir compared to the headwaters (Supplement Table 1). Moreover, there is a very conspicuous and strong increase in TSM along the lower main Tana (Fig. 3a) where the river flows through semi-arid plains for ~700 km, and where no tributaries discharge in the dry season. Based on data from the dry season sampling in 2008, Bouillon et al. (2009) suggested that resuspension of internally stored riverbed sediments could offer an explanation for the gradual downstream increase in TSM observed during low flow conditions. An alternative interpretation for this downstream increase in TSM below the reservoirs is that the lower Tana River is in a non-equilibrium state with respect to sediment transport. Past studies have documented similar impacts of upstream damming to downstream river networks (Scodanibbio and Mañez, 2005), such as river channel incision, associated riverbank erosion and downstream sedimentation (Rosgen, 1997). In the case of the Tana River, Maingi and Marsh (2002) reported that following the construction of Masinga dam, river meandering rates have decreased and the river channel of the lower Tana has deepened. Our observations of strongly increasing TSM concentrations during different stages of the hydrograph thus suggest that much of the sediment generated in the lower section of the Tana River, at least during periods of lower discharge, is derived from the collapse of incised and unstable riverbanks, whereas during the wet season, high TSM concentration are likely contributed by both riverbank erosion and surface erosion.

The contribution of bank sediments in explaining the increasing TSM load along the lower Tana River appears to be consistent with OC data from riverbank soils. The high TSM loads coincide with lower %POC values and higher  $\delta^{13}\text{C}_{\text{POC}}$  signatures, and a comparison with bank soil data illustrates that these could represent an end-member consistent with observations on the riverine POC (Fig. 11b).

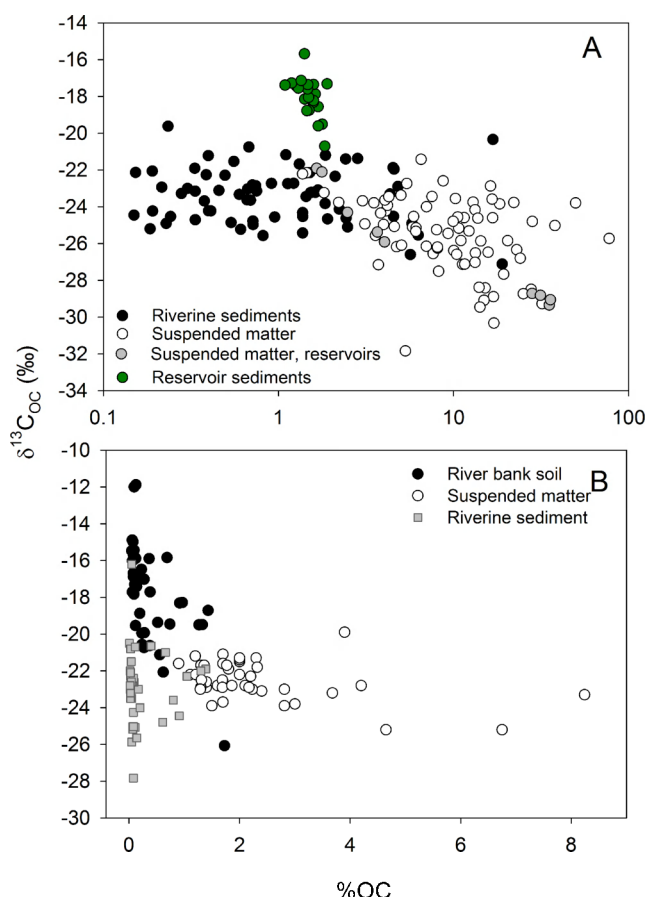
Variations in <sup>7</sup>Be/<sup>210</sup>Pb<sub>xs</sub> ratios form an important tool for tracing suspended particles along the river continuum (Matisoff et al., 2005; Saari et al., 2010). In the context of



**Fig. 10.** Overview of results of  $^{7}\text{Be}/^{210}\text{Pb}_{\text{xs}}$  measurements on suspended sediment samples in the Tana River during wet season and end of wet season: **(A)** altitudinal profile of  $^{7}\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratios, and the estimated % new sediment, **(B)** altitudinal profile of the estimated suspended matter age, **(C)** relationship between suspended matter age and TSM concentrations, and **(D)** relationship between suspended matter age and %POC.

identifying the sources of sediments in the lower Tana River, these data allow us to make an analysis of the relative importance of surface erosion (material with high  $^{7}\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratios) versus riverbed resuspension or riverbank collapse (material with low  $^{7}\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratios, Whiting et al., 2005). Although the number of samples is limited, our data show a number of interesting patterns which allow to put some first order constraints on the origin of riverine suspended matter (Fig. 10). First, along an altitudinal gradient, differences between seasons are not very pronounced (Fig. 10a, b) since variations along the riverine continuum within a sampling season are quite strong. Secondly, when plotting the average of suspended sediments versus TSM concentrations, there appears to be a gradual increase in age with increasing TSM during dryer conditions, with one site showing exceptionally high sediment age (with an estimated contribution of new sediment of 0 %, Fig. 10c). This suggests that during low flow conditions, the increasing TSM concentrations downstream are caused by inputs of older sediments, with bank erosion and/or resuspended sediments being the main candidate sources. A contribution by riverbank collapse would contribute  $^{7}\text{Be}$ -deficient sediment to the river suspended matter load (Whiting et al., 2005), since it brings in deeper soil

layers with an older radionuclide signature. Internal resuspension of river sediments would have a similar effect on  $^{7}\text{Be}/^{210}\text{Pb}_{\text{xs}}$  ratios, but as noted above, this mechanism less likely accounts for the large downstream increase in TSM observed during dry conditions. During the wet season, however, the much higher TSM concentrations do not follow this trend, as they show sediment ages in the same range as those observed at much lower TSM concentrations during dryer conditions (Fig. 10c). This suggests a contribution of recently eroded material during the wet season, as also indicated by the decreasing sediment age downstream (Fig. 10b). Despite the evidence for recently eroded sediment, the estimated % contribution of new sediment is overall relatively low (8–20 % in the lower Tana River during the wet season, Fig. 10a). Finally, it can be noticed that when pooling the different data, the suspended matter samples representing more recently eroded material correspond to those with higher %POC values (Fig. 10d), consistent with topsoil erosion which is expected to have a higher organic matter content than deeper soil layers or riverbanks.



**Fig. 11.** Comparison between (A) % OC vs.  $\delta^{13}C_{OC}$  for tributaries upstream of Masinga reservoir, (B) % OC vs.  $\delta^{13}C$  for the lower Tana River.

#### 4.2 Longitudinal changes in riverine organic carbon cycling

The high %POC and POC:Chl *a* ratios in the upstream reaches (Supplement Table 1) suggest that POC is predominantly terrestrial, and the low  $\delta^{13}C_{POC}$  values point towards C3 plant species, which are dominant in the high altitude headwater catchments. The  $\delta^{13}C_{POC}$  values increase downstream in contrast to patterns observed in the Amazon basin (Cai et al., 1988; Townsend-Small et al., 2005; Aufdenkampe et al., 2007), although a similar pattern has been reported in a tropical river system in Cameroon (Bird et al., 1994b). Such a downstream increase in  $\delta^{13}C_{POC}$  could result from a combination of two processes: (i) altitudinal differences in the  $\delta^{13}C$  signature of C3 vegetation, and/or (ii) a shift towards a higher contribution of C4 vegetation at lower altitudes. Regarding the first mechanism,  $\delta^{13}C$  values of C3 plants have been reported to increase with decreasing mean annual precipitation (e.g. Kohn, 2010). The rainfall pattern in Tana River basin decreases from 2200 mm yr<sup>-1</sup> at high altitudes to 450 mm yr<sup>-1</sup> in lower and drier Tana catchment

(Brown and Schneider, 1998). Employing these precipitation data together with the empirical relationship between altitude, precipitation and  $\delta^{13}C$  of C3 vegetation established by Kohn (2010), the average C3 vegetation is expected to have average signatures of -28.7 and -26.5 ‰ for the highest and lowest altitudes, respectively, i.e. a shift of +2.2 ‰. This shift is much smaller than the observed shift of ~7 ‰ in our dataset, (Fig. 4a). This indicates that the downstream increase in  $\delta^{13}C$  values is to a large extent due to increased contributions from C4 vegetation or C4-dominated soil organic matter. One notable exception to this elevational pattern is the much higher than expected C4 contribution at some of the high altitude sites (Aberdares, Mt. Kenya), where POC show distinctly higher  $\delta^{13}C$  signatures (Fig. 4a). This observed C4 contribution is explained by the frequent occurrence of *A. amethystinus*, a tussock-forming C4 grass species in high altitude sites (> 3000 m, see Tieszen et al., 1979; Wooller et al., 2001), for which our own  $\delta^{13}C$  measurements range between -13.6 and -12.1 ‰.

The downstream increase in C4 vegetation as reflected in  $\delta^{13}C_{POC}$  values is related to an increasing aridity and the associated vegetation gradient, where forested ecosystems at high altitudes gradually shift towards savannah dominated ecosystems along the lower main Tana. Based on a simple mixing model, and using end-member values for C4 and C3 vegetation of -12.1 and -27.6 ‰ respectively, the estimated C3 contribution in the POC pool in the lower main Tana is surprisingly high (63 %), despite the open savannah vegetation in the lower altitude Tana basin probably due to contribution from riverine forest. Past studies from other tropical rivers suggest minimal contribution of POC from algal sources in fluvial systems (Bird et al., 1994a, b). The  $\delta^{13}C$  signatures for POC at Masinga (Bouillon et al., 2009) and Kamburu dams showed depleted  $\delta^{13}C$  values, low POC : Chl *a* ratios, high % POC and low POC : PN ratios, thus reflecting POC contributions from algal sources (Supplement Table 1; Fig. 4a, b). This effect was particularly pronounced during dry season campaign (Bouillon et al., 2009). Yet, in our riverine samples, there is a negligible contribution of phytoplankton to the POC pool as confirmed by the high POC : Chl *a* ratios.

The  $\delta^{13}C$  values for Masinga dam sediment cores were surprisingly high (-19.5 to -17.3 ‰) and inconsistent with the values measured in tributaries feeding into the Masinga reservoir (Fig. 11b). These signatures similarly do not match the phytoplankton in the reservoir (grey symbols in Fig. 11b), suggesting that selective retention of particles associated with the C4 fraction or/and preferential mineralization of isotopically light POM could be responsible for these unexpected  $\delta^{13}C$  signatures. Indeed, there appear to be more  $^{13}C$ -depleted signatures in the surface layers, increasing downcore coinciding with a loss of OC (Fig. 9b). Since phytoplankton  $\delta^{13}C$  signatures in this reservoir is found to be quite  $^{13}C$ -depleted, the downcore variations would be consistent with a preferential loss of more labile in situ production.

Nevertheless, the  $\delta^{13}\text{C}$  values found in deeper layers still reflect a C4 contribution which is much higher than would be expected based on  $\delta^{13}\text{C}_{\text{POC}}$  signatures in the inflowing rivers (Fig. 11b).

Preferential mineralisation of the C3 component of riverine inputs would conflict with the hypothesis proposed by Wynn and Bird (2007) that C4 derived organic matter decomposes faster than C3-derived material. One possible mechanism to reconcile these results is related to particle sorting effects, whereby the C4 component is well protected on the finer particles and that our samples, collected towards the outflow of the reservoir, represent this finer fraction (which would be consistent with the high SA values, Fig. 8a). A first-order estimate of post-depositional C losses can be obtained by comparing the %OC data between the upper and lower layers of the deepest sediment core. This way, we estimate a  $\sim 30\%$  OC loss thus suggesting a relatively high burial efficiency of organic C ( $\sim 70\%$ ) in the Masinga reservoir. The burial efficiency of OC in our study is significantly higher than the  $\sim 40\%$  reported in other temperate and tropical lakes (Sobek et al., 2009; Kunz et al., 2011), but it should be stressed that our estimate is derived from a limited number of data. Nevertheless, even this coarse estimate underscores the significant role reservoirs play as sinks in global C cycle (Cole et al., 2007; Battin et al., 2008; Tranvik et al., 2009). The surface area (SA) for suspended matter along lower main Tana ( $60\text{--}80\text{ m}^2\text{ g}^{-1}$ ) were within the same range as those reported by Bouillon et al. (2009) but are much higher than those reported for coastal sediments, estuaries and rivers ( $< 50\text{ m}^2\text{ g}^{-1}$ ) (Mayer, 1994; Keil et al., 1997; Aufdenkampe et al., 2007). Compared to the TSM, the riverine sediment showed a much larger range in SA due to the sandy and muddy deposits in the riverbed. As expected (Mayer, 1994; Keil et al., 1997), riverine sediment %OC showed a positive correlation with SA (Fig. 8b), a strong indication of protective organic matter adsorption to mineral surface areas. For coarser, sandy sediments (low SA values), %OC were generally higher than expected for the “monolayer equivalent” (Mayer, 1994), whereas the opposite was true for more clay-rich riverine sediments (higher SA). This would be consistent with a significant fraction of non-bound particulate matter in coarser sediments, while most of the particulate C in fine-grained sediments is more strongly bound to clay minerals. In contrast, soil %OC did not show significant relationship with corresponding SA (Fig. 8b), and the majority of soil samples had %OC values above the monolayer equivalence lines, which is consistent with a contribution from non-bound plant-derived organic matter. The OC : SA ratios for riverine sediments were consistently lower than those of soils with similar SA values, suggesting that riverine OC particles have been subjected to extensive degradation losses. All reservoir sediments and suspended matter samples showed high SA values of  $> 60\text{ m}^2\text{ g}^{-1}$ , and organic C loadings were always below the monolayer equivalent zone. The observed range of OC : SA values in these suspended matter and reservoir

sediment samples ( $0.14\text{--}0.53$  and  $0.16\text{--}0.25\text{ mg OC m}^{-2}$ , respectively) are markedly lower than the range previously observed in other large river systems such as the Amazon, Fly, Columbia, and Hung He (typically between  $0.25$  and  $1$ ; see Keil et al., 1997), and fall more in the range of values found in coastal or marine sediments (Aufdenkampe et al., 2007). These low OC : SA values thus suggest a very stable organic C pool which has undergone extensive degradation of the more labile fractions during erosional and riverine transport and retention cycles.

The relationship between %POC and TSM followed an inverse relationship as reported for other world rivers (Meybeck, 1982). Two different hypotheses have been proposed to explain this relationship (Thurman, 1985; Ludwig et al., 1996). First, decreasing %POC in suspended matter with increasing TSM concentrations could reflect the variable contribution of the autochthonous C produced by riverine phytoplankton. Secondly, this pattern may reflect mixing between more organic-rich surface soil runoff and/or direct litter contributions, and deeper soil-derived sediments with reduced organic C loading. In our study, the high POC : Chl *a* ratios (Fig. 4b) strongly favour the second hypothesis. Only for the reservoirs (Kamburu and Masinga) do our data suggest that the elevated %POC is explained by in-situ phytoplankton production. The elevated %POC recorded in headwater tributaries corresponds with high POC : PN ratios (Supplement Table 1), indicating OC is majorly derived from allochthonous fresh plant materials, while low %POC values recorded in lower main Tana, particularly during wet season campaign, are due to dilution by soil mineral particles (from mechanical erosion associated with surface runoff during flash floods during the wet season and bank instability during dry season). During wet season sampling, high amount of terrigenous and lithological materials originating from soil and/or bank erosion, characterized by low organic C content is a dominant characteristic. The %POC relationship from our data fits well with an empirical model based on Ludwig et al. (1996) data in the lower TSM range (up to  $\sim 1000\text{ mg l}^{-1}$ ), but %OC values are markedly higher than global averages in the higher TSM range ( $> 1000\text{ mg l}^{-1}$ ). In addition, %POC was generally higher than soil %OC, particularly in higher altitude sites due to additional contributions from the riparian vegetation as direct litter inputs or topsoil detritus.

DOC concentrations in the present study ( $0.2$  to  $6.9\text{ mg l}^{-1}$ ) are relatively low compared to those reported for other African rivers (range  $0.6$  to  $51.2\text{ mg l}^{-1}$ ; Martins, 1983; Seyler et al., 1995; Coynel et al., 2005; Brunet et al., 2009; Spencer et al., 2010), but consistent with average values for rivers crossing semi-arid climates as reported by Spitzzy and Leenheer (1991). The altitudinal profiles show contrasting patterns during different seasons: for the dry season, concentrations were consistently low throughout the basin (Bouillon et al., 2009), increased downstream during the wet season (Fig. 5a), though highly variable in lower

altitude (< 2000 m), or showed consistently higher values in the high-elevation sites (end of wet season, Fig. 5a) in Aberdare and Mt. Kenya headwaters, which may be attributed to presence of peatlands and swamps. DOC in high mountain streams are typically much lower than those of other natural waters (Meybeck, 1982; Hedges et al., 2000). However, most of these studies were conducted at higher latitudes where organic-rich peat soils do not occur (Townsend-Small et al., 2005). The generally higher DOC concentrations during the wet and end of wet season would be consistent with a terrestrial-derived origin of DOC, which is also most likely given the minimal contribution of phytoplankton to the POC pool. The downstream increase in DOC concentrations during wet season may be associated with efficient soil organic matter degradation in hotter lower Tana. DOC : POC ratios were relatively low and ranged from 0.02 in the lower reaches of Tana River main channel to 5.5 in the headwaters. DOC typically dominated in the tributaries ( $59 \pm 21\%$ ) while POC dominated in the main Tana River (DOC contribution of  $34 \pm 23\%$ ), which is typical for highly erosive and turbid systems and in line with the general trend of lower DOC : POC ratios with increasing TSM (Meybeck, 1982; Ittekkot and Laane, 1991; Middelburg and Herman, 2007; Ralison et al., 2008; Bouillon et al., 2009). The global average contribution of DOC to the total riverine OC pool is highly variable, ranging between 10 and 90 % (Meybeck, 1982) but recent estimates put global mean DOC contribution at  $73 \pm 21\%$ , and  $61 \pm 30\%$  for tropical systems (Alvarez-Cobelas et al., 2010). Contrary to the downstream trend observed in  $\delta^{13}\text{C}_{\text{POC}}$  values (Fig. 4a),  $\delta^{13}\text{C}$  signatures of DOC were generally stable (Fig. 5b). The weak correlation between  $\delta^{13}\text{C}_{\text{DOC}}$  and  $\delta^{13}\text{C}_{\text{POC}}$  (Fig. 6a) suggests that the exchange of C between POC and DOC pools (through adsorption and desorption reactions, *sensu* Middelburg and Herman, 2007) is limited.

### 4.3 Links between terrestrial and aquatic carbon pools

Soil % OC showed a marked altitudinal gradient, with high values in high altitude sites and consistently decreased to low values in sites along the lower Tana River (Fig. 3b). This altitudinal gradient in soil OC is in accordance with previous and more large-scale datasets on soil OC stocks in Kenya (Batjes, 1996, 2004), and is also observed in other large-scale studies such as in the Amazon basin (e.g. Townsend-Small et al., 2005; Aufdenkampe et al., 2007). A similar gradient was observed in riverine sediment % OC (Fig. 3b). Such gradients are typically explained by the associated temperature gradient, which leads to less efficient soil organic matter degradation in colder, high-altitude regions (Couteaux et al., 2002; Finlay and Kendall, 2007). As expected (e.g. Townsend-Small et al., 2005), both soil and sediment POC / PN ratios showed an altitudinal gradient, although more pronounced in sediments ( $R^2 = 0.25$  and  $0.37$ , respectively). The stable isotope composition of soil organic matter in principle reflects

the isotope signatures of the vegetation. Thus, soil organic matter  $\delta^{13}\text{C}$  values of about  $-27\%$  and  $-13\%$  are expected in areas dominated by C3 and C4 plants, respectively (Finlay and Kendall, 2007; Kendall et al., 2001). Although  $\delta^{13}\text{C}_{\text{soil}}$  values in the present study do not show systematic patterns with altitude, the values exhibited the full range of C3 to C4 signatures ( $-28.5$  to  $-13.2\%$ ) consistent with the variable vegetation patterns within the catchment. The distribution of C3 and C4 grasses in Kenya has been documented by Tieszen et al. (1979), and they found a clear altitudinal shift of a complete C4-dominance below 2000 m to a dominance of C3 grass species above 3000 m. The  $\delta^{13}\text{C}_{\text{sediment}}$  values ( $-27.8$  to  $-16.2\%$ ) show a more narrow range of values with less variability than surface soils, considering sediments integrate soil inputs from larger areas and so are more mixed than spot samples in soils. This concurs with data from Bird et al. (1994b) that  $\delta^{13}\text{C}_{\text{sediment}}$  values are controlled and/or reflective of the dominant vegetation type present in the river catchment, among other factors such as altitude. It should be stressed that estimates of C3 and C4 contributions using soil  $\delta^{13}\text{C}$  data refer to C inputs from these two vegetation types, and do not necessarily reflect their relative standing biomass due to potential differences in their relative productivity and degradability of litter. Gillson et al. (2004), for example, demonstrated that soil  $\delta^{13}\text{C}$  data in Kenyan mixed C3–C4 savannas significantly underestimated local C3 plant biomass.

The relationship between  $\delta^{13}\text{C}_{\text{soil}}$  values and  $\delta^{13}\text{C}_{\text{DOC}}$  and  $\delta^{13}\text{C}_{\text{POC}}$  values for tributaries (Fig. 6b) shows that DOC and POC in the aquatic system usually have a stronger C3 contribution than soils in the subcatchments (with the obvious caveat that our soil samples are not necessarily representative of the entire subcatchment). Organic matter in some of the tributaries also appears to be partially derived from direct litter inputs, given the higher % OC than observed in surface soils.

## 5 Conclusions

Generally, suspended matter and POC delivery in Tana River was highest during high-flow conditions, with the majority of the suspended load being generated in the lower section of the Tana River. We propose that riverbank erosion, coupled with sediment pulses from ephemeral streams form the main sources of these high TSM loads. Thus, the cascade of reservoirs on the Tana River at mid-altitude appear to be very efficient traps for suspended material from high-altitude regions, but also result in a disequilibrium in the lower course of the river, with increased sediment mobilisation downstream. The  $\delta^{13}\text{C}$  values constrained from bulk C organic measurements show that C3 derived organic matter dominates the riverine DOC and POC pools, with important C4 contributions mainly in the high-altitude regions and in the lower Tana. The generally high POC : Chl *a* ratios suggest

there is a negligible contribution from in-stream phytoplankton production except in Kamburu and Masinga reservoirs. The  $\delta^{13}\text{C}$  values from sediments in Masinga and Kamburu reservoirs do not reflect phytoplankton production but rather selective retention of the C4 fraction of the organic matter – a rather unique observation considering C4 organic matter is normally preferentially mineralized over C3. Despite limited data,  $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$  measurements point towards a combination of older sediment sources (bank erosion) and surface erosion as significant sources of riverine suspended matter, the latter particularly during high flow periods.

**Supplementary material related to this article is available online at:** <http://www.biogeosciences.net/9/2905/2012/bg-9-2905-2012-supplement.pdf>.

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