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Dissolved organic carbon lability and stable isotope shifts during microbial decomposition in a tropical river system

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Abstract

A significant amount of carbon is transported to the ocean as dissolved organic carbon (DOC) in rivers. During transport, it can be transformed through microbial consumption and photochemical oxidation. In dark incubation experiments with water from the Tana River, Kenya, we examined the consumption of DOC through microbial decomposition and the associated change in its carbon stable isotope composition ($\delta^{13}C$). In 15 of the 18 incubations, DOC concentrations decreased significantly by 10 to 60 %, with most of the decomposition taking place within the first 24–48 h. After 8 days, the remaining DOC was up to 3 ‰ more depleted in ^{13}C compared with the initial pool, and the change in $\delta^{13}C$ correlated strongly with the fraction of DOC remaining. We propose that the shift in $\delta^{13}C$ is consistent with greater microbial lability of DOC originating from herbaceous C_4 vegetation than DOC derived from woody C_3 vegetation in the semi-arid lower Tana. The findings complement earlier data that riverine C sources do not necessarily reflect their proportion in the catchment: besides spatial distribution, also processing within the river can further influence the riverine $\delta^{13}C$.

1 Introduction

Rivers form the main connection between the terrigenous and oceanic organic carbon (OC) pools. Although rivers were previously seen as mere conduits of water and material, this is no longer the case (Cole et al., 2007; Battin et al., 2009; Aufdenkampe et al., 2011). Indeed, from the 1.9 Pg C yr^{-1} (Cole et al., 2007; Regnier et al., 2013) to 2.7 Pg C yr^{-1} (Battin et al., 2009) estimated to be globally entering inland waters, only 0.9 Pg C yr^{-1} is delivered to the ocean (Cole et al., 2007; Battin et al., 2009; Regnier et al., 2013). Of the total OC flux, 73 ± 21 % is exported as dissolved carbon (Alvarez-Cobelas et al., 2012). Despite the significant amount of terrigenous carbon entering the river systems, relatively little organic material with a terrigenous signature can be found in the ocean (Raymond and Bauer, 2001; Bianchi and Bauer, 2011; Marìn-Spiotta et al.,

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2014). Therefore, it is important to have a better understanding of the changes OC is subjected to and at which point those changes occur during their transport towards the oceans. Two processes, photochemical oxidation and microbial consumption, are able either to mineralize the terrigenous OC, or transform it in such a way that its characteristics resemble the oceanic OC (Bianchi and Bauer, 2011; Lalonde et al., 2014; Marìn-Spiotta et al., 2014). When this transformation of the OM characteristics occurs during transport in the rivers, it may lead to inconsistent characteristics between the terrestrial input, what is present in the river and the OM which is delivered to the ocean, if the transformation processes are not fully understood.

Photochemical processes can occur directly, when the chromophoric dissolved organic matter (DOM) becomes excited under the influence of UV and visible light, leading to transformation within the molecules, or indirectly when free radicals are formed which react with organic compounds (Amon and Benner, 1996; Lalonde et al., 2014). Compared with carbohydrates, lignin components are found to be much more susceptible to photochemical degradation, despite their resistance to biological degradation (Opsahl and Benner, 1998; Opsahl and Zepp, 2001; Spencer et al., 2009). As lignin is more depleted in ^{13}C than the bulk DOM, decomposition of lignin would lead to a ^{13}C enrichment of the remaining DOC pool (Opsahl and Zepp, 2001). An increase in the $\delta^{13}C$ signature of DOC under the influence of UV light has indeed been observed in different river systems such as the Congo, Amazon, and Mississippi rivers (Opsahl and Zepp, 2001; Spencer et al., 2009; Lu et al., 2013; Lalonde et al., 2014).

The biodegradable fraction of DOC can be quantified by the loss of DOC by microbial consumption in dark incubation experiments (Servais et al., 1989). Several experiments have combined the effect of photochemical oxidation with microbial incubation, either by exposing filtered water to UV light followed by the addition of inoculum (Amon and Benner, 1996; Lalonde et al., 2014), or by allowing both processes to act simultaneously (Benner and Kaiser, 2011; Lu et al., 2013). These studies have consistently found that photochemical oxidation broke down a larger fraction of the DOC, compared to biological consumption (Amon and Benner, 1996; Benner and Kaiser, 2011; Lu et al.,

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2013; Lalonde et al., 2014). Furthermore, microbial and photochemical processes exert greater effect in combination than independently (Benner and Kaiser, 2011; Lu et al., 2013). However, photochemical processes only take place in the light penetrated upper layer of a river, while microbial consumption can take place in the entire water column. Depth-integrated estimates for the Amazon River indicate that microbial consumption is the dominant process affecting DOC degradation, accounting for a loss of ca. 0.75 % of the DOC per day, while it is only 0.01 % for photochemical oxidation (Amon and Benner, 1996). Studies have not found a significant change in $\delta^{13}C$ associated with microbial consumption of DOC, with the exception of the Congo and Parana rivers, which experienced a decrease in $\delta^{13}C$ by 1.2 and 2.5 ‰ (Lalonde et al., 2014). According to Lalonde et al. (2014), the different behavior for these rivers might be due to the importance of the C_4 carbon fixation pathway in their catchments.

In the discussion about processes affecting the stable carbon isotope signature of DOC, it is important to distinguish between isotope fractionation and selective decomposition. In processes subjected to isotope fractionation, there is a preferential use of the light or heavy isotopes of a homogeneous substrate because it is energetically more favorable. When the original substrate is not homogeneous, the isotope signature of the different components might be different. If one of those components decomposes at a faster rate than others (i.e. selective decomposition takes place), the isotope signature of the remaining substrate will shift towards the isotope signature of the less degradable component. During the degradation of DOC in aquatic systems, selective decomposition might be the main reason for changes in isotope signatures; Opsahl and Zepp (2001) have demonstrated that the isotope shift during photochemical oxidation is caused by the preferential decomposition of lignin components, which are isotopically lighter than the remaining ^{13}C-enriched carbohydrates.

We measured DOC concentration and the corresponding $\delta^{13}C_{DOC}$ signatures at high temporal resolution at two stations ca. 385 km apart on the lower Tana River, Kenya during three different campaigns. During the first campaign, we observed a significant downstream decrease in DOC concentration (from 3.30 to 2.36 mg L^{-1}). At the same

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time, we noticed a decrease in $\delta^{13}C_{DOC}$ (from −22.6 to −24.6 ‰). These findings suggested that significant DOC processing took place in the lower Tana River. However, quantifying decomposition rates as well as understanding decomposition mechanisms requires more detailed information than can be obtained from river time series alone. Therefore, we performed dark incubation experiments during the two last campaigns in order to assess the stability of DOC over the travel time of the water between both stations (ca. 5 days). We focused on the microbial decomposition of DOC, as light penetration was limited due to the high sediment load of the river, typically $> 100\,mg\,L^{-1}$ in the lower Tana (Bouillon et al., 2009; Tamooh et al., 2012, 2014). We also tested whether decomposition dynamics was significantly affected by the presence of POC and suspended sediment. The presence of POC could affect microbial degradation kinetics and DOC mineralization as it may function as a source of DOC.

2 Material and methods

The Tana River catchment ($95\,500\,km^2$) is characterized by a strong variation in climate: high rainfall (up to $3000\,mm\,yr^{-1}$) and relatively low temperatures (around 10 °C) occur in the highlands of the source area of the Tana, while the area around Garissa is very warm (around 35 °C) and receives an annual amount of ca. $350\,mm\,yr^{-1}$, with high interannual variability. The rainfall follows a bimodal distribution resulting in high discharge from April to June and from November to January.

The variability in climate results in strong variations in vegetation composition (Fig. 1). The overall coverage of the catchment with C_4 vegetation is 59 %, based on the revised isoscape map (using the Global Land Cover 2000 map and estimates of crop %) of Still and Powell (2010) which was converted to a ratio of C_4 vegetation cover based on a 2-source mixing scenario with as end members C_3 vegetation and C_4 vegetation with a $\delta^{13}C$ of respectively −27 and −12 ‰. Between the sampling sites, the river is fringed with tropical forest (whereby the total floodplain is seldom wider that 5 km), while savannah and open shrubs dominate outside of the floodplain.

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Water samples were taken from the lower Tana River at Garissa and near Garsen (Fig. 1). The distance along the river between the sampling points is 385 km, and only ephemeral tributaries, which hold water during only a few days per year, are present along this stretch of the river. Sampling took place during the wet seasons in May–June, 2013 and in April–May, 2014. In 2013, maximum discharge in Garissa reached 750 $m^3 s^{-1}$ which resulted in extensive flooding between the two sampling locations (but not upstream of Garissa), while only two small discharge peaks (up to 280 $m^3 s^{-1}$) occurred in 2014.

Grab water samples were taken from the middle of two bridges crossing the river. One 40 mL subsample was used to determine the initial DOC concentration. This water was vacuum filtered on a pre-combusted GF/F filter (pore size: 0.7 µm) and subsequently filtered with a 0.2 µm Sartorius Minisart syringe filter. The filtration was started as soon as possible after sampling, but due to the high sediment load in the water, it could take up to 2 h before the filtration was finished. Finally, 50 µL of H_3PO_4 was added for preservation. These samples were stored in the dark until analysis, which was within 4 months of sampling.

The remainder of the grab water sample was used to monitor DOC degradation. In 2013, the degradation rate of DOC was measured under two different treatments: with and without removal of particulate organic carbon (POC). In the first treatment, 500 mL of unfiltered water was stored in a glass bottle wrapped in Al foil. In the second, 500 mL of river water was first filtered to 0.2 µm as described above for DOC sampling. After filtration, 5 mL of unfiltered river water was added to serve as inoculum. Similar to the unfiltered set-up, the water was then kept in foil-covered glassware. To avoid large changes in temperature, both bottles were submerged either directly in the river water, or in a coolbox with water as an isolator from outside temperature changes. Water temperature was regularly measured and ranged between 25 and 30 °C. At days 2, 4, 6, 8 and 10, a subsample of ca. 40 mL was extracted from the incubation bottle, filtered with a syringe filter (Sartorius Minisart, pore size: 0.2 µm) and preserved with

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50 µL of H_3PO_4 in glass vials with Teflon-coated screw caps. We carried out 4 series of incubation experiments (both filtered and unfiltered) at each location.

In 2014, 5 incubation series were carried out at each location, but only with filtered water (second treatment). The methodology was identical to the one used in 2013, except that subsamples were taken at days 1, 2, 3, 5 and 8 in order to provide a higher time resolution during the early stages of the incubations.

DOC concentration and isotopic signature were measured with a wet oxidation TOC analyzer (IO Analytical Aurora 1030W) coupled with an isotope ratio mass spectrometer (ThermoFinnigan DeltaV Advantage). Calibrations were based on a 2-point calibration (IAEA-C6: δ^{13}C −10.4 ‰ and an internal standard, sucrose: δ^{13}C −26.99 ‰). Based on replicates of the standards, the error in the concentration measurements was < 3 % and the standard deviation for the δ^{13}C measurements was < 0.2 ‰.

Decay rates, i.e. absolute rates of DOC loss per unit of time, over the whole incubation period were calculated based on the concentration difference between the day of in situ sampling (day 0) and day 8, which is the last common day between the measurements in 2013 and 2014. Initial decay rates were calculated over the first 2 days.

We calculated the concentration (C_{min}) and δ^{13}C signature ($\delta^{13}C_{min}$) of the DOC fraction lost to mineralization during the incubation period based on a 2-source mixing scenario:

$$C_{min} = C_{init} - C_{fin} \quad (1)$$

$$\delta^{13}C_{min} = \frac{C_{init} \cdot \delta^{13}C_{init} - C_{fin} \cdot \delta^{13}C_{fin}}{C_{init} - C_{fin}} \quad (2)$$

The initial concentration (C_{init}) and δ^{13}C signature ($\delta^{13}C_{init}$) were those measured on day 0, while the final concentration (C_{fin}) and δ^{13}C signature ($\delta^{13}C_{fin}$) were those measured on day 8. The seven series for which the relative error on the calculated C_{min} was higher than 50 % (due to very slow mineralization rates and hence, minor differences between C_{init} and C_{final}) were excluded from this part of the discussion

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of the results. For the series that were retained, the standard error on the isotopic signature of the mineralized DOC was estimated to be equal or less than 0.4 ‰, based on standard error propagation methods.

3 Results and discussion

3.1 Comparison of incubation experiments with and without POC

In the incubation series with relatively limited decomposition of DOC, the presence of POC did not result in significant changes in concentration between both treatments (Fig. 2a, Table 1). In all other cases was a significant difference between the filtered and unfiltered incubation series, whereby the final concentration of DOC was systematically higher in the samples without POC by ca. 10 %. A similar pattern was observed for $\delta^{13}C_{DOC}$ (Fig. 2b, Table 1), whereby the samples with POC were slightly more depleted in ^{13}C than the ones without POC, with on average ca. 0.3 ‰ difference. These two findings indicate that there was no substantial net addition of DOC originating from the POC pool within the time frame of our sampling. Mineralization rates were slightly enhanced in experiments with POC, likely due to the higher biomass of the heterotrophic microbial community in the presence of suspended matter. As this enhancement was relatively minor and because of the covariations between changes in DOC and $\delta^{13}C_{DOC}$ during both treatments, the unfiltered incubation series is treated as equivalent to the filtered ones for the remainder of the discussion.

3.2 Change in DOC concentration during microbial degradation

The general pattern in the concentration of DOC was a reduction within the first 24 to 48 h (Fig. 3a, Supplement Table S1). After this initial period, during which up to 60 % of the DOC was lost, the concentration remained relatively stable. Initial concentrations over the whole dataset ranged between 1.35 and 5.43 mg L^{-1}, with an average of

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2.98 mg L^{-1}. By day 8 of the incubation, this range was reduced to 1.28–4.20 mg L^{-1}, and an average concentration of 1.96 mg L^{-1}. Out of all series, only 6 samples from the upstream station (Garissa) in 2013 (three filtered ones and the corresponding unfiltered ones) showed minor degradation of DOC (a change of < 10 % of the initial concentration). This limited decrease in concentration can be related to the low initial concentration which was for all those samples below 2 mg L^{-1} and which might consist completely of the recalcitrant DOC, which is also still present at the end of the series where mineralization took place (Fig. 4).

Paired *t* tests over all the filtered series, indicated that the concentration at day 2 was significantly different ($p < 0.05$) from the initial concentration, with a mean difference of 0.91 mg L^{-1}. The concentration difference between day 2 and day 8 over all the filtered series was also significant (paired *t* test, $p < 0.05$), with an average decrease in concentration of 0.09 mg L^{-1}. The rate of decay of DOC ranged between 0.002 and 0.320 mg L^{-1} day over the whole incubation (day 0 to day 8), with on average 0.127 mg L^{-1} day, while the decay rate during the first two incubation days reached up to 1.50 mg L^{-1} day, with an average of 0.456 mg L^{-1} day. Similar to our experiments, Moody et al. (2013) observed an average decline of 47 % in DOC after 10 days dark incubation of water from a peat-covered catchment. They also observed that the majority of the degradation took place during the first two days, while degradation continued thereafter at a much lower rate (Moody et al., 2013).

3.3 Changes in stable isotope signatures of DOC during microbial degradation

Overall, $\delta^{13}C_{DOC}$ signatures decreased consistently during microbial degradation (Fig. 3b, Table 1). However, there was considerable variation in magnitude of change between the different series. Some incubation series, mainly in 2013 at Garissa and in 2014 at Garsen, experienced hardly any change, while other series, especially in 2013 at Garsen, experienced a decrease up to 3.0 ‰. Initial $\delta^{13}C$ values ranged between −25.0 and −21.7 ‰ with an average value of −23.3 ‰ for the whole dataset,

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which is in line with previous measurements for the lower Tana River (Bouillon et al., 2009; Tamooh et al., 2012). Towards the end of the incubation (day 8), $\delta^{13}C$ values had decreased significantly, ranging between −25.3 and −23.3 ‰ (avg. −24.2 ‰).

The $\delta^{13}C_{DOC}$ values at day 2 were significantly different from initial $\delta^{13}C$ values (paired t test, $p < 0.05$) over all the filtered incubation series, with a decrease of 0.8 ‰. In contrast to the concentration, no significant change in $\delta^{13}C$ was detected between day 2 and day 8.

3.4 Characterization of mineralized and remaining C

The change in $\delta^{13}C$ was positively related to the proportion (%) of DOC still present after incubation (Fig. 5). A stronger reduction in DOC led to a more ^{13}C depleted residue, implying that the mineralized fraction of the DOC was enriched in ^{13}C vs. the bulk initial DOC pool. The regression equation for a linear fit over the averaged points per incubation series over the whole dataset was $\Delta\delta = -3.5 + 0.038 \times$ (%DOC remaining) (R^2 0.605). However, two series with a strong reduction in DOC, but relatively little change in isotopic signature can be seen as outliers (Fig. 5). After removal of the latter data points, the regression equation became $\Delta\delta = -4.5 + 0.048 \times$ (%DOC remaining), with a higher R^2 value of 0.817.

The isotopic characteristics of the mineralized DOC were clearly different from the initial DOC as well as from the remaining DOC (Fig. 6). The mineralized fraction of the DOC was more enriched in ^{13}C than the initial or remaining DOC, with average values of −21.2, −23.1 and −24.3 ‰ for the mineralized, initial and remaining carbon pools for all the observations. The concentration of the mineralized DOC was on average lower than that of the DOC which was more resistant to microbial degradation.

3.5 Removal mechanism and origin of DOC

Analogous to an isotopic shift due to selective photochemical oxidation of certain compounds, selective decomposition during microbial oxidation could be the key mecha-

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nism to explain the shift in $\delta^{13}C$ that we observed during DOC decomposition, whereby the isotopically heavier carbohydrates were preferentially decomposed. However, if such a mechanism were to be generally valid, a similar shift would be expected in other types of aquatic systems (irrespective of the C_3/C_4 dominance in the catchment), yet previous studies have typically shown little or no change in $\delta^{13}C$ during microbial degradation of DOC (Lu et al., 2013; Lalonde et al., 2014). However, a similar decrease in $\delta^{13}C_{DOC}$ due to microbial degradation has been shown for both the Congo and Parana rivers (Lalonde et al., 2014). One characteristic which both river systems have in common with the Tana River, is the presence of C_4 vegetation within their catchment. A higher decomposition rate for the C_4-derived DOC, as reported for soil organic carbon (Wynn and Bird, 2007), would indeed be consistent with the observed isotopic shift.

It is, however, not clear whether the different decomposition rates are inherently related to the different photosynthetic pathways used by C_3 and C_4 vegetation, or to the fact that in tropical regions such as the Tana River catchment, C_3 vegetation consists of shrubs and trees, which are more resistant to degradation, while C_4 vegetation consists of grass species, which are more easily degraded. The latter option would appear more likely, as a study directly comparing the decomposition of C_3 and C_4 grasses has shown a greater decomposition rate for C_3 grasses (Ross et al., 2002). More dedicated studies using a similar experimental approach as used here, but with mixtures of DOC originating from both C_3 and C_4 grasses would be required to verify the latter hypothesis.

Microbial degradation was high during the initial phase (first 48 h) in both sampling sites. Considering the water travel time (~ 5 days) between these sites, the high reactivity even at the downstream site implies that there is not merely a downstream transport of DOC which is progressively mineralized, but that a replenishment of the labile DOC pool must occur. Possible sources include (1) the POC suspended in the water which may release C into the DOC pool, (2) advection by the tributaries, (3) inputs from the floodplain during inundation, (4) DOC release from river bed sediments, and (5)

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groundwater inputs. Only the first source was explicitly tested for in the experiments in 2013, and it appeared that after 48 h, there was no net effect of the presence of POC. This does not completely rule out POC as a source of DOC, as ambient conditions in a river setting are still different than in our experimental setup. The advection of DOC by tributaries is unlikely, as their water flow is very erratic, likely even absent in 2014, while the presence of labile DOC was fairly constant. Input from the flooded floodplain will have been important in Garsen during the flooding in 2013 as DOC concentrations were significantly higher. However, it can not explain the presence of labile DOC during the wet season of 2014 when no considerable flooding took place. The last two options, river bed sediments and groundwater flow, are speculative, as no information on them is yet available. The analysis of optical characteristics of the dissolved organic matter pool (Jaffé et al., 2008; Lambert et al., 2015) could be a valuable complementary approach in order to understand the origin and processing of DOC in rivers.

4 Conclusions

Our experiments demonstrated that in the lower Tana River, a fraction of the DOC is highly susceptible to decomposition, similar to observations in other large river systems. While it was previously considered that bacterial mineralization of labile dissolved OM generally has little influence on $\delta^{13}C_{DOC}$ signatures, our results show that such a change should be taken into account, at least when considering environments with mixed C_3/C_4 inputs. Differences in the rate of decomposition of the DOC originating from C_3 and C_4 vegetation will lead to an underestimation of the C_4-derived carbon input in catchments if the residence time between the input of carbon and the sampling location allows significant microbial degradation.

In addition, the high reactivity of the DOC at both sites has raised the question about the origin of the labile DOC pool. The applied method was only able to exclude POC as a likely source of labile DOC in the experimental setup. Further research, includ-

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ing optical characterization, would be required to shed more light on the dynamical replacement of the labile DOC pool in river systems.

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Table 1. Concentration and isotopic signatures at the start (day 0) and the end (day 8) of the incubation series (the full dataset including all intermediate measurements, can be found in the Supplement).

Site[a]	yr	Date[b]	Filtered[c]	Initial C ($mg\,L^{-1}$)	Final C ($mg\,L^{-1}$)	% Remaining[d]	Initial $\delta^{13}C$ (‰)	Final $\delta^{13}C$ (‰)	$\Delta\delta$ (‰)[e]
GSA	2013	04/05	U	2.60	1.48	57	−22.8	−25.0	−2.2
GSA	2013	15/05	U	1.54	1.48	96	−24.3	−24.5	−0.2
GSA	2013	26/05	U	1.35			−24.4		
GSA	2013	05/06	U	1.41	1.39	99	−23.9	−23.3	0.6
GSA	2013	04/05	F	2.60	2.07	80	−22.8	−23.3	−0.5
GSA	2013	15/05	F	1.54	1.43	93	−24.3	−24.0	0.3
GSA	2013	26/05	F	1.35	1.28	95	−24.4	−24.2	0.1
GSA	2013	05/06	F	1.41	1.34	95	−23.9	−23.6	0.3
GSN	2013	03/05	U	5.43	3.68	68	−25.0	−25.3	−0.3
GSN	2013	14/05	U	4.09	2.43	59	−23.5	−24.7	−1.3
GSN	2013	26/05	U	4.00	1.80	45	−21.9	−24.8	−2.9
GSN	2013	06/06	U	3.26	1.58	49	−21.6	−24.4	−2.7
GSN	2013	03/05	F	5.43	4.20	77	−25.0	−24.7	0.3
GSN	2013	14/05	F	4.09	2.69	66	−23.5	−24.4	−0.9
GSN	2013	26/05	F	4.00	1.93	48	−21.9	−24.3	−2.4
GSN	2013	06/06	F	3.26	1.66	51	−21.6	−23.6	−2.0
GSA	2014	02/04	F	4.99			−23.5		
GSA	2014	11/04	F	2.99	2.23	74	−23.0	−24.7	−1.7
GSA	2014	20/04	F	4.57	2.01	44	−22.4	−24.3	−1.9
GSA	2014	29/04	F	2.25	1.46	65	−22.1	−23.7	−1.5
GSA	2014	08/05	F	1.59	1.34	85	−23.1	−23.5	−0.4
GSN	2014	06/04	F	3.91	1.81	46	−23.9	−24.1	−0.3
GSN	2014	15/04	F	2.11	1.87	89	−24.3	−24.8	−0.5
GSN	2014	24/04	F	2.98	2.44	82	−24.0	−24.0	0.0
GSN	2014	03/05	F	2.40	1.91	80	−23.4	−23.4	0.0
GSN	2014	12/05	F	2.34	1.56	67	−22.3	−24.0	−1.7

[a] GSA, Garissa and GSN, Garsen. [b] Date of day 0 of the incubation series. [c] U, unfiltered for incubation; F, filtered with addition of inoculum.
[d] Proportion of initial DOC concentration remaining at the end of the incubation. [e] Change in $\delta^{13}C$ between start and end of the incubation.

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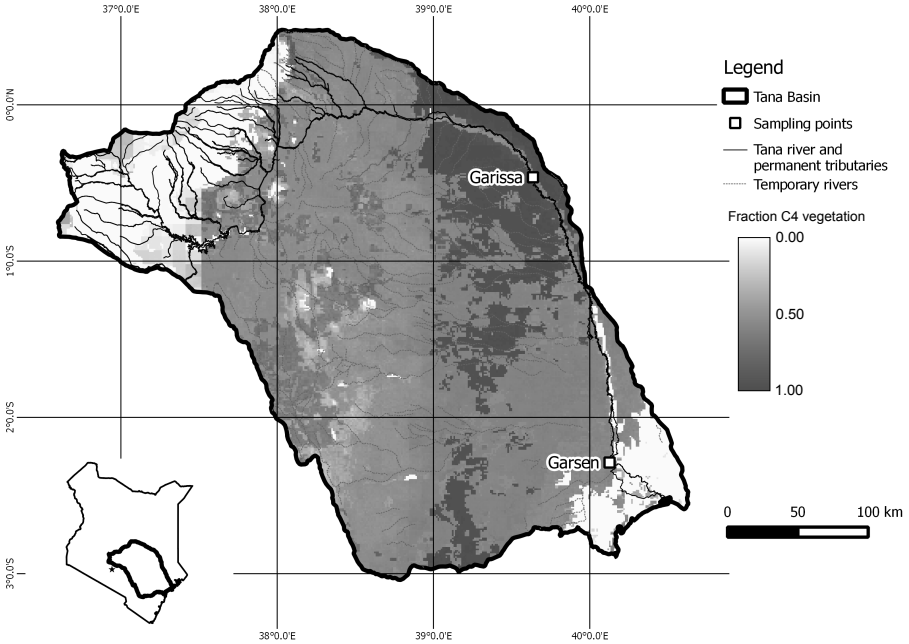

Figure 1. The Tana River with the indication of the two sampling locations in the lower catchment. The shading represents the fraction of C_4 vegetation, based on the isoscapes of Still and Powell (2010). The inset indicates the Tana River basin within Kenya.

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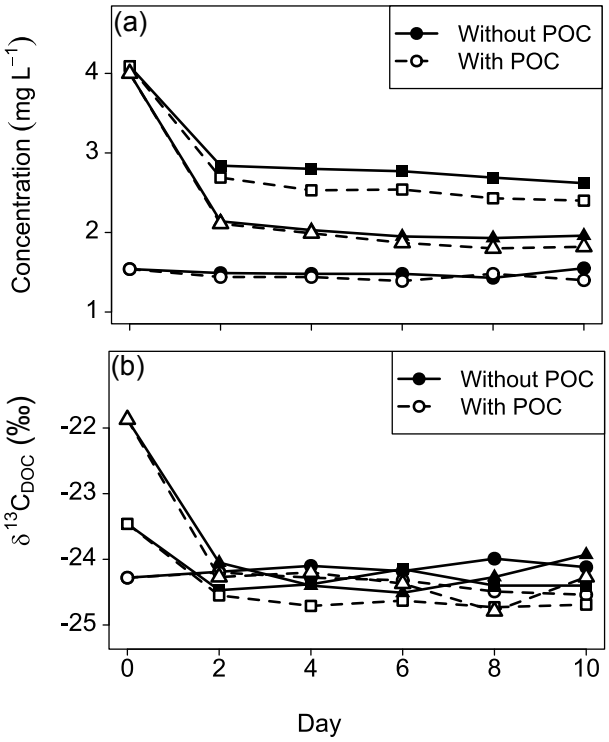

Figure 2. Comparison of evolution of **(a)** DOC concentration and **(b)** stable carbon isotope ratio of DOC ($\delta^{13}C_{DOC}$) over time, for incubations with POC (unfiltered) and without POC (filtered). The three incubation series (Garissa 15 May 2013 (circles), Garsen 14 May 2013 (squares) and Garsen 26 May 2013 (triangles)) are representative of the eight data series, as they give an example of the low, medium and high response of the DOC. No consistent difference was found between the different sampling sites. The full dataset for all incubations can be found in the Supplement.

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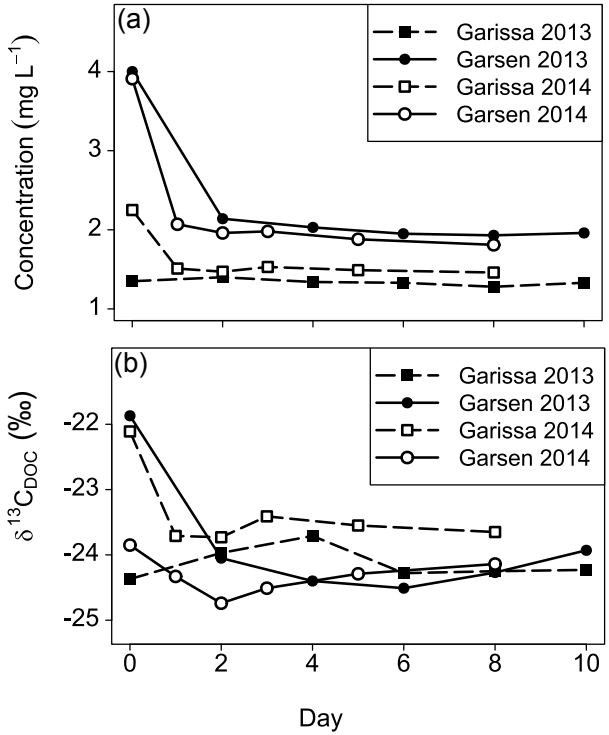

Figure 3. Evolution of **(a)** DOC concentration and **(b)** carbon stable isotope signature of DOC ($\delta^{13}C_{DOC}$) during the 8 to 10 day incubations. Both panels show data from one incubation series per sampling site and per year (Garissa 26 May 2013, Garsen 26 May 2013, Garissa 29 April 2014, Garsen 6 April 2014), providing representative examples of the low, medium and high response of the DOC. No consistent difference was found between the different sampling sites or sampling years. The full dataset and a similar figure with all the incubation series without POC can be found in the Supplement.

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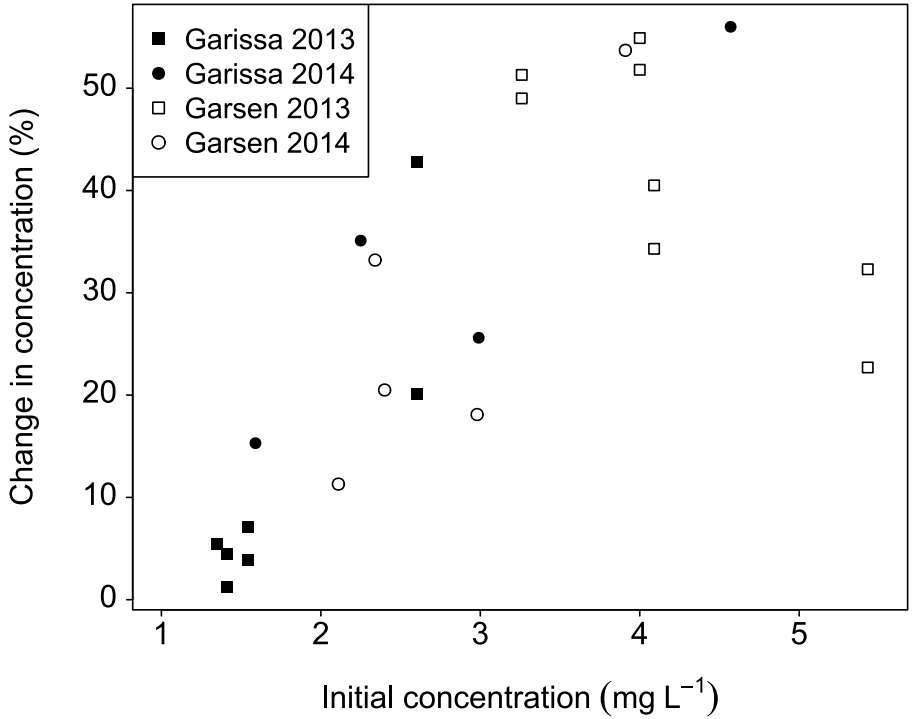

Figure 4. Change in initial concentration (day 0) and final concentration (day 8) vs. the initial concentration of the DOC. All available data are represented.

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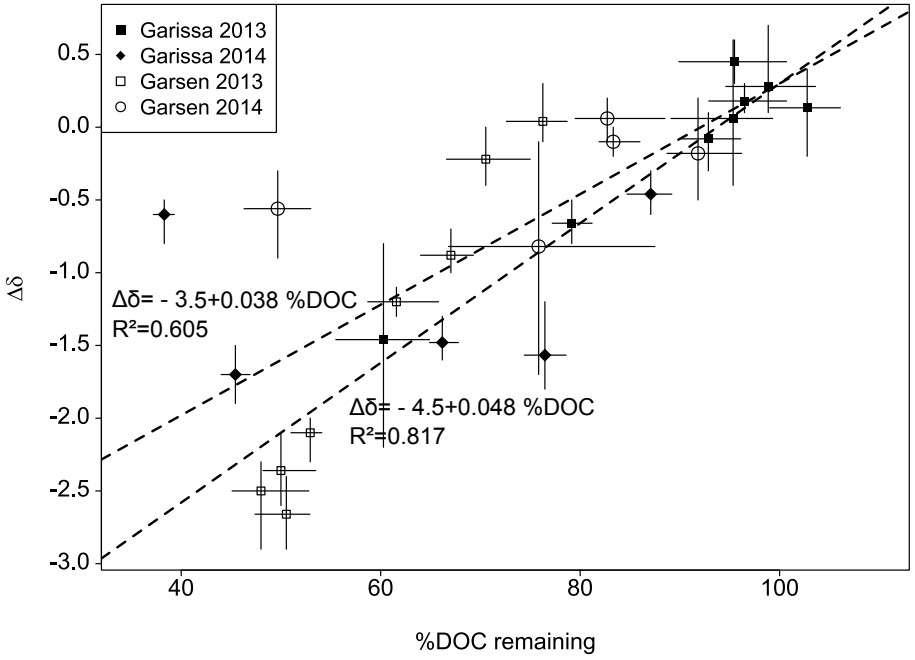

Figure 5. Change in isotopic signature between initial concentration (day 0) and later in the incubation series ($\Delta\delta$) vs. the proportion (%) of DOC remaining after incubation. The points are average values over the five measurements per series and the lines indicate minimum and maximum values within that series. One regression line is with two outliers included, the second is without the outliers. Both filtered and unfiltered series are represented.

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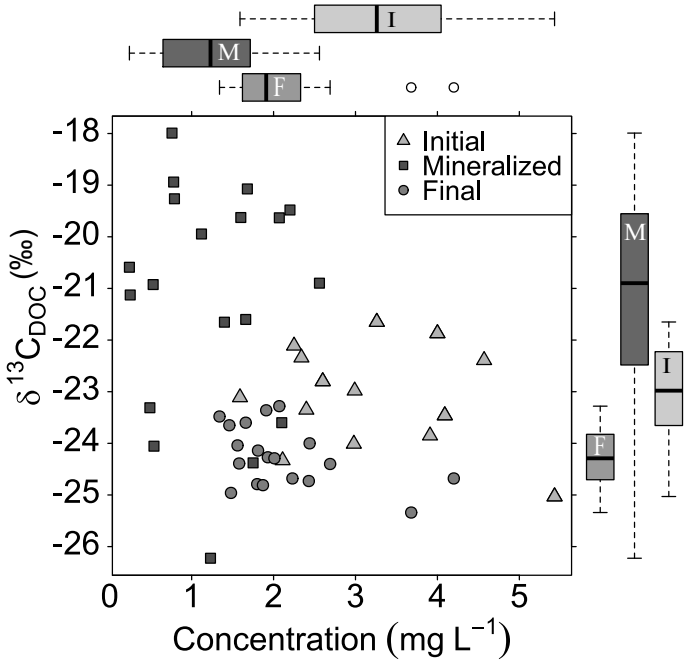

Figure 6. Calculated values of the concentration and isotopic signature of the mineralized DOC pool, for incubation series that experienced a sufficiently high loss of DOC. The horizontal box plots indicate the distribution of the concentration while the vertical ones indicate the distribution of the stable isotope signature for the initial (I), mineralized (M) and final (F) DOC. Incubation series with and without POC are represented, as long as the relative error on the concentration was less than 50 %.

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