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The age of terrestrial carbon export and rainfall intensity in a temperate river headwater system

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Abstract Riverine dissolved organic carbon (DOC) supports the production of estuaries and coastal ecosystems, constituting one of the most actively recycled pools of the global carbon cycle. A substantial proportion of DOC entering oceans is highly aged, but its origins remain unclear. Significant fluxes of old DOC have never been observed in temperate headwaters where terrestrial imports take place. Here, we studied the radiocarbon age of DOC in three streams draining forested headwater catchments of the river Mulde (Ore Mountains, Germany). In a 4 week summer precipitation event DOC aged at between 160 and 270 years was delivered into the watershed. In one stream, the DOC was modern but depleted in radiocarbon compared to other hydrological conditions. The yield was substantial and corresponded to 20–52 % of the annual DOC yields in wet and dry years, respectively. The analysis of long-term data suggested that the DOC export in extreme precipitation events added to the annual yield and was not compensated for by lower exports in remaining periods. We conclude that climate change, along with additional processes associated with human activities, channels old soil carbon into more rapidly cycled carbon pools of the hydrosphere.

Keywords DOC · DIC · Radiocarbon · 14C · Catchment · Reservoir

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Introduction

While river carbon received attention in global carbon flux estimates (Battin et al. 2008), the age of river carbon is a matter of particular interest. The earlier view that riverine dissolved organic carbon (DOC) is derived from contemporary terrestrial biomass and therefore must be distinguishable from ancient DOC in ocean interiors (Williams and Druffel 1987; Hedges et al. 1997) has been questioned (Ludwig 2001; Raymond and Bauer 2001a). More recent studies have revealed that a significant proportion of riverine DOC is in fact of old origin, originating from terrestrial production of hundreds to more than a thousand years ago (Raymond and Bauer 2001a, b; Raymond et al. 2004; Wang et al. 2006). This was in line with the observation that old terrestrial carbon contributes substantially to the energetic basis of riverine food webs (Caraco et al. 2010). There are some identified processes that can account for this import of old DOC, almost all with anthropogenic causes. They include the

melting of glaciers (Hood et al. 2009), thawing of permafrost soils (Guo et al. 2007), conversion of native landscapes to agriculture and urbanization (Sickman et al. 2010), burning of fossil fuels (Stubbins et al. 2012) and municipal wastewater release (Griffith et al. 2009). One notable report of old ages of DOC stems from an intermittently-flowing, highly erosive mountainous river (Masiello and Druffel 2001). However, process studies in river headwaters, the common sites of terrestrial imports, have identified "modern" carbon almost exclusively as the source of riverine DOC (Schiff et al. 1997; Palmer et al. 2001; Neff et al. 2006; Longworth et al. 2007; Evans et al. 2007; Waldron et al. 2008; Billett et al. 2011; Huey 2011). This means that the carbon was enriched with "bomb"-^{14}C derived from nuclear testing after the year 1950 ($\Delta^{14}C > 0$ ‰).

Current understanding suggests that at base flow conditions DOC up to 3,700 years old enters the streams by groundwater inflow (Schiff et al. 1997; Evans et al. 2007). However, the flux rates are negligible as low discharges are combined typically with low groundwater DOC concentrations (Schiff et al. 1997; Pabich et al. 2001; Evans et al. 2007; O'Donnell et al. 2010). With rising water tables and increasing discharge, progressively younger DOC is mobilized by seepage from the topsoil litter layer near the stream slopes (Schiff et al. 1997; Laudon et al. 2011). However, there is no known scenario suggesting that old DOC can be mobilized in headwater catchments to constitute a significant fraction of total DOC.

Study area and methods

We studied radiocarbon concentrations in DOC and dissolved inorganic carbon (DIC) from three streams at four contrasting hydrologic conditions as well as from the downstream reservoir at Muldenberg. The conditions refer to moderate spring and summer discharges, dry summer base flow and a rain event (Table 1). The sampling day during the event fell within the 6 % of days with the most intense precipitation, as recorded between 1960 and 2010. The streams, Rote Mulde, Weiße Mulde and Saubach, each drain small catchments of 4–5 km^2 area, situated at 700–950 m a.s.l. at the ridge of the Ore Mountains (Erzgebirge), Germany (Fig. 1). They are forested with Norway spruce and spots of hornbeam. The quartz-porphyry bedrock is predominantly covered by shallow or moderate deep peaty topsoil. The influence of agriculture or wastewater was negligible. The stream sampling stations were located about 200 m upstream from the inflows into the reservoir. The reservoir integrated the stream supplies and provided information on carbon isotopes from streams in the past. We took the samples from 2 m depth (mixed surface layer). In addition, we sampled once a natural seepage spring without mounting in a shallow depression in a forest stand (Weiße Mulde catchment) and from a stone-built outlet collecting shallow strata water from the above slope (Saubach catchment, Fig. 1).

Within the framework of a 'monitoring program' (1993–2010) conducted by the State Reservoir Administration (SRA), precipitation was recorded close to the reservoir dam using a rain gauge. Discharges were measured at the outlet of the reservoir. Samples for DOC, sulphate and pH were collected on a monthly basis. In an 'isotope program' (2008–2010) we sampled carbon isotopes, DOC and DIC at four specific hydrologic conditions (i–iv, Table 1). During this period, discharges were additionally recorded at the three stream sampling stations. The water level was monitored every 15 min in well defined masoned channels before thin-plate notched weirs.

Samples for DOC were filtered in the monitoring program using low-blank 0.45 µm membranes and were measured by the analytical staff at the SRA laboratory using infrared gas absorption (TOC-VCPN, Shimadzu). In the 'isotope program' samples were processed by the staff at the UFZ chemical laboratory. Pre-combusted (500 °C, 4 h) GF/F filters ($\sim$0.7 µm pore size) and a Hightoc analyzer (Scalar) were used. Analytical differences between the two filtration methods were negligible. Sulphate concentrations were analyzed at the SRA laboratory by ion chromatography (ICS-1100, Dionex).

For determination of $\Delta^{14}C$ and $\partial^{13}C$, we collected samples of 1–5 l volume from the streams and springs as well as from the reservoir from 2 m depth using a water sampler (Limnos, Turku, Finland). In addition, two samples of fresh leaves were collected at several locations in the Weiße Mulde catchment to obtain valuations for the ^{14}C-concentration of recent terrestrial source carbon. All glassware including sampling bottles were rinsed twice with 0.1 N HCl and Nanopure water and were baked at 500 °C for four hours. Stoppers were covered with baked aluminum foil.

Table 1 Radiocarbon concentration in DOC and DIC at specific hydrological conditions (i–iv) as well as in two springs

Conditions, date	Sample	DOC[a] (mg C l^{-1})	DIC[a] (mg C l^{-1})	Δ^{14}C-DOC[b] (‰)	^{14}C-DOC age[c] (yr BP)	∂^{13}C-DOC[a] (‰)	Δ^{14}C-DIC (‰)
Streams and reservoir							
i, 25 Aug 2008	Rote Mulde	10.9	1.1	14 ± 5	Modern	−26.9 ± 0.0	17 ± 7
	Weiße Mulde	7.5	0.8	42 ± 6	Modern	−26.8 + 0.0	19 ± 4
	Saubach	5.3	0.7	24 ± 5	Modern	−26.9 + 0.1	n.d.
	Reservoir	6.9	1.2	36 ± 4	Modern	−27.6 ± 0.1	11 ± 6
ii, 28 Apr 2009	Rote Mulde	5.7	0.3	22 ± 4	Modern	−26.3 ± 0.1	19 ± 3
	Weiße Mulde	5.1	0.3	37 ± 3	Modern	−26.6 ± 0.0	36 ± 3
	Saubach	2.3	0.2	22 ± 3	Modern	−25.5 ± 0.3	11 ± 2
	Reservoir	7.2	0.4	39 ± 3	Modern	−26.9 ± 0.2	31 ± 3
iii, 23 Sep 2009	Rote Mulde	9.2	1.7	−8 ± 4	6	−27.0 ± 0.3	7 ± 3
	Weiße Mulde	5.4	0.9	13 ± 3	Modern	−27.0 ± 0.1	8 ± 3
	Saubach	3.6	1.0	−21 ± 3	110	−27.2 ± 0.0	-27 ± 5
	Reservoir	5.5	0.6	25 ± 3	Modern	−27.7 ± 0.0	17 ± 3
iv, 17 Aug 2010	Rote Mulde	24.1	0.2	−33 ± 3	210	−26.8 ± 0.3	33 ± 3
	Weiße Mulde	23.0	0.3	−40 ± 3	268	−26.3 ± 0.4	28 ± 4
	Saubach	15.3	0.2	11 ± 3	Modern	−26.4 ± 0.3	16 ± 3
	Reservoir	6.8	0.4	−27 ± 3	162	−26.9 ± 0.1	49 ± 3
Springs							
27 Apr 2009	Spring SB[d]	0.8	6.6	−24 ± 3	134	−31.4 ± 1.2	33 ± 3
11 Aug 2009	Spring WM[e]	0.8	1.9	−15 ± 3	60	−25.7 ± 0.3	15 ± 3

The Δ^{14}C-POC of fresh leaves, a reference of recent terrestrial carbon, equalled 45 ± 3 ‰ and 51 ± 3 ‰ in 2008 and 2009, respectively

[a] Mean of duplicate measurements. The deviations from mean (0.5 ranges) were ≤0.1 mg C l^{-1} for DOC, except 17 Aug. 2010 ≤ 0.4 mg C l^{-1}, as well as <0.1 mg C l^{-1} for DIC

[b] The values of Δ^{14}C (single analysis ± analytical error) and of ∂^{13}C (mean of triplicates ± SD) express the isotope concentration as per mil (‰) deviation relative to analytical standards see section ("Methods")

[c] The age, that is the time since degradation of the parent plant organic matter started, increases with decreasing Δ^{14}C. Given numbers refer to years before 1950 (conventional radiocarbon age) (Stuiver and Polach 1977)

[d] Spring in Saubach catchment (Fig. 1)

[e] Spring in Weiße Mulde catchment (Fig. 1)

Samples were filtered within 16 h using pre-combusted GF/F filters. The DOC was enriched in a first step through evaporation at 60 °C and bubbling with UHP nitrogen. The gas stream did not cause precipitations in a control barium hydroxide solution, confirming that it was free of inorganic carbon. The aim of using evaporation was to reduce the risk of contamination by oil backstreaming from the rotary pump into the sample that can occur during long freeze drying (Burr et al. 2001). Evaporation was stopped when the volume was reduced to about 30 ml, containing 7–40 mg DOC. The samples were colored dark brown, as the presence of inorganic salts was not significant (electric conductivity in original samples 58–122 µS cm^{-1}), with the exception of one spring (Saubach, 330 µS cm^{-1}). Precipitates were removed by sonification from glass walls. We tested the efficiency of evaporation using DOC derived from alder leaves or peat and estimated a recovery of 88 %. The evaporated samples were acidified with H_3PO_4 (pH < 1). At the Leibniz-Laboratory for Radiometric Dating and Isotope Research, Kiel, Germany, the samples were freeze dried and combusted at 900 °C in the presence of CuO and a silver catalyst. The CO_2 was reduced with H_2 at 600 °C to graphite (Nadeau et al. 1998) for accelerator mass spectrometry (AMS). The ^{14}C concentrations were analyzed with respect to oxalic acid II standard and corrected for process and

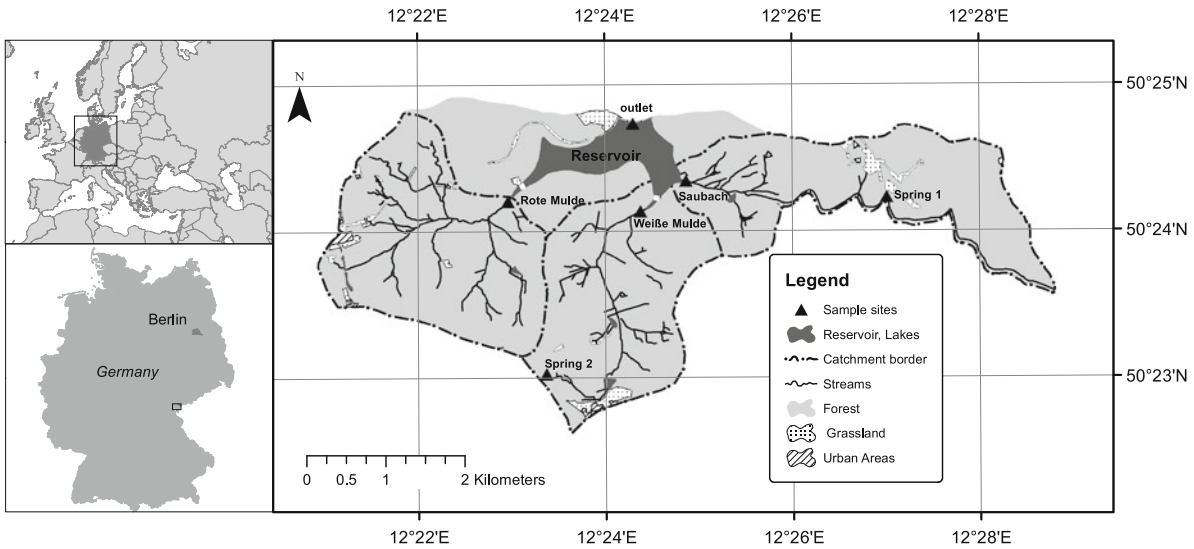

Fig. 1 Map of the reservoir Muldenberg catchment and of the locations of the sampling sites. The streams Rote Mulde and Weiße Mulde enter predams of the reservoir. The stream Saubach was connected eastward to a 4-km-long concreted open channel, crossing a steep hillslope with gentle incline. The channel was formerly used for timber transport. The subcatchment in the north around the reservoir was drained by a number of small temporary streams (not shown)

instrument blanks and for isotope fractionation using $\partial^{13}C$ measured online by AMS (Stuiver and Polach 1977). For analysis of ^{13}C concentrations, aliquots of evaporated and acidified samples were freeze dried and then sent to the Stable Isotope Facility at the University of California, Davis, USA, for conventional isotopic ratio mass spectrometry (MS). The $\partial^{13}C$ values were expressed relative to standard Vienna PeeDee Belemnite.

For determination of carbon isotopes in DIC, we collected samples with a volume of 5 l (springs) or 20 l (other locations) in glass bottles or airtight plastic carboys, respectively. The large sample volumes accounted for low DIC concentrations (Table 1) and aimed to minimize the impact of potential contaminations. Samples were acidified (pH < 2) using HCl (37 %) and bubbled for four hours with UHP nitrogen. The outstripped CO_2 was precipitated in a saturated barium hydroxide solution that was filtered under a nitrogen stream with 0.2 µm pore size membranes prior to use. The precipitates were stored in wrapped flasks in a desiccator containing a nitrogen atmosphere. Controls of filtered barium hydroxide solutions showed no signs of contamination by atmospheric CO_2. At the Kiel AMS site, the carbonate precipitates were hydrolyzed using phosphoric acid at 90 °C. For analysis of ^{14}C-DIC by AMS, the CO_2 was processed as described above. There was no analysis of ^{13}C-DIC by MS.

To calculate flux rates (DOC yields) during the 'isotope program' (2008–2010, Fig. 2) we used discharges from stream stations. For statistical analyses covering the 'monitoring program' (1995–2010, Table 2) we used total discharges from the outlet of the reservoir (see above) multiplied by constant specific stream quota. The latter were derived from the discharge of the specific stream relative to the combined discharges of all streams calculated each day in 2009 (Rote Mulde 44 ± 7 %, Weiße Mulde 39 ± 6 %, Saubach 17 ± 8 % mean ± SD of daily stream quota). We calculated yields on the basis of daily averages of discharge and linearly interpolated DOC concentrations. For a stream of comparable size in an adjacent watershed, the errors of DOC yield calculations were <20 % with similar sampling regime (Büttner and Tittel 2013). Within the rainfall event (iv, see below), there were only two DOC samples available. To achieve a conservative estimate of the yield, we assumed that concentrations dropped between samples to a concentration equal to the mean of all samples of that stream in the three sampling years (9.4 mg l^{-1}). For the analysis of runoff ratios (discharge relative to precipitation) and their relationship to DOC (Fig. 3), we selected summer precipitation

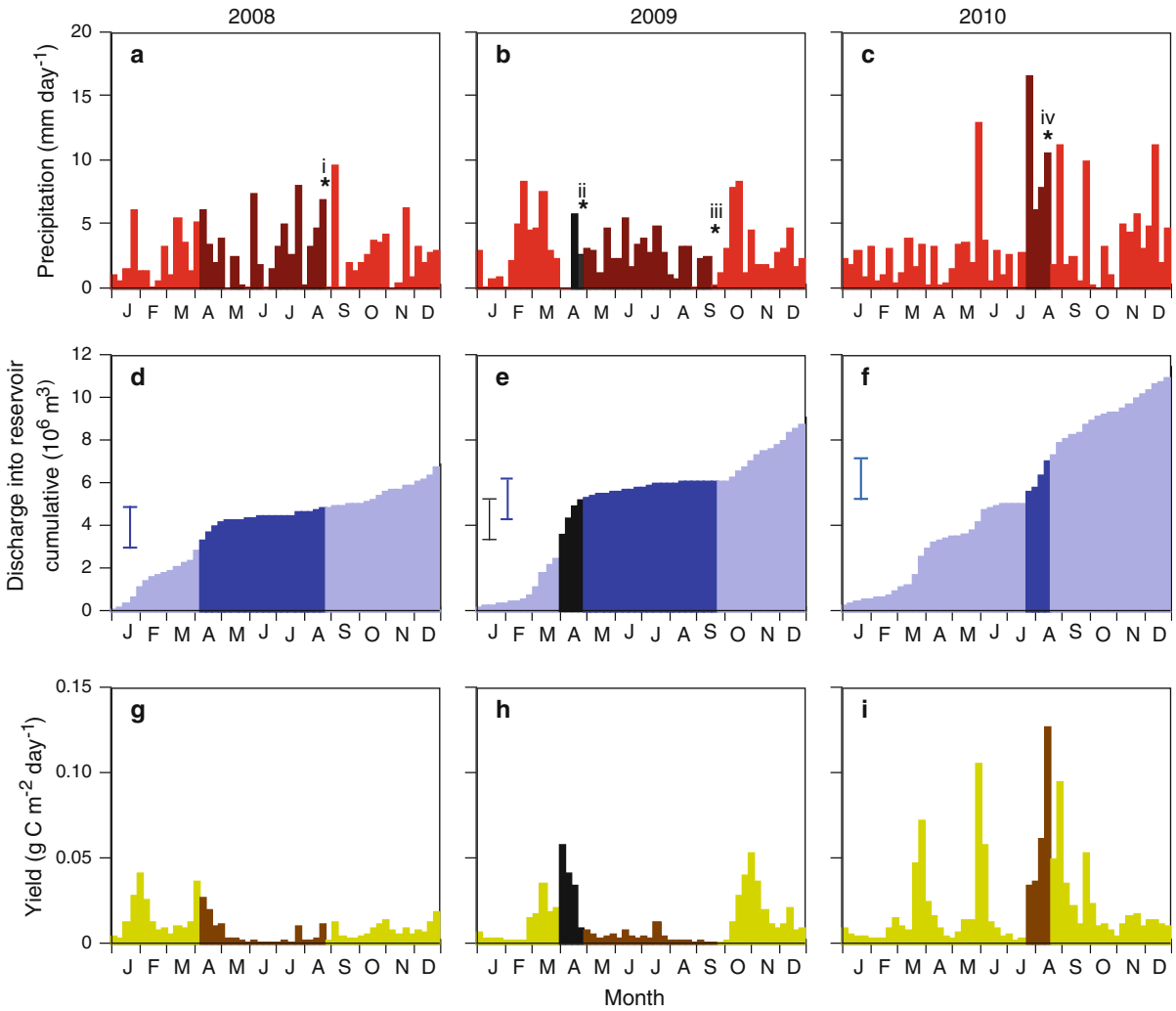

Fig. 2 Hydrology and DOC flux. **a–c**, Precipitation. **d–f**, discharge. **g–i**, DOC yield. *Columns* show weekly means, except discharge (**d–f**), where *columns* indicate the volume accumulated until the end of the week. *Asterisks* indicate sampling dates, *Roman numbers* refer to hydrologic conditions (see text). *Highlighted phases* denote the time over which stream inflows replaced the volume of the reservoir layer before it was sampled (cumulative discharge $\sim 2 \times 10^6$ m^3, vertical range symbols, see section "Methods")

events (June to September) from the monitoring program in which DOC measurements were available near the time of the discharge peak ($n = 12$ events). We considered only summer events to exclude potential effects of a reduced microbial activity on soil DOC generation. The runoff ratio (RR) was calculated as $RR = (Q–Q_{base})/P$, where Q represents the event-cumulated discharge, Q_{base} the base flow as the minimum discharge the day before the start and during the event, and P the cumulated precipitation.

We have additionally sampled the surface layer of the reservoir, which received the inflows of Rote Mulde and Weiße Mulde. Both inflows previously warmed up in shallow predams, which retain the stream inflows before they enter into the main reservoir. The smaller Saubach did not pass a predam. Its water may have stratified in part below the surface layer. To obtain information about the hydrologic conditions from which the stream inflows and our reservoir samples were derived, we calculated how long the inflows had been occurring. We assumed that the discharges replaced the water of the surface layer. The time for replacement was derived graphically by cumulating the discharges of the three streams over

Table 2 Regression parameters predicting the annual yield of DOC and the annual mean DOC concentration

Parameter 1	Parameter 2	Parameter 3	R^2	F
Prediction of DOC Yield				
Precipitation			0.48	42.49
Precipitation	Extreme frequency (−)		0.58	30.56
Precipitation	Extreme frequency (−)	Sulphate (−)	0.66	27.95
Prediction of DOC Concentration				
Sulphate (−)			0.22	13.28
Sulphate (−)	Precipitation		0.40	14.87
Sulphate (−)	Precipitation	Extreme intensity (−)	0.58	20.48

Parameters include the annual precipitation in the years 1995-2010 integrated over the three catchments (711–1412 mm year^{-1}), the annual mean sulphate concentrations in the three individual streams (10.8–23.5 mg l^{-1}, Fig. 3), and two estimates of temporal variation in precipitation (extreme frequency and extreme intensity, section "Methods"). Minus symbols indicate negative statistical relationships, e. g. DOC decreased with rising sulphate. Extreme intensity did not increase R^2 in DOC yield and extreme frequency did not increase R^2 in DOC concentration. All regressions were significant at the $P < 0.001$ level (3 streams × 16 yr, $n = 48$)

time, before the sample-taking and until the volume of the layer was achieved ($\sim 2 \times 10^6$ m^3, Fig. 2d–f highlighted areas). As discharge in the surface layer was likely overestimated regarding Saubach inflows, the actual inflows may have ranged further back than estimated. In the four sampled conditions (i–iv, Fig. 2) the reservoir was thermally stratified. However, there was mixing in the first 2 weeks of April 2009 and weak stratification thereafter. The reservoir sample in this condition (ii) may also have contained older water before snowmelt, which started at the end of March (Fig. 2e, highlighted phase).

For data management, calculations and statistics we used the program package MATLAB. The multiple regression analysis (Table 2) was performed by applying the conventional procedure of stepwise removing predictive variables using the partial F-test values (Draper and Smith 1998). Extreme intensity denoted the maximum precipitation of five consecutive days of a year (49–174 mm) (Haylock and Nicholls 2000). Extreme frequency represented the number of days within a year with precipitation ≥95 % from all daily precipitations within the observation period (8–25 days year^{-1} ≥ 14.2 mm day^{-1}) (Haylock and Nicholls 2000). The analysis was based on data of the long-term monitoring program.

Hydrologic conditions

Sampling was conducted in August 2008 (i), in late summer conditions characterized by moderate antecedent precipitation (Fig. 2a). The discharges contributing to the reservoir sample had accumulated since April (Fig. 2d, highlighted area). This indicates that the reservoir sample represented stream contributions from summer and spring, but not from the previous winter's snowmelt. Then, in April 2009 (ii, Fig. 2b), we sampled during representative spring conditions characterized by high discharge and moderate antecedent precipitation. Here, the water in the reservoir was derived from spring precipitation, from snowmelt as well as from previous winter baseflow (Fig 2e, see above). Dry conditions prevailed in September 2009 (iii, Fig. 2b) where there was zero to very low discharge in the 4 weeks prior to sampling. The precipitation total was only 36 mm. The reservoir accumulated the discharge from the streams over this dry period and the preceding time frame from late spring, including the entire summer (Fig 2e). Finally, we collected samples in August 2010 (iv, Fig. 2c) after heavy rainfalls. In 4 weeks, precipitation accumulated to 288 mm, which was the third highest value for an equal period since the beginning of records in 1960. The water in the reservoir originated from this period (Fig 2f).

Results

Modern carbon was identified in August 2008 (i) and April 2009 (ii) from both stream and reservoir samples (Table 1). The DOC must have consisted of a mixture of recently fixed carbon with a Δ^{14}C value equal to or

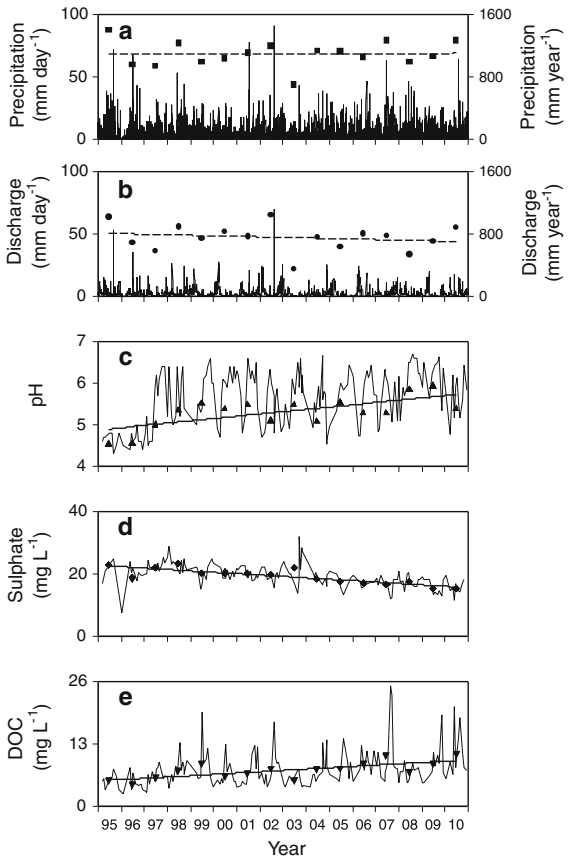

Fig. 3 Increase of DOC concentration between 1995 and 2010, shown for the example of the Rote Mulde. Symbols and regression lines refer to annual means (right y-axis in a, b). **a** Precipitation (n.s.). **b** Discharge (n.s.). **c** pH ($P = 0.017$). **d** Sulphate ($P < 0.001$). **e**, DOC ($P = 0.003$). DOC concentrations also increased in both other streams, i.e. in Weiße Mulde ($P = 0.006$) and in Saubach ($P = 0.001$) (not shown). There was no significant increase of yields in time series of individual streams ($n = 16$, not shown). However, if annual yields were normalized within stream time series and then pooled for all streams, the yields of DOC increased significantly ($P = 0.025$, $n = 48$, not shown)

larger than fresh organic carbon of sampling years ($\Delta^{14}C$ 48 ± 3 ‰, Table 1), plus a contribution of old DOC produced before the year 1950 ($\Delta^{14}C < 0$ ‰). During the summer dry conditions (iii), however, two streams contained a higher proportion of pre-1950 DOC ($\Delta^{14}C$ −21 to −8 ‰). These values corresponded to those obtained in two DOC samples of groundwater-fed springs in the catchment ($\Delta^{14}C$ −24 to −15 ‰, Table 1). It is likely that DOC from groundwater contributed to stream DOC during summer dry conditions (Schiff et al. 1997; Evans et al. 2007). The DOC of the third stream, Weiße Mulde, was of modern origin, although with higher contributions of pre-1950 DOC compared to moderately wet conditions (i, ii). The highest ^{14}C concentrations were found in the reservoir, suggesting that old groundwater DOC was significant only during dry-condition sampling, while modern DOC prevailed during earlier moderate precipitation.

On the other hand, continuing rainfall in summer 2010 (iv) had mobilized old DOC, analyzed from two streams and the reservoir ($\Delta^{14}C$ −40 ‰ to −27 ‰). The radiocarbon age equalled 270–160 yr BP. The third stream, Saubach, was connected to a concrete open channel (Fig. 1), allowing effective supplies from the overland flow only. Old carbon contributed less to DOC in Saubach, suggesting that old DOC was not primarily transported overland at this steep hillslope. We observed that the channel was dry in September 2009 (iii) when the connected Saubach carried old DOC. Except for one sample, $\Delta^{14}C$ values of DIC were modern, indicating recently fixed soil organic matter as the likely source of the DIC rather than carbonate rock. The concentrations of DOC were the lowest from the groundwater (0.8 mg l^{-1}); DOC varied in streams largely around 6 mg l^{-1} but was exceptionally high during the rainfall event (iv, 15-24 mg l^{-1}, Table 1). The DOC concentrations have risen since the early to mid-nineties, concurrently with a decrease in acid load (Fig. 3c–e). The latter was based on the reduction of anthropogenic depositions of sulfur and nitrogen oxides (Sucker et al. 2011).

Discussion

We found modern DOC at moderately dry and moderately wet conditions as well as at high discharges during snowmelt. Old groundwater carbon contributed to stream DOC during the summer drought, although the yield was negligible (0.001 g C m^{-2} d^{-1}). In the extreme precipitation event, high amounts of old DOC were mobilized (0.044 g C m^{-2} d^{-1}). The time-integrating reservoir samples also revealed modern DOC ages under moderate conditions and old DOC from the rainfall event. In the reservoir, the DOC quality can change, e.g. by photosynthetic production or photochemical degradation of DOC. Both processes would enrich the DOC in ^{13}C (Bidigare et al. 1997; Spencer et al. 2009). However, the $\Delta^{13}C$-DOC values in the reservoir were

close to those in the streams and consistent with a terrestrial source. Therefore, it can be assumed that these processes did not significantly influence the isotopic composition and the age of the DOC in the reservoir.

Earlier studies suggested that increasing precipitation escalates the contribution of modern DOC from topsoil layers to surface runoff (Schiff et al. 1997; Laudon et al. 2011). Our results demonstrate a step change occurring if rainfall intensities increase and become extreme; then the consequences lead to the mobilization of old carbon in exceptionally high concentrations. We evaluated potential mechanisms (1–4) that could be causing this step change. (1) During the event, old particulate organic carbon was mobilized by erosion. A fraction was not retained on the 0.7 μm pore size filters and was analyzed as DOC. (2) Some processes have increased the decomposition rate of soil organic matter during the event. (3) Large changes in dissolved ions or pH or the destruction of soil peds by high erosive forces have triggered carbon previously bound to minerals to be released. (4) During the event, hydrologically less connected areas became connected to the stream, delivering old DOC. Starting with mechanism (1), we do not have indication for substantial soil erosion during the event. The soil was covered by coniferous tree needles and vegetation and we did not observe signs of substantial surface erosion. With respect to ion concentrations (3), electric conductivity and major ions (dissolved Si, Ca, Mg, Na) were not different in the event compared to situations (ii) and (iii) (no data in situation i), except lower K were found in the event. Overall, we do not see arguments supporting mechanisms (1) and (3), which suggest that changes in erosion and dissolved ions caused old DOC ages in the event. In addition, increased microbial decomposition during precipitation (2) was rather unlikely to be a factor. The latter may applies to dry ecosystems where microbial activity depends on seasonal inputs of water.

To evaluate if less connected areas became active in the event (4), we first calculated the discharge relative to precipitation (runoff ratio) for a number of rainfall events (Fig. 4a). The runoff ratio increased with increasing precipitation. This is often observed and explained by the fact that saturated hydraulic conductivities increase nonlinearly towards the soil surface. Rising groundwater levels progressively increase the lateral transport and the stream runoff (transmissivity feedback, Kendall et al. 1999). Typically, the DOC concentrations also rise rapidly, as more organic-rich surface soil layers are drained in this process. If precipitation and runoff ratios further increase, there are two scenarios, leading to different conclusions with respect to the activation of less connected areas (4). First, the increase in precipitation can continue up to a point at which the soil becomes saturated. Now, additional rain is transported overland to the stream (saturation excess flow, Troch et al. 1993), and its typically DOC-poor water dilutes the stream DOC (Casper et al. 2003; Laudon et al. 2011). Furthermore, the amount of DOC that can be mobilized from the drained area may be limited, and additional discharge decreases DOC values. If this scenario applies, we expect that with increasing runoff ratios of rainfall events, the DOC concentrations first increase and then decrease steadily. We refer to runoff ratios here rather than precipitation, as the former includes the effects of antecedent soil wetness. The second scenario is based on the assumption that upland and riparian zones remain disconnected from each other for much of the year, or even several years. Only rarely during rainfall events does a shallow groundwater system, all the way along the hillslope, connect the two zones creating a strong hydrological gradient that enables significant transport not only of water but also of dissolved matter to the stream that had previously accumulated in the upland zone (Stieglitz et al. 2003; Ocampo and Sivapalan 2006). If this scenario applies, we expect that opposite trends appear by dilution versus mobilization processes, representing a decrease in DOC due to saturation excess or limited availability (see above) and an increase in DOC due to connection of upland areas, respectively. Our analysis of rainfall events shows that this second scenario likely applies (Fig. 4b). Starting from events with low runoff ratios, there was a steep increase in DOC from one event to the next, indicating progressive drainage of surface DOC. However, events with higher runoff ratios around 0.3 were characterized by high as well as low DOC values (Fig. 4b grey area), suggesting that activation of upland DOC became significant, but its contribution varied between events relative to riparian DOC. At high runoff ratios, stream DOC concentrations were rather high, which was consistent with significant contributions of upland DOC. Actually, DOC concentrations up to 83 mg l^{-1} in surface water of small depressions in the Rote Mulde catchment

were found (Herzsprung et al. 2012) and were in agreement with this second scenario. If upland zones are rarely or partially connected to the stream, old DOC may accumulate. On the other hand, old DOC ages from the event cannot be explained by the first scenario, as modern DOC is expected in the topsoil layers of riparian zones (Palmer et al. 2001).

The DOC yield integrated over the four-week rainfall event (iv) was estimated at 1.2 g C m^{-2}. This equalled 20 % of the annual yield in 2010, the wettest year, 37 % of the yield in 2009 and 52 % in 2008, the driest year (Fig. 2g–i). This shows that the transport of old carbon in extreme precipitation events can constitute a substantial fraction of the annual DOC export. It has previously been unclear if natural processes in temperate headwaters mobilize old DOC. The initial assumption that selective mineralization of contemporary riverine DOC shifts the composition towards old compounds (Raymond and Bauer 2001b) was questioned by more recent data (Hood et al. 2009). Bedrock and land use type have been tested as potential factors in small watersheds in North America, but Δ^{14}C-DOC ages were unrelated and almost all modern (Longworth et al. 2007). Although our study included only forested catchments, the results point to hydrologic connectivity as a key factor. If the results can be transferred to other catchments, it may not only be an issue of climate but also of catchment topography. The mobilization of upland DOC appears restricted to catchments with high upslope accumulated area and is influenced by a complex interplay of hillslope angle, bedrock permeability and soil depth (Hopp and McDonnell 2009; Pacific et al. 2010).

There is observational evidence from a number of countries that rainfall is increasingly occurring in more intensive events but less frequently (New et al. 2001), and these events are associated with longer or more severe periods of drought (Schär et al. 2004). Climate models suggest that this trend will continue in the future (Kharin et al. 2007). If the results of this study apply to other watersheds, more old DOC will be delivered to surface waters. This can also be the effect of some other processes, including polar warming, fossil fuel burning, landscape change and wastewater release (Hood et al. 2009; Guo et al. 2007; Sickman et al. 2010; Griffith et al. 2009, Stubbins et al. 2012). Together, this suggests that human activities are destabilizing carbon pools within the soil and the old carbon is being channelled into smaller but more rapidly cycled carbon pools in river networks, estuaries and the atmosphere.

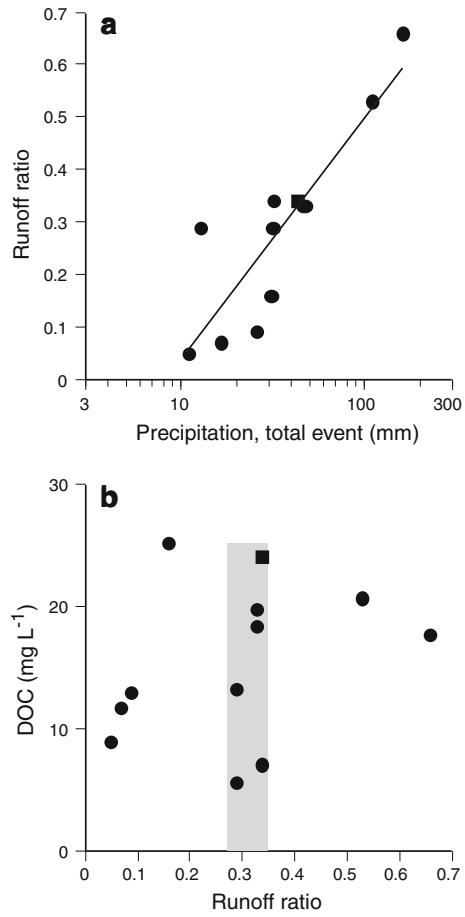

Fig. 4 Runoff generation in the Rote Mulde catchment. **a** runoff ratio (runoff/precipitation) increased with event-integrated precipitation ($R^2 = 0.77$, $P < 0.001$, $n = 12$ events). **b** Runoff ratio and stream DOC concentration. Further explanation see text. The *square symbol* denotes the event yielding old DOC (Fig. 2, Table 1, hydrological condition iv). The event with the highest precipitation and runoff ratio shown contributed to the highest gauge level of River Elbe at Dresden since the year 1275 (here 145 mm on 12 and 13 August 2002, 312 mm within 24 h in other areas, Ulbrich et al. 2003)

To test how climate change affects the yields of DOC, we evaluated data of the monitoring program collected between 1995 and 2010. Overall, the yield was related primarily to annual precipitation (Table 2). At a given precipitation, however, yields were lower in years with more extreme events. Taken together, the final effect on DOC yield depends on whether extreme events increase the annual precipitation or were compensated by longer or more severe

periods of dryness. In our dataset, years with a higher frequency of extreme events were also years with higher precipitation ($R^2 = 0.72$, $P < 0.001$, $n = 16$, linear relationship). This implies that the DOC yield rose with increasing frequency of extreme events ($R^2 = 0.30$, $P < 0.001$, $n = 48$, power relationship). From both isotope data and regression analysis we concluded that old DOC delivered in extreme events was not saved by lower exports at other times of the year and added to the annual yield.

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