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Continuous flux of dissolved black carbon from a vanished tropical forest biome

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Humans have used fire extensively as a tool to shape Earth's vegetation. The slash-and-burn destruction of Brazil's Atlantic forest, which once covered over 1.3 million km^2 of present-day Brazil and was one of the largest tropical forest biomes on Earth[1], is a prime example. Here, we estimate the amount of black carbon generated by the burning of the Atlantic forest, using historical records of land cover, satellite data and black carbon conversion ratios. We estimate that before 1973, destruction of the Atlantic forest generated 200–500 million tons of black carbon. We then estimate the amount of black carbon exported from this relict forest between 1997 and 2008, using measurements of polycyclic aromatic black carbon collected from a large river draining the region, and a continuous record of river discharge. We show that dissolved black carbon (DBC) continues to be mobilized from the watershed each year in the rainy season, despite the fact that widespread forest burning ceased in 1973. We estimate that the river exports 2,700 tons of DBC to the ocean each year. Scaling our findings up, we estimate that 50,000–70,000 tons of DBC are exported from the former forest each year. We suggest that an increase in black carbon production on land could increase the size of the refractory pool of dissolved organic carbon in the deep ocean.

The tropical Atlantic forest once covered >1.3 million km^2 of today's Brazil[1] (Fig. 1). The forest was the continuation of the Amazon rainforest with similar species composition and productivity[2]. Its destruction started with the arrival of the Europeans in the sixteenth century. However, in 1850 more than 95% of its original area remained intact[1]. In the 1850s, massive clearing started with broadax and firebrand[2] and in 1973 less than 15% of the forest was left[1]. Today, 8% of its original extension remains, mainly as secondary forest distributed over small patches in mountainous regions[1].

Forest fires produce airborne combustion products and residues on and in the ground. A major part of these residues is charcoal, or black carbon, which by definition is any blackened form of plant material whose chemical structure has been altered as a result of heating by fire[3]. The wide range of charring temperatures in wildfires produces a continuum of black carbon moieties ranging from slightly altered biopolymers to highly condensed polycyclic aromatic compounds. Owing to their particular chemical and physical properties, the latter can be preserved over centuries and millennia in soils[4] and are ubiquitous in soils and sediments[3,5]. Charring of biomass therefore provides a shortcut between the active and geological carbon cycle by chemically modifying recently produced biopolymers into black carbon that may survive microbial decomposition over geological timescales[6]. This hypothesis has been challenged[4], but despite the potential relevance for global biogeochemical cycles, our knowledge on the turnover of black carbon remains fragmentary. After years of microbial attack in soils, charcoal can become partially soluble and may thus be lost from soils by leaching[7–9]. DBC may then enter the ocean through rivers[10–12]. Contrary to suspended material that is mainly deposited on continental shelves, DBC is potentially distributed throughout the ocean and may impact biogeochemical processes on a global scale. Indeed, the global pool of thermally altered dissolved organic matter in the global ocean exceeds 12 Pg carbon[13], which points towards a considerable flux of DBC from the continents into the ocean.

In this study we determined the load of DBC in Paraíba do Sul River (Fig. 1) from 1997 to 2008 on a biweekly (14 days) basis. The Paraíba do Sul has a length of 1,145 km and drains an area of 55,400 km^2, making it the largest river that exclusively drains former Atlantic forest. Of the original 100% forest cover of the drainage area, 10.7% is left in small fragmented patches[14]. Average rainfall during the 11-year period of sampling was 1,009 mm yr^{-1} (ranging between 690 mm in 2000 and 1,550 mm in 2005). Half of the annual rainfall occurred in the three-month period from November to January.

DBC was determined on a molecular level as the sum of polycyclic aromatic carbon. This method covers the spectrum of the black carbon continuum that has experienced the highest temperatures[15] and is among the most stable components of charred biomass. This is also the fraction of black carbon that is found dissolved throughout the deep ocean[13]. The concentration of DBC in the river fluctuated with seasons, with highest concentrations during the period of high water discharge (Fig. 2). Burning (of mainly sugarcane and pasture) almost exclusively occurred in the dry seasons, coinciding with minimum concentrations of DBC in the river, which excludes direct deposition as a significant source. During peak flow conditions in the rainy seasons, DBC reached concentrations of up to 29 µmol carbon l^{-1} (7% of bulk dissolved organic carbon). During base flow in the dry seasons, the concentrations of DBC were low and fell below detection limits

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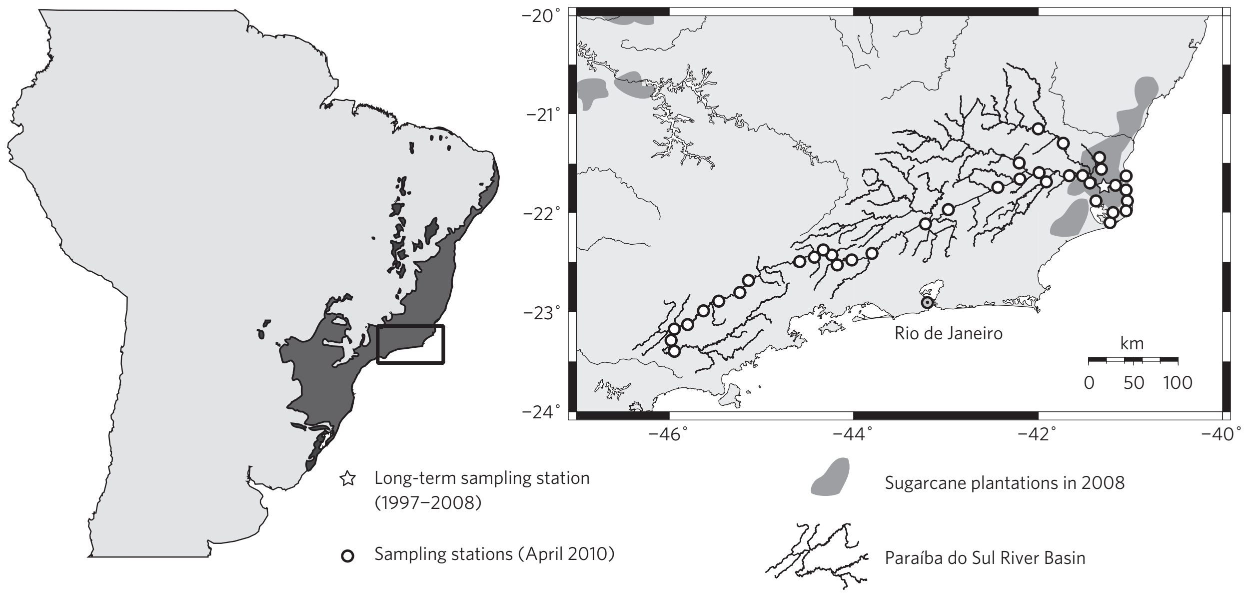

Figure 1 | The study area. The original coverage of the tropical Atlantic forest in the year 1500[1] (dark shading, left panel) was reduced to about 8%, consisting of fragmented patches. Today's production (right panel) of black carbon in the drainage basin of Paraíba do Sul River (the area outlined by the box in the left panel) is largely due to pre-harvest burning of sugarcane in the lower part of the catchment area.

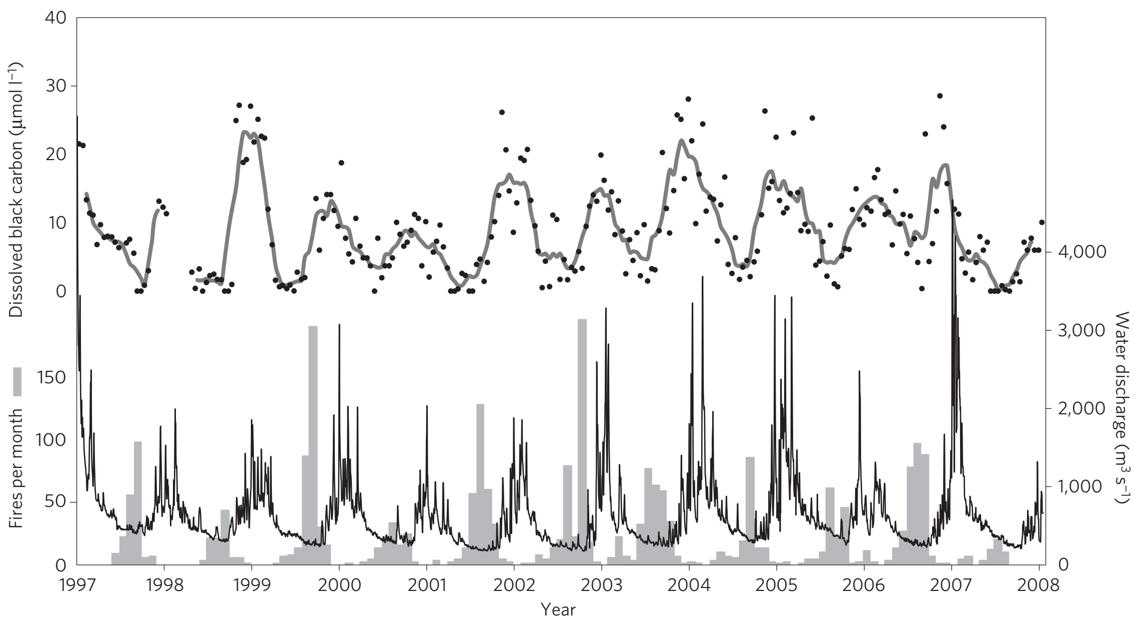

Figure 2 | Time series of Paraíba do Sul River for 1997–2008. Biweekly black carbon concentrations and daily water discharge (http://hidroweb.ana.gov.br/) at Campos dos Goytacazes, and occurrence of fires in the entire drainage basin, as detected by the satellite NOAA-12 (http://sigma.cptec.inpe.br/queimadas/). Biweekly measurements of DBC (dots) and three-months moving averages (lines). The analytical error of DBC concentrations (coefficient of variance of triplicate analysis) is <5% (ref. 19).

($0.2\,\mu$mol carbon l^{-1}) in years of minimum water discharge. Further examination of discharge versus concentration relationships indicated the mixing of distinct bodies of water in the river[16]. Base flow water was depleted in black carbon presumably owing to predominant input of groundwater. During the rainy season, input of soil waters or surface runoff with elevated black carbon and dissolved organic carbon content mixed with base flow in the river (see Supplementary Fig. S1). DBC and dissolved organic carbon concentrations highly significantly correlated in the river ($p < 0.001$), which is consistent with the proposed mixing of two water bodies.

The annual load of DBC was calculated from the DBC concentrations and daily water discharge data (Fig. 2). On average 2,700 tons of DBC were carried per year from Paraíba do Sul River into the ocean (lower and upper 95% confidence limit: 2,300–3,100 tons yr^{-1}). Normalized to the drainage area of the basin, this load results in a yield of 0.05 ± 0.01 tons $km^{-2}\,yr^{-1}$. Present production rates of black carbon in the drainage basin (Fig. 3) are not sufficient to explain this yield. Pasture and open grass land cover 74% of the basin today. Part of this land is managed by fire. Satellite information was used to determine an average fire-return cycle of 25 years from 1997 to 2008 and estimate an annual production of polycyclic aromatic black carbon from grasslands of 80–320 tons. In the lower reaches of the basin there are extensive sugarcane plantations (Fig. 1) where pre-harvest

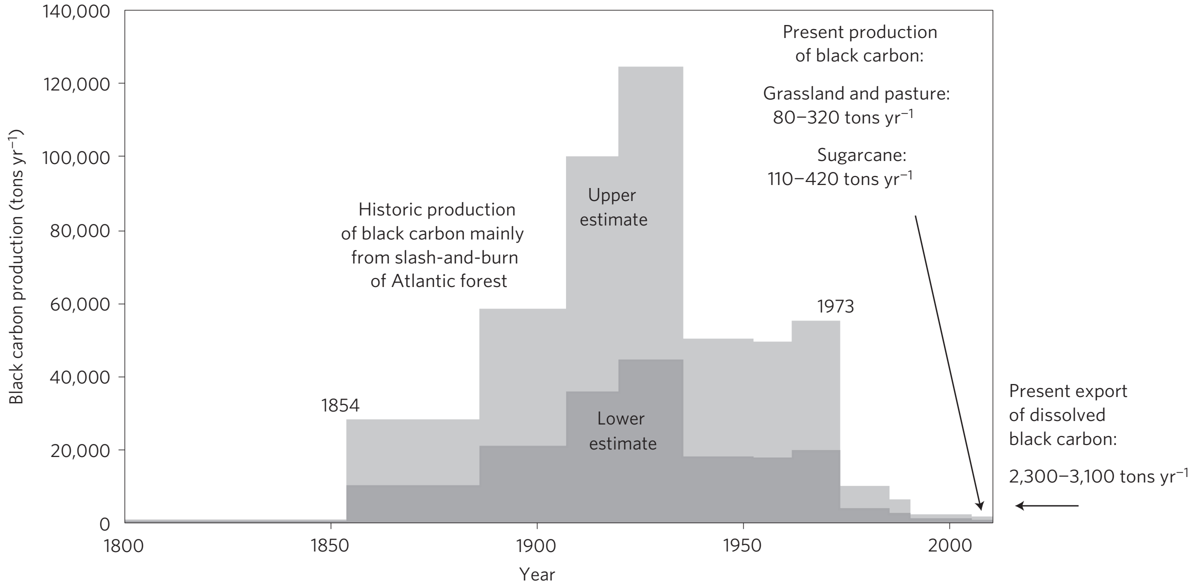

Figure 3 | History of black carbon production in the drainage basin of Paraíba do Sul River for the past 200 years. Annual production rates are for the polycyclic aromatic fraction of black carbon. The rate shown for the period 1800–1854 also represents the period 1500–1800. Black carbon was mainly produced by slash-and-burn clearing of the Atlantic forest. Today's production is mainly due to pasture management and pre-harvest burning of sugarcane.

burning is annually applied to facilitate harvest. Annual production of polycyclic aromatic black carbon from sugarcane burning in the basin of Paraíba do Sul River was estimated to be between 110 and 420 tons. Most of this black carbon was released to the atmosphere and deposited in the vicinity (<100 km distance) of the burning site. Significant leaching of black carbon from sugarcane soils should be reflected in increased concentrations in the lower reaches of the river. To address this last point, samples were collected from the river and its tributaries in April 2010 (Fig. 1). In the main stem, DBC concentrations fluctuated around the average of 15.5 $\mu mol\, l^{-1}$. Concentrations up- and downstream were statistically not different from one another. Minor tributaries, channels and lakes showed higher variability, but did not noticeably impact the river because of their low discharge relative to the main stem.

In sum, the present production of black carbon from biomass burning was on average 190–740 tons yr^{-1}. Atmospheric deposition from fossil-fuel burning is probably low in comparison. The emission of polycyclic black carbon from the two metropolitan areas of Rio de Janeiro and São Paulo was estimated to be approximately 6,000 tons yr^{-1}. Only a small fraction of this annual production deposits in the basin of Paraíba do Sul River because the basin is isolated by mountain ranges and the prevailing wind direction is from the northeast, blowing away from the metropolitan centres. Wet (rain) and dry deposition was collected over a period of one month in April 2010 in Campos dos Goytacazes, which, with 400,000 inhabitants, is the largest city in the basin of the Paraíba do Sul. The rain contained black carbon concentrations below the detection limit (0.2 $\mu mol\, l^{-1}$), confirming negligible deposition of black carbon outside the burning period of the year.

In summary, the load of DBC in the river was 3–16 times higher than today's production rate. Historically, black carbon production rates were several orders of magnitude higher than today (Fig. 3). Over a period of approximately 120 years, a total of 2.8–7.2 million tons of polycyclic black carbon were produced. Assuming a first-order kinetic for the release of DBC from the soils to the river, and assuming dissolution of black carbon as the only removal mechanism from soils, the half-residence time of black carbon in the system would be 630–2,200 years. It is likely that on this timescale polycyclic aromatic black carbon is also lost by complete oxidation to CO_2 and through erosion in particulate form; therefore, this estimated half-residence time is an upper limit.

To assess the standing stock of leachable black carbon from the soils, an extreme rain event was simulated by mixing soil with ultrapure laboratory water. Soil from secondary Atlantic forest released on average (±standard deviation) 0.60 μmol DBC g^{-1} (±0.05), soil from pasture 0.24 $\mu mol\, g^{-1}$ (±0.07) and sugarcane soil only 0.10 $\mu mol\, g^{-1}$ (±0.01), even though the organic carbon content was highest in the last of these. The management practice in the sugarcane plantation had evidently reduced the pool of soluble black carbon, possibly owing to differences in black carbon molecular structure or changes of soil properties. The molecular compositions of DBC in all of the soil leachates and the river were indistinguishable, whereas freshly produced DBC from sugarcane burning had a much higher degree of condensation. If the above numbers are extrapolated to the entire basin, such an extreme rain event would release 70,000 tons of DBC from the upper soil (20 cm), illustrating that the available pool of soluble black carbon by far exceeds the determined export rates.

On the basis of the data presented, historic clearing of the Atlantic forest was the main source of DBC in the Paraíba do Sul. This is consistent with the observation that black carbon becomes more soluble after decades of ageing in soils[7,9]. More than 35 years after the main burning events in the former Atlantic forest, the release and transport of black carbon was driven by hydrology. The Paraíba do Sul River catchment drains a representative area of former Atlantic rain forest in terms of climate, elevation distribution, soil properties and modern land use[1,2,14]. Extrapolating from the Paraíba do Sul catchment suggests the total land–ocean flux of DBC from the entire cleared area of Atlantic forest in Brazil is 50,000–68,000 tons yr^{-1} at present. Thus, a very small fraction of less than 0.0025% of the past annual net primary production[2] of the Atlantic forest is exported annually in the form of DBC at present. This export was evident more than 35 years after the main burning event and did not decrease during the 11-year period of our study. This flux may continue for centuries, as indicated by estimated residence times. DBC is virtually inert in the deep ocean on the timescale of centuries to millennia[13].

Therefore, even minor injections of this DBC into the deep ocean will impact global biogeochemical cycles on centennial to millennial scales. Future studies should address the stability of DBC at the sea surface as it is not known what fraction of DBC survives long-distance transport from the river mouths to the deep ocean[17]. The disappearance of the Atlantic forest provides a worst-case scenario for tropical forests worldwide, most of which are being cleared at an increasing rate. The comparably fast mobilization of DBC from soils and its apparent recalcitrance in the deep ocean suggest that an increase of black carbon production on land may alter the size of the refractory dissolved organic matter pool in the deep ocean on the long term.

Methods

For detailed Methods we refer the reader to the Supplementary Information. Sampling was performed in a two-week interval from January 1997 to February 2008 from a bridge in Campos dos Goytacazes (Fig. 1). For molecular analysis, DBC was concentrated using ultrafiltration. In April 2010, the river, tributaries, lakes and channels were sampled at 58 stations (Fig. 1), and DBC was concentrated using solid-phase extraction[18]. Soil samples were taken at three locations in the lower part of the catchment area from secondary lowland Atlantic forest, a sugarcane plantation and pasture grassland. Aqueous extracts of the soils were analysed for DBC.

Dissolved organic carbon was determined as carbon dioxide after catalytic high-temperature combustion. For the determination of black carbon, a wide range of different analytical methods exists, each addressing a different spectrum of the black carbon continuum[15]. In this study, DBC was determined at the molecular level using the benzenepolycarboxylic acid (BPCA) method[19]. This method specifically quantifies condensed aromatic moieties. The relative proportion of the eight different detectable BPCAs gives indications on the degree of condensation and the size of the polycyclic aromates. The concentration of DBC was calculated from the concentrations of the individual BPCAs (ref. 19).

The historic black carbon production from Atlantic forest was estimated as follows. Since 1500, a forested area of 49,500 km^2 was cleared by the slash-and-burn practice in the drainage basin of Paraíba do Sul River, 48,600 km^2 of this area in the period between 1854 and 1973 (ref. 1). Experimental evidence[3,20–22] indicates total black carbon production of 160–420 tons carbon per square kilometre during fire-clearing of tropical Amazon rainforest. On the basis of these numbers, we estimate a total black carbon production in the course of the destruction of the Atlantic forest in the drainage basin of Paraíba do Sul River of 8–21 million tons, and 200–500 million tons of black carbon from a total cleared Atlantic forest area of 1.2 million km^2. The total production of polycyclic aromatic black carbon in the drainage basin was approximately 2.8–7.2 million tons. For the historic production of black carbon in the studied drainage area (Fig. 3), the reported historic coverage of Atlantic forest in the region[1] was scaled to the area of the Paraíba do Sul River Basin.

Pasture and open grass land cover 74% of the basin today[14]. During the period of this study, an area of 1,500 km^2 of grassland burned every year in the catchment area, as detected by the NOAA-12 satellite (http://sigma.cptec.inpe.br/queimadas/) and by using published conversion factors[23]. On the basis of these numbers, the standing stock of carbon biomass in these grasslands[24] and published black carbon conversion rates for grasslands[3], we estimate an annual production of polycyclic aromatic black carbon from grasslands in the drainage area of 80–320 tons yr^{-1}. The burning of above-ground biomass in sugarcane plantation produces a total amount of burned residues[25] of 0.5–2.2 tons km^{-2}. As sugarcane burns extraordinarily fast[26], the stalks and soil are charred only at the very surface. A soil charring depth of 1.5 cm (refs 27,28) adds less than 0.1 tons km^{-2} charred residue through charring of the root carbon pool at this depth[29]. We determined a black carbon content (after the BPCA method) in the above-ground fire residue of 13%. The total production area of sugarcane of 1,370 km^2 remained stable during the course of this study. On the basis of these numbers, we calculated an annual production of polycyclic aromatic black carbon from sugarcane burning in the basin of Paraíba do Sul River of 110–420 tons yr^{-1}.

We estimated the emission rate of black carbon from the metropolitan areas of São Paulo and Rio de Janeiro by scaling the published values for South and Central America[30] to the population of the metropolitan area of São Paulo and the state of Rio de Janeiro.

For the calculation of DBC loads, daily discharge values from the Brazilian Agência Nacional de Águas (http://hidroweb.ana.gov.br/) were used. On the basis of concentration versus discharge trajectories analysis, and validation tests of outputs from load models (http://water.usgs.gov/software/loadest/), the following procedure yielded the most reliable results. The discharge data were averaged for two-week periods starting one week before and ending one week after the DBC measurement was made. The DBC concentration was then multiplied by the average discharge to generate loads for each two-week period. These were then used to calculate an average annual load for the study period. A bootstrap routine was used to calculate upper and lower 95% confidence levels for the mean load.

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Author contributions

The idea of this study was jointly developed by C.E.d.R. and T.D. All authors contributed to sampling, chemical analysis and/or data interpretation, and to the general discussion. T.D. led the writing of the manuscript and the drafting of the figures. All authors provided input into the drafting and the final version of the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to T.D. or C.E.d.R.

Competing financial interests

The authors declare no competing financial interests.