Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans

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Global biomass burning generates 40 million to 250 million tons of charcoal every year, part of which is preserved for millennia in soils and sediments. We have quantified dissolution products of charcoal in a wide range of rivers worldwide and show that globally, a major portion of the annual charcoal production is lost from soils via dissolution and subsequent transport to the ocean. The global flux of soluble charcoal accounts to 26.5 ± 1.8 million tons per year, which is ~10% of the global riverine flux of dissolved organic carbon (DOC). We suggest that the mobilization of charcoal and DOC out of soils is mechanistically coupled. This study closes a major gap in the global charcoal budget and provides critical information in the context of geoengineering.

Charcoal, or black carbon (BC), is a molecularly diverse organic product of incomplete combustion of biomass and fossil fuels (*1*–*3*). It is ubiquitous in the environment, where it slowly decomposes (*4*), but part of it is preserved for thousands of years (*5*). Global biomass burning generates an estimated 40 to 250 mega–metric tons (MMT) of BC per year (*6*) (MMT = 10^{12} grams), and 5 to 40% of total soil organic carbon (OC) is estimated to be BC (*7*–*10*). The global BC stock in sediments, soils, and waters combined is 300 to 500 giga–metric tons of carbon (*11*). BC has been considered as extraordinarily stable in the environment. However, current production rates exceed estimates of decomposition rates. According to this mismatch, there should be more BC than total OC in soils (*12*, *13*). This paradox indicates that a relatively labile BC pool must exist, allowing for considerable losses from soils. Measurements of BC age in boreal forest soils of ~652 years (*14*) agree with reported BC degradation rates on centennial time scales (*11*, *15*, *16*), suggesting that microbial degradation and erosion of BC may be more substantial than previously believed. A meta-analysis of the current knowledge on BC degradation in soils (*4*) indicates turnover times of less than 100 years. Alternatively, multiple pools of BC were suggested in the same study (*4*), with about half of the BC turning over in 3 years, whereas the other half may persist in soils over millennia. This range of reactivity is probably a function of charring temperature and source material, but also, environmental factors such as soil properties and fauna play a role in BC decomposition (*4*, *17*, *18*). In addition to complete oxidation into CO_2 and particle erosion (*19*), BC can also be mobilized from soils in dissolved form as dissolved BC (DBC) (*11*, *20*–*23*). A recent study showed that even decades after major slash and burn, DBC was efficiently mobilized in large quantities from the soils of a former tropical forest biome in Brazil (*21*). The fact that >2% of the marine dissolved OC (DOC) pool has a heat-induced molecular signature (*24*) also points toward considerable fluxes of DBC from land to ocean. If BC dissolution in soils is an important

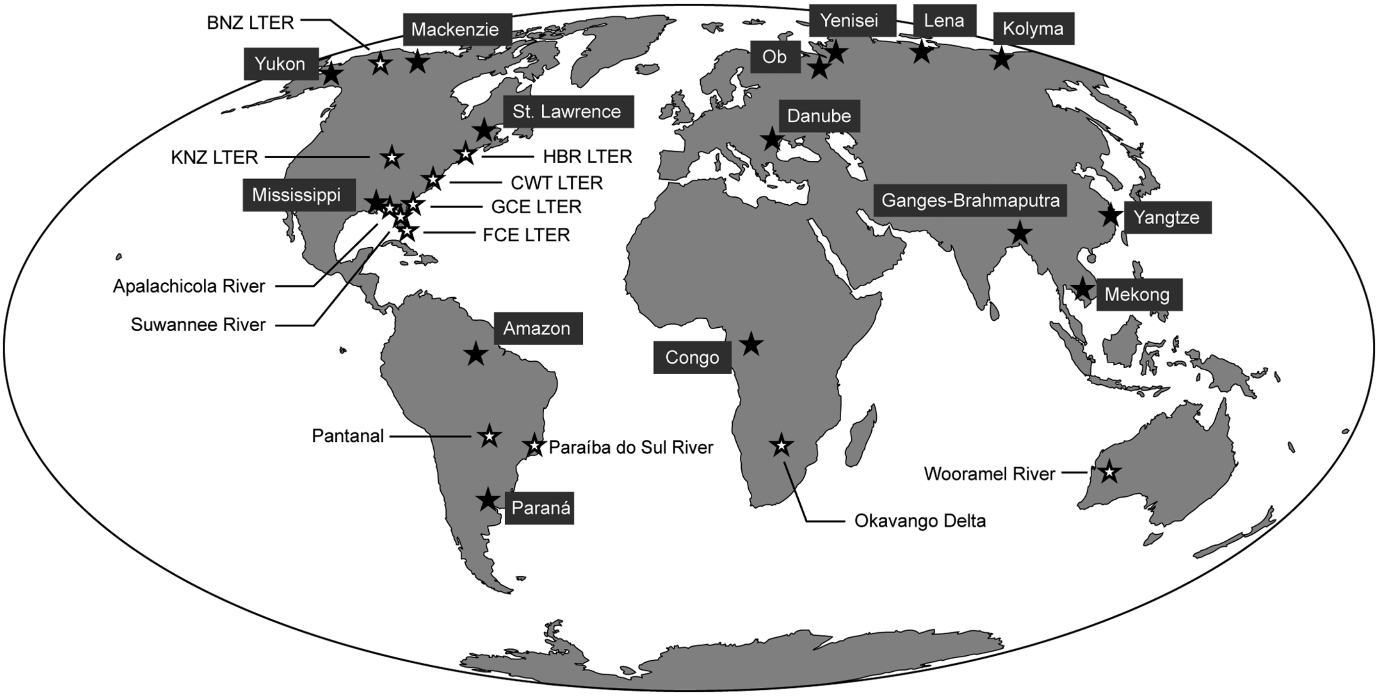

Fig. 1. Map of global freshwater DBC sampling sites. Black stars indicate major world rivers, and white stars indicate all other sites, including minor to intermediate rivers and wetland-associated streams, including Long-Term Ecological Research (LTER) sites. BNZ, Bonanza Creek; KNZ, Konza Prairie; HBR, Hubbard Brook; CWT, Coweeta; GCE, Georgia Coastal Ecosystems; FCE, Florida Coast Everglades.

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translocation process in terrestrial systems, the transfer of this material to marine environments may be critical in establishing global mass balances for BC. However, few data on DBC loads are available for rivers (*21*, *23*), and this quantitative information is too limited to reliably estimate land-ocean fluxes on a global scale.

The objective of this study was to provide an estimate of the global flux of DBC from land to ocean through rivers. For this purpose, we determined the concentration of DBC in rivers globally (Fig. 1) across a wide range of sizes, from major rivers to headwater streams and wetland watersheds, and geographically from the Arctic to the southern midlatitudes.

DBC was determined on a molecular level as the sum of polycyclic aromatic carbon (*25*). This polycyclic aromatic fraction forms at the highest temperatures (*7*) and is among the most stable components of charred biomass. It is also the fraction of BC that is found dissolved throughout the deep ocean (*24*). The limitation of our analytical window to polycyclic aromatic carbon implies that the global DBC flux calculations reported here are conservative underestimates and comprise a lower limit of the actual fluxes. We studied 174 freshwater samples in order to assess the average and variability of DBC and DOC concentrations on a globally representative scale. Sampling was not necessarily intended to resolve seasonal or site-specific features, such as climate, elevation, or vegetation. Replicate samples from the same locations and season were averaged so as to avoid domination of the statistics by only a few sampling locations, thus reducing the overall data set to 109 data points. Each data point represents a distinct main stem, tributary, wetland system, or season from 27 different river systems and wetlands. These samples include 15 of the largest rivers worldwide, such as the Amazon, Congo, and major Arctic rivers. We appended the data set with results from previous case studies (*20*–*22*).

The DBC concentrations varied strongly among the freshwater systems, ranging from 1.94×10^{-3} to 2.77 mg carbon liter^{-1} (average ± SD of 0.48 ± 0.55 mg carbon liter^{-1}). DBC comprised from 0.1 to 17.5% of DOC (average ± SD of 7.1 ± 3.6%). Despite this apparent variability, DBC and DOC concentrations were highly correlated [correlation coefficient (r^2) = 0.88, n = 109 data points, $P < 0.0001$]. Recent case studies that examined the relationship between DOC and DBC (*20*–*22*), as well as soil BC and soil organic matter (*10*, *26*), are consistent with our observation. Because our DOC and DBC concentrations were not normally distributed, we grouped the samples according to their DOC concentrations into 15 groups for further statistical analysis (Fig. 2). The slope of the resulting regression indicates that the global DOC pool contains 10.6% DBC (±0.7%, on a 95% confidence level, n = 15 DOC concentration groups). The intercept of the regression was not significantly different from zero. If the original ungrouped data are used for the regression, the resulting slope and intercept are statistically not different from the grouped data, but the estimates for the error margins (confidence intervals) are lower because of the higher number of data points (n = 109 data points). The major world river samples followed the regression of the whole data set, suggesting that natural integration occurs in big watersheds.

We took advantage of this highly significant relationship between DBC and DOC concentrations to convert published data for global river loads of DOC into DBC loads. The estimated annual DBC flux from land to ocean is about 26.5 ± 1.8 MMT of carbon per year, based on a flux of riverine DOC of 250 MMT of carbon per year (*27*). The global DOC flux contains considerable margins of uncertainty. As refinements of global DOC flux estimates become available, updates on global DBC fluxes can be easily made on the basis of the observed relationship between DOC and DBC.

Although a wide range of variability among individual rivers was observed as expected, the global linear relationship between DOC and DBC concentrations appears enigmatic on a first view. It suggests that the diagenetic processes driving the release of DOC and DBC from soils are related. The close coupling between DBC and DOC fluxes indicates that the release and subsequent sorption and desorption processes of DBC are a complex function of environmental factors and soil properties, just as for bulk DOC. The aging of BC in soils seems critical in facilitating its transfer to the aqueous phase (*21*, *22*, *28*). During aging, the condensed aromatic ring structures of charcoal are functionalized over time with hydroxyl and carboxylic groups on their periphery (*11*, *29*), conferring them not only some limited aqueous solubility but also binding capacities to mineral surfaces in soil (*10*, *11*). As an alternative explanation, DOC could be directly involved in the physical translocation process of soil BC to DBC. As for hydrophobic organic pollutants, the presence of dissolved organic matter may serve as a mobilizing agent through hydrophobic interactions.

According to our data, it is clear that DBC is globally ubiquitous in freshwater environments. Approximately 26.5 MMT carbon of DBC enter the oceans every year, which is in the same order of magnitude as the estimated range of the annual production of BC from vegetation fires (40 to 250 MMT carbon year^{-1} of BC) (*6*). Although other soil processes—such as microbial oxidation, sorption of DBC on aquifer materials, erosion, and reburning—also may contribute to the loss of soil BC, our study shows that DOC is an important environmental intermediate for both transfer and storage of BC. With continued anthropogenic perturbations to watersheds (such as slash-and-burn agriculture) and global climate change impacts (such as permafrost thaw) leading to an increase in terrestrial DOC export from land to the oceans, the flux of DBC is expected to increment equivalently. Bio-char applications to soils have been proposed as an effective means of carbon sequestration (*30*). This activity may further

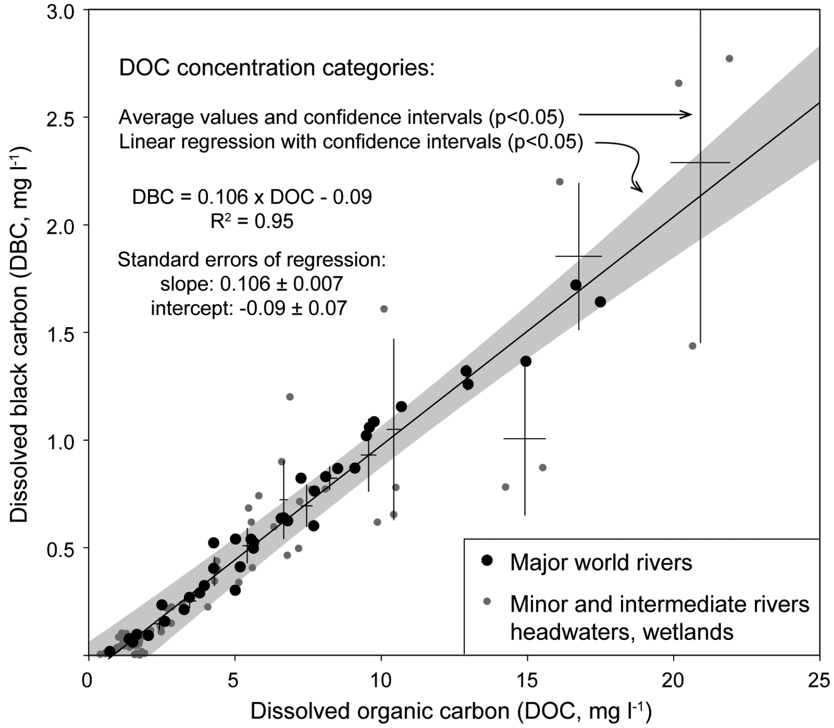

Fig. 2. DBC versus DOC concentrations of global rivers. The regression parameters are for the average values of 15 DOC concentration groups (crosses). Raw data regression yields the same slope and intercept, but the confidence intervals are smaller because of the larger number of samples.

enhance the translocation and export of DBC to marine systems. The environmental consequences of this are presently unknown but may be reflected in the reduction of DOC bioavailability and associated effects on microbial loop dynamics and aquatic food webs. Our data suggest that we apply our existing knowledge on DOC production, storage, and movement in soils to ensure that biochar applications are implemented sustainably and managed in ways to minimize riverine DBC fluxes.

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Supplementary Materials

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Resilience and Recovery of Overexploited Marine Populations

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Recovery of overexploited marine populations has been slow, and most remain below target biomass levels. A key question is whether this is due to insufficient reductions in harvest rates or the erosion of population resilience. Using a global meta-analysis of overfished stocks, we find that resilience of those stocks subjected to moderate levels of overfishing is enhanced, not compromised, offering the possibility of swift recovery. However, prolonged intense overexploitation, especially for collapsed stocks, not only delays rebuilding but also substantially increases the uncertainty in recovery times, despite predictable influences of fishing and life history. Timely and decisive reductions in harvest rates could mitigate this uncertainty. Instead, current harvest and low biomass levels render recovery improbable for the majority of the world's depleted stocks.

Recovery of overexploited marine populations would be a "win-win" outcome for fisheries and conservation, easing pressure on wild populations and associated ecosystems (*1*–*3*), and ultimately enhancing catches, revenues, and food security (*4*–*6*). Recognizing the global importance of recovery, the United Nations (UN) 2002 World Summit on Sustainable Development proposed that global fisheries be rebuilt to maximum sustainable yield (MSY) levels by 2015 (*5*, *7*). Echoing this call, several countries, including Australia and the United States, mandated rebuilding in their fisheries legislation. In Europe, a proposed new Common Fisheries Policy (CFP) aims to rebuild fisheries to MSY levels by 2020 (*8*). Although exploitation rates have been reduced and population declines halted in some regions (*9*, *10*), stock biomass remains below that of maximum sustainable yield (B_{MSY}) for the majority of commercially exploited fishes (*6*, *10*, *11*). By 2010, only ~1% of global stocks requiring rebuilding had been successfully rebuilt (*9*), suggesting that the UN's 2015 recovery target will not be met (*5*). Here, we empirically examine the time frames needed to recover the world's depleted stocks.

Fisheries operate in complex systems, and the factors driving recovery remain uncertain. Simple theoretical models predict that most overfished stocks should recover to B_{MSY} in less than a decade if fishing mortality is sufficiently reduced (*12*). The slow recovery of some populations, however, has led to increased investigation of their resilience to overfishing (*13*, *14*). Allee effects (*13*, *15*), reduced productivity attributable to adverse environmental conditions (*16*, *17*), and the evolution of life-history traits caused by high fishing mortality (*18*, *19*) have been proposed as causes of impaired recoveries. Although such effects may be identifiable retrospectively [e.g., (*20*)], it remains unclear whether recoveries are predictable, given these potentially adverse effects of long-term exploitation and altered ecosystem states.

To gain insight into the recovery process, we investigated the importance of fishing mortality relative to life history, exploitation history, and other hypothesized drivers of recovery for 153 marine fish and invertebrate stocks for which stock assessments indicated that population biomass had declined below half of B_{MSY} (table S1) (*11*, *21*). We modeled recovery times—the number of years between depletion ($B < 0.5\ B_{\mathrm{MSY}}$) and recovery to B_{MSY}—for 184 depletion events, using a Bayesian regression model based on

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