Mangroves, a major source of dissolved organic carbon to the oceans

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[1] Organic matter, which is dissolved in low concentrations in the vast waters of the oceans, contains a total amount of carbon similar to atmospheric carbon dioxide. To understand global biogeochemical cycles, it is crucial to quantify the sources of marine dissolved organic carbon (DOC). We investigated the impact of mangroves, the dominant intertidal vegetation of the tropics, on marine DOC inventories. Stable carbon isotopes and proton nuclear magnetic resonance spectroscopy showed that mangroves are the main source of terrigenous DOC in the open ocean off northern Brazil. Sunlight efficiently destroyed aromatic molecules during transport offshore, removing about one third of mangrove-derived DOC. The remainder was refractory and may thus be distributed over the oceans. On a global scale, we estimate that mangroves account for >10% of the terrestrially derived, refractory DOC transported to the ocean, while they cover only <0.1% of the continents' surface.

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1. Introduction

[2] Mangroves fringe most of the tropical coasts worldwide, but they are generally considered hostile, foul-smelling, muddy environments, which may explain why they have gained very little public and scientific attention compared to the colorful coral reefs or tropical rain forests. The 2005 tsunami event has demonstrated in a dramatic way the importance of mangroves as a natural barrier against the ocean, and their relevance for commercially important fish species is well documented [*Mumby et al.*, 2004]. Furthermore, ocean margins, including mangroves, link the carbon cycles of land and ocean. Tidal transport from coastal wetlands (''outwelling'') [*Dittmar et al.*, 2001], along with riverine fluxes [*Opsahl and Benner*, 1997], provide the most important sources of terrigenous organic matter to the ocean. About 50% of net primary production in mangroves is exported as organic matter to the ocean [*Robertson et al.*, 1992; *Dittmar and Lara*, 2001a, 2001b; *Jennerjahn and Ittekkot*, 2002] which is almost 2 orders of magnitude higher than the global average for terrestrial ecosystems (0.7%) [*Spitzy and Leenheer*, 1991]. Mangrove-derived detritus and suspended particles generally settle within the inner shelf area. Mangroves contribute ~15% to the organic carbon globally accumulating in marine sediments [*Twilley et al.*, 1992; *Jennerjahn and Ittekkot*, 2002].

[3] The importance of ocean margins and intertidal systems for organic carbon burial in sediments is well recognized [*Hedges et al.*, 1997; *Jennerjahn and Ittekkot*, 2002] as well as their contribution to dissolved organic matter (DOM) inventories of the oceans' interior [*Bauer and Druffel*, 1998]. Several studies consistently indicate that a significant fraction of mangroves' primary production can be exported via tidal currents as DOM [*Nixon et al.*, 1984; *Twilley*, 1985; *Boto and Wellington*, 1988; *Ayukai et al.*, 1998; *Dittmar et al.*, 2001; *Dittmar and Lara*, 2001a]. Tidally mediated flux of sediment pore water to the ocean seems to be the principal pathway of DOM outwelling [*Dittmar and Lara*, 2001b]. Surprisingly, despite the enormous ecological differences among the studied mangroves in Brazil [*Dittmar et al.*, 2001], Australia [*Boto and Wellington*, 1988] and North America [*Twilley*, 1985], the area-normalized DOM export from mangroves appears to be independent of location. These organic solutes may be transported farther offshore and globally distributed through the currents of the ocean conveyor belt. Despite the global relevance, a baseline for DOM outwelling from mangroves has not been established, and the fate of mangrove-derived DOM in the ocean is unclear. It is not known whether coastal outwelling of DOM can impact the oceans' elements budgets beyond the direct vicinity of the mangroves, and whether mangrove-derived DOM survives transport into the oceans.

[4] The tools for tracing terrigenous organic matter in the ocean are extremely limited. Isotopic differences can be used to distinguish terrigenous and algal-derived organic matter [e.g., *Dittmar et al.*, 2001] because terrestrial C3-plants and aquatic primary producers have distinctive stable carbon-isotope ratios ($\delta^{13}C$). Isotopic fractionations caused by degradation are usually small compared to the sharp isotopic differences between terrigenous and algal-derived organic matter in coastal zones.

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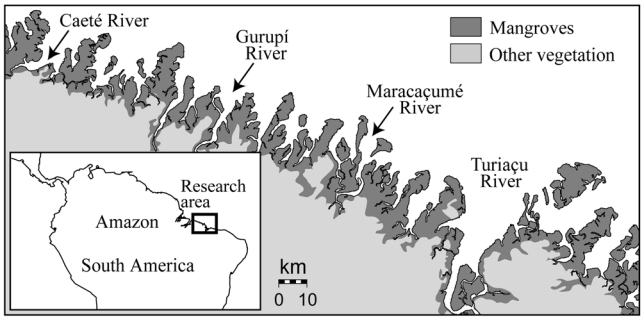

Figure 1. Distribution of mangroves (~6700 km^2) in the research area, estimated from Landsat satellite images. The mangrove area that influences the sampled shelf area extends farther southeast and comprises a total of ~10,000 km^2 mangroves.

On a molecular level, lignin is the only unambiguous tracer for terrigenous DOM [*Meyers-Schulte and Hedges*, 1986], and has been applied to identify mangrove-derived DOM in north Brazilian coastal waters [*Dittmar et al.*, 2001]. Spectroscopic properties (fluorescence and absorbance spectra) can also be useful to identify the source of DOM at the scale of coastal environments [e.g., *Moran et al.*, 1991]. Exposure to sunlight, however, sharply decreases lignin concentration [*Opsahl and Benner*, 1998] and spectroscopic activity of DOM within a few days. If not properly addressed these molecular changes may cause artifacts in source identification.

[5] Molecular changes during outwelling can be monitored via proton nuclear magnetic resonance spectroscopy (NMR) which has provided key insights into structural details of natural organic matter over the last decades [e.g., *Hedges et al.*, 2002; *Simpson et al.*, 2003]. Modern proton NMR spectroscopy is extremely sensitive, and because it is unselective, quantitative structural information on fundamental building blocks, and of chemical environments within, is readily obtained.

[6] The objectives of this study were (1) to provide a first baseline on DOC outwelling from mangroves to the ocean and (2) to identify major processes responsible for removal and chemical modification of mangrove-derived DOM in the ocean. The study was performed on the scale of an entire mangrove-shelf system (Figure 1) that integrates information of ~10,000 km^2 of north Brazilian mangroves. The mangroves belong to the major and most pristine forests in the world, representing ~70% of Brazil's and ~20% of Americas' mangroves [*Spalding et al.*, 1997]. A combined approach of stable carbon isotopes and NMR was used to quantify mangrove-derived DOM on the North Brazilian shelf and to identify molecular modifications that may occur during outwelling.

2. Materials and Methods

2.1. Sampling and Field Analyses

[7] Sampling was performed from the cutter *Tubarão II* during the dry season in October/November 2001 at 40 stations, covering the North Brazilian shelf southeast of the Amazon estuary along transects from the mangroves to the shelf edge (>100 km offshore). The mangroves are a well-developed mixed forest of *Rhizophora mangle* and *Avicennia germinans*, with a low abundance of *Laguncularia racemosa*, all species reaching heights of 20 m or more. The water column of the shallow shelf (water depths mostly <30 m) was well mixed by action of waves, which reached heights of 4 m, and strong diurnal tidal currents. Therefore water sampling was restricted to the surface. Water column stratification was checked with profiles of physicochemical parameters (Multipar-CTD). Water flux profiles were obtained on the transects with an acoustic Doppler current profiler (RD Instruments). Water currents over the shelf exhibited very regular sinusoidal tidal fluctuations. Net water transport over the shelf (component of the North Brazil Current) was calculated from depth-integrated current data. The error (confidence interval P = 0.05) of mean water transport includes methodological errors but also irregularities in water flow caused, for example, by winds. Rivers were sampled from bridges.

[8] As a reference for mangrove-derived DOM, pore water was extracted from mangrove sediments from surface to 1.5 m depths at three different locations in the Caeté Estuary. Most of the area is flooded biweekly during spring tides, when the tidal range is 4–5 m. Sampling was performed during the dry season in October 2001 at neap tide, so that the site was not flooded during the period of sampling. To obtain pore water, three holes of 1.5 m depth were carefully dug into the mangrove sediment. After the holes were filled with water, the water was evacuated 2 times before sampling, to reduce effects of disturbance and contamination. The salinity of the different pore water samples ranged between 25.0 and 30.9, and DOC concentrations between 0.65 and 2.77 mM.

[9] Processes that occur during outwelling were simulated in a two-step degradation experiment. First, sterile-filtered (0.2 μm pore size) mangrove DOM was exposed to natural sunlight for up to 14 days in precombusted (550°C) glass ampoules (30 mm × 150 mm). For sampling, triplicates (three ampoules) were removed every second day, immediately filtered through precombusted Whatman GF/F filters, and kept frozen (−18°C) until further analyses. Subsequently, degradation was monitored in microbial incubation experiments with aliquots of photodegraded DOM as well as original DOM in triplicate batches of 3–5 L in the dark. An estuarine microbial community from the Caeté Estuary, i.e., surface water which was 3-μm-filtered to remove detritus and phytoplankton, served as inoculum. A headspace of air eliminated possible oxygen limitation during all experiments. In terms of light-energy, the 14 days of the photodegradation experiment compares to several years in the ocean, because only the upper few centimeters of the water column on the continental shelf is actually penetrated by UV-light.

2.2. Sample Preparation

[10] Immediately after sampling, all samples were filtered (0.2 μm pore size) and aliquots stored frozen in muffled glass ampoules or polyethylene bottles for the analysis of DOC and nutrients, respectively. To isolate DOM, aliquots

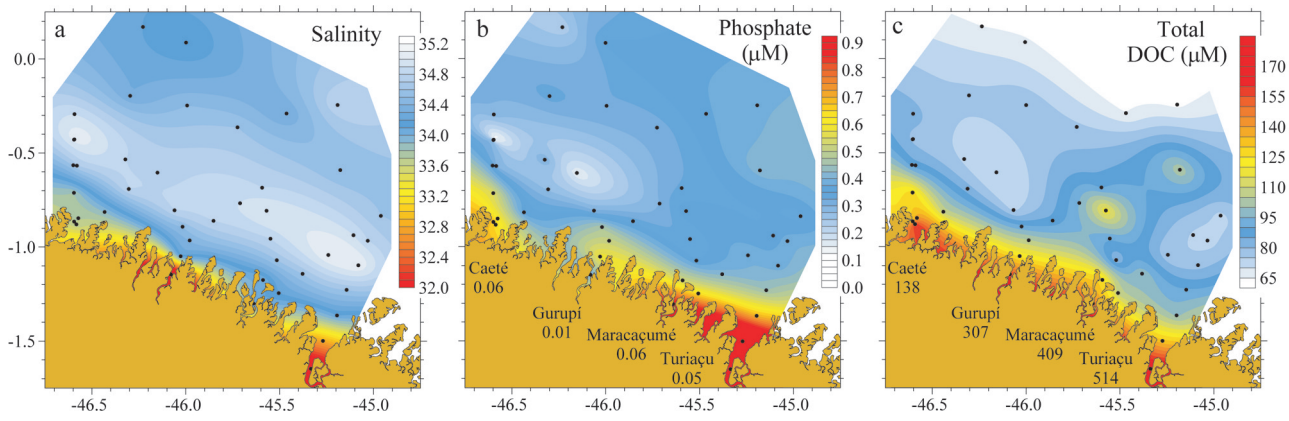

Figure 2. Salinity, dissolved *o*-phosphate and dissolved organic carbon (DOC) concentrations (μM) on the North Brazilian shelf and in corresponding rivers, southeast of the Amazon Estuary; with sampling stations (black dots). River concentrations are given below their respective names.

of all samples were acidified (pH = 2) with 10 M HCl and pumped through solid-phase extraction cartridges (C18, Varian Bond Elut). DOM was eluted onboard with methanol. The eluted samples were freeze-dried and stored at −18°C in the dark. The solid-phase extraction was checked with artificial seawater blanks (DOC < 0.5 μM). Freeze-dried blank extracts did not contain significant amounts of DOC. Sample extracts were checked for trace contamination with C_{18}-compounds via nuclear magnetic resonance spectroscopy. In order to minimize possible artifacts introduced by selective isolation of specific compounds classes, the same DOM extraction procedure was applied to all samples and end-members. The extraction efficiency for DOC was 39 ± 3%.

2.3. Chemical Analyses

[11] Physicochemical parameters, inorganic nutrients, and chlorophyll *a* were determined using standard methods [*Grasshoff et al.*, 1999]. DOC was determined by high-temperature catalytic oxidation with a modified MQ Scientific TOC analyzer [*Peterson et al.*, 2003]. Detection limit was 10 μM C. The method was repeatedly checked with seawater reference material [*Hansell*, 2001]. Stable carbon-isotope ratios were measured on freeze-dried DOM extracts (isolated from seawater by C18 solid-phase extraction) by combustion on a Carlo Erba NC2500 interfaced through a Finnigan ConFlo II to a Finnigan Delta XL IRMS. The method was calibrated with nicotinic acid and routinely checked with standard reference material. Stable carbon-isotope ratios are expressed as $\delta^{13}C$ relative to the Pee Dee Belemnite standard. Proton detected (one- and two-dimensional, homo- and hetero-nuclear $^{1}H/^{13}C$) NMR spectra [*Schmitt-Kopplin et al.*, 1998; *Hertkorn et al.*, 2002] were acquired from 0.1–1.2 mg of freeze-dried DOM isolates in 500 μL 0.1 N NaOD and organic solvents with a 5-mm z-gradient $^{1}H/^{13}C/^{15}N$ TXI cryogenic probe using 90° excitation pulses on a Bruker DMX 500 NMR spectrometer. The 1D ^{1}H NMR spectra were recorded in 0.1 N NaOD using the first increment of the presat-NOESY sequence (4.7-s acquisition time, 15.3-s relaxation delay, 320 scans, 1-ms mixing time, 1-Hz exponential line broadening). All variances of average values given in the text are expressed as confidence intervals (P = 0.05).

3. Results and Discussion

[12] DOC concentrations on the North Brazilian shelf decreased from ≤196 μM, in the mangrove-fringed estuaries, to values ≥64 μM offshore (Figure 2). Offshore DOC concentrations were slightly elevated compared to the background concentration of the deep equatorial Atlantic (<50 μM) [*Hansell and Carlson*, 1998], indicating an additional source of DOC on the shelf. This source can be terrestrial input or aquatic production (in situ or advected from the adjacent ocean). To distinguish between terrestrial and algal DOC sources, we determined stable carbon-isotope ratios ($\delta^{13}C$) of DOC, which we isolated by solid-phase extraction. The $\delta^{13}C$ values of DOC that we extracted from the rivers in our sampling area ranged from −26.8 to −30.4‰ (Figure 3). For the mangrove end-member we determined $\delta^{13}C$ on photodegraded mangrove pore water, in order to minimize possible artifacts introduced by isotopic fractionations during degradation. The $\delta^{13}C$ value of mangrove-derived DOC was −31.4‰, similar to reported values for mangrove litter [*Dittmar and Lara*, 2001c]. The slightly higher value in the rivers, when compared to mangroves, is probably due to algal growth in the rivers. In contrast, $\delta^{13}C$ in marine DOC is clearly different: DOC that we extracted from Atlantic deep water (~4000 m water depth) had an average $\delta^{13}C$ value of −23.7‰.

[13] To distinguish DOC from rivers and DOC from mangroves, salinity was used as a tracer: River water is fresh, in contrast to mangrove waters which are brackish to marine. Freshwater input to the shelf was small, and salinity was close to the background value of the Equatorial Current (Figure 2). This is in sharp contrast to the river-dominated shelf region northwest of the Amazon Estuary, but the North Brazil Current prevents water from the Amazon River flowing southward [*Geyer et al.*, 1996] into the studied shelf region. On the shelf, DOC concentration was inversely correlated with salinity (P < 0.01), indicating mixing of essentially two sources with different salinities. On the

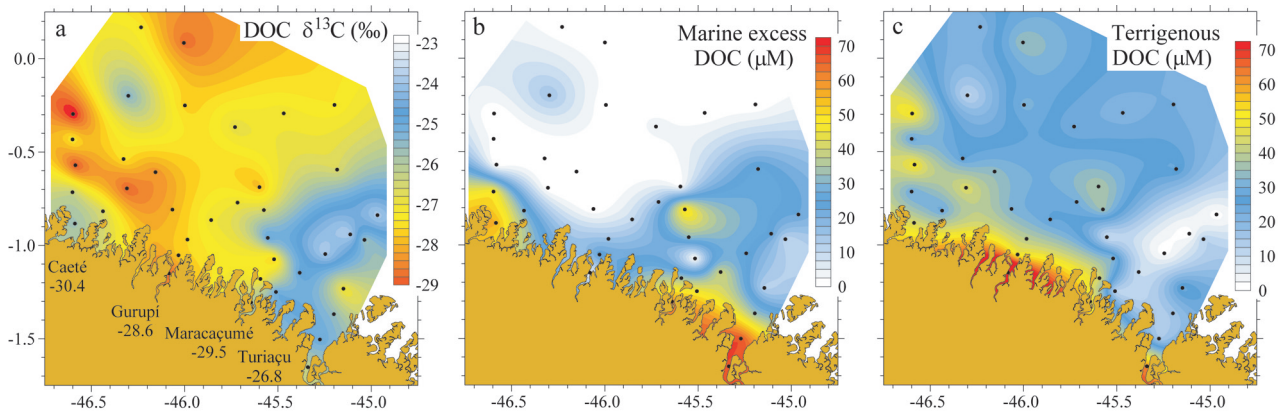

Figure 3. Stable carbon-isotope ratios ($\delta^{13}C$, ‰) of dissolved organic carbon (DOC) and DOC concentrations (μM) split into the different sources on the North Brazilian shelf. Marine excess DOC is algal-derived DOC that exceeds the marine background, and terrigenous DOC is mainly derived from mangroves. The proportion of the different sources to total DOC was estimated from $\delta^{13}C$ values.

basis of this correlation, the theoretical concentration of DOC in freshwater can be estimated from the intercept, assuming conservative mixing of only marine and riverine sources. This calculation results in a theoretical freshwater DOC concentration of 1900 ± 300 μM, which is almost an order of magnitude higher than the concentrations we actually measured in all adjacent rivers and the values published for the Amazon River [*Moreira-Turcq et al.*, 2003]. Since riverine inputs cannot explain the inverse correlation between salinity and DOC concentrations on the shelf, the main source of terrigenous DOC to the shelf must be brackish mangrove waters. Rivers are only a minor DOC source to the shelf southeast of the Amazon Estuary, although only ~5% of the fluvial catchment areas in this region are covered by mangroves.

[14] The contribution of mangrove DOC to the marine DOC pool can be calculated from $\delta^{13}C$ values, using a simple two-source mixing model. For the mangrove end-member, we used a $\delta^{13}C$ value of −31.4‰ and for the marine end-member −23.7‰. Isotopic fractionations on the shelf, which might introduce errors in the mixing model, are assumed to be small, because we used photodegraded, refractory DOM as a reference for mangrove DOM. All samples and end-members (including rivers, mangrove and ocean end-member) were prepared and analyzed in exactly the same way in order to avoid artifacts. The calculated marine DOC concentration was corrected for the marine background (~50 μM) to illustrate the actual in situ marine production of DOC [*Carlson*, 2002]. The concentration of the marine "excess" DOC, i.e., DOC derived from algae production on the shelf and in the coastal zone, decreased sharply from >60 μM in the vicinity of the mangroves to values close to zero on the shelf (Figure 3). Excess DOC-concentrations correlated significantly with phosphate concentrations (Figure 2; $P < 0.001$). The primary source of phosphate on the shelf is coastal outwelling and rivers. The correlation between phosphate and excess DOC indicates a local source of "excess" DOC rather than advection from the open ocean. Very low chlorophyll *a* concentrations (<0.05 mg m^{-3}) and very low nitrate concentrations (<0.1 μM) on the outer shelf corroborate these findings.

[15] In contrast to marine DOC, terrigenous DOC was more homogenously distributed on the shelf and did not exhibit sharp gradients (Figure 3), with the exception of some patches of elevated terrigenous DOC concentrations, which were probably outwelling plumes from the mangroves. The average terrigenous DOC concentration was 60 ± 20 μM in the estuaries and decreased to 26 ± 5 μM on the shelf, of which at least 21 μM were mangrove-derived (estimated from salinity). Even at the outermost stations, where intrusion of Amazon River water could not be totally excluded, the terrigenous DOC concentration exceeded the estimated riverine DOC concentration by at least a factor two. Mangrove-derived DOM is therefore a main source of DOC on the North Brazilian shelf. The high offshore concentration of mangrove-derived DOC and the lack of a distinct gradient from nearshore to offshore are most intriguing features, because they imply that mangrove-derived DOC is transported faster offshore than it is removed from the water column. Our flux measurements (see below) indicate complete turnover of shelf waters on the timescale of 1 year. Consequently, a major fraction of mangrove-derived DOM seems to be refractory. This finding was further corroborated by our degradation experiments.

[16] In order to simulate modifications occurring within the water column during outwelling, mangrove DOM from three independent pore water samples (n = 3) was exposed to natural sunlight and an estuarine microbial community. During the photodegradation experiments, the DOC concentration decreased asymptotically to 71 ± 8% of its initial value, and to 61 ± 9% during the subsequent biodegradation (Figure 4). Original (nonphotodegraded) DOM was more resistant to biodegradation than photodegraded DOM. The optical properties changed dramatically during photodegradation. The color of the sample was initially like black tea. The color almost completely disappeared after 2–4 days of sunlight exposure and the carbon-normalized UV absorption was significantly reduced.

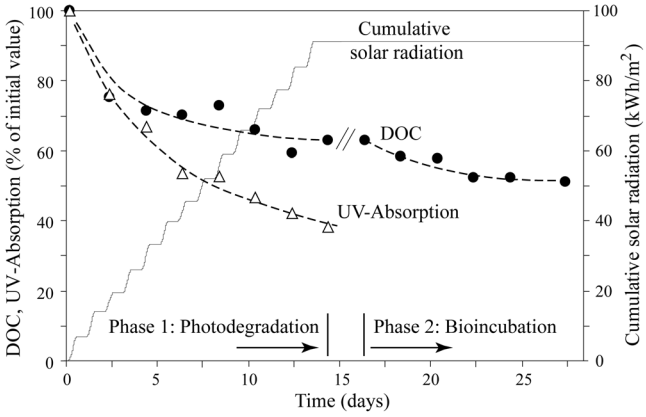

Figure 4. A two-phase degradation experiment of a mangrove pore water sample. Phase 1 is photodegradation of sterile-filtered DOM with natural sunlight. Phase 2 is dark incubation of photodegraded DOM with an estuarine microbial community. Dissolved organic carbon (DOC) concentrations and UV-absorption (250 nm) are normalized to initial values (%); solar radiation is expressed as cumulative energy (kWh/m^2).

[17] The change in DOC concentration and optical properties is reflected in the change in chemical characteristics. High-resolution nuclear magnetic resonance spectroscopy (^{1}H NMR) showed almost complete degradation of aromatic compounds and significant decrease of carboxylic acids (''functionalized aliphatics'') during photodegradation (Table 1). The observed alterations of the chemical signature induced by exposure to natural sunlight show a striking similarity with chemical changes from nearshore to offshore (Table 1). It can be concluded that a major part of terrigenous DOM on the shelf is photo-bleached mangrove-derived organic matter. This DOM is refractory to further microbial and photochemical degradation and may be distributed worldwide through ocean currents. The destruction of aromatic structures during photodegradation makes it difficult to trace terrigenous, including mangrove-derived, DOM through the global conveyor belt into the deep ocean basins. The most established tracer techniques for terrigenous DOM (UV-absorption, fluorescence and molecular lignin-phenol analyses) are based on detection of photo-sensitive compound classes and may thus underestimate the concentration of photochemically modified terrigenous material.

[18] To allow comparison with other mangrove and terrestrial ecosystems, we calculated the area-normalized discharge of mangrove-derived refractory DOC. The concentrations of mangrove-derived DOC on the North Brazilian shelf were estimated to be >21 μM on average (see above). The mean transport of water over the continental shelf via the North Brazil Current was 0.18 ± 0.04 Sv (1 Sv = 10^6 m^{3}s^{-1}) during our study. This flux consisted mainly of water input from outer shelf areas [*Johns et al.*, 1998], which is mixed on the shelf by tidal and wind forces. We calculated the corresponding export of mangrove-derived DOC to be >1.2 × 10^{11} mol C per year from the considered shelf. This estimate probably represents a lower limit, because higher water transport was observed in longer-term oceanographic studies in adjacent shelf areas [*Johns et al.*, 1998]. The extent of DOC outwelling to the ocean becomes more evident when normalized to the drainage area. About 12 mol DOC were exported per m^2 mangrove and year, exceeding the area-normalized export from the drainage basins of the Amazon or any other major river in the world [*Spitzy and Leenheer*, 1991] by at least 1 order of magnitude.

[19] In order to identify the mangrove's impact on global biogeochemical cycles we sought to establish a baseline for DOC outwelling and extrapolate our results on a global basis. Our research area represents approximately 6% of the global mangroves. In comparing our results with previous studies we confront two major difficulties. (1) All earlier estimates were based on areas of a few km^2 or less and reflect the intrinsic heterogeneity of mangroves and the uncertainties of flux estimates in tidal systems. We largely reduced these restrictions by integrating the impact of ~10,000 km^2 of mangroves. (2) Litter and detritus that flush out of the mangroves are rapidly decomposed inshore and nearshore, releasing soluble compounds to the water column [*Wafar et al.*, 1997]. All previous studies were performed within the mangrove forests, therefore not considering DOC released from detritus and leaves in the nearshore water column.

[20] To circumvent these issues we estimated the global DOC export from mangroves via an independent approach. The most comprehensive review on litter fluxes in mangroves to date [*Jennerjahn and Ittekkot*, 2002] concludes that the global annual average for litter fall in mangroves is ~38.3 mol C m^{-2} yr^{-1}. For this estimate, data from mangroves in Asia, Oceania, and South and North America were integrated. Within the first weeks of litter diagenesis, >75% of organic carbon can be lost [*Dittmar and Lara*,

Table 1. Molecular Transformation of Dissolved Organic Matter During Outwelling From Mangroves Offshore, and Transformations Induced by Sunlight[a]

	Proportion of Hydrogen in Structural Groups, %				
Assignment	Mangrove DOM	Estuarine DOM	Nearshore DOM	Offshore DOM	Photodegraded Mangrove DOM
Aromatics	7.5	4.3	4.0	1.1	2.3
Acetal	3.8	2.2	2.1	1.4	1.6
Carbohydrates	20.8	17.7	13.8	12.0	10.4
Functionalized aliphatics	31.8	24.1	22.6	18.9	16.5
Aliphatics	36.1	51.7	57.5	66.6	69.2

[a]Characteristic alterations that were experimentally induced by photodegradation resemble natural changes from inshore to offshore. Structural groups were assigned to chemical shift ranges [*Hertkorn et al.*, 2002] from liquid-state high-resolution proton nuclear magnetic resonance spectroscopy (^{1}H NMR).

2001c], most of it to the dissolved pool [*Benner et al.*, 1990]. *Wafar et al.* [1997] estimated that ~60% of litter fall is ultimately transformed into DOM. Approximately half of the released DOC is labile to microbial degradation [*Wafar et al.*, 1997]. By combining this information, we conclude that ~11.5 mol C m^{-2} yr^{-1} of DOC, which is not easily degradable, is exported from mangroves. This value, that includes DOC flushing out of the sediments as well as DOC that is released from detritus and leaves in the water column, is in good agreement with our direct estimates from northern Brazil (12 mol C m^{-2} yr^{-1}).

[21] Previous small-scale studies, where DOC release from litter was not included, yielded lower fluxes. DOC export from a north Brazilian mangrove tidal-creek [*Dittmar and Lara*, 2001a] was estimated to be 4.0 mol C m^{-2} yr^{-1}. A Florida mangrove area [*Twilley*, 1985] exported 3.1–3.7 mol C m^{-2} yr^{-1}, and a mangrove tidal creek in Australia [*Ayukai et al.*, 1998] exported 1.8 mol C m^{-2} yr^{-1}. The amount of DOC-outwelling from an adjacent Australian mangrove is unclear [*Boto and Wellington*, 1988; *Ayukai et al.*, 1998]. Significant outwelling of DOC is also reported for Malaysian mangroves [*Nixon et al.*, 1984]. This general agreement confirms our assumption that DOM outwelling is a general feature of most mangroves, largely independent of their location, and that litter export is an important factor for DOM fluxes. Mangroves in Africa, where no data on DOM outwelling are available, probably behave similar to mangroves in America, Australia, and Southeast Asia.

[22] We obtained the global DOC flux from mangroves to the ocean by multiplying the results from our two independent area-normalized estimates with the surface area globally covered by mangroves: DOC export from mangroves is approximately 2.2×10^{12} mol C yr^{-1} which is similar to the annual Amazon River discharge. Mangroves cover<0.1% of the continents, but they probably account for >10% of the DOC globally transported from the continents to the ocean.

[23] Since mangroves play a major role for the DOM exchange between continents and oceans, their rapid decline over the recent decades [*Valiela et al.*, 2001] may already have reduced the flux of terrigenous DOM to the ocean, impacting one of the largest organic carbon pools on Earth. The potential consequences of this observation on global element cycles and climate place an enormous responsibility on society to preserve these environments.

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