

Biogeochemistry of the Dumai River estuary, Sumatra, Indonesia, a tropical black-water river

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Abstract

The biogeochemistry of the Dumai River estuary in eastern Sumatra, Indonesia, was studied in order to obtain information on the sources, transformation, and fate of organic matter. Between October and December 2003, water, total suspended matter (TSM), and sediments were sampled along a salinity gradient during four campaigns, and plants and soils were collected from the catchment. Water samples were analyzed for dissolved inorganic nutrients and dissolved organic carbon (DOC). The concentrations of organic carbon (C_{org}) and total nitrogen (N) and the stable carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotope distributions were determined in TSM, sediments, plants, and soils. The pH as well as the concentrations of dissolved inorganic nutrients and TSM were very low in the river and increased toward the sea. A maximum DOC concentration of $5,050 \mu\text{mol L}^{-1}$ was measured in the river, and concentrations decreased toward the sea. Low-gradient relief and a dense vegetation cover, and hence little weathering and erosion, appear to be responsible for low river loads of dissolved nutrients and TSM in this black-water river. Leaching from extensive peat soils in its catchment may account for the high DOC content of the Dumai River. Peat swamps drained by numerous small rivers are estimated to cover $3.3 \times 10^4 \text{ km}^2$ in eastern Sumatra, suggesting that leaching of DOC may be a significant source of carbon to the adjacent coastal seas. A comparison with “normal” rivers shows that black-water rivers can export similar amounts of DOC from catchments that are orders of magnitude smaller. Thus, export from small black-water rivers may be quantitatively more significant for the global DOC input into the ocean than previously thought.

Tropical rivers contribute about 60% of water, sediment, and organic carbon input into the ocean. Indonesia is among the regions with maximum weathering and erosion rates, and hence maximum dissolved and particulate river fluxes, on Earth (Ludwig et al. 1996; Gaillardet et al. 1999; Syvitski et al. 2005). However, as yet, little attention has been paid to the leaching of dissolved organic matter from lowland peat soils in the tropics. The Indonesian island of Sumatra has both high mountains and steep gradients with high weathering and erosion rates along its western coast and lowlands covered by extensive peat swamps with low weathering and erosion rates on its eastern side. On the one hand, tropical peatlands are one of the largest terrestrial carbon stores, but on the other hand, they export more organic carbon per unit area than any other significant biogeographical land type in the world (Freeman et al. 2001a; Page et al. 2002). In many cases, peatlands are drained by so-called black-water rivers. These dark-colored

rivers are characterized by a low pH, low concentrations of dissolved inorganic nutrients and suspended sediments, and high amounts of dissolved organic carbon (DOC) (e.g., Vegas-Vilarrubia and Rull 1988). The almost exclusively organic nature of the soil and low mineral content are responsible for the acidic character and low suspended load. The South American Rio Negro and Caroni are the most prominent examples of this river type. They are tributaries of two of the largest rivers in the world, the Amazon and Orinoco. Mostly, black-water rivers are small streams that have been considered quantitatively insignificant for carbon input into the ocean. However, it has been suggested that the release of DOC from peatlands may change dramatically during times of global warming and changes in moisture distribution (Freeman et al. 2001a; Tranvik and Jansson 2002). It is conceivable that black-water rivers are more important for carbon cycling than previously thought. With regard to this, the existing knowledge on the biogeochemistry of black-water rivers is astoundingly small.

Here, we present results of a biogeochemical study carried out in the Dumai River estuary, Sumatra, Indonesia. It is a small black-water river that drains the vast lowland peat soils of eastern Sumatra. The biogeochemical characteristics of the Dumai River are compared to those of other black-water rivers, and the role of the latter for DOC export into the ocean is examined.

Materials and methods

Study area—The Dumai River is located in the province of Riau on the Indonesian island of Sumatra (Fig. 1). It is

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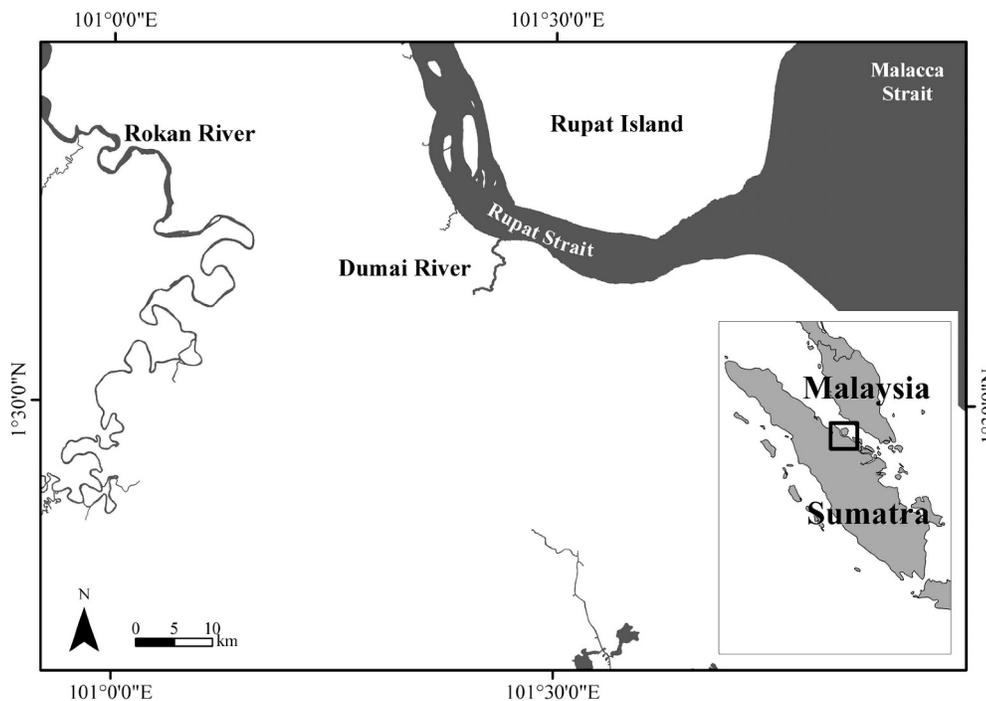


Fig. 1. Map of the investigated area in the province of Riau, Sumatra, Indonesia.

a lowland river with low steepness and has an approximate length of 12 km and average depth of 6 m. Tropical peat swamp and lowland forest form the major vegetation in the river catchment. Small patches of land near the coast are used for agriculture, the major part of which is used for the cultivation of rice and coconut palms. The estuary is fringed by a mangrove forest. The major soil type in the catchment is tropical forest peat (Laumonier 1997). Consequently, the river's water is dark brown to black. The Dumai River flows through the city of Dumai and discharges into Rupert Strait, the passage between the islands of Sumatra and Rupert. It is strongly influenced by the tides, the amplitude of which varies between 0.5 m and 3 m between neap and spring tide (mesotidal range). Climate of the region is governed by the monsoons. Due to its equatorial position, seasonality is weak. The annual average precipitation in Dumai is 2,500 mm, and the major rainy periods occur between March and May and September and November (Fig. 2).

Sampling—Four sampling campaigns were carried out in the Dumai River and its estuary between October and December 2003. Sampling stations were distributed along a salinity gradient from zero salinity at spring high tide at steps of ~ 5 units toward the sea.

The Dumai River estuary was sampled for water, suspended matter, and sediments. Plants and soils of the potential terrestrial organic matter sources were also sampled, i.e., mangrove, rice fields, *Nypa* palms. Water was filtered through precombusted (10 h, 450°C) Whatman GF/F filters. Filters, sediments, plants, and soil samples were dried at 50°C. For DOC analysis, 10 mL of water was filtered into precombusted (4 h, 450°C) glass ampoules, acidified to pH 2 with 1 mol L⁻¹ HCl, and then sealed. For

analysis of dissolved inorganic nutrients, 25 mL of filtered water was preserved with HgCl₂ (20 g L⁻¹) and kept frozen in polyethylene vials. Surface sediment samples from the estuary were collected during the first sampling campaign with a simple self-made grab.

Physicochemical and current velocity measurements—Conductivity, dissolved oxygen (DO), temperature, and pH were measured using WTW LF196, WTW Oxi96, and Knick 913XPH meters, respectively. Water depth was measured with a handheld echosounder (Plastimo Echotest II). Current velocity was determined using an Ekman style 231WA300 GEMWARE current meter. The following formula was used to calculate current velocity: $V =$

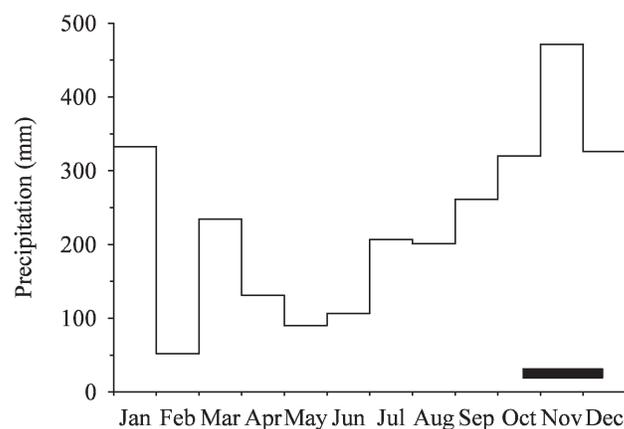


Fig. 2. Average monthly precipitation at CALTEX Meteorological Station, Dumai airport, in 2003. The black bar denotes the sampling period from 13 October to 15 December 2003.

$0.257N + 0.0039$, where V is current velocity (m s^{-1}), and N is the number of propeller revolutions per second.

Analyses—Dissolved inorganic nutrients (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , and $\text{Si}[\text{OH}]_4^-$) were determined using a Skalar-SAN-plus continuous-flow autoanalyzer and detected spectrophotometrically as a colored complex (Grasshoff et al. 1999). To correct for the water color, absorption of the samples was measured without chemicals first, and the values were subtracted from those obtained with chemicals. Precision of the method was better than 3.4%, and all nutrient concentrations were near the detection limit. DOC was measured by high-temperature catalytic oxidation (680°C) with a Dohrmann Rosemount DC-190 instrument equipped with a standard catalyst that consisted of Al_2O_3 particles with 0.5% Pt (Skoog et al. 1997). Precision of the method was better than 1%.

Soils, sediments, and plant samples were crushed and homogenized in an agate mortar and pestle prior to analysis. Total carbon, C_{org} , and total N analyses were carried out by high-temperature oxidation in a Carlo Erba NA 2100 elemental analyzer (Verardo et al. 1990). C_{org} was determined similarly after removal of carbonate by acidification with 1 mol L^{-1} HCl and subsequent drying at 40°C . Inorganic carbon was calculated by subtraction of organic carbon from total carbon. Precision of the method was better than 4.5% for carbon and better than 8% for nitrogen. $\delta^{15}\text{N}$ was determined in a Finnigan Delta Plus gas-isotope-ratio mass spectrometer after high-temperature combustion in a Flash 1112 EA elemental analyzer. $\delta^{15}\text{N}$ is given as ‰ deviation from the nitrogen isotope composition of atmospheric air. $\delta^{13}\text{C}_{\text{org}}$ was determined similarly after removal of carbonate by adding 1 mol L^{-1} HCl and subsequent drying at 40°C . $\delta^{13}\text{C}_{\text{org}}$ is given as ‰ deviation from the carbon isotope composition of the Peedee belemnite (PDB) standard. The standard deviation of replicate measurements was 0.2‰.

Discharge calculation—Cross-sectional area of the river was calculated from measurements of its width and depth with a handheld echosounder along the cross-sectional river profile. River discharge (Q) was then calculated from current velocity (CV) and cross-sectional area (CSA) using the formula: $Q (\text{m}^3 \text{ s}^{-1}) = CV (\text{m s}^{-1}) \times CSA (\text{m}^2)$. Discharge measurements were not corrected for tidal currents. However, the tidal component should be small because discharge measurements were performed during slack high tide.

Results

The results of the physicochemical measurements and biogeochemical analysis conducted along a salinity gradient displayed little temporal variation over the four sampling campaigns.

Physicochemical data, dissolved nutrients, and DOC—Water temperature ranged between 27.9°C and 32.0°C and generally displayed a slight increase toward the sea. The pH displayed a strong gradient, from a minimum of 4.0 at zero

salinity to a maximum of 8.7 at the seawater end. From river to sea, nitrate increased from $<0.5 \mu\text{mol L}^{-1}$ to $\sim 4.5 \mu\text{mol L}^{-1}$, phosphate decreased from a maximum of $3.2 \mu\text{mol L}^{-1}$ to $0.5 \mu\text{mol L}^{-1}$, and silicate increased from $0.5 \mu\text{mol L}^{-1}$ to $25.8 \mu\text{mol L}^{-1}$ (Fig. 3). Nitrite was not detectable, and ammonium, with a maximum of $0.7 \mu\text{mol L}^{-1}$ in the river, decreased toward the sea. In a similar manner, DO concentration and saturation increased from minimum values of 1.9 mg L^{-1} and 23.9% to 7.0 mg L^{-1} and 98.0%, respectively, while DOC decreased from $5,050 \mu\text{mol L}^{-1}$ to $600 \mu\text{mol L}^{-1}$ from river to sea (Fig. 4).

Suspended matter concentration and its biogeochemical composition—The concentration of total suspended matter (TSM) varied between 5.3 mg L^{-1} and 6.8 mg L^{-1} at zero salinity and did not display any trend with salinity (Table 1). Maximum TSM concentration was observed in the salinity range between 10 and 20 and, in particular, during the first sampling campaign at spring tide, during which a maximum tidal amplitude of 2.5 m was recorded between high and low tide. Maximum C_{org} and N ranged between 9.0% and 12.2% and 0.8% and 1.2% of TSM, respectively, at zero salinity and decreased drastically toward the sea. $\delta^{13}\text{C}_{\text{org}}$ varied between -28.7‰ and -27.4‰ in the river and increased moderately toward the sea. $\delta^{15}\text{N}$ varied between 0.7‰ and 7.3‰ and did not display any trend with salinity except for a narrowing of the range from river to sea.

Biogeochemical composition of sediments, plants, and soils—In sediments, maximum concentrations of C_{org} and N of 11.2% and 0.3%, respectively, were measured at Sta. 1 in the river. Seaward, C_{org} varied between 1.2% and 5.0%, and N varied between $<0.1\%$ and 0.3% without displaying any trend. $\delta^{13}\text{C}_{\text{org}}$ ranged between -29.6‰ and -27.2‰ , and $\delta^{15}\text{N}$ ranged between 2.4‰ and 4.7‰, which is in the range of the plants and soils that form the major part of the land cover/use (Table 1).

Discussion

The very low pH, low concentrations of dissolved nutrients and TSM, and the high DOC content qualify the Dumai River as a typical black-water river. The sources and fate of the dissolved and particulate river loads are discussed below.

Sources and fate of suspended and sedimentary organic matter—The SE Asian/western Pacific region is generally characterized by high weathering and erosion rates and hence high river loads of suspended sediments (e.g., Milliman and Meade 1983; Gaillardet et al. 1999; Milliman et al. 1999). When compared to those, however, weathering and erosion are minimal in the Dumai River catchment due to the low gradient, low river discharge, and the large surface covered by peatlands, which results in the observed low TSM concentration in the Dumai River. Despite a slight increase of $\delta^{13}\text{C}_{\text{org}}$ toward the sea, which points to a small contribution of marine organic matter (OM), suspended particulate OM appears to originate

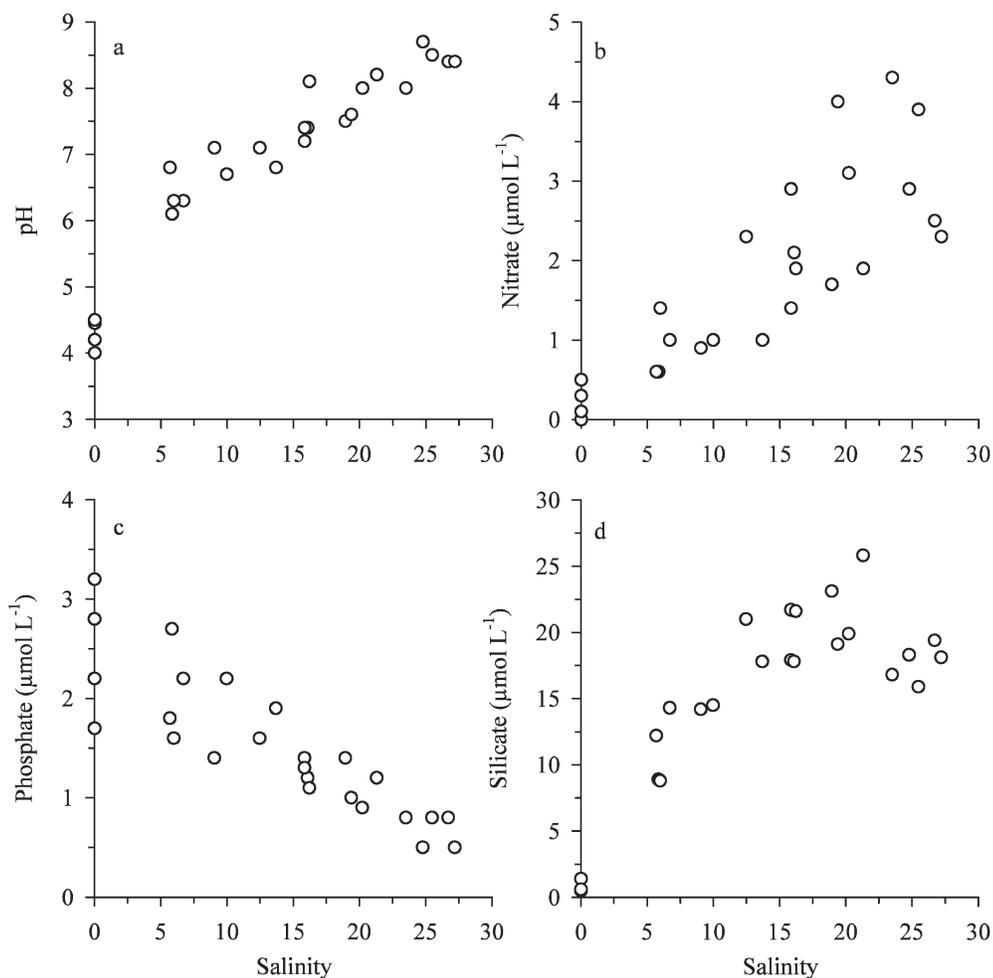


Fig. 3. The (A) pH, (B) dissolved nitrate, (C) dissolved phosphate, and (D) dissolved silicate concentrations vs. salinity in the Dumai River estuary.

mainly from the surrounding vegetation and soils, as indicated by a C:N ratio basically between 10 and 20 and a $\delta^{13}\text{C}_{\text{org}}$ value between -29% and -27% . While $\delta^{13}\text{C}_{\text{org}}$ values of sediments and TSM fall within the same range,

the C:N ratio of sediments is higher by a factor of two over that of TSM (Table 1). Preferential decomposition of labile nitrogenous OM compounds, such as amino acids, for example, may be responsible for the high C:N ratio (e.g.,

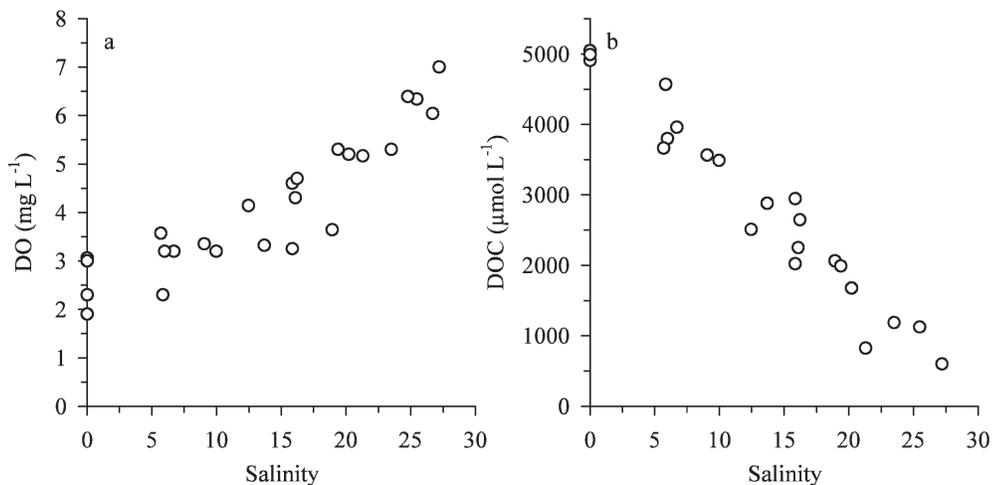


Fig. 4. Concentrations of (A) DO and (B) DOC vs. salinity in the Dumai River estuary.

Table 1. Biogeochemical characteristics of TSM and sediments from the Dumai River estuary and plants and soils from the river catchment. Data for TSM and sediments displayed here are from samples obtained during the first sampling campaign. Coordinates of stas. 1–7: 101°25.909'E, 01°40.260'N; 101°25.777'E, 01°40.504'N; 101°25.844'E, 01°40.609'N; 101°25.891'E, 01°40.640'N; 101°26.121'E, 01°40.798'N; 101°26.130'E, 01°40.814'N; 101°26.074'E, 01°40.930'N.

Sample	Salinity (mg L ⁻¹)	TSM (%)	N (%)	C _{org} (%)	C:N	δ ¹³ C _{org} (‰)	δ ¹⁵ N (‰)
TSM							
Sta. 1	0.0	5.9	0.9	10.9	12.1	-28.7	0.7
Sta. 2	6.7	74.2	0.3	3.8	12.7	-28.0	2.5
Sta. 3	13.7	164.5	0.2	3.1	15.5	-28.0	5.1
Sta. 4	15.8	209.2	0.2	2.9	14.5	-28.0	6.2
Sta. 5	18.9	136.7	0.1	2.4	24.0	-28.0	5.1
Sta. 6	21.3	81.8	0.1	2.1	21.0	-27.7	4.1
Sta. 7	26.7	88.0	0.1	2.7	27.0	-27.8	5.2
Sediments							
Sta. 1	0.0		0.3	11.2	37.3	-29.5	3.0
Sta. 2	6.7		0.2	4.6	27.9	-27.8	2.5
Sta. 3	13.7		0.0	1.4	33.0	-27.4	4.4
Sta. 4	15.8		0.1	4.2	32.1	-28.2	2.4
Sta. 5	18.9		0.0	1.3	30.6	-27.5	4.7
Sta. 6	21.3		0.1	5.0	39.2	-29.6	3.1
Sta. 7	26.7		0.1	1.2	24.4	-27.2	4.5
Plants and soils							
Mangrove leaf (green)			1.3	44.3	34.1	-27.5	2.9
Mangrove leaf (fallen)			0.7	43.5	64.6	-27.9	3.9
Rice plant			2.0	38.9	19.9	-29.0	7.9
<i>Nypa</i> fruit			1.4	44.3	31.2	-26.2	4.1
<i>Nypa</i> leaf			1.2	44.8	38.6	-26.7	0.7
Rice soil			0.1	1.8	34.3	-23.9	4.3
Mangrove soil			0.1	3.5	19.4	-27.8	3.4

Jennerjahn and Ittekkot 1999). It indicates that sedimentary OM has undergone severe degradation. δ¹⁵N is almost similar in TSM and sediments and falls in the range of the potential terrestrial sources (Table 1). It is also similar to the δ¹⁵N of TSM and sediments from the Brantas River, a river on the Indonesian island of Java that has a high load of suspended sediments mainly originating from agricultural soils (Jennerjahn et al. 2004). The relatively high TSM concentration in the estuarine mixing zone of the Dumai River appears to result almost exclusively from resuspension. The low C_{org} content of TSM there is probably a mixture of recycled sedimentary OM with minor contributions of freshly produced autochthonous OM.

Sources and fate of dissolved nutrients and DOC—Extremely low nutrient concentrations as a result of low weathering and erosion are a typical feature of black-water rivers. Salinity-related gradients of pH and nutrients indicate that conservative mixing is a major determinant of the observed distribution patterns in the Dumai River estuary.

Ocean-derived nitrate appears to be the source for the very low autochthonous estuarine OM production. Phosphate concentration in the Dumai River is in the same range as in the Brantas River and in other mangrove creeks and estuaries (e.g., Alongi et al. 1992; Dittmar and Lara 2001; Jennerjahn et al. 2004). In contrast to nitrate, phosphate decreases from maximum values in the river with increasing salinity toward the sea (Fig. 3). Sulfate reduction in the suboxic or anoxic peat swamps may have bound iron in sulfides that originally were bound in iron-phosphorus compounds. This mechanism has been observed in freshwater wetlands (e.g., Lucassen et al. 2004). The maximum phosphate and minimum DO content of river water at zero salinity indicates that phosphate may have been released from the peat swamps by this mechanism.

The extremely high DOC concentration of >5,000 μmol L⁻¹ in the dark-colored water of the Dumai River is the highest measured in world rivers so far (e.g., Degens et al. 1991; Table 2). Physicochemical characteristics of the high-DOC water are important factors for the production and decomposition of OM. Leaching from litter and peat soils is the major source of dissolved organic matter (DOM) in the Dumai River. In general, carbohydrates and amino acids are major labile compounds of DOM, while humic and fulvic substances make up the more refractory portion (Schlesinger 1991). The humic and fulvic substances on average make up 60–80% of riverine DOM, and the maximum portions are found in black-water rivers and swamps (Moran and Hodson 1990; Leff and Meyer 1991; Spitzy and Leenheer 1991). High concentrations of phenolic compounds usually found in peatlands inhibit biodegradation by reducing activity of biodegradative hydrolase enzymes. This is of particular importance under anoxic conditions. Activity of the enzyme phenol oxidase, which requires bimolecular oxygen, is severely constrained under anoxic conditions. Therefore, the lack of oxygen prevents phenol oxidase from eliminating phenolic compounds, which, in turn, reduces biodegradation of OM substantially (Wetzel 1992; Vuorinen and Saharinen 1996; Freeman et al. 2001b). These processes in combination with the low river discharge may explain the extremely high DOC concentration in the vicinity of this anoxic peat swamp forest, which is inundated during most times of the year.

In the river, maximum DOC concentrations coincide with minimum DO concentration and saturation of 2–3 mg L⁻¹ and of 20–40%, respectively. Physical mixing of river and seawater appears to be a major factor for the decrease of DOC and increase of DO toward the sea. However, a nonlinear relationship between these indicates that the decrease of DOC cannot be explained solely with conservative mixing. A statistically significant relationship (exponential decay) suggests DOM degradation in the estuary (Fig. 5). The tidal input of bimolecular oxygen may have activated phenol oxidase to eliminate phenolic compounds, which, in turn, may have resulted in degradation of the DOM leached from the anoxic peat swamps. Biodegradability of vegetation- and soil-derived DOC has been demonstrated in a tropical wet forest in Costa Rica. DOC concentrations of up to 13 mg L⁻¹ were measured in throughfall (rainwater falling through tree canopy), litter

Table 2. Biogeochemical characteristics of black-water rivers. References: *, this study; 1, Baum et al. (2007); 2, Valentine and Zepp (1993); 3, Leff and Meyer (1991); 4, Vegas-Vilarrubia and Rull (1988); 5, Castillo et al. (2004); 6, Richey et al. (1990); 7, Hastenrath et al. (1999). DIN, dissolved inorganic nitrogen; #, nitrate only.

River	pH	DOC ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	DIN ($\mu\text{mol L}^{-1}$)	Ref.
Dumai, Sumatra, Indonesia (averages at Sta. 1)	4.3	4,983	0.7	1.7–3.2	1.0	*
Siak, Sumatra, Indonesia	5.2–7.8	554–2,594	1.6–89.1	0.2–36.7	7.9–67.9	1
Mandau (tributary of Siak)	4.4–4.9	1,939–3,568	2.9–49.9	0.6–15.4	5.8–28.1	1
Suwannee, Georgia, USA	5.5–6.5	3,920				2
Ogeechee, Georgia, USA		417–1,667				3
Orinoco tributaries						
San Jaime	4.6	783	1.4			4
Cauo Buja	5.2	792	3.6			4
Caroni	5.1	442	6.1			4
Autana, Venezuela	4.7	658		<0.1	2.9#	4, 5
Sipapo	4.9	542	4.1	0.1	2.6#	4, 5
Atabapo	4.0	450	3.4			4
Chola	3.8	625	5.3			4
Loro	3.7	633	5.9			4
Darigua	3.7	675	4.9			4
Uniabo	3.7	617	5.1			4
Negro	3.9	633	7.2			4
Guiania	3.9	600	5.2			4
Amazon tributary						
Rio Negro	4.6	542–883	57.0			6, 7

leachate, and soil solution, of which 23–46% was biodegraded within 7 d. There, the soil solution had a range of 41–46% and displayed the maximum biodegradable fraction of DOC (Schwendenmann and Veldkamp 2005). In the Dumai River estuary, the DOC concentration at the seaward end was still in the range of $600 \mu\text{mol L}^{-1}$ despite substantial degradation. This is much higher than in numerous rivers from all climatic zones around the world (e.g., Ludwig et al. 1996).

Relevance of black-water rivers for DOC export to the ocean—Information on the biogeochemistry of black-water rivers is scarce, and so their possible quantitative significance for the oceanic DOC budget is as yet unexplored. For this purpose, we calculated DOC export for the Dumai River and the few other black-water rivers for which the respective information was available from the literature. Our budget relied on simple short-term discharge calculations without correction for the tidal current. Due to these constraints, our calculated DOC export may be an overestimate. We measured a discharge of $16 \text{ m}^3 \text{ s}^{-1}$, which results in an annual total of $0.5 \text{ km}^3 \text{ yr}^{-1}$. Multiplied by the mean concentration of 59.8 mg L^{-1} , DOC export from the Dumai River is estimated to be $30.2 \times 10^6 \text{ kg yr}^{-1}$. Even though this may be an overestimate, its total export is very low on a global scale, even when compared to other black-water rivers.

Two examples from South America highlight the relative significance of black-water rivers for fluvial DOC input into the oceans. The Rio Negro and Caroni are black-water tributaries of the Amazon and the Orinoco, respectively. While the Rio Negro makes up only 12.2% of the Amazon's

catchment, it contributes 32.3% of its DOC load. Similarly, the Caroni makes up 9.3% of the Orinoco's catchment, but contributes 17.0% of its DOC load (Vegas-Vilarrubia and Rull 1988; Richey et al. 1990; Hastenrath et al. 1999). On a global scale, riverine DOC input into the ocean tends to increase with catchment size (Ludwig et al. 1996). The same appears to hold true for black-water rivers. When compared to "normal" rivers, however, black-water rivers export similar amounts of DOC from catchments that can be

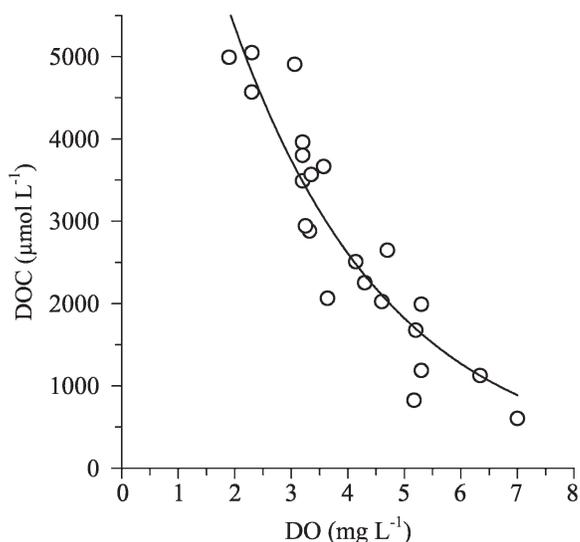


Fig. 5. DOC vs. DO in the Dumai River estuary. $\text{DOC} = 11,016 \times e^{-0.36\text{DO}}$, $r = 0.99$, $n = 22$.

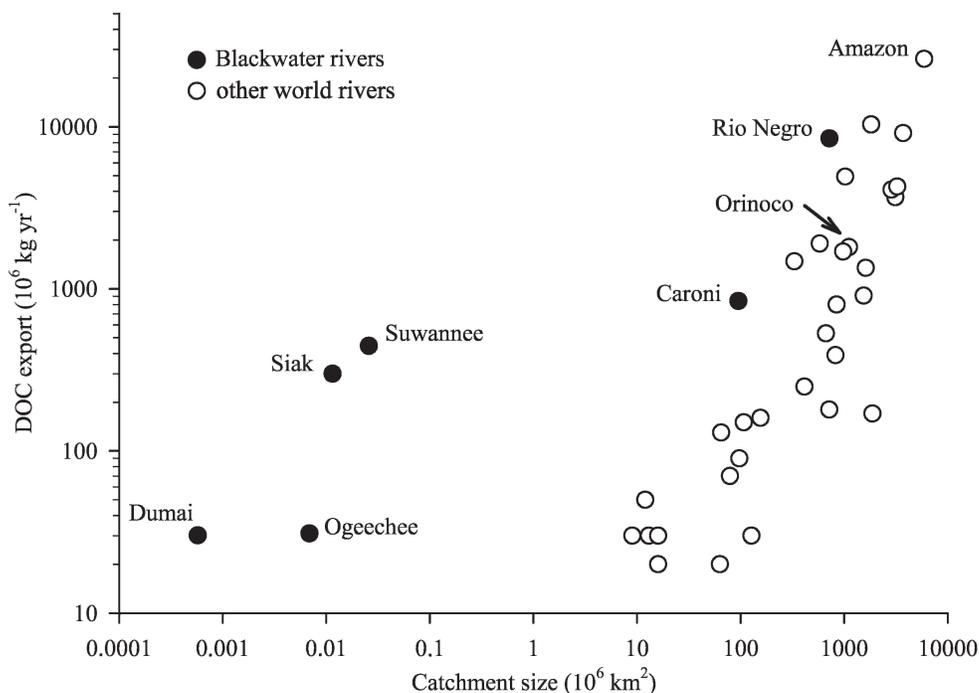


Fig. 6. DOC export vs. catchment size for several black-water rivers and some world rivers. Data are from Vegas-Vilarrubia and Rull (1988), Richey et al. (1990), Leff and Meyer (1991), Valentine and Zepp (1993), Ludwig et al. (1996), Hastenrath et al. (1999), McCallum and Hickey (2001), World Resources Institute (2003), Castillo et al. (2004), and Baum et al. (2007). No official data are available on the catchment size of the Dumai River. The estimate used was derived from a map and therefore has a high uncertainty.

orders of magnitude smaller, particularly in the case of small rivers that drain peatlands (Fig. 6). This indicates that the numerous small black-water rivers that drain the 3.3×10^4 km² of peatlands in eastern Sumatra (Thia-Eng et al. 2000) are very efficient DOC sources for the adjacent coastal sea. On a global scale, it is conceivable that DOC export from black-water rivers is quantitatively more significant than previously thought. This is corroborated by findings of Baum et al. (2007), who estimated the DOC export of Indonesian rivers draining peatlands to be on the order of 17×10^9 kg yr⁻¹, which is about 8% of the global total DOC input into the ocean.

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