JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, G03029, doi:10.1029/2007JG000626, 2008

Spatial and seasonal dynamics of riverine carbon fluxes of the Brantas catchment in East Java

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Received 19 October 2007; revised 6 May 2008; accepted 25 June 2008; published 30 August 2008.

[1] Dissolved and particulate organic and inorganic carbon concentrations and flux were measured from July 2005 to June 2006 in the Brantas River basin, a midsized tropical mountainous river and the second largest in Java. There were large seasonal differences in carbon fluxes. Dissolved inorganic carbon (DIC) fluxes were 9.3 times greater and dissolved organic carbon (DOC) fluxes were 532 times greater in the wet season (October to April) than in the dry season. These large contrasts in concentration lead to large differences in load between dry and wet months. In the wet season between January and April, DIC and DOC fluxes are 66% and 87%, respectively, of the total annual fluxes. Most of the annual fluxes of total suspended solids (2.7 × 106 t a^{-1}), total dissolved solids (2.3 × 106 t a^{-1}), DIC (0.26 × 106 t a^{-1}), and DOC (0.2 × 106 t a^{-1}) are transported into the Madura Strait. Accordingly, the Brantas River ranks number 17 among the top 20 rivers that originate at elevations above 3000 m. The concentration of DIC is consistently high all yearlong due to carbonate weathering in the river basin, except in the middle part of the basin, whereas the concentration of DOC is highly seasonal because of variations in biological activities. The total inorganic carbon concentration substantially exceeded the total organic carbon concentration, but the differences decreased from January to April when DOC increased sharply. The carbon budget indicates that the upstream river is a carbon source, and the middle sections of the river are a carbon sink. No carbon trapping was observed by the several impoundments over the basin while sediment trapping was obvious.

Citation: Aldrian, E., C.-T. A. Chen, S. Adi, Prihartanto, N. Sudiana, and S. P. Nugroho (2008), Spatial and seasonal dynamics of riverine carbon fluxes of the Brantas catchment in East Java, *J. Geophys. Res.*, *113*, G03029, doi:10.1029/2007JG000626.

1. Introduction

[2] The flux of terrestrial carbon from continents to the ocean by river runoff and wetland discharge is an important component of the global organic carbon cycle [*Hedges et al.*, 1992]. For example, an estimated 0.25–0.4 × 10^{15} g of dissolved organic carbon (DOC) is discharged to the oceans by the world's rivers each year [*Meybeck*, 1982; *Chen*, 2004]. Rivers deliver both particulate and dissolved organic matter to coastal regions via estuaries. Erosion and delivery of sediment are a function of river runoff, basin morphology, tectonics, bedrock lithology, basin area and human activities such as damming. Because of their erosive ability, small drainage basin areas, high topographic relief, relatively young and erodible rocks, and heavy tropical rainfall, small mountain rivers that drain the highstanding islands of the East Indies transport a disproportionately large amount of sediment to the ocean. For instance, *Milliman and Syvitski* [1992] showed that small and midsized rivers can carry a sediment load that is one to two orders of magnitude larger than that carried by major river systems. East Indies rivers, according to *Milliman and Syvitski* [1992], may discharge as much as 9 × 10^9 t annually, or about half of the total sediment flux to the ocean. *Milliman and Meade* [1983] had previously estimated that more than 70% of the sediment that enters the oceans come from rivers that drain southern Asia and Oceania, as a result of mountainous terrain, erodible strata often impacted by human activities such as deforestation and agriculture [e.g., *Milliman et al.*, 1987; *Douglas*, 1996], and seasonally heavy rainfall. *Milliman et al.* [1999] estimated that rivers in Java may discharge about 0.33 × 10^9 t a^{-1} of sediment. Interestingly, they also estimated that although small mountainous islands such as Java deliver a small amount of sediment annually, the rough terrain results in sediment yields of three times from that of large islands in the East Indies.

[3] Estimates of the riverine carbon flux to the coast vary greatly in part because of a lack of quantitative estimates

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0148-0227/08/2007JG000626$09.00

from much of the world [*McKee*, 2003]. However, as explained above, small mountainous rivers may be a much more important source of organic carbon to the ocean than previously thought [*Kao and Liu*, 1996, 1997; *Lyons et al.*, 2002; *Blair et al.*, 2003; *Gomez et al.*, 2003; *Komada et al.*, 2004]. The total organic carbon (TOC) flux from small mountainous rivers in Asia-Oceania alone has been estimated to be 21–38% of the total oceanic input [*Schlünz and Schneider*, 2000], but this range is very wide. The TOC flux from rivers to the marine environments is estimated to be about 55% in the dissolved form (DOC) [*Ludwig et al.*, 1996; *Chen*, 2004]. *Baum et al.* [2007] suggested a total Indonesian DOC export of ~21 Tg a^{-1}, representing ~10% of the global riverine DOC input to the ocean. The TOC flux may be greatly affected in the future by changes in the climate [*Tranvik and Jansson*, 2002].

[4] Flowing riverine water constitutes an important link in global biogeochemical cycles. This water transports organic matter from terrestrial sources and generates organic material within aquatic environments [*Hedges et al.*, 2000]. The hydro-meteorological pattern from the rainfall and river hydrology is important to understanding better the biogeochemical processes that occur in the rivers down to the estuary. The Brantas River is one of Indonesia's most important catchments for the "rice bowl" of Java and is important to the nation's industrial activity. Several researchers have assessed the water quality of the Brantas River basin. *Hart et al.* [2001] and *Sudaryanti et al.* [2001] introduced and evaluated the use of the biological assessment of the condition of the Brantas River using the Australian River Assessment System (AUSRIVAS). The Brantas River authority (Perum Jasa Tirta I) has a well-established integrated catchment management system [*Booth et al.*, 2001] that has been used to collect and maintain a long record of hydrometeorological and water-quality data by online monitoring system [*Marini and Weilguni*, 2003]. *Jennerjahn et al.* [2004] established the biogeochemistry at the mouth of the Brantas River, and the Wonokromo and Porong rivers during the dry season and suggested that the fluvial export of dissolved substances over one of the mouths of the Brantas River was larger during the rainy season than at other times of the year. In spite of this, the inner catchment area from upstream to downstream and the spatial and temporal distributions of the sediment and carbon fluxes that contribute to the coastal processes have not yet been established.

[5] The purpose of this study is to establish the spatiotemporal pattern of the sediment and carbon fluxes over the Brantas catchment that could be used for the broader patterns of carbon fluxes in the region. The contribution of the 12 regulated reservoirs and the way in which damming works in a tropical, monsoonal, mountainous midsize river [*Vörösmarty et al.*, 1997; *Chen*, 2002], will also be investigated. This study involves intensive sampling and measurements between July 2005 and June 2006 at sites from upstream to downstream. The spatiotemporal carbon budget is established from dissolved organic carbon, dissolved inorganic carbon, particulate organic carbon and particulate inorganic carbon concentrations, which hereinafter are denoted DOC, DIC, POC and PIC, respectively. To our knowledge, this is the first time seasonal carbonate chemistry and fluxes for any river basin are studied in Indonesia, if not in the entire tropical Southeast Asia.

2. Material and Methods

2.1. Study Area

[6] The Brantas catchment covers about 11050 km^2 or approximately 35% of the area of East Java Province (Figure 1), extending approximately from 111°30′E to 112°45′E and 7°20′S to 8°20′S. The total length of the main river stream is 320 km, which is the second largest in Java. The annual average rainfall reaches 2330 mm (average between 1991 and 2005) and about 80% falls during the rainy months. The total potency of surface water reaches 12 billion m^3, while the total dam capacity in the area of interest is only 2.6–3 billion m^3 annually. Major dams and reservoirs were built in the 1970s and 1980s, mainly for power generation, irrigation and flood control. Twelve dams, the largest of which is the Karang Kates Dam, were built along the mainstream and tributaries of the Brantas River and they have been managed by a special authority; the Perum Jasa Tirta I (PJT I). The number of residents in the Brantas basin was around 13.7 million in 1994 and 15.5 million in 2003 (about 16 million nowadays) or approximately 43.2% of the total population of East Java. The population density over the basin area is about 1.5 times the provincial average. Rapid demographic changes and pressure from the population in the 20th century have altered Java's landscape and ecology. Over the last two decades, the average yearly per capita water consumption has doubled from 400 to 800 m^3, predominantly because of the agricultural sector, which uses about three quarters of the available water. Almost all of the available water is consumed during the dry season. However, nearly 500 industries directly discharge their effluents, contributing a BOD load of approximately 125 t d^{-1} [*Binnie & Partners (Overseas) Ltd*, 1999]. Most discharge comes from the pulp and paper mills and sugarcane processing plants, monosodium-glutamate production, tanneries and dyes, coconut-oil and metal-fabrication industries. Industry is responsible for 80% of the pollution of the river, despite the heavy discharge of domestic waste [*Marini and Weilguni*, 2003]. Other human activities such as deforestation, intensive agriculture (mainly rice cultivation), urban and industrial waste disposal, the formation of levees and sand and limestone minings in the downstream portion, river diversion and the conversion of the estuarine mangroves to aquaculture ponds alter the flow regime and the amount and composition of substances that are transported by the river and discharged into the Madura Strait.

[7] The Brantas River originates near the volcano Arjuno, streams southward, westward, northward and finally diverts into three branches in the coastal lowlands (Figure 1) close to the provincial capital Surabaya. The source of Brantas is surrounded by high mountains, Mt. Kelud, Mt. Arjuna, Mt. Anjasmoro, Mt. Semeru and Mt. Bromo with heights 1731 m, 3339 m, 2277 m, 3675 m and 2392 m, respectively. The first and the last mountains are still active volcanoes. In the middle stream is Mt. Wilis, with a height of 2552 m. On the slopes within the river channels of Mt. Semeru and under a humid climate, erosion rates rank among the

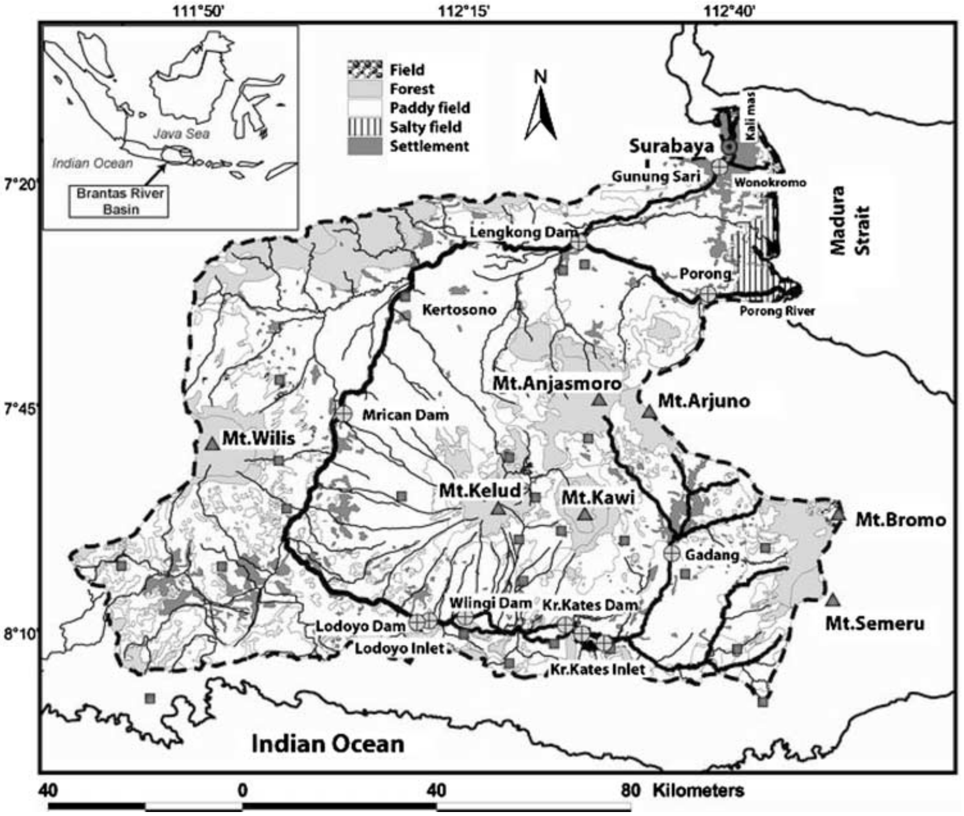

Figure 1. The Brantas River basin in East Java, Indonesia. Rain gauge stations (squares), as well as discharge and carbon sampling stations (crossed circles) are marked.

highest (105–106 $m^3\ km^{-2}\ a^{-1}$) recorded anywhere in the world [*Lavigne*, 2004].

[8] Sediment yields are dominated by rain-triggered lahars, which occur every rainy season extending from October to April in several drainage basins of Mt. Semeru [*Lavigne*, 2004]. The Porong River and the Wonokromo River are the two major branches that divert at approximately 40 km before Surabaya and discharge into the Madura Strait, while the smaller Kali Mas River diverts from the Wonokromo River at about 10 km before Surabaya into the narrowest part of the Madura Strait north of the city after it passes the city. The mouth of Wonokromo River is 30 km north of the Porong River, which is the major branch that transports water and sediment. During the wet season, when almost 80% of the water supplied by the Brantas is diverted to the Porong, its average discharge can be around 600 $m^3\ s^{-1}$, and may rise to 1200 $m^3\ s^{-1}$ in extremely wet years [*Hoekstra et al.*, 1989]. In El Niño years, however, the discharge can be much lower because precipitation is reduced. High sediment loads, particularly in the wet season cause the Porong River to have a strongly prograding delta. During the dry season, most of the flow is mainly diverted to the town of Surabaya and the discharge of the Porong is extremely low [*Hoekstra*, 1989]. The monsoons dominate the climate, such that eastern Java experiences only one wet season from October to April, which is also the period of peak river discharge, which was about 217 $m^3\ s^{-1}$ (1991–1996 annual average [*Jennerjahn et al.*, 2004]).

2.2. Sampling and Preparation of Samples

[9] Rainfall, hydrology and water quality data for the Brantas River were collected and managed by the Perum Jasa Tirta I (PJT I) as the catchment regional authority. Hydrometeorological data for the Brantas River are the best yet collected for any catchment in Indonesia. Daily rainfall data have been available since 1955, while hydrological and water quality data have been available since 1991. Moreover, since 1991, the local authority has modernized data collection using an integrated automatic telemetry system [*Marini and Weilguni*, 2003]. Hydrology or discharge data are available at many check points - especially at dam inlets, dam outlets and irrigation stations. Seven primary sampling locations were used from July 2005 until June 2006 to represent different regions from upstream to downstream (Table 1). These locations were at Gadang, Karang Kates Dam, Lodoyo Dam, Mrican Dam, Lengkong Dam, Porong and Gunung Sari, which are marked by crossed circles in Figure 1. The latter two are stations over two major branches of Brantas that flow to the coast. Daily rainfall data from 26 rain gauge stations throughout the catchment area were also used herein.

[10] Water samples were collected once per month from July 2005 to June 2006 using a water sampler device. They were collected from the midlayers at about 70–80% river depth or at the point of maximum velocity in the middle of the river and at the left and right river banks (composite samples) at all stations. Temperature, salinity (conductivity), dissolved oxygen and pH were measured in situ. Filtration was performed only after the pH had been determined. The

Table 1. Water Quality Sampling Locations From July 2005 to June 2006

Longitude (East)	Latitude (South)	Station Name	Remarks
112.632	8.024	Gadang	upstream
112.434	8.157	Karang Kates Dam	upstream
112.182	8.149	Lodoyo Dam	middle stream
112.024	7.765	Mricam Dam	middle stream
112.459	7.446	Lengkong Dam	middle stream
112.698	7.543	Porong	downstream
112.719	7.307	Gunung Sari	downstream
112.506	8.191	Karang Kates inlet	Jan–Apr 2006
112.464	8.173	Karang Kates middle	Jan–Apr 2006
112.248	8.142	Wlingi inlet	Jan–Apr 2006
112.197	8.146	Lodoyo inlet	Jan–Apr 2006

samples were kept in fully filled narrow-necked and sealed glass bottles and stored in the dark at 4°C to minimize the error associated with CO_2 degassing prior to analysis. DO was measured in situ using a portable DO meter after calibration with an oxygen zero and by using titration.

[11] Water samples were filtered through 0.45 μm glass fiber filters into glass bottles, preserved with mercury chloride ($HgCl_2$) solution (20 gl^{-1}) until the final concentration reached 10 mg/L, and kept frozen at -20°C until analysis. Water samples for total suspended matter (TSM) filtration were taken from PE tanks, cooled and stored in the dark until filtration. The TSS values were derived using a gravimetric analyzer. Samples were filtered over precombusted (5 h, 450°C) Whatman GF/F filters and dried at 40°C.

2.3. Analyses

[12] Water samples were analyzed in the Water Quality Laboratory of the Ministry of Public Works in Surabaya for dissolved and particulate carbon. Although data up to June 2006 were obtained and analyzed, the TOC analyzer did not function well after April. Therefore data for carbon parameters were obtained only up to April 2006, while nutrient and sediment parameters were obtained up to June 2006. The carbon contents were analyzed using a Shimadzu TOC 5000 Analyzer with a combustion temperature of 680°C. TOC and DOC standardizations were conducted using potassium hydrogen petalat $C_8H_5KO_4$, while TIC and DIC standardization were conducted using sodium carbonate Na_2CO_3 and sodium bicarbonate $NaHCO_3$. The organic and inorganic carbon contents of the total and dissolved carbon were measured. Then, the particulate carbon was determined from their differences. pCO_2 was calculated from pH and total dissolved inorganic carbon (DIC) [*Frankignoulle and Borges*, 2001].

[13] Elementary and isotopic analyses were conducted at a laboratory of the Zentrum für Marine Tropenökologie in Bremen, Germany. Parameters measured in that laboratory included particulate inorganic carbon (PIC) and particulate organic carbon (POC) of the residue of filtered papers. Actual measurements were conducted in Bremen with a Finnigan Delta Plus gas isotope ratio mass spectrometer [see *Jennerjahn et al.*, 2004], and these measurement values were compared to calculated particulate carbon from the Shimadzu results.

3. Results

3.1. Hydrologic System

[14] The climate over the Brantas catchment is dominated by a strong monsoonal system with a large contrast between the dry and rainy seasons and is strongly modulated by El Niño Southern Oscillation [*Aldrian and Susanto*, 2003]. During the last five decades, this catchment has experienced the impact of global climate change by some prolonged dry periods and a persistent

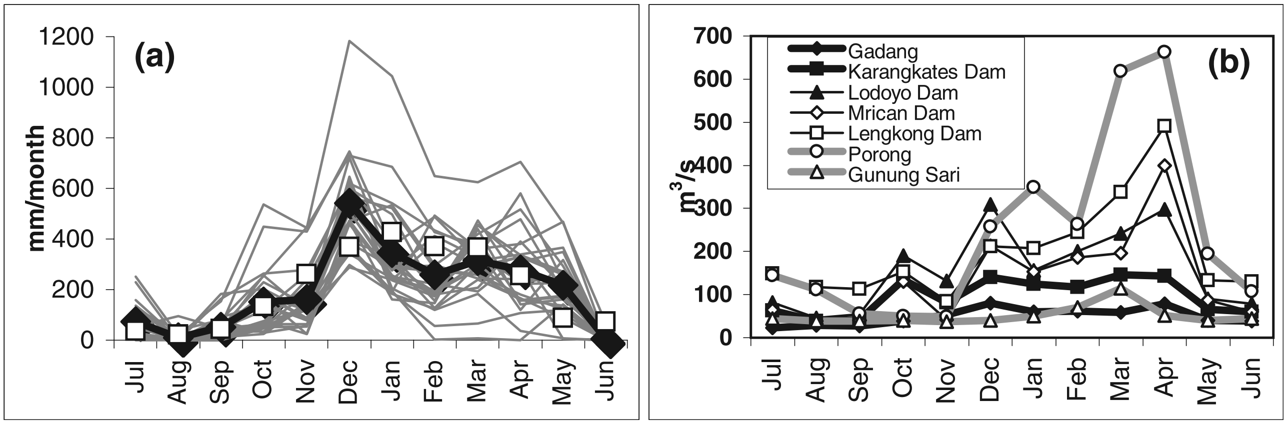

Figure 2. (a) Annual rainfall patterns of 26 rain gauge stations from July 2005 to June 2006 with average (solid thick lines) and monthly averages over 15 years from 1991 to 2005 (open squares) and (b) river discharges from upstream (thick black lines), through middle stream (thin lines) to downstream (thick gray lines).

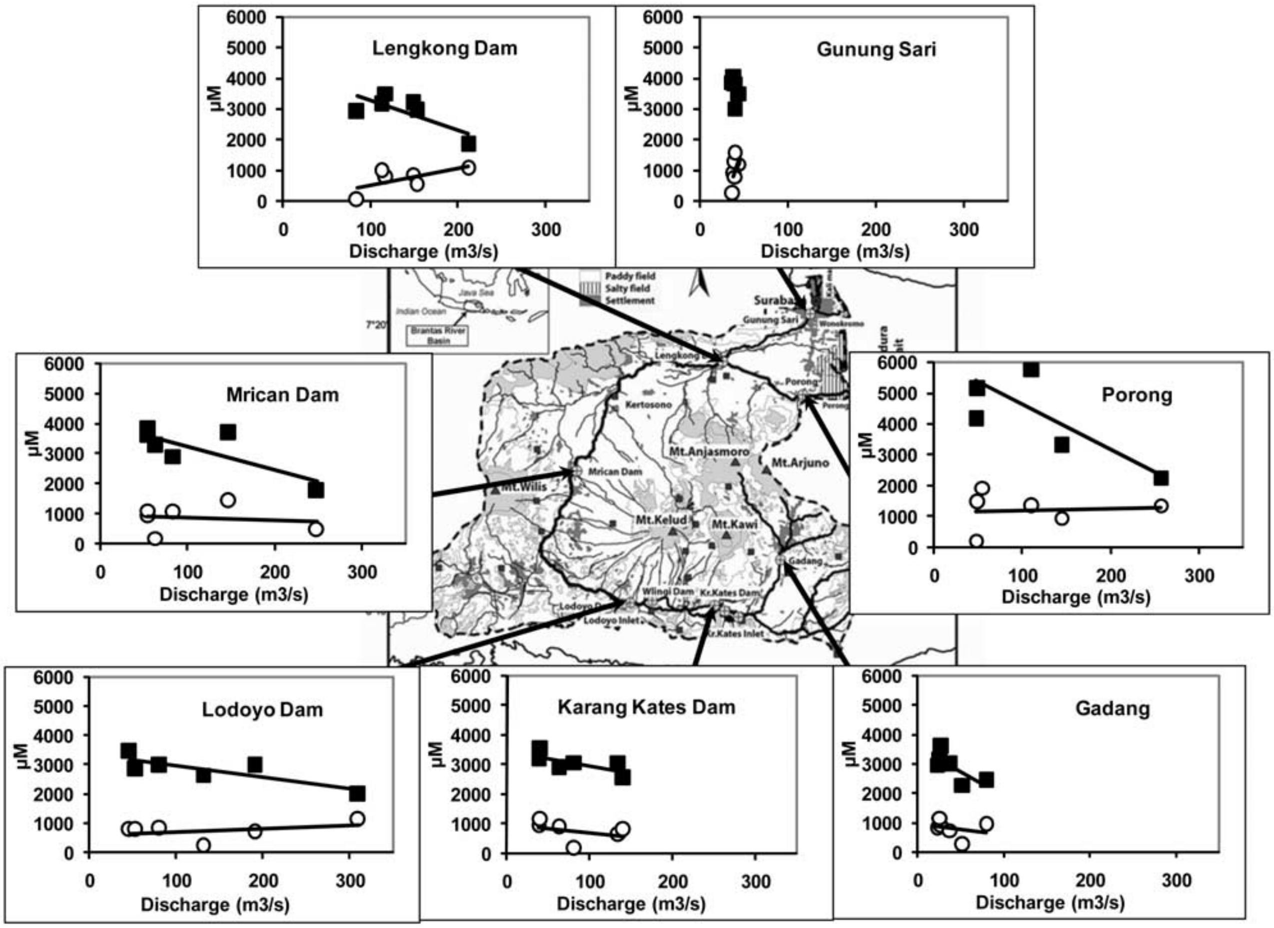

Figure 3. TOC (open circles) and TIC (solid squares) versus discharge between July 2005 and April 2006.

reduction of the annual precipitation [*Aldrian and Djamil*, 2008]. Observations made during the study period reveal that the dry season is between June and September while the rainy season is between October and April, as presented in Figure 2. The largest peak is observed in January, while the second largest, in April, is associated with a transitional period. The sampling period herein, which is from July 2005 to June 2006, is regarded as a normal year, based on a comparison with the recent 15 year average, but with much more rainfall in December than its monthly average.

[15] The water discharge patterns over the Brantas River do not exactly follow the rainfall pattern. The existence of 12 dams in various locations may to some extent contribute to the actual pattern. During the period of this study, the discharge was maximum in April instead of in December consistently from the upstream to the downstream sampling sites. A comparison with inflows and outflows of respective dams reveal that the patterns are consistent with the aforementioned annual pattern. Accordingly, the presence of the cascading dams along the Brantas River does not affect the upstream to downstream flows. In fact, all of the dams, except for the Karang Kates Dam, are daily controlled, such that the daily outflow directly follows the daily inflow. Hence, the pattern is homogenous, as presented in Figure 2b. Another pattern is the increase of discharge from upstream to downstream locations.

3.2. Temporal TOC and TIC Variations

[16] During the dry and transitional periods (July to October), the TIC concentrations from 2000 to 4000 μM (μmol/L) typically exceed the TOC concentration of approximately 1000 μM - especially in the upstream and midstream areas. In the downstream area, the TIC exceeded 5000 μM at Porong. Based on Table 2, the negative correlations of TIC with discharge are significant for all stations except the Gunung Sari station. However, the correlations between TOC and discharge are positive but weak at all stations. Moreover, Table 2 indicates that DIC and TIC are significantly correlated ($p < 0.001$) with discharge in the upstream regions, while DOC and TOC are significantly and positively correlated with discharge in the downstream regions. These phenomena suggest, however, that the terrestrial runoff, phenomenon caused by the river discharge, significantly controls the TIC concentration during the dry period, implying that the chemical weathering of the geological rock, such as limestone, produces more carbon in the runoff, perhaps as a result of the groundwater outflow, than from other soil and vegetation. Limestone can be found in the southern side of the

Table 2. Correlations Among Carbon Parameters and Discharge (Q), Fractions of Dissolved Carbon, and Percentage Ratio of Particulate[a]

		Gadang	Kr. Kates Dam	Lodoyo Dam	Mrican Dam	Lengkong Dam	Gunung Sari	Porong
Various correlations	DOC–TOC	(a) 0.991	(a) 0.995	(a) 0.994	(a) 0.980	(a) 0.988	(a) 0.954	(a) 0.962
	DIC–TIC	(a) 0.963	(a) 0.995	(a) 0.993	(a) 0.932	(a) 0.994	(a) 0.983	(a) 0.992
	POC–TOC	0.590	0.382	0.300	0.436	0.471	0.564	(b) 0.803
	PIC–TIC	0.293	0.406	(b) 0.612	0.411	−0.158	0.177	−0.214
	POC–TDS	(c) 0.738	−0.241	0.556	0.583	0.497	(c) 0.656	(a) 0.906
	POC–TSS	(c) 0.728	0.533	(c) 0.719	0.435	(a) 0.884	(a) 0.937	(a) 0.963
	TOC–Q	0.546	0.492	0.542	(c) 0.735	(a) 0.909	(b) 0.778	(b) 0.847
	TIC–Q	(b) −0.774	(b) −0.801	(b) −0.793	−0.417	0.004	−0.451	−0.624
	DOC–Q	0.467	0.535	0.489	(c) 0.674	(a) 0.876	0.621	(c) 0.687
	DIC–Q	(c) −0.696	(b) −0.775	(c) −0.786	−0.420	−0.018	−0.531	(c) −0.688
	POC–Q	(b) 0.782	−0.221	0.578	0.533	0.553	(b) 0.773	(a) 0.957
	PIC–Q	−0.401	−0.529	−0.494	−0.093	0.207	0.392	(c) 0.677
Average ratio of dissolved to total	DOC/TOC	0.818	0.827	0.860	0.779	0.854	0.790	0.805
	DIC/TIC	0.976	0.967	0.938	0.917	0.968	0.958	0.938
Percentage ratio POC to total suspended matter	max (%)	1.66	1.48	1.01	1.91	1.03	1.75	1.74
	avg (%)	0.72	0.80	0.57	0.78	0.45	0.80	0.71
	min (%)	0.02	0.09	0.03	0.14	0.02	0.06	0.15
Percentage ratio PIC to total suspended matter	max (%)	1.44	1.05	1.00	2.84	0.56	1.08	0.96
	avg (%)	0.37	0.35	0.39	0.86	0.21	0.35	0.34
	min (%)	0.05	0.08	0.06	0.01	0.04	0.07	0.04

[a] A negative correlation between a carbon parameter and Q indicates a dilution effect. Here (a), (b), and (c) represent significant levels of 0.001, 0.05, and 0.1, respectively.

upstream region up to the Lodoyo Dam and in the northern side of the downstream region from the Kertosono gauge station to the Kali Mas branch near Surabaya city. Figure 3 demonstrates that TIC concentrations typically decrease during the period of ascending discharge between July and December, while the TOC concentrations increase because DOC in the soil starts to leach out. In the period of high discharge between January and April, TOC values exceed TIC values.

[17] There is a large contrast between the TOC concentrations in the dry and wet seasons, while less contrast for TIC in both seasons. In contrast to the TOC, higher concentrations of TIC occur in the dry period while lower concentrations in the wet period due to the dilution effect. In fact, TIC is inversely related to discharge (Figure 3) as the result of the dilution effect by the rain. All sites reveal this dilution effect except at Lengkong Dam, where probably the water is drained greatly for agricultural use in the midstream region. The dilution relationship is inferred from the correlation between the TIC and DIC, whose correlations at all sites and all months are significantly strong (Table 2). This implies that a higher inorganic content is associated with a higher dissolved portion. Accordingly, during the high discharge period, discrepancies from this relationship are due to the nondilution effect (nonphysical effect) of TOC or may be due to biological activity.

3.3. Temporal DOC and DIC Variations

[18] The DOC and DIC dominate the TOC and TIC, respectively, in their proportions and temporal variations (Table 2) at all stations. The average DIC/TIC ratio was much higher than the DOC/TOC ratio. As shown in Figure 4, the DOC was generally below 1000 μM in the dry period and between 2000 and 3000 μM in the wet period. However, the DIC concentration varied from about 2000 to 4000 μM, except at Porong Bridge, which recorded over 6000 μM. The higher DIC concentrations over Porong were due to the contribution of a large marble factory in its tributary at about 5 km up-stream from the sampling station. From July to December DIC was mostly two to three times higher than DOC in the entire basin except at Porong, where the magnitude of DIC was up to four times that recorded in September suggesting that the DOC concentration tends to increase, but the DIC concentration tends to decrease during the wet period. This phenomenon was identified at all sampling stations. The differences between DOC and DIC then gradually diminished to the range of 2000 to 3000s μM between January and April. The comparisons of temporal distributions of DOC and DIC imply that the solutes do not have similar controls and their transformation follow similar mechanisms.

[19] The situation for particulate carbon is rather different than for dissolved as neither PIC nor POC follows a common seasonal pattern. POC is typically much higher than the PIC. The POC concentrations range from 6.3 to 1425 μM: the value was highest in Gunung Sari in March 2006. Table 2 presents POC as a percentage of total suspended matter, which has ranges between 0.02 to 1.99%.

[20] Particulate matter, unlike dissolved carbon, does not exhibit a seasonal trend because of terrestrial agricultural waste output. $\delta^{13}C^*_{POC}$ signatures were examined to determine the source of the particulate organic matter. All of the isotope data from the 80 POC samples collected from all stations between August 2005 and March 2006 reveal terrestrial sources of POC, with $\delta^{13}C^*_{POC}$ from −32.77‰ to −19.67‰. Most values show two clusters ranging between −29‰ and −26‰ and between −25‰ and −23‰ (Figure 5).

[21] From Figure 6, POC over the Brantas River has a strong dependency to the erosion factor such as total suspended sediment (TSS) and the discharge. Although the correlations do not apply for all sampling stations, they apply well in nonregulated dam stations such as Porong, Gunung Sari, Gadang and Lengkong. Figure 6 plots the relationships between some POC concentrations and TSS

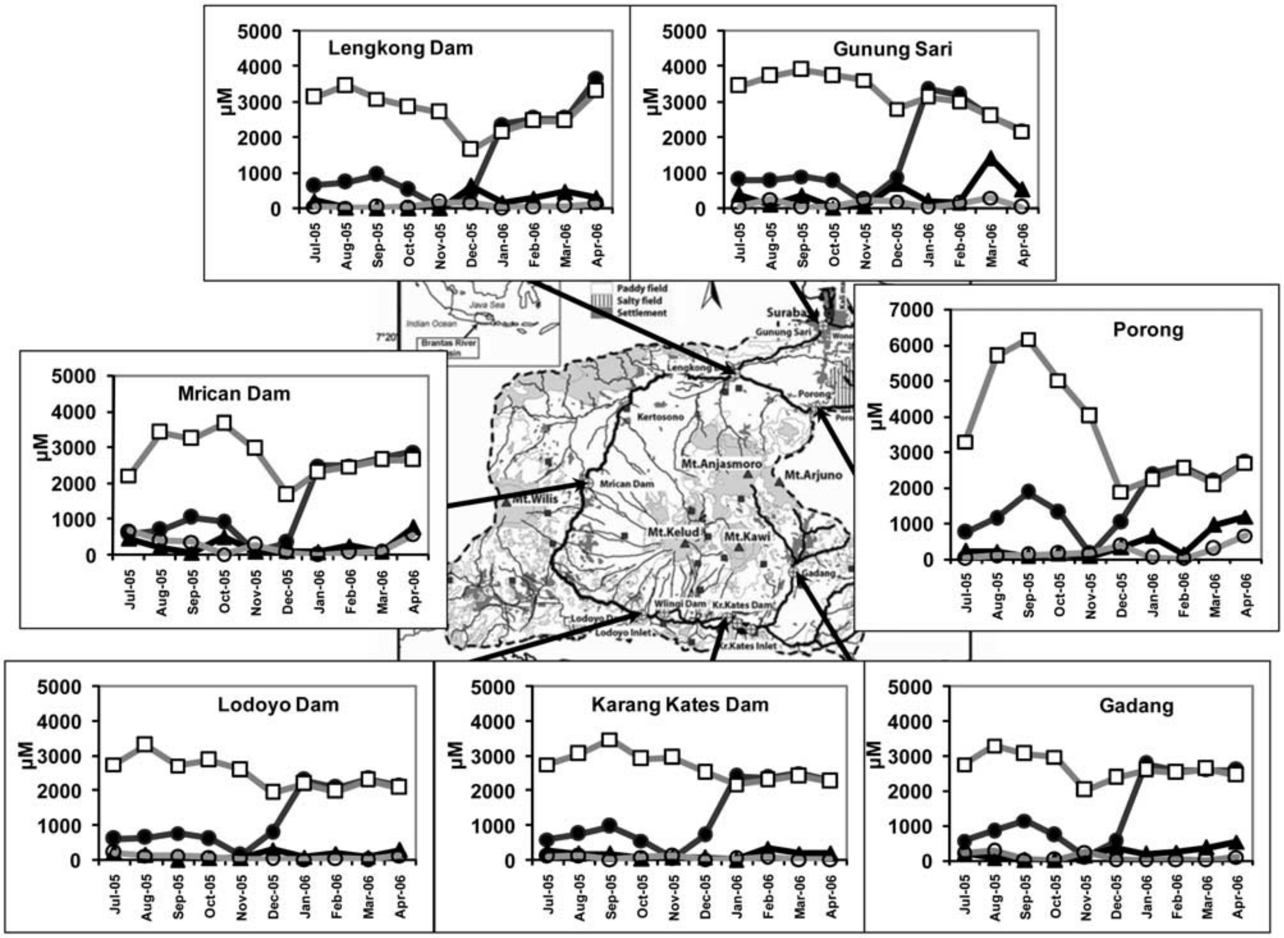

Figure 4. Spatio- and temporal-variabilities of DOC (solid circles), DIC (open squares), POC (solid triangles), and PIC (open circles) for the Brantas River basin from July 2005 to April 2006.

fluxes. Notably, at stations with high discharge, such as in Lengkong and in Porong, the correlations are significant, while for the Gunung Sari and Gadang with low discharge flow, as occurs in most of the world's river [*Ittekkot*, 1988], POC contributes more to TSS. A similar relationship has been reported in Parana River, Argentina [*Depetris and Gaiero*, 1998]. Significant correlations exist between POC and discharge (Figure 6b) in Gadang, Gunung Sari and Porong.

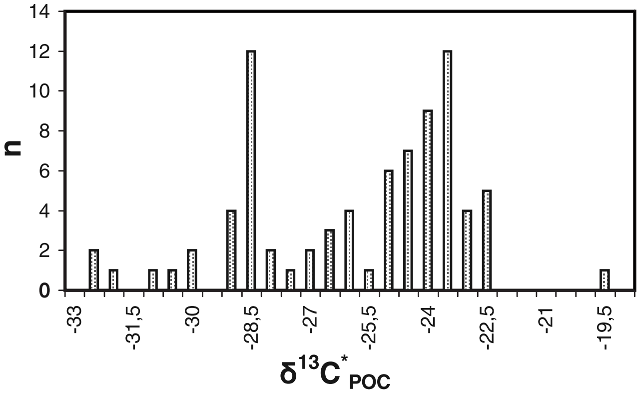

Figure 5. Histogram of $\delta^{13}C^*_{POC}$ for all stations.

[22] Figure 7 plots the CO_2 partial pressure (pCO_2) from the Brantas River, and shows net CO_2 fluxes to the atmosphere all yearlong at almost all sampling stations. Although exact data for the fluxes are not known due to a lack of wind data, all values except those for August in Porong and for February in Gunung Sari, exceed the atmospheric level ($\sim$370 μatm). The values range from 126 to 8776 μatm. The pattern is regular during the ascending period along the Brantas River, where the source of carbonate weathering is obviously in the upper and downstream areas, while in midstream, pCO_2 is relatively low. For the subsequent four months or during high discharge, this regularity fails and the midstream exhibits a strong increase in pCO_2 as the middle stream starts to act as the carbon source in January and reaches its peak in March. This period coincides with the period of strong erosion or carbonate weathering. Additionally, a significant relationship ($p < 0.0001$) exists between pCO_2 and acidity, but not between DIC and pCO_2 (R^2 of only 0.056). The isotopic composition of DIC therefore depends not only on the relative proportions of silicate and carbonate minerals that are being weathered but also on the source of acidity.

3.4. Carbon and Impact of Damming

[23] Since January 2006, more sampling stations have been added over the two largest dams, Karang Kates and

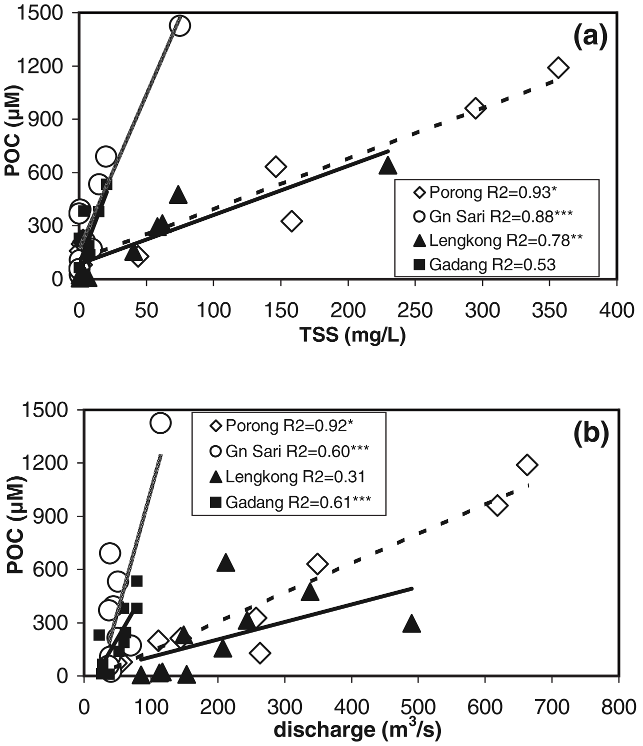

Figure 6. POC concentration versus (a) TSS fluxes and (b) discharge in nonregulated dam stations with R^2 values for respective regression lines. In regulated dams in the middle stream the TSS values are highly sensitive to seasonal discharge change. Additionally, the contrast between TSS values in the dry and wet season is very high (Figure 8) in comparison to the contrast of POC, which is more stable. *, **, and *** represent significant levels of 0.0001, 0.001, and 0.1, respectively.

Lodoyo, to investigate the impact of damming on the carbon cycle. Additional sampling locations over the Karang Kates Dam are located at the inlet and in the middle reservoir. The sampling location after the reservoir is quite far from the outlet and the effects of turbulence and evasion are not considered herein. The Wlingi Dam between these two large dams is daily regulated. For these additional sampling locations, all samples were collected near the surface. *Milliman* [1997] suggested that particularly in the second half of the 20th century, the diversion and damming of rivers have led to an overall reduction of sediment inputs into the ocean. As presented in Figure 8, DIC and DOC in the cascade dam varied in the range 1500 to 2700 μM. DOC varied less, with higher concentrations than DIC, especially in the middle reservoir of the Karang Kates Dam from January to April. The middle of the reservoir did not show a significant increase in DIC nor DOC concentration. Normally when trapping occurs, the middle of the reservoir has a higher concentration than the outlet. Thus, obvious trapping of organic and inorganic matter occurs in January and February only, while in other months, no obvious trapping occurs. Therefore, no evidence of carbon trapping occurs in this cascade dam system, perhaps because of the smallness of the reservoir that can trap carbon and because of respiration activity that may be responsible for the variation of DOC in the middle of Karang Kates. Another possible explanation is that the water samples taken from the reservoir system may not be representative as only surface water was sampled. Although some trapping may occur over the Karang Kates Dam, the Lodoyo Dam does not exhibit any trapping at all. The Lodoyo Dam is a daily regulated dam whose total inflow and outflow are kept the same.

[24] The pH over the cascading dam shows significant changes before and after the Karang Kates Dam. The large pH change is not followed by large changes in TIC from the after-dam values, perhaps suggesting that the pH changes are caused not by limestone but by other sources. Indeed, the dissolved oxygen is supersaturated at the inlet and in the middle of this dam (not shown). This fact clearly indicates that biological productivity has removed CO_2, hence lowering pCO_2 but raising pH. The large body of water at Karang Kates acts as a sink of atmospheric CO_2 since the calculated pCO_2 in surface water is below the atmospheric level ($\sim$370 μatm).

3.5. Fluxes of Dissolved Carbon

[25] Unfortunately, the sampling period does not cover the entire year but only ten months. Nevertheless, the general annual pattern, presented in Figure 9, was established using the available data. The figure presents the calculated carbon fluxes from upstream to downstream. Unlike POC, the DOC and DIC fluxes along the Brantas River follow the annual variation of the discharge pattern. Therefore, the fluxes of DOC and DIC are autocorrelated with river discharge. The DIC fluxes range from 66 to 1852 Ton/day and about 2.582 $\times$ 10^5 t a^{-1} is discharged from Porong into the estuary. The DOC flux ranges from 3.53 to 1878 Ton/day and about 2.023 $\times$ 10^5 t a^{-1} is discharged from Porong into the estuary. DIC typically dominates the fluxes and increases from upstream to downstream stations. Notably, the data herein are sampled at the outlet of those dams, and therefore differ slightly from those presented above in the section on the impact of damming. Moreover, dams after the Karang Kates dam are daily regulated dams. Also, the high erosion rates that occur after the dam outlets may keep carbon fluxes high. The branch at Gunung Sari always had lower fluxes than the Porong branch because the discharge through Gunung Sari was persistently low.

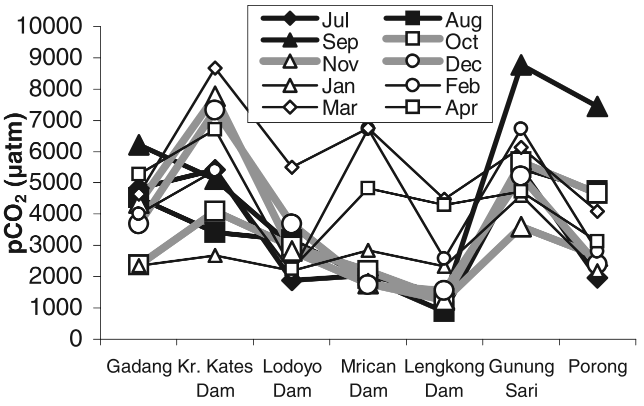

Figure 7. Partial CO_2 pressure (pCO_2) from upstream to downstream from July 2005 to April 2006.

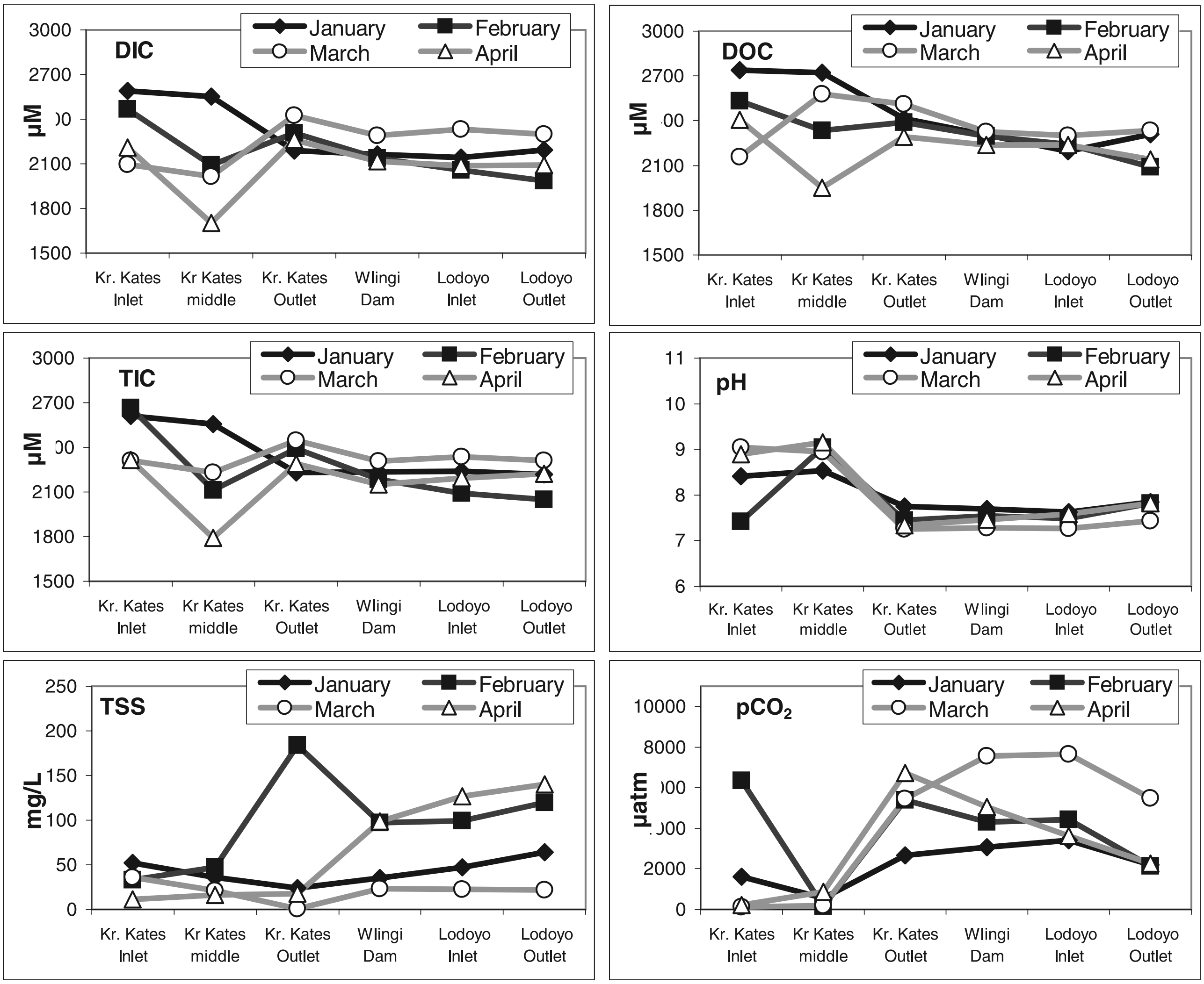

Figure 8. Effect of damming on carbon budget in upstream dams at an additional four sampling stations from January to April 2006.

[26] Like the temporal variations of DIC and DOC concentrations, carbon fluxes are dominated by DIC during the dry season and less dominant during the wet season. In November (Figure 9), all fluxes are low because the surface runoff recedes, and the groundwater discharge has not yet started. During the peak of groundwater discharge in April, both DIC and DOC fluxes increase rapidly. The difference between the fluxes in the dry and wet seasons is large at all stations. At each particular station, the DIC varies between high discharge and low discharge by a factor of 3 to 9.3 (highest at Porong) from upstream to downstream. The factor for DOC varies between 32 and 532 (highest at the Lengkong Dam). The fluxes in only four months between January and April comprised 66% and 87% of the total annual fluxes of DIC and DOC, respectively. The data demonstrate that the estimated annual water discharge from the Porong outlet is about 7.523 km^3 a^{-1} and through the Gunung Sari outlet is 1.6 km^3 a^{-1}.

4. Discussion

[27] The hydrology data herein show that the maximum discharge in April, and not in December, is caused by the groundwater outflow after the period of subsurface accumulation/retention in the catchment. Thus, the required retention time from maximum rainfall to maximum discharge is approximately four months. Also, at the peak of the rainy season, between October and December, the underground soil water holding capacity may not have been saturated. Accordingly, rainfall during this period does not contribute directly to the surface runoff, as evidenced by the low runoff in November. Hence, the runoff peak in April was caused by groundwater outflow. A third possibility involves the control or regulation of dam outflow, since the water that was partially retained during the rainy season, especially over the Karang Kates Dam was released in April. However, the more downstream, the peak flow in April gets larger as the consequence of accumulated discharge from tributaries. Furthermore, secondary data from PJT 1 show that the surface water retention time from the Karang Kates Dam outlet to the estuary is only about 28 h. If in April the release of discharge was controlled solely by the Karang Kates outlet, such a short water travel time would not take place. In other words, the first two possibilities are quite convincing.

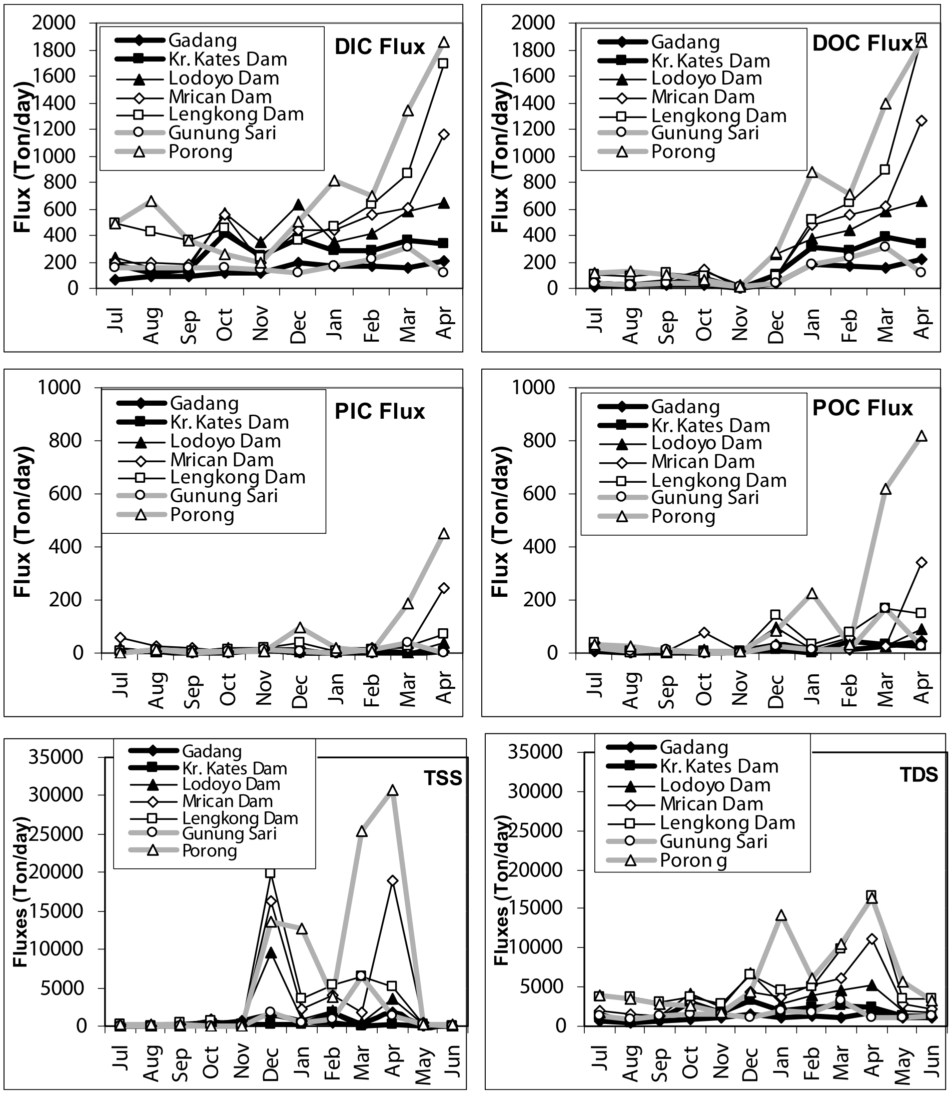

Figure 9. Annual pattern of DIC, DOC, PIC, POC, TSS, and TDS fluxes.

[28] The increase in DOC during the rainy season at all stations is associated with biological activity. For example, rice planting patterns in Java follow the marked seasonality of rainfall [*Naylor et al.*, 2001]. For each month (not shown), the differences among DOC data from all stations are not very large, but the variation among DIC data are large because carbonate weathering is unevenly distributed. The DIC and TIC at Porong during the dry season is much higher than at other sites because of the contribution from a marble factory, as mentioned above. The DOC concentration values of 2000–3000 μM during the rainy season and below 1000 μM during the dry season are comparable to those over the Siak River in central Sumatera, which are between 560 and 2594 μM [*Baum et al.*, 2007]. Riverine DOC is produced primarily by the leaching of leaf litter within the stream, and by groundwater inflows that infiltrated through organic rich areas of the soil [*Boulton et al.*, 1998]. Such DOC is composed of primarily humic substances [*Ertel et al.*, 1986] with lesser amounts of polysaccharide carbohydrates and amino acids [*Volk et al.*, 1997]. Part of this material can be taken up by bacteria [*O'Connell et al.*, 2000] and up to only about 10% of riverine DOC can be respired as it passes through the estuary [*Moran et al.*, 1999].

[29] As for the comparison of the particulate carbon from other studies, POC concentrations in this study (between 6.3 to 1425 μM) is comparable to other Javanese rivers', which are between 175 and 511 μM in the Solo River and 393 μM in the Serayu River [*Li et al.*, 1995]. Meanwhile, percentages of POC to total suspended matter recorded in that study were between 1.28 and 1.48% for the Solo River and 1.29% for the Serayu River, which is comparable to values in this study (between 0.02 to 1.99%).

[30] According to *Meyers and Lallier-Vergès* [1999] the range of $\delta^{13}C^*_{POC}$ in this study is related to C3 land plants. For a detailed investigation of the source of POC, usually the isotope method is associated with some amino acid measurements or ^{15}N isotope data. Here, we utilize secondary sources of information from other measurements made in the estuary of the Brantas River. According to *Jennerjahn et al.* [2004], the range of isotopes herein corresponds to the agricultural waste from rice plants and rice soil. The value

Table 3. Comparison of $\delta^{13}C^*_{POC}$ Signatures From Several Rivers Around the World

River	$\delta^{13}C^*_{POC}$ (‰)	Source
York	−28.2 to −30.0	*Raymond and Bauer* [2001]
Parker	−30.0 to −33.7	*Raymond and Bauer* [2001]
Small mountainous, Papua New Guninea	−22.3 to −32.6	*Raymond* [1999]
Amazon	−26.6	*Raymond and Bauer* [2001]
Brantas	−32.77 to −19.67	this paper

of −19.67‰ from one sample is associated with sugarcane soil. Values below −29‰ for seven samples correspond to the near estuary sources such as Avicennia and Sonneratia Alba leaves [*Jennerjahn et al.*, 2004]. From the comparison of other $\delta^{13}C^*_{POC}$ signatures as shown in Table 3 the values in this study are similar to those of small mountainous rivers of Papua New Guinea [*Raymond*, 1999].

[31] The organic geochemical processes of the Brantas River, unlike its inorganic hydrochemistry, are still poorly understood. The source of riverine organic carbon can be divided into three categories [*Degens*, 1982]; an allochthonous pool derived from terrestrial organic matter, an autochothonous pool originated from in situ biological production and the anthropogenous pool derived from industrial, domestic and agricultural wastes. According to Figure 9, the DOC flux variability between stations was smaller than the DIC variability, suggesting that the dominant source of DIC is associated with carbonate weathering. Moreover, DOC fluxes differ greatly between the dry and wet periods, but the DIC fluxes differ less. Agricultural waste and other biological products in the wet season are important sources of this DOC contrast. The variation of DIC over those periods is driven primarily by the large contrast of discharge values. In the case of DOC concentration, large seasonal differences are due to high biological activity. In fact, the DO values over the Brantas catchment (Table 5) vary seasonally, as an indicator of biological activity in the wet period and eutrophication in the dry season. That table also indicates that oxygen seems to be undersaturated in the river. Probably, another source of inorganic carbon is the respiration within the water column or the sediments. Imported organics (e.g., from agriculture) will to a certain extent be metabolized by aquatic heterotrophs, consuming O_2 and producing CO_2. Additionally, Figure 9 also indicates a strong increase in DIC and DOC carbon sources in the middle stream in March and April, while this area acts as a sink for carbon by the end of the dry period (look at Figure 10). Like DIC distribution, Gunung Sari becomes a sinking place for DOC, where concentrations are higher than other sampling stations are detected.

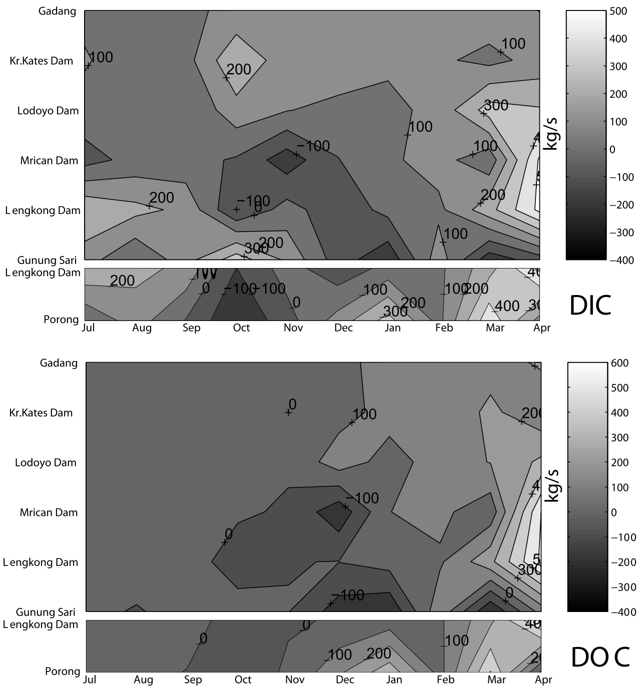

Figure 10. (top) DIC and (bottom) DOC fluxes from (top) upstream to (bottom) downstream. The diagram was calculated using the different fluxes between the respective sampling site and the upstream site. The spatial fluxes for Porong and Gunung Sari were calculated using the differences between their values and those at Lengkong Dam.

[32] The calculations herein yield TSS flux values (Table 4) of about 3.0×10^6 t a^{-1} from the Brantas to the estuary. This number is within the range of observed values that had been measured by Perum Jasa Tirta I (PJT I) at Lengkong from 1991 to 1997, which was from 0.43×10^6 t a^{-1} during El Nino in 1997 to 3.82×10^6 t a^{-1} in 1995. The TSS flux in this study, 3.0×10^6 t a^{-1}, is typical of a normal year. Since the Brantas River basin is a typical Java River basin, TSS and TDS fluxes for the whole Java can be estimated based on the data provided in Table 4. The calculation based on the Brantas River catchment area of 11050 km^2 or approximately 8.7% of the area of Java, yields extrapolated TSS and TDS fluxes over Java of 3.45×10^7 and 3.25×10^7 t a^{-1}, respectively. Notably, this extrapolation does not take into account variety of basin location (e.g., east versus west coast) as well as the influence of the dams in other basins. *Milliman et al.* [1999], however, estimated that fluxes from Java may reach 3.3×10^8 t a^{-1} or ten times larger than the value extrapolated value of this study, which is 3.45×10^7 t a^{-1}. The discrepancies may come from intensive irrigation system that was built in mid 1980s and 1990s. Thus there are significant differences on loading patterns of sediment and carbon during *Hoekstra*'s [1989] study and the present study. In the present study, the carbon and sediment fluxes that leak out from the main river stream may eventually reach the estuary through small tributaries other than main outlets through Porong and Gunung Sari.

Table 4. Estimated Sediment and Carbon Loads From Brantas to the Estuary and Catchment Yields

Parameter	Porong Load (10^3 t a^{-1})	Gunung Sari Load (10^3 t a^{-1})	Brantas Yield (t km^{-2} a^{-1})
DIC	258.2	60.7	28.86
DOC	202.3	37.2	21.67
PIC	15.5	4.0	1.77
POC	37.9	9.5	4.29
TSS	2661.7	345.6	272.15
TDS	2288.0	544.6	256.34

Table 5. Dissolved Oxygen Concentration at Sampling Stations in Dry (July) and Rainy Seasons (January)[a]

	Sampling Locations						
Month	Gadang	Kr. Kates Dam	Lodoyo Dam	Mrican Dam	Lengkong Dam	Gunung Sari	Porong
Jul	4.54	1.51	5.70	5.35	6.74	2.23	5.64
Jan	7.40	5.00	7.97	6.77	6.57	3.78	7.17

[a] Units are in mg/L.

[33] In comparison to other small mountainous rivers, the carbon yields for POC and DOC over Brantas are similar to those of the Sepik River in Papua New Guinea [*Burns et al.*, 2001], which has POC and DOC yields of 15.5 and 5.8 t km^{-1} a^{-1}, respectively. Results of this study are much higher than most of small mountainous rivers in New Zealand as reported by *Carey et al.* [2005]. However, the values in this study are smaller than the mountainous Sikkim River, Himalaya with POC and DOC yield values of 28 and 67 t km^{-1} a^{-1}, respectively [*Sharma and Rai*, 2004]. The total sediment yield from the Brantas River at about 272 t km^{-2} a^{-1} is similar to that of the Ganges River (530 t km^{-2} a^{-1}), which ranks number 17 among the top 20 rivers that originate at elevations above 3000 m [*Chen et al.*, 2004] and above those of the Indus (260 t km^{-2} a^{-1}), Yangtze (250 t km^{-2} a^{-1}) and Amazon River (190 t km^{-2} a^{-1}).

[34] Another way to illustrate the carbon fluxes is to present the spatial and temporal trend from upstream to downstream (Figure 10). The net changes of carbon fluxes is an indication of source if the number is positive and an indication of sink if the number is negative. In most cases, the whole river basin is the source of carbon except in the middle stream between Mrican Dam and Gunung Sari from October to January and between Lengkong Dam and Gunung Sari in March. Although the period between October and January is in the middle of rainy season and discharge is not at the minimum, carbon is removed during this time of the year. The most likely cause is the high intensity of irrigation and the uptake of carbon associated with the paddy fields during this period in the middle and downstream areas. In the midstream, carbon and sediment loadings within the mainstream of Brantas are redistributed into smaller irrigation channels and flows to tributaries into the coast. Moreover, this area exhibits low carbonate weathering as explained above. The removal of both DIC and DOC at midstream between October and January suggests the uptake of DIC and the decomposition of DOC, perhaps by heterotrophic microbes. The high DO content (Table 5) and high discharge multiply the rates of biological uptake and excretion in the rainy season. The DIC and DOC fluxes peak occurs in April or when the riverine discharge peaks. DO is a good indicator of biological activity. In general, the DIC and DOC flux analyses indicate that the upstream river is a carbon source, the middle stream is a carbon sink and the downstream is a net source.

5. Conclusions

[35] Small mountainous river discharge into the oceans along with sediment material within is important for global biogeochemical cycle. Little is known about the carbon and sediment fluxes from a small mountainous tropical river. Assessments of the contribution of such a small river to the global budget are sometimes misleading due to less knowledge on seasonal basis. The Brantas River basin is a good example for closing the information gap on this issue. Moreover, the volcanic activity in the upstream region, ever changing climate and anthropogenic activities provide a good estimates for representing similar river type in the region. Regarding this, large contrasts between wet and dry seasons were described and how the carbon and sediment concentration as well as their respective fluxes behave were elucidated.

[36] TIC concentration was much higher than TOC, although the gap got closer from January onward. Carbon flux was dominated by TIC especially in the source region during the dry season and in the midstream. The upstream is a carbon source, and the middle stream is a carbon sink. Damming traps organic carbon rather than inorganic carbon. The high inorganic carbon is derived from chemical weathering of the limestone. The upstream cascade dam exhibited varying carbon dynamic on monthly basis. DIC concentrations were persistently high throughout the year because of carbonate weathering in the upstream and downstream, whereas DOC concentrations were highly seasonal because of biological activity.

[37] **Acknowledgments.** The authors would like to thank the SARCS project 94/01/CW and the National Science Council of the Republic of China, Taiwan (NSC 95-2621-Z-ID-005), for financially supporting this research. The authors offer special thanks to Didik Agus Wijanarko and his staff at the Water Quality Laboratory in Surabaya for support in the field, the Jasa Tirta Public Corporation (PJT I) for support in the field and in compiling discharge and rainfall data, and Yudha Setiawan Djamil for data processing and illustrations. The authors are very grateful to V. Ittekkot, Tim Jennerjhan, Dorothee Dasbach, and Matthias Birkicht from Zentrum für Marine Tropenökologie (ZMT), Bremen, Germany, for laboratory equipment and assistance. Two reviewers provided a positive and detailed review which greatly enhanced the quality of the manuscript. The final version of the manuscript was prepared while E. Aldrian was a visiting scholar, supported by the Aim for the Top University Plan (94C030200), at National Sun Yat-Sen University, Taiwan. The editor is appreciated for his editorial assistance.

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