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# INFLUENCE OF STRONG MONSOON-DOMINATED CLIMATE ON BIOGEOCHEMISTRY OF THE HEAVILY ANTHROPOGENIC IMPACTED BRANTAS RIVER ESTUARIES AND MADURA STRAIT COASTAL WATER, EAST JAVA, INDONESIA

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## Abstract

Brantas River basin and Madura Strait in East Java Indonesia, are subject to heavily change in land use and land cover, and Brantas River Basin is a very important densely populated area in East Java, Indonesia for agriculture, industry as well as for settlement. The aim of the research is to elucidate the fate of transformation of bio-elements (organic carbon, Nitrogen (N), Phosphorus (P), and Silicate (Si)) and its seasonal variability. The contrast river discharge combined with tide generates the distinctive mixing zone during rainy and dry season. Dissolved Inorganic Nitrogen (DIN) and Dissolved Inorganic Phosphorus (DIP) concentrations in the river are high and decrease to the very low value seaward. N:P ratio has seasonal variation due to large discrepancy of DIN and DIP supply from land to the sea. Dissolved Inorganic Silicate (DSi) in river and estuaries is extremely higher than the average in the world (> 150 mM). Chlorophyll-a (Chl-a) in dry season in the coastal water is higher than the rainy season. Due to high Total Suspended Matter (TSM), the primary production is limited by the light in the coastal water.

**Keywords:** Biogeochemistry, Brantas Rives, Madura Straits, Indonesia.

## INTRODUCTION

River-borne materials that are delivered to the coastal zone are exposed to many dynamic processes that result in steep biogeochemical gradient on the continental shelf (Daag *et al.*, 2004). In the recent years the role of estuaries in the exchange of $CO_2$ within coastal zone received considerable attention (Gatusso *et al.*, 1998). Temporal and spatial dynamics in the estuarine/plume regions will vary largely depending on the freshwater forcing function. The plume dynamic is affected by some physical controlling variables, namely seasonal variations in river discharge, temperature, wind forcing and solar radiation. Meybeck (1982) stated that nitrogen (N) and phosphorus (P) input into rivers around the world increase dramatically in 20th century as a result of intensive agriculture, industrial and municipal waste water discharge. N and P are two essential nutrients for all phytoplankton groups. N and P concentrations are strongly influenced by human activities. Therefore, N and P received much attention in eutrophication studies. However, only a few phytoplankton requires silicate (Si), and Si concentration is not directly influenced by human activities. Si source is mainly from natural weathering silicate mineral from soil (Treguer *et al.*, 1995). The fate of carbon (C), N, P and Si in high latitude estuaries like in North Atlantic Basin is largely determined by the residence time in the system (Bianchi, 2007). Large fractions of particulate materials are trapped in the estuarine area, and never reach the continental shelf. Nevertheless, in the large river in tropical country

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like Amazon 70% of total nitrogen bypass estuary (Bianchi, 2007).

As a result of rapid pattern of development there is growing concern of increasing contribution of Southeast Asia on global environment degradation. The countries of Southeast Asia are among the highest population growth rate in the world and their economy rely on living resources from land and sea. The coastal zone of this area is vulnerable to changes in sea level rise, flooding and storm surge that result from monsoonal climate change (Talaue-McManus, 2001). Hence, there is an urgent need to better understanding on interaction between human and environment in particular on how biogeo-chemical and hydrological cycles respond to change in land use and land cover, and what is the implication of these and land based activities to the marine environment.

The aim of this research is to present the result of biogeochemical observation in Brantas River estuaries and Madura Strait coastal water in order to elucidate the fate of transformation of bio-elements (organic carbon, N, P, and Si) and its seasonal variability. This area is a subject of heavily change in land use and land cover, and Brantas River Basin is a very important densely populated area in East Java, Indonesia for agriculture, industry as well as for settlement.

## MATERIALS AND METHODS

### Introduction to the study area

Madura Strait (MS) is located between East Java at the west and south, Madura Island at the north, and Bali Strait at the east (Fig. 1). The strait is connected to the Java Sea through the narrow and shallow channel of Surabaya Strait (SS) that is 14 km wide at the eastern entry, 2.4 km at its narrowest part, and 4.6 km at the north exit. Surabaya Harbour is located in the centre of the channel. Surabaya, the capital city of East Java, is the second biggest city in Indonesia and the main harbour in the eastern part of Indonesia. Because of its importance, the channel is dredged regularly to maintain its depth in order to be able to provide safe shipping routes in the Indonesian archipelago. MS is relatively shallow water with the maximum depth of about 40 m located in the east. MS can be considered as a semi-enclosed, rectangular tidal basin with a uniform width and is characterized by smooth and regular sloping bottom topography,

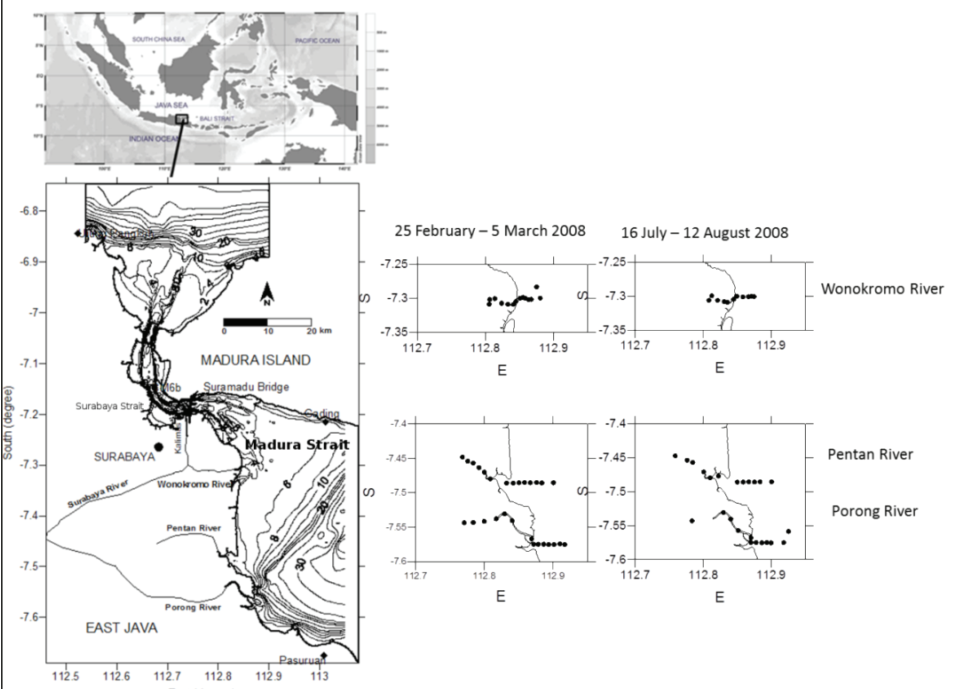

**Figure 1.** Study area of Brantas River estuaries and bathymetric map of Madura Strait coastal water (left panel). Sampling stations in Wonokromo Rivers (upper part), Pentan River and Porong River (lower part) in Rainy Season and Dry Season.

although it is not entirely closed due to the presence of the SS. A tidal transport through SS is estimated to be only 10% (25000 $m^3s^{-1}$) of that through MS (220000 $m^3s^{-1}$) (Hoekstra, 1989). Currents are strongest near Surabaya but gradually decrease in a southward direction.

Brantas River (see Fig. 2) is an important river in East Java. The river origin is in Arjuno Mountain in Malang, and the stream flows clockwise, passing through Malang, Blitar, Tulungagung, Kediri, Mojokerto, and Surabaya before debouching into Madura Strait (Fig. 1). The length of this river is 320 km and it is the second longest river in East Java after Bengawan Solo.

There are seven dams in the stream of Brantas River with its main function for irrigation and water storage. The number of population in Brantas River Basin nowadays is around 16 million or approximately 43% of total population in East Java. Large population altered land use, land cover and ecology. Water is mostly consumed for agriculture sector. There are nearly 500 industries discharge their effluent directly to the river, contributing approximately 500 t $d^{-1}$ of biology oxygen demand (BOD) load (Aldrian *et al.*, 2008). Moreover, watershed degradation and sedimentation are the severe problem in the Brantas River Basin. Erosion is a severe problem in the upstream area of Brantas River. Perum Jasa Tirta I of Malang documented the gross and effective storage of eight reservoirs of Brantas decreased to 405 mill $m^3$ (62.6%) and 343 mill $m^3$ (71.6%), respectively because of sedimentation (Hidayat *et al.*, 2008). One slope in the upstream area of Brantas catchment has the highest erosion rank in the world (105-106 $m^3$ $km^{-2}$ $year^{-1}$) and it is due to the rain-triggered lahar which occurs every rainy season dominated by sediment yields (Aldrian *et al.*, 2008).

## Materials

We collected surface water samples from two Brantas tributaries namely Wonokromo River and Porong River (Fig. 1). We also collected samples from Pentan River; smaller river that is located in down-stream of Brantas River basin. Sampling period is from 25 February to 5 March 2008 (herein after Rainy Season) and from 16 July to 12 August

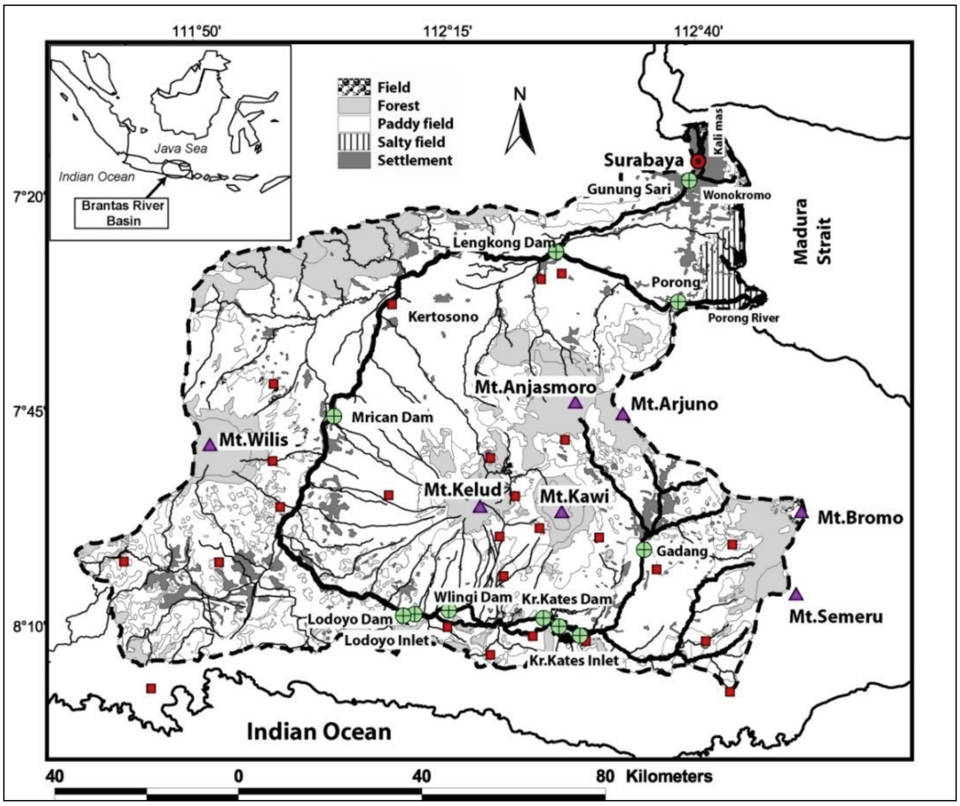

**Figure 2.** Land use and land cover of Brantas River Basin (after Aldrian *et al.,* 2008).

2008 (herein after Dry Season). The samplings site extents from 8 km inside the river until 5-10 km from the coastline (Fig. 1).

Water samples were collected using bucket taken from small boat at the depth of about 1 meter below the surface. Temperature, pH, salinity and dissolved oxygen concentration of water were measured insitu using WTW multiparameter probe instrument at the same level with water samples. Water samples for nutrients analysis were filtered in the lab of Water Quality of East Java, Surabaya through single use membrane filters into prewashed polyethylene bottles, preserved with mercury chloride solution and kept frozen until analysis. Water samples for total suspended matter (TSM) filtration were taken in polyethylene tanks, cooled and stored in the dark until filtration. Water samples for dissolved nutrients ($NH_4^+$, $NO_3^-$, $PO_4^-$, $Si(OH)_4^-$), TSM, chlorophyll-a and organic carbon were analyzed in the laboratory of Center for Marine Tropical Ecology (ZMT) in Bremen, Germany. Actual methodology of the nutrient and TSM analysis has been described in Jennerjahn *et al.* (2004). Chlorophyll-a was analyzed with spectrophotometer as described by Grasshoff *et al.* (1999). For analysis of organic carbon, the reader was suggested to read Baum *et al.* (2007).

Daily discharge data of Brantas River and its tributaries (Porong and Wonokromo Rivers) were provided by Perum Jasa Tirta I (PJT I) of Brantas River Catchment Authority Office.

## RESULTS AND DISCUSSION

### Hydrology

Aldrian and Susanto (2003) divides Indonesian region into three zones with different variation of rainfall, namely monsoonal pattern, equatorial pattern and local pattern. Brantas River catchment is dominated by monsoonal pattern with a large contrast between the dry and rainy seasons and is strongly modulated by El Nino Southern Oscillation (ENSO). Minimum rainfall occurs in June or July and the maximum occurs in December or January. The period where the

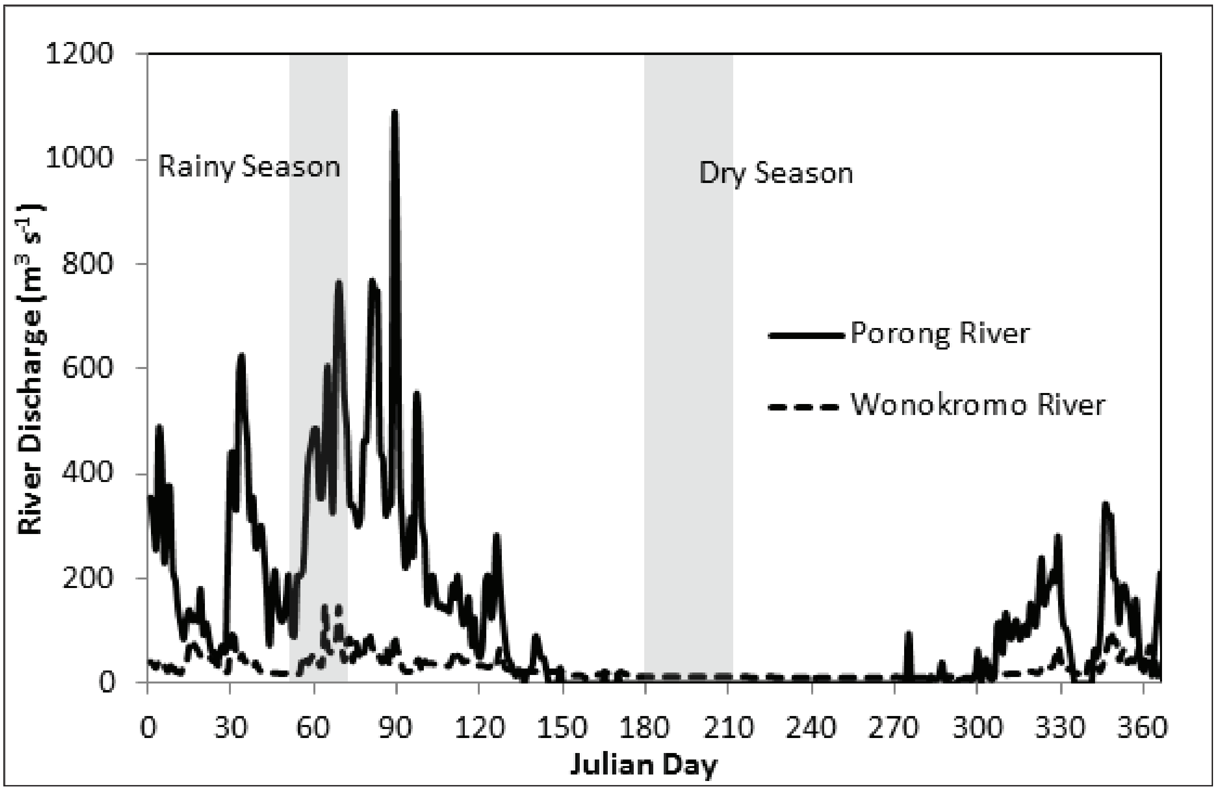

**Figure 3.** Daily river discharge (in m3 s-1) of Porong River (solid line) and Wonokromo River (dashed line) from 1 January to 31 December 2008. The shaded areas indicate sampling period 25 Feb-5 March (herein after Rainy Season) and 16 July – 12 August 2008 (herein after Dry Season).

obsevation take place is a unique case of La Nina and a positive IOD (Indonesian Ocean Dipole) that is revealed by Nino3 and IOD index from the NOAA and JAMSTEC data (Yulihastin *et al.*, 2003, unpublished). The anomalies of precipitation all over Indonesia is positive. Therefore, sampling periods in March and August 2008 are regarded as La Nina year.

Figure 3 showed the daily discharge of Porong River and Wonokromo River in the year of 2008. High river discharge starts from early November, reaching its maximum in end of March, instead of December or January. The maximum discharge of Wonokromo River was 150 $m^3/s$ and Porong River was 1072 $m^3/s$ that recorded on March 4 and March 29, respectively. The maximum discharge in Porong was much higher than its annual average of 600 $m^3/s$. The minimum river discharge shown by flat line was from June to September. The large discrepancy of discharge between two rivers was due to the discharge regulation by the gate at Lengkong (Fig. 2) where Brantas River branched to Porong and Surabaya River. During high precipitation the flow was usually directed to Porong River that had less industries and population to avoid the flood in the city of Surabaya.

### Salinity, pH, and dissolved oxygen (DO)

The influence of the freshwater discharge was obvious on plot of surface water salinity distribution as shown by Fig. 4a - c. The salinity shift existed in each river during dry and rainy seasons. In Wonokromo River during dry season zero salinity was observed at 5 km upstream and salinity increases down-stream. Freshwater from river mixed with saline water from the off shore area at the coastline (indicated as zero in the figures), and increased sharply to the maximum value up to 35. In the contrary, during rainy season when the discharge was high, the plume of low salinity water pushed the saline water off the estuary, therefore the front developed around 3 km off shore from the coastline. During sampling

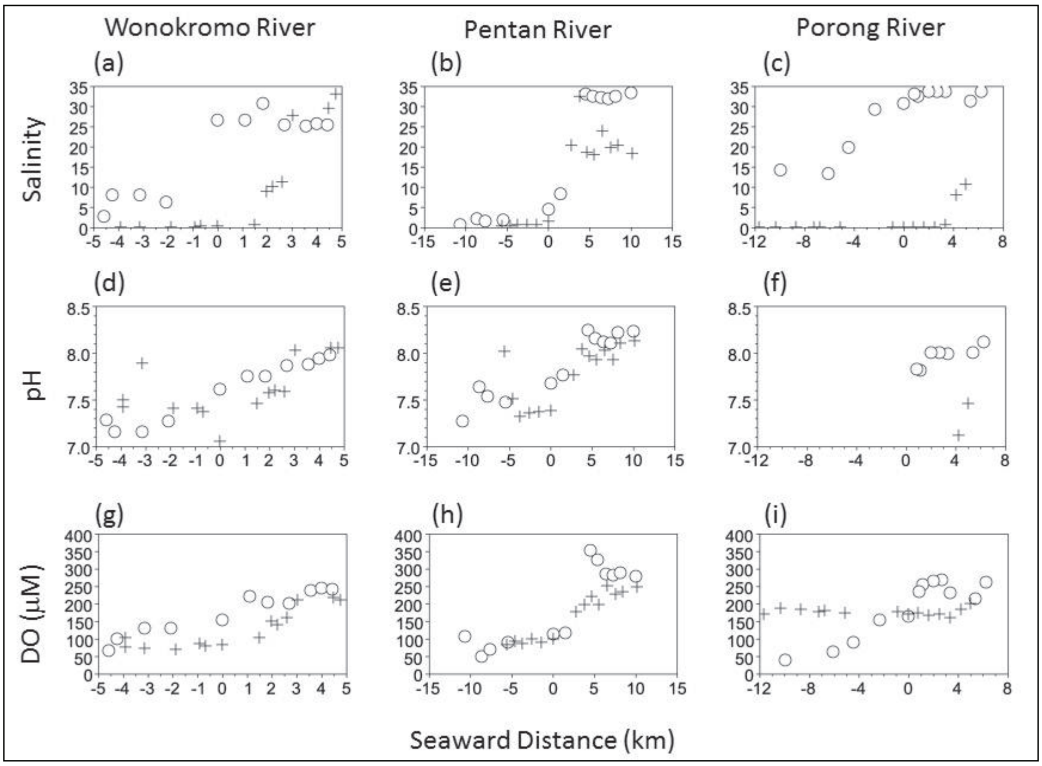

**Figure 4.** Longitudinal distribution of salinity (a, b, c), pH (d, e, f) and dissolved oxygen (g, h, i) in Wonokromo, Pentan and Porong Rivers. Circles denote dry season data, and plus marks denote rainy season data.

time, the estuarine front was visible and indicated by the bubbling and turbid water, and often accompanied by the clustered debris transported from the land. Sea water penetrated Pentan River up to 10 km from the coastline during dry season. Meanwhile, in the rainy season the mixing zone became shorter and it existed in the coastal water. The water became saline already in the river mouth. Porong River showed contrast mixing zone compared to Wonokromo River and Pentan River. During dry season, when the discharge of Porong was almost zero, the saline water penetrated up to 12 km upstream, and salinity increased from 15 to 20 at -5 km, 30 at -2 km. In contrast, the discharge of Porong during rainy season was around 10 times of two other rivers. Therefore zero salinity was observed until 4 km off shore. However, the mixing zone existed around 5 km offshore.

pH is an important property of aqueous solution because it affects chemical and biochemical processes such as chemical reactions, equilibrium conditions and biological toxicity (Dickson 1984, Milero *et al.*, 2009 in Marion *et al.*, 2011). During dry season, pH value in Wonokromo (Fig. 4d) varied between 7.4 at 5 km upstream and 8.20 at 5 km off shore. In the rainy season, the range of pH was narrower, from 7.4 to 8.1. The variability of pH in Pentan River (Fig. 4e) during dry and rainy seasons was larger than that of Wonokromo. In dry season, low pH was observed at -10 km, and then increased to its maximal value of 8.25 at 5 km offshore. In rainy season, low pH was observed between -5 to 0 km. However, higher pH were found to the more upstream station from that. At the coastal water, seawater pH increased. Unfortunately, the pH data from Porong River (4f) was not available in rainy season 2008 due to the malfunction of the instrument. PH at the river mouth of Porong during dry season was 7.8 and it increased to 8.2 at 6 km offshore.

In Wonokromo River and Pentan River (Fig. 4g-h), DO concentrations in the freshwater during both seasons were very low. Their concentrations were below 100 μm or between 30-40% saturation. Oxygen concentration increased in coastal water as freshwater mixed with saline water. Porong River (Fig. 4i) had different behavior from the other rivers. Low DOs below 100 μm or below 40% saturation were observed from -10 to -4 km during dry season, and then increased seaward. However, we did not observe low DO during rainy season. High discharge increased the flow velocity in the river, hence generated the turbulence and enabled oxygen entering the water column via diffusion processes at air-water interface. DO concentration from inner estuary to the coastal area varied between 162 to 202 μm or above 70% saturation.

## Nutrients (DIN, DIP, and DSi)

Dissolved Inorganic Nitrogen (DIN) concentration varied conservatively in three rivers in both seasons (Fig. 5a-c). $R^2$ of linear regression of DIN versus salinity (figure are not shown) for Wonokromo, Pentan and Porong were > 0.85, except in Pentan River during dry season that had less value (0.6). We observed higher concentration of DIN (160 μm) at the upper part of Wonokromo River, changed slightly until -2 km, and then decreased sharply to 16 μm at 1.8 km from the coastline and lower than 2 μm at the most outer part of the estuary. DIN concentration pattern in Pentan River in dry season was curious. We observed 23 μm of DIN at upstream station, increased to 100 μm at the next station, and increased linearly until coastline. DIN decreased abruptly seaward. In the rainy season, we did not find any dramatic change in DIN concentration in Pentan River. We observed maximal DIN of 80 μm at upstream and minimum 30 μm at the coastal water during rainy season in Porong. Maximal concentration of DIN in upstream area of Porong River was 70 μm and 150 μm in dry season and rainy season, respectively. DIN decreased until less than 1 μm in the coastal water. However, the influence of river discharge was obvious during rainy season. High concentration of DIN (60 μm) could be still observed at the end of transect at 5 km offshore. The DIN composition in three rivers was different between two seasons. DIN mainly consisted of nitrate in rainy season due to nutrient transport from land, and ammonium in dry season due to the regeneration of organic matter.

Fig.5d, 5e and 5f show transects of DIP in Wonokromo, Pentan and Porong River, respectively. Linear regression of DIP versus salinity revealed different result with DIN. DIP behaved conservatively in Wonokromo River in rainy season, and in Pentan River in both seasons

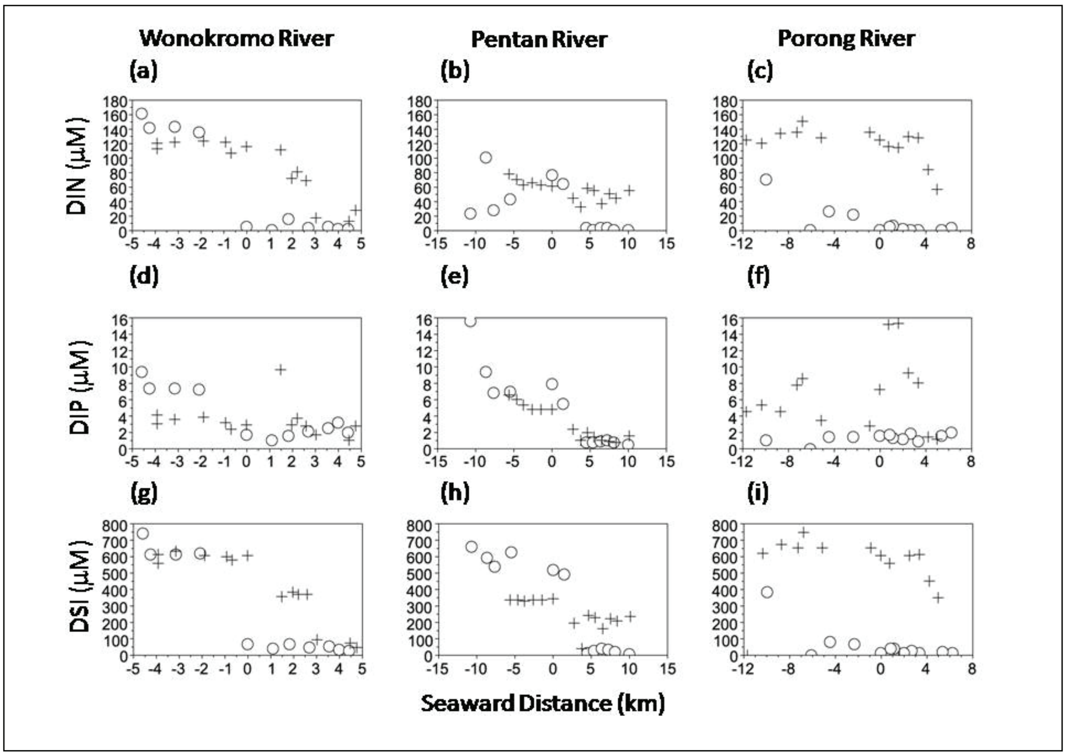

**Figure 5.** Longitudinal distribution of DIN (a, b, c), DIP (d, e, f) and DSi (g, h, i) in Wonokromo, Pentan and Porong Rivers. Circles denote dry season data, and plus marks denote rainy season data. Units are in μm.

and it was indicated by $R^2 > 0.8$. However, DIP had a weak relationship with salinity in Porong River in rainy season, and neither did in dry season. High concentration of DIP in Porong River during rainy season may result from high load of fertilizer that is used in agriculture and domestic waste. Moreover, increase of DIP during rainy season in Porong River is in good agreement with low salinity (Fig. 4). This may indicate that the source of DIP is from the river. Maximal DIP concentration in dry season in Wonokromo River was 9.5 μm in upstream station and minimal 1 μm at the coastline. DIP was slightly increased in the coastal water. Observed DIP in the same river during rainy season was lower to 4.2 μm at upstream station and then undulated seaward.

DSi in three rivers (Fig. 5g-i) behaved more conservative which was indicated by $R^2$ of salinity and DSi ranged between 0.76-0.93 in rainy season, and 0.76 - 0.99 in dry seasons. DSi concentrations in Brantas River, its tributaries and coastal water of Madura Strait were surprisingly high. In dry season the maximal DSi were 750 μm in Wonokromo River (Fig. 5g), 700 μm in Pentan River (Fig. 5h), and 400 μm in Porong River (Fig. 5i). Those highest concentrations were observed at the most upstream part of each transect. DSi decreased sharply at coastal area in three estuaries. In the contrary, in rainy season high DSi concentrations were observed even in the coastal water. Different from two other rivers, highest DSi concentration in Porong was observed in rainy season. The slope of DSi was gentle from the river to coastal water; therefore we still observed 400 μm DSi at 5 km from the coastline.

### N:P and N:Si ratio

In order to investigate the nutrient limitation for primary production in the estuarine of Brantas Rivers, we plot N:P (Fig. 6a-c) and N:Si ratio (Fig. 6d-f). In Wonokromo River, N:P ratios in dry season were slightly higher than 16, and then decreased in the coastal water. In contrast, in rainy season the concentration of DIN was increased, hence we observed high N:P ratio in the river until 3 km from the shoreline. Nevertheless, we found low N:P ratio in the coastal water. Pentan River had low N:P ratio in all station from upstream to

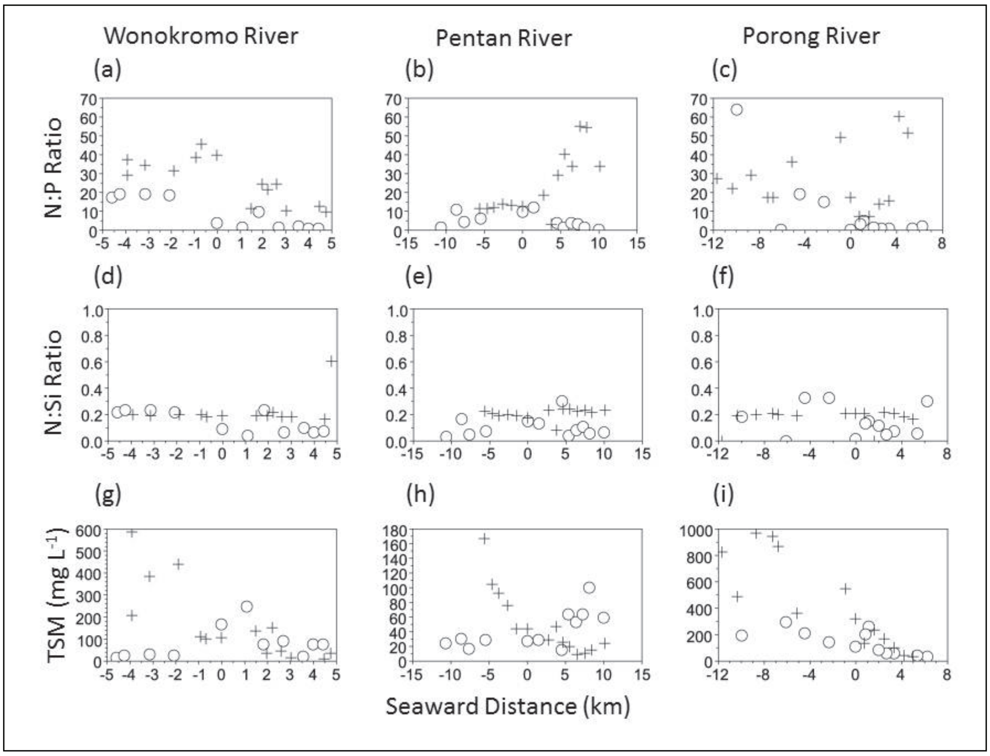

**Figure 6.** Longitudinal distribution of N:P ratio (a, b, c), N:Si ratio (d, e, f) and TSM (g, h, i) in Wonokromo, Pentan and Porong Rivers. Circles denote dry season data, and plus marks denote rainy season data. Unit of TSM is in mg/L.

downstream during dry season. Interestingly, we observed N:P ratio lower than 16 in rainy season in the river, but it became higher and reach its maximum N:P ratio 55:1 at 8 km off shore. High N:P ratio was observed at the most upstream point in Porong River (64:1) and at -4 km (19:1) during dry season, instead the other station showed N:P ratio much lower than Redfield ratio of 16. In rainy season when DIN supply were high, N:P ratio in the Porong River were mostly higher than 16 from upstream to downstream except at four stations between coastline to 4 km off shore. From that point, the N:P ratio increased again up to 60:1.The N:Si ratio in those rivers was always lower than 1, indicating that DIN will be used up earlier than DSi in primary production. In rainy season, N:Si ratio was almost constant from upstream to downstream, except at the coast end where N:Si ratio elevated to 0.6 in Wonokromo River. However, N:Si ratio slightly decreased during dry season in the coastal water. In Pentan River N:S1 varied between 0.18 – 0.25 along its transect, except at 5 km. Nevertheless, N:Si ratio in this river had broader variation (0.05 – 0.3) during dry season.

## TSM, POC, DOC, and Chlorophyll-a

We collected TSM from Wonokromo, Pentan and Porong River in dry season as well as rainy season (Fig. 6g-i). We observed low TSM concentration (< 50 mg/l) at the river end station in Wonokromo River during dry season. The maximum TSM was at the coastline and decreased again seaward. In contrast, river supplied large TSM in rainy season, therefore the concentration of TSM elevated to the maximum 600 mg/l at the river end station, and decreased linearly to the shore. Pentan River had less turbid water compared to Wonokromo. TSM during dry season increased up to 120 mg/l at 8 km offshore, before decreased again at 10 km. In rainy season, TSM at -5 km (end of transect) was 180 mg/l, and then decreased gradually seaward. In Porong River, TSM was higher than two previous rivers in dry season and then decreased linearly seaward. In rainy season, TSM in Porong had maximum concentration 1000 mg/l and decreased seaward.

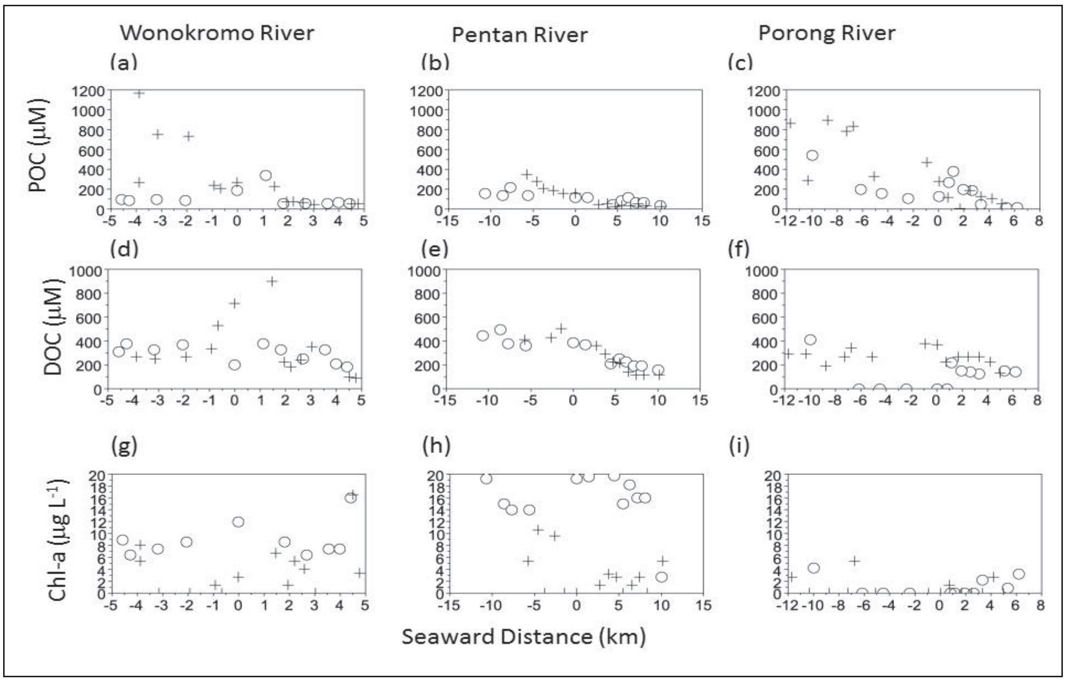

**Figure 7.** Longitudinal distribution of POC (a,b,c), DOC (d, e,f) and Chlorophyll a (g,h,i) in Wonokromo, Pentan and Porong Rivers. Circles denote dry season data, and plus marks denote rainy season data. Units of POC and DOC are μM. Unit for chlorophyll a is in μg/L.

Fig. 7a-c showed transect of the particulate organic carbon (POC) measurement in three rivers. POC in Wonokromo River showed large difference between two seasons in the river stations. Highest POC concentration was detected at -4 km in the rainy season, and then decreased seaward to almost similar value with that during dry season. We found similar phenomenon landward from the river mouth in Pentan and Porong River. Maximum concentration of POC was observed in the river-end station, and then decreased gradually to the river mouth. The distribution of POC in the coastal water was nearly similar during both seasons. It is possible that the POC sink in the inner part of estuary, meanwhile main part of POC in the sea is the phytoplankton.

The range of dissolved organic carbon (DOC) concentration in Wonokromo and Pentan Rivers were high in rainy season (see Fig. 7d-f). Maximum DOC in Wonokromo River was around 950 μm at the river mouth, and 500 μm in Pentan River mouth. The origin of high DOC is from domestic sewage that exists along the river. Meanwhile, maximum DOC in Porong was around 420 μm that was observed in dry season at upstream part of transect. The seasonal variability of DOC near the mixing zone of Wonokromo River was obvious. However, DOC concentration in Pentan River was almost similar at all stations except three stations that were located between -5 km to the shoreline that was exceptionally high. Unfortunately, there was only one data of DOC at the river end of transecting that showed highest DOC, and no additional data in the river. Higher DOC was observed in the coastal water during rainy season than that during dry season in Porong.

The spatial and temporal variability of chlorophyll-a in three tributaries were shown in Fig.7g-i. In general, the seasonal variability of chl-a was not very strong in Wonokromo River, although the maximum chl-a 16 μg/l observed far from the coast in dry season. In contrast, Pentan River showed strong seasonal variability of chl-a, with the high Chl-a concentration during dry season at all station except at the sea-end station. Unfortunately, we did not have many data in Porong River. High chl-a was observed at the river end station during both dry and rainy seasons.

## DISCUSSION

Brantas River and Madura Strait are located around equator where the temperature of water and atmosphere is nearly the same throughout the year.

In addition, this area also receives no significant different solar radiation throughout the year. Thus, wind forcing and seasonal river discharge are two important factors that control the dynamic of the plume and its biogeochemical variability. Aldrian *et al.* (2008) argued that the retention time from maximum rainfall to maximum discharge is approximately four months. In addition, at the peak of rainy season (between October and December) the underground soil water is not saturated. The rainfall does not contribute directly to the surface runoff. Hence, the groundwater outflow caused the runoff peak and discharge in Brantas River in the end of Maret-April. It was evidenced in the daily discharge data 2008 (Fig. 3). Moreover, intensive rainfall during 2008 as La Nina year produced maximal discharge 1172 $m^3$ $s^{-1}$ in Porong River, which is double of its average discharge of around 600 $m^3s^{-1}$ (Hoekstra, 1989).

DSi concentration from tributaries of Brantas River and surrounded coastal water are exclusively high and it is more than four times its world average silicic acid 150 μm (Treguer *et al.*, 1995). DSi concentration in Brantas estuaries is higher than the other tropical rivers such as Amazon (132 μm), subtropical river such as Pearl River (120-170 μm) and temperate river such as Mississippi River (108 μm) (Cai *et al.*, 2004). River contributes about 80% DSi to the world ocean (Treguer *et al.*, 1995). The first pathway from river to the ocean is by chemical weathering of silicate minerals, either directly via surface run off or indirectly via groundwater flow (Treguer *et al.*, 1995). The Brantas River Basin is bracketed by volcanic massif, and contains two active volcanoes: Mt. Semeru to the east and Mt. Kelud near the basin center.

Volcanic ash is both a major source of soil fertility and a primary cause of sedimentation (Rodger *et al.*, 2002). Jennerjahn *et al.* (2006) documented that in general DSi yield in tropical rivers was higher than subtropical rivers due to natural factors such as climate, geology and geomorphology rather than anthropogenic factors such as river regulation, urban or industrial waste disposal. We deduce that high DSi in Brantas River and Madura Strait source is from the weathering of high volcanic ash soil that is eroded by high precipitation during La Nina year, and then delivered by high surface run off to the river and groundwater flow. The abundant source of DSi had the consequence to the diatom dominated phytoplankton in the coastal water of Madura Strait (Jennerjahn *et al.*, 2004; Damar, 2008).

High discharge during rainy season shifted the mixing zone 2-10 km (Fig. 4a, 4c). Lower freshwater DO mixed with higher DO of seawater off shore. High discharge also washed DIN, DIP and DSi from the river into coastal water (Fig. 4g-i). Concentration of DOC increased at -1 to 2 km, and then decreased again (Fig 5). Decomposition of POC, which is settled at that area (Fig. 4a-f) could be the reason of high DOC as indicated by low DO at the same area (Fig. 4d, and 4i). In dry season, low river discharge allowed salt water penetration upstream during high tide, made brackish water development up to river-end station (Fig. 4a and c). Low pH at the end-river station was observed, and then increases due to the mixing with seawater. Drastic change of concentration of nutrients (DIN, DIP and DSi) at the river mouth indicated intensive biological process. $NH_4$ was dominant component of DIN in dry season. Denitrification is thought to be prominent process of net nitrate removal in estuary that takes place in a water column under condition oxygen depletion or anoxic/suboxic sediment (Dahnke *et al.*, 2008). High TSM at the coastline that well corresponds with Chl-a indicating that suspended matter contains a lot of phytoplankton. Lower load of TSM during dry season, made the coastal water turbidity lower, hence the light penetration during dry season was better than rainy season to generate higher primary production.

Porong River showed different phenomena with Wonokromo River. During dry season, the water in the river was almost stagnant without flow, therefore there was no additional oxygen from the atmosphere (aeration). Moreover, there was accumulation of organic matter in the bottom water that consumed oxygen. However, the concentration of DIN remained high. Hence it was possible that the decomposition of organic matter consumed oxygen, mineralization process occurred and then released $NH_4$ to the water column increases DIN in the river. The result of decomposition was also shown by high DOC at upstream station.

POC, DOC, TSM and chl-a concentrations in the Brantas estuaries showed strong seasonal variability (Fig. 6 and 7). POC concentration in rainy season in this study is comparable with the results of Aldrian *et al*. (2008), and 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). In general, POC concentration in the Brantas river estuaries and coastal area were lower than that in the Jakarta Bay area that was range between 200 μm–650 μm in February 2007 (Nugrahadi *et al.*, 2009). DOC concentration in this study was much lower that observed by Aldrian *et al.* (2008) in the same river such as Porong and Wonokromo. Aldrian *et al.* (2008) observed DOC in August 2005 and March 2006, which were 1000 μm and up to 3000 μm, respectively. This discrepancy is because the station location of Aldrian *et al*. (2008) was about 20 km upstream than our study. Large seasonal differences of DOC are due to high biological activity in the Brantas and Madura Strait coastal water. This fact was also supported by the seasonal variation of DO as explained above. DOC in the river was primarily produced 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). Environmental covering area also influences to the DOC concentration. It was evidenced by high DOC in Wonokromo river mouth at -1 to 2 km where the mangrove was densely populated because Wonokromo estuary had a function as mangrove touristic area. We could obtain interesting information from the relationship among TSM, POC and Chl-a in Pentan River (Fig. 6h, 7b, 7h). In the dry season, suspended sediment content in the water column was low, turbidity decreased, hence increased solar penetration in the water. Consequently, high Chl-a (Fig. 7g) occurred in the river and coastal area. In contrast, in the rainy season TSM, POC, and DOC were elevated to the maximum concentration in three rivers. Variability of POC has strong dependency on the erosion factor such as river discharge and TSM concentration in three estuaries during rainy season.

Ambient nutrient ratios are usually compared to idealized phytoplankton stoichiometry in the marine environment (Redfield *et al.*, 1963). However, such comparison is only indicative of the potential limitation of phytoplankton growth by a given nutrient (Dorth and Whitledge, 1992). The concentration of DSi in the rivers and coastal area of Madura Strait revealed no seasonal variation throughout the year. It was far beyond the limiting levels of diatoms uptake of DSi (0.1 mg/L or 36 μm, Martin-Jezequel *et al.*, 2000). Therefore, diatoms growth in Madura Strait coastal water is never limited by DSi. In dry season, DIN concentration in the river is high due to the low flow and intensive agriculture fertilizer and sewage discharge (Jennerjahn *et al.*, 2004). Hence, N:P ratio in Wonokromo and Porong rivers were mostly higher than the Redfield ratio of 16. In dry season, N:P ratio in the coastal plume decreased to below 16, indicating that nitrogen was the limiting nutrient for the primary production. In contrast, in rainy season, there was excess nitrate-dominated DIN in the river and coastal plume of Madura Strait. N:P ratio in Wonokromo and Porong Rivers are higher than the Redfield ratio. Pentan River had N:P near 16, but then increased up to 60:1 in the coastal zone. This indication may lead to the hypothesis that there was a shifting limiting factor for phytoplankton growth. However, this is different from P limitation in the other coastal regime such as Xiamen coast, Chesapeake Bay, and Pearl River Estuary where excess N is followed with P depletion (K. Yin *et al.*, 2004). In addition, we have to consider turn over time of P that is much shorter than N (Tanaka *et al.*, 2006), elevation of DIP concentration and high TSM in the river and coastal area, therefore we argue that higher N:P ratio did not necessarily mean potential P limitation. Jennerjahn *et al.* (2004) believed that the primary production in river during dry season appear to be limited by light rather than phosphorus-limited due to high turbidity. Moreover, contrast freshwater discharge in the coastal water leads to longer residence time during dry season than rainy season that controls the higher biological productivity in the coastal area of Madura Strait (Nugrahadi *et al.*, in submission). Thus, it will be a challenged to investigate the mechanism of biogeochemical process coupled with hydrodynamic regime in this area in the near future.

## SUMMARY

This paper presents a study on seasonal variation of nutrients concentrations in the river, their fate and their consequence to the ecosystem of the estuary and coastal area in the heavily anthropogenically impacted environment. Large contrast between rainy and dry seasons were described and inter relationship among nutrients were elucidated. In summary, biogeo-chemical properties of Brantas River Estuaries and Madura Strait coastal water are as follows,

1) Contrast of seasonal variation of river discharge associating with tide generates different length of mixing zone between dry and rainy season.
2) pH is low in the river due to high POC and DOC, meanwhile pH is high in sea due to dissolved inorganic carbon (DIC) consumption by Chl-a.
3) DO in river is low due to decomposition and low flow rate during dry season. DO is high in the sea due to photosynthesis by high Chl-a.
4) DIN and DIP concentration in Brantas Estuaries and Madura Strait are high. Furthermore, DSi concentration was extremely high and it was four times higher than its average concentration in the World Rivers due to natural characteristic of the river basin.
5) N:P ratio has seasonal variation due to large discrepancy of DIN and DIP supply from land to the sea through the river.
6) Chl-a is high during dry season when the TSM is low, despite very low concentration of nutrients. N:P ratio is high in the estuaries, however concentration of DIP increases with high TSM. This indicates that light is the limiting factor for the primary production.

Madura Strait receives large seasonal and spatial variation of nutrient supply. Largest nutrient input is during rainy season and Porong River has the largest contribution due to high river discharge. However, beside nutrient supply, the other physical process such as water residence time may play a very important role controlling biological activity in the coastal water of the area, which will be studied in the near future. Moreover, this study describes the qualitative approach on biogeochemical aspect of the river and estuary that is averaged into seasonal scale. Nevertheless, there may be some valuable aspects that vary in the shorter time scale. Therefore, a simple ecosystem model will be applied in the future to cope valuable insight into pathways of organic matter transfer in ecosystem

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## REFERENCE

Aldrian E. and R.D. Susanto. 2003. Identification of three dominant rainfall regions within Indonesia and their relationship to sea surface temperature. *Int. J. Climate.*, 23: 1435–1452.

Aldrian, E., C-T. A. Chen, S. Adi, Prihartanto, Sudiana, N. and S.P. Nugroho. 2008. Spatial and seasonal dynamics of riverine carbon fluxes of the Brantas catchment in East Java. *J. Geophys. Res.*,113,G.03029,doi:10.1029/2007JG000626.

Baum, A., T. Rixen and J. Samiaji. 2007. Relevance of peat draining rivers in cenral Sumatera for the riverine input of disssolved organic carbon into the ocean. *Estuarine, Coastal and Shelf Science,* 73: 563–570.

Bianchi, S. 2007. *Biogeochemistry of estuaries.* Oxford Univ. Press, pp 720.

Boulton, A. J., S. Findlay, P. Marmonier, E. H. Stanley, and H. M. Valett. 1998. The functional significance of the hyporheic zone in streams and rivers. *Annual Review of Ecology and Systematics*, 29: 59–81.

Cai, Y., L. Guo, and T. A. Douglas (2008), Temporal variations in organic carbon species and fluxes from the Chena River, Alaska, Limnol. Oceanogr.,53, 1408–1419.

Daag, M., R. Benner, S. Lohrenz, D. Lawrence. 2004. Transformation of dissolved and particulate materials on continental shelves influence by large rivers: plume processes. *Continental Shelf Research*, 24: 833–858.

Dahnke, K., E. Bahlmann, K. Emeis. 2008. A nitrate sinks in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary. *Limnology and Oceanography*, 53(4): 1501–1514.

Damar, A. 2008. Dynamics in the Brantas River Estuary, Java, Indonesia. Coastal Environments: Focus on Asian: 173-189.

Dickson, A.W. Maki, and W.A. Brungs, eds., Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems. Proceedings of the Sixth Pellston Workshop, Florissant, CO, August 12-17, 1984. Pergamon Press, New York. pp. 219-244.

Dorth, Q. and T.E. Whitledge. 1992. Does nitrogen or silicon limit nitrate phytoplankton production in the Mississippi river plume and nearby regions. *Continental Shelf Research,* 12: 367–789.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast, Carbon and carbonate metabolism in coastal aquatic ecosystems, *Annu. Rev. Ecol. Syst.*, 29, 405– 433, 1998.

Grasshoff, K., K. Kremling, M. Ehrhardt. 1999. Methods of seawater analysis. *Willey-VCH, Weinheimm*, 632p.

Hoekstra, P (1989). River outflow, depositional process and coastal morph dynamics in a monsoon-dominated deltaic environment, East Java. *Netherland Geographic Studies*, 209p.

Hidayat, Fahmi, H. M. Sungguh, Harianto. 2008. Impact of climate change on floods in Bengawan solo and Brantas River Basins, Indonesia. *Presentation paper at 11th River Symposium September 2008*, Brisbane, Australia

Jennerjahn T.C, B.A. Knoppers, W.F.L. de Souza, G.J. Brunskill, E.I.L. Silva and Seno Adi. 2006. Factors controlling dissolved silica in tropical rivers. The Silicon cycle. Human perturbations and impacts on aquatic systems (eds. V. Ittekkot, D. Unger, C. Humborg, and N.Tac An). *SCOPE 66, Island Press*. Washington D.C., p29–51.

Jennerjahn, T.C., V. Ittekkot, S. Klopper, S. Adi, S.P. Nugroho, N. Sudiana, A. Yusmal, Prihartanto, G. Gaye-Haake. 2004. Biogeochemistry of a tropical river affected by human activities in its catchment: Brantas River estuary and coastal waters of Madura Strait, Java, Indonesia. *Estuarine, Coastal and Shelf Science,* 60: 503–514.

Li, W., J. Dagaut, A. Saliout. 1995. The application of sterol biomarkers to the study of the sources of particulate organic matter in the solo River System and Serayu River, Java, Indonesia. *Biogeochemistry*, 31: 139–154.

Martin-Jézéquel, V., M. Hildebrand, and M. A. Brzezinski. 2000. Silicon metabolism in diatoms: Implications for growth. *J. Phycol*., 36, 821–840.

Meybeck, M. 1982. Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci*., 282: 401–450.

Millero FJ, Woosley R, Ditrolio B, Waters J (2009) Effect of ocean acidification on the speciation of metals in sea water. Oceanography 22:72−85.

Nugrahadi, M.S., K. Duwe, F. Schroeder, D. Goldmann. 2010. *Seasonal variability of the water residence time in the Madura Strait, East Java, Indonesia*. In submission.

Nugrahadi, M.S., T. Yanagi, I.G. Tejakusuma, S. Adi, R. Darmawan. 2009. Dissolved and particulate carbon in Jakarta Bay, Indonesia. *Mar. Res. Indonesia*, 34:11–16.

Redfield A.G., B.H. Ketchum, F. A. Richards. 1963. *The influence of organism on the composition of seawater.* In: Hill, M.N. (ed). *The Sea*, 2, 26–77.

Rodger, D., Livieu, G., Robert, C. 2002. Paleoceanographic signi¢cance of sediment color on western North Atlantic drifts: Origin of color. *Marine Geology* 189: 25–41.

Talaue-McManus, L. 2001. *Global change in the coastal zone the case of South-east Asia.* LOICZ Newsletter, September 2001, Texel.

Tanaka, T., P. Henriksen, R. Lignell, K. Olli, J.Seppälä, T.Tamminen and T. F. Thingstad. 2006. Specific affinity for phosphate uptake and specific alkaline phosphatase acti-vity as diagnostic tools for detecting phosphorus-limited phyto-plankton and bacteria. *Estuaries and Coasts*, 29: 1226–1241.

Treguer, P., D.M. Nelson, A.J.v-Bennekom, D.J. DeMaster, A. Leynaert, B. Queguiner. 1995. The Silica balance in the world ocean: a reestimate. *Science,* 268: 375–379.

Yin, K., Lin, Z., and Ke, Z. 2004. Temporal and Spatial Distribution of Dissolve Oxygen in the Pear River Estuary and Adjacent Coastal Waters. *Continental Shelf Research,* 24: 1935–1948.

Yulihastin E., N. Febrianti, Trismidianto. 2009. *Impacts of El Nino and IOD on the Indonesian Climate.* http://www2.ims.nus.edu.sg/Programs/09fluidss/files/~Report_Swadhin%20Behera.pdf