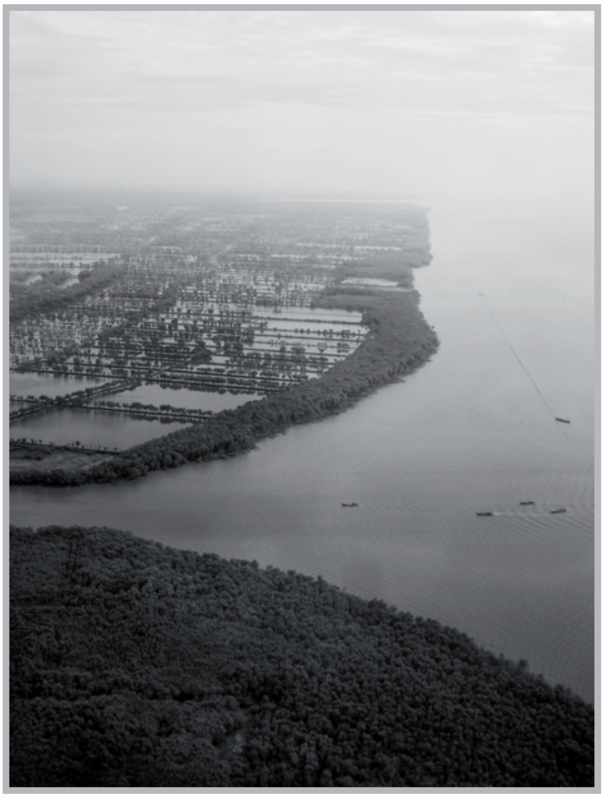
Sources and fate of particulate organic matter in the sediments of the Brantas estuary, Java, Indonesia



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vorgelegt von

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CONTENTS

ABSTRACT

The important role of coastal sediments in the global carbon cycle in terms of transformation, accumulation, remineralization, and burial has been widely recognized. In this context, especially the sediments along the tropical coasts of Southeast Asia and Oceania are crucial due to their high sediment input to the ocean and the intense human activities within the coastal zone. However, most of the studies on coastal organic matter (OM) cycling were conducted in temperate regions and knowledge about tropical coastal ecosystems is still scarce.

The present study aimed to investigate the spatio-temporal variations of sedimentary processes as well as their dependence on natural processes and anthropogenic influences in the coastal waters of the Brantas estuary, East Java. The Brantas River is the second largest river of Java and its catchment exemplifies a coastal zone of Southeast Asia heavily impacted by human activities. During four expeditions in the rainy and dry season of 2008 and the rainy seasons of 2010 and 2011, surface samples and sediment cores were taken and analyzed for a variety of biogeochemical parameters, such as amino acids, stable isotopes or ammonium pore water concentrations.

Regional and seasonal distribution patterns of sedimentary OM characteristics were predominantly determined by the quantity and composition of the riverine material input. Regional variations mainly resulted from strongly differing discharge rates between the two main river arms, the Porong and the Wonokromo. Compared to the Wonokromo River input, the manifold higher discharge of the Porong River resulted in a much higher accumulation of terrestrial material in the adjacent estuary. The riverine organic matter was mainly derived from soil. The reactivity of the riverine OM was lower than that of the freshly produced marine OM. As their respective portions in the sediments determined the magnitude and spatial gradients of the OM reactivity in the estuarine sediments, lowest values were found off the Porong. The lower reactivity of sedimentary OM at the Porong estuary resulted in a lower OM degradation rate compared to the Wonokromo estuary. Consequently, benthic ammonium fluxes, which strongly depend on the amount of remineralized OM, were higher at the Wonokromo estuary. However, benthic ammonium supply was a considerable year-round source for the Brantas estuarine waters. Seasonal variations of OM reactivity occurred as, according to the monsoonal cycle, the discharge rates in both rivers were strongly enhanced during the rainy season. This resulted in an overall higher input of terrestrial, refractory material to the estuary and led to a lower reactivity of sedimentary OM. However, regional differences of ammonium fluxes and OM reactivity exceeded seasonal variations. Nevertheless, focusing only on the Porong estuary, material deposition and burial rates were significantly affected by seasonal river discharge variations. Due to the much higher riverine particulate organic carbon (POC) input in the rainy season that by far exceeded benthic remineralization rates, huge amounts of POC were buried. In contrast to this phase of accumulation, the dry season can be considered as a period of degradation, given that the low amounts of sedimenting POC are immediately remineralized or were even decomposed in the water column.

Overall, compared to other marine environments the sediments at the Brantas estuary are characterized by a low reactivity of sedimentary OM due to a strong degradation of organic matter that is caused by intense tide-induced resuspension processes occurring in the shallow Brantas estuary. The high benthic ammonium fluxes and very high POC burial rates substantiate the role of coastal sediments as important sources and sinks in nutrient cycles.

ZUSAMMENFASSUNG

Im Rahmen des globalen Kohlenstoffskreislauf besitzen küstennahe Sedimente eine wichtige Rolle im Hinblick auf Umwandlungs-, Akkumulations-, Zersetzungs- und Ablagerungprozesse. In diesem Zusammenhang sind insbesondere die Sedimente in Südostasien und Ozeanien aufgrund der dortigen hohen Eintragsraten und des enormen anthropogenem Einflusses im Küstenbereich hervorzuheben. Die bisherigen Studien des Kohlenstoffeskreislauf in Küstenzonen konzentrieren sich jedoch weitgehend auf die gemäßigten Breiten, wohingegen tropische Küstenökosysteme bislang unzulänglich erforscht sind.

Die vorliegende Dissertation untersucht die räumlich-zeitliche Variation von benthischen Prozessen im Brantas-Ästuar (Ost-Java) sowie deren Abhängigkeit von natürlichen und anthropogenen Umwelteinflüssen. Der Brantas ist der zweitgrößte Fluss Javas und sein Einzugsgebiet ist stark durch menschliche Aktivitäten geprägt. Während vier Expeditionen in der Regen- und Trockenzeit 2008 sowie den Regenzeiten von 2010 und 2011 wurden Oberflächenproben und Sedimentkerne gewonnen, an welchen biogeochemische Parameter wie bspw. Aminosäuren, stabile Isotope und Ammoniumkonzentrationen im Porenwasser untersucht wurden.

Regional und saisonal schwankende Eigenschaften des organischen Materials in den Küstensedimenten wurden vorrangig durch Menge und Zusammensetzung der Flusseinträge bestimmt. Regionale Unterschiede sind vornehmlich auf die unterschiedlichen Abflussraten der beiden Hauptarme des Brantas, der Porong und der Wonokromo, zurückzuführen. Deutlich höhere Abflussraten des Porongs führten dabei zu einer höheren Akkumulation von terrestrischem, organischem Material in dessen angrenzendem Mündungsbereich. Das vom Fluss transportierte organische Material stammte überwiegend aus Bodenmaterial. Es wies eine geringere Reaktivität auf als frisches marines organisches Material. Folglich war die Reaktivität des organischen Materials in den ästuarinen Sedimenten am geringsten vor der Porongmündung. Die geringere Reaktivität führte zu einer ebenfalls geringen Degradation von organischem Material. Dies wiederum resultierte in deutlich reduzierten benthischen Ammonium-Stoffflüssen, welche generell stark von der Menge des remineralisierten organischem Material abhängig sind. Ungeachtet der regionalen Schwankungen stellten die benthischen Ammoniumflüsse über das ganze

Jahr hinweg eine wichtige Ammoniumquelle des Ästuars dar. Saisonale Schwankungen der Reaktivität des benthischen organischen Materials resultierten aus den stark erhöhten Schwankungen der Abflussraten während der Regenzeit. Dies führte zu einem stärkenen Eintrag an terrestrischem, refraktärem Material, dessen Ablagerung im Ästuar eine Verringerung der Reaktivität des organischen Materials zur Folge hatte. Trotz der starken saisonalen Unterschiede der Abflussraten überlagerten jedoch die regionalen Unterschiede der Sedimenteigenschaften und Ammonium-Stoffflüsse die saisonal auftretenden Schwankungen. Betrachtet man ausschließlich die Sedimente des Porong-Ästuars so wurden die Akkumulationsraten signifikant durch die saisonalen Unterschiede beeinflusst. Da die Flusseinträge von partikulärem organischem Kohlenstoff in der Regenzeit die remineralisierten Mengen bei weitem überstiegen, wurden große Mengen des angelieferten Materials sedimentiert. Dahingegen stellte sich die Trockenzeit als eine Phase der Degradation dar, in welcher die geringen Flusseinträge sofort remineralisiert wurden.

Im Vergleich zu anderen marinen Gebieten zeichnen sich die Sedimente des Brantas-Ästuars durch eine geringe Reaktivität des abgelagerten organischen Materials aus. Der Hauptgrund dafür liegt in einer starken Degradation, welche durch tidenabhängige Resuspensionsprozesse im flachen Brantas-Ästuar ausgelöst werden. Die, global betrachtet, hohen benthischen Ammonium-Stoffflüsse und sehr hohen Sedimentationsraten von partikulärem organischem Material bekräftigen die Rolle der küstennahen Sedimente als wichtige Quellen sowie Senken in Nährstoffkreisläufen.

1 INTRODUCTION

1.1 Coastal zones and estuaries – relevance and threats from global scale to an Indonesian estuary

Estuaries and coastal waters, which are the interface between land and ocean, cover approximately 7 % of the surface area of the world's ocean (Gattuso et al., 1998). There is a huge variety of coastal ecosystems, ranging from tidal flats, salt marshes, seagrass meadows to coral reefs. All of them are characterized by multiple biogeochemical gradients and processes (e.g. Alongi, 1998). Despite their relatively small areal dimensions, coastal zones are highly productive (30% of the total net oceanic primary production), have some of the highest biotic diversity in the world and support at least 90% of the global fish catch (Holligan, 1992; Alongi, 1998). The high productivity is primarily driven by nutrient and organic matter (OM) inputs from rivers, but also groundwater and atmospheric input as well as upwelling and exchanges with offshore waters are important coastal nutrient sources. Under the interactions of various highly dynamic physical, chemical and biological processes the land-derived material can be substantially modified and recycled within estuarine and coastal environments before reaching the open ocean (e.g. Bianchi, 2007). Furthermore, a significant part of the terrestrial material is retained in these crucial land-ocean pathways, where e.g. 80 % of the global organic carbon (OC) burial takes place (Berner, 1989; Hedges and Keil, 1995). Thus, estuarine and coastal waters play a key role in global nutrient cycling and have a high ecological as well as economical value (e.g. Costanza et al., 1997; Crossland et al., 2005; Jickells, 1998)

These important and valuable marine ecosystems also belong to the most perturbed areas, as human activities and settlement concentrate along coasts and estuaries throughout the world (e.g. Crossland et al., 2005). About 44 % of the global population lives in the coastal zone (100 km distance from the coast, LOICZ) and the coastal population density is disproportionally increasing to the global population (Shi and Singh, 2003). Impacts of coastal population pressure, which are already visible, will further increase in the future.

These are mainly:

a) alterations of nutrient cycles (e.g. nutrient enrichment),

b) physical restructuring of the environment (e.g. dredging),

c) alterations of the hydrological river regimes and associated changes of freshwater flow and sediment discharge (e.g. damming and water diversions),

d) harvesting and overexploitation of living and nonliving resources,

e) chemical contamination due to extensive industrialization,

f) introduction of non-native species (Hobbie, 2000).

It becomes apparent that the understanding of the dynamics of land-ocean interactions, coastal processes and the influence of human interventions is fundamental to estimate global nutrient cycling and to evaluate complex and sustainable management issues, especially with respect to the biogeochemical and physical processes that regulate the chemistry and biology of estuaries (Bianchi et al., 1999; Crossland et al., 2005). Most of the knowledge of how coastal ecosystems are functioning has been derived from the temperate regions and cannot be easily transferred to tropical coastal zones, as these show essentially different features, e.g. regarding climatic, hydrological or erosion processes (e.g. Alongi, 1998). Thus, more investigations of the heterogeneous tropical coastal environments are needed for the evaluation and understanding of global biogeochemical budgets and processes, especially with regard to the increasing human impacts burdening these regions. ***Southeast Asia*** is particularly crucial in this respect as it exhibits the highest population pressure and most intense environmental changes within the coastal zone, followed by Europe and North America (Elvidge et al., 1997; Nicholls and Small, 2002) (Fig. 1).

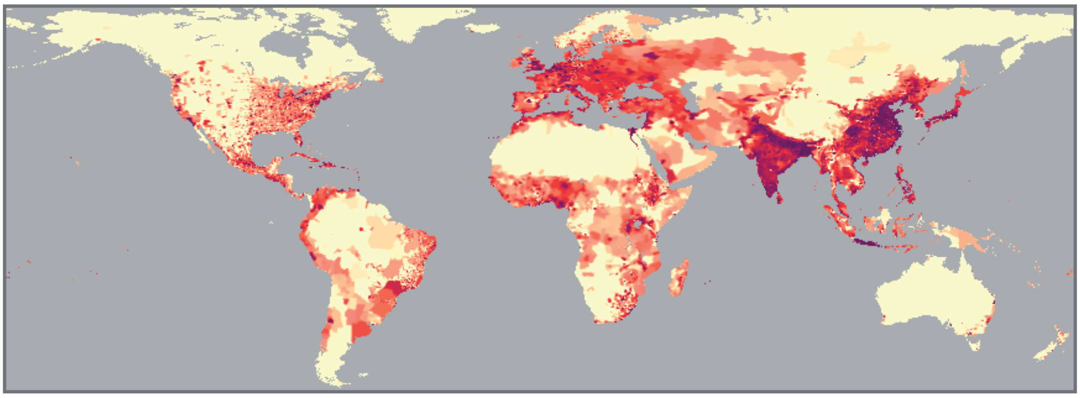

Figure 1 Population density of the world (from SEDAC)

Furthermore, Southeast Asia plays a key role in global nutrient cycles due to the very high material discharge into the oceans and the associated high accumulation and burial of material. It was estimated that the rivers of Southern Asia and Oceania contribute to more than 70% of the oceans sediment input (Fig. 2, Milliman and Meade, 1983). Milliman and Syvitski (1992) emphasized the large export capacity of the small mountainous rivers of these region and Milliman et al. (1999) calculated that the high-standing islands of the "East Indies" (predominantly Indonesia) alone transport a disproportionally high sediment amount to the ocean (20 to 25 % of the global sediment export). Among an overall increased sediment load under human influence particularly Indonesia shows strong enhancements of modern sediments loads, what has been largely ascribed to deforestation (Syvitski et al., 2005). This indicates the high intensity of human modification proceeding in Indonesia. The strong population pressure becomes extremely visible on the ***Island of Java*** where more than half of the nation's population lives (230 Mio inhabitants and 4th Rank world wide, Worldbank). Associated environmental problems have increased and the landscape has changed strongly due to intense deforestation that took place especially in the last decades for agricultural purposes, such as rice cultivation, or for the construction of aquaculture ponds along the coast (Boomgaard, 1992; Fox, 2005; Whitten et al., 1996).

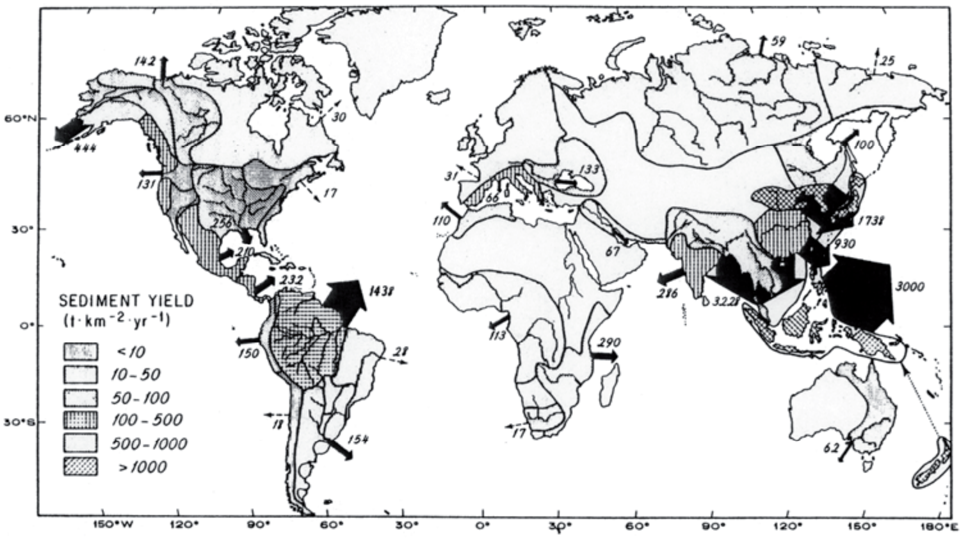

Figure 2 Annual discharge of suspended sediment from various drainage basins in the world. Width of arrows corresponds to relative discharge. Numbers refer to average annual input in millions of tons (from Milliman and Meade, 1983)

The catchment area and coastal zone of the second largest river of Java, the ***Brantas River***, is one of the most densely populated regions in Indonesia and notably affected by human activities. It comprises an area of 11050 km² (Whitten et al., 1996) and exhibits a population density of more than 1000 inhabitants per km². The Brantas river basin is nowadays one of the nation's major areas of agricultural cultivation (Booth et al., 2001). The intensive agriculture and a strong urbanization as well as industrialization created the demand for various river regulations (e.g. six reservoirs, dams, etc.) that strongly alter the discharge regime (Sudaryanti et al., 2001). Additional factors like deforestation, sand mining or the conversion of estuarine mangroves to aquaculture ponds enhanced the environmental degradation (Römer-Seel, 2003). Apart from the flow regime, these perturbations alter the amount and composition of substances that are transported by the river and discharged into the coastal sea where it might result in alterations of coastal nutrient cycles (Jennerjahn et al., 2004).

Besides the numerous human influences, the river discharge regime is controlled by a strong monsoonal system that it is characterized by the alteration of a wet season (West-Northwest monsoon) lasting from November until April and a dry East-Southeast monsoon prevailing from May until October. The rainfall rates average 2300 mm per year with 80 % precipitating during the wet season (Aldrian and Djamil, 2008). The rainfall shows strong interannual variations and also exhibits different precipitation rates within the catchment area that comprises high volcanic complexes in the south and large alluvial plains in the coastal lowland (Whitten et al. 1996). Due to the high abundance of volcanoes and volcanic eruptions, a tremendous production of highly erodible material is present and high erosion from the mountain slopes and the alluvial plains, which are intensively used by agriculture, supply a considerable amount of sediment to the river (Lavigne and Gunnell, 2006). The total sediment yield of the Brantas River is about 256 t km²/year (Aldrian et al., 2008). The highly fluctuating precipitation involves an unequal annual river runoff with strongest pulses in the wet season. The discharge is disproportionally distributed to the main river arms Porong (major channel) and Wonokromo (minor channel) that branch out in the coastal lowland and discharge into the Madura Strait (Fig. 3). Thus, the estuary of the Brantas River comprises the eastern part of the Madura Strait where salinity distributions in the coastal waters vary strongly with the seasonally varying river discharge and the tides (e.g. Hoekstra et al., 1989). The estuary and nearshore coastal waters are characterized by extensive tidal flats and a strong resuspension action of currents and tides that range within a micro- to mesotidal scale (Hoekstra, 1989; Hoekstra et al., 1989).

Thus, the Brantas River can be characterized as a mid-sized tropical mountainous river that is, on the one hand, strongly affected by variations in monsoonal precipitation and, on the other hand, strongly influenced by human activities in its catchment.

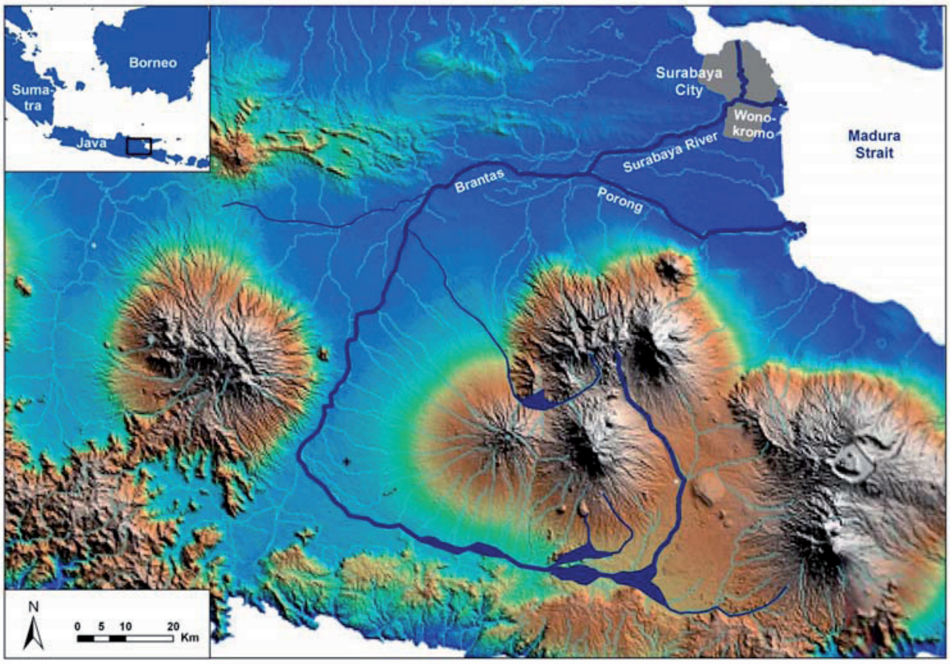

Figure 3 The Brantas River in East Java (modified from Mazzini et al., 2000)

1.2 The role of sediments in coastal environments

Sediments play a significant role in OM decomposition and nutrient recycling in marine ecosystems. Especially in coastal environments that receive huge material inputs and are characterized by closely coupled benthic-pelagic processes, sediments have an important regulatory and buffering function (Jørgensen, 1996). This is, firstly, based on their high storage capacity for OM and, secondly, due to the fact that the retention and release of nutrients via the sediment-water interface can largely influence the nutrient dynamics (e.g. Kemp et al., 1990; Caffrey et al., 2002). On the one hand, sediments can be a significant sink for nutrients in shallow coastal systems, e.g. through denitrification. This important process of nutrient removal in coastal marine sediments can reduce large amounts of the nitrogen inputs to the coastal environment to gaseous nitrogen (N_2, N_2O) and, therefore, largely influence the coastal nitrogen budgets (e.g. Seitzinger, 1988). On the other hand, the benthic remineralization of OM can supply substantial nutrient amounts to the overlying water column that are comparable or even higher than those contributed by local rivers (e.g. Billen, 1978; Conley et al., 1997; Friedrich et al., 2002). Thus, a major fraction of the nutrient requirements of the pelagic primary producers can be provided by benthic fluxes (e.g. Rowe et al., 1975; Nixon, 1981). In contrast to the open ocean, where huge parts of the organic matter are recycled within the water column, the sediments in shallow estuarine environments are largely involved in the mineralization of the land-derived and primary produced OM, since the settling times for organic detritus are relatively short and the supply is immense (e.g. Graf, 1992).

The decomposition of organic matter in marine sediments proceeds through a sequence of electron acceptors that is determined by the energy yield for microorganisms, which drives the remineralization processes (e.g. Froehlich et al., 1979). Since oxic respiration is the most energetic oxidation reaction, oxygen is depleted first followed by the reduction of nitrate > manganese oxide > iron oxide > sulfate and methane fermentation (e.g. Canfield, 1993; Thamdrup and Canfield, 2000), whereby the individual reaction can overlap each other (Fig. 4). Simultaneous to the oxidation of organic matter, the electron acceptors can also be consumed during the reoxidation of the reduced inorganic products originating during decomposition (e.g. Hensen et al., 2006). Several factors can influence the relative importance of the diverse mineralization pathways, e.g. sedimentation rate, bottom water chemistry and sediment composition (for review see e.g. Jørgensen, 1983; Henrichs and Reeburgh, 1987).

The rates of benthic degradation are highly variable and they are determined by a variety of factors like the quantity (availability) and quality (reactivity) of OM, metabolic activity of sediment microbial communities, the availability of electron acceptors, sediment accumulation rates, mineral protection or the oxygen exposure time (e.g. Canfield, 1994; Keil et al., 1994a; Hartnett et al., 1998; Keil et al., 2004). As microorganisms first break down the most readily metabolizable material, the rate of decomposition changes with the degradation status (or reactivity) of the organic material. The residual organic detritus becomes more and more refractory with increasing time (and depth) and at the same time less reactive towards microbial decay resulting in slower organic matter degradation rates (Stanier et al., 1980; Hulthe et al., 1998; Van Cappellen et al. 2002).

The transport of the remineralized nutrients from the sediment to the water column proceeds mainly via molecular diffusion, macrobenthic activities, advective transport of porewater and episodic events like the resuspension of surficial sediments (Berner, 1980; Mortimer, 1999; Huettel et al., 2003; Almroth et al., 2009).

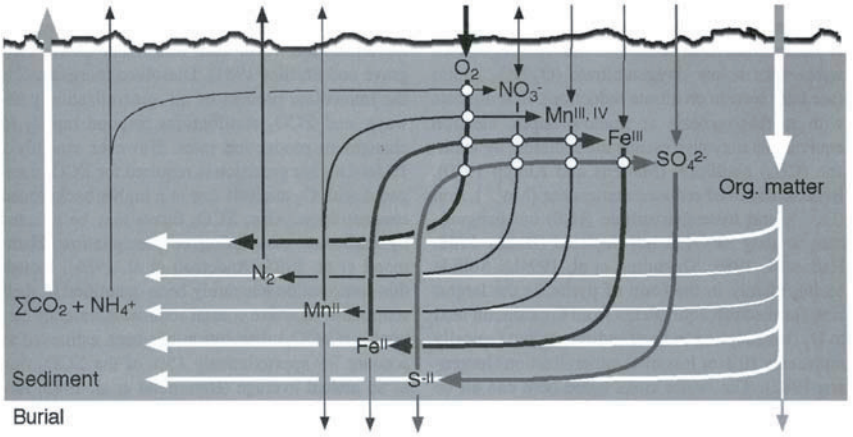

Figure 4 Schematic view of the various mineralization pathway during the decomposition of OM. Circles at intersections indicate reoxidation reactions (from Thamdrup and Canfield, 2000).

A huge part of the deposited material is recycled and the organic matter that escapes these remineralization pathways becomes permanently buried. The burial of organic matter in the marine sediments is one of the crucial sink mechanisms controlling the global distribution and cycling of major elements like C, N, P, and S (e.g. Berner, 1989; Kump, 1992). It has been widely observed, that an increasing fraction of the deposited organic matter escapes degradation with increasing sedimentation rate (e.g. Müller and Suess, 1979; Henrichs and Reeburgh, 1987; Tromp et al., 1995). Due to the high material delivery and its rapid deposition in coastal regions the sediments in these areas are sites of enhanced preservation and, thus, accumulation of organic matter. Especially the high sediment yields of fluvial systems in Southeast Asia and Oceania become important in this regard. As they account for a disproportionally high fraction of the global material fluxes to the ocean (e.g. Milliman and Syvitski, 1992; Nittrouer and Kuehl, 1995) these subtropical and tropical coastal regions became potential significant burial sites on global scale.

Thus, on shorter (benthic fluxes) and larger (burial of organic matter) timescales, coastal sediments are significant for regional and global nutrient cycling and there is a need to understand and quantify the involved processes.

1.3 Motivation and Objectives

This thesis was conducted within the project MADURA-Monitoring. It is affiliated to the German-Indonesian program SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) that aims to investigate scientific, social and economic issues related to the management of the Indonesian coastal ecosystems and their resources.

The main objective of the subproject MADURA-Monitoring was to investigate the spatial-temporal variations of biogeochemical cycles and associated controlling processes as well as their dependence on natural processes and anthropogenic influences in the coastal waters of the Brantas estuary located at the eastern part of the Madura Strait. Locally, this knowledge, in combination with the survey of the river material inputs, is essential to, 1.) assess the impact of the natural variations and the human activities in the hinterland for the coastal ecology, 2.) establish a sustainable management of the coastal ecosystem and its natural resources, which are of fundamental value for the local population. With relevance to global processes, the investigations of the biogeochemical cycling in the Brantas estuary could provide knowledge from one of the most crucial regions with regard to human perturbations, as the Brantas River catchment and the adjacent coastal waters exemplify a coastal zone of Southeast Asia heavily impacted by human activities. Furthermore, high mountains in the catchment area, its size of 11050 km² and high erosion rates as well as high sediment yields classify the Brantas River as one of the important mountainous rivers that are crucial within global budgets concerning sediment fluxes to the ocean (e.g. Milliman and Syvitski, 1992). Therefore, the Brantas coastal region is an excellent study area to assess coastal ecosystem functions and its biogeochemical cycling within the globally important region of Southeast Asia. Additionally, it helps to close the gap of knowledge on biogeochemical processes in tropical coastal regions, where much less research was conducted compared to temperate regions.

In a preliminary study, first insights on biogeochemical processes in the Brantas River and its estuary could be gained (Jennerjahn et al., 2004). However, many questions are left open for a profound understanding of the coastal processes or even arose from these first findings, partly due to the fact that sampling was conducted only during one season. Thus, almost no knowledge was obtained regarding the seasonal variations of the river input via the two main river channels and their distribution, transformation processes, and retention in the adjacent coastal waters. Great differences can be expected in this respect due to natural seasonal variations (monsoonal system) and the various human activities (e.g. river regulations, intensive agriculture) in the hinterland. Furthermore, during the preliminary study sustenance of primary production in the coastal waters was observed despite a rapid decrease of nutrients in offshore direction, what raised the questions if there may be other nutrient sources available than those related to the river discharge, such as benthic nutrient supply.

These questions were investigated concomitant to the general aim of understanding the regional and temporal variations of coastal biogeochemical processes in the Brantas estuary. Therefore, comprehensive samplings of water, suspended matter, surface sediments and sediment cores were performed in the rainy and dry season of 2007 and 2008 and additional field campaigns were carried out to a smaller extent in the rainy season of 2010 and 2011. The investigations of the spatial and temporal biogeochemical changes in the different river branches and the costal water column are discussed within the thesis and publications of I. Jänen.

The present thesis concentrates on the sedimentary processes in the Brantas estuary, which are examined with special regard to natural and anthropogenic land-based impacts on the coastal ecosystem. These comprise, on the one hand, the potential influence of human activities in the catchments via the riverine input and, on the other hand, the overall high riverine material export of the Brantas River and its seasonal changes (monsoonal system) as well as its regional variation due to the different discharge rates of the two main river channels.

Considering these aspects and with respect to the important role of sediments in the processing of OM in coastal environments, this study aims

A) to define the sources of sedimentary OM and its seasonal and regional distribution and deposition,
B) to investigate the processes of OM degradation and their influencing factors,
C) to quantify benthic fluxes and estimate their importance for the estuarine nutrient cycling,
D) to determine the burial of particulate organic carbon (POC) in the estuarine sediments.

These objectives are discussed in three manuscripts written in the context of this thesis. The fundamental question combining all three manuscripts is about the fate of OM in the sediments of the Brantas estuary (Fig. 5). In the first manuscript (1) the characteristics of sedimentary OM and especially its reactivity towards microbial decay is examined in relation to the OM sources. This knowledge is important for the further investigation of the decomposition of sedimentary OM as it can be strongly influenced by a varying quantity and quality of OM supply (objectives A and B). These factors also determining the amount of remineralized nutrients, whose quantification and relevance for the coastal nutrient pool is estimated in the second manuscript (2; objectives B and C). Besides a benthic nutrient supply to the water column the OM remineralization also determines the amount of OC that is buried in the sediments. This important sink function of the sediments within global carbon budgets is quantified in the third manuscript (3; objective B and D)

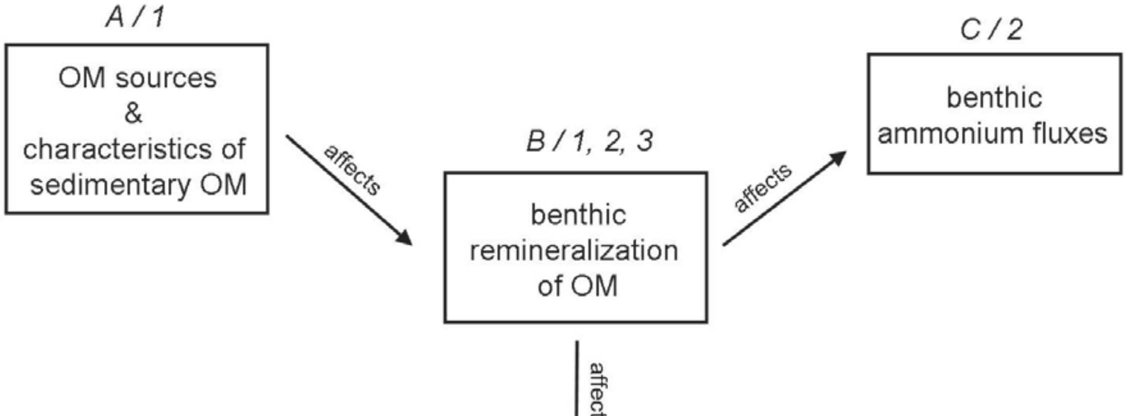

Figure 5 Topics and relationships addressed in the present thesis (1-3 number of manuscripts, A-D = objectives)

1.4 Publication outline

This study includes three manuscripts. Two of them have been submitted to international journals and the third will be submitted soon.

Manuscript I

Sources and degradation of sedimentary organic matter in coastal waters off the Brantas River, Java, Indonesia

by Claudia Propp, Ingo Jänen, Tim Jennerjahn

C.P. developed the concept of this study. Field work in Indonesia was conducted by C.P and I.J.. Laboratory work was carried out by C.P. The evaluation of the data was done by C.P. who also wrote the manuscript with editorial help of all authors.
The manuscript has been submitted to the Asian Journal of Water, Environment and Pollution.

Manuscript II

Variability of benthic ammonium fluxes in the Brantas River estuary, Java, Indonesia

by Claudia Propp, Ingo Jänen, Frank Wenzhöfer, Matthias Zabel and Tim Jennerjahn

The concept of the study was developed by C.P.. Field work in Indonesia was conducted by C.P and I.J.. Laboratory work was carried out by C.P. who also evaluated the data and wrote the manuscripts with scientific and editorial advice from F.W., M.Z. and T.J.
The manuscript has been submitted to Estuarine, Coastal and Shelf Science.

Manuscript III

Seasonal variation of carbon burial in the estuary of a mid-sized tropical mountainous river

by Claudia Propp, Ingo Jänen, Martina Löbl, Frank Wenzhöfer and Tim Jennerjahn

C.P and M.B. developed the concept of this study. Field work in Indonesia was conducted by C.P and I.J.. Laboratory work was carried out by C.P. and I.J. The data was evaluated by C.P., F.W., M.L. and T.J.. C.P. wrote the manuscript with editorial help of F.W. and M.L.
The manuscript is in preparation for submission.

2 MANUSCRIPT I

Sources and degradation of sedimentary organic matter in coastal waters off the Brantas River, Java, Indonesia

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Abstract

Organic matter (OM) processing in estuaries is crucial in the marine environment as significant quantities of OM are buried or modified in these land-ocean-interactions zones. Southeast Asia is globally important in this regard because of high sediment inputs to the ocean and intense human modifications in the coastal zone, as exemplarily can be observed in the catchment of Java's second largest river, the Brantas. In order to investigate sedimentary OM processing, surface sediments and short sediment cores were sampled in its estuary in the rainy and dry season of 2008. $\delta^{13}C_{org}$, $\delta^{15}N$, C/N ratios and amino acids and hexosamines were used to determine the sources, transformation and fate of estuarine sedimentary organic matter. Ranges in $\delta^{13}C_{org}$ of -24.9 to -20.1 ‰, in $\delta^{15}N$ of 3.5 to 5.4 ‰ and a C/N ratio of 7.9 to 16.5 in the sediments indicate a mixture of freshly produced marine algae and degraded terrestrial soil organic matter. The relative contributions of the autochthonous and allochthonous OM in the estuarine sediments differed according to the amount and dispersal of the land-derived material. As the discharge of the two main river arms, the Porong and the Wonokromo River, showed strong differences with up to fivefold higher values in the Porong River in the rainy season, the highest proportion of terrestrial OM was found off the Porong river mouth that received the highest riverine runoff. Also the lowest sedimentary reactivity was detected in this region as displayed by amino acids (AA) and hexosamines (HA). AA+HA ranged between 0.76 to 5.25 mg g^{-1}, amino acid bound carbon between 5.9 to 22.6 % and the AA/HA ratio between 4.2 – 13.0. Furthermore, a reduced intensity of OM degradation was observed in front of the Porong River outlet, what has been attributed to the high quantity of depositing material and the low reactivity of the surface sediments. In a global context the reactivity of sedimentary OM from the Brantas estuary was in the range of degraded sediments from offshore regions or stations at greater water depth. It indicates that severe OM degradation based on a strong tidally induced resuspension of sediments in the turbid and well mixed waters of the shallow Brantas estuary is responsible for burial of refractory carbon.

Keywords: sediments, organic matter, organic matter degradation, stable carbon isotopes, amino acids, Indonesia, East Java, Brantas estuary

Introduction

Estuaries and their adjacent areas are the main connection between terrestrial and marine environments. Significant quantities of terrestrial and marine organic matter (OM) are deposited in these regions of high primary production that is largely sustained by the riverine nutrient inputs (e.g. Prahl et al., 1994; McKee et al., 2004; Bianchi, 2007). Thus, estuaries and coastal zones are a significant sink of OM in the marine environment and play an important role in the global organic carbon cycle (e.g. Berner, 1989; Hedges and Keil, 1995; Hedges, 1997). Determining the origin and composition of OM and processes that affect its distribution, degradation and preservation in coastal zones is therefore fundamental for a comprehensive understanding of the fate of OM in the marine environment. In this respect, recent studies revealed a strong degradation of OM along tropical coasts and shelves that is based on intensive resuspension of sediments caused by high tidal energy and coastal currents (e.g. Aller and Blair, 2006).

The identification of OM provenances of estuarine sedimentary OM can be based on elemental, isotopic and molecular biomarkers, whereby a simultaneous use of two or more tracers can considerably improve the determination (e.g. Thornton and McManus, 1994). Organic carbon/nitrogen atomic ratios (C/N ratio) and carbon and nitrogen isotopic composition have been widely used to define the origin of sedimentary OM in estuarine sediments, which predominantly derives both from terrestrial and marine sources (Shultz and Calder, 1976; Peters et al., 1978; Fry and Sheer, 1984; Meyers, 1994). The application of these tracers relies on fundamental differences in the use of carbon and nitrogen sources during biosynthesis of OM in terrestrial and aquatic ecosystems that result in clearly distinguishable $\delta^{13}C$ and $\delta^{15}N$ (e.g. Degens, 1969; Peterson and Fry, 1987; Meyers, 1994; Kendall, 1998). The C/N ratios differ due to the abundance of cellulose in vascular plants and its absence in marine produced OM that is instead rich in proteins (e.g. Meyers, 1994). Nevertheless, especially the C/N ratio and $\delta^{15}N$ signal of OM can change during various processes like the ammonium adsorption by sediments or degradation processes (e.g. Müller, 1977; Rosenfeld, 1979; Thornton and McManus, 1994).

Amino acids (AA) and hexosamines (HA) account for significant parts of the organic carbon and organic nitrogen in most organisms with (Lee, 1988) and are labile relative to bulk nitrogen and carbon (Ittekkot, 1988; Cowie and Hedges, 1992). The analysis of these labile compounds provides a useful tool to evaluate the degradation status or reactivity of particulate OM in estuaries that can be either influenced by decomposition in general, or in particular by a different reactivity of OM from land-derived and marine sources (e.g. Cowie and Hedges, 1992; Dauwe and Middelburg, 1998). Due to the generally refractory character of riverine material, which predominantly results from high contributions of strongly degraded soil, a distinction can be made towards the freshly produced marine phytoplankton, e.g. by its high contributions of amino acids to bulk OC (e.g. Cowie and Hedges, 1992; Ittekkot et al., 1984). Based on changes of the amount and composition of AA and HA occurring during decay, degradation processes can be detected, for example, by the calculation of the degradation index (DI, Dauwe and Middelburg, 1998) or the reactivity index (RI, Jennerjahn and Ittekkot, 1997) but also AA/HA ratios can be used to determine the reactivity of OM as decreasing values indicate increasing OM degradation based on the fact that AAs are preferentially lost during degradation compared to HAs (Müller et al., 1986; Haake et al., 1992; Unger et al., 2005).

The intensity of OM degradation during early diagenesis in sediments determines the OM preservation and does strongly depend on specific local environmental conditions. It is influenced by organic carbon flux, bulk sedimentation rate, water depth, oxygen concentration in the bottom water and related extent of bioturbation of surface sediments (Aller et al., 1985; Hartnett et al., 1998). The rate of degradation slows down with increasing sediment depth which is primarily due to the decreasing OM reactivity as the remineralization of the more labile OM, which breaks down easily, proceeds first and the more refractory material concentrates with depth (e.g. Canfield, 1993; Hulthe et al., 1998; Thamdrup and Canfield, 2000; Burdige, 2007). An appropriate way to detect these downcore variations is the measurement of the more labile compounds of OM, like amino acids and hexosamines.

Due to the fact that tropical and subtropical estuaries receive ~70 % of the freshwater and ~74 % of the sediment discharge to the world's oceans (Milliman and Meade, 1983), the investigation of the sources and fate of the OM in these coastal areas is especially important for the global carbon cycle. This knowledge is fundamental to understand coastal ecosystem processes as sediments play a very important role in shallow, coastal environments due to their large storage capacity and their buffering function considering the retention and release of nutrients (e.g. Jørgensen, 1996). The islands of Indonesia are particularly relevant in this respect as they presumable contribute 20 to 25 % of the global sediment export (Milliman et al., 1999). Furthermore, the coastal zones of Southeast Asia are among the regions with the strongest human modifications around the world (Nicholls and Small, 2002) that most probably strongly affect the ecology and elemental cycles of the adjacent coastal ecosystems. However, much less is known about tropical coastal ecosystem functions than from temperate regions (e.g. Alongi, 1998).

The most urbanized region in Indonesia corresponds to the catchment area of the second largest river of Java, the Brantas River. Its estuary receives high riverine inputs that are on one hand seasonally varying (monsoonal cycle) and on the other hand disproportionally distributed to the two main river outlets and its nearshore, extensive muddy tidal flats. This study investigates the seasonal and regional variations of sedimentary OM in this tropical estuary and aims to determine the sources of the OM, their mixing and spatial distribution as well as the reactivity and the degradation of the sedimentary OM.

The study area

The Brantas River is located at the eastern coast of Java, Indonesia. With a length of 320 km it is the second largest river of the island and drains a catchment area of 11050 km^2 (Whitten et al., 1996) accounting for approximately 35 % of the East Java Province. The

Brantas River originates in high volcanic mountains and diverts into the three branches Porong, Wonokromo and Mas in the coastal lowlands (Fig. 1a). The overall discharge of the Brantas River fluctuates enormously during the year, depending on seasonal climatic changes which are dominated by a strong monsoonal system. This is characterized by the alteration of a wet season (West-Northwest monsoon) from November to April and a dry season from May until October dominated by the East-Southeast monsoon. The average annual rainfall amounts to 2300 mm yr^{-1} (Aldrian and Djamil, 2008), of which 80 % precipitates during the wet season. This coincides with a peak in water and material discharge of the two main river channels Wonokromo and Porong that discharge into the Madura Strait.

The Porong represents the major water and sediment transporting branch. During the rainy season, about 85 % of the runoff is discharged through the Porong channel. In contrast, during the dry season the significantly lower river discharge occurs in a large part via the Surabaya River and the Wonokromo (Hoekstra, 1989b). These natural discharge trends were enhanced by river regulations that result in an average discharge of 47 and 20 m^3 s^{-1} in the Wonokromo and 264 to 50 m^3 s^{-1} in the Porong River during the rainy and dry seasons, respectively (2003-2007, Jasatirta Public corporation, pers. comm.). The Brantas River has a very high sediment load, especially during the rainy season (Hoekstra, 1989b). This is promoted by very high erosion and denudation rates (Lavigne and Gunnell, 2006) that result from generally favorable natural conditions for high mechanical and chemical weathering on the one hand (e.g. Gaillardet et al., 1999) and human interventions on the other hand, e.g. severe deforestation for the benefit of cash-crop growing areas and the absence of protecting riverbank stripes (Römer-Seel, 2003). The different water runoff via the two main river channels indicate a lower and more stable material supply to the Wonokromo estuary throughout the year compared to the Porong estuary, which receives the predominant part of the high river material discharge in the rainy season. The riverine material is distributed to the extensive intertidal flats at the Brantas estuary. Their depth averages around 1-2 m below sea level and water level fluctuations occur on a micro- to mesotidal scale during mixed diurnal-semidiurnal tidal cycles (Hoekstra et al., 1989).

The Brantas catchment is nowadays the most urbanized region in Indonesia (approximately 16 million inhabitants) and it is one of the nation's major regions of cultivation where nearly half of the area is used for agriculture, mainly rice cultivation (Booth et al., 2001). Numerous efforts have been made to regulate the water resources. This involves the building of dams, reservoirs or irrigation installations for the purpose of power generation as well as flood control and in order to meet the increasing demand of water for domestic, industrial and agricultural water purposes. In this context, a declining water quality has been noticed that is mainly caused by domestic wastewater disposal and occurs especially in urban areas (Ramu, 2004).

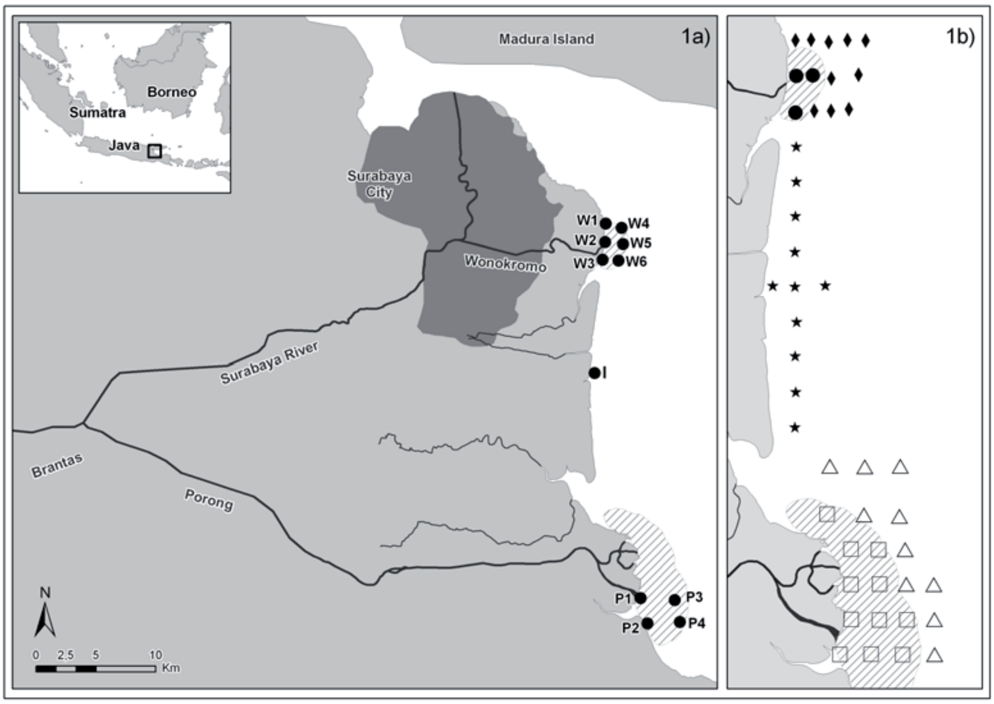


Figure 1 Sampling sites of (a) sediments cores and (b) surface sediment samples including river plume extension in the rainy season. Sediment cores are distinguished in cores taken at the Wonokromo estuary (W1-W6), the Porong estuary (P1-P4) and the intermediate region (I). Surface sediment sampling sites are subdivided into 5 regions (☐ Porong proximal, △ Porong distal, ● Wonokromo proximal, ◆ Wonokromo distal, ★ intermediate region). River plume extensions are indicated by hatched areas.

Material and Methods

Stations and sample treatment

In the rainy (February) and the dry (July) season of 2008 surface sediments and short sediment cores were sampled in the coastal waters of the Brantas estuary. In water depths between 0.5 and 25 m, 46 (rainy season) and 48 (dry season) surface sediment samples were collected during each field campaign using a Van Veen grab. Samples were taken along transects perpendicular to the coast in front of the Wonokromo river mouth (= Wonokromo estuary, 3 transects) and the Porong river mouth (= Porong estuary, 6 transects) (Fig. 1b). The transects were sub-divided into proximal and distal regions relative to the coastline (Fig. 1b). The boundaries between proximal and distal stations were set according to the respective river plume extension that was defined by satellite images, total suspended matter (TSM) contents and salinity values (Fig. 1 a, b). Additionally, a further transect was sampled parallel to the coast between these two estuaries (intermediate region). The surface sediment layer (1 cm) was sampled and split. One half, taken for geochemical analyses, was frozen, freeze-dried (Alpha 1-2 LDplus, CHRIST) and ground (RETSCH Planetary Ball Mill PM 100, 500 rpm). The other half was stored cool and dark in small plastic bags until grain size measurements.

Short sediment cores were taken at 11 stations in the rainy season and at 12 stations in the dry season of 2008. Four cores were situated at the Porong estuary (P1-P4) and five (rainy season, except W5)/ six cores (dry season) at the Wonokromo estuary (W1-W6) (Fig. 1a). Within ~500 m and ~2 km distance to the coast they were taken from water depths between 0.3 and 1.4 m. One station was located in the intermediate region close to the coastline (I). For sampling, a hand-corer (HYDRO-BIOS) and plastic liners with a length of 60 cm and a diameter of 7 cm were used. The cores, whose length varied between 25 and 45 cm, were sliced in 5 cm intervals. Samples were split for grain size analyses and geochemical analyses and further processed like the surface sediment samples.

Analytical methods

Total carbon (TC), total nitrogen (TN) and total organic carbon (TOC) concentrations were analyzed by high-temperature combustion in a *Carlo Erba NA 2100* element analyzer (Verardo et al., 1990). TOC measurements took place after the removal of carbonate by acidification with 1N HCL and subsequent drying at 40°C (analytical errors OC <0.05 %, N <0.01 %). The total organic carbon is reported in weight percent (%) and the ratio of OC and TN is discussed as C/N ratio in the following.

The organic carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotopic composition were determined in a *Thermo Finnigan Delta Plus* mass spectrometer after high temperature combustion in a *Flash EA 1112* elemental analyzer. Sediment material was decarbonated with 150 µl of 1N HCl and dried at 40 °C for the $\delta^{13}C_{org}$ determination. $\delta^{13}C_{org}$ and $\delta^{15}N$ results are given as per mil relative to Vienna PDB standard and nitrogen isotopic composition of atmospheric air, respectively, based on the following equation:

$$\delta R = (R_{sample}/R_{standard} - 1) \times 1000 \qquad \text{with } R = {}^{13}C/{}^{12}C \text{ or } R = {}^{15}N/{}^{14}N$$

The amount and monomeric composition of total hydrolysable amino acids (AA) and total hydrolysable hexosamines (HA) were analyzed with a *Biochrom 30* Amino Acid Analyzer after hydrolysis with 6 N HCl for 22 h at 110 °C. The individual monomers were separated with a cation exchange resin and detected fluorometrically. A detailed method description is given by Jennerjahn and Ittekkot (1999).

The grain size distribution was determined using a laser particle analyzer HORIBA LA-300. For homogenization, 0.1 to 0.4 g sediment was suspended in ~30 ml distilled water and sodiumphosphate ($NaPO_4$) was added (1-2 g). Further disaggregation of the particles was achieved with ultrasonication (15 seconds). The measurements of the suspension were performed in water dispersion according to the Mie Scattering Theory (Mie, 1908).
The grain size is commonly strongly correlated to the content of OM that adsorbs onto mineral surfaces (e.g. Keil et al., 1994b). Since fine particles have the largest surface area and due to the fact that the fine grain size fraction <20 µm (clay, fine and medium silt) showed the best correlation with the OC content in our data set (data not shown), we used this fraction for the characterization of the grain size distribution.

Statistics

For a synoptic presentation of the data, sediment core characteristics were consolidated via *locally weighted scatter plot smoothing* (LOESS) (e.g. Hastie and Tibshirani, 1990). The analyses were performed with the program *R*.

Results

Surface sediments

The organic carbon content of surface sediment samples varied from 0.3 to 1.5 % (Fig. 2a). Sediments at the Porong estuary showed values between 0.3 and 1.5 %. An increase in sedimentary OC was observed towards the offshore sampling sites. This gradient was more distinctly pronounced in the dry season. Except for significantly higher values directly in front of the Wonokromo river mouth in the dry season (average of the proximal area = 1.1 %), lower values were found at the Wonokromo estuary compared to the Porong estuary (Table 1). The sediments in the intermediate region displayed higher OC contents towards the Porong estuary and lower values in northward direction to the Wonokromo (Fig. 2a).

Highest C/N values were found at the proximal area of the Porong estuary in the rainy season (mean 11.4, Table 1, Fig. 2d). Besides an overall decline of values during the dry season, lower C/N ratios were observed with increasing distance to the coastline in both seasons. At the Wonokromo estuary, this gradient was only apparent during the dry season (Table 1). During the entire year, the intermediate region had the lowest values (annual average: 9.2).

The $\delta^{13}C_{org}$ of the sediments ranged between -24.9 ‰ and -20.1 ‰. The Porong and the Wonokromo estuary had higher values in offshore direction, with the proximal samples showing slightly higher values during the dry season (Table 1, Fig. 2c). Highest $\delta^{13}C_{org}$ values in the coastal sediments were found in the intermediate region, with a slight decline during the dry (-20.8 ‰) compared to the rainy period (-21.5 ‰).

Amino acids and hexomsamines contents in sediments were found in quantities of 0.62 to 5.67 mg g^{-1} and 0.09 to 0.75 mg g^{-1}, respectively. The concentrations of both compounds were correlated (rainy season $R^2 = 0.78$, $p<0.05$; dry season $R^2 = 0.79$, $p<0.05$) and are discussed as the sum of AA+HA. Lowest values were found at the Porong estuary, where higher AA+HA-contents were observed in the distal (annual average = 3.93 mg g^{-1}) compared to the proximal sediments (annual average = 2.18 mg g^{-1}) (Table 1). This spatial trend was more pronounced in the dry season. Such a gradient was not found at the

Wonokromo estuary, where the highest values were detected in the proximal stations during the dry season (Table 1, Fig. 2b). The sediments in the intermediate region exhibited an annual average of 3.93 mg g^{-1} AA+HA with slightly higher values in the dry season.

Based on the fact that the factor coefficients of a PCA carried out with our amino acid data were not in agreement with the factor coefficients calculated and used by Dauwe and Middelburg (1998) to calculate the DI, i.e. our data appeared not to be determined by degradation alone, we decided not to apply this indicator. Furthermore, strongly varying non-protein amino acids in our data prohibited the calculation of reliable (robust) RI's that could be compared with each other. Instead, we use the percentages of amino acid bound carbon and the ratio of amino acids to hexosamines (AA/HA ratio) that both decrease with OM degradation (e.g. Cowie and Hedges, 1992; Unger et al., 2005). This is based on the fact that these sum parameters are more robust as compared to variations of single monomers like the non-protein amino acids and therefore provide a more consistent data set.

Despite the general correlation of AA and HA, their relative contents varied within the sediments leading to a differing AA/HA ratio. It ranged between 4.2 and 13 and was highest in the sediments of the intermediate region and lowest at the Porong estuary (Fig. 2e). This ratio was higher in the entire coastal region during the dry season. During both seasons, sediments of the Porong estuary had higher ratios in offshore direction, which was more pronounced in the rainy season (Table 1). This gradient could not be found at the Wonokromo estuary, where to the contrary strongly elevated values were observed in the proximal compared to the distal stations in the dry season.

The percentages of amino acid bound carbon (AA-C%) showed similar seasonal and spatial trends as detected for the AA/HA-ratio (Table 1, Fig. 2f). The contribution of AA-C% ranged between 5.9 % at the Porong estuary and 22.6 % in the intermediate region.

The grain size of sediments from the Brantas estuary was dominated by the clay and silt size fractions (<20 µm) (Table 1). The most fine-grained material was found at the distal stations in the Porong estuary, where it amounted to 87 % on average. At the Wonokromo estuary, this grain size fraction amounted to an average of 57 % in both seasons except for the proximal samples taken in the dry season, which exhibited the overall most coarse-grained sediments. In the sediments from the intermediate region the proportion of the <20 µm fraction was ~70 %.

Table 1 Mean value, standard deviation and range of total organic carbon, C/N ratio, carbon and nitrogen isotopic composition, amino acid characteristics and grain size of the surface sediment samples at the Brantas estuary.

		OC [%]	C/N ratio	$\delta^{13}C_{org}$ [‰]	$\delta^{15}N$ [‰]	AA+HA [mg/g]	AA-C [%]	AA/HA ratio	grain size [<20µm]
rainy season 2008	**Porong-proximal n=10-12**								
	Average	**0.84**	**11.4**	**-22.8**	**4.6**	**2.28**	**8.6**	**5.0**	**77.4**
	Stdv	0.26	2.1	0.9	0.3	0.43	1.6	0.5	23.6
	Range	0.27 - 1.15	8.3 - 16.5	-24.3 - -21.0	4.1 - 5.0	1.53 - 2.74	5.9 - 10.7	4.2 - 5.8	15.1 - 95.5
	Porong-distal n=9-10								
	Average	**1.06**	**9.7**	**-21.7**	**4.4**	**3.80**	**12.9**	**5.9**	**87.9**
	Stdv	0.10	0.8	0.7	0.3	0.97	2.8	0.5	5.1
	Range	0.93 - 1.28	8.6 - 10.6	-22.7 - -20.7	4.0 - 4.9	2.68 - 5.21	9.4 - 17.2	5.3 - 6.7	77.7 - 95.5
	Wonokromo-proximal n=3								
	Average	**1.05**	**10.4**	**-22.8**	**3.9**	**3.61**	**13.1**	**6.7**	**58.8**
	Stdv	0.48	0.5	0.9	0.3	1.48	1.7	0.4	29.8
	Range	0.49 - 1.33	10.1 - 11.0	-23.5 - -21.8	3.6 - 4.1	1.95 - 4.82	11.3 - 14.7	6.3 - 7.0	24.8 - 80.0
	Wonokromo-distal n=9-10								
	Average	**0.74**	**10.4**	**-21.7**	**4.5**	**2.63**	**12.1**	**6.6**	**53.0**
	Stdv	0.24	0.5	0.5	0.2	0.87	1.8	0.6	22.0
	Range	0.30 - 0.97	8.6 - 13.0	-22.7 - -20.7	4.2 - 5.1	1.2 - 4.1	9.4 - 15.7	6.0 - 7.9	16.6 - 80.3
	intermediate region n=11								
	Average	**0.95**	**9.4**	**-20.8**	**4.3**	**3.74**	**14.9**	**7.6**	**69.4**
	Stdv	0.19	0.7	0.4	0.3	0.93	3.3	1.4	13.6
	Range	0.65 - 1.20	8.5 - 10.5	-21.5 - -20.3	3.8 - 4.7	2.37 - 5.23	8.5 - 21.0	6.7 - 11.5	49.8 - 88.7
dry season 2008	**Porong-proximal n=12-13**								
	Average	**0.80**	**10.5**	-22.7	4.1	**2.09**	**9.3**	**6.5**	**57.5**
	Stdv	0.35	1.3	1.0	0.4	0.96	2.0	2.3	19.4
	Range	0.27 - 1.47	8.1 - 13.1	-24.9 - -21.0	3.5 - 5.1	0.76 - 4.26	6.0 - 13.6	4.6 - 13.0	24.3 - 84.0
	Porong-distal n=11-12								
	Average	**1.11**	**8.8**	**-21.8**	**4.4**	**4.05**	**13.4**	**6.9**	**87.3**
	Stdv	0.07	0.6	0.7	0.4	0.74	2.1	1.0	7.6
	Range	0.96 - 1.19	7.9 - 9.7	-23.2 - -20.8	4.0 - 5.1	2.69 - 5.25	8.8 - 16.9	5.2 - 8.2	69.2 - 96.1
	Wonokromo-proximal n=2								
	Average	**0.57**	**10.7**	**-22.2**	**4.1**	**2.11**	**13.7**	**8.7**	**25.6**
	Stdv	0.40	0.9	0.6	0.1	1.65	1.4	0.5	21.5
	Range	0.29 - 0.86	10.1 - 11.4	-22.7 - -21.8	4.0 - 4.2	0.94 - 3.27	12.7 - 14.7	8.3 - 9.0	10.4 - 40.9
	Wonokromo-distal n=8-10								
	Average	**0.73**	**10.1**	**-21.8**	**4.5**	**2.23**	**11.1**	**6.6**	**58.3**
	Stdv	0.14	0.7	0.6	0.5	0.89	2.3	1.0	26.0
	Range	0.56 - 0.95	8.8 - 10.9	-22.4 - -20.1	3.7 - 5.1	1.16 - 3.56	7.2 - 14.0	5.5 - 8.3	2.7 - 82.7
	intermediate region n=11								
	Average	**0.97**	**9.0**	**-21.5**	**4.8**	**4.12**	**16.2**	**8.3**	**70.1**
	Stdv	0.26	0.5	0.5	0.4	1.31	2.8	0.7	19.0
	Range	0.57 - 1.34	8.4 - 9.9	-22.3 - -20.9	4.3 - 5.4	2.3 - 6.27	12.0 - 22.6	7.6 - 9.5	33.7 - 89.7

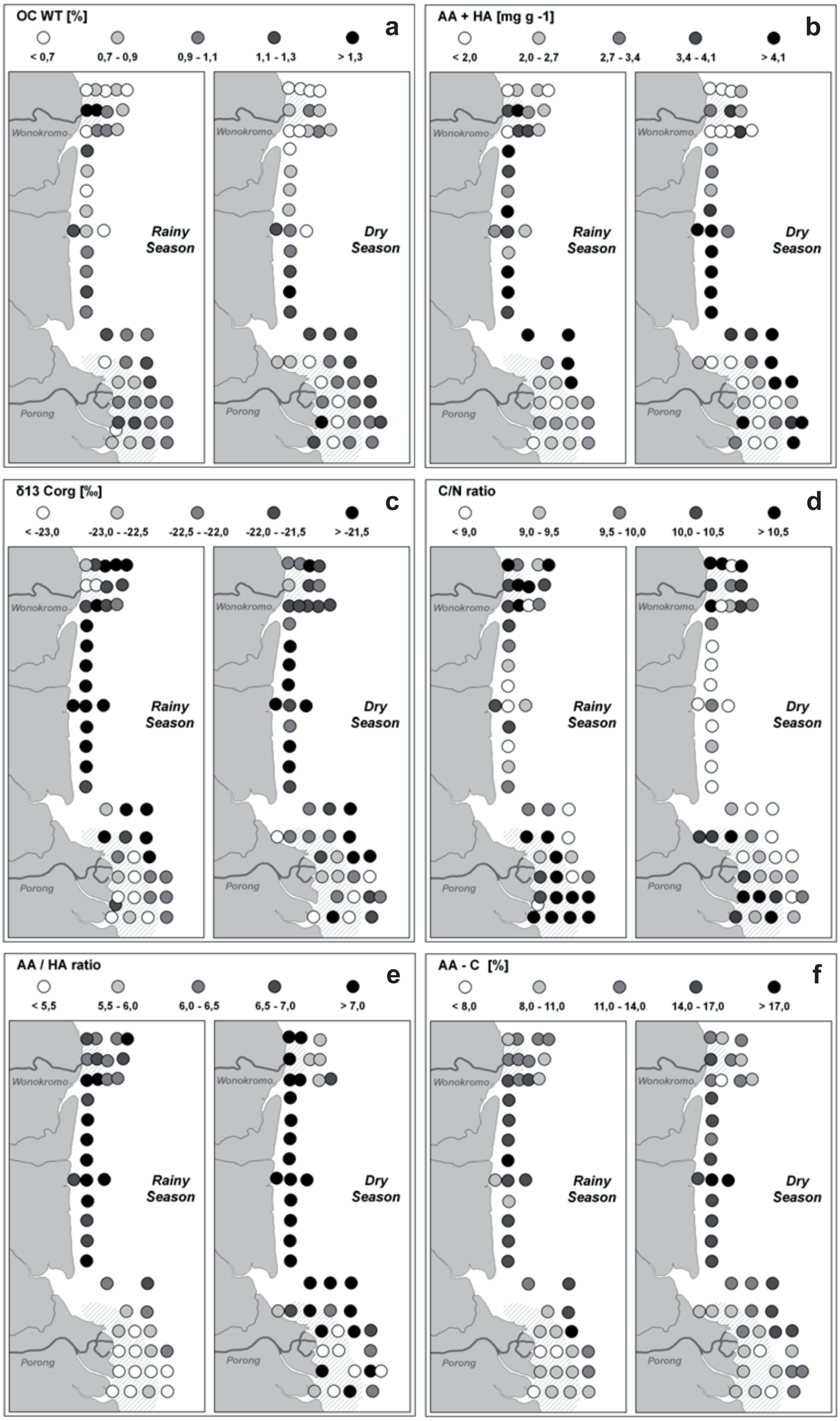


Figure 2 Spatial distribution of (a) organic carbon, (b) total hydrolysable amino acids + hexosamines, (c) carbon isotopic composition, (d) C/N ratio, (e) amino acid/hexosamines ratio, (f) amino acid bound carbon in surface sediments at the Brantas estuary in the rainy and dry season of 2008.

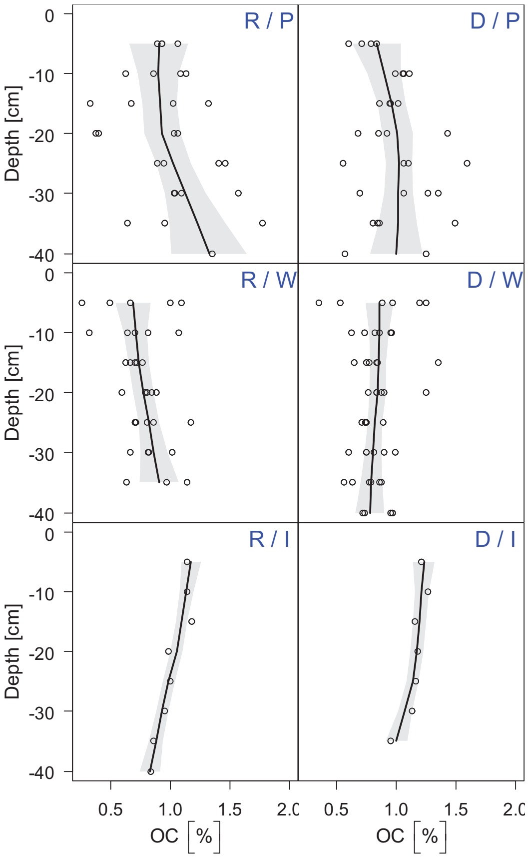
Sediment cores

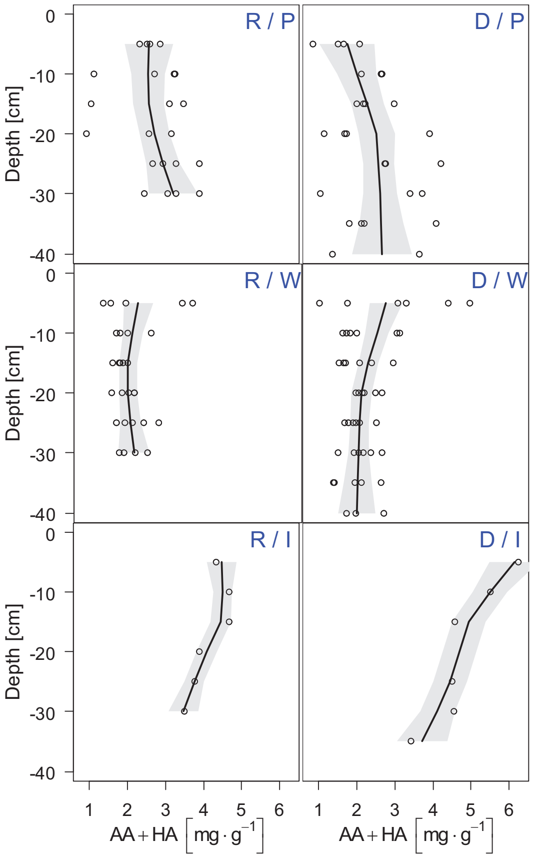
Organic carbon in the sediment cores ranged between 0.3 to 2.0 % (Fig. 3). Values were in the same range in all three areas. The cores in the Wonokromo and the Porong estuary showed strong fluctuations with depth (ranges: P= 0.3 - 1.8 %, W= 0.3 – 1.4 %). Several cores displayed a downcore increase at both estuaries but no significant overall trend could be observed as the confidence intervals of the upper and lower sediment layers overlapped. The core taken at the intermediate region exhibited a small range of values (0.8 – 1.3 %) and a marginal decrease with depth.

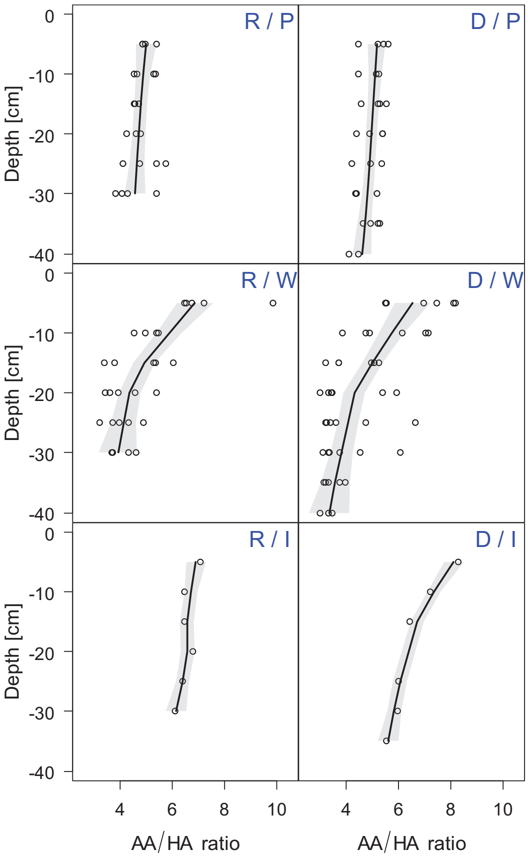
Total AA+HA were found in quantities of 0.85 to 6.24 mg g^{-1}. The core in the intermediate region exhibited generally the highest values (3.42 – 6.24 mg g^{-1}) and showed a distinct decline of AA+HA contents with depth. This was more pronounced in the dry season due to higher values in the upper sediment layers (Fig. 3). Like the OC content, the AA+HA content varied strongly and ranged between 1.02 – 4.97 mg g^{-1} off the Wonokromo and 0.85 – 4.21 mg g^{-1} off the Porong. Slight changes with increasing depth were observed at both estuaries in the dry season, when several cores showed a slight increase of AA+HA at the Porong estuary and a decline of values was detected in most of the cores of the Wonokromo estuary.

AA-C% ranged between 5.3 – 19.8 % and the AA/HA ratio between 2.9 – 10.4. Both parameters revealed a significant decrease with depth in all cores taken at the Wonokromo estuary (Fig. 3). In contrast, at the Porong estuary, most of the sediment cores showed constant values with depth. The core of the intermediate region showed a significant decline of AA-C% and AA+HA in the dry season.

The grain-size fraction <20 μm varied between 14 and 98 % and fluctuated strongly in most sediment cores. No significant trends were observed at the Wonokromo and the Porong estuary. However, many cores at the Porong estuary showed a decline of the fraction <20 μm in the upper half of the cores in the rainy season and an opposite trend in the dry season. At the Wonokromo estuary, the sediment became more fine-grained with increasing depth. Within core I, overall high values were detected.


R / P
D / P
R / W
D / W
R / I
D / I
Depth [cm]
0
-10
-20
-30
-40
0.5
1.0
1.5
2.0
OC [%]


R / P
D / P
R / W
D / W
R / I
D / I
Depth [cm]
0
-10
-20
-30
-40
1
2
3
4
5
6
AA + HA [mg · g^{-1}]


R / P
D / P
R / W
D / W
R / I
D / I
Depth [cm]
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-10
-20
-30
-40
4
6
8
10
AA/HA ratio

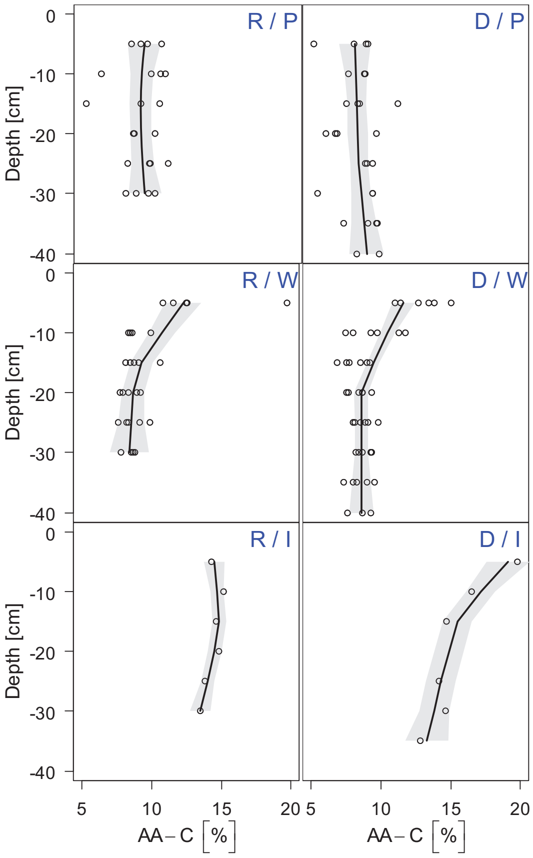
R / P
D / P
R / W
D / W
R / I
D / I
Depth [cm]
0
-10
-20
-30
-40
5
10
15
20
AA – C [%]

Figure 3 Downcore distribution of total organic carbon (OC), total hydrolysable amino acids and hexosamines (AA+HA), amino acid/hexosamines ratio and amino acid bound carbon (AA-C) in short sediment cores sampled at the Porong estuary (P, 4 cores), Wonokromo estuary (W, 5-6 cores) and the intermediate region (I, one core) in the rainy (R) and dry (D) season of 2008.

Discussion

Sources of organic matter

Porong estuary

The $\delta^{13}C_{org}$ of the surface sediments at the Porong estuary ranged between -24.9 and -21 ‰ and the C/N ratio between 7.9 to 16.5 in both seasons of 2008 and showed higher ($\delta^{13}C_{org}$) as well as lower (C/N ratio) values in the distal compared to the proximal stations (Table 1, Fig. 4). $\delta^{15}N$ values varied between 3.5 and 5.0 ‰ and revealed no spatial pattern.

It has been widely observed that the OM in estuarine sediments is a mixture of terrestrial and marine sources (e.g. Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998; Yu et al., 2010). The land-derived OM that is transported to estuaries via rivers can be a very heterogeneous composition of autochthonous and allochthonous material (e.g. Fry and Sherr, 1984; Mook and Tan, 1991). Freshwater phytoplankton shows $\delta^{13}C_{org}$ values lower than –26 ‰, C/N ratio from 4 to 10 and a $\delta^{15}N$ signal between 5 and 8 ‰ (e.g. Sigleo and Macko, 1985; Cai et al., 1988; Meyers, 1994).

Other potential major sources of riverine particulate OM in the agricultural dominated Brantas River catchment area are vascular plant debris and underlying soils from the main crop rice (C_3 plant) and other important crops like maize and sugarcane (C_4 plants) as well as soybean and cassava (C_3 plants) (Badan Pusat Statistik Republik Indonesia). Vascular plants exhibit C/N ratios above 20 and the C_3 and C_4 type differ in their carbon isotopic composition (C_3 plants $\delta^{13}C_{org}$ ~-27 ‰, C_4 plants ~-14 ‰; e.g. Rullkötter 2006, Meyers 1994). Rice and sugar cane plants sampled in the Brantas river basin exhibit $\delta^{13}C_{org}$ values of -28.1 and –12 ‰, C/N ratios of 29 and 54 as well as $\delta^{15}N$ values of 1.2 and -2.7 ‰, respectively (Jennerjahn et al., 2004). Soils from freshly sewn and harvested rice fields in the Brantas region are characterized by $\delta^{13}C_{org}$ of -26 and -23.4 ‰, C/N ratios of 20.7 and 22.1 and $\delta^{15}N$ signal of 2.0 and 2.9 ‰, the soil of sugar cane fields exhibits values of -20

‰ ($\delta^{13}C_{org}$), 20.6 (C/N) and 3.7 ‰ ($\delta^{15}N$) (Jennerjahn et al., 2004). Due to the large erosion rates in the region (Lavigne and Gunnell, 2006) the soil OM can contribute in larger amounts. This is indicated by data of suspended matter obtained in the Brantas River that shows a mixture of possible OM sources, but is mainly dominated by terrestrial soil underlying C_3 plants (Jänen, unpubl. data) and also a previous study investigating the Brantas catchment suggests a high input of agricultural soil via the river (Jennerjahn et al., 2004). This is in general agreement with numerous observations of riverine OM composition (Meybeck, 1982; Ittekkot and Arian, 1986; Ludwig and Probst, 1998). Suspended matter taken at high salinity stations in the Brantas estuary exhibited $\delta^{13}C_{org}$ values of -20 and -22 ‰ and C/N ratios of 8 to 10 as well as a $\delta^{15}N$ signal around 6 ‰ (Jänen, unpubl. data). They are similar to those reported for marine algae from low latitudes, which range between -18 and -22 ‰ ($\delta^{13}C_{org}$), 4-10 (C/N ratio) and 6-10 ‰ ($\delta^{15}N$) (Fry and Sherr, 1984; Fischer, 1991; Meyers, 1994; Currin et al., 1995; Middelburg and Nieuwenhuize, 1998).

Due to the extensive cultivation of rice and other C_3 plants in the catchment, we suggest a dominance of terrestrial soil of C_3 plants in the riverine material that is intensively mixed with marine algae OM in the coastal sediments (Fig. 4). The gradient of $\delta^{13}C_{org}$ and the C/N ratio in offshore direction point to an increasing portion of marine OM in offshore direction (Fig. 5 a, b). We ascribe this gradually changing mix of the OM sources to a rapidly nearshore settling of (terrestrial) particles, which occurs due to a pronounced bottom friction and fast deceleration of the river flow velocity at the shallow Porong river mouth (Hoekstra, 1989b). This is corroborated by a declining content of suspended matter in offshore direction (Jänen, unpubl. data). The decrease in turbidity commonly leads to an increase in light penetration enabling phytoplankton to use the river nutrients more efficiently at the edge of the plume (Aller et al., 1985). Therefore, we infer a much higher input of freshly produced marine OM to the distant Porong sediments. By comparison, the contribution of planktonic material is most likely reduced in the sedimentary OM at the proximal stations based on the high turbidity and the strong nearshore settling of terrestrial organic and lithogenic material. The latter, furthermore, might also have a quantitative dilution effect on the sedimentary OM of the proximal stations, where lower contents of OC and AA+HA were observed compared to the distal stations (Table 1). This suggestion is based on the fact that a stronger sedimentation of particles is usually accompanied by a higher settling of mineral particles from the river load (e.g. Rullkötter, 2006).

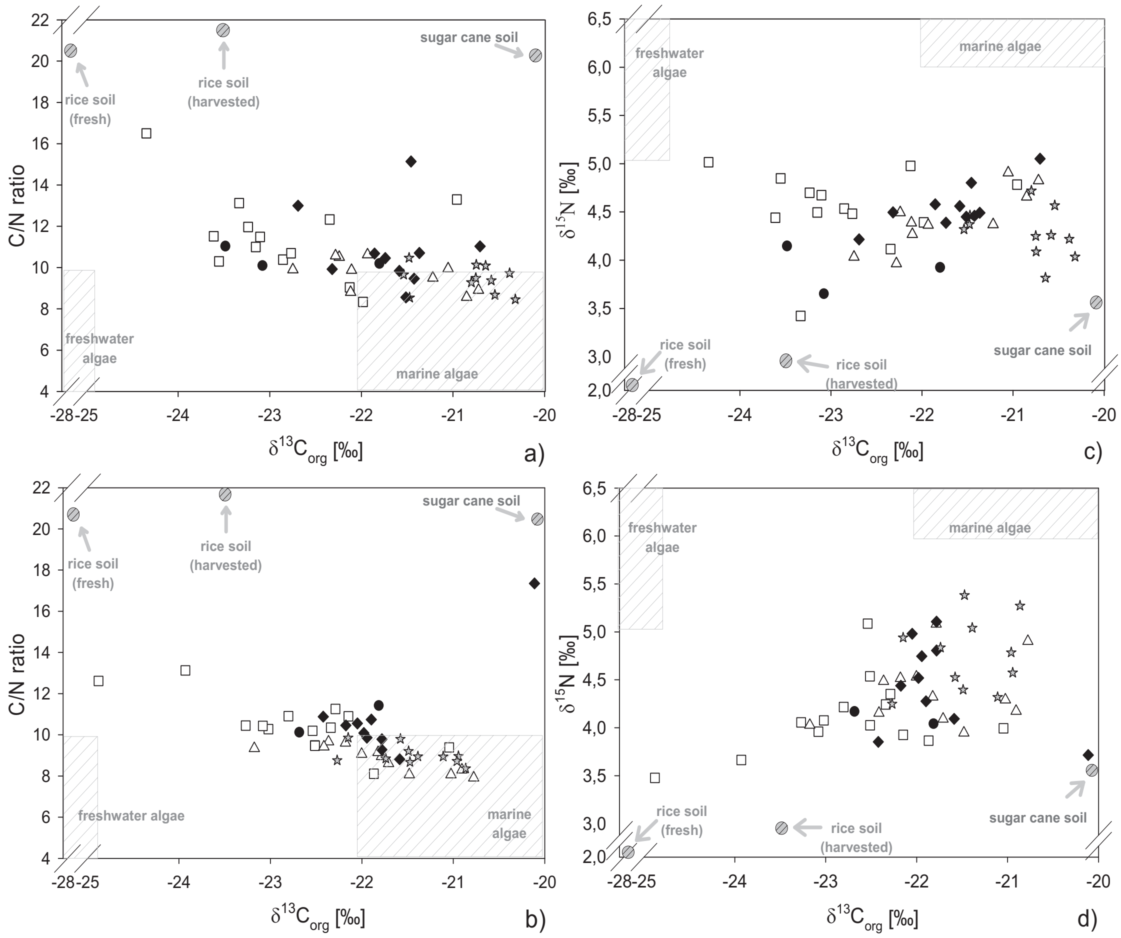

Figure 4 Stable carbon and nitrogen isotopic composition ($\delta^{13}C_{org}$ and $\delta^{15}N$) and C/N ratios of surface sediments at the Brantas estuary. a) $\delta^{13}C_{org}$ and C/N in the rainy season; b) $\delta^{13}C_{org}$ and C/N in the dry season; c) $\delta^{13}C_{org}$ and $\delta^{15}N$ in the rainy season; d) $\delta^{13}C_{org}$ and $\delta^{15}N$ in the dry season. Surface sediment sampling sites are subdivided into 5 regions (□ Porong proximal, △ Porong distal, ● Wonokromo proximal, ◆ Wonokromo distal, ★ intermediate region).

A high accumulation of terrestrial organic material can also affect the reactivity of sedimentary OM since degraded soil and vascular plant debris are commonly referred to be more refractory than freshly produced marine OM. They contain less labile compounds like amino acids (Cowie and Hedges, 1992; Jennerjahn et al., 1999; Unger et al., 2005). The percentages of amino-acid bound carbon and the AA/HA ratio of the estuarine sediments at the Porong estuary showed increasing values in offshore direction in both seasons (Table 1, Fig. 5 c, d) that indicate a higher reactivity with increasing distance from the coast. This could on the one hand result from a higher proportion of labile (more reactive) marine OM in the distal sediments. On the other hand, a less intense degradation of organic material in the slightly deeper offshore region than in the shallow highly turbid proximal waters is conceivable, based on the fact that the latter are characterized by strong resuspension processes (Hoekstra, 1989a) that are known to enhance the degradation of OM (e.g. Ståhlberg et al., 2006)

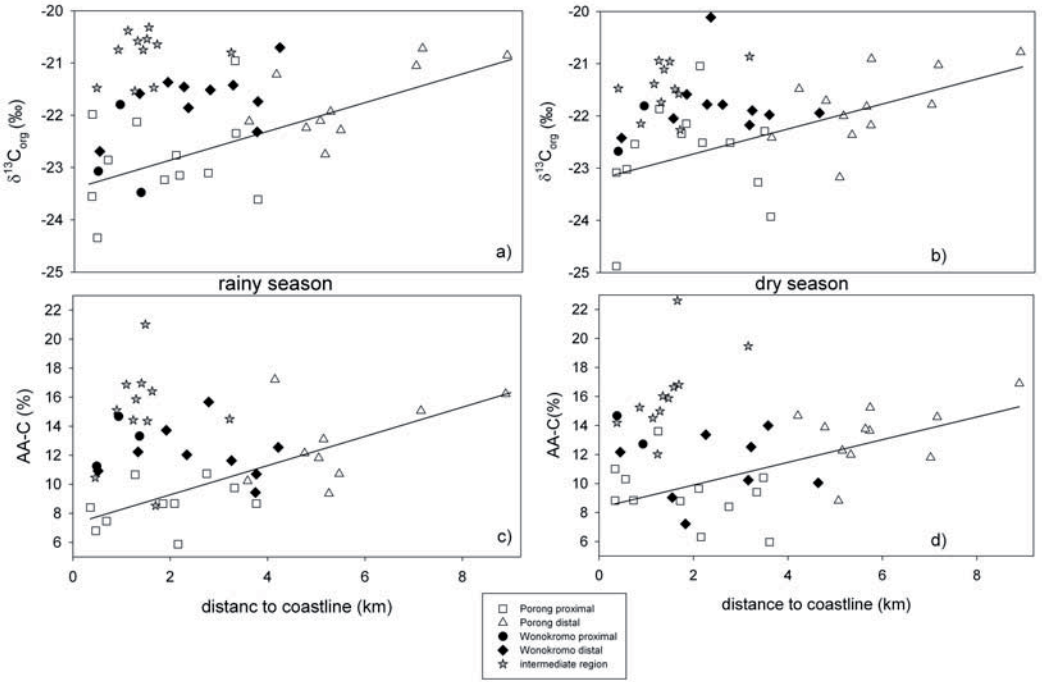

Figure 5 Stable carbon isotopic composition (a= rainy season/ b= dry season) and percentages of amino acid bound carbon (AA-C%) (c= rainy season/ d= dry season) of the surface sediments plotted against the distance to the coastline. Surface sediment sampling sites are subdivided into 5 regions: □ Porong proximal, △ Porong distal, ● Wonokromo proximal, ◆ Wonokromo distal, ★ intermediate region. (regression Porong estuary: Fig. 5a) $R^2=0.42$, $p<0.01$; Fig. 5b) $R^2=0.33$, $p<0.01$; Fig. 5c) $R^2=0.56$, $p<0.01$ $R^2=0.37$, $p<0.01$)

Besides these spatial variations, the AA-C% and the AA/HA ratio were higher and the C/N ratio was lower during the dry compared to the rainy season while, in contrast, $\delta^{13}C_{org}$ displayed constant values (Table 1, Fig. 2). It points to a more reactive sedimentary OM and a higher proportion of freshly produced phytoplankton during the dry season. This most probably resulted from the varying discharge of the Porong River that decreases from 264 $m^3\ s^{-1}$ in the rainy to 50 $m^3\ s^{-1}$ in the dry season (2003-2007, Jasatirta Public corporation, pers. comm.). Thus, the input of terrestrial material as well as the turbidity was much lower during that time and hence most likely promoted the phytoplankton production in the whole estuary. Furthermore, the reactivity as well as the $\delta^{13}C_{org}$ of riverine suspended matter sampled in the downstream part was higher in the dry season (Jänen, unpubl. data). This indicates a higher production of riverine/ estuarine phytoplankton that usually display ranges between -30 and –25 ‰ $\delta^{13}C_{org}$ (e.g. Goni et al., 2006). The transport of this material during less freshwater discharge and its mixing with marine phytoplankton might have led to the constant sedimentary $\delta^{13}C_{org}$ signal in the estuary. Seasonal variations were also observed for $\delta^{15}N$. The values at the proximal stations were higher in the rainy than in the dry season (Table 1, Fig. 4 c, d). It has been widely observed that, among other factors, $\delta^{15}N$ values increase with degradation (e.g. Saino and Hattori, 1980; Peterson and Fry, 1987). Based on the much higher discharge rates in the rainy season, it is conceivable that the seasonal increase at the proximal sites result from a stronger erosion and transport of older, degraded soil from the river bed and the subsequent deposition of this material near to the river mouth.

Wonokromo estuary

The sediments at the Wonokromo estuary showed ranges of $\delta^{13}C_{org}$, C/N ratio and $\delta^{15}N$ similar to those found at the Porong estuary and therefore likewise indicate a mixture of terrestrial and marine OM (Fig. 4). During both seasons, sedimentary $\delta^{13}C_{org}$ at the Wonokromo estuary displayed higher values in the distal compared to the proximal sediments, which was more pronounced in the rainy season (Table 1). Although this trend was more distinct at the Porong estuary, we attribute this offshore directed increase to an enhanced proportion of marine OM in the more distal sediments. In contrast, the regional distribution of the OC and AA+HA content as well as of the AA/HA-ratio and AA-C% differed strongly from the spatial patterns found at the Porong estuary. In the proximal sediments of the Wonokromo estuary we observed notably higher OC and AA+HA contents than in the distal sediments in the rainy season (Table 1, Fig. 2 a, b). This spatial difference most probably resulted from a high deposition of riverine particulate organic matter (POM) directly in front of the river mouth, which rapidly decreases in offshore direction due to the small river plume. A dilution effect, like observed at the Porong estuary, is unlikely in the proximal sediments due to lower TSM and higher POC contents in the Wonokromo compared to the Porong River (Jänen, unpubl. data). In the dry season, the OC and AA+HA content were much lower at the proximal stations and a much lower portion of the <20 μm fraction was observed in these sediments (Table 1). A relationship between OM and grain size has been widely observed in marine sediments and is based on the adsorption of OM to inorganic particles (e.g. Keil et al., 1994b; Mayer, 1994; Hedges and Keil, 1995). Thus, the loadings of OM increase with increasing surface area of inorganic particles and fine grained sediments have a higher sorptivity than course grained sediments. Therefore, we conclude that the lower OC and AA+HA contents in the dry season are related to the seasonal grain size difference of the proximal sediments (Table 1).

In contrast to the Porong estuary, the sedimentary AA/HA ratios and AA-C% did not increase with distance to the coast in the rainy season and even showed significantly higher values in the proximal region in the dry season (Table 1, Fig. 2 e, f). Moreover, the values were generally higher in the proximal sediments off the Wonokromo than off the Porong. These trends most probably result from a higher reactivity of suspended material in the Wonokromo compared to the Porong River that was detected in both seasons. Furthermore, a strong increase of the reactivity from rainy to dry season was observed for the Wonokromo riverine material (Jänen, unpubl. data). We basically ascribe this seasonal variation and the difference between both rivers to a varying production of fresh, autochthonous OM. The riverine primary production can be strongly controlled by the available amount of light and nutrients. Thus, the much higher TSM concentrations in the Porong River, which reduce the light availability, can result in a lower primary production. It has been documented that inputs of urban wastewater and sewage can be extensively decomposed in warm tropical waters and the resultant high amounts of remineralized nutrients could trigger an autochthonous riverine primary production (e.g. Carreira et al., 2002). Additionally, the sewage material itself might contribute to a higher reactivity of the riverine material, as it is usually rich in proteins (e.g. Wu et al., 2007). Within the Brantas catchment, the urban area of Surabaya is the most rapidly industrialized region (Sudaryanti et al., 2001) where the maximum amount of pollution load with the river basin is generated (Ramu, 2004). Therefore, we conclude that a higher input of urban materials to the Wonokromo River lead to a higher primary production, and thus a higher reactivity, of the Wonokromo suspended material. The enhanced reactivity of riverine suspended matter in the dry season is most probably associated with a stronger primary production during the lower river discharge in the dry season (dry season: 20 $m^3 s^{-1}$, rainy season: 47 $m^3 s^{-1}$ 2003-2007, Jasatirta Public corporation, pers. comm.).

The transport of the freshly produced riverine material is limited to the very proximal regions of the Wonokromo estuary due to the overall lower discharge of the Wonokromo River and the small river plume. This input most probably enhanced the reactivity of the proximal sediments in both seasons. In the rainy season, it resulted in equal values equal to those at the distal stations that contained a higher proportion of labile marine OM. In the dry season, the deposition of the much more reactive riverine suspended matter result in strongly enhanced reactivities in the proximal sediments.

Intermediate Region

The overall lower C/N ratios as well as higher $\delta^{13}C_{org}$ values, AA+HA concentrations, percentages of AA-C and AA/HA ratios compared to the Wonokromo and Porong estuary (Table 1, Fig. 4 a, b; Fig. 5) indicate a higher portion of marine OM in sediments from the intermediate region. Due to the distance to the main river mouths terrestrial OM can only be transported to the sediments at the intermediate region in a reduced amount via longitudinal coastal currents, by diffusive terrestrial runoff or via smaller drainage channels located along the coastline between the Wonokromo and the Porong river mouths. In the dry season, higher AA/HA ratios, AA-C%, AA+HA contents as well as slightly lower C/N ratios point to less terrestrial influence than observed in the rainy season (Table 1, Fig. 2) because of lower precipitation and hence lower diffusive terrestrial input via the small draining channels.

Interestingly, $\delta^{13}C_{org}$ decreased from -20.8 ‰ in the rainy to -21.5 ‰ in the dry season although terrestrial input was lower. Suspended matter in the intermediate region also displayed lower $\delta^{13}C_{org}$ values in the dry season and the nutrient concentrations were lower (Jänen, unpubl. data). Despite lower terrestrial runoff nearly constant Chlorophyll *a* throughout the year (Jänen, unpubl. data) indicate little variation in primary production in the dry season. This suggests an increased nutrient recycling in the water column at that time. It has been found that the fractionation against the heavier $^{13}C_{org}$ increases with enhanced respiration (Degens et al., 1968), what implies an enrichment of $^{13}C_{org}$ -depleted compounds and therefore a lighter isotopic planktonic signal within a more heterotrophic system. It is conceivable that the lower $\delta^{13}C_{org}$ of suspended matter at the intermediate region in the dry season was caused by an enhanced heterotrophic cycling. Accordingly, seasonal variations in this fractionation of carbon isotopes by plankton were probably responsible for the seasonal changes of the sedimentary $\delta^{13}C_{org}$. In the rainy season, $\delta^{15}N$ was in the same range as in sediments at the Porong and Wonokromo estuary, but was higher in the dry season (Table 1, Fig. 4 c, d). $\delta^{15}N$ varies with the strength of isotopic fractionation. It gets lower under abundant nutrient supply due to the higher discrimination against the heavier isotope ^{15}N (e.g. Fry and Peterson, 1987). Therefore we conclude that the seasonal changes of $\delta^{15}N$ can be ascribed to a lower isotopic fractionation during the reduced nutrient supply in the dry season (see above).

Organic Matter Degradation

The OC as well as the AA+HA content strongly varied within the sediment cores and showed no significant trend with depth at the Wonokromo and Porong estuary but a slight decrease of values in the intermediate region (Fig. 3). Due to the fact that OM commonly adsorbs onto mineral surfaces (e.g. Hedges and Keil, 1995) and therefore are higher in fine grained sediments due to the higher mineral surface area, the fluctuations of OC and AA+HA content might be ascribed to co-occurring high fluctuations of the grain-size as indicated by correlation of the grain size fraction <20 µm with the OC content of cores taken at the Wonokromo estuary and the intermediate region (W: $R^2= 0.6$, $p<0.05$, I: $R^2= 0.7$, $p<0.05$). This correlation diminished in the Porong cores ($R^2= 0.3$, $p>0.1$) what could be based on large amounts of discrete terrestrial plant debris deposited at the Porong estuary that can hamper grain-size measurements and indicate that adsorption is not the only control of OC in Porong sediments.

AA-C% and AA/HA generally decrease with increasing degree of degradation (e.g. Cowie and Hedges, 1992; Haake et al., 1992). The AA-C% varied between 5.3 and 19.8 % and the AA/HA ratio ranged from 2.9 to 10.4 (Fig. 3). Both parameters showed basically the same trend of more constant values in the Porong cores and a stronger decline of values in the Wonokromo cores and the core taken in the intermediate region.

In accordance with the surface sediment data of the proximal subregions, the least reactive material was found in the upper 5 cm of the Porong sediment cores (Fig. 3). The uppermost sediment layers in the cores taken at the Wonokromo estuary had a higher reactivity, mainly due to a higher reactivity of the settling riverine suspended matter. The core of the intermediate region showed a high reactivity of the upper sediment as well because of a higher portion of labile marine OM. While the reactivity decreased only slightly downcore the Porong sediments, a strong decline of the OM reactivity was observed in the Wonokromo estuary. Thus, the degradation of OM appeared to be much stronger in the Wonokromo estuary, hence OM preservation, or burial efficiency (Betts and Holland, 1991; Reimers et al., 1992; Harnett et al., 1998), was higher at the Porong estuary.

Hartnett et al. (1998) discussed that the burial efficiency and preservation of OM depends on its contact time with oxygen (“oxygen exposure time”). Among other factors, primary production rate, bottom water oxygen content and the overall sedimentation rate are important in this respect. The latter controls the rate at which organic material moves out of the oxygenated upper sediment layers and therefore escapes the intense oxic respiration (e.g. Canfield, 1993; Hartnett et al., 1998; Henrichs and Reeburgh, 1987). It is conceivable that this influencing factor on the oxygen exposure time is much more pronounced in front of the Porong river mouth based on the huge river discharge difference between both rivers (mainly in the rainy season: Wonokromo = 47 $m^3 s^{-1}$, Porong = 264 $m^3 s^{-1}$). It is likely that the higher sediment accumulation at the Porong estuary results in a higher burial rate than in front of the Wonokromo river mouth which receives less material delivery. This implies that the OM had less time for degradation in the oxygenated upper sediment zone in the Porong estuary. Thus, a higher amount of OM could be preserved and buried in Porong sediments.

Another factor that most probably leads to the higher degradation intensity at the Wonokromo estuary is the higher OM reactivity of the surface sediment in this region. As the upper sediment layers contain a higher proportion of more labile material that breaks down easily, the degradation of OM could proceed faster and stronger than in the more refractory Porong sediments that are more resistant to decomposition. It has often been observed that initially less reactive OM is stored more efficiently than more labile material (e.g. Aller et al., 1985). In those cases other boundary conditions were similar, whereas in our study area different sedimentation patterns coincided with a different initial OM reactivity. Therefore, we can not clearly determine which factor predominantly causes the different OM preservation.

However, the importance of sedimentary OM reactivity for the intensity of degradation is discernable from seasonal changes occurring at the intermediate region core station. The lower AA/HA ratios in the upper sediment layers indicate a lower reactivity in the rainy season. This was possibly caused by a higher diffusive terrestrial runoff or outwelling of mangrove-derived OM in the high rainfall season (e.g. Dittmar et al., 2001). Apparently, the lower reactivity of the surficial sediment in the rainy season lead to an overall lower degradation intensity and therefore a better preservation of the less reactive OM compared to the stronger decay of OM in the dry season, when OM reactivity of the uppermost sediment layer was much higher (Fig. 3). These changes occurred independently of varying sedimentation rates and therefore point to the importance of OM reactivity as a control factor for OM decay rates at the Brantas estuary.

In addition to the differing burial rates and sedimentary OM reactivity, the activity of macrobenthos might also have influenced the extent of degradation in our study area. Macrobenthic activity generally could enhance the oxygen supply mainly due to porewater irrigation (e.g. Archer and Devol, 1992) and therefore increase the degradation of sedimentary OM. The establishment of a well-developed benthic community can be promoted by high fractions of labile organic material and can be impaired by strong material accumulations (Rhoads et al., 1985; Alongi, 1991). This indicates better settlement conditions at the Wonokromo estuary. Benthos data obtained for the Wonokromo and Porong estuary support this assumption as it pointed to a much stronger animal abundance off the Wonkromo (Yusli, University of Bogor, pers.comm). Therefore, we suggest a higher benthic activity and thus a stronger impact of this oxygen-biasing factor at the Wonokromo estuary and the intermediate region what likely have enhanced the OM degradation in these areas.

We conclude that the high sedimentation rate of mineral and more refractory material at the Porong estuary and the higher reactivity of the OM at the Wonokromo estuary and in the intermediate region determined the regionally strongly different decline of OM reactivity.

Brantas sedimentary organic matter in the global context

To put the characteristic of the sedimentary organic matter in our study area into a global context, we compare them with surface sediment data measured in other coastal environments (Table 2). $\delta^{13}C_{org}$ are higher than values found in estuarine sediments of the Philippines and Vietnam that are characterized by extensive mangrove stands (Kennedy et al., 2004). $\delta^{13}C_{org}$ of mangroves plants range between -25 and -30 ‰ (e.g. Marguillier et al., 1997; Bouillon et al., 2008) and mangroves soil reveals values around –27 ‰ (Jennerjahn and Ittekot, 2002). The lower values at sites of the Philippines and Vietnam likely occur by a high input of leaves and soil OM from the mangrove forest, e.g. by outwelling (e.g. Dittmar et al., 2001). High inputs of mangroves material can not be assumed at the Brantas estuary due to scarcely existing mangrove stands along the coastline what results from the strong decrease of the natural mangrove forest for the construction of aquaculture ponds (Römer-Seel, 2003). This and the high inputs from terrestrial OM from the hinterland might be the reason for the comparatively higher $\delta^{13}C_{org}$ in our study area. In contrast, $\delta^{13}C_{org}$ and $\delta^{15}N$ are lower compared to sediments of the Delaware estuary (Cifuentes et al.,

1988) or the open estuary of the Kallada River (Jennerjahn et al., 2008) which is most probably a result of the predominantly planktonic origin of the organic matter reported for these estuaries in relation to the high proportions of terrestrial material found in the Brantas estuarine sediments. Whereas a high primary production was detected in the Delaware estuary, the low amount of terrestrial material in the open estuary of the Kallada River has been ascribed to a high deposition of river-derived material in the upper parts of the estuary. At the Brantas estuary, a high phytoplankton production is not probable due to the predominantly very high turbidity. Moreover, a strong settling of huge amounts of material transported by before the river outlet like observed for the Kallada River are not very likely due to the much higher discharge of the Brantas River. This and a lower erodibility in the Kallada catchment most probably also reduced the transport of lithogenic terrestrial material resulting in a less dilution of the estuarine sediments by mineral material and therefore comparatively higher organic contents in the Kallada estuary.

The $\delta^{13}C_{org}$ of the coastal sediments in front of the Ayeyarwaddy River in the northern Andaman Sea (Ramaswamy et al., 2008) ranges in the same interval, or even slightly higher, as the Brantas estuarine sediments although samples were taken in much more regions (~ 50-250 km) where a higher input of marine material could be suggested. This is based on the higher water and material discharge of the Ayeyarwaddy River that transports the terrestrial material much further than the comparatively lower outflow of the Brantas River. Nevertheless, increasing $\delta^{13}C_{org}$ and the OC content indicate an offshore directed increase of marine OM contributions like observed at the Brantas estuary. Another example of intense offshore material transport is the Fly River delta where sediments exhibited $\delta^{13}C_{org}$ values of -26.5 to -25.8 ‰ even 50 km of the coast (Goni et al., 2006). The strongly different spatial extension of the terrestrial signal between the three coastal areas furthermore indicates how fast the settling of riverine material takes place at the Brantas estuary due to its shallow morphology.

The concentrations of amino acids and hexosamines are lower than at the Potamac estuary (Sigleo and Shultz, 1993) that is characterized by a high primary production and seasonally anoxic conditions. This entails a higher deposition of freshly produced planktonic material and better preservation conditions for OM than in the turbid, well mixed Brantas estuary.

The AA + HA contents, AA-C% and the AA/HA ratio of shelf and slope sediments along the Brazilian coast (Jennerjahn and Ittekkot, 1997), in the Western Arabian Sea and the Oman Basin (Suthhof et al., 2000), the Pearl River estuary (Chen et al., 2004) as well as in the Kara Sea (Unger et al., 2005) are similar to those at the Brantas estuary. Compared to the Brantas estuary, all these sampling sites are either located in a larger distance to the coast or in greater water depths. Therefore, it can be suggested that the sedimentary OM deposited in these areas was subject to a notable degradation during redistribution processes or while sinking through the water column or both (e.g. Suess, 1980; Thomsen et al., 2002). The similarity of the AA + HA contents, the AA-C% and the AA/HA ratio of the shallow, nearshore sediments at the Brantas estuary and the sampling sites listed above suggest a relatively strong degradation of the sediments in our study area. This high OM decomposition most likely results from the intense resuspension processes that have been observed at the Brantas estuary. These are based on flat morphology of the extensive tidal and subtidal flats and the strong resuspensive action of tidal currents and waves (Hoekstra 1989a) that are known to strongly enhance the degradation of OM in shallow coastal areas (e.g. Valeur et al., 1995; Pusceddo et al., 2005; Ståhlberg et al., 2006). Furthermore, the year-round high tropical temperature might additionally enhance the microbial-driven decomposition of OM. The data suggests that the "incinerator" function for OM attributed to tropical shelf systems in recent studies (e.g. Aller and Blair, 2006) already occurs in much more nearshore coastal regions exposed to high tidal energy, like intertidal flats.

Table 2 Organic carbon content (OC), C/N ratios, carbon and nitrogen isotopic composition ($\delta^{13}C_{org}$ and $\delta^{15}N$) and amino acid characteristics (AA+HA = total hydrolysable amino acids and hexosamine content, AA-C% = amino acid bound carbon, AA/HA ratio) in coastal sediments ("-" = no data; mean value in parentheses).

	location	OC [%]	C/N ratio	$\delta^{13}C_{org}$ [‰]	$\delta^{15}N$ [‰]	AA+HA [mg g^{-1}]	AA-C [%]	AA/HA ratio
Indonesia[a]	Brantas River (open) estuary	0.27 - 1.47 (0.88)	7.9 - 16.5 (10.1)	-24.9 - -20.3 (-22.0)	3.48 - 5.38 (4.4)	0.76 - 6.27 (3.1)	5.9 - 22.6 (12.5)	4.2 - 13.0 (6.9)
East Coast USA[b]	Delaware estuary	-	-	-21.4 - .20.0	7.1 - 8.2	-	-	-
India[c]	Kallada River (open) estuary	2.0	10.8	-20.9	6.6	-	-	-
Philippines, Vietnam[d]	mangrove coast	2.1 - 16.0	23 - 43.3	-23.6 - -28.1	-	-	-	-
Thailand, Myanmar[e]	Andaman Sea	0.08 - 2.66	2.7 - 34.2	-26.4 - 20.5	3.2 - 6.5	-	-	-
Papua New Guinea[f]	Fly River delta	0.8 - 1.6	12 - 17	-26.5 - -25.8	-	-	-	-
East Coast USA[g]	Potomac estuary	-	-	-	-	20.5*	-	-
Arabian Sea[h]	Western Arabian Sea, Oman Basin	0.9 - 3.45	4.8 - 8.5	-	-	2.1 - 8.5	9.8- 11.4	-
China[i]	Pearl River estuary	-	-	-	-	0.9 - 2.9	11.7 - 16.2	-
Brazil[j]	shelf sediments	1.43	9.8	-	-	4.4	12.0	8.0
	slope sediment	1.09	7.7	-	-	3.4	10.4	5.7
Siberia[k]	Kara sea	1.1 - 2.1		-	-	0.35 - 8.27*	10.3 - 14.3	8.0 - 9.8

[a] This study
*only AA [mg g^{-1}]
[b] Cifuentes et al., 1988
[c] Jennerjahn et al., 2008
[d] Kennedy et al., 2004
[e] Ramaswamy et al., 2008
[f] Goni et al., 2006
[g] Sigleo and Shultz, 1993
[h] Suthhof et al., 2000
[i] Chen et al., 2004
[j] Jennerjahn and Ittekkot, 1997
[k] Unger et al., 2005

Summary and conclusion

Terrestrial soil OM and marine derived organic material are the dominant sources of the sedimentary OM in the Brantas estuary. Their respective contributions in the sediments depend on the seasonal and regional variations of the river discharge that is disproportionally distributed between the two main river outlets, the Porong and the Wonokromo. As the reactivity of these autochthonous and allochthonous sources exhibit strong differences, their final balance determines the magnitude and spatial gradients of the OM reactivity in estuarine sediments. Sedimentary OM at the Porong estuary, which receives the highest terrestrial inputs, was less reactive than sedimentary OM in the intermediate region, where freshly produced marine OM dominates over the terrestrial due to the distance to the river mouths. A reduced river and diffusive runoff in the dry season lead to an overall decreasing input of terrestrial material. Next to a different amount and dispersal of terrestrial material its composition also has an impact on the estuarine sediments. This is most pronounced at the Wonokromo estuary that receives highly reactive OM in the dry season. The high reactivity of the riverine material is based on a high autochthonous production that is most probably intensified by the inputs and remineralization of urban wastewaters. The spatial differences in sediment accumulation and OM reactivity of the surficial sediments result in a higher intensity of OM degradation at the Wonokromo estuary and the intermediate region compared to the Porong estuary. This implies a higher preservation and storage of OM in the area of the highest sedimentation, the Porong estuary.

On a global scale, the reactivity of the shallow Brantas estuarine sediments is similar to sediments located in greater depth or distance to the coast that have undergone considerable degradation during redistribution or sinking processes. This point to a substantial degradation of OM during intense resuspension processes in the turbid waters above the extensive tidal flats characterizing the Brantas estuary. The flat morphology also leads to a comparatively rapid settling and thus less extension of terrestrial input into coastal water in comparison with other estuarine systems.

It has been elucidated in our study that the quantity and quality of riverine material can largely influence estuarine sediment characteristics and the intensity of OM degradation in the Brantas estuary. As the characteristics of land-derived material, in turn, generally depend on the processes in the catchment area, perturbations of the river discharge regime and other anthropogenic influences like the wastewater disposal or intensified agriculture can strongly influence the OM in estuarine sediments. Due to the fact that sediments have an important regulatory effect in coastal ecosystems (e.g. Jørgensen, 1996) our results indicate that changes of sedimentary characteristics and processes should be monitored with regard to increasing human impacts in the coastal zone.

Acknowledgments

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3 MANUSCRIPT II

Variability of benthic ammonium fluxes in the Brantas River estuary, Java, Indonesia

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Abstract

Diffusive fluxes of ammonium through the sediment-water interface were determined by calculations from pore water concentration gradients in intertidal flat sediments of the tropical Brantas River estuary during the rainy and dry season in 2008. The estuary receives a generally high, but seasonally as well as regionally varying amount of terrestrial material via the two main arms of the second largest river of Java. The diffusive fluxes ranged between 0.16 and 4.30 mmol m^{-2} d^{-1} and sediments were a source of ammonium throughout the year. A significantly lower ammonium release was observed in the river mouth area that receives a higher influx of terrestrial material. It is conceivable that an unequal mixing of terrestrial (more refractory) and marine (more labile) organic matter in front of the two river outlets, which is based on the striking different discharge rates, led to a different total reactivity of sedimentary organic matter as revealed by the amount and composition of amino acids. This affects both remineralization rates and benthic ammonium fluxes. Benthic turnover times were calculated (1.3 to 17 days). A comparison of the ammonium input via the river and the benthic recycling over a certain area revealed that the benthic ammonium fluxes account for at least half of the riverine input. Hence, benthic ammonium release contributed a significant amount to the estuarine nutrient pool.

Keywords: sediment-water interface, benthic flux, ammonium, organic matter, remineralization, amino acids, Indonesia, East Java, Brantas estuary

Introduction

Benthic-pelagic coupling plays a critical role for nutrient cycling in shallow estuarine and coastal ecosystems. There, sediments can on the one hand act as a sink due to uptake and temporary retention of nutrients, e.g. by denitrification (Seitzinger, 1987). On the other hand, they can also serve as a nutrient source in these highly productive land-ocean transition zones, as they are important sites for the decomposition of the high amounts of organic matter produced in the water column and delivered by rivers (Nixon, 1981; Graf, 1992). As a result of the recycling processes, substantial amounts of nutrients and carbon are released from the sediments to the overlying water, providing a significant source for primary producers (e.g. Billen, 1978; Nixon, 1981; Callender and Hammond, 1982,). This "internal" supply can account for 30 to 100 % of the annual nitrate and ammonium requirements for the primary production (Blackburn and Hendriksen, 1983), which is often limited by the availability of nitrogen (Ryther and Dunstan, 1971). In general, ammonium is used preferentially to nitrate by phytoplankton (e.g. McCarthy and Eppley, 1972). Especially in coastal environments, the importance of benthic recycled ammonium can be considered as high, since a major part of recycled nitrogen released from the sediments to the water is in the form of NH_4^+ (e.g. < 60 % Blackburn and Hendriksen, 1983; 70-100 % Pratihary, 2009) and the relevance of ammonium fluxes relative to nitrate increases with decreasing water depth (Hopkinson et al., 2001).

Benthic regeneration has been widely studied and a high variability of fluxes as well as a multitude of temporal and spatial patterns observed indicate a complex interplay between various chemical, physical and biological factors that affect the exchange processes at the sediment-water interface. Release of ammonium from sediments is basically controlled by the rate of organic matter remineralization and by the transport processes through the sediment (e.g. Jahnke et al., 2000). Whereas the first is governed by the quantity of organic material, its composition and lability (e.g. Westrich and Berner, 1984; Jensen et al., 1990), the latter is controlled by concentration differences between the pore water and overlying water (e.g. Asmus, 1986), molecular diffusion (Berner, 1980), bioturbation and –irrigation (Aller, 1980; Mortimer et al., 1999) and the activity of benthic microalgae (Sundbäck and Graneli, 1988), which can contribute to the retention of nutrients in the sediment. In addition, rates of benthic ammonium fluxes can be modified by numerous other factors like temperature (e.g. Forja et al., 1994; Asmus et al., 2000), adsorption and desorption processes (e.g. Gardner et al., 1991), nitrification and denitrification (e.g. Kemp et al., 1990) as well as hydrodynamic conditions (e.g. resuspension, Huettel et al., 2003).

The effects of the multiple influencing factors controlling the benthic nutrient exchange processes can interact in many different ways and are difficult to separate. Consequently, data can not be transferred from one region to another and each study area requires specific investigations (e.g. Forja et al., 1994). To contribute to the understanding of potential influencing factors we here present a study of benthic fluxes influenced by highly seasonal variations in rainfall and river discharge, a main characteristic of the tropics. Since data on benthic regeneration from these regions are scarce when compared to temperate latitudes, our results on benthic ammonium fluxes in the estuary of Java's second largest river, the Brantas, help to close this gap. This tropical river and the adjacent coastal system are characterized by a strong anthropogenic influence and high delivery and thus accumulation of material, disproportionally distributed to the two main river outlets and its nearshore, extensive muddy tidal flats. We investigated how ammonium exchange rates alter with a seasonally strongly changing material accumulation and whether the impacts of intense anthropogenic activities within the catchment influence the benthic fluxes. Thereby, we focused on the relation between amino acid characteristics and ammonium fluxes. In order to assess the importance of the benthic ammonium exchange for the coastal nutrient cycling in the Brantas estuary, their magnitude was compared with the ammonium input by the river and benthic turnover times were calculated.

Material and methods

Study area

The Brantas River is located at the eastern coast of the Indonesian island of Java. It is the second largest river system of Java with a length of 320 km that drains a catchment area of

11050 km^2 (Whitten et al., 1996) or approximately 35 % of East Java Province. In the coastal lowlands the Brantas River diverts into three branches (Fig. 1). The main river channels Wonokromo and Porong discharge both into the Madura Strait. During the year, the discharge fluctuates enormously depending on the seasonal climatic changes that are dominated by a strong monsoonal system. It is characterized by the alteration of a wet season (West-Northwest monsoon) lasting from November until April and a dry East-Southeast monsoon prevailing from May until October.

The average annual rainfall in this region is about 2300 mm yr^{-1} (Aldrian and Djamil, 2008), from which 80 % precipitates during the wet season when also the predominant part of water and material discharge takes place, with maximum values in the Porong River. The seasonally averaged discharge values vary between 47 and 20 m^3 s^{-1} in the Wonokromo and 264 to 50 m^3 s^{-1} in the Porong River during rainy and dry seasons, respectively (2003-2007, Jasatirta Public corporation, pers. comm.).

The high sediment loads of the Brantas River are promoted by very high erosion and denudation rates (Lavigne and Gunnell, 2006). In front of the Porong river mouth a substantial part of the huge sediment load carried during the wet season is rapidly deposited due to a pronounced bottom friction and fast deceleration of flow velocity creating a strongly prograding delta (Hoekstra, 1989a). In the dry season the quantities are expected to be very low, since at this time the major part of water and material discharge supplied by the Brantas is diverted into the Surabaya River and with this to the Wonokromo (Hoekstra, 1989a; Hoekstra et al., 1989). This indicates a more stable supply to the Wonokromo estuary throughout the whole year, relative to the Porong estuary. Both estuaries have extensive tidal flats with depths of 1-2 m below sea level and exhibit water level fluctuations on a micro- to mesotidal scale during mixed diurnal-semidiurnal tidal cycles (Hoekstra et al., 1989).

During the last decades, numerous efforts were conducted to regulate the water resources in the Brantas region, which is one of the nation's major area of cultivation (Booth et al., 2001) and nowadays among the most densely-populated regions in Indonesia (approximately 16 million inhabitants). Human interferences enhance the naturally varying discharge regime of the river. Amongst other activities, dams, reservoirs and irrigation installations have been built and dredging as well as river diversions are carried out in order to meet the increasing demand of domestic, industrial and agricultural water supply and for the purpose of power generation and flood control.

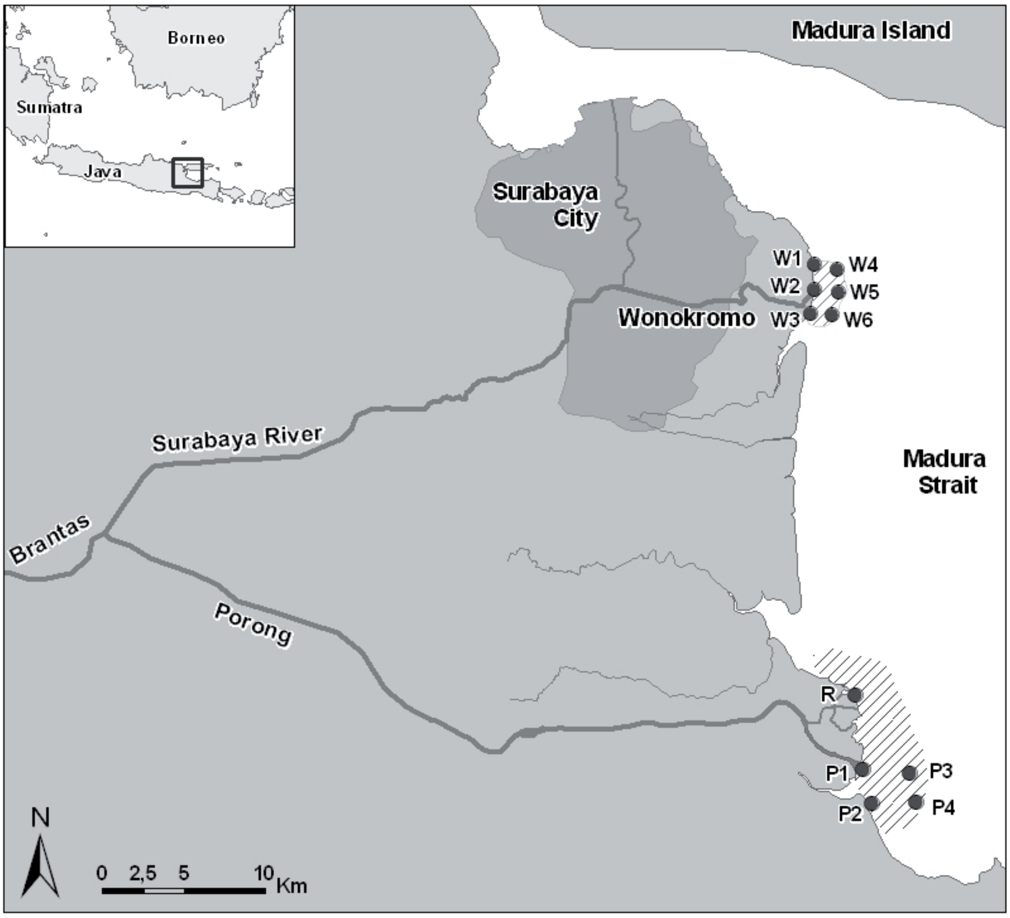

Figure 1 Sampling sites and river plume extensions in the rainy season of the study area Plume extensions were defined by satellite images, total suspended matter content and salinity.

Sampling and sample treatment

Sediment cores were taken from two sampling sites on the intertidal flats of the Brantas River estuary (Fig. 1) during two expeditions in February and August 2008. Five cores were taken off the Porong (P1-4 & R) and six off the Wonokromo (W1-6) river mouth, sampled in two north-south transects near and within ~ 2 km distance of the coast. Site R was considered as a reference station because it was situated in a sheltered bay rather distant to the main river mouth of the Porong receiving only little river input. Therefore, data obtained for site R were not included in the average values and ranges calculated for the Porong sampling site but rather used as a station of less riverine impact. All cores were taken from water depth between 0.3 and 1.4 m with a hand-corer (HYDRO-BIOS) containing a plastic liner with a length of 60 cm and a diameter of 7 cm. The length of the retrieved sediment cores varied between 25 and 45 cm and they were stored at in-situ temperature in a water bath until bottom and pore water was extracted, which took place approximately 12 to 20 hours after sampling.

Before the extraction of the pore water, bottom water was removed with syringes and filtered through 0.45 µm filters into 50 ml plastic bottles for nutrient analysis fixed with 50 µl $HgCl_2$ (32-%). Pore water samples for nutrient analysis (10 ml) were obtained with rhizons (ECOTECH, length: 5 cm, pore size: 0.1 – 0.2 µm), penetrating the cores through predrilled holes, and vacuum syringes. Samples were stored in PE centrifuge tubes and 10-20 µl $HgCl_2$ (32 %) were added for preservation. Pore and bottom water samples were stored cool and dark until further analyses.

After pore water extraction, sediment cores were sliced in 5 cm intervals. Samples for geochemical analyses (see below) were taken in glass vials and freeze-dried (Alpha 1-2 LDplus, CHRIST). The dried sediment core samples were ground and homogenized in a RETSCH Planetary Ball Mill PM 100 at 500 rounds per minute.

Analytical methods

Total organic carbon concentrations (TOC) in sediment samples were analyzed by high-temperature combustion in a *Carlo Erba NA 2100* element analyzer (Verardo et al., 1990). For the analysis, ~ 30 mg of sediments were weighed in silver cups for organic carbon measurements, which took place after removal of carbonate by acidification with 1N HCL and subsequent drying at 40°C (analytical error < 0.05 %). Total hydrolysable amino acids (THAA) were analyzed with a Biochrom 30 Amino Acid Analyzer after hydrolysis with 6 N HCl for 22 h at 110°C. The individual monomers were separated with a cation exchange resin and detected fluorometrically. A detailed method description is given by Jennerjahn and Ittekkot (1999). Ammonium was detected spetrophotometrically as specific colored complex, applying the manual indigo-blue-method (Grasshoff et al., 1999).

Flux calculations

Assuming steady state conditions, diffusive fluxes across the sediment-water interface were calculated from the steepest concentration gradients in the upper sediment horizon (1-5 cm), according to Fick`s first law of diffusion:

$$J = -\phi \text{ x } D_0 \text{ x } (1- \ln\phi^2)\text{-1 x } \partial C / \partial x$$

where J is the diffusive flux, ϕ is porosity, D_0 is the substance-dependent diffusion coefficient in water, θ^2 is the tortuosity and $\partial C / \partial x$ is the concentration gradient. D_0 for ammonium is 1.85×10^{-9} m^2 s^{-1} at a water temperature of 25 °C (Boudreau, 1997).

Statistics

A two sample t-test assuming unequal variances was performed for testing the differences of mean regional fluxes and sediment TOC as well as THAA values (Table 1), whereas F-tests were carried out to test for identical regression lines in different regions. It was tested whether the given data set was better described via two different regression lines ($p < 0.05$) or whether one regression line was appropriate ($p > 0.05$).

Results and discussion

Regional variability of ammonium fluxes related to organic matter composition

The overall average ammonium release of sediments from the Brantas estuary (taking both estuaries into account) during the dry season in 2008 was 1.67 mmol m^{-2} d^{-1}, with the lowest flux observed in front of the Porong estuary (0.22 mmol m^{-2} d^{-1}) and the highest at the Wonokromo estuary (4.30 mmol m^{-2} d^{-1}) (Fig. 2).

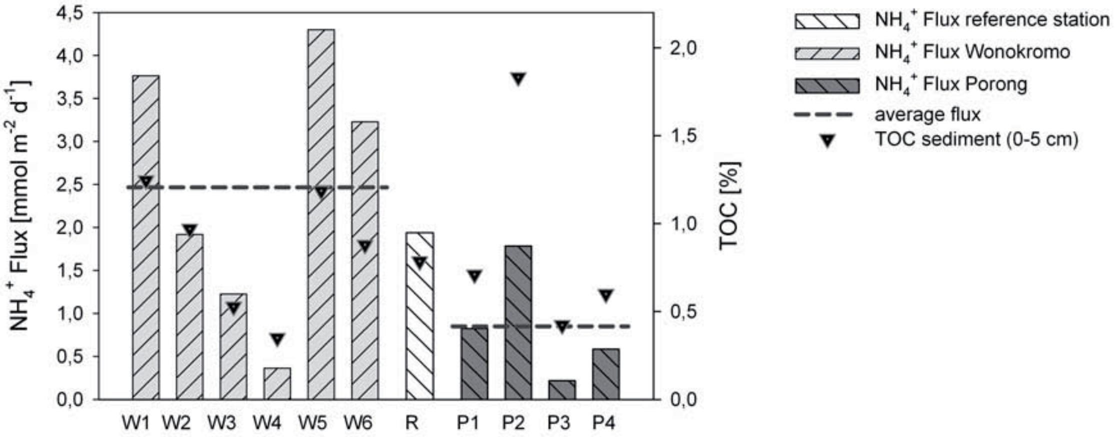

Figure 2 Ammonium fluxes and organic carbon content of sediments from the Wonokromo and Porong estuary during dry season 2008.

A regional difference was observed as the mean benthic ammonium flux of 2.47 mmol m^{-2} d^{-1} at the Wonokromo estuary clearly exceeded the average of 0.85 mmol m^{-2} d^{-1} at the Porong estuary. However, both estuaries showed a high intraregional variation of the benthic ammonium release. This variability was more pronounced in front of the Wonokromo river mouth (0.36 to 4.3 mmol m^{-2} d^{-1}) than off the Porong (0.22 to 1.79 mmol m^{-2} d^{-1}), where the reference station (R) had the highest flux with 1.94 mmol m^{-2} d^{-1}.

The large variation of diffusive benthic ammonium fluxes and the different mean fluxes off Wonokromo and Porong could have arisen from many factors, e.g. nutrient concentrations in the overlying water, benthic denitrification and nitrification, macrofaunal activities and temperature (e.g. Hendriksen and Kemp, 1988; Asmus et al., 2000; Caffrey et al., 2002; Sakamaki et al., 2006), several of which can be excluded from having an influence at the Brantas estuary. No significant temperature effect is expected due to rather constant year-round temperatures of around 28 °C in the region (1999-2009, Utah State University). Furthermore, no correlation was found between ammonium concentrations of overlying bottom waters and pore waters (data not shown). Based on the observation of black colored upper sediment layers that indicate a very small oxygen penetration depth in the estuarine sediments of our study area we conclude that nitrification processes were also insignificant.

In contrast, a correlation existed between the organic carbon of the upper sediment layer (0-5 cm) and the benthic ammonium release rates. The total organic carbon content varied between 0.4 and 1.3 % at the Wonokromo and 0.6 to 1.8 % at the Porong estuary (Fig. 2). However, intraregional variations were higher than interregional differences. The respective arithmetic means were similar at both estuaries (W: 0.86 % TOC; P: 0.99 % TOC). Ammonium fluxes were significantly correlated with the surface sediment organic matter content, but with different regression slopes for the two estuaries (Fig. 3a). Intercepts slightly below zero indicate a minor contribution of ammonium from other sources, e.g. nitrate reduction (Koike and Hattori, 1978; Sorensen, 1978) or the mineralization of dissolved organic nitrogen (Pantoja and Lee, 2003). The slope and thereby the rate of ammonium release at a given concentration of sedimentary organic carbon is significantly lower at the Porong than at the Wonokromo estuary ($p \leq 0.01$ for F-test on identical regression lines). Based on these correlations the organic carbon content appears to be the first order control factor that regulates the ammonium fluxes. However, due to the fact that TOC does not differ significantly between both estuaries, the strong disparity of the regression slopes reveals a different regional intensity of benthic recycling that can not be explained by the amount of organic matter. It is therefore conceivable that a different composition of the organic material deposited off both river mouths was responsible for this disparity.

Amino acids, the building blocks of proteins, comprise the major part of organic nitrogen and considerable amounts of organic carbon in most organisms (e.g. Lee, 1988; Cowie and Hedges, 1994) and as a consequence, represent up to 50 % of TOC and 100 % of organic nitrogen in recent coastal marine sediments (e.g. Lee and Wakeham, 1987; Burdige and Martens, 1988; Lee, 1988). They are labile relative to bulk nitrogen and carbon, which makes them more susceptible to biodegradation (e.g. Lee, 1988). At the sediment-water interface, amino acids can account for 35 % of C and 71 % of N remineralized (Cowie and Hedges, 1992), values that reflect their high importance for ammonium production. During their degradation, the molar composition of amino acids changes (e.g. Dauwe and Middelburg, 1998). These changes can be used as a sensitive indicator for the degradation status of particulate organic matter (POM), for transformation processes and, to a certain extent, it also offers clues for the sources of the material (Ittekkot et al., 1984; Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Jennerjahn and Ittekkot, 1999; Jennerjahn et al., 1999).

Total hydrolyzable amino acids were found in quantities of 0.73 to 4.35 mg g^{-1}, with generally lower values off the Porong (mean = 1.91 mg g^{-1}) than off the Wonokromo (mean = 2.68 mg g^{-1}) and an overall average of 2.37 mg g^{-1} (Table 1). Like the sedimentary organic carbon content, the amino acid concentration is positively correlated with the benthic ammonium fluxes at the Wonokromo and the Porong estuary. Again, the regression slopes differ significantly (Fig. 3b, $p \leq 0.05$ for F-test on identical regression lines), indicating that the bulk amino acid content alone does not explain the regional differences.

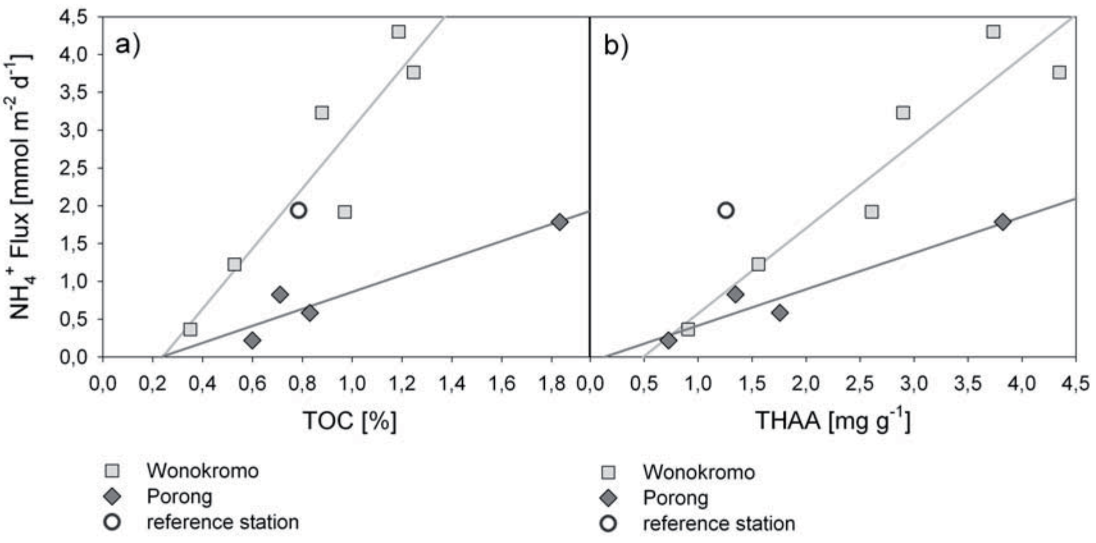

Figure 3 Ammonium flux as a function of (a) total organic carbon content and (b) amino acids content during the dry season 2008 ((a): Wonokromo $R^2 = 0.84$, Porong $R^2 = 0.92$; (b) Wonokromo $R^2 = 0.89$, Porong $R^2 = 0.89$).

The lower ammonium release at a given amount of THAA and TOC in front of the Porong is associated with lower concentrations of amino acid bound nitrogen and carbon, a discrepancy indicating differences in the composition of organic material between both estuaries. Percentages of amino acid bound nitrogen (AA-N%) and carbon (AA-C%) have been found high in fresh and/or planktonic organic material and low in land-derived organic matter but decreasing with ongoing degradation (Ittekkot and Arain, 1986; Cowie and Hedges, 1992; Jennerjahn et al., 1999; Unger et al., 2005). The much lower percentages of amino acid bound carbon and nitrogen in the sediments off the Porong (7.8 and 29.6 %) than off the Wonokromo (12.9 and 44.8 %, see also Table 1) exhibit the more refractory nature of sedimentary organic matter from the Porong estuary. Additionally, two other indicators, namely non-protein amino acids and the reactivity index (RI) also displayed regional differences (Table 1). The non-protein amino acids β-alanine and γ-aminobutyric acid typically increase with increasing diagenetic alteration (Lee and Cronin, 1982; Ittekkot et al., 1984; Cowie and Hedges, 1994). At the same time, a preferential degradation of the more labile aromatic amino acids tyrosine and phenylalanine has been observed (Cowie and Hedges, 1992; Jennerjahn and Ittekkot, 1999). The ratio of aromatic vs. non-protein amino acids – the reactivity index (RI) – can be used as an indicator for organic matter reactivity, whereby higher values refer to more fresh material (Jennerjahn and Ittekkot, 1997). The mole percentages of β-alanine and γ-aminobutyric acid were on average higher in the Porong than in the Wonokromo sediments (2.2 mole-% vs. 1.6 mole-%, respectively) while RI values displayed an opposite trend (2.3 and 3.3, respectively). All parameters together can be regarded as an "index of diagenetic maturity" (Cowie and Hedges, 1992) and concordantly indicate that the sedimentary organic matter in front of the Porong is less reactive than in front of the Wonokromo.

Table 1

Mean value, standard deviation and minimum/ maximum value of ammonium fluxes, total organic carbon content (TOC) and amino acid characteristics (THAA = total hydrolysable amino acids, AA-C% = amino acid bound carbon, AA-N% = amino acid bound nitrogen, non-prot. AA = non-protein amino acids, RI = reactivity index – see text for more information) of sediments from the Wonokromo and Porong estuary.

dry season 2008	NH_4^+-Flux [mmol m^{-2} d^{-1}]	TOC [%]	THAA [mg g^{-1} sed]	AA-C [%]	AA-N [%]	non-prot. AA [mol %]	RI
p-value*	$P \leq 0.05$	$P \geq 0.05$	$P \geq 0.05$	$P \leq 0.05$	$P \leq 0.05$	$P \leq 0.05$	$P \leq 0.05$
Porong (n= 5)							
mean	**0.85**	**0.99**	**1.91**	**7.8**	**29.6**	**2.2**	**2.3**
stdev.	0.67	0.12	1.17	1.8	8.1	0.2	0.2
range	0.22 - 1.79	0.60 - 1.83	0.73 - 3.82	5.2 - 11.7	18.8 - 38.1	2.0 - 2.6	2.1 - 2.6
Wonokromo (n= 6)							
mean	**2.47**	**0.86**	**2.68**	**12.9**	**44.8**	**1.6**	**3.3**
stdev.	1.54	0.36	1.29	1.5	4.6	0.2	0.4
range	0.36 - 4.30	0.35 - 1.25	0.91 - 4.35	11.0 - 15.0	40.6 - 53.1	1.4 - 1.8	2.6 - 3.8

*p-value of t-test

The reactivity or degradation state of sediments was found to be directly linked to the production of ammonium and mineralization of amino acids (Pantoja and Lee, 2003). In Chilean coastal surface sediments Pantoja and Lee (2003) determined the composition and decay rates of sedimentary THAA and compared the results with the production of ammonium measured at the same time and sites (Thamdrup and Canfield, 1996). The data showed a decreasing recycling capability of organic matter in more diagenetically altered sediments. This correlation has also been found during the quantification of sulfate reduction rates measured during laboratory studies of planktonic organic matter decomposition (Westrich and Berner, 1984), whereby stronger degraded plankton material decomposed more slowly than fresher (more labile) plankton. The close relationship allows an assessment of mineralization rates from the sedimentary amino acid composition (Pantoja and Lee, 2003) and is even more important if it is considered, that up to 80 % of the total nitrogen regeneration and 20 to 60 % of the ammonium production in coastal sediments can be accounted for by amino acid decomposition (Burdige and Martens, 1988; Pantoja and Lee, 2003). From this and the high importance of the organic matter reactivity as a decay-controlling parameter (Westrich and Berner, 1984), we conclude that the observed ammonium flux rate differences were related to the differences in reactivity of Wonokromo and Porong sedimentary organic matter.

This regional inhomogeneity, in turn, was most likely caused by different amounts and compositions of terrestrial and marine organic matter settling in front of the two river mouths. In general, both estuaries receive inputs of allochthonous land-derived material introduced by the rivers as well as autochthonous marine plankton (Jennerjahn et al., 2004; Jaenen, unpubl. data). The latter represents the comparatively more labile and most reactive organic matter source. This is mainly due to the fact that marine plankton contains more amino acids than vascular plants and degraded soil organic matter, which contribute largely to riverine suspended matter (e.g. Meybeck,1982; Ittekkot and Arian, 1986; Cowie and Hedges, 1992; Aller et al., 1996). In other tropical rivers, the riverine organic material has been found to be stronger degraded and more depleted in amino acids in the rainy than in the dry season (e.g. Ittekkot and Arain, 1986). The same seasonal trend was observed in the Brantas catchment, where the riverine material differed between rainy and dry season with higher relative percentages of labile organic matter in the dry season in both rivers (Jennerjahn et al., 2004; Jaenen, unpubl.data). In the rainy season, the period of peak river discharge, we suggest a stronger accumulation of more degraded riverine organic matter at the Porong estuary. This is due to the much higher river discharge of the Porong River at this time (~85 % of the total discharge in the rainy season). Besides seasonal differences in discharge we also observed differences in the reactivity of organic matter that was transported by the two river arms. In the rainy season, the suspended material transported by the Wonokromo River had a higher reactivity compared to that of the Porong River (RI averages in rainy season = 10.7 and 3.5, respectively) (Jaenen, unpubl. data). As both rivers branch from the Brantas River, this distinction was possibly caused by the input of large amounts of urban wastewaters and sewage into the Wonokromo River from the urban area of Surabaya. On the one hand, the sewage material itself might have contributed to a higher reactivity of the riverine material, as it is usually rich in proteins (e.g. Wu et al., 2007). On the other hand, the additional nutrient input might have triggered autochthonous riverine primary production (e.g. Carreira et al., 2002).

We suggest that the differences in supply and reactivity of the riverine organic material in both rivers, which were more pronounced in the rainy season, led to the regionally different organic matter reactivity of the estuarine sediments. Thus, the proportion of the more labile marine autochthonous material was much lower in the Porong estuarine sediments due to the enormous amount of refractory, amino acid-poor organic material delivered by the Porong River. In contrast, the Wonokromo estuary received a lower amount of terrestrial material that was, in addition, more reactive compared to the material transported by the Porong River. Therefore, the deposition of this material and a higher contribution of marine organic matter was responsible for the observed higher organic matter reactivity in front of the Wonokromo River.

The sheltered location and the distance to the main river mouth presumably prevent reference station R from receiving a high input of terrestrial organic material (Fig.1) as most of the riverine material is rapidly deposited in front of the river mouth (Hoekstra, 1989a). Especially in the dry season, the river plume does not reach this site due to the much lower river discharge. A higher RI value (3.2) as well as a lower mole percentage of the non-protein amino acids (1.6 mole-%) at station R indicate a higher proportion of labile marine material than at stations P1 to P4. Therefore, ammonium fluxes at given amounts of TOC and THAA were in the same range as off the Wonokromo (see Fig. 3 a, b). Thus, station R might be considered as a more “marine site” at the Porong estuary that is less or not affected by the very high material delivery of the river. It emphasizes, that the delivery and accumulation of terrestrial organic matter is an important influencing factor for the overall degradational status of the Brantas estuarine sediments.

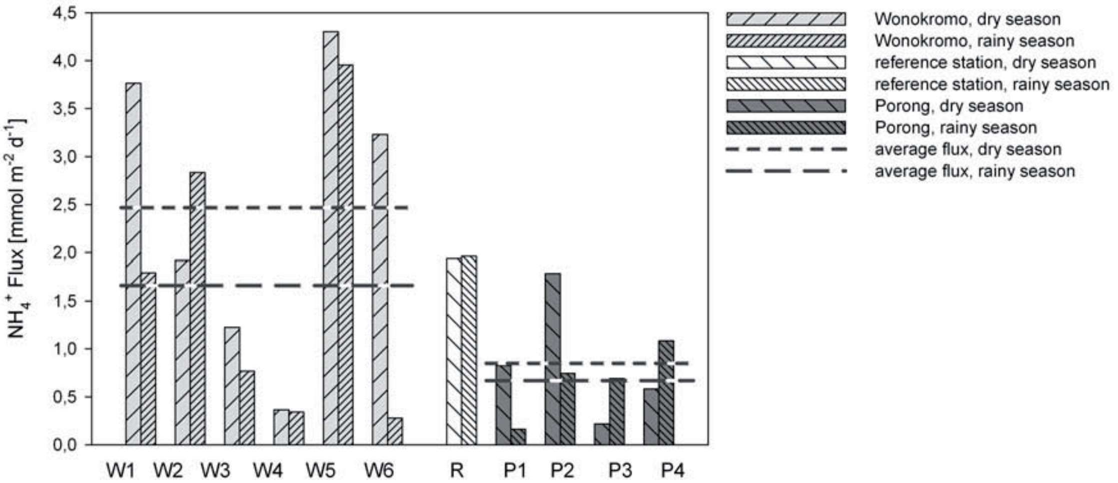

Figure 4 Ammonium fluxes at the Wonokromo and Porong estuary during rainy and dry season 2008.

Seasonal variability of ammonium fluxes

The regional distinction of benthic ammonium release between both estuaries was also observed in the rainy season of 2008, when the fluxes ranged between 0.16 mmol m^{-2} d^{-1} and 3.95 mmol m^{-2} d^{-1} and the mean values were 0.67 mmol m^{-2} d^{-1} and 1.66 mmol m^{-2} d^{-1} at the Porong and Wonokromo estuary, respectively (Fig. 4). We ascribe these similar seasonal trends to the fact that the decisive quantitative difference of terrestrial material supply and accumulation takes place in the rainy season. The resultant disparity of the reactivity of Wonokromo and Porong estuarine sediments remains throughout the year as the lower amount and more similar range of both river run-offs in the dry season can not modify the regional trend.

Despite the ammonium fluxes displaying an overall regional distinction during both seasons there were partly strong seasonal variations at single stations (Fig. 4). At the Wonokromo estuary, the most notable changes were observed at station W1 and W6. The difference at station W6 can be related to a strong variation in the flux determining organic carbon content (rainy season = 0.26 %, dry season = 0.88 %). Based on the fact the sedimentary organic matter is correlated with the sediment surface area and therefore has a high affinity for fine-grained sediments (e.g. Hedges and Keil, 1995) this discrepancy might result from the much larger particle size in the rainy season (grain size fraction <20 µm: 58 % in dry season, 17 % in rainy season) that we ascribe to a small dislocation of the sampling station (due to sampling problems). The decrease at station W1 might be also associated with a decline of the sedimentary organic matter (dry season TOC = 1.26 %, THAA = 4.35 mg g^{-1}; rainy season TOC = 1.00 %, THAA = 2.94 mg g^{-1}) which could not be explained further by the available data.

Strong changes of fluxes were also observed at the Porong estuary where the ammonium fluxes decreased at stations P1 and P2 and increased at stations P3 and P4 from the dry to the rainy season. The latter most probably can be attributed to the generally higher total organic carbon and total amino acids content at the Porong estuary in the rainy season (dry season TOC = 0.99 %, THAA = 1.91 mg g^{-1}; rainy season TOC = 1.14 %, THAA = 2.75 mg g^{-1}). We ascribe this enhancement to the much higher material supply in the rainy season that resulted in an overall higher amount of sedimentary organic material placed available for benthic remineralization. In contrast, the decrease of fluxes at P1 and P2 from the dry to the rainy season may be related to the constantly high freshwater discharge in the rainy season. An infiltration of freshwater into the uppermost centimeters of the sediments at these two stations located closely to the river mouth is likely (bottom water salinity: P1 = 0.2 and P2 = 8.0, respectively). This could have led to a reduction of ammonium fluxes since sediment-ammonium binding, which occurs presumably by ion exchange or adsorption and prevents diffusion through the surface sediment layer (e.g. Rosenfeld, 1979), appears to be stronger in freshwater and suppressed in seawater sediments. Ion pairing of ammonium and seawater ions in conjunction with a blockage of sediment cation exchange sites by seawater cations (Boatman and Murray, 1982) allows a larger quantity of mineralized ammonium to diffuse out of the sediment than in freshwater systems (Gardner et al., 1991). Thus, it is conceivable that the strong freshwater outflow during the rainy season inhibited the efflux of ammonium at stations P1 and P2.

Despite these variations at single stations, we found no statistically significant seasonal differences between the fluxes at the Wonokromo and Porong estuary. The diffusive ammonium exchange between the sediment and the overlying water column at the Brantas estuary was directed out of the sediment throughout the year and thus the sediments act as a regionally distinct but seasonally relatively consistent year-round source of ammonium for the coastal waters.

Relevance of the benthic ammonium fluxes in the Brantas estuary

In addition to their quantitative relevance for coastal nutrient cycles, benthic ammonium regeneration as well as other benthic nutrient fluxes are considered to confer a certain stability to the ecosystem, because they provide a more constant supply to the overlying water column in contrast to daily, seasonally and interannual variations in the rate of pelagic recycling and river nutrient inputs (Billen, 1978; Claquin et al., 2010). In order to evaluate the importance of this stabilizing internal estuarine ammonium source for the nutrient pool at the Wonokromo and Porong estuary we used different approaches.

We calculated the potential turnover times for ammonium in the water column, which is the time needed by the benthic fluxes to replace the water column nutrient inventory. Water column ammonium concentrations from the shallow areas, which correspond to the core sampling stations and average river plume extensions, were integrated over the site-related mean water depth of 2.2 m and divided by the regional corresponding benthic ammonium input. As seasonal variations were not significant, benthic ammonium fluxes represented the respective annual average values of both estuaries (W = 2.07 mmol m^{-2} d^{-1}, P = 0.76 mmol m^{-2} d^{-1}). In the rainy season, when the average ammonium concentrations in the water column were almost similar in both regions (W = 4.3 mmol m^{-3}, P= 5.5 mmol m^{-3}), the higher benthic ammonium flux at the Wonokromo estuary could replace the water column ammonium stock more than three times faster than the much lower fluxes at the Porong estuary (4.9 days at the Wonokromo vs. 17.0 days at the Porong estuary). Due to the lower river discharges, which resulted in overall reduced estuarine mean water column values (W = 2.1 mmol m^{-3}, P = 0.4 mmol m^{-3}, respectively), the turnover rates were generally higher in the dry season. Due to the fact that the standing stock of ammonium was much lower off the Porong river mouth at that time, the smaller benthic ammonium release there was sufficient to yield faster turnover times than the higher fluxes at the Wonokromo estuary (W = 1.3 days, P = 2.3 days). Another way to assess the impact of benthic recycling is to compare this internal source and the external nutrient supply by the rivers (e.g. Aller and Benninger, 1981). We calculated the mean ammonium river inputs for the respective plume areas (W = 8.1 km^2, P = 43.8 km^2) and obtained a river ammonium yield of 2.76 mmol m^{-2} d^{-1} for the Wonokromo and 1.46 mmol m^{-2} d^{-1} for the Porong estuary. Owing to the lack of distinct freshwater end-points in the dry season, mainly due to strong tidal intrusions into the rivers, calculations could only be made for the rainy season of 2008. For the respective benthic fluxes we used the average values from the rainy season, but considered only the time period when parts of the intertidal sediments were submerged (1/3 of the plume areas were exposed to air for on average 4.2 hours). This resulted in an estuarine flux of 1.56 mmol m^{-2} d^{-1} at the Wonokromo and 0.79 mmol m^{-2} d^{-1} at the Porong estuary.

The calculations demonstrate that the benthic release accounts for more than one third of the total ammonium supply (= estuarine benthic flux + riverine input) at the Wonokromo and Porong estuary, respectively. It is conceivable that the relative proportion of the benthic input is much higher in the dry season due to the overall lower river supply of nutrients, especially at the Porong estuary. This is corroborated by the faster benthic turnover rates in the dry season.

We conclude that the benthic ammonium release provides a varying, but yet considerable proportion to the estuarine nutrient pool, since it represents at least half of the riverine input at both sites. Our calculations further indicate that the relevance of the benthic fluxes for the pelagic ammonium inventory varies between seasons according to the fluctuating river discharge. Therefore, the benthic contribution is more important in the dry than in the rainy season. Furthermore, the lower seasonal run-off variations of the Wonokromo River were responsible for a lower seasonal fluctuation of benthic turnover times at the Wonokromo than at the Porong estuary.

Compared to other estuarine and near shore sediments our ammonium exchange rates are at the upper end of measured diffusive benthic fluxes (Table 2). This indicates the quantitative importance of the benthic ammonium input into the Brantas estuary, which represents an estuary of a tropical mountainous medium-sized river. However, it has to be considered that due to methodological differences, our calculated fluxes based on pore water profiles most likely still underestimate the net release of nutrients into the overlying waters compared to total flux estimates measured with benthic chambers (e.g. Callender and Hammond, 1982; Rutgers van der Loeff et al., 1984; Qu et al., 2005). Thus our study implies that sediments are important ammonium sources for these tropical coastal environments.

Table 2

Ammonium exchange rates in coastal and estuarine sediments* (n.d. = no data).

NH_4^+ flux [mmol m^{-2} d^{-1}]		coastal site	Region	Authors
diffusive flux	total flux			
0.4 - 2.6	**0.8 - 5.2**	estuary	West India	Pratihary, 2009
0.6 - 2.5	**0.3 - 5.0**	intertidal flat	France	Feuilliet-Girard et al., 1996
0.02 - 1.3	**0.4 - 1.4**	mudflat	California	Caffrey et al., 2002
0.82	**2.3**	estuary	East coast USA	Lyons et al., 1982
0.6 - 3.9	**-3.1 - 26.0**	estuary	East coast USA	Callender and Hammond, 1982
-2.7 - 6.1	**-1.8 - 25.9**	estuary	UK	Mortimer et al., 1998
n.d.	**-11.8 - 13.2**	tidal flat	Japan	Sakamaki et al., 2006
n.d.	**-0.4 - 4.0**	lagoon/ estuary	Brazil	Niencheski and Jahnke, 2002
0.07 - 5.2	**n.d.**	lagoon	Puerto Rico	Corredor and Morell, 1989
0.2 - 1.6	**n.d.**	intertidal flat	Portugal	Falcão and Vale, 1998
0.2 - 4.3	**n.d.**	intertidal flat	Indonesia	This study

*negative values represent uptake by the sediment

Summary and conclusions

In the Brantas estuary, benthic ammonium fluxes were directed from the sediment to the water column throughout the year. They showed a wide range of values that were in the same order of magnitude as reported from other studies in shallow and nearshore coastal environments, whereby the maximum efflux rates obtained in this study are among the highest diffusive flux rates worldwide.

Benthic turnover times and a comparison of the river and benthic ammonium input revealed a considerable contribution of the sedimentary ammonium release to and their high potential importance for the estuarine nutrient pool and the intense cycling processes.

Our study showed that variations of ammonium fluxes can be provoked by a different supply and accumulation as well as a different composition of terrestrial organic material depositing in coastal sediments. At the Brantas estuary, the dissimilar influx of riverine material via the two main river outlets resulted in an unequal proportion of marine (more labile) and terrigenous (more refractory) sedimentary organic matter in front of the two river mouths. Accompanied by a different reactivity of riverine organic matter between both rivers that potentially resulted from anthropogenic impacts, this led to a different degradational status of the estuarine sediments and entailed the observed regional ammonium flux disparities.

Our example suggests that the amount and quality of delivered material is the most crucial factor of influence for benthic ammonium fluxes in coastal regions with high seasonal or regional discharge variations, like the tropical regions. Human activities in river catchments can bias this factor in various directions, e.g. on the one hand they can alter the input of the refractory terrestrial material due to deforestation or the building of reservoirs and on the other hand wastewater disposal can enhance the reactivity of the transported organic matter. As those impacts become much more intense these days, we suggest that the interplay between these anthropogenic effects, which modify the amount and the quality of the riverine material export, will have an increased impact on benthic flux characteristics and coastal nutrient recycling processes in the future and outweigh the effects of naturally induced seasonal discharge variations.

Acknowledgments

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4 MANUSCRIPT III

Seasonal variation of carbon burial in the estuary of a mid-sized tropical mountainous river

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Abstract

On the basis of riverine particulate organic carbon (POC) discharge and benthic carbon remineralization rates we evaluated the carbon turnover of an estuary receiving inputs from the major arm of Java's second largest river, the Brantas, whose discharge is strongly influenced by the monsoonal cycle. We calculated the POC load for the rainy season as well as for the dry season of 2008 ($6.3 * 10^3$ t C/ month and $0.4 * 10^3$ t C/ month, respectively). Benthic remineralization rates were obtained by core incubation experiments carried out in 2008 and 2011. They amount to 19.3 g C/ m^2/ month in the rainy season and 24.5 g C/ m^2/ month in the dry season. Mass balance calculations revealed that due to the low material supply in the dry season all of the discharged riverine POC was remineralized in the water column. Therefore, the accumulation of riverine material takes place exclusively in the rainy season when on average a maximum of 98.8 g C/ m^2/ month are buried. The dry season is characterized by a prevailing decomposition of sedimentary POC resulting in an annual burial of 322.5 g C/ m^2/ year. Our results emphasize the high storage potential of POC in tropical estuaries receiving high sediment yields and reveal its seasonal character under monsoonal influence.

Keywords: particulate organic carbon, remineralization, burial, Indonesia, East Java, Brantas estuary

Introduction

Coastal ecosystems and estuaries are the major connection between land and sea and thus play a key role in linking terrestrial and marine organic carbon (OC) cycles. These regions receive high riverine inputs of terrestrial particulate and dissolved organic matter (OM) and are the main sites of its transformation, deposition, remineralization and burial (Hedges and Keil, 1995; Aller, 1998; McKee et al., 2004; Burdige, 2007). The quantity of riverine carbon fluxes is an important component of the global carbon cycle (e.g. Degens et al., 1991) and depends on the size of the drainage basin, steepness of basin morphology, bedrock erodibility, climate conditions (precipitation, temperature), vegetation cover and human activities (Milliman and Syvitski, 1992; Ludwig et al., 1996; Gao, 2010). Recent estimates amount to a global terrestrial riverine OC input of ~400 x 10^{12} g and approximately half of it is present in particulate form (e.g. Ittekkot and Laane, 1991; Meybeck, 1993; Schlünz and Schneider, 2000). It has been calculated that about 70 % of the sediment transported to the worlds oceans by rivers derived from southern Asia and Oceania (Milliman and Meade, 1983). Furthermore, the high importance and sediment yields of smaller mountainous rivers compared to the major world rivers have been ascertained (Milliman and Syvitski, 1992). Especially the high-standing islands of the East Indies, which feature rather small drainage basin areas, contribute a disproportionally high amount to the global riverine sediment export (20-25 %) although they account only for about 3 % (Milliman and Meade, 1983; Milliman et al., 1999). River sediment inputs have increased strongly under human influence and the tropics, in particular Indonesia, are the regions most influenced by increased sediment loads (Syvitski et al., 2005).

As the particulate organic carbon discharged by rivers is roughly 2-3 times as much as buried in marine sediments, a burial efficiency of terrestrial OM of 33-50 % is suggested, which depends on the amount of terrestrial OM that escapes remineralization in the water column and marine sediments (Berner, 1989; Hedges and Keil, 1995; Burdige, 2007). Marine OM produced in the euphotic layer is degraded up to 90 % while sinking through the water column, hence only a very small fraction reaches the seafloor (Suess, 1980).

The particulate organic material reaching the marine sediments is either remineralized or buried in the sediment (e.g. Berner, 1980; Canfield, 1993). The OM mineralization occurs according to a sequence of redox reactions, where oxygen is the initial oxidant for organic carbon as it is the energetically most favorable electron acceptor (Fröhlich et al., 1979; Canfield 1993).

The supply of OM to the sediments is the main factor of influence on the oxygen exposure time (Harnett et al., 1998) and the composition of OM (sources), the benthic mineralization as well as the preservation of sedimentary OM (e.g. Burdige, 2007). The amount of deposited material itself depends on the input of riverine material (terrestrial OM), surface water productivity (marine OM) and water depth (Hedges et al., 1997; Alongi, 1998). Thus, rates of benthic mineralization, material deposition and burial are highly variable and increase over several orders of magnitude from slowly accumulating deep sea to rapidly accumulating near shore deposits (e.g. Middelburg et al., 1997). On a global scale, approximately 90 % of the organic matter burial occurs in deltaic and associated shelf environments (Berner, 1982; Jörgensen, 1983; Hedges and Keil, 1995) and coastal sediments account for 50 % of the benthic mineralization although covering only 7 % of the oceans surface (Middelburg et al., 1997).

The dispersion, deposition and transformation of particulate organic matter in coastal regions are controlled by a complex interplay of factors such as riverine fluxes, coastal biological processes (like microbial decay), water depth and seabed morphology, wave and tidal energy, and local hydrographic conditions (McKee et al., 2004). However, very little is known about the effects of seasonal dynamics of riverine OM discharge and deposition on coastal biogeochemical cycles. The intensive organic matter cycling in estuaries and near shore coastal environments is critical in constraining global biogeochemical processes, especially Southeast Asia and Oceania. As these regions are highly variable and most have not been studied in detail they are so far difficult to include in global assessments (Henrichs and Reeburgh, 1987; Wollast, 1991; Nittrouer et al., 1995 in Aller et al. 2004).

The present study examines the seasonal variability of terrestrial POC transport of the Brantas, the second largest river of the Indonesian island of Java, and its effects on the mineralization and burial rates in adjacent coastal sediments. By comparing riverine POC loads with POC remineralization, we give a first overview on annual and seasonal POC budgets in this tropical coastal region.

Material and Methods

Study site

The Brantas River is a mid-sized tropical mountainous river that drains an area of 11.020 km² and discharges into the Madura Strait, a shallow part of the Java Sea (Fig. 1, Whitten, 1996). Its overall discharge fluctuates enormously during the year, depending on seasonal climatic changes which are dominated by a strong monsoonal system. The average annual rainfall amounts to ~2300 mm yr^{-1} (Aldrian and Djamil, 2008), of which 80 % precipitates during the rainy season. Our investigations focus on the estuary of the major branch, the Porong River, which transports almost 80 % of water supplied by the Brantas in the rainy season. According to the monsoonal cycle, the Porong River is characterized by immense seasonal discharge variations, resulting in about 5-fold increased discharge rates in the rainy season (~296 m^3/ s, November-March) compared to the dry season (~48 m^3/ s, April-October) (2003-2008, Jasatirta Public corporation, pers. comm.).

These naturally strong seasonal changes are intensified due to river regulations carried out by the integrated catchment management system of the Brantas River authority (Jasatirta Public corporation), for flood control and to meet the increasing demand of water for domestic, industrial and agricultural water purposes in one of the most urbanized regions in Indonesia (Booth et al., 2001).

The Brantas River has a very high sediment load, especially during the rainy season (Hoekstra, 1989a, b) and exhibits a total sediment yield of about 272 t km^{-2} yr^{-1}. This is promoted by very high erosion and denudation rates (Lavigne and Gunnell, 2006) that result from generally favorable natural conditions for high mechanical and chemical weathering on the one hand (e.g. Gaillardet et al., 1999) and human interventions on the other hand, e.g. severe deforestation and extensive agriculture (Römer-Seel, 2003). The transported riverine material load is rapidly deposited in the coastal water off the Porong river mouth due to a pronounced bottom friction and fast deceleration of the river outflow velocity within the flat estuary morphology, forming a strongly prograding delta (Hoekstra, 1989b). Furthermore, a strong resuspensive action of waves and tidal currents was observed at the Porong estuary (Hoekstra, 1989a)

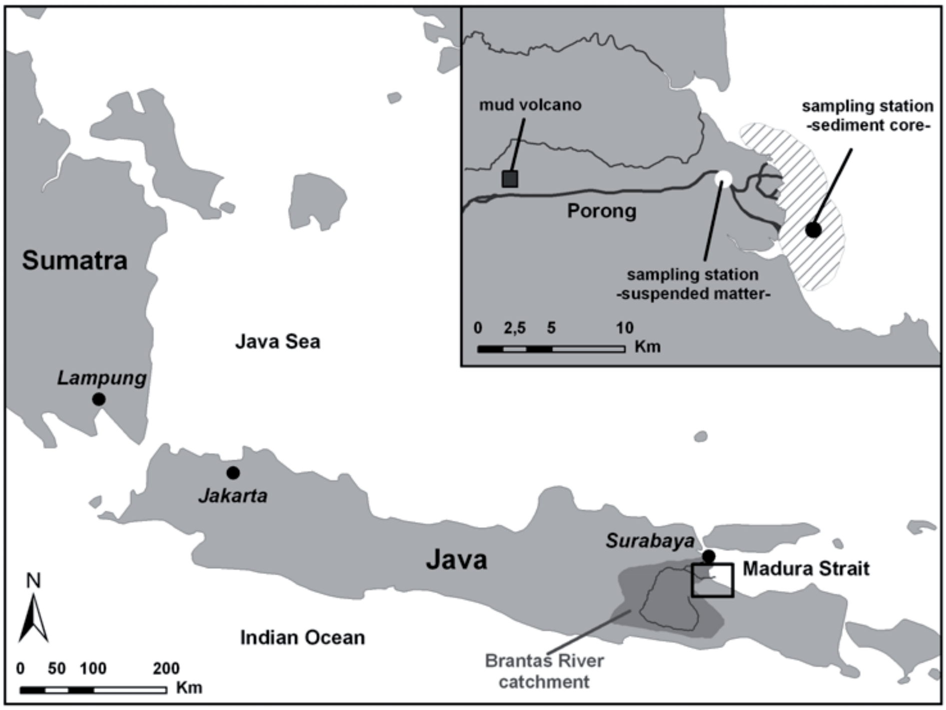

Figure 1 Brantas River catchment area, sampling sites and the Porong river plume extension (hatched area).

Selection of riverine sampling sites

The selection of riverine sampling sites was adjusted to the influence of the mud-volcano "LUSI", erupted in 2006 nearby the Porong river banks (e.g. Davies et al., 2008). Its mud is pumped via huge tubes into the river and changes the biogeochemical characteristic of dissolved and particulate OM at the point of inlet (Jänen, unpubl. data).

Given that the biasing effects of the mud input are locally restricted and rapidly decreases downstream (Jänen, unpubl. data) we want to minimize their potential influence on our calculation and sampled the riverine water shortly before the branching of the Porong River into its major and minor outlet (Fig.1).

POC analysis

To collect the riverine total suspended matter (TSM) the river water was filtered over precombusted Whatman GFF filters, which were subsequently dried at 40 ºC. Concentrations of POC were analyzed by high-temperature combustion in a *Carlo Erba*

NA 2100 element analyzer (Verardo et al., 1990) after the removal of carbonate by acidification with 1N HCl.

Calculation of riverine POC load & estuarine POC deposition rate

The calculation of the riverine POC-input into the Porong estuary is based on POC data from two expeditions carried out in the rainy season (March) and dry season (August) in 2008, and on monthly averaged discharge data of the Porong River available for the years 2003-2008 from the Jasa Tirta Coporation, Malang, Indonesia.

According to the discharge hydrographs of the Porong River from the years 2003 to 2008, the discharge data set was defined in a “rainy” period, from December to April, and a “dry” period, from May to November. Annual and seasonal riverine POC loads were obtained by the multiplication of the average seasonal POC concentration with the monthly averaged river discharge of the years 2003 to 2008 and the subsequent respective addition of the obtained monthly POC-loads.

For the calculation of the areal deposition rate of riverine POC in the Porong estuary we divided the annual/ seasonal average POC-input by the area of the average river plume extension of 43.8 km² (Fig. 1). This was defined under the consideration of satellite images, total suspended matter contents and salinity values.

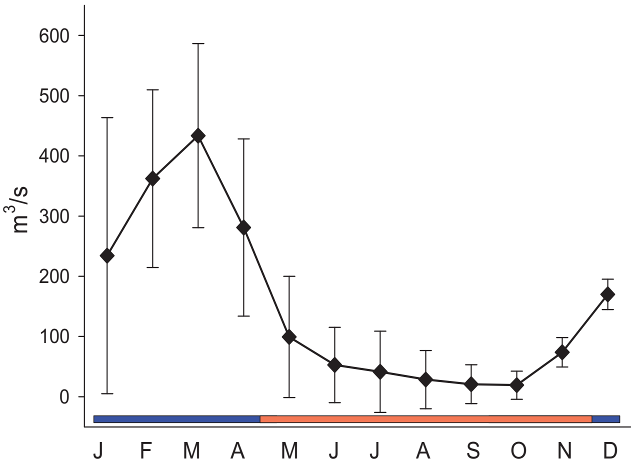

Figure 2 Porong River discharge (monthly average and standard deviation; blue and orange bars indicate rainy season and dry season, respectively; 2003-2008 Jasatirta Public corporation).

Determination of benthic carbon mineralization rates

The rate of benthic carbon mineralization was determined via the total oxygen uptake (TOU) of the sediments, which represents the most widely used proxy to estimate benthic carbon mineralization (e.g. Thamdrup and Canfield, 2000). This is based on the fact that oxygen is the ultimate electron acceptor during carbon oxidation, as it is either consumed via oxic respiration of OM or during the reoxidation of reduced species produced by anaerobic degradation processes. Thereby, the TOU slightly underestimates the total carbon oxidation due to minor sink of electrons via N_2-release from denitrification or the burial of sulfide (mainly FeS) during sulfate reduction (e.g. Canfield et al., 2005).

The benthic O_2 uptake was measured directly by incubation of enclosed sediment cores (e.g. Smith and Hinga, 1983). The cores were taken on the subtidal flats in front of the Porong river mouth during three expeditions in March (rainy season) and August (dry season) 2008 as well as in March (rainy season) 2011. They were obtained from water depth between 0.9 and 1.4 m with approximately 2 km distance to the main river mouth by the use of a hand-corer (HYDRO-BIOS) containing a plastic liner with a length of 60 cm and a diameter of 7 cm. The cores were darkened and placed in an incubation bath kept at in situ water temperature. After carefully sealing the core tops under the exclusion of air bubbles, the incubations started approximately 30 minutes after retrieval. The overlying water (18 to 29 cm) was kept homogenized by a small rotating stirrer that was fixed to the upper cap. During the 4 to 8 hours of incubation time, oxygen concentration was measured continuously with an oxygen probe (HACH, LDO/ HQ 10). The TOU (mmol/ m^2/ day) was calculated from the linear regression of the oxygen concentration variations versus time using the equation

$$\mathrm{TOU} = ((\Delta C/\Delta t)\ V_{\mathrm{BW}}/A_{\mathrm{core}})$$

where dC/dt ($\mu M\ h^{-1}$) is the concentration change over incubation time, V_{BW} (cm^3) is the volume of overlying water in the enclosed sediment core, and A_{core} (cm^2) is the sediment area enclosed by the core. To convert the oxygen-based measurements of benthic mineralization to carbon equivalents we used the generally applied respiration quotient of 1.0 ($RQ = \Delta CO_2/-\Delta O_2$) (e.g. Hopkinson and Smith, 2005; Williams and del Giorgio, 2005).

Results and Discussion

Potential deposition of terrestrial particulate organic matter in the estuary

Influenced by the annual monsoonal cycles, the Porong River exhibits water discharge rates of high seasonal variability, with average values of 7.7 * 10^8 m^3/ month in the rainy season (December-April) and 1.3 * 10^8 m^3/ month in the dry season (May-November). POC concentrations are higher during the rainy season (8.23 mg/ L) compared to the dry season (1.90 mg/ L), which is likely to be attributed to increased soil erosion during the months of peak rainfall. The intense variations of river discharge rates and POC concentrations consequently lead to a highly variable seasonal riverine POC load. The average POC input into the Porong estuary in rainy season is 6.3 * 10^3 t C/ month whereas only about 0.4 * 10^3 t C/ month reaches the estuary via the Porong River in dry season. These loadings result in an annual riverine POC input of 34.3 * 10^3 t C/ year.

It has been commonly observed that a large portion of the terrestrial material discharged into coastal waters is trapped in estuaries (e.g. Chen et al., 1999; Chen, 2010). In the tropics, a large proportion of mud and organic detritus deposit in the deltaic systems as rapidly extending intertidal banks or mudbanks in shallow subtidal areas (Alongi, 1991). The fast sedimentation of particles is attributed to a massive supply of lithogenic material by the rivers that serve as mineral ballast and facilitates a rapid sinking of particle aggregates and furthermore provide a protective effect to the organic matter (e.g. Armstrong et al., 2002). A rapid settling of material was also observed earlier at the Porong estuary and has been ascribed to the flat river mouth morphology and the high bed friction of the river outflow (Hoekstra, 1989a,b; Nolting et al., 1989). Furthermore, Hoekstra (1989b) concluded that the input of sediment largely exceeds the transport capacity of coastal currents and waves what results in the rapid progradation of the delta system. Thus, we suppose that the by far predominant part of the riverine POC load is deposited together with the overall rapid settling of particles in the proximal area off the river mouth. With respect to the further budget calculations, we therefore presume that all of the POC transported by the river is accumulating in the area of the mean river plume extension (43.8 km^2). This results in an annual riverine POC deposition of 789 g POC m^2/ year in the Porong estuary. According to the strongly varying seasonal POC loads also the deposition rates vary enormously within a year. Approximately 92 % of the annually deposited riverine POC settles in the rainy season, what implies an average monthly sedimentation of 144.6 g C/ m^2/ month in the five months of peak river discharge. In contrast, only 9.4 g C/ m²/ month are deposited in the dry season.

Benthic mineralization of particulate organic carbon

The mineralization of sedimentary organic carbon was determined via the total oxygen uptake rates of the estuarine sediments measured via incubation experiment.

All incubations showed a decrease of oxygen concentrations what indicated an overall uptake of oxygen by the sediments in the Porong estuary (Table 1). TOU rates varied between 66.1 and 87.5 mmol/ m^2/ day resulting in carbon mineralization rates between 18.5 and 24.5 g C/ m^2/ month. Oxygen uptake in the dry season exceeded the values in the rainy season about ~20 mmol/ m^2/ day (or ~5 g C/ m²/ month). This seasonal variability is likely to be attributed to different characteristics of POC transported by the river. According to Ittekkot (1988) riverine POC can be divided into a more labile fraction (LPOC) and a more refractory part (RPOC) that account for 35 and 65 % of the total POC input to the oceans, respectively. The contribution of the more labile POC decreases with increasing total suspended matter concentrations (Ittekkot, 1988) what implies a higher proportion of RPOC during times of high water and material discharge. These findings corroborate the higher reactivity of riverine suspended matter in the Porong River in the dry season compared to the rainy season 2008 (Jänen, unpubl. data). A similar seasonal trend was also found in surface sediments of the proximal Porong estuary (Propp et al., submitted). Thus, the higher O_2-consumption rates in the dry season most probably result from the accumulation of comparatively more labile riverine POC, which is remineralized faster than rather refractory POC supplied in the rainy season. Also, increased pelagic primary production during dry season due to less total suspended matter concentrations (rainy season 126 mg/ L, dry season 94 mg/ L; Jänen, unpubl. data) and preferential water column irradiance might be a source of labile organic matter remineralized the sediment. The Porong river estuary is highly turbid throughout the year, caused by high bed friction of the river outflow inducing strong mixing processes and a high resuspensive action of tidal currents in the shallow estuary (Hoekstra, 1989a). It seems likely that primary production in the Porong river estuary is potentially strongly light limited as often observed in highly turbid waters, where heterotrophic activities then dominate (e.g. Cole et al., 1992; Fishez et al., 1992) so that the estuary becomes net heterotrophic (Smith and Hollibough, 1993; Heip et al., 1995; Frankignoulle et al., 1998). We therefore assume that most of the organic matter remineralized in the Porong estuary is of riverine origin rather than directly produced within the estuary by benthic or pelagic primary production

The average benthic remineralization amounts to 22.3 g C/ m^2/ month. Our benthic remineralization rates are high compared to results of an extensive compilation of estuarine benthic respiration rates by Hopkinson and Smith (2005) as their average is 12.5 g C/ m^2/ month covering large seasonal and spatial variability. Our high values most probably result from the high sediment yields of the Brantas catchment or/ and the very close proximity of the sampling site to the river mouth. Thus, very high POC input and accumulation compared to other sampling areas are likely. The high OM deposition at the proximal Porong estuary involves comparatively higher benthic mineralization rates and sedimentary oxygen demand than in within greater distance to the coast or greater depth. For example, Lohse et al. (1998) detected mineralization rates of 19.0, 7.8 and 4.3-7.8 g C/ m^2/ year in the shelf, slope and lower slope sediments of the European continental margin, respectively, but also the average of data compiled from coastal oceans (<200 m; Burdige, 2007) is with ~41.4 g C/ m^2/ year much lower than the mineralization rates measured at the Porong estuary. Furthermore constantly high temperatures of tropical waters generally enhance remineralization rates compared to lower latitudes (e.g. Asmus et al., 2000).

Table 1 Water and POC discharge of the Porong River into the Porong estuary. Deposition, oxygen consumption and carbon mineralization rates in the Porong estuary

	water discharge (m^3/ month)	POC input (t C/ month)	deposition rate (g C/ m^2/ month)	O_2-consumption (mmol/ m^2/ day)	benthic carbon mineralization (g C/ m^2/ month)
average rainy season (March 2008 & 2011)	$7.7*10^{-8}$	$6.3*10^{-3}$	144.6	68.6 (66.1 - 72.6)*	19.3 (18.5 - 20.4)*
average dry season (August 2008)	$1.3*10^{-8}$	$0.4*10^{-3}$	9.4	87.5	24.5
annual average				73.4	22.3
annual sum	$4.7*10^{-9}$	$34.3*10^{-3}$	789.3		

*range; n = 3

Potential POC budget for the Porong estuary

Based on our measurements and the above outlined presumptions, we here want to suggest a potential POC budget for the Porong estuary, which aims to function as an initial conceptual framework for the understanding of carbon cycling in a widely unknown ecosystem, rather than as a completed ecosystem analysis. The potential POC budget was made for the dry as well as the rainy season and annual averages were calculated, based on the following equation:

$$\mathbf{POC_{burial} = POC_{river} + P_{pelagic} + P_{benthic} - R_{pelagic} - R_{benthic}}$$

with POC_{burial} representing the burial of POC , POC_{river} representing the delivery of POC by the Porong river, $P_{pelagic}$ the production of POC in the water column (phytoplankton primary production), $P_{benthic}$ the production of POC in the benthic (microphytobenthos primary production), $R_{pelagic}$ the amount of remineralization in the water column, and $R_{benthic}$ the amount of the amount of remineralization in the sediment. This POC budget assumes no export of POC from the Porong estuary (Fig. 3).

We applied the following values:

$\mathbf{POC_{river}}$: riverine POC deposition

$\mathbf{P_{pelagic}}$ and $\mathbf{P_{benthic}}$: assumed to be insignificant due to light limitation caused by high turbidities.

$\mathbf{R_{pelagic}}$: since data are lacking, estimates from a study of net ecosystem metabolism (NEM) conducted in shallow estuarine environments of the United States (Caffrey, 2004) were applied. Since temperature highly influence remineralization (e.g. Sampou and Kemp, 1994) we only considered summer values (n=42) from the study of Caffrey (2004). This amounts to a monthly average of -26.5 g C/ m²/ month.

$\mathbf{R_{benthic}}$: as measured

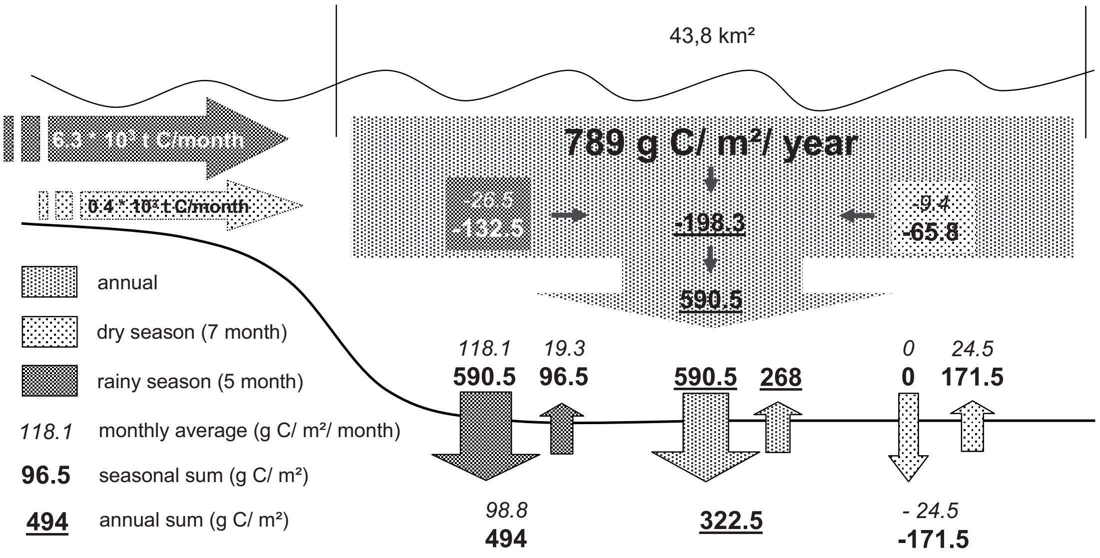

Figure 3 Potential POC budget established for the Porong estuary.

Due to the fact that the POC deposition rates strongly vary between the seasons, the burial rates are highly variable throughout the year (Fig. 3).

On condition that a part of the introduced riverine POC is decomposed by pelagic processes and is therefore not settling to the Porong estuarine sediments, the calculated maximum potential deposition rates (see above) are reduced. In the rainy season, the subtraction of an assumed pelagic respiration of -26.5 g C/ m²/ month results in deposition rates of 118.1 g C/ m²/ month. These amounts of depositing POC can not be decomposed at the sediment surface as indicated by average mineralization rates of 19.3 g C/ m²/ month. This leads to a burial rate of approximately 98.8 g C/ m²/ month and an associated burial efficiency of 83.7 % (= the fraction of OC delivered to the sediment that becomes buried). Thus, in the rainy season the sediments act as a considerable sink for riverine POC. In the dry season, in contrast, the subtraction of pelagic POC respiration yields negative values due to the very low potential deposition rates of 9.4 g C/ m²/ month and no riverine material is deposited. Concurrently, benthic remineralization rates change only slightly what indicates that the sedimentary standing stock of OC that accumulates during the rainy season fuels remineralization during the dry season. The negative data obtained from calculation with the data from the dry season reveals the limitations of applying a hypothetical NEM due to the fact that these negative values indicate other OM sources for pelagic respiration than riverine POC but can not be further discussed due to the hypothetical approach. Nevertheless, it can be estimated that a loss of -26.5 g C/ m²/ month during the five month of the rainy season and a maximal possible pelagic respiration of -9.4 g C/ m²/ month of riverine POC in the dry season results in a annually pelagic respiration of about -198.3 g C/ m²/ year of riverine POC. This is equivalent to 25.1 % of the annual riverine POC input and amounts to an annual deposition of 590.5 g C/ m². While the riverine POC is only depositing in the rainy season, the benthic mineralization is high throughout the year. This results in a phase of POC accumulation in the rainy season (98.8 g C/ m²/ month) and a period of POC degradation in the dry season (-24.5 g C/ m²/ month). The annual benthic POC remineralization amounts to 268 C/ m², corresponding to 45.4 % of the POC deposited in the estuary per year. Thus, despite a considerable potential pelagic loss of POC, the amount of yearly settling organic material exceeds the annual loss of POC via benthic remineralization and an annual burial rate of 322.5 g C/ m² can be assumed.

The burial rates in this study are very high compared to rates measured in other marine environments. Thus, 0.6 to 6.5 g C/ m²/ year of organic carbon burial were detected along the shelf, slope and deep sea sediments of the NW Indian Ocean (Naqvi, 2010), 0.8 to 13.1 g C/ m²/ year were measured at the Bay of Biscay (500 – 2800 m, Mouret et al., 2010) and arctic sediments taken in depths of 36 m revealed burial rates of 25.3 g C/ m²/ year (Rysgaard et al., 1998). These examples illustrate the trend of increasing burial rates with increasing water depth. Therefore, the very high burial rates observed in this study in the rainy season can be clearly attributed to the very close proximity to the coastline and the river mouth of the sampling site and the associated high material deposition rates. Furthermore, the preservation of OM in nearshore sediments is often enhanced by rapid deposition rates (Hedges and Keil, 1995) and large surface area of fine sediment particles (Keil et al., 1994b; Mayer, 1994). This may also be the case at the Porong estuary based on the large amount of lithogenic material carried by the river (Hoekstra, 1989a,b) and the high fraction of fine grained particles in the estuarine sediments (fraction <20µm = ~ 87 %, Propp et al., submitted). Another study, where sampling stations were located in ultimate proximity to the coastline, was carried out in the northeastern Australian estuary receiving the inputs from the Herbert River. Burial rates in 0.5 m depth averaged 180 g C/ m²/ year and rates in 5-20 m depth amount to roughly 20.4 g C/ m²/ year (Brunskill et al., 2002). This example again demonstrates the depth dependence of burial rates but it also exhibits lower values than found at the Porong estuary despite similar depth. The Herbert River discharges nearly the same amount of water as the Porong River (~5 * 10^9 m^3/ year; Porong River = 4.7 * 10^9 m^3/ year) but it transports only 28.8 * 10^3 tones of OC, what implies a POC load of about 14.4 * 10^3 t C. Thus, the lower burial rates of these proximal waters compared to the intertidal flats in front of the Porong River most probably results from the lower riverine POC supply. Moreover, it emphasizes the high sediment yield of the Brantas catchment given that the Herbert River catchment area got almost the same size as the one of the Brantas River.

Summary and Conclusions

In this study, we tried to establish a POC budget for the proximal Porong estuary that receives POC inputs from the second largest river of Java.

We can conclude that the monsoonal driven pulsed river input of the Porong River leads to strongly different deposition rates of the riverine material in the rainy and dry season. Given that benthic mineralization rates show relatively constant values, these changes in POC supply have a direct regulatory effect on the burial rates that are much higher in the rainy season. Benthic POC degradation is high compared to other marine environments and decomposes approximately a fifth part of the riverine POC depositing in rainy season. In the dry season, the much lower riverine POC input is most probably degraded by pelagic respiration before reaching the sediment. This results in burial efficiencies of ~84 % in the rainy and 0 % in the dry season.

Apparently, the strongly different amounts of POC supply have no major effect on benthic mineralization rates. This indicates that the benthic system is not limited by carbon, which is abundant in the sediments also during the dry season due to the large standing stock of sedimentary OC. However, the decay rates apparently enhance with inputs of more labile OM in the dry season. Next to burial efficiencies, the pulsed material input might have an influence on the relative importance of the various carbon oxidation pathways, as these are related to the sedimentation rate (amongst other factors) and anaerobic degradation generally becomes more important with increasing material deposition (Jørgensen, 1983; Canfield, 1993).

Our data suggests that tidal flats at river dominated estuaries are important sites for POC degradation and simultaneously have a very high potential storage capacity. Especially estuaries and coastal zone adjacent to mountainous tropical rivers of Southeast Asia and Oceania that are discharging in shallow areas, e.g. like many Indonesian and Malaysian Rivers that flow into the shallow Sunda Sea, can therefore be considered as significant sites of organic carbon burial.

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5 SUMMARY AND CONCLUSIONS

The present study investigates the processing of OM in the estuary of the second largest river of Java, the Brantas River. It originates in high volcanic complexes and discharges high amounts of terrestrial material to the coastal ocean that is eroded from the agricultural most intensively used catchment area. While tracking the pathway of estuarine sedimentary organic matter from its sources to its burial, the main focus of this thesis is to quantify the benthic remineralization of OM and to understand the determining processes. A variety of biogeochemical tools, such as the measurement of stable isotopes and amino acids as well as pore water nutrient analyses, show that the quantity and composition of the riverine material delivered to the estuary are the overall predominant influencing factors that determine the deposition and characteristics of sedimentary OM, its remineralization and the amount of material that becomes buried.

The strong impact of the riverine material discharge on the characteristics of OM in the coastal sediments is indicated by the observation that respective contributions of the main organic matter sources, namely terrestrial soil OM and marine phytoplankton, show strong regional changes dependent to different discharge rates of the two main river channels Wonokromo and Porong. The naturally manifold higher discharge of the Porong River is intensified due to river regulations and results in a much higher accumulation of terrestrial material in its estuary compared to the Wonokromo estuary. Despite the high material inputs, the terrestrial OM is not transported to distant offshore regions. This is unusual for rivers with high discharge rates and can be attributed to the flat river mouth morphology and an associated rapid settling of particles. Given that the reactivity of the autochthonous and allochthonous OM exhibit strong differences, their final balance determines the magnitude and spatial gradients of the OM reactivity in the estuarine sediments. Hence, the sedimentary OM in the Porong estuary has a lower reactivity than OM in sediments in front of the Wonokromo river mouth or the coastal region between the two main river outlets. This difference induced by discharge variations is intensified by a higher reactivity of suspended matter in the Wonokromo River that results from a higher riverine phytoplankton production, possibly triggered by wastewater disposal in the area of Surabaya, the second largest city of Indonesia. Due to the fact that the discharge rates in

both rivers are strongly enhanced in the rainy season the Brantas estuarine sediments are, besides regional variations, also characterized by minor seasonal changes. Most likely accompanied by a stronger erosion generated through the higher precipitation, the elevated discharge rates lead to a higher input of terrestrial, refractory organic material to the whole estuary (via river discharge and diffuse runoff) and consequently to an all over decreasing reactivity of sedimentary OM during rainy season.
On a global scale, the OM reactivity of the shallow Brantas estuarine sediments is similar to that of sediments located in greater depth or distance to the coast that have undergone considerable degradation during redistribution or sinking processes. This similarity points to a substantial degradation of particulate OM in the turbid waters of the Brantas estuary that strongly decreases the OM reactivity. This high OM decay is generated by the intense tide-induced resuspension processes occurring at the extensive tidal flats, as well as by the high tropical temperatures triggering microbial activity. This suggests that the "incinerator" function for OM attributed to tropical shelf systems in recent studies (e.g. Aller and Blair, 2006) already occurs in much more nearshore coastal regions exposed to high tidal energy, like tidal flats.

The reactivity of sedimentary OM, that has been addressed in the first manuscript, is an important factor for the benthic degradation of OM, as more labile material like freshly produced phytoplankton is decomposed much faster than more refractory organic matter, such as woody material containing high amounts of lignin (e.g. Cowie and Hedges, 1992; Hulthe et al.,1998). Therefore, the regionally diverse reactivity of the sedimentary organic material provokes spatial differences regarding the degradation of OM in the Brantas estuarine sediments. Furthermore, the lower reactivity of nearshore Porong sediments is associated with the overall high accumulation, and thus burial, of riverine material in front of the Porong River mouth that reduces the oxygen exposure time of OM at the surface sediments (another crucial factor for the degradation of OM, e.g. Hartnett et al. 1998). The combination of both important controlling factors results in a significantly lower intensity of OM degradation in the proximal sediments of the Porong estuary compared to the more reactive sediments at the Wonokromo estuary and the intermediate coastal region that both receive lower amounts of terrestrial material. This was demonstrated by a lower decrease of amino acids (manuscript I), which are labile relative to bulk OC, and lower diffusive benthic nutrient exchange rates of ammonium (manuscript II) at the Porong estuary. However, the benthic fluxes are an overall year-round source of ammonium for the

Brantas estuarine waters. The diffusive benthic ammonium fluxes measured at the Brantas estuary are high compared to other coastal environments and they have a high potential importance for the local coastal nutrient cycling throughout the year. They account for at least half of the river ammonium input, even during the rainy season when the river discharge is very high. During this season, the benthic turnover time (= time needed by the benthic fluxes to replace the water column nutrient inventory) is higher at the Wonokromo estuary than at the Porong estuary. This partly results from the higher benthic ammonium fluxes at the Wonokromo estuary but is mainly referable to the higher ammonium supply via the Porong River and the consequently enhanced ammonium nutrient concentrations in the estuarine waters. However, the benthic turnover times generally decrease in the dry season due to the overall strongly reduced river nutrient discharge. The high diffusive fluxes detected in this study emphasize the importance of sediment nutrient supply in shallow coastal ecosystems, even though they most likely still underestimate the net release of ammonium into the overlying waters compared to total flux estimates measured with benthic chambers (e.g. Callender and Hammond, 1982).

The amount of OM that is not remineralized in upper sediment layers becomes buried in the deeper sediments and is removed from the global carbon cycle for a longer time (e.g. Burdige, 2007). The rate of burial increases with rapid accumulation rates and therefore very high burial rates can be expected in the coastal sediments of Oceania that receive the highest riverine POC worldwide. Results from a POC budget calculation obtained in this study for the sediments in front of the Porong river mouth substantiate this assumption, as extremely high burial rates were estimated. However, it is difficult to rank the obtained results amongst those in Oceania, as almost no data exist for estuarine sediments in this region despite their global relevance in terms of riverine material input. The burial rates at the Porong estuary are very high compared to other marine environments worldwide and indicate the importance of catchment sediment yields for the amount of buried material. Moreover, the calculated burial rates demonstrate a very high seasonality of POC burial. Due to the strongly enhanced riverine POC input and deposition in the rainy season and a comparatively low variations of benthic remineralization of POC, the burial at the Porong estuary exclusively takes place in the rainy season. This might be an important consideration for future budget calculation in regions characterized by strong monsoonal cycles and should be considered in yearly projections.

6 PERSPECTIVES

This study yields insights into the biogeochemical processes of a tropical estuary in a globally very important region of OM input, remineralization and burial. Nonetheless, many aspects of sedimentary OM processing could not be addressed and questions remain due to methodological limitations on the one hand and the overall complexity of coastal ecosystems on the other hand.

Thus, for example the application of a hand corer for sediment core retrieval limited the sampling to sites up to 1.4 m water depth, whereby incubation and pore water extraction could not be carried out in further offshore regions. Furthermore, the role of benthic organisms could not be clarified. As benthic microalgae can strongly influence benthic production and/ or respiration processes and microorganism basically drive most of the reactions investigated in this study, information about their abundance, different metabolic rates or the composition of the specific benthic communities are missing for a complete and detailed understanding of the examined processes (Cahoon, 1999; Canfield et al., 2005). Given that diffusive benthic fluxes calculated in this study based on pore water profiles, generally underestimate the total sediment-water exchange rates, the measurements of total fluxes appear to be more suitable for the estimation of the relevance of benthic nutrient supply for coastal nutrient cycles.

The results of this study substantiate the importance of resuspension processes for the decomposition of OM but unfortunately, detailed resuspension patterns were not explored to confirm this assumption. Besides its importance for OM degradation, resuspension processes can enhance the benthic nutrient release, affect the dispersion and redistribution of particles and potentially influence the marine primary production that strongly depends on light availability (e.g. Wright and Nittrouer, 1995; Huettel et al., 2003). Due to this close benthic-pelagic coupling that is characteristic for energetic tropical deltaic systems (Aller, 1998), there is a need to further study resuspension processes in the shallow, tidally influenced Brantas estuary to comprehensively understand the pathways of organic matter.

For that reason, it is furthermore important to distinguish specific constituents of particulate organic matter. Isotopic differences ($\delta^{13}C_{org}$ and $\delta^{15}N$) between terrestrial and marine organic matter were used in this study to differentiate between inputs from these two sources. The significance of those results is, however, limited to a certain extent as signals from different sources overlap. A more precise identification of the sources and age of organic matter components would be provided by ^{14}C measurement or organic carbon biomarkers (e.g., plant pigments, lipids, lignin-phenols, etc.) (e.g. Pearson et al., 2001; Raymound and Bauer, 2001; Peters et al., 2005). The combination of specific biomarkers and stable carbon isotopes currently provides the best approach to separate carbon source inputs to sediments and to trace their pathways during further processing.

Despite the limitations of this study, the obtained data contribute to the understanding of biogeochemical OM cycling in tropical coastal ecosystems. In particular, the study demonstrates the high influences of quantity and composition of river discharge on coastal ecosystem processes. Due to the importance of riverine material inputs for benthic mineralization and burial rates, an increasing influence of human alterations on sedimentary organic matter processing can be expected in areas of enhanced human activities in the coastal zone, like Southeast Asia. This influence comprises for example the enhancement or reduction of sediment yields due to the construction of dams or due to deforestation, respectively. Therefore, more studies in these regions are required to assess changes of the global carbon budgets under human influence, like recently highlighted by Syvitski et al. (2005a, b).

Sedimentary processes are only one aspect of the complex interacting coastal processes and only interdisciplinary investigations can lead to a comprehensive and precise understanding of the various interactions between the different ecosystem compartments. As this can not be realized in all coastal ecosystems worldwide, the establishment of model regions appears to be reasonable for this purpose. Profound knowledge of one specific coastal system might then be consulted to understand processes in other systems, where less data is available. As the Brantas River catchment is a very good example for coastal zones affected by intensive and steadily increasing human activities, and as it furthermore reveals very high sediment yields, this area could be considered as a model region for the globally important regions of Southeast Asia and Oceania. The global importance together with the unique setting of two major river arms that are differently influenced by human impact as well as the availability of long time data of river management (starting from the 1970th, Jasatirta Public Corporation, pers comm.) and a good local infrastructure provides a good basis and interesting prospects for further research.

However, as every ecosystem consists of numerous interlinked compartments and processes, especially the heterogeneous coastal environments, field research like the present study is essential for a comprehensive understanding of coastal ecosystem processes.

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ERKLÄRUNG

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