

**Impact of sugar cane cultivation on
biogeochemistry and
phytoplankton dynamics in a tropical
lagoon and estuary in Brazil**

Dissertation submitted by

Gertrud Spörl

In partial fulfillment of the requirements for the degree of
Doctor of Natural Sciences (Dr. rer. nat.)

Leibniz Center for Tropical Marine Ecology
Faculty of Biology/ Chemistry
University of Bremen

April 2011



Advisory Committee:

Reviewer: Prof. Dr. Kai Bischof
University of Bremen

Reviewer: PD Dr. Tim Jennerjahn
Leibniz Center for Tropical Marine Ecology, Bremen

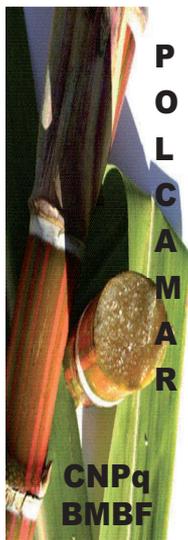
Examiner: Prof. Dr. Ulrich Saint-Paul
Leibniz Center for Tropical Marine Ecology, Bremen

Examiner: Prof. Dr. Herwig Stibor
European Institute for Marine Studies Technopole
Brest-Iroise, France

This thesis was conceived and written at the Leibniz Center for Tropical Marine Ecology, Bremen, as part of the bilateral German Brazilian project POLCAMAR (POLLution from sugar CAne in MARine systems).

This work was conducted in cooperation with the Universidade Federal Alagoas (UFAL), Maceio, Universidade Federal Fluminense (UFF), Niteroi and Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF), Campos dos Goytacazes in Brazil.

The project was funded by the German Ministry for Research and Education (BMBF), grand number (03F0455D).



Contents

Contents

Abbreviations	I
Abstract	II
Zusammenfassung	V
Outline of publications	IX
1. Scientific Background and Objectives	1
1.1 Eutrophication – a global concern	1
1.2 Consequences of eutrophication	3
1.3 Cultivation and history of sugar cane in Brazil	5
1.4 Environmental problems of sugar cane agriculture	7
1.5 State of aquatic systems in Brazil affected by sugar cane cultivation	9
1.6 Objectives and Hypotheses	11
2. Material and methods	14
2.1 Study areas	14
2.2 Field work	18
2.3 Analytical work	18
3. Results and synoptic discussion	21
3.1 Factors controlling the availability and distribution of nutrients and organic matter	21
3.2 Source, sink and transformation of nutrients	26
3.3 Composition and distribution of organic matter	39

3.4 Implication of results	42
3.5 A global view on eutrophication	43
4. Perspectives	46
5. References	49
Publications	
Chapter I	64
Chapter II	100
Chapter III	144
Presentations and Co-author Publications	179
Acknowledgements	180
Erklärung	183

Abbreviations

Abbreviations

Chl a	Chlorophyll a
C _{org}	Particulate organic carbon
C/N	Molar ratio of C _{org} and PN
DIN	Dissolved inorganic nitrogen
DON	Dissolved organic nitrogen
$\delta^{13}\text{C}_{\text{org}}$	Organic carbon isotope ratio
$\delta^{15}\text{N}$	Nitrogen isotope ratio
HABs	Harmful algal blooms
MML	Mundau Manguaba Lagoon
NH ₄ ⁺	Ammonium
NO ₂ ⁻	Nitrite
NO ₃ ⁻	Nitrate
NO _x ⁻	Nitrite + nitrate
OM	Organic material
PN	Particulate nitrogen
PO ₄ ³⁻	Phosphate
PSR	Paraiba do Sul River
Si(OH) ₄	Silicate
TSM	Total suspended matter

Abstract

Sugar cane cultivation has become the main land use in northeast and southeast Brazil and it is still increasing because of a growing national and international demand of sugar and biofuel. Shallow coastal lagoons and estuaries are the linkage between terrestrial and marine environments and are susceptible to anthropogenic modifications. Little is known about the impact of sugar cane cultivation in these systems.

Aim of this study was to gain knowledge on the impact of effluents from sugar cane cultivation on the biogeochemistry and phytoplankton dynamics in two shallow coastal systems affected by sugar cane monoculture in their watersheds, a coastal lagoon and an estuary in Brazil. In the Mundau Manguaba Lagoon (MML), water samples were collected at the beginning and end of the dry season during five expeditions between September 2007 and February 2009. Additionally, sediment cores were taken in March 2007. In the Paraíba do Sul River (PSR), samples were taken during the rainy (January) and dry (September) season 2008.

The main elements of this study were the determination and characterization of nutrients (nitrate, nitrite, ammonium, silicate, phosphate) and total suspended matter (TSM) as well as phytoplankton communities in the MML and the PSR. Particulate organic matter (C_{org} , PN) and stable carbon and nitrogen isotopes ($\delta^{13}C$, $\delta^{15}N$) were determined in TSM of surface water in the MML and PSR and sediments of the MML. Inorganic nutrients were measured in the water samples. Phytoplankton abundance,

Abstract

biomass and community composition were identified in the MML. Effects of nutrient enrichment caused by fertilizer runoff from sugar cane fields on phytoplankton communities in the MML were experimentally simulated. Chlorophyll a (chl a) was used to estimate phytoplankton biomass in the PSR.

Nutrients and organic matter derived from fertilizer runoff in the catchment area of the PSR were transported from the river and its tributaries to the estuary and subsequently to adjacent coastal waters during the rainy season because of high river discharge. Reduced river discharge and long residence time during the dry season led to an increase in chl a amount and retention of allochthonous and autochthonous material inside the system.

Nutrient concentrations in the MML were mainly governed by the rivers which drain the sugar cane dominated catchment area. A seaward nutrient decrease coincided with high phytoplankton biomass inside the lagoons and was the result of fast nutrient uptake by algae. Parts of the organic matter were removed from the water column due to sedimentation and were recycled or stored in the sediments of the lagoons. Other parts of the organic matter were exported from the Manguaba and Mundau lagoons into adjacent coastal waters due to tidal currents.

Phytoplankton community and diversity were highly variable in both lagoons because of rapidly changing salinity and nutrient concentrations as well as residence time. Thus, temporal and spatial phytoplankton

distributions and shifts between cyanobacteria and diatom dominated communities were observed in the MML.

Nutrient enrichment experiment conducted in order to simulate high nutrient input from fertilizer runoff showed a direct response of phytoplankton communities. Diatoms were the main profiteers due to permanently high silicate concentrations in tropical aquatic ecosystems. Alterations in the nutrient ratios affected by high nitrogen and phosphate inputs from sugar cane cultivation lead to a shift in phytoplankton communities and consequently influence the entire food web dynamics in the lagoons.

It can be concluded that lagoons and estuaries play an important role for nutrient and organic matter cycles in the coastal ecosystems affected by sugar cane cultivation in the northeast and southeast regions of Brazil. Seasonal variations in fertilizer runoff, geomorphology of the system and biological processes are the main factors that control the material distribution, composition and finally the retention of nutrients and organic matter inside the system or the outwelling from the system into adjacent coastal waters.

Zusammenfassung

Zuckerrohranbau ist die vorherrschende Landnutzung im Nordosten und Südosten Brasiliens. Aufgrund einer ständig steigenden nationalen und internationalen Nachfrage nach Zucker und Biodiesel, dehnt sich der Anbau von Zuckerrohr weiterhin aus. Damit einhergehende Landnutzungsänderungen können drastische Auswirkungen auf flache, küstennahe Ökosysteme wie Lagunen und Ästuare haben, die als Bindeglied zwischen terrestrischen und marinen Lebensräumen fungieren. Bisher ist nur wenig über den Einfluss von Zuckerrohranbau und die daraus resultierenden Wechselwirkungen auf diese Systeme bekannt.

Ziel dieser Arbeit war, den Einfluss von Abwässern aus Zuckerrohrmonokulturen auf die Biogeochemie und Phytoplaktodynamiken in einem küstennahen Lagunensystem und einem Ästuar in Brasilien zu untersuchen. In der Mundau Manguaba Lagune (MML) wurden während fünf Expeditionen zwischen September 2007 und Februar 2009 jeweils zu Beginn und am Ende der Trockenzeit Wasserproben genommen. In einer ersten Beprobungskampagne im März 2007 wurden Sedimentkerne aus beiden Lagunensystemen gezogen. Der Fluß Paraíba do Sul (PSR) wurde jeweils während der Regen- und Trockenzeit 2008 beprobt (Januar und September).

Die Bestimmung und Charakterisierung von Nährstoffen (Nitrat, Nitrit, Ammonium, Silikat, Phosphat) und suspendiertem Material (TSM) in der MML und im PSR, ebenso wie die Bestimmung und Quantifizierung von

Phytoplanktongemeinschaften in der MML standen im Mittelpunkt dieser Untersuchung. Des Weiteren wurden partikuläres organisches Material (C_{org} , PN) und stabile Kohlenstoff- und Stickstoffisotope ($\delta^{13}C$, $\delta^{15}N$) des TSM im Oberflächenwasser der MML und des PSR, sowie im Sediment der MML bestimmt. Phytoplanktonabundanz, deren Biomasse und die Zusammensetzung der Gemeinschaften wurde in der MML untersucht. Auswirkungen von erhöhtem Nährstoffeintrag durch Dünger aus Zuckerrohrfeldern auf Phytoplanktongemeinschaften in der MML wurden experimentell simuliert. Im PSR wurde Chlorophyll a (Chl a) zur Abschätzung von Phytoplanktonbiomasse verwendet.

Nährstoffe und organisches Material aus den Zuckerrohranbaugebieten im Einzugsbereich des PSR wurden während der Regenzeit aufgrund der hohen Abflussmenge direkt vom Fluß und seinen Zuflüssen ins Ästuar und die angrenzenden Küstenbereiche exportiert. Dagegen führten geringe Abflussmengen und eine lange Verweilzeit des Wassers im Fluß während der Trockenzeit zu einem Anstieg der Chl a Menge und einem Rückhalt von allochthonem und autochthonem Material innerhalb des Systems.

Nährstoffkonzentrationen in der MML wurden vorwiegend durch die Flüsse bestimmt, welche Nährstoffe aus dem Zuckerrohr dominierten Einzugsgebiet eintragen. Die Nährstoffkonzentrationen nahmen entlang eines Gradienten vom Fluß zum Ozean hin ab. Dabei nahm gleichzeitig die Phytoplanktonbiomasse in der Lagune zu, was auf eine schnelle Aufnahme der Nährstoffe durch Phytoplankton hindeutet. Das suspendierte Material

sedimentierte entweder in der MML ab, wo es wiederaufbereitet wurde oder wurde, beeinflusst durch die Tide, in küstennahe Gewässer exportiert.

Kurzzeitige Veränderungen in Salinität, Nährstoffkonzentrationen, sowie der Verweildauer des Wassers in den Systemen können zu einer hohen Variabilität in der Phytoplanktongemeinschaft und –diversität führen. Folglich wurden zeitliche und räumliche Unterschiede in der Verteilung des Phytoplanktons in der MML beobachtet, ebenso wie Veränderungen der Gemeinschaften, die entweder von Kieselalgen oder Cyanobakterien dominiert wurden.

Mit Hilfe eines Anreicherungsexperiments, bei dem der hohe Eintrag von Nährstoffen aus Düngern nachgestellt wurde, konnte gezeigt werden, dass Phytoplanktongemeinschaften direkt auf diese Nährstoffhöhung reagieren. Durch die permanent hohen Silikatkonzentrationen in tropischen Gewässern, profitieren Kieselalgen am stärksten vom zusätzlichen Nährstoffeintrag, was sich in ihrer Zellzahl und Biomasse widerspiegelt. Änderungen in der Nährstoffzusammensetzung durch hohe Stickstoff- und Phosphatzufuhr aus dem Anbau von Zuckerrohr kann somit zu einer Veränderung in der Phytoplanktongemeinschaft führen und dadurch die Dynamik im gesamten nachfolgenden Nahrungsnetz in den Lagunen beeinflussen.

Aus den Ergebnissen dieser Untersuchung wird deutlich, dass Lagunen und Ästuare eine wichtige Rolle im Kreislauf von Nährstoffen und organischem Material in Küstenökosystemen in Nord- und Südost-Brasilien

spielen, die stark vom Zuckerrohranbau beeinflusst sind. Saisonale Unterschiede im Eintrag von Düngemitteln, die Geomorphologie des jeweiligen Systems, sowie biologische Prozesse sind wichtige Faktoren, die sowohl die Verteilung als auch die Zusammensetzung und letztendlich das Verweilen von Nährstoffen und organischem Material in einem System steuern oder zu einem Austrag in den Küstenozean führen.

CHAPTER I

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn

Phytoplankton biomass and composition in a tropical lagoon in NE Brazil affected by sugar cane monoculture in its catchment

The project on sugar cane impact on water quality and biogeochemistry in aquatic systems in Brazil was initiated by T. Jennerjahn. The particular idea of this study was developed by G.Spörl. Data sampling and analyses were conducted by G. Spörl. The paper was written by G. Spörl with scientific and editorial advice by the co-authors. The manuscript is submitted to Estuaries and Coasts.

CHAPTER II

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn, Svenja Beilfuss,
Enaide Melo-Magalhães, Paulo Petter, Bastiaan Knoppers

Phytoplankton dynamics along a salinity and nutrient gradient in a sugar cane impacted tropical lagoon in northeast Brazil

The project on sugar cane impact on water quality and biogeochemistry in aquatic systems in Brazil was initiated by T. Jennerjahn. The particular idea of this study was developed by G.Spörl. Field work was conducted by G. Spörl, P. Petter and B. Knoppers. Phytoplankton calculations were carried out by G.Spörl. Nutrient analysis was conducted by G. Spörl and P. Petter. Phytoplankton identification and counting were conducted by G.Spörl, S.

Beilfuss and E. Melo-Magalhães. The paper was written by G. Spörl with scientific advice by the co-authors. The manuscript is in preparation.

CHAPTER III

Gertrud Spörl, Carlos E. Veiga de Carvalho, Bastiaan Knoppers, Tim Jennerjahn

Effect of sugar cane monoculture on organic matter composition and dynamics in a tropical coastal lagoon in Brazil

The project on sugar cane impact on water quality and biogeochemistry in aquatic systems in Brazil was initiated by T. Jennerjahn. The particular idea of this study was developed by G. Spörl. Data sampling was conducted by G. Spörl with support of C. E. Veiga de Carvalho, B. Knoppers and T. Jennerjahn. Data analyses and writing of the manuscript were conducted by G. Spörl with improvements by the co-authors. The manuscript is submitted to *Estuarine, Coastal and Shelf Science*.

1. SCIENTIFIC BACKGROUND AND OBJECTIVES

1.1 Eutrophication – a global concern

Increasing nutrient loads entering aquatic systems have been reported from all over the world (Filoso et al., 2003; Paerl et al., 2006; Smith, 2003; Turner and Rabalais, 1994; Turner and Rabalais, 2003). These high nutrient concentrations are mainly due to anthropogenic inputs from e.g. rapidly growing urbanization, industrial development, the expansion of aquaculture and the increasing input from agricultural effluents.

High nutrient concentrations in a system in combination with an increase in organic matter (OM), e.g. algae and aquatic plants are usually defined as eutrophication. However, a number of definitions have been proposed by different authors depending on the emphasis of their impact. Vollenweider (1992) e.g. defined “Eutrophication - in its more generic definition that applies to both fresh and marine waters – is the process of enrichment of waters with plant nutrients, primarily nitrogen and phosphorous that stimulates aquatic primary production and in its more serious manifestations leads to visible algae blooms, algae scums, enhanced benthic algal growth of submerged and floating macrophytes”. Another very short but accurate definition was given by Nixon (1995): “eutrophication is an increase in the rate of supply of organic matter to an ecosystem”.

Human derived phosphorus and nitrogen in organic or inorganic form are the most important nutrients responsible for eutrophication. Phosphorus is

generally the nutrient, which limits primary production in freshwater ecosystems, whereas nitrogen is often the limiting factor in brackish or marine aquatic environments (Howarth, 1988; Schindler, 1974; Talling and Lemoalle, 1998). However, these nutrients can also be co-limiting for the primary production in an aquatic ecosystem (Fisher et al., 1992; Rudek et al., 1991). Elevated transport of nitrogen and phosphorus to aquatic systems can consequently diminish the limitation and support higher primary productivity. In a final step, it can even trigger phytoplankton blooms (Anderson et al., 2002).

Large parts of tropical and subtropical aquatic systems are nitrogen depleted due to the removal of biologically available nitrogen by microbial denitrification (Deutsch et al., 2001; Gruber and Sarmiento, 1997). However, mainly during the first weeks of the rainy season elevated nutrient loads induced by out-washing of fertilizers from the soils of cultivated areas enter the aquatic systems. Increased agricultural runoff may fuel large phytoplankton blooms, as it was observed in the Gulf of California, where blooms occurred shortly after fertilization and irrigation of agricultural fields (Beman et al., 2005).

Other nutrients, such as silicon or iron, can additionally influence the abundance of phytoplankton species and consequently change the composition of a community (Hecky and Kilham, 1988). Silicon, which is a product of rock and soil weathering, is an important nutrient for the abundance and distribution of diatoms, as it is incorporated into the diatom's frustule (Egge and Aksnes, 1992). However, if silicon becomes

limited, shifts from diatom to non biomineralizing communities or even an increase in harmful algal blooms, e.g. cyanobacteria, in coastal waters can be observed (Officer and Ryther, 1980). Consequently changes in silicon concentration can influence phytoplankton community and species abundance and subsequently the food chain as diatoms are an important food source for higher trophic levels (Cushing, 1989).

1.2 Consequences of eutrophication

Increased nutrient loads can result in a wide variety of changes in the ecosystem. The changes in nutrient availability and stoichiometry influence the phytoplankton abundance and community structure and generally result in higher chlorophyll a values. Finally, an increase in algal biomass in the system can lead to the occurrence of nuisance and harmful algal blooms (HABs) in different frequencies (Béthoux et al., 2002; Hallegraeff, 1993; Piehler et al., 2004). A well investigated example is the bloom of *Pseudo-nitzschia spp.* on the Louisiana shelf in the extended plume of the Mississippi River, which can be traced back to the 1950s. Mainly in spring, increased nutrient loads directly lead to the development of this toxic species and its increase in cell abundance. Microcosm experiments have also shown that the increase in biomass of *Pseudo-nitzschia spp.* responded directly to nutrient pulses (Dortch et al., 2000; Dortch et al., 1997; Parsons et al., 2002). The occurrence of HABs can affect animal and human health by the production of toxins. Direct consumption or indirect exposure to contaminated fish can cause illness and mortality.

Transport of high loads of nutrients and organic material into coastal regions can severely damage and destroy seagrass beds or coral reefs (Burkholder et al., 2007; Chazottes et al., 2002; McGlathery, 2001). Shading due to micro- and macroalgal growth and consequently high biomass in addition to suspended matter in the water column can lead to seagrass and coral declines and reduction in species diversity. Macroalgae can overgrow seagrasses and old corals, inhibit the recruitment of juvenile corals and lead to hypoxic or anoxic conditions (Lapointe et al., 2004 and references therein). Therefore economically important resources, e.g. fishery and tourism, can be negatively impacted by alterations of the ecosystem (Nixon, 1995).

Top down factors such as grazing by microzooplankton, e.g. heterotrophic flagellates, control the phytoplankton production and biomass (Mallin and Paerl, 1994; Sellner et al., 1993). However, during algal blooms, phytoplankton is not completely grazed due to poor food quality or even the presence of toxic species. Consequently, dead algae sink to the bottom of the system, been deposited in the surface sediments and the decomposition of this organic material use the oxygen, which can result in hypoxic or even anoxic conditions in the aquatic environment (Zhang et al., 2010). As soon as the oxygen concentration decreases to a critical level, the organisms in the ecosystem will escape if possible or suffer high mortalities (Diaz and Rosenberg, 2008).

1.3 Cultivation and history of sugar cane in Brazil

Generally regions in southern and eastern Asia show proportionally high increase in nutrient load due to population growth, increasing industrialization and changes in land use associated with increased fertilizer application (Seitzinger et al., 2002a). In many other countries, land use change due to the increased production of biofuel will also alter the nutrient transport from the catchment area to the sea (Rabalais et al., 2009 and reference therein). In many tropical countries the cultivation of sugar cane is increasing because it is more and more used for the production of biofuel.

Brazil is the biggest sugar cane producer in the world, followed by India and Australia (FIAN and GTZ, 2002). During the last decades, the cropping land for sugar cane increased from 2 million ha to more than 7 million ha. Since 1975, the PROALCOOL program, which was promoted by the Brazilian government, led to an enormous increase in sugar cane production. Triggered by the global energy crisis and the oil price shock, the government postulated the production of alcohol as fuel in the automobile sector. In 2002, the sugar cane industry started another very dynamic growth period, following up the PROALCOOL initiative in 1975. Today, the main products of sugar cane - sugar and ethanol, have a leading role in the Brazilian agribusiness. More than half of the sugar cane production is used for the production of ethanol (UNICA, 2001).



Figure 1: Major sugar cane cultivation areas in Brazil (modified from UNICA, 2010)

The states of Alagoas and Pernambuco in the northeast of Brazil are the homeland of sugar cane production due to their topography, the warm and humid climate and fertile soils. More than 80% of the agricultural areas in northeast Brazil are actually covered by sugar cane monocultures (Goldemberg et al., 2008). During the last decades, the cultivation areas expanded and shifted to the states of Sao Paulo and Minas Gerais in the southeast of Brazil, because these flat areas are more suitable for mechanisation (Fig. 1). Today, about 75% of the sugar production and around 80% of the alcohol production take place in the state of Sao Paulo

(FIAN and GTZ, 2002 and references therein; UNICA, 2001). The different climatic zones all over Brazil enable sugar cane cultivation and consequently sugar and alcohol production during the whole year.

1.4 Environmental problems of sugar cane agriculture

The cultivation of sugar cane and its processing in factories are accompanied by several environmental problems. The expansion of sugar cane monocultures led to direct and indirect deforestation during the last decades. The clear-cutting of forests made way for new sugar cane production areas. However, sugar cane agriculture also spread out in areas, which were previously used for the cultivation of other crops and pasture. Consequently, new agricultural areas were needed to replace the lost pasture and crop lands, which resulted in further deforestation. Almost 95% of the rainforest along the coast of the Atlantic Ocean in Brazil, which is the most diverse rainforest in the world and rich in endemic species, is already deforested because of these agricultural practices (FIAN and GTZ, 2002).

Soil erosion by wind and water is another problem of sugar cane cultivation, which may result in soil loss and consequently cause a large reduction of agricultural yields, as was observed in the northeast of Brazil (Cavalcanti et al., 2000; Sparovek et al., 1997). Soil compaction caused by the use of heavy farm machinery increases the surface runoff in deforested regions and can lead to heavy flooding after strong rainfalls, which destroy fields, harvests, as well as human infrastructure and houses.

It is a widely-used practice in Brazil to burn off the sugar cane fields before the harvest. This procedure mainly removes the foliage of the sugar cane plant, which makes it easier to cut and transport. The smoke and ash in the atmosphere from the burning can cause strong air pollution and health problems (Guarnieri and de Martino Jannuzzi, 1992). Furthermore, the natural vegetation is being destroyed resulting in a negative impact on the flora and fauna.

The cultivation of sugar cane as monoculture requires additional application of fertilizer (e.g. NPK (nitrogen-phosphorus-potassium) fertilizer or special fertilizers with trace elements) to regenerate the nutrient pool in the soil, which is leached during the growth of the sugar cane plants. In addition, pesticides and herbicides are used to reduce weeds and pests in the sugar cane fields, mainly on the young sugar cane plants. Besides chemical fertilizer, sugar cane products like vinasse and bagasse, byproducts of the sugar cane distillation in the factories and the smashed sugar cane fibers after the processing in the factories, respectively, are applied in the fields as organic fertilizer. Contaminated soils and water bodies are the result of the widespread and intensive use of agrochemicals and high fertilizer concentrations. During the last years, the increase of sugar cane monocultures has coincided with a strong increase in fertilizer application. Brazil is one of the largest consumers of agrochemicals worldwide with an average consumption of about 3.12 million tones of fertilizer in 2006 (Martinelli and Filoso, 2008).

1.5 State of aquatic systems in Brazil affected by sugar cane cultivation

Coastal lagoons and estuaries are dynamic environments, as they are influenced by terrestrial and marine inputs (Fig. 2). These systems are affected by the interaction of a wide range of abiotic factors (e.g. light, salinity, water temperature, residence time, nutrients) and biotic factors (e.g. primary production, grazing, competition). Land use change and subsequent anthropogenic inputs are a main component which controls the phytoplankton dynamics in estuaries and coastal lagoons (Ferreira et al., 2005; Wehr and Descy, 1998).

Intensive agriculture in combination with the increased use of fertilizer and pesticides raise the nitrogen and phosphate load in rivers. Transformations in the nutrient cycle and resulting changes in the phytoplankton community have been reported from e.g. subtropical regions like the Mississippi River and the Gulf of Mexico (Turner and Rabalais, 1994; Turner and Rabalais, 2003). Generally, high nitrogen and phosphorus loads from waste water effluents and fertilizer runoff have almost doubled during the last decades (Bouwman et al., 2005; Meybeck, 1982; Vollenweider, 1992). However, land use change in tropical regions and its impact on aquatic systems is not well investigated.

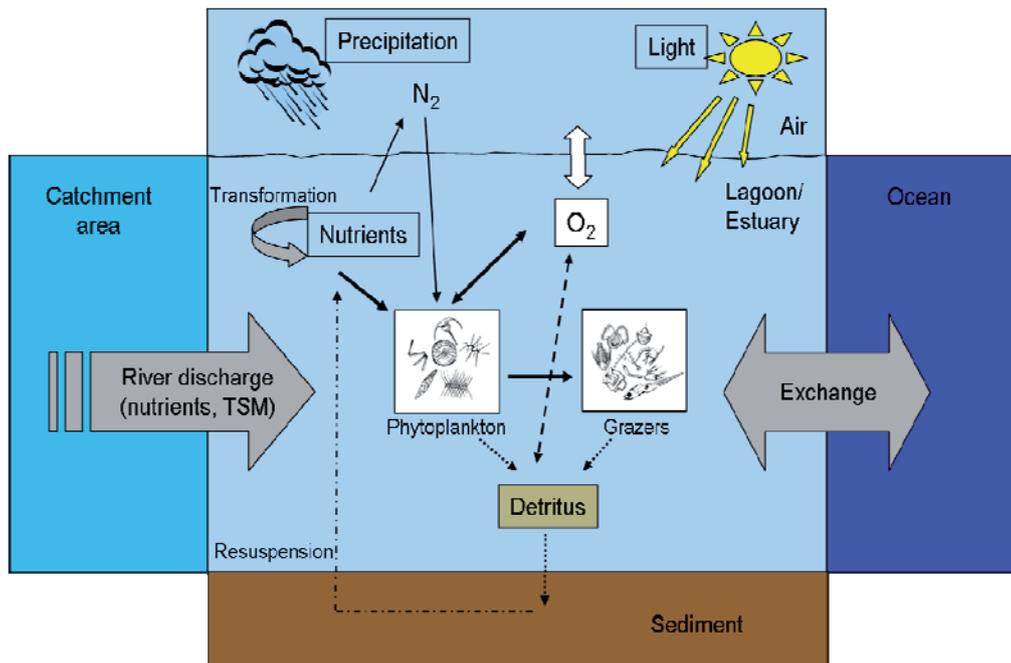


Figure 2: Schematic diagram of the interactions of biotic and abiotic variables inside the lagoon/ estuary (modified from Solidoro et al., 2005).

High rates of nitrogen export into rivers draining catchment areas, which are mainly cultivated by sugar cane, have been reported e.g. for the Piracicaba River basin (Filoso et al., 2003). The Piracicaba River in southeast Brazil is a tributary, which discharges into the Parana River. It is located in a region that is intensively used by agriculture and industries. Highest nitrogen concentrations ($\sim 200 \mu\text{M}$) in this river have been measured in areas with a high proportion of agricultural and urban land use, whereas lowest concentrations occurred in landscapes covered by pasture and forest. The average annual flux of nitrogen ($18\,900 \text{ tons N yr}^{-1}$) in the Piracicaba River increased by a factor of 15-20 from the headwaters to the lower reaches, although the discharge was only 7 times higher. Total net anthropogenic input into the system reached about $4\,500 (\pm 900) \text{ kg N km}^{-2} \text{ yr}^{-1}$. Generally nitrogen inputs into the system were clearly higher than

outputs, which points to intensive transformation processes such as denitrification or burial inside the river (Filoso et al., 2003).

1.6 Objectives and Hypotheses

The growing sugar cane cultivation and sugar cane production in Brazil coincides with an increasing use of fertilizer in the catchment area of rivers. Knowledge regarding the consequences of effluent runoff from sugar cane fields and sugar cane factories into aquatic ecosystems in Brazil is limited. The main objectives of the present study were to identify the sources, transformation processes and fate of nutrients and organic material from the effluents of sugar cane cultivation and to study their effects on the biogeochemistry and phytoplankton dynamics in the tropical Mundau Manguaba lagoon (MML), and the Paraíba do Sul (PSR) River and Estuary in Brazil. Both study areas are influenced by sugar cane cultivation in their watersheds and sugar cane processing factories. The distribution of nutrients, particulate organic carbon and nitrogen as well as phytoplankton biomass were investigated in the MML and PSR during five expeditions from March 2007 to February 2009. C/N ratios and stable carbon and nitrogen isotopes of organic material were determined to identify the sources and distribution of organic matter in the lagoon and estuary.

Two hypotheses were addressed based on the following assumptions:

1.

Effluents, which can be attributed to sugar cane cultivation and production, are either from fertilizer runoff from sugar cane fields or from point sources, such as the waste water from the sugar cane factories.

Hypothesis 1

Fertilizer runoff as well as effluents from sugar cane industry enhance nutrients and phytoplankton biomass in the Mundau Manguaba lagoon and Paraiba do Sul River.

2.

Nutrient and organic matter cycling as well as phytoplankton biomass production in coastal aquatic environments generally depend on the geomorphology of a system and the seasonal variability in an area. This also has an effect on the transformation and fate of nutrients and organic matter introduced into a system through effluents from sugar cane cultivation and processing in its catchment area.

Hypothesis 2

Long water residence time and consequently high filtering capacity derived by the rather closed morphology of the Mundau Manguaba lagoon leads to a lower export of nutrients and organic matter to adjacent coastal waters compared to the open Paraiba do Sul estuary.

The results obtained from this study will help to develop an understanding regarding the effects of sugar cane cultivation on water quality and phytoplankton biomass and composition in the main sugar cane cultivation areas in Brazil. This is the first study in the region that elucidates the impact of sugar cane cultivation in combination with phytoplankton biomass and species diversity.

Specifically the results will help to understand the influence of sugar cane cultivation in the Mundau Manguaba lagoon and Paraiba do Sul River, which were used as case study sites. Furthermore the results regarding changes in organic matter, nutrient distribution and composition in these systems can be used to develop a general understanding of the effects of sugar cane cultivation on organic material and nutrient cycling in tropical lagoons and estuaries.

2. MATERIAL AND METHODS

2.1 Study areas

The two study areas, Mundau Manguaba Lagoon system (MML) in northeast and Paraiba do Sul River (PSR) in southeast Brazil, are located in tropical and subtropical regions, respectively. Both study sites have huge amounts of sugar cane monocultures in their catchment areas which, in addition to sugar cane factories along the rivers and tributaries, can influence the nutrient cycling and biogeochemistry of the aquatic environments. Over the last decades, human activities and mainly the cultivation of sugar cane has more than doubled and led to an increase in fertilizer use (Macedo et al., 2008).

Mundau Manguaba Lagoon (MML)

The MML is located in the state of Alagoas. It consists of two shallow lagoons, which are connected by a narrow channel system, lined with mangroves and linked to the ocean (Fig. 3). The channels of the two lagoons are separated in a joint outlet by a sand bar and discharge into the Atlantic Ocean. The area of the whole lagoon system is 79 km² with an average depth of 2 m. The Manguaba lagoon with an area of 43 km² is surrounded by sugar cane fields, while the 24 km² Mundau lagoon is additionally receiving untreated effluents from the city of Maceio which actually has about 900,000 inhabitants (ANA, 2005; Oliveira and Kjerfve, 1993). The tropical climate is characterized by a dry season from

Materials and Methods

November to March and a rainy season from May to August with an average annual precipitation of 1654 mm. The Mundau River annually discharges an average of $33.5 \text{ m}^3\text{s}^{-1}$ into the Mundau lagoon, Paraiba do Meio and Sumauma River $17.6 \text{ m}^3\text{s}^{-1}$ and $5 \text{ m}^3\text{s}^{-1}$, respectively, into the Manguaba lagoon (Oliveira and Kjerfve, 1993; Souza et al., 2003). During the rainy season, the lagoons are strongly influenced by freshwater and sediment transport in the rivers, while, during the dry season, river flow is low and the system is mainly controlled by tidal variation.

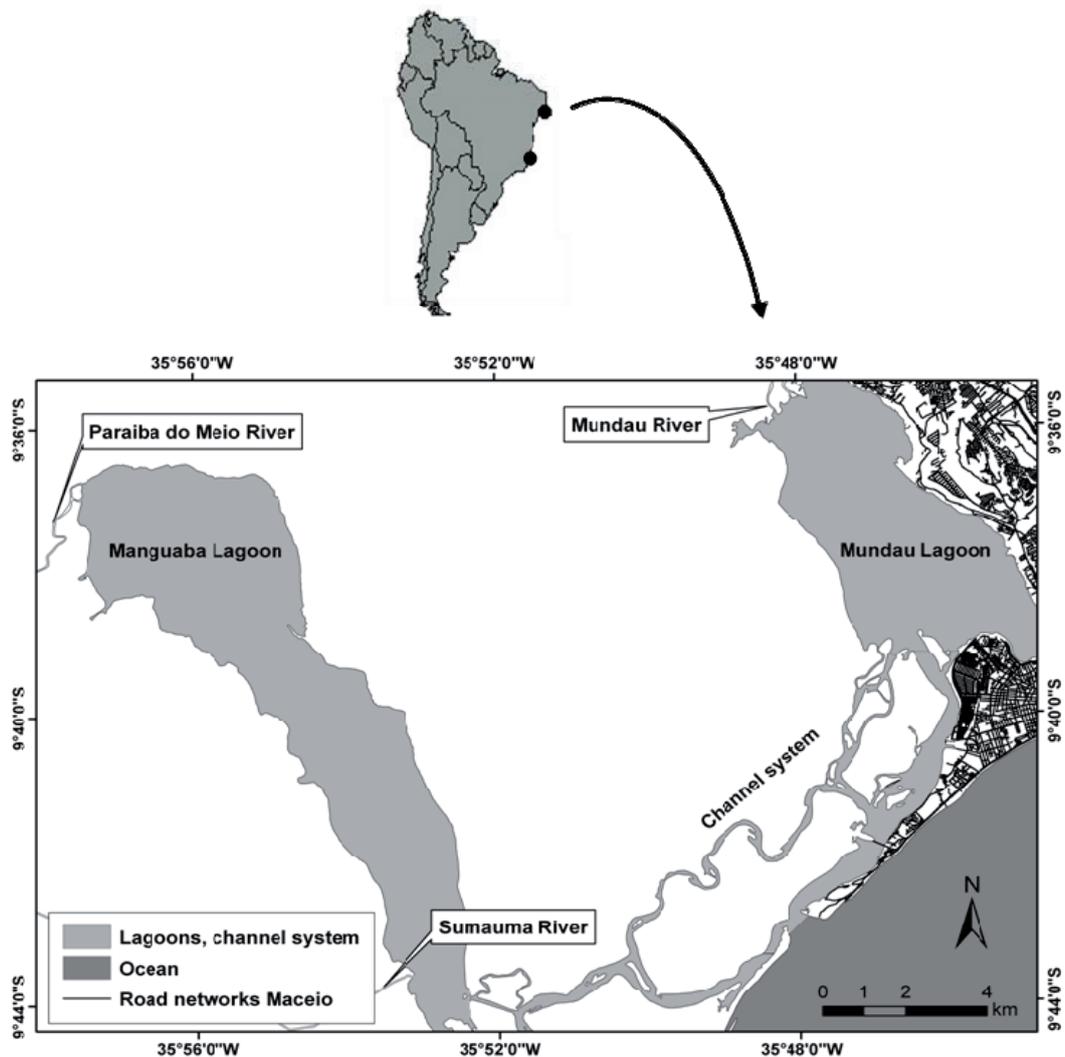


Figure 3: Map of the Mundau Manguaba lagoon in northeast of Brazil.

Most of the tidal energy from semi-diurnal tides dissipates in the connecting channels between the ocean and the lagoons. The different sizes of the lagoons and the channels cause an average water residence time of around 1-2 weeks for Mundau lagoon and 5-7 weeks for Manguaba lagoon (Oliveira and Kjerfve, 1993).

In northeast Brazil which is the second largest sugar cane production area of the country, planting and fertilization of sugar cane starts between January and March which is the end of the dry season. At the beginning of the dry season, in September/October, harvesting of sugar cane and subsequently the sugar production in the factories starts.

Paraíba do Sul River (PSR)

The PSR is a medium sized river, which drains the most industrialized states Rio de Janeiro, São Paulo and Minas Gerais. It is about 1145 km long with an area of 55 400 km² (Fig. 4). The subtropical climate shows a clear precipitation regime with a rainy season from November to January and a dry season between June and August. Annual rainfall in the river basin ranges between 1000 and 3000 mm. During the dry period, the water discharge of the PSR can be very low (180 m³s⁻¹), while heavy precipitation during the rainy season can raise the discharge to up to 4380 m³s⁻¹ and can cause heavy flooding (DNAEE, 1983; Rosso et al., 1991).

The Pomba River and the Muriaé River are two main tributaries, which drain into the lower PSR. At the mouth of the PSR several channels,

lakes, swamps and mangrove areas form a huge delta. Land use in the PSR catchment area is mainly urban development, extensive cattle farming and agriculture. The PSR supplies the agriculture and industry in its basin with water, which is also used for human consumption. Effluents from the agriculture fields or sewage can affect the water quality of the river.

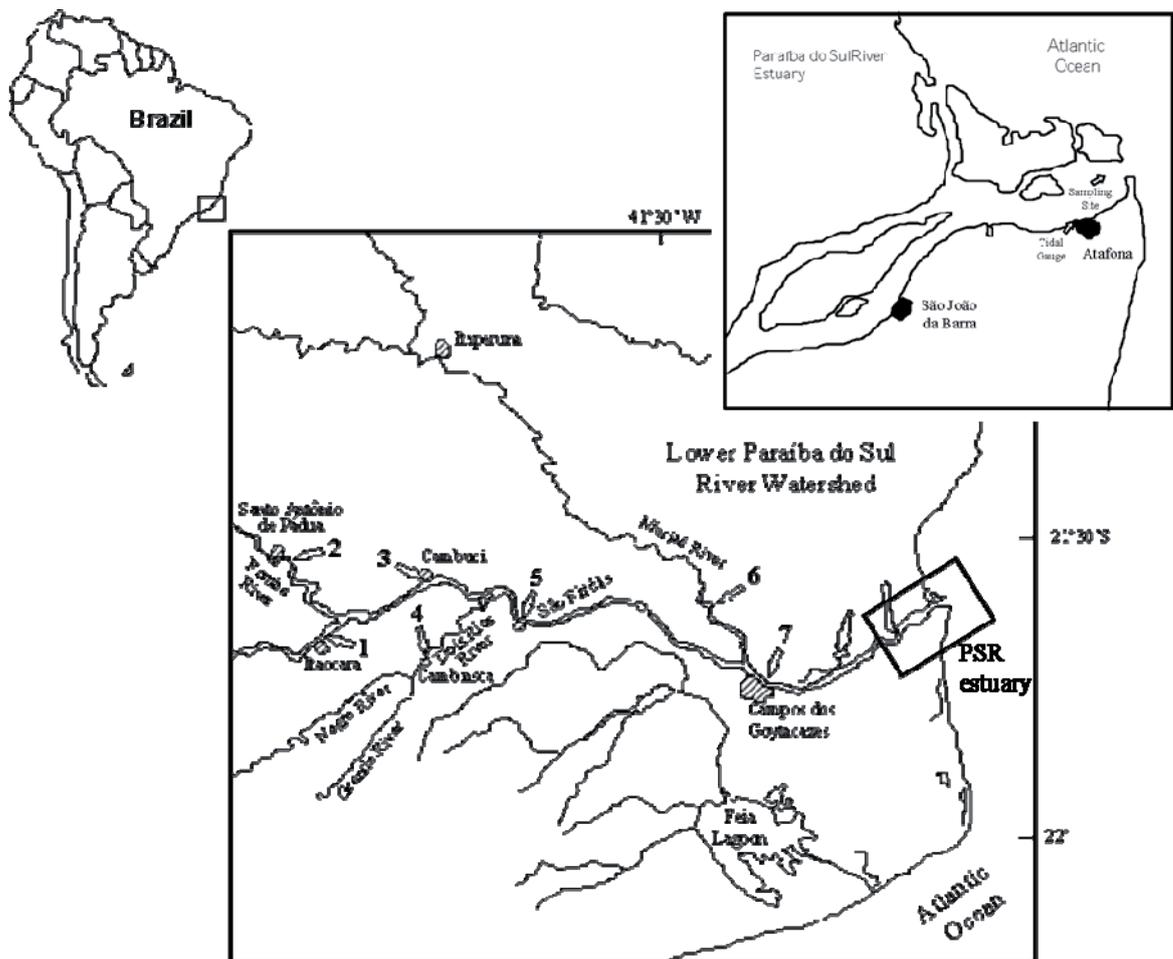


Figure 4: Map of the Lower Paraíba do Sul River basin including the sampling stations in the tributaries (2 (Pomba River), 4 (Dois Rios River), 6 (Muriaé River)) and the PSR (1, 3, 5, 7). The PSR estuary is subdivided into the main estuary and a smaller second channel (modified from Carvalho et al., 2002; Krüger et al., 2004).

2.2 Field work

In the MML, surface water samples were taken along a gradient from marine to freshwater during two expeditions at the beginning of the dry and harvesting season in September 2007 and October 2008 and at the end of the dry season in February 2008 and 2009. In March 2007, four sediment cores (30 - 50 cm) were collected in each lagoon on a gradient from the upper to the lower lagoon area and sliced in 2 cm layers. According to hydrodynamic and geographical characteristics, the lagoons were subdivided into three units: the channels (estuary), the lagoons and the rivers (freshwater).

In the PSR and the adjacent coastal area, surface water samples were taken in January and September 2008 during the rainy and dry season, respectively. Sampling stations were located in the mangrove and estuarine area in the lower part of the PSR. Additional samples were collected in the smaller tributaries Pomba River, Dois Rios and Muriaé River (Fig. 4).

2.3 Analytical work

During the sampling campaigns in the MML and PSR, water samples for the different analyses were collected with a Niskin bottle near the surface (~0.5 m depth) and stored cool and dark until filtration. Salinity, temperature and oxygen concentrations were measured directly with a *WTW MultiLine* multiparameter sensor.

Materials and Methods

Water samples for nutrient analyses (nitrite, nitrate, ammonium, phosphate and silicate) were filtered through single use membrane filters into prewashed PE bottles and stored frozen or fixed with mercury chloride until the analysis according to Grasshoff et al. (1999). Dissolved inorganic nutrients were analyzed using a continuous flow analyzing system (Skalar SAN++System). Nitrate+nitrite (NO_x^-), nitrite (NO_2^-), phosphate (PO_4^{3-}) and silicate ($\text{Si}(\text{OH})_4$) were detected spectrophotometrically and ammonium (NH_4^+) fluorometrically (Grasshoff et al., 1999). Determination limits for the different nutrients were $0.08 \mu\text{M}$ (NO_x^-), $0.04 \mu\text{M}$ (NO_2^-), $0.05 \mu\text{M}$ (NH_4^+), $0.06 \mu\text{M}$ (PO_4^{3-}) and $0.17 \mu\text{M}$ ($\text{Si}(\text{OH})_4$) according to DIN 32645. The coefficient of variation of the procedure was $<3.4\%$.

For chlorophyll a (chl a) analysis, water was filtered through *Whatmann* GF/F filters which then were stored frozen until the analyses. Chl a concentrations were determined following the method of Jeffrey and Humphrey (1975).

Analyses of particulate organic carbon (C_{org}) and particulate nitrogen (PN) of total suspended matter, sediment, soil and plant material were carried out by high temperature combustion using a Carlo Erba NA 2100 elemental analyser. For the analysis of particulate organic carbon (C_{org}), dried particulate matter (40°C) was acidified with 1N hydrochloric acid to remove inorganic carbon. Repeated measurements of standard samples gave a precision of 0.1% for organic carbon and 0.01% for nitrogen.

The nitrogen ($\delta^{15}\text{N}$) and organic carbon ($\delta^{13}\text{C}_{\text{org}}$) isotopes were determined with a Finnigan Delta Plus mass spectrometer coupled to a Flash 1112 EA elemental analyser. For the determination of $\delta^{13}\text{C}_{\text{org}}$, samples were acidified by adding 1N HCl to remove the carbonate, and dried at 40 °C. The precisions of the method given by an internal standard were 0.2 ‰ for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$.

3. RESULTS AND SYNOPTIC DISCUSSION

The main focus of this thesis was to determine the influence of effluents from sugar cane cultivation and production on aquatic ecosystems. Two different aquatic ecosystems in Brazil, a rather closed lagoon system and an open estuary, were used as case study sites to investigate the sources, the transformation processes and the fate of nutrients and organic matter derived from sugar cane agriculture and associated industrial processes and their potential impact on aquatic environments. The findings of this study will help to understand the influence of effluents from sugar cane cultivation on water quality and phytoplankton composition in the lagoon and the estuary, respectively. Furthermore the results regarding changes in organic matter distribution and composition in these systems can be used to develop a general understanding of the effects of sugar cane cultivation on organic material cycling in tropical lagoons and estuaries.

3.1 Factors controlling the availability and distribution of nutrients and organic matter

The input of nutrient and organic matter in coastal systems is generally controlled by environmental factors including precipitation, salinity, residence time and sedimentation. Furthermore light intensity, temperature and biological interactions, such as predation and competition, play an important role in the nutrient and organic matter cycling via uptake and

release by phytoplankton and biomass production (Ferreira et al., 2005; Wehr and Descy, 1998).

Table 1: Inorganic nutrient concentrations in the upper PSR and its tributaries in the rainy and dry season 2008

Location	NO₂⁻ [μM]	NO₃⁻ [μM]	NH₄⁺ [μM]	PO₄³⁻ [μM]	Si(OH)₄ [μM]	n
Rainy season						
Pomba River	-	-	-	-	-	-
Muriaé River	3,3	18,3	2,5	0,4	75,4	1
Dois Rios	3,2	16,3	3,4	0,5	62,3	1
PSR	3.0 - 3.5	31.0 - 34.9	2.8 - 4.4	0.4 - 0.5	66.3 - 91.6	3
Dry season						
Pomba River	28.1 - 34.7	0.3 - 0.4	1.8 - 2.0	0.2 - 0.5	176.3 - 206.0	2
Muriaé River	0.3 - 0.4	61.5 - 113.8	1.8 - 36.9	0.3 - 1.0	114.65 - 184.2	2
Dois Rios	0.1 - 0.3	50.6 - 57.6	0.9 - 14.3	0.4 - 0.5	234.1 - 239.7	2
PSR	0.2 - 0.6	37.5 - 97.7	0.9 - 14.7	0.3 - 0.9	119.8 - 181.3	8

During the rainy season high river discharge and consequently huge water volumes can flush through estuaries, as it was described for the Paraíba do Sul River (PSR) (Krüger et al., 2004). Also during the sampling in January 2008, high discharge rates in the PSR led to freshwater dominance at the stations sampled and a shift of the salinity gradient in the coastal waters. Inhibited intrusion of marine water into the PSR estuary caused similar nutrient concentrations in the upper and lower river basin (Tab. 1; Fig. 5 to

7). Dilution effects by nutrient-poor marine water, which generally affect estuarine areas, could not be observed in the inner parts of the PSR during sampling due to the high river discharge. Although TSM concentrations were high during the rainy season, the proportion of organic matter was only small and coincided with low chlorophyll a concentrations (Tab. 2). Similar trends in the PSR were already observed by Figueiredo (1999), who suggested that about 90% of the TSM was transported during the rainy season due to erosion of soil from sugar cane fields in the catchment area by heavy rainfall and organic matter input from field surface runoff.

During the dry season when the river had low discharge, phytoplankton biomass increased and contributed more to organic material of the PSR, whereas TSM concentrations simultaneously decreased (Tab. 2). Lower nutrient concentrations during the dry seasons seemed to be rather a consequence of nutrient uptake by phytoplankton than of mixing with nutrient-poor marine water, as almost no salinity was measured inside the estuary during sampling.

However, studies of other estuaries showed that mainly during low river discharge the intrusion of marine water can have a strong effect inside the estuary because of changing salinities and therefore an influence of processes therein (Paerl, 2009; Perez et al., 2010). Salinity can additionally increase in the system by evaporation, especially when the water surface to volume ratio is high. This effect seemed to be weakened during the night because of a reduced evaporation (Hollins and Ridd, 1997).

Table 2: Particulate matter, chlorophyll a and C/N distribution in the PSR and its catchment area in the rainy and dry season in 2008.

Location	Distance to shoreline [km]	TSM [mg l ⁻¹]	Corg [%]	PN [%]	C/N	Chlorophyll a [µg m ⁻³]	n
Rainy season							
Pomba River	156,3	107.9 ± 55.0	2.3 ± 0.1	0.2 ± 0.1	15.8 ± 5.9	-	2
Muriaé River	68,2	129.1 ± 60.1	2.2 ± 0.8	0.3 ± 0.0	9.6 ± 3.9	-	2
Dois Rios	129,2	91.9 ± 29.5	2.8 ± 0.6	0.5 ± 0.1	7.2 ± 0.3	-	2
RPS	39.8 - 135.3	127.6 ± 34.1	8.9 ± 2.9	1.1 ± 0.4	10.0 ± 1.5	-	8
Main estuary	0.3 - 35.0	87.1 ± 29.7	4.3 ± 2.5	0.7 ± 0.5	7.8 ± 2.4	1.9 ± 0.6	14
Second channel	0.7 - 4.8	50.8 ± 32.6	4.4 ± 2.9	0.6 ± 0.5	9.4 ± 1.8	4.6 ± 4.6	10
Mangrove	1.5 - 3.6	19.5 ± 6.2	8.9 ± 2.9	1.1 ± 0.4	10.0 ± 1.5	5.2 ± 0.6	10
Offshore	1.0 - 4.3	33.0 ± 30.4	4.3 ± 2.5	0.7 ± 0.5	7.8 ± 2.4	-	3
Dry season							
Pomba River	156,3	15.5 ± 1.2	10.4 ± 4.8	1.2 ± 0.5	9.6 ± 0.9	1.4 ± 0.1	2
Muriaé River	68,2	9.5 ± 1.7	7.4 ± 0.7	0.7 ± 0.1	11.8 ± 0.1	5.6 ± 3.4	2
Dois Rios	129,2	9.2 ± 0.3	13.0 ± 8.8	1.9 ± 1.6	9.2 ± 2.5	-	2
RPS	39.8 - 135.3	10.7 ± 1.8	7.6 ± 2.4	1.0 ± 0.4	9.6 ± 1.2	7.0 ± 6.2	8
Main estuary	0.1 - 34.5	12.9 ± 7.8	9.4 ± 5.9	1.3 ± 0.8	8.6 ± 0.9	15.0 ± 9.2	18
Second channel	0.6 - 3.4	22.1 ± 14.2	5.1 ± 3.4	0.7 ± 0.4	8.4 ± 0.6	12.9 ± 7.5	10
Mangrove	0.8 - 4.1	14.2 ± 3.8	5.3 ± 1.7	0.7 ± 0.2	8.3 ± 30.9	7.2 ± 2.6	10
Offshore	0.6 - 11.0	23.9 ± 8.4	4.5 ± 3.5	0.6 ± 0.5	8.1 ± 0.8	2.4 ± 1.5	6

The influence of salinity in the PSR estuary governed by the rainfall regime in its catchment area and the tidal intrusion is usually higher during the dry season (Krüger et al., 2004). Furthermore, the geomorphology of the system and its connection to the ocean in combination with the tidal amplitude are factors that influence the variation of salinity in the system and therefore the nutrient and organic matter distribution. In an estuary like the PSR, nutrients and organic material were transported to adjacent coastal waters mainly during the rainy season because of the high river

discharge. During the dry season when the river discharge and also the flushing rate were low, nutrients were transformed inside the system by phytoplankton uptake which resulted in high organic material production (Tab. 2). Due to the low flushing rate of the river the material might sediment inside the system.

Not only seasonal conditions also the spatial differences play an important role in salinity concentrations, as it was demonstrated in the MML (Chapter I, Chapter II). Size and geomorphologic structure together with river discharge controlled the intrusion of marine water into the lagoons and resulted in different residence time. Long residence time in shallow systems like coastal lagoons favour a higher and faster biomass production and accumulation compared to rivers with high flushing rates (Cloern, 1996; Knoppers et al., 1991). The restrained exchange with marine water in these semi- enclosed system leads to sedimentation of dead algal material inside the lagoons as it could be observed in the particulate organic carbon content of the surface sediments in the MML (Chapter III).

Key findings

- ◆ **Seasonal and spatial variations in the nutrient concentrations/availability of a tropical estuarine system are controlled by both riverine discharge and salinity intrusion. These variations are more pronounced in the open PSR estuary than in the semi-enclosed MML.**
- ◆ **During the dry season, long water residence time in the MML and PSR cause an increased production of autochthonous**

material and its accumulation in the sediments compared to the rainy season, when the systems are flushed by precipitation runoff.

3.2 Source, sink and transformation of nutrients

Nutrient cycling in estuaries and lagoons is generally affected by inputs from diffuse and point sources like surface water, groundwater, atmospheric deposition, recycling in the water column or sediment as well as sewage or industrial effluents (Paerl et al., 2002; Vitousek et al., 1997). Diffuse sources of nutrients are of huge concern as they are usually large and widespread and therefore difficult to control. For example, 75% of nitrogen and phosphorus inputs into the Chesapeake Bay came from diffuse sources, whereas 25% derived from point sources (Boynton et al., 1995).

Fertilizer runoff from sugar cane fields in Brazil can be a main contributor to diffuse nutrient sources. Though, the use of nitrogen fertilizer (80 – 100 kg N ha⁻¹ yr⁻¹) on sugar cane fields in Brazil is low compared to other countries, e.g. the USA and the Netherlands with about 150 kg N ha⁻¹ yr⁻¹ and 300 kg N ha⁻¹ yr⁻¹, respectively (Martinelli and Filoso, 2008). However, several studies have demonstrated that only 20 to 40% of the fertilizer is assimilated by the sugar cane plants, whereas a huge part remains in the soil (Basanta et al., 2003; Oliveira et al., 2000).

Phosphorus and dissolved inorganic nitrogen (DIN) in the PSR in 2008 showed higher concentrations in the rainy season compared to the dry season (Tab.1) The DIN in the river consisted mainly of nitrate. This is a main component of the fertilizer used in Brazil (FAO, 2004). Similar results were also reported for the PSR in the rainy season in 2001 where nitrate was ~ 95% of the total DIN (Krüger et al., 2004). The high nitrate proportion pointed to runoff from fertilized sugar cane fields and from nearby areas due to precipitation as it was suggested by Carvalho et al. (1995). Increased phosphate concentrations in the PSR estuary during the rainy season can be similar to nitrogen a result of surface runoff from the soils in the drainage basins, as phosphorus is a content of the fertilizers used for the sugar cane cultivation (Fig. 6).

Nitrogen concentrations in the MML showed similar trends, mainly at the beginning of the dry season, with high proportions of nitrate in the rivers which drain into the lagoons (Chapter I, II). Because of heavy rain showers some days before the sampling outwash from the fertilized sugar cane soils seemed to be the source for the nitrogen input.

Usually, studies have focused on DIN as nutrient source in aquatic environments, but several works have shown that dissolved organic nitrogen (DON) comprises a larger part (up to 70%) of the total dissolved nitrogen pool (Lewis et al., 1999; Meybeck, 1982; Seitzinger and Sanders, 1997).

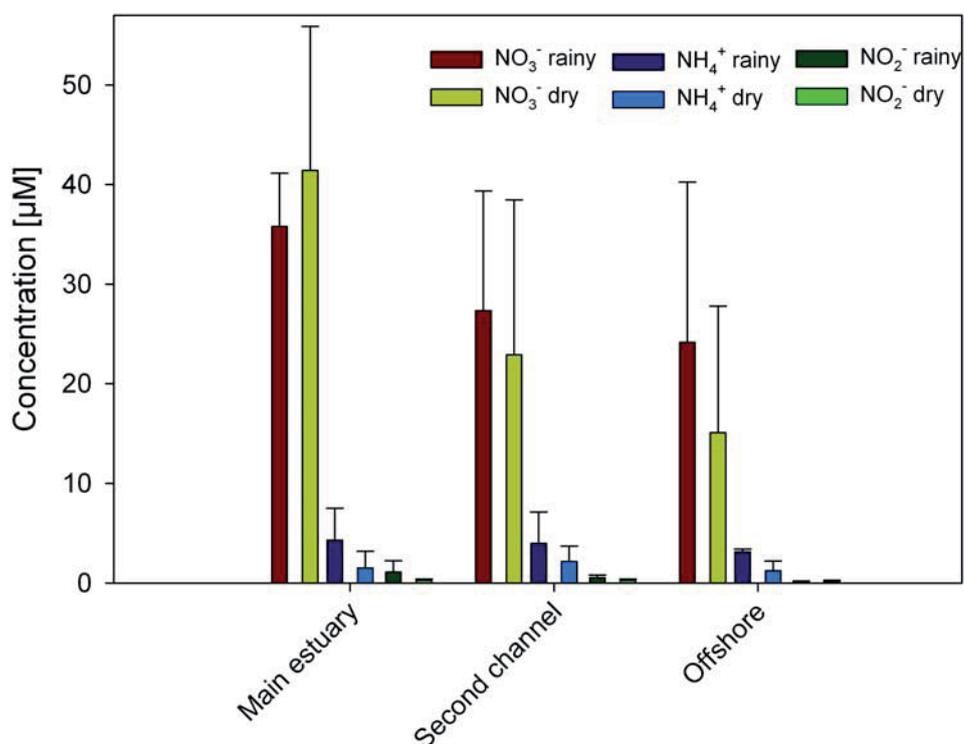


Figure 5: Nitrogen concentrations (average + SD) and distribution in the PSR estuary (main channel and second channel) and the ocean in the rainy and dry season in 2008.

In Brazil, vinasse and bagasse, which are dissolved and particulate organic by-products of the sugar and alcohol production, are additionally used as fertilizer on the fields in the catchment area of the rivers. During processes like ammonification and nitrification, DON from organic fertilizers can be converted into ammonium by bacteria. This can further be oxidised to nitrate which was measured in high concentrations in the PSR estuary (Fig. 5). Similar results could be found e.g. in the Piracicaba River in south Brazil. In this region sugar cane is the main land use and about two-thirds of the average total nitrogen export consisted of DON (Filoso et al., 2003). These findings support the suggestion that high DON concentrations from sugar cane cultivation can strongly contribute to the TDN pool in these

systems. Consequently, besides DIN from fertilizers also organic nitrogen from sugar cane cultivation could add to the nitrogen concentrations in these areas.

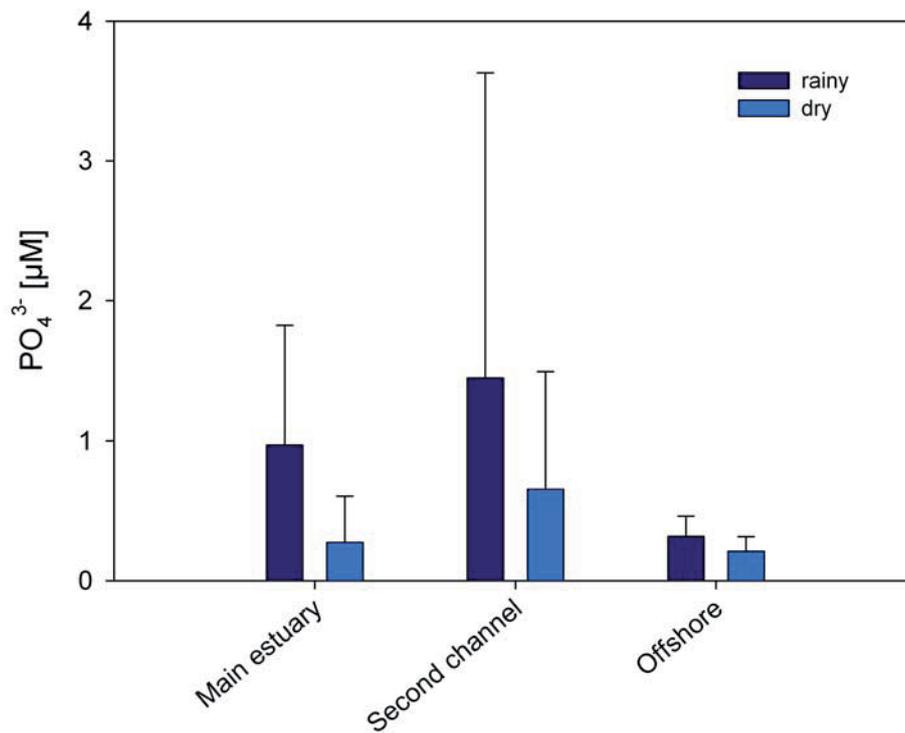


Figure 6: Phosphate concentrations (average + SD) and distribution in the PSR estuary (main channel and second channel) and the ocean in the rainy and dry season in 2008.

Groundwater and atmospheric input can also be sources for elevated nitrate concentrations in the PSR and in the MML during the dry season (Fig. 5; Chapter II). Groundwater can receive increased nutrient loads due to fertilizer use in sugar cane agriculture. During the season of low river discharge, nutrient enriched groundwater has more time to mix with water in the system, which could lead to high nitrate concentrations. Elevated inputs of enriched groundwater into the aquatic environment can increase

DIN concentrations and therefore, affect algae growth and biomass production (Laroche et al., 1997).

Atmospheric deposition after sugar cane burning at the beginning of the dry season which is an usual procedure in the northeast and southeast of Brazil can also increase the nutrient availability in adjacent ecosystems. Phosphate and nitrate are already known as sources for additional nutrient contribution to a system either adsorbed to fine particles or from particles of nitrous oxides in the atmosphere. It is estimated that 20 – 40% of atmospheric nitrogen from industrial, agricultural or urban sources is added to estuarine and coastal waters (Driscoll et al., 2001; Fisher and Oppenheimer, 1991; Paerl, 1995). Paerl (1997) demonstrated experimentally that rainwater can noticeably contribute to the nitrogen pool due to its enrichment in DIN.

Sugar cane factories in Brazil work mainly during the harvesting season. Nutrient enriched effluents from waste waters, released from the washing of sugar cane stems in the mills and from processes during the sugar and ethanol production, are drained into the adjacent rivers. These nutrient input can contribute to the total nutrient pool, but it is probably of minor importance in the course of a whole year because it is often a small and only temporal supply. Although nutrient concentrations from samples in the PSR and Paraíba do Meio collected in direct adjacency to sugar cane factories were not noticeably enriched compared to the other river water samples maybe because of the fast mixing with this water.

Silicon is not directly linked to eutrophication in aquatic environments because chemical weathering of silicon rocks and minerals as the main sources of dissolved silica, in rivers, are natural and not man made (White and Brantley, 1995). Tropical river basins are important regions for the transport and chemical weathering processes of dissolved silica due to their climate conditions. Therefore, tropical rivers have generally higher dissolved silica concentrations compared to temperate systems (Jennerjahn et al., 2006). But in combination with an enrichment of nitrogen and phosphorous it can lead to fast phytoplankton production (Chapter I).

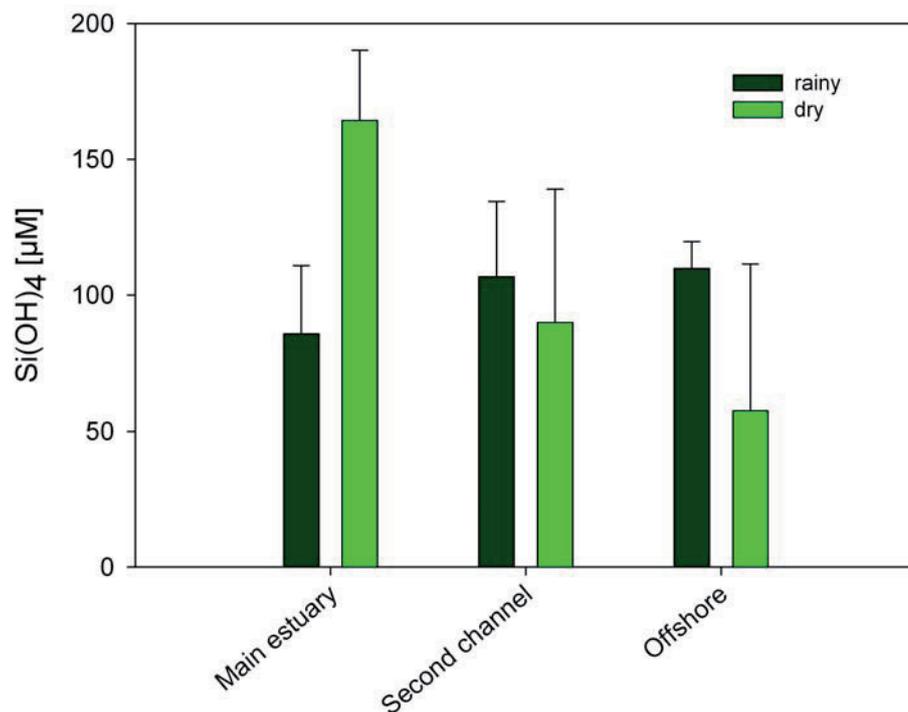


Figure 7: Silicate concentrations (average + SD) and distribution in the PSR estuary (main channel and second channel) and the ocean in the rainy and dry season in 2008.

The PSR and the rivers of the MML showed dissolved silicate concentrations between 62.3 and 239.7 μM and 58.8 to 440.8 μM ,

respectively (Tab. 1, Fig. 7, Chapter I, II). The observed values fit into the amount described for tropical rivers, which have an average concentration of $\sim 190 \mu\text{M}$ (Jennerjahn et al., 2006). The high silicate values in the MML and in the PSR are likely a result of soil leaching in these areas, where latosols, which are rich in silicon, are the main soil type covering the catchment areas of the rivers (Carvalho and Torres, 2002; Oliveira and Kjerfve, 1993; Scheffer and Schachtschabel, 2002). Higher concentrations in the PSR during the dry season can be the result of the longer residence time and, therefore, of a better interaction between groundwater and coterminous soil systems (Fig. 7). These exposures can lead to an increase in dissolved silicate concentration, as it was suggested by Carvalho et al. (1995).

Moreover, the recycling of diatom shells can be an additional source to the high concentration of silicate in waters. Diatoms occurred in high abundance in the MML during the different seasons and the enrichment with nitrogen and phosphorus favored diatom growth because of the high silicon availability (Chapter I). Sugar cane, which is cultivated in the surrounding areas and hinterland of the MML and the PSR, can uptake silicate and store it mainly in its leaves in the form of phytoliths (Keeping et al., 2009; Savant et al., 1999). After the burning of the plants, which is an usual procedure in the northeast and southeast of Brazil, the sugar cane ash and also the sugar cane organic material, which is produced during the processing in the sugar cane factories, still contain silicon (Keeping et al., 2009; Le Blond et al., 2010). Used as organic fertilizer, sugar cane fibres are recycled in the fields and make silicon again as an available nutrient.

Water hyacinth blooms were frequently observed in September and October in the river and the transition zone in MML (Chapter I, II). Water hyacinths extract nutrients from the water and accumulate silicate in their root tissues (Rodriguez et al., 1998). Uptake by plants and release of silicate from decaying plant material can affect the silicate pool in the water column on a temporal scale. However, the recycling of silicate compared to nitrogen and phosphorus generally takes more time in an aquatic environment and leads to longer silica retention in the sediment and, therefore, in the system (Conley et al., 1993).

Nutrients released from the sediments during resuspension are a further important nutrient source in shallow coastal ecosystems. Its magnitude is dependent on wave actions and mixing processes in the water column triggered by the tide. Nutrients, which are stored in the sediments and/or which get recycled in the interface between surface sediments and the water column due to biodegradation of dead and sunken organic matter, can be resuspended and become available in the water column (Eyre and Ferguson, 2002; Trimmer et al., 1998). This effect was observed in the channels of the MML where tidal intrusion led to resuspension and thus an increase in nutrient concentration (Chapter II).

Biogeochemical processes, e.g. nitrification, denitrification or nitrogen fixation as well as accumulation, can remove nitrogen and phosphorus from the aquatic systems (e.g. Nixon et al., 1996 and references therein). In relation to eutrophication, nutrient enrichment can lead to intensive biological transformations due to e.g. primary production and also

degradation of organic material as demonstrated in the enrichment experiment and the sediments of MML (Chapter I, III). These transformations can modify the system through subsequent processes. Bound in organic matter, the nutrients can retain for a short time in the system before they get released from degraded material through the microbial loop and again available for phytoplankton (Seitzinger et al., 2002b).

Nutrients from fertilizer runoff of leached agricultural soils can reach estuaries and lagoons and support the phytoplankton growth and organic matter accumulation in these areas as it was simulated in the enrichment experiment (Chapter I). Enrichment with nitrogen and phosphorus together resulted in highest total biomass indicating a synergetic effect (Chapter I). However, the disproportional N loading from anthropogenic input can also increase the potential for a periodic phosphorus limitation in a system (Sylvan et al., 2006).

However, low nutrient concentrations can be a huge advantage for functional groups that can fix atmospheric nitrogen, such as cyanobacteria in the MML, which can use this nitrogen directly for their metabolism. Thereby fixed N_2 gets reduced to NH_3 , NH_4^+ or organic nitrogen compounds which can in parts directly be released as shown during the bloom of the N-fixing cyanobacterium *Trichodesmium* (Capone et al., 1994; Glibert and Bronk, 1994). Thus, additional nutrients can be added to the system and alterations in water chemistry and consequently in the biogeochemistry can be detected (Anderson et al., 2002).

Temporal nutrient pulses or elevated nutrient concentration is the result of fertilizer use in sugar cane cultivation. This in turn can diminish the existing nutrient limitation and result directly in phytoplankton growth and increased biomass as observed in the MML (Chapter II). These new autochthonous material can also be registered as elevated organic carbon content in the TSM of the water column and in the surface sediment of the system (Table 2; Chapter III).

Mallin et al. (1993) demonstrated that nitrate components from fertilizer outwash, due to rainfall in the upper watershed of the Neuse river, were directly related to primary production in the lower reaches of the estuary. However, results from PSR indicated that high nutrient concentrations during the rainy season are not always linked to a high primary production, because the flushing rate of the river and the turbidity transported huge sediment loads and hampered the production of chlorophyll a, which resulted in low phytoplankton biomass (Tab. 2). In contrast, elevated nitrate concentrations in the MML enhanced the phytoplankton growth, which resulted in high biomasses and its accumulation in the system due to high residence times (Chapter I, II, Cloern, 1996; Knoppers et al., 1991).

However, not only the nutrient concentration, but also the composition of the available nutrient pool plays an important role for phytoplankton species abundance and composition. Klausmeier et al. (2004) showed that the widely accepted Redfield ratio for nitrogen to phosphorus of 16 represents an average N:P ratio for marine phytoplankton which can vary strongly on a species-specific level. Rhee (1978) showed the N:P ratio of 30 is best for

the *Scenedesmus* development. Results from the growth of chlorophytes at high N:P ratio in the enrichment experiment with a natural community from the MML agreed with these findings (Chapter I).

Alterations in the nutrient stoichiometry due to human activities in coastal ecosystem or the hinterland may modify natural phytoplankton communities, which can support harmful or potentially toxic algae blooms with subsequent cascading impacts on higher trophic levels in the food web (Glibert, 2007 and references therein; Humborg et al., 1997; McClelland and Valiela, 1998). Phytoplankton species in the MML shifted mainly between diatoms and cyanobacteria depending on the season and nutrient input from the fertilizer application (Chapter I). It was observed that cyanobacteria bloom frequency increased throughout the year inside the MML. Thereby the dominant cyanobacteria species were *Anabaena spiroides* and *Microcystis aeruginosa* which reached chlorophyll a concentrations of up to 800 $\mu\text{g l}^{-1}$ (Medeiros, 1996; Melo-Magalhaes et al., 1998).

In contrast to temperate regions, high silicate concentrations in tropical aquatic systems hamper the growth of nuisance algae as long as nitrogen and phosphorus are above the threshold level for phytoplankton requirements, because diatoms can immediately outcompete other algal groups, if N or P are supplied (Chapter I). This is supported by the results from other studies, where it was found that high nutrient concentrations affect phytoplankton communities and available silicate favors diatom growth (Del Amo et al., 1997a; Del Amo et al., 1997b; Foullaron et al.,

2007; Piehler et al., 2004 and references therein). But the enhancement of phytoplankton biomass could further result in self shading and act as a principal component that can repress phytoplankton growth (Cloern, 1999; Cullen and Lewis, 1988).

Salinity, which usually can be linked to nutrient-low marine water, seems to be another important factor for the shift of phytoplankton composition and diversity in brackish water systems (Kies, 1997; Kirst, 1989; Muylaert and Sabbe, 1999; Rijstenbil, 1988). Strong temporal changes in tidal intrusion in the MML affected salinity and nutrient availability and consequently the phytoplankton communities. Highest phytoplankton diversity was detected in the incoming rivers dominated by typical freshwater species whereas lowest phytoplankton diversity and species abundance were observed under brackish water conditions in the MML (Chapter II). Nutrient limitation in these areas is usually controlled by freshwater discharge, enhancing the system with nutrients from the catchment area.

Water bodies at the freshwater-marine water interface like estuaries and semi- enclosed coastal lagoons can act as filters for incoming nutrients and organic matter and therefore be considered as sink which mainly depends on the season and the residence time of the water. These findings were detected in the PSR and the Manguaba lagoon during the dry season with low flushing rates and high chlorophyll a concentrations due to algal biomass production (Tab 1; 2; Chapter I). But they can also act as source of nutrients and organic matter due to the out wash of the material into the adjacent coastal waters which depends on the tidal export like in the

Mundau lagoon or on high river discharge, like in the PSR during the rainy season (Tab. 1; Chapter II).

Key findings

- ◆ **Fertilizer runoff from sugar cane fields in Brazil is an important diffuse source of nutrients to estuarine and coastal systems, especially during the rainy season, when fertilizers are washed out from the fields into the estuary.**
- ◆ **Diffuse sources from sugar cane cultivated areas contribute more to nutrient availability in the MML and PSR than punctual sources like sugar cane factory effluents.**
- ◆ **Seasonality and geomorphology are the key factors that rule the retention, dilution and biomass production in the MML and PSR. During the rainy season, high river discharge in the PSR export nutrients and organic matter to adjacent coastal waters. In contrast low river discharge during dry season leads to retention of nutrients and organic matter inside both systems, the MML and PSR.**
- ◆ **The nutrient enrichment experiment suggests that high fertilizer input from sugar cane cultivation changes the nutrient ratio in the system, which results in a phytoplankton shift and promotes diatom growth due to high silicate concentrations in tropical aquatic environments.**

3.3 Composition and distribution of organic matter

The composition of particulate suspended and sedimentary organic matter contains information of organic material sources, as well as their mixing in the system and subsequently their deposition in the sediment and degradation (Budge and Parrish, 1998; Heip et al., 1995). In the MML, signals from sugar cane were detected, either from plant material or by-products from sugar cane processing in the fields or from the soils of sugar cane cultivation areas (Chapter III).

Additional sources from autochthonous production of phytoplankton and waste water material from the city of Maceio formed parts of the particulate material in the lagoons (Chapter III). These findings were also described for the MML by Costa et al. (2011), who used lipid biomarkers as indicator. Seasonal differences resulted in a higher phytoplankton biomass production at the beginning of the dry season (Chapter II). Due to a longer residence time in Manguaba lagoon and also higher productivity, more sedimentary organic matter was detected there. In contrast, the higher $\delta^{15}\text{N}$ values in the surface sediments of the Mundau lagoon pointed to sewage input, which was also detected in the TSM of the water column (Chapter III). Usually, most of the labile living material, e.g. bacteria and plankton is recycled fast with parts of detritus (Laane et al., 1987).

High TSM in the PSR during the rainy season in combination with low organic matter content pointed to high sediment or soil material loads in the river (Tab. 2). Stable carbon and nitrogen isotopes in the PSR suggested

outwash from sugar cane fields and soil runoff, which were transported directly to the sea by high river discharge.

Material transport in small and midsized rivers has been often underestimated in the calculations of budgets as it was shown that e.g. their sediment load is much larger than those of major rivers (Milliman and Syvitski, 1992). Particulate organic matter in rivers can contribute to the total organic export in a range from 4% to 97% depending on the river type (Golladay, 1997; Jacobson et al., 2000). The annual organic carbon transported by rivers is about 0.4 Gt, in which the higher proportion is dissolved material (Hedges et al., 1997; Ludwig et al., 1996).

High C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ of TSM in the PSR indicate that the material was composed of both phytoplankton and terrestrial organic matter (Fig. 8, Tab. 2). The high $\delta^{15}\text{N}$ values in the PSR coincided with high nitrate concentrations and high chlorophyll a values during the dry season. Strong interactions between groundwater and river water in the PSR can lead to an enrichment of ^{15}N as groundwater of farmland can have an $\delta^{15}\text{N}\text{-NO}_3$ up to 8.9‰ (Li et al., 2007). Further fractionation of the nitrate by phytoplankton can increase the ^{15}N as it was suggested for high $\delta^{15}\text{N}$ values of the TSM in the MML (Chapter III). Thus, substantial changes in estuaries and coastal lagoons, mainly due to anthropogenic environmental changes, will affect the biogeochemical cycle in these systems and consequently in the adjacent coastal ocean.

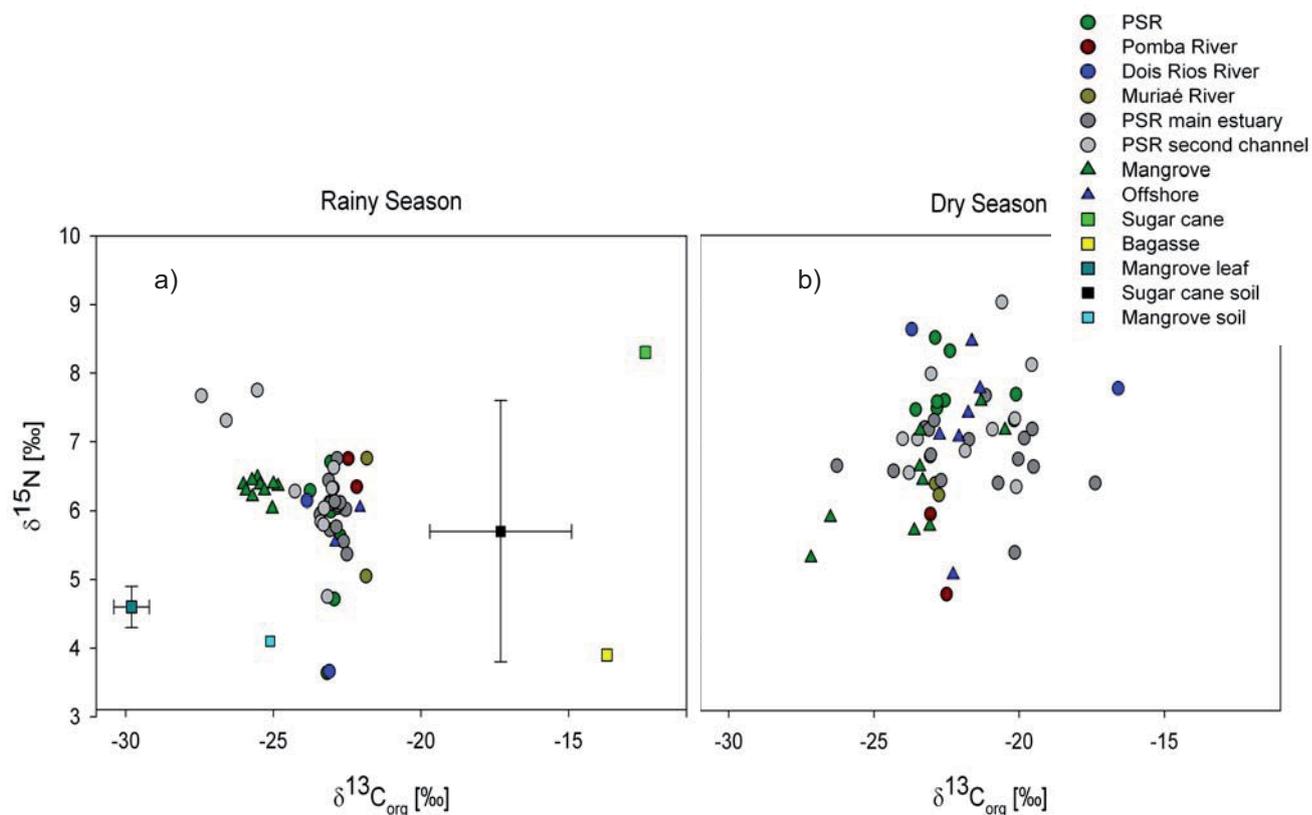


Figure 8: Stable organic carbon and nitrogen isotope distribution of the PSR, its tributaries, the mangrove channel and the ocean in the rainy (a) and dry (b) season 2008 and potential end members. Values for sugar cane, bagasse, sugar cane soil, mangrove leaf and mangrove soil are given in averages (+ SD) in figure 8a.

Key findings

- ◆ Sugar cane plant and soil material contributes to the total suspended matter in the MML and PSR.
- ◆ During the dry season, the MML and PSR act as filter for organic material derived by sugar cane cultivation. During the rainy season, soil and organic material derived from sugar cane fields are exported directly from the PSR to adjacent coastal waters.

3.4 Implication of results

Several studies deal with nutrient enrichment by land use changes and fertilizer application in tropical regions, but information about the impact of agricultural intensification from sugar cane cultivation on aquatic environments in Brazil and its consequences are scarce (Barros et al., 2010; Carreira et al., 2002; Jennerjahn et al., 2004; Seitzinger et al., 2002a). The nutrient concentration and distribution as well as the characterization of TSM and sediment indicated an impact of sugar cane agriculture on aquatic environments like it was shown for the case study sites, MML and PSR. Thereby the impact from diffuse sources like organic and inorganic fertilizer input seemed to be more important than effluents from sugar cane factories. These nutrient concentrations directly influenced phytoplankton biomass and diversity in the system (Chapter I, II).

However, it was also shown that annual changes of material transport and nutrient concentrations were caused by a combination of biological and physico-chemical processes. Seasonal variations, salinity, river discharge and the geomorphology of the system are important factors which affect dynamics in these aquatic systems (Tab. 1, 2, Chapter II). These processes coupled with phytoplankton abundance, control transformation, retention and release of nutrients and organic matter in these aquatic environments. Human impact due to an enrichment of nutrients which are usually natural compounds of the system may modify the properties of the system.

Rather closed systems, like shallow coastal lagoons, can act as a filter and retain nutrients and allochthonous material in the system as they are removed from the water column by sedimentation (Chapter III). This can consequently result in a high production potential to transform and degrade organic material before it reaches the open ocean. In contrast, during times of high river discharge in the rainy season, open estuaries can transport nutrients and material directly to coastal zones with low productivity inside the river-estuarine system. As a consequence the balance of the biogeochemical cycling in the coastal zone can be disturbed and change the abundance and composition of phytoplankton communities. This can further result in changes of the subsequent food web (Cloern, 2001; Sommer et al., 2002).

3.5 A global view on eutrophication

In general, nitrate concentrations in the MML and PSR were above the level described for rivers with only low impact by agriculture like the Amazon River in Brazil (GEMS, 2002). But many coastal systems have experienced increased nitrate concentrations due to fertilizer runoff from agricultural dominated catchment areas in tropical to temperate regions. Rivers like the Brantas River, Indonesia, and the Changjiang River, China, showed nitrate concentrations which were similar to that measured in the PSR during the rainy season (Jennerjahn et al., 2004; Liu et al., 2003). Much higher concentrations were observed in the Pinios River, Greece, in

the Schelde or the Rhine estuary, Netherlands (Bellos et al., 2004; GEMS, 2002; Kromkamp and Peene, 1995).

The considerably low nitrate concentrations in the MML and the PSR during the dry season coincided with high phytoplankton biomass and were a result of reduced fertilizer runoff and uptake by algae. The phytoplankton biomass mainly in the MML was in the upper range compared to values of other coastal ecosystems such as the Patos Lagoon, Brazil, the estuary of the subtropical Tamsui River, Taiwan, the Guadiana estuary, south-west Iberia, and Bizerte Lagoon, western Mediterranean (Abreu et al., 1995; Domingues et al., 2005; Hlaili et al., 2006; Wu and Chou, 2003). The enhanced phytoplankton biomass was mainly the result of long residence time in combination with high silicate concentrations which fit into the values described for tropical rivers (Jennerjahn et al., 2006). An enrichment of nutrients by high fertilizer runoff from sugar cane fields will consequently change the nutrient ratio in the system and play an important role for the entire food web dynamics. A change in phytoplankton composition towards non biomineralizing communities as observed in many temperate regions is not to be expected in these tropical systems because of the high silicate supply.

In conclusion, phytoplankton biomass and composition in combination with nutrient concentration can be useful to identify trophic conditions of a system. But also variations in the season should be considered for the characterization of the system. Although nitrate and phosphate concentrations in the MML are low, the high phytoplankton biomass even

during the dry season determined eutrophic conditions in the lagoons. The nutrient concentrations in the PSR during rainy season were similar to those of the Brantas River which is under heavy human impact. Both the MML and PSR seemed to be impacted by sugar cane cultivation depending on the season, which lead to eutrophic conditions in the system with potential consequences for the adjacent coastal waters.

4. PERSPECTIVES

Most of the studies dealing with nutrient and organic matter dynamics and fluxes in coastal areas focused on large rivers, like the Amazon and Sao Francisco River in Brazil (Dagg et al., 2004; Hedges et al., 1986a; Knoppers et al., 2006). However, there is a deficit regarding information on the contribution of nutrients and organic matter from medium and small sized rivers or lagoons to the ocean. Therefore quantification of nutrient loads from effluents of sugar cane cultivation areas would be necessary to calculate budgets in order to estimate their contribution to global budget.

The increasing demand of sugar and biofuel in Brazil and probably worldwide, will lead to an increase of cultivation areas and fertilizer application in future. Atmospheric input in sugar cane cultivation areas, runoff from diffuse and point sources as well as the transport of plant and soil material into the systems will further increase nutrient and organic matter concentrations in the sea water on a global scale and cause eutrophic conditions with several ecological consequences like e.g. hypoxia. The determination and control on point sources is relatively easy, but future control needs to be concentrated on diffuse terrestrial and aerial inputs.

Besides inorganic nitrogen and its interactions, main emphasis of future research should focus on organic nitrogen, as it can be available in great proportions and influence primary production and diversity (Berg et al., 2001; Seitzinger et al., 2002b). However, ecosystems are variable in

sensitivity and in response to enhanced nutrient loads, which can lead to changing trophic states and different degrees of ecosystem resilience. This can mainly be due to the complex interaction of light and nutrient limitation as well as the influence of residence time and ecological interactions of phytoplankton biomass to nutrient enrichment, which will affect the export of nutrients and phytoplankton biomass to the adjacent ocean (Cloern, 2001).

Changes in the abundance and composition of phytoplankton communities will also occur due to changing nutrient ratios from fertilizer application and its runoff. This can lead to the appearance of noxious algal blooms as observed e.g. in the Gulf of Mexico, USA (Dortch et al., 2000). This will further result in changes of the subsequent food web due to low quality food (Cloern, 2001; Sommer et al., 2002). However HABs can also have serious effects in fish kills because of toxin production and thus affect the local population.

It seems that a linear response of nutrient loads to eutrophication does not occur in such systems, because of their high complexity (Howarth and Marino, 2006). These systems can function like a buffer for the incoming material due to a natural assimilative capacity. However, the effects of eutrophication resulting from sugar cane cultivation could exceed this buffering function. As a consequence nutrients and total suspended matter are transported directly to adjacent coastal waters and the balance of the biogeochemical cycling in the coastal zone can be disturbed.

Thus, it is necessary to understand the ecosystem functioning and the interaction between phytoplankton primary production and nutrient patterns throughout the year to develop appropriate management strategies. Additionally, management strategies in Brazil should implement the reduction in fertilizer application as well as treatment of sewage and waste water from soil runoff and factories. This in the end can improve the nutrient and organic matter balance in the aquatic systems and lower the risk from the negative consequences like HABs and hypoxic or anoxic conditions.

5. REFERENCES

- Abreu, P.C., Hartmann, C. and Odebrecht, C., 1995. Nutrient-rich saltwater and its influence on the phytoplankton of the patos lagoon estuary, Southern Brazil. *Estuarine, Coastal and Shelf Science*, 40(2): 219-229.
- ANA, 2005. *Elaboração do Plano de Ações e Gestão Integrada do Complexo Estuarino-Lagunar Mundaú/Manguaba - CELMM*, Agencia Macopmaö de Aguas; <http://www.ana.gov.br>, Brazil.
- Anderson, D., Glibert, P. and Burkholder, J., 2002. Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. *Estuaries and Coasts*, 25(4): 704-726.
- Barros, G.V., Martinelli, L.A., Oliveira Novais, T.M., Ometto, J.P.H.B. and Zuppi, G.M., 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil). *Science of the Total Environment*, 408(10): 2226-2232.
- Basanta, M.V. et al., 2003. Management effects on nitrogen recovery in a sugarcane crop grown in Brazil. *Geoderma*, 116: 235-248.
- Bellos, D., Sawidis, T. and Tsekos, I., 2004. Nutrient chemistry of River Pinios (Thessalia, Greece). *Environment International*, 30(1): 105-115.
- Beman, M.J., Arrigo, K.R. and Matson, P.A., 2005. Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature*, 434(7030): 211-214.
- Berg, G., Glibert, P., Jørgensen, N., Balode, M. and Purina, I., 2001. Variability in inorganic and organic nitrogen uptake associated with riverine nutrient input in the Gulf of Riga, Baltic Sea. *Estuaries and Coasts*, 24(2): 204-214.
- Béthoux, J.P., Morin, P. and Ruiz-Pino, D.P., 2002. Temporal trends in nutrient ratios: chemical evidence of Mediterranean ecosystem changes driven by human activity. *Deep Sea Research Part II: Topical Studies in Oceanography*, 49(11): 2007-2016.

-
- Bouwman, A.F., Van Drecht, G., Knoop, J.M., Beusen, A.H.W. and Meinardi, C.R., 2005. Exploring changes in river nitrogen export to the world's oceans. *Global Biogeochemical Cycles*, 19(1): GB1002.
- Boynton, W., Garber, J., Summers, R. and Kemp, W., 1995. Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries and Coasts*, 18(1): 285-314.
- Budge, S.M. and Parrish, C.C., 1998. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. *Organic Geochemistry*, 29(5-7): 1547-1559.
- Burkholder, J.M., Tomasko, D.A. and Touchette, B.W., 2007. Seagrasses and eutrophication. *Journal of Experimental Marine Biology and Ecology*, 350(1-2): 46-72.
- Capone, D.G., FERRIER, M.D. and CARPENTER, E.J., 1994. Amino Acid Cycling in Colonies of the Planktonic Marine Cyanobacterium *Trichodesmium thiebautii*. *Applied and Environmental Microbiology*, 60(11): 3989-3995.
- Carreira, R.S. et al., 2002. Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: an elemental, isotopic and molecular marker approach. *Marine Chemistry*, 79(3-4): 207-227.
- Carvalho, C.E. and Torres, J.P., 2002. The ecohydrology of the Paraíba do Sul River, Southeast Brazil. In: H. Salz and W.K. Kundzewicz (Editors), IAHS Special Publication no. 6, Wallingford, UK.
- Carvalho, C.E.V. et al., 1995. Dinâmica de amônia, nitrito, nitrato, fosfato e sílica em três situações de vazão (alta, média e baixa) do Rio Paraíba do Sul, RJ, em sua porção inferior em 1994/95, Anais do V Congresso Brasileiro de Geoquímica e III Congresso de Geoquímica dos países de língua portuguesa, Niterói, Rio de Janeiro.
- Carvalho, C.E.V., Salomao, M.S.M.B., Molisani, M.M., Rezende, C.E. and Lacerda, L.D., 2002. Contribution of a medium-sized tropical river to the particulate heavy-metal load for the South Atlantic Ocean. *The Science of The Total Environment*, 284(1-3): 85-93.

References

- Cavalcanti, C. et al., 2000. Programa de apoio ao desenvolvimento sustentável da Zona da Mata de Pernambuco; <http://www.fundaj.gov.br/tpd/135.html>.
- Chazottes, Le, C.-A., Peyrot, C. and Cuet, 2002. The effects of eutrophication-related alterations to coral reef communities on agents and rates of bioerosion (Reunion Island, Indian Ocean). *Coral Reefs*, 21(4): 375-390.
- Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. *Review of Geophysics*, 34(2): 127-168.
- Cloern, J.E., 1999. The relative importance of light and nutrient limitation of phytoplankton growth: a simple index of coastal ecosystem sensitivity to nutrient enrichment. *Aquatic Ecology*, 33(1): 3-15.
- Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series*, 210: 223-253.
- Conley, D.J., Schelske, C.L. and Stoermer, E.F., 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Marine ecology progress series*. Oldendorf, 101(1-2): 179-192.
- Costa, T., Araújo, M., Knoppers, B. and Carreira, R., 2011. Sources and Distribution of Particulate Organic Matter of a Tropical Estuarine-Lagoon System from NE Brazil as Indicated by Lipid Biomarkers. *Aquatic Geochemistry*, 17(1): 1-19.
- Cullen, J.J. and Lewis, M.R., 1988. The kinetics of algal photoadaptation in the context of vertical mixing. *Journal of Plankton Research*, 10(5): 1039-1063.
- Cushing, D.H., 1989. A difference in structure between ecosystems in strongly stratified waters and in those that are only weakly stratified. *Journal of Plankton Research*, 11(1): 1-13.
- Dagg, M., Benner, R., Lohrenz, S. and Lawrence, D., 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes. *Continental Shelf Research*, 24(7-8): 833-858.

-
- Del Amo, Y. et al., 1997a. Impacts of high-nitrate freshwater inputs on macrotidal ecosystems. I. Seasonal evolution of nutrient limitation for the diatom-dominated phytoplankton of the Bay of Brest (France). *Marine Ecology Progress Series*, 161: 213-224.
- Del Amo, Y., Quéguiner, B., Tréguer, P., Breton, H. and Lampert, L., 1997b. Impacts of high-nitrate freshwater inputs on macrotidal ecosystems. II. Specific role of the silicic acid pump in the year-round dominance of diatoms in the Bay of Brest (France). *Marine Ecology Progress Series*, 161: 225-237.
- Deutsch, C., Gruber, N., Key, R.M., Sarmiento, J.L. and Ganachaud, A., 2001. Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO₂. *Global Biogeochemical Cycles*, 15(2): 483-506.
- Diaz, R.J. and Rosenberg, R., 2008. Spreading Dead Zones and Consequences for Marine Ecosystems. *Science (Washington)*, 321(5891): 926-929.
- DNAEE, 1983. Bacia do Paraíba do Sul, Boletim Fluviométrico F 5.02. Departamento Nacional de Águas e Energia Elétrica.
- Domingues, R.B., Barbosa, A. and Galvao, H., 2005. Nutrients, light and phytoplankton succession in a temperate estuary (the Guadiana, south-western Iberia). *Estuarine, Coastal and Shelf Science*, 64(2-3): 249-260.
- Dortch, Q. et al., 2000. *Pseudonitzschia* spp. in the northern Gulf of Mexico: Overview and response to increasing eutrophication, Symposium on Harmful Marine Algae in the U.S. December 4-9, 2000 Marine Biological Laboratory, Woods Hole, Massachusetts, pp. 27.
- Dortch, Q. et al., 1997. Abundance and vertical flux of *Pseudo-nitzschia* in the northern Gulf of Mexico. *Marine Ecology-Progress Series*, 146(1-3): 249-264.
- Driscoll, C.T. et al., 2001. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. American Institute of Biological Sciences.
- Egge, J.K. and Aksnes, D.L., 1992. Silicate as regulating nutrient in phytoplankton competition. *Marine ecology progress series*, 83(2-3): 281-289.

References

- Eyre, B.D. and Ferguson, A.J.P., 2002. Comparison of carbon production and decomposition, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgae and macroalgae-dominated warm-temperate Australian lagoons. *Marine ecology progress series*, 229: 43-59.
- FAO, 2004. Fertilizer use by crop in Brazil. In: F.a.A.O.o.t.U. Nations (Editor). Food and Agriculture Organization of the United Nations, Rome, pp. 1-64.
- Ferreira, J.G., Wolff, W.J., Simas, T.C. and Bricker, S.B., 2005. Does biodiversity of estuarine phytoplankton depend on hydrology? *Ecological Modelling*, 187(4): 513-523.
- FIAN and GTZ, 2002. Economic, social and ecological impacts on Brazil of accelerated liberalisation of the European sugar market. In: D.G.f.T.Z. GmbH (Editor). Deutsche Gesellschaft für Technische Zusammenarbeit GmbH, Heidelberg, pp. 1-59.
- Figueiredo, R.O., 1999. Transporte de carbono e nitrogênio no baixo Paraíba do Sul: fluxos e processos. PhD Thesis, Universidade Estadual do Norte Fluminense, Campos dos Goytacazes, RJ, Brazil.
- Filoso, S. et al., 2003. Land use and nitrogen export in the Piracicaba River basin, Southeast Brazil. *Biogeochemistry*, 65(3): 275-294.
- Fisher, D.C. and Oppenheimer, M., 1991. Atmospheric Nitrogen Deposition and the Chesapeake Bay Estuary. *Ambio*, 20(3/4): 102-108.
- Fisher, T.R., Peele, E.R., Ammerman, J.W. and Harding, L.W.J., 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine ecology progress series*, 82(1): 51-63.
- Foullaron, P. et al., 2007. Response of a phytoplankton community to increased nutrient inputs: A mesocosm experiment in the Bay of Brest (France). *Journal of Experimental Marine Biology and Ecology*, 351(1-2): 188-198.
- GEMS, 2002. Global Environmental Monitoring System www.gemswater.org.
- Glibert, P.M., 2007. Eutrophication and Harmful Algal Blooms: A Complex Global Issue, Examples from the Arabian Seas including Kuwait Bay, and an Introduction to the Global Ecology and Oceanography

-
- of Harmful Algal Blooms (GEOHAB) Programm. *International Journal of Ocean and Oceanography*, 2(1): 157-169.
- Glibert, P.M. and Bronk, D.A., 1994. Release of Dissolved Organic Nitrogen by Marine Diazotrophic Cyanobacteria, *Trichodesmium* spp. *Applied and Environmental Microbiology*, 60(11): 3996-4000.
- Goldemberg, J., Coelho, S.T. and Guardabassi, P., 2008. The sustainability of ethanol production from sugarcane. *Energy Policy*, 36(6): 2086-2097.
- Golladay, S.W., 1997. Suspended Particulate Organic Matter Concentration and Export in Streams. *Journal of the North American Benthological Society*, 16(1): 122-131.
- Grasshoff, K., Kremling, K. and Ehrhardt, M.E., 1999. *Methods of Seawater Analysis*. third ed. Wiley-VCH(Weinheim): 600 pp.
- Gruber, N. and Sarmiento, J.L., 1997. Global patterns of marine nitrogen fixation and denitrification. *Global Biogeochemical Cycles*, 11(2): 235-266.
- Guarnieri, L.C. and de Martino Jannuzzi, R., 1992. Proálcool : Impactos Ambientais. *Revista Brasileira de Energia*, 2(2).
- Hallegraeff, G.M., 1993. A review of harmful algal blooms and their apparent global increase*. *Phycologia*, 32(2): 79-99.
- Hecky, R.E. and Kilham, P., 1988. Nutrient Limitation of Phytoplankton in Freshwater and Marine Environments: A Review of Recent Evidence on the Effects of Enrichment. *Limnology and Oceanography*, 33(4): 796-822.
- Hedges, J.I. et al., 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography*, 31(4): 717-738.
- Hedges, J.I., Keil, R.G. and Benner, R., 1997. What happens to terrestrial organic matter in the ocean? *Organic Geochemistry*, 27(5-6): 195-212.
- Heip, C.H.R. et al., 1995. Production and consumption of biological particles in temperate tidal estuaries. In: A.D. Ansell, R.N. Gibson and M. Barnes (Editors), *Oceanography and Marine Biology: an Annual Review*. UCL Press, London, pp. 1-149.

References

- Hlaili, A., Chikhaoui, M.A., El Grami, B. and Mabrouk, H., 2006. Effects of N and P supply on phytoplankton in Bizerte Lagoon (western Mediterranean). *Journal of Experimental Marine Biology and Ecology*, 333(1): 79-96.
- Hollins, S. and Ridd, P.V., 1997. Evaporation over a tropical tidal salt flat. *Mangroves and Salt Marshes*, 1(2): 95-102.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology*, 19: 89-110.
- Howarth, R.W. and Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography*, 51(1): 364-376.
- Humborg, C., Ittekkot, V., Cociasu, A. and Bodungen, B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature*, 386(6623): 385-388.
- Jacobson, P.J., Jacobson, K.M., Angermeier, P.L. and Cherry, D.S., 2000. Variation in material transport and water chemistry along a large ephemeral river in the Namib Desert. *Freshwater Biology*, 44(3): 481-491.
- Jeffrey, S.W. and Humphrey, G.F., 1975. New spectrophotometric equations for determining chlorophylls a, b, c₁ and c₂ in algae, phytoplankton and higher plants. *Biochem. Physiol. Pflanz.*, 167: 191-194.
- Jennerjahn, T.C. et al., 2004. Biogeochemistry of a tropical river affected by human activities in its catchment: Brantas River estuary and coastal waters of Madura Strait, Java, Indonesia. *Estuarine, Coastal and Shelf Science*, 60(3): 503-514.
- Jennerjahn, T.C. et al., 2006. Factors Controlling Dissolved Silica in Tropical Rivers. In: V. Ittekkot, D. Unger, C. Humborg and T.A. An (Editors), *The Silicon Cycle, Human Perturbations and Impacts on Aquatic Systems*. SCOPE, Washington, pp. 29-51.
- Keeping, M.G., Kvedaras, O.L. and Bruton, A.G., 2009. Epidermal silicon in sugarcane: Cultivar differences and role in resistance to sugarcane borer *Eldana saccharina*. *Environmental and Experimental Botany*, 66(1): 54-60.

-
- Kies, L., 1997. Distribution, biomass and production of planktonic and benthic algae in the Elbe Estuary. *Limnologica*, 27(1): 55-64.
- Kirst, G.O., 1989. Salinity Tolerance of Eukaryotic Marine Algae. *Annual Review of Plant Physiology and Plant Molecular Biology*, 41(1): 21-53.
- Klausmeier, C.A., Litchman, E., Daufresne, T. and Levin, S.A., 2004. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature*, 429(6988): 171-174.
- Knoppers, B., Kjerfve, B. and Carmouze, J.P., 1991. Trophic state and water turn-over time in six choked coastal lagoons in Brazil. *Biogeochemistry*, 14: 149-166.
- Knoppers, B., Medeiros, P.R.P., de Souza, W.F.L. and Jennerjahn, T., 2006. The São Francisco Estuary, Brazil. *Hdb Env Chem*, 5(Part H): 51-70.
- Kromkamp, J. and Peene, J., 1995. Possibility of net phytoplankton primary production in the turbid Schelde Estuary (SW Netherlands). *Marine Ecology-Progress Series*, 121(1-3): 249-259.
- Krüger, G.C.T., de Carvalho, C.E.V. and Suzuki, M.S., 2004. Dissolved nutrient, chlorophyll a and DOC dynamic under distinct riverine discharges and tidal regimes at the Paraíba do Sul River Estuary, R.J., Brazil. *Journal of Coastal Research*, 39: 1-8.
- Laane, R.W.P.M., Etcheber, H. and Relexans, J.C., 1987. Particulate organic matter in estuaries and its ecological implications for macrobenthos. In: E.T. Degens, S. Kempe and G. Weibin (Editors), *Transport of Carbon and Minerals in Major World Rivers*. SCOPE/UNEP, Hamburg, pp. 71-91.
- Lapointe, B.E., Barile, P.J. and Matzie, W.R., 2004. Anthropogenic nutrient enrichment of seagrass and coral reef communities in the Lower Florida Keys: discrimination of local versus regional nitrogen sources. *Journal of Experimental Marine Biology and Ecology*, 308(1): 23-58.
- Laroche, J. et al., 1997. Brown Tide blooms in Long Island's coastal waters linked to interannual variability in groundwater flow. *Global Change Biology*, 3(5): 397-410.

References

- Le Blond, J.S., Horwell, C.J., Williamson, B.J. and Oppenheimer, C., 2010. Generation of crystalline silica from sugarcane burning. *Journal of Environmental Monitoring*, 12(7): 1459-1470.
- Lewis, W.M., Melack, J.M., McDowell, W.H., McClain, M. and Richey, J.E., 1999. Nitrogen yields from undisturbed watersheds in the Americas. *Biogeochemistry*, 46(1): 149-162.
- Li, X., Masuda, H., Koba, K. and Zeng, H., 2007. Nitrogen Isotope Study on Nitrate-Contaminated Groundwater in the Sichuan Basin, China. *Water, Air, & Soil Pollution*, 178(1): 145-156.
- Liu, S.M. et al., 2003. Nutrients in the Changjiang and its tributaries. *Biogeochemistry*, 62(1): 1-18.
- Ludwig, W., Probst, J.L. and Kempe, S., 1996. Predicting the oceanic input of organic carbon by continental erosion. *Global Biogeochemical Cycles*, 10(1): 23-41.
- Macedo, I.C., Seabra, J.E.A. and Silva, J.E.A.R., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy*, 32(7): 582-595.
- Mallin, M.A. and Paerl, H.W., 1994. Planktonic Trophic Transfer in an Estuary: Seasonal, Diel, and Community Structure Effects. *Ecology*, 75(8): 2168-2184.
- Mallin, M.A., Paerl, H.W., Rudek, J. and Bates, P.W., 1993. Regulation of estuarine primary production by watershed rainfall and river flow. *Marine Ecology-Progress Series*, 93(1-2): 199-203.
- Martinelli, L.A. and Filoso, S., 2008. Expansion of sugarcane ethanol production in Brazil: environmental and social challenges. *Ecological Applications*, 18(4): 885-898.
- McClelland, J.W. and Valiela, I., 1998. Changes in food web structure under the influence of increased anthropogenic nitrogen inputs to estuaries. *Marine Ecology-Progress Series*, 168: 259-271.
- McGlathery, K.J., 2001. Macroalgal blooms contribute to the decline of seagrass in nutrient-enriched coastal waters. *Journal of Phycology*, 37(4): 453-456.

-
- Medeiros, P.R.P., 1996. Influencia da Agroindustria canvieira na qualidade de água do rio Mundaú, Maceio (Al.). Boletim de Estudos de Ciencias do Mar, UFAL: 127-228.
- Melo-Magalhaes, E.M., Lira, M.C.A. and Cavalcanti, M.O., 1998. Floracoes de algas cianoficeas no complexo estuarino Mundaú-Manguaba, Alagoas-Brasil. Boletim de Estudos de Ciencias do Mar, UFAL, 10: 1-13.
- Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. American Journal of Science, 282: 401-450.
- Milliman, J.D. and Syvitski, J.P.M., 1992. Geomorphic/tectonic control of sediment discharge to the ocean: The importance of small mountainous rivers. Journal of Geology, 100(5): 525-544.
- Muylert, K. and Sabbe, K., 1999. Spring phytoplankton assemblages in and around the maximum turbidity zone of the estuaries of the Elbe (Germany), the Schelde (Belgium/The Netherlands) and the Gironde (France). Journal of Marine Systems, 22(2-3): 133-149.
- Nixon, S. et al., 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry, 35(1): 141-180.
- Nixon, S.W., 1995. Coastal Marine Eutrophication: A definition, social causes, and future concerns. Ophelia 41: 199-219.
- Officer, C.B. and Ryther, J.H., 1980. The possible Importance of Silicon in Marine Eutrophication. Marine Ecology Progress Series, 3: 83-91.
- Oliveira, A.M. and Kjerfve, B., 1993. Environmental Responses of a Tropical Coastal Lagoon System to Hydrological Variability: Mundau-Manguaba, Brazil. Estuarine, Coastal and Shelf Science, 37(6): 575-591.
- Oliveira, J.I.C.s.M.d. et al., 2000. Nitrogen dynamics in a soil-sugar cane system. Scientia Agricola, 57: 467-472.
- Paerl, H., Dennis, R. and Whittall, D., 2002. Atmospheric deposition of nitrogen: Implications for nutrient over-enrichment of coastal waters. Estuaries and Coasts, 25(4): 677-693.
- Paerl, H.W., 1995. Coastal Eutrophication in Relation to Atmospheric Nitrogen Deposition - Current Perspectives. Ophelia, 41: 237-259.

References

- Paerl, H.W., 1997. Coastal Eutrophication and Harmful Algal Blooms: Importance of Atmospheric Deposition and Groundwater as "New" Nitrogen and Other Nutrient Sources. *Limnology and Oceanography*, 42(5): 1154-1165.
- Paerl, H.W., 2009. Controlling Eutrophication along the Freshwater-Marine Continuum: Dual Nutrient (N and P) Reductions are Essential. *Estuaries and Coasts*, 32: 593-601.
- Paerl, H.W., Valdes, L.M., Peierls, B.L., Adolf, J.E. and Harding, L.W., 2006. Anthropogenic and climatic influences on the eutrophication of large estuarine ecosystems. American Society of Limnology and Oceanography, Inc., School of Oceanography, WB-10 University of Washington Seattle WA 98195 USA.
- Parsons, M.L., Dortch, Q. and Turner, R.E., 2002. Sedimentological Evidence of an Increase in Pseudo-nitzschia (Bacillariophyceae) Abundance in Response to Coastal Eutrophication. *Limnology and Oceanography*, 47(2): 551-558.
- Perez, B., Day, J., Justic, D., Lane, R. and Twilley, R., 2010. Nutrient stoichiometry, freshwater residence time, and nutrient retention in a river-dominated estuary in the Mississippi Delta. *Hydrobiologia*: 1-14.
- Piehl, M.F., Twomey, L.J., Hall, N.S. and Paerl, H.W., 2004. Impacts of inorganic nutrient enrichment on phytoplankton community structure and function in Pamlico Sound, NC, USA. *Estuarine, Coastal and Shelf Science*, 61(2): 197-209.
- Rabalais, N.N., Turner, R.E., Diaz, R.J. and Justic, D., 2009. Global change and eutrophication of coastal waters. *ICES Journal of Marine Science: Journal du Conseil*, 66(7): 1528-1537.
- Rhee, G.Y., 1978. Effects of N:P Atomic Ratios and Nitrate Limitation on Algal Growth, Cell Composition, and Nitrate Uptake. *Limnology and Oceanography*, 23(1): 10-25.
- Rijstenbil, J.W., 1988. Selection of phytoplankton species in culture by gradual salinity changes. *Netherlands Journal of Sea Research*, 22(3): 291-300.
- Rodriguez, S.A., Avila-Perez, P. and Barcelo-Quintal, I., 1998. Bioaccumulation of chemical elements by water hyacinth

- (*Eichhornia crassipes*) found in “Jose Antonio Alzate” dam samples in the State of Mexico, Mexico. *Journal of Radioanalytical and Nuclear Chemistry*, 238(1): 91-95.
- Rosso, T.C.A., Neves, C.F. and Rosman, P.C.C., 1991. O estuário do Rio Paraíba do Sul: perspectivas em um cenário de variação do nível do mar. In: E.d.A. 3 (Editor), *Simpósio Brasileiro de Recursos Hídricos 9 & Simpósio Luso Brasileiro de Hidráulica e Recursos Hídricos*, Rio de Janeiro., pp. 578-586.
- Rudek, J., Paerl, H.W., Mallin, M.A. and Bates, P.W., 1991. Seasonal and hydrological control of phytoplankton nutrient limitation in the lower Neuse River Estuary, North Carolina *Marine Ecology-Progress Series*, 75(2-3): 133-142.
- Savant, N.K., Korndörfer, G.H., Datnoff, L.E. and Snyder, G.H., 1999. Silicon nutrition and sugarcane production: A review. *Journal of Plant Nutrition*, 22(12): 1853 - 1903.
- Scheffer, F. and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde*. Spektrum Akademischer Verlag GbmH, Heidelberg.
- Schindler, D.W., 1974. Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management. *Science*, 184(4139): 897-899.
- Seitzinger, S.P. et al., 2002a. Global Patterns of Dissolved Inorganic and Particulate Nitrogen Inputs to Coastal Systems: Recent Conditions and Future Projections. *Estuaries*, 25(4B): 640-655.
- Seitzinger, S.P. and Sanders, R.W., 1997. Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. *Marine Ecology-Progress Series*, 159: 1-12.
- Seitzinger, S.P., Sanders, R.W. and Styles, R., 2002b. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. *Limnology and Oceanography*, 47: 353–366.
- Sellner, K., Brownlee, D., Bundy, M., Brownlee, S. and Braun, K., 1993. Zooplankton grazing in a Potomac River cyanobacteria bloom. *Estuaries and Coasts*, 16(4): 859-872.
- Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems: a global problem. *Environmental science and pollution research international*, 10: 126-139.

References

- Solidoro, C., Pastres, R. and Cossarini, G., 2005. Nitrogen and plankton dynamics in the lagoon of Venice. *Ecological Modelling*, 184(1): 103-123.
- Sommer, U., Stibor, H., Katchikis, A., Sommer, F. and Hansen, T., 2002. Pelagic food web configurations at different levels of nutrient richness and their implications for the ratio fish production:primary production. *Hydrobiologia*, 484(1): 11-20.
- Souza, M.F., Kjerfve, B., Knoppers, B., Landim de Souza, W.F. and Damasceno, R.N., 2003. Nutrient budgets and trophic state in a hypersaline coastal lagoon: Lagoa de Araruama, Brazil. *Estuarine, Coastal and Shelf Science*, 57(5-6): 843-858.
- Sparovek, G., Well, M.M., Ranieri, S.B., Schnug, E. and Silva, E.F., 1997. The life-time concept as a tool for erosion tolerance definition. *Scientia Agricola*, 54(Número especial. Piracicaba): 130-135.
- Sylvan, J.B. et al., 2006. Phosphorus Limits Phytoplankton Growth on the Louisiana Shelf During the Period of Hypoxia Formation. *Environmental Science & Technology*, 40(24): 7548-7553.
- Talling, J.F. and Lemoalle, J., 1998. *Ecological Dynamics of Tropical Inland Waters*. Cambridge University Press, Cambridge, 451 pp.
- Trimmer, M., Nedwell, D.B., Sivyver, D.B. and Malcolm, S.J., 1998. Nitrogen fluxes through the lower estuary of the River Great Ouse, England: The role of the bottom sediments. *Marine Ecology Progress Series*, 163: 109-124.
- Turner, R.E. and Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi river delta. *Nature*, 368: 619-621.
- Turner, R.E. and Rabalais, N.N., 2003. Linking Landscape and Water Quality in the Mississippi River Basin for 200 Years. *Bioscience*, 53(6): 563-572.
- UNICA, 2001. *Energia da Cana-de-Açúcar e Redução do Efeito Estufa.*, São Paulo.
- UNICA, 2010. *Do álcool ao etanol: trajetória única*, Sao Paulo.
- Vitousek, P.M. et al., 1997. Human alteration of the global nitrogen cycle: Causes and consequences. *Ecological Applications*, 7: 737-750.
- Vollenweider, R.A., 1992. Coastal marine eutrophication: principles and control. *Science of the Total Environment Supplement*: 1-20.

- Wehr, J.D. and Descy, J.P., 1998. Use of phytoplankton in large river management. *Journal of Phycology*, 34(5): 741-749.
- White, A.F. and Brantley, S.L., 1995. Chemical weathering rates of silicate minerals; an overview. *Reviews in Mineralogy & Geochemistry*, 31(1): 1-22.
- Wu, J. and Chou, T., 2003. Silicate as the limiting nutrient for phytoplankton in a subtropical eutrophic estuary of Taiwan. *Estuarine, Coastal and Shelf Science*, 58(1): 155-162.
- Zhang, J. et al., 2010. Natural and human-induced hypoxia and consequences for coastal areas: Synthesis and future development. *Biogeosciences*, 7 1443-1467.

CHAPTER I

Phytoplankton biomass and
composition in a tropical lagoon in
NE Brazil affected by sugar cane
monoculture in its catchment

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn

Submitted to *Estuaries and Coasts*



Phytoplankton biomass and composition in a tropical lagoon in NE Brazil affected by sugar cane monoculture in its catchment

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn

ABSTRACT

During the dry season in October 2008 spatial variations in dissolved inorganic nutrients and the phytoplankton community in the Manguaba lagoon, affected by sugarcane monoculture, were studied to determine the effects of agricultural effluents on nutrient dynamics and phytoplankton biomass. Dissolved inorganic nitrogen and phosphate are with 14.9 and 2.8 μM highest in the river and decreased seaward. The same trend was observed for silicate ranging between 27.6 and 440.9 μM . Total phytoplankton biomass in the lagoon reached up to $2.4 \cdot 10^3 \text{ mg C L}^{-1}$. In order to simulate nutrient inputs from agriculture and the response of phytoplankton enrichment experiments were conducted, resulting in an immediate respond of phytoplankton communities to additions of nitrogen and phosphorus. High Si:N and Si:P ratios favour the growth of diatoms. Thus, altered nutrient ratios due to excessive agricultural runoff from sugar cane fields in the system play an important role for the entire food web dynamics in the lagoon.

KEYWORDS

Tropical coastal lagoon, sugar cane monoculture, phytoplankton community, nutrient concentration, enrichment experiment, Brazil

INTRODUCTION

Coastal lagoons are shallow ecosystems which are highly productive and characterized by high nutrient input from river discharge and a limited exchange with the ocean (Knoppers et al., 1991; Taylor et al., 1995). High nutrient inputs into these lagoons are often due to human activities in the hinterland such as agriculture, discharge of untreated sewage or industrial effluents. Hence, resulting high nitrogen and phosphorus loads can lead to eutrophication (Filoso et al., 2003; Turner and Rabalais, 1994; Turner and Rabalais, 2003). Eutrophication affects nutrient stoichiometry and results consequently in enhanced phytoplankton biomass (Sutcliffe and Jones, 1992) and changes in phytoplankton species composition (Duarte et al., 2000). Negative effects of eutrophication on ecosystems like harmful algal blooms, hypoxic events or the degradation and loss of seagrass beds have been reported (McGlathery, 2001; Rabalais et al., 1996; Zhang et al., 2010).

Coastal lagoon phytoplankton communities are often highly diverse as they are composed of freshwater and marine species. Phytoplankton dynamics are controlled by environmental factors including light intensity, temperature, salinity, sedimentation, nutrients and biotic interactions such

as predation and competition (Ferreira et al., 2005; Wehr and Descy, 1998). In tropical areas seasonal variations in light and temperature are often small. Therefore variations in nutrient amount and composition are the major controls of phytoplankton biomass and species composition.

Phytoplankton on average requires dissolved inorganic nitrogen (DIN) and phosphate (PO_4) in the ratio of 16:1 noted as the Redfield ratio for best growth (Klausmeier et al., 2004)). Optimum silicate (Si) uptake for diatoms in relation to nitrogen is around a ratio of 1:1 (Rahm et al., 1996). However nutrient consumption can vary among species, depending on species-specific nutrient uptake kinetics, storage capacities and assimilation (Tilman et al., 1982).

In tropical marine regions nitrogen limitation is particularly widespread and often controls primary production (Quiblier et al., 2008). An input of anthropogenic nitrogen and phosphorous by rivers into coastal ecosystems will also lower the Si:N and Si:P ratios in these systems and thereby influence phytoplankton species composition, especially in diatom dominated communities (Conley et al., 1993).

Mainly during the last decades of the 20th century human activities may have changed the nutrient availability in aquatic coastal ecosystems of Brazil considerably. For the production of ethanol as an alternative fuel in the automobile sector the cultivation of sugar cane was expanded from 2 million ha to 7 million ha (UNICA, 2001). Therefore further needs of agricultural area led to deforestation. Additionally, intensive use of

fertilization on the sugar cane fields and high productivity in the sugar cane industry followed. These activities resulted in high N discharge rates into rivers draining watersheds or passing by factories where industrial wastewaters are released (Filoso et al., 2003; Martinelli and Filoso, 2008).

An increase of phytoplankton biomass resulting from eutrophication is often accompanied by shifts in species composition and a reduction in species diversity. But there are various other factors controlling the phytoplankton biomass and community composition in coastal ecosystems. As yet little is known on the impact of effluents from sugar cane monoculture on the amount and composition of nutrient availability and subsequent effects on phytoplankton distribution and composition in lagoons and adjacent coastal waters in Brazil. The shallow coastal Manguaba lagoon which is affected by sugar cane monocultures in its catchment area was used as a case study site.

The objectives of this study were:

- (i) to estimate the spatial variation of nutrient availability in the Manguaba lagoon affected by freshwater discharge and tidal variation during times of low precipitation,
- (ii) to assess the response of phytoplankton community from Manguaba lagoon to nitrogen and phosphorus during an enrichment experiment in order to simulate high nutrient input from sugar cane monoculture.

STUDY AREA

The Mundau Manguaba lagoon complex is located in northeast Brazil, in the state of Alagoas (latitudes 9°35' and 9°36'S, longitudes 35°44' and 35°58'W). It consists of two lagoons which are connected to each other by a narrow channel system fringed with mangroves and connected to the ocean (Fig. 1). The channels of the two lagoons are separated in a joint outlet by a sand bar and discharge into the ocean. The area of the whole system is 79 km² with an average depth of 2 m. The Manguaba lagoon has an area of 43 km² and is surrounded by sugar cane fields (Oliveira and Kjerfve, 1993). The Paraiba do Meio and Sumauma rivers discharge 17.6 m³s⁻¹ and 5.0 m³s⁻¹, respectively, into the Manguaba lagoon (Oliveira and Kjerfve, 1993; Souza et al., 2003).

The tropical climate is characterized by a dry season from September to February and a rainy season from March to June with an average annual precipitation of 1654 mm (Fig. 2). Rainfall strongly influences the lagoon by freshwater and sediment transport from the rivers while during the dry season the system is mainly controlled by the semi – diurnal tides because of low river flow. Most of the tidal energy dissipates in the connecting channel between the ocean and the lagoon. According to this effect in combination with the size of the lagoon, the Manguaba lagoon has an average residence time of around 5-7 weeks (Oliveira and Kjerfve, 1993).

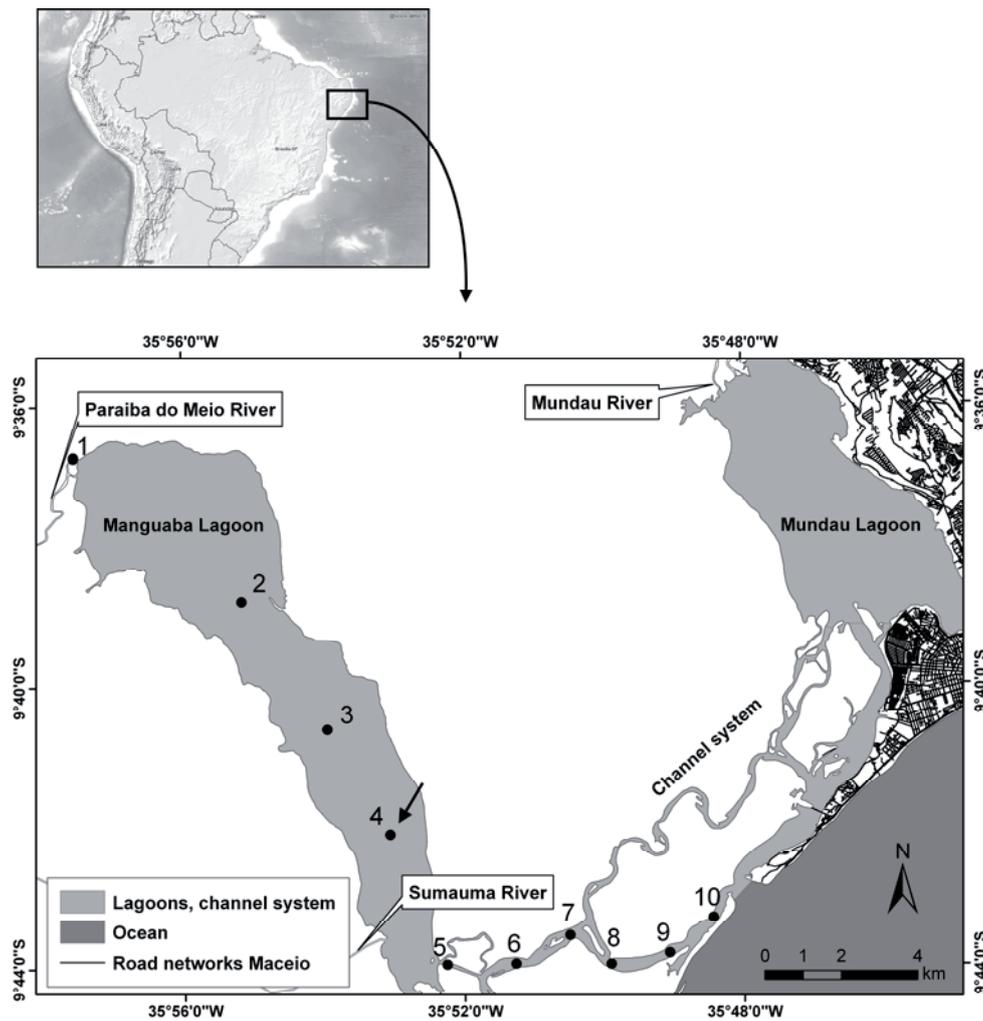


Figure 1: Map of the investigated area, Mundau Manguaba lagoon system, in northeast Brazil. Black points (●) denote sampling stations along the gradient, the arrow (←) shows the station where the water was taken for the enrichment experiment, white areas (□) around the lagoons represent sugar cane fields.

Over the last three decades human activities and mainly the cultivation of the sugar cane has more than doubled (Macedo et al., 2008). The attendant increase in fertilizer use and population growth have probably increased the nutrient loads of the rivers. In northeast Brazil which is the second largest sugar cane production area of the country the planting and simultaneously the fertilization of sugar cane starts at the end of the dry

season in January to March. At the beginning of the dry season in September/October the harvesting of sugar cane and subsequently the sugar production in the factories starts. Mainly during the first weeks of the rainy season after the out washing of e.g. fertilizers from the soils increased nutrient availability in Mundau Manguaba lagoon is expected.

MATERIAL AND METHODS

Field sampling and sample preparation

Samples were taken along a salinity gradient. According to hydrodynamic and geographical characteristics the lagoon system is divided into three different units: the channel (estuary), the lagoons and the river (Fig. 1). Water samples for nutrients, chlorophyll a and phytoplankton were collected near surface (~ 0.5 m depth) in October 2008 (Oct 08). Samples were taken with a Niskin bottle and kept dark and cool until filtration. Water samples for nutrient analysis were filtered through single use membrane filters (0.45 µm pore size) into prewashed PE bottles, fixed with mercury chloride solution and kept frozen until analysis. Water for chlorophyll a determination was filtered through *Whatmann* GF/F filters and stored frozen until the analysis. Samples for the determination of phytoplankton composition and biomass were sampled directly from surface water with 250 ml brown glass bottles. The phytoplankton samples were fixed with Lugol's iodine and kept in darkness.

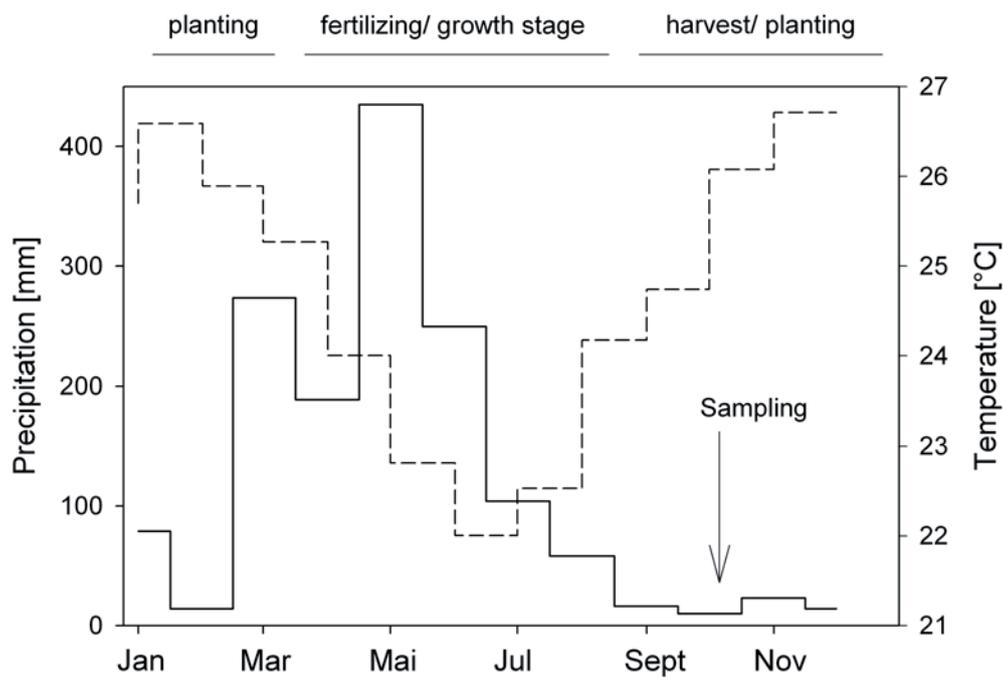


Figure 2: Monthly precipitation (continuous line) and temperature (dashed line) in the investigated period 2008 and sugar cane cultivation cycle in this region.

Experimental design and sampling

To experimentally investigate the situation with a potential high nutrient input into the Manguaba lagoon and hence changes in stoichiometry, we carried out a controlled enrichment experiment in laboratory mesocosm systems. For that purpose 150 liters of surface water were taken at one station in the Manguaba lagoon (latitudes $9^{\circ}42.090$, longitudes $35^{\circ}52.843$) on 13th October 2008 in the beginning of the dry season where low nutrient concentrations in the lagoon were expected. The sampled lagoon water was filtered through a 200 μm mesh nylon gauze to remove large zooplankton.

The samples were moved to 10 litre polyethylen (PE) mesocosms and held in the laboratory under equal temperature and light conditions for 8 days with an average temperature of 26.2°C which is similar to the water temperature in the lagoon. The mesocosms were enriched with nutrients and the following treatments were established: (I) control, (II) enriched with 40 µM phosphorus (KH₂PO₄) (+P), (III) enriched with 50 µM nitrogen (NaNO₃)(+N) and (IV) enriched with 40 µM phosphorus (KH₂PO₄) and 50 µM nitrogen (NaNO₃) (+NP) every second day. We replicated each treatment three times and in total the set up existed of 12 mesocosms.

Water of each treatment was sampled in the beginning, every second day immediately before enriching and at the end of the experiment. To reduce sedimentation processes the mesocosms were shaken manually several times per day. Natural light and day-night conditions were ensured. The water was analysed for nutrients and chlorophyll a every second day. Total algal biomass and phytoplankton species composition was determined in the beginning and at the end of the experiment.

Analyses

Salinity, temperature, pH and dissolved oxygen of the surface water were measured directly with a *WTW MultiLine* multiparameter sensor. Dissolved inorganic nutrients (nitrite, nitrate, ammonium, silicate and phosphate) of surface water were determined according to Grasshoff et al. (1999).

Chlorophyll a was determined spectrophotometrically after extracting from filters in 90% acetone for 24h at 4°C in darkness (Jeffrey and Humphrey, 1975). Phytoplankton was identified and counted with an inverted Zeiss *Axiocvert 200* microscope according to Utermöhl (1958). After sedimentation in the chambers, at least 400 cells were counted to keep a counting precision of $\pm 10\%$ (Lund et al., 1958), if possible. Biovolume of the species was calculated using geometric configurations (Hillebrand et al., 1999) and converted into biomass and cell carbon content (Cc) according to Rocha and Duncan (1985). The equation $Cc = aV^b$ was used for the inverted microscopy with $a = 0.12$ and $b = 1.051$. Phytoplankton composition will be represented in the following taxonomic classes: Cyanophyta, Bacillariophyta and Chlorophyta.

Statistics

A one-way analysis of variance (ANOVA) was used to test differences in phytoplankton cell density during the experiment. These differences between the start and the end of the enrichment in all treatments were tested by an additional Post-hoc Tukey's test. The relationship between diatom fraction and diatom biomass with nutrients and nutrient ratios were determined using Pearson correlation. All tests were carried out in STATISTICA 9.

RESULTS

Variation in physico-chemical properties, nutrient concentrations and ratios

Water temperature in the Manguaba lagoon system was on average 28.3 °C with lowest values in the channel connecting the lagoon with the ocean. Salinity varied between 0.1 and 18.1. The average pH was 8.0 (Tab. 1). Nutrient concentrations in Manguaba lagoon showed spatial patterns and fluctuated with the tide. Therefore highest nutrient concentrations (DIN, PO₄, Si) were measured in the Paraiba do Meio while they declined downstream in the lagoon and reached lowest values close to the shore (Fig. 3).

The composition of DIN varied in the Manguaba system. Nitrite concentrations in the system were <1.0 µM. The ammonium concentration (1.5 µM) in the Paraiba do Meio was much lower than nitrate (13.0 µM) and declined towards the ocean. Very high silicate concentrations (440 µM) were measured in the Paraiba do Meio and decreased seaward. The nutrient peak measured inside the Manguaba lagoon had maximum concentrations of phosphate (2.2 µM) and DIN (26.8 µM; Fig. 3). The high silicate concentrations in the system resulted in high average dissolved Si:N ratios which increased from river to channel due to decreasing DIN values (Tab. 1). Average N:P ratios ranged between 6.8 - 32.1 in the system with highest values in the channel because of very low phosphate concentrations.

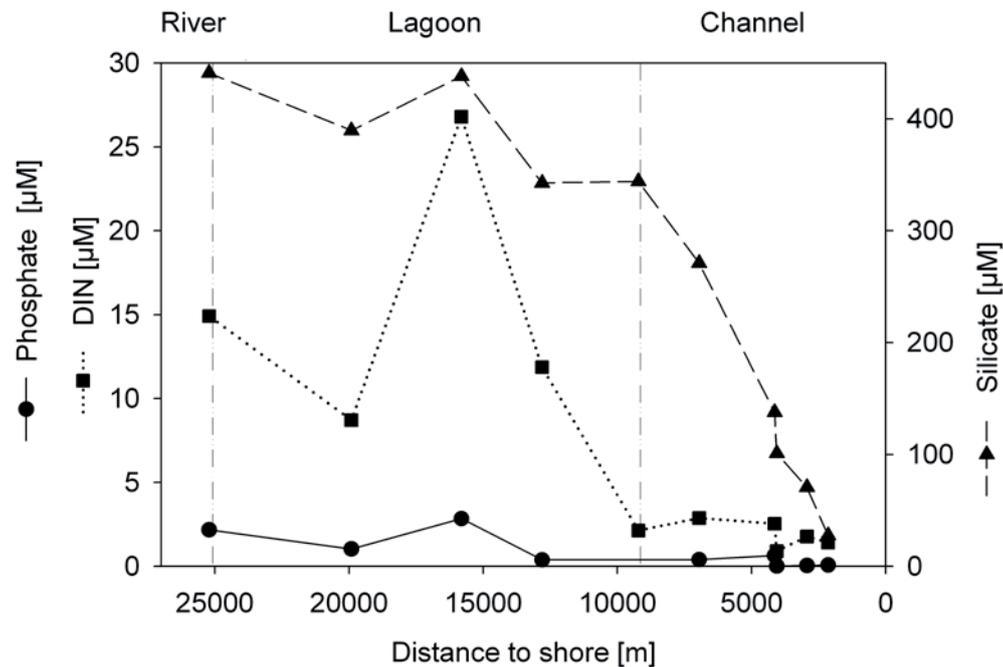


Figure 3: Variations in nutrient concentrations (DIN (■), PO_4 (●), Si (▲)) along the distance to shore at sampling stations in the Manguaba lagoon. Dashed lines divide the Manguaba lagoon system into river, lagoon and channel.

Spatial changes in phytoplankton community and biomass

Average chlorophyll a concentrations showed a high spatial variation with maximum values of $47.0 \mu\text{g L}^{-1}$ inside the channel and minimum concentrations in the river ($2.9 \mu\text{g L}^{-1}$; Tab. 1).

Phytoplankton cell density and composition changed from river to lagoon and channel. Total phytoplankton abundance was low inside the rivers. Highest cell abundance ($47.5 \cdot 10^6 \text{ cells L}^{-1}$) and also algal biomass was observed in the transition zone between the lagoon and the channel and was followed by a decrease towards the ocean (Fig. 4). In the transition zone, phytoplankton biomass consisted to 50% of Cyanobacteria, mainly of

Table 1: Minimum, maximum and average values with standard deviation for temperature, salinity, depth, pH, Si:N and N:P ratios and chlorophyll a measured in Paraiba do Meio River, Manguaba lagoon and channel.

		River n=1	Lagoon n=3	Channel n=6
Temperature (°C)	Min		28,0	23,3
	Max	27,6	28,8	28,3
	AVG (± STDEV)		28.3 (± 0.4)	26.6 (± 2.3)
Salinity	Min		0.1	0.6
	Max	0.1	0.5	18,1
	AVG (± STDEV)		0.3 (± 0.2)	12.0 (± 9.4)
Depth (m)	Min		0,9	1,6
	Max	4,6	3,4	4,3
	AVG (± STDEV)		2.2 (± 1.3)	2.4 (± 1.0)
pH	Min		7,5	7,9
	Max	7,6	8,4	9,0
	AVG (± STDEV)		7.8 (± 0.5)	8.3 (± 0.4)
Si:N	Min		16,4	19,6
	Max	29,6	44,7	161,9
	AVG (± STDEV)		30.0 (± 14.2)	80.1 (± 52.5)
N:P	Min		8,4	4,0
	Max	6,8	31,4	92,6
	AVG (± STDEV)		16.4 (± 13.0)	32.1 (± 36.2)
Chlorophyll a ($\mu\text{g L}^{-1}$)	Min		7,5	16,8
	Max	2,9	27,2	47,0
	AVG (± STDEV)		16.0 (± 10.1)	30.7 (± 12.6)

long *Anabaena sp.* chains. Bacillariophyta dominated phytoplankton biomass in the river and northern part of the lagoon and also in the channel and were composed mainly of large *Cyclotella sp.*. Inside the lagoon phytoplankton biomass was low and Cyanobacteria were the main group (Fig. 4). Maximum Chlorophyta values were observed in the transition zone from the lagoon to the channel with *Coelastrum* and *Eudorina* as main

genera whereas *Scenedesmus* was the only Chlorophyta that was observed in the river station.

Pearson correlation indicated that DIN is negatively correlated with diatom biomass in the Munguaba lagoon ($r = -0.71$; $p = 0.02$), whereas the Si:N ratio is positively correlated with diatom biomass ($r = 0.65$; $p = 0.04$).

Nutrient enrichment experiment

The initial mean concentrations of inorganic nutrients in the lagoon water used for the experiment were $1.6 \mu\text{M}$ for phosphate (PO_4) (SD = 1.1) and $17.5 \mu\text{M}$ for DIN (SD = 2.6) (Fig. 5). Phosphate was mainly consumed after day 2 of the enrichment. The uptake was higher in samples after day 4 to which only phosphate (+P) was added compared to the treatment to which +NP were added (Fig. 5a). Added nitrogen (+N) was directly consumed within the first 4 days of incubation in the treated samples, followed by a decrease in uptake and an increase in dissolved nitrogen concentration (Fig. 5b). Silicate concentration decreased in all enriched samples after day 6 except for the control (Fig. 5c)

In the beginning of the experiment the mean chlorophyll a concentration was $27.2 \mu\text{g L}^{-1}$. Chlorophyll a responded in all enriched treatments and showed highest concentration in +NP addition ($80.7 \mu\text{g L}^{-1}$), indicating a synergetic effect of these nutrients. After an increase of phytoplankton biomass the control declined rapidly to minimum values of $8.8 \mu\text{g L}^{-1}$ until the end of the experiment (Fig. 5d).

Initial Si:N ratios ranged from 13.2 to 24.1 and increased until day 2 in all treatments. Highest ratios were detected on day 4 in treatments +N because of very low DIN concentrations in these samples. Reduced uptake of DIN and therefore higher concentrations of nitrogen in +N and +NP samples resulted in a decrease of the Si:N ratio. A continuous increase in dissolved Si:N ratios could only be detected in the control treatments over the time of the experiment.

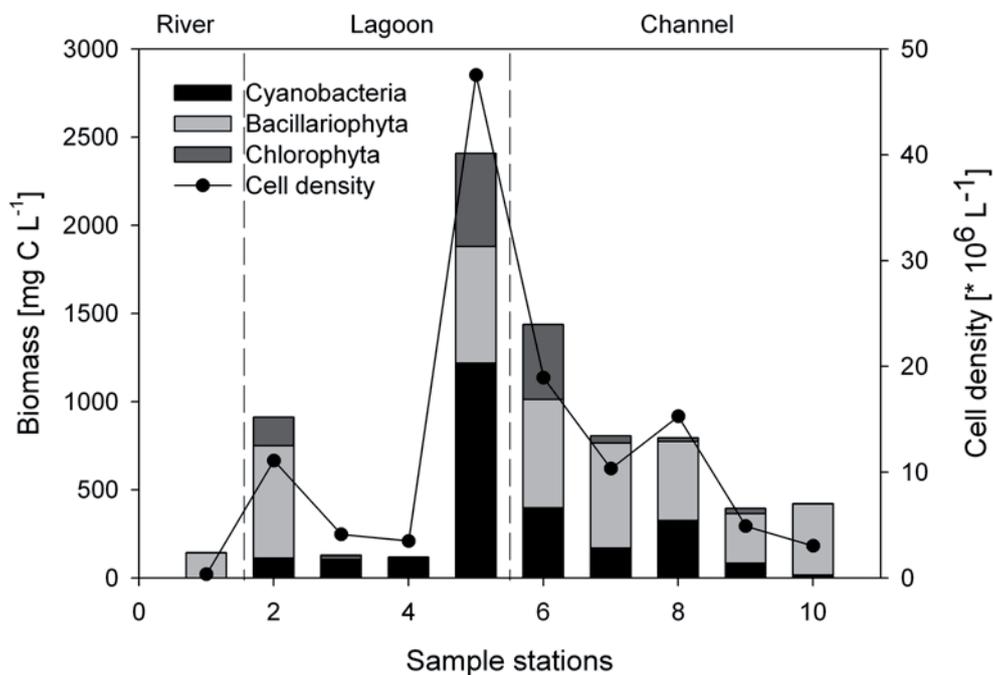


Figure 4: Phytoplankton biomass of Cyanobacteria, Bacillariophyta and Chlorophyta and their total abundance in the Manguaba lagoon along a freshwater – marine gradient. Dashed lines divide the Manguaba lagoon system into river, lagoon and channel.

The addition of nutrients resulted in a considerable enhancement in phytoplankton cell density. An increase in Bacillariophyta was observed from an initial cell count of 6.5×10^6 cells L⁻¹ to a maximum of 15.4×10^6 cells L⁻¹ in nutrient enriched samples. Only samples with N - addition

showed significant differences ($p < 0.02$) in cell densities between the start and the end of the experiment. Chlorophyta cell density increased in all treatments, but differences were only significant in treatments where +NP was added ($p < 0.02$). There, cell number grew from 1.8×10^6 cells L^{-1} at the beginning to a maximum of 6.6×10^6 cells L^{-1} at the end of the experiment. In contrast, Cyanophyta decreased significantly ($p < 0.0003$) to values between 12 – 24 % of the initial abundance in nutrient enriched treatments and the control. The maximum phytoplankton cell count was measured in samples enriched with both nutrients (+NP; up to 23.9×10^6 cells L^{-1} , mainly consisting of diatoms).

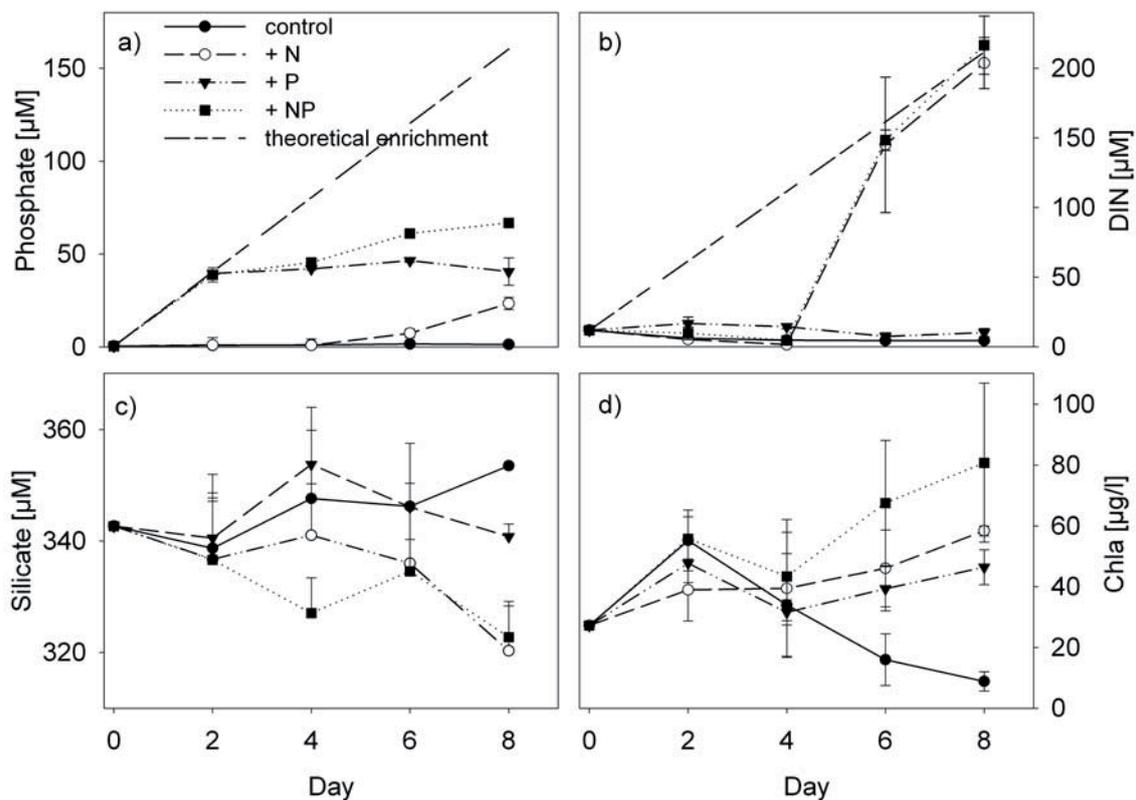


Figure 5: Time series of phosphate (a), DIN (b), silicate (c) and chlorophyll a (d) concentrations (mean \pm SD, $n=3$) during the enrichment experiment and theoretical concentration line for phosphate (a) and nitrogen (b) after enrichment.

The initial total phytoplankton biomass increased from $1.4 \cdot 10^3 \text{ mg C L}^{-1}$ to $1.7 \cdot 10^3 \text{ mg C L}^{-1}$ in the control until the end of the experiment (Fig. 6). In the beginning, Cyanobacteria, dominated by *Anabaena sp.*, contributed 15 % of the total phytoplankton biomass in the control, whereas Bacillariophyta and Chlorophyta made up 51 % and 34 %, respectively. At the end of the experiment Cyanobacteria and Bacillariophyta decreased to 2 % and 35 % of the total biomass in the control whereas the biomass of Chlorophyta increased to 63 % ($1.1 \cdot 10^3 \text{ mg C L}^{-1}$). Nutrient enrichment had strong effects on the total biomass of all treatments.

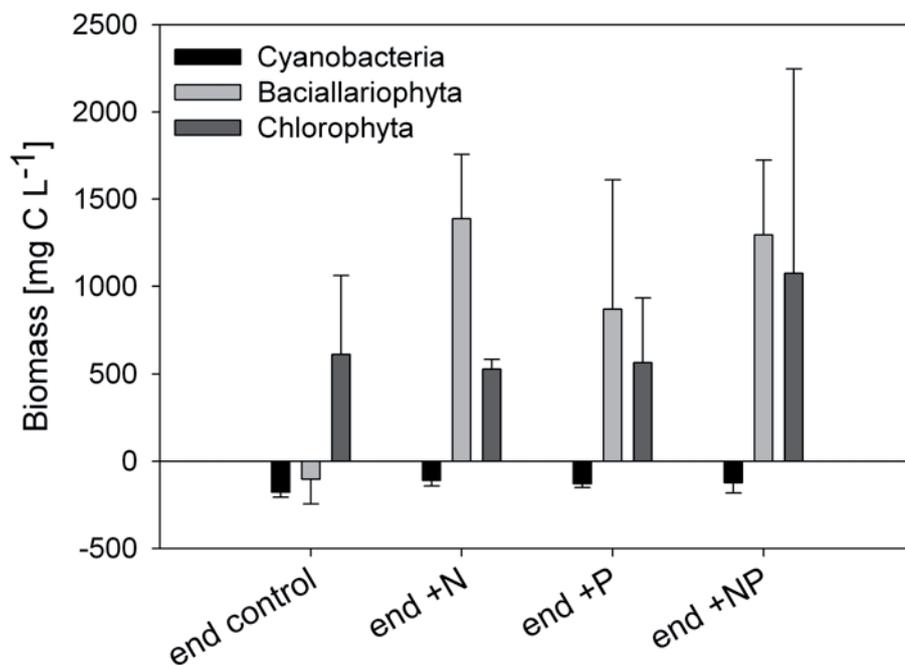


Figure 6: Effect of nutrient enrichment on the average phytoplankton biomass (mean \pm SD, $n = 3$) in the different treatments between the beginning and the end (after 8 days) of the experiment.

Cyanobacteria biomass decreased significantly between the beginning and the end of the experiment in all treated samples ($p_N < 0.02$, $p_P < 0.008$, p_{NP}

< 0.01, ANOVA followed by Tukey's *post-hoc* test) and differed significantly from the control ($p_C < 0.0008$). Total phytoplankton biomass increased strongest in the +NP treatment ($3.6 * 10^6$ mg C L⁻¹; Fig. 6). These increases were mainly due to the growth of fast growing species such as small Chlorophyta and Bacillariophyta like *Cyclotella sp.* and *Scenedesmus sp.*. Additionally, the growth of Bacillariophyta biomass in treatments only enriched with +N was very close to +NP enriched treatments and showed clear differences in diatom biomass between start and end of the experiment ($p_N < 0.02$ and $p_{NP} < 0.02$, ANOVA followed by Tukey's *post-hoc* test). The biomass of Cyanobacteria in nutrient enriched samples generally decreased to 2 – 3% of the total phytoplankton biomass ($0.08 - 0.1 * 10^3$ mg C L⁻¹).

DISCUSSION

Variations in nutrient availability and phytoplankton community in the Manguaba lagoon

During the last decades, lots of tropical aquatic systems have to deal with increased anthropogenic pressures such as agricultural development. Especially during times of high precipitation, high nutrient loads are expected in the rivers from out washing processes in the surrounding fields and the hinterland, whereas water of marine origin with reduced nutrient amount reached the lagoon preferentially during dry periods. The spatial variation of physico-chemical water properties, nutrients and biological activity like e.g. phytoplankton growth in the Manguaba lagoon are

characterized by daily and seasonally varying freshwater inputs and the tidal exchange between the lagoon and the ocean.

In general, the concentrations of dissolved inorganic nutrients (dissolved inorganic nitrogen, phosphate, silicate) were high at the river station. In October 2008 DIN consisted mainly of nitrate in the Paraiba do Meio River which enters the Manguaba lagoon. It is probably the result of diffuse inflow from the fertilized sugar cane soils caused by heavy rain showers some days before the sampling. The low concentrations of nitrogen and phosphorus in the lagoon in combination with the increased chlorophyll a values compared to the river suggest fast nutrient uptake by algae.

Concentrations $<1.0 \mu\text{M}$ for DIN and $<0.1 \mu\text{M}$ for PO_4 are usually considered to be limiting for algal growth (Fisher et al., 1992). At some sampling points in the channel, DIN concentrations were close to this threshold due to dilution with nutrient depleted seawater. Phosphate concentrations in the channel were often below the threshold value of $0.1 \mu\text{M}$ and phosphorus was consequently the limiting nutrient in October 2008. Usually phosphorus is considered to be the main limiting nutrient in temperate freshwater systems (Schindler, 1974) whereas nitrogen limitation dominates in marine ecosystems (Howarth, 1988; Talling and Lemoalle, 1998). On the seaward gradient of nutrients a particular peak was detected inside Manguaba lagoon. This pattern pointed to an additional nutrient source probably from sediment recycling as silicate, phosphate and DIN were increasing at this station possibly due to punctual turbulences.

Silicate also decreased seaward, but concentrations at all stations were very high and not limiting for diatom growth. The rapid decrease of silicate in the channels coincided with elevated Bacillariophyta biomass and points to a fast uptake by these algae. Diatom growth is considered to become silicate limited when the ratio of silicate to dissolved inorganic nitrogen falls below 1 and silicate concentrations are less than 2 μM (Egge and Aksnes, 1992; Turner et al., 1998). A decrease of silicate below this threshold could inevitably effect the algae composition and result in changes of the pelagic food web. A reduction in diatom availability would affect zooplankton, the main food of fish, which often favour diatoms over other phytoplankton (Officer and Ryther, 1980).

In Manguaba lagoon the Si:N ratio was between 16 to 162 and the concentration of silicate never fell below 27.6 μM . The high silicate values in the lagoon are most probably a result of soil leaching in this area where latosols are the main soil type covering the northeast of Brazil and which are rich in silicon (Oliveira and Kjerfve, 1993; Scheffer and Schachtschabel, 2002). Moreover, the recycling of diatom shells can add to the constantly high concentration of silicate in the shallow water column of the well mixed lagoon. Sugar cane which is cultivated around the lagoon and in its hinterland can also take up silicate and store it mainly in its leaves in the form of so called phytoliths (Keeping et al., 2009; Savant et al., 1999).

After the burning of the plants, the sugar cane ash and also the sugar cane organic material, which is formed during the processing in the sugar cane factories, still contain silicon. (Le Blond et al., 2010). Used as organic

fertilizer sugar cane fibres are recycled on the fields and make silicon again available as nutrient.

Water hyacinth blooms were frequently observed in September and October in the river and the transition zone to the lagoon. Water hyacinths extract nutrients from the water and accumulate silicate in their root tissues (Rodriguez et al., 1998). Uptake by plants and release of silicate from decaying plant material could also affect the temporal variation of silicate concentrations in the water column.

Phytoplankton abundance in the Manguaba lagoon in October 2008 was high compared to other studies conducted in this region (Melo-Magalhaes et al., 2009). Cell density increased from a few hundred per liter in the river up to 47.5×10^6 cells L^{-1} . Primary production and accumulation of biomass in rivers and channels with high flushing rates is lower compared to lagoons where longer water residence times favour high biomass accumulation (Cloern, 1996; Knoppers et al., 1991). Accordingly phytoplankton biomass was higher in Manguaba lagoon which is an almost closed lagoon with low flushing rates and therefore a residence time of 5-7 weeks (Oliveira and Kjerfve, 1993).

Compared to other tropical and temperate coastal ecosystems e.g. Patos Lagoon estuary (southern Brazil), the estuary of the subtropical Tamsui River (northern Taiwan), the Guadiana estuary (south-west Iberia) and Bizerte Lagoon (western Mediterranean), the phytoplankton biomass of Manguaba lagoon is in the upper range of the values (Abreu et al., 1995;

Domingues et al., 2005; Hlaili et al., 2006; Wu and Chou, 2003). The low phytoplankton biomass in the above mentioned regions were often the result of nutrient limitation, mainly silicate, besides factors like shading or turbidity.

Subdivided into groups, phytoplankton biomass in Manguaba lagoon was dominated by Bacillariophyta except for the southern part of the lagoon and its transition zone to the channel where Cyanophyta mainly composed the biomass. The most abundant Bacillariophyta was *Cyclotella*, a solitary species which is typically found in brackish water environments (Reimann et al., 1963). *Anabaena* as the most important heterocystous cyanobacteria in the lagoon is capable to grow in waters with low nitrogen which is typical for many estuarine and coastal systems. This cyanobacteria is known as a N₂-fixing species that can bring additional nitrogen into the aquatic environment (Kohl et al., 1982). In Manguaba lagoon *Anabaena spiroides* was considered as the dominant species during the dry period (Melo-Magalhaes et al., 2009) most probably because of low nitrogen effluents from sugar cane fields in the catchment during this season. Therefore the annual succession of phytoplankton in Manguaba lagoon can change during the year depending on the community composition as well as on the availability and stoichiometry of nutrients.

Phytoplankton response to nutrient enrichment

Distinct differences in algal abundance were detected in the enrichment experiment between the control and the treatments. This indicates that algal groups responded immediately to increases in N and P

concentrations, as also reported from other coastal areas (Hlaili et al., 2006; Piehler et al., 2004; Smith, 2006; Tomasky et al., 1999).

The addition of N or P alone led already to an increase in total phytoplankton abundance and biomass, but enrichment with N and P together resulted in highest total biomass indicating a synergetic effect. Tamminen and Andersen (2007) reported similar phytoplankton biomass changes in bioassays from the Baltic Sea with strongest chlorophyll a response in treatments with combined N and P addition. They categorized the response of phytoplankton into P, N and combined limitation according to species – specific nutrient storage abilities. They also demonstrated that different phytoplankton species can adapt their metabolism by stocking nutrients in their cells and use these reserves for growing when the required nutrients were not present in the water.

In our experiment, diatoms showed the strongest response to nutrient addition and replaced chlorophytes and cyanophytes as dominant phytoplankton groups. Diatoms are known to have high uptake and growth rates and can accumulate higher biomass compared to other algae groups as long as they are not limited by silicate availability (Kudela and Dugdale, 2000). Silicate concentrations in the lagoon and thus also in our experiment were very high and had no limiting effect on the growth of diatoms. In temperate regions silicate is often a limiting nutrient because of initially low silicate concentrations and regularly appearing diatom spring blooms which lead to silicate depletion in the water column or even silicate limitation which resulted in the collapse of these spring blooms (Domingues et al.,

2005; Fisher et al., 1992). After these blooms, diatom biomass decreases and at the same time an increase in green algae biomass can be observed (Domingues et al., 2005). Hence low silicate concentrations and high N:P ratios favour growth of green algae whereas diatom growth is enhanced at high N:P and Si:P ratios (Roelke et al., 1999).

In our experiment a mean N:P ratio in the water of the control (24.6) at the start was higher than the Redfield ratio, suggesting initial P limitation whereas it was much lower in the control at the end (7.7). This points to intensified nitrogen uptake by phytoplankton over time as phosphorus concentrations were constant. At the end of the experiment, green algae showed a maximum contribution to the total phytoplankton biomass in the control. High N:P ratios are ideal for the growth of chlorophytes. Rhee (1978) showed that best N:P ratios for *Scenedesmus* development is 30. Increased nitrogen and phosphate concentrations which are expected during the rainy season from the effluent from sugar cane fields could initiate the growth of chlorophytes in Manguaba lagoon. But increasing Si:N ratios until day four of the experiment showed that enriching with N leads to a fast nitrogen and silicate consumption and results in high diatom biomass. It seems that diatoms could immediately outcompete other algal groups if N or P were supplied as it was shown in other studies (Piehler et al., 2004 and references therein).

Ecological consequences of nutrient enrichment

In tropical systems with high silicate concentrations, such as the Manguaba lagoon, an increase in nitrogen and phosphorus amounts will immediately benefit diatom growth and biomass production. An increase in nutrient availability in an aquatic system, like the input of fertilizer from agriculture, may result in rapid production and changes in phytoplankton biomass as we demonstrated in our enrichment experiment. It may eventually lead to phytoplankton blooms which are either short-term events or even periodical.

But changes in phytoplankton biomass and composition can also be caused by artificial constructions like dams. Thereby a decrease in nutrient loads to the rivers and coastal areas is caused due to the removal of nutrients in the reservoir sediment. These alterations in nutrient stoichiometry can consequently lead to radical shifts in phytoplankton communities. The most notable example for temperate regions is the construction of the dam in the Danube River which coincided with a decrease of dissolved silicate concentrations in its discharge and consequently changes in primary production in the Black Sea from diatom dominated communities to non-siliceous forms. This artificial lake effect cause longer water residence times and affected Si:N ratios stronger than changes caused by eutrophication. These decreased Si:N ratios resulted in an increase in phytoplankton cell number, composition and changes in bloom frequencies in the north western Black Sea (Humborg et al., 1997).

The development of blooms depends on the nutrient availability, the phytoplankton composition, its fast reproduction and biomass accumulation. Changes in the nutrient mix often lead to blooms of nuisance algae which are of lower food quality for higher trophic levels. Cyanobacteria which were detected mainly during the dry season in the Manguaba lagoon as reported by Melo-Magalhaes (2009) are very common nuisance algae in freshwater environments and cause often toxic blooms which can have serious health impacts on animals and humans. Diatom blooms in contrast are usually seen as an effective enhancement of classical pelagic food chains from algae via copepods to fish and less often connected with negative effects of nuisance algae stopping food web flow already at the beginning (Sommer et al., 2002). Nevertheless, high phytoplankton biomass accumulation of diatoms can also have negative ecosystem consequences resulting from strong self shading and increased mortality. The decomposition of sinking dead phytoplankton leads to oxygen depletion in deeper waters and can cause hypoxic or anoxic events in these systems (Zhang et al., 2010). A high residence time of the water body can exacerbate these phenomena because of the usually limited water circulation and exchange times in lagoon systems compared to open estuaries.

SUMMARY AND CONCLUSION

Over the last decades, there has been an increase in sugar cane cultivation in Brazil, mainly planted as monocultures which led to an increasing use of

fertilizer comprised of nitrogen, phosphate and potassium (FAO, 2004). Nutrient analyses in the Manguaba lagoon have shown that high concentrations of nutrients were carried to the lagoon by the rivers where they were rapidly consumed by phytoplankton.

Our mesocosm experiment showed that the addition of nutrients promoted mainly diatom growth because of the high silicate availability in the system. Thus the increased input of nutrients from sugar cane monocultures could lead to phytoplankton proliferations as simulated in the experiment. As high silicate concentrations seem to be a general phenomenon in the investigated tropical lagoon system it is conceivable that diatoms would be the main profiteers of increased nutrient availability, resulting in a probably high biomass flow to copepods and fish. Generally an increase in total nitrogen and total phosphate concentrations will modify Si:N and Si:P ratios. Aquatic systems in temperate regions will be strongly affected by harmful algae blooms due to silicate limitation during phytoplankton succession. In contrast, high silicate availability in tropical areas will give a competitive advantage for diatoms and thereby prevent the growth of often toxic cyanophytes or even restrain blooms of nuisance algae.

ACKNOWLEDGEMENTS

We would like to thank our Brazilian partners from the POLCAMAR project for their support during our work in Brazil. We especially thank Liliane

Tonial and the staff from UFAL in Maceio for their assistance during the expedition and for providing information and facilities and Bastiaan Knoppers for all his support. We also thank Svenja Beilfuss and Matthias Birkicht for laboratory work at ZMT. Financial support by the German Federal Ministry for Education and Research (BMBF) is gratefully acknowledged (Grant No. 03F0455D).

REFERENCES

- Abreu, P.C., Hartmann, C. and Odebrecht, C., 1995. Nutrient-rich saltwater and its influence on the phytoplankton of the patos lagoon estuary, Southern Brazil. *Estuarine, Coastal and Shelf Science*, 40(2): 219-229.
- Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. *Review of Geophysics*, 34(2): 127-168.
- Conley, D.J., Schelske, C.L. and Stoermer, E.F., 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Marine ecology progress series*. Oldendorf, 101(1-2): 179-192.
- Domingues, R.B., Barbosa, A. and Galvao, H., 2005. Nutrients, light and phytoplankton succession in a temperate estuary (the Guadiana, south-western Iberia). *Estuarine, Coastal and Shelf Science*, 64(2-3): 249-260.
- Duarte, C.M., Agusti, S. and Agawin, N.S.R., 2000. Response of a Mediterranean phytoplankton community to increased nutrient inputs: A mesocosm experiment. *Marine Ecology Progress Series*, 195: 61-70.

-
- Egge, J.K. and Aksnes, D.L., 1992. Silicate as regulating nutrient in phytoplankton competition. *Marine ecology progress series*, 83(2-3): 281-289.
- FAO, 2004. Fertilizer use by crop in Brazil. In: F.a.A.O.o.t.U. Nations (Editor). Food and Agriculture Organization of the United Nations, Rome, pp. 1-64.
- Ferreira, J.G., Wolff, W.J., Simas, T.C. and Bricker, S.B., 2005. Does biodiversity of estuarine phytoplankton depend on hydrology? *Ecological Modelling*, 187(4): 513-523.
- Filoso, S. et al., 2003. Land use and nitrogen export in the Piracicaba River basin, Southeast Brazil. *Biogeochemistry*, 65(3): 275-294.
- Fisher, T.R., Peele, E.R., Ammerman, J.W. and Harding, L.W.J., 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine ecology progress series*, 82(1): 51-63.
- Grasshoff, K., Kremling, K. and Ehrhardt, M.E., 1999. *Methods of Seawater Analysis*. third ed. Wiley-VCH(Weinheim): 600 pp.
- Hillebrand, H., Duerselen, C.D., Kirschtel, D., Pollinger, U. and Zohary, T., 1999. Biovolume calculation for pelagic and benthic microalgae. *Journal of Phycology*, 35(2): 403-424.
- Hlaili, A., Chikhaoui, M.A., El Grami, B. and Mabrouk, H., 2006. Effects of N and P supply on phytoplankton in Bizerte Lagoon (western Mediterranean). *Journal of Experimental Marine Biology and Ecology*, 333(1): 79-96.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology*, 19: 89-110.
- Humborg, C., Ittekkot, V., Cociasu, A. and Bodungen, B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature*, 386(6623): 385-388.
- Jeffrey, S.W. and Humphrey, G.F., 1975. New spectrophotometric equations for determining chlorophylls a, b, c₁ and c₂ in algae, phytoplankton and higher plants. *Biochem. Physiol. Pflanz.*, 167: 191-194.
- Keeping, M.G., Kvedaras, O.L. and Bruton, A.G., 2009. Epidermal silicon in sugarcane: Cultivar differences and role in resistance to sugarcane

- borer *Eldana saccharina*. *Environmental and Experimental Botany*, 66(1): 54-60.
- Klausmeier, C.A., Litchman, E., Daufresne, T. and Levin, S.A., 2004. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature*, 429(6988): 171-174.
- Knoppers, B., Kjerfve, B. and Carmouze, J.P., 1991. Trophic state and water turn-over time in six choked coastal lagoons in Brazil. *Biogeochemistry*, 14: 149-166.
- Kohl, J.G., Baierova, J. and Dudel, G., 1982. Die Bedeutung der Stickstoff-fixierenden Blaualgen für den Stoffhaushalt stehender und gestauter Binnengewässer. *Acta Hydrochimica et Hydrobiologica*, 10(5): 415-437.
- Kudela, R.M. and Dugdale, R.C., 2000. Nutrient regulation of phytoplankton productivity in Monterey Bay, California. *Deep Sea Research Part II: Topical Studies in Oceanography*, 47(5-6): 1023-1053.
- Le Blond, J.S., Horwell, C.J., Williamson, B.J. and Oppenheimer, C., 2010. Generation of crystalline silica from sugarcane burning. *Journal of Environmental Monitoring*, 12(7): 1459-1470.
- Lund, J.W., Kipling, G. and LeCreen, E.D., 1958. The inverted microscope method of estimating algae numbers and the statistical basis of estimation by counting. *Hydrobiologia*, 11: 143-170
- Macedo, I.C., Seabra, J.E.A. and Silva, J.E.A.R., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy*, 32(7): 582-595.
- Martinelli, L.A. and Filoso, S., 2008. Expansion of sugarcane ethanol production in Brazil: environmental and social challenges. *Ecological Applications*, 18(4): 885-898.
- McGlathery, K.J., 2001. Macroalgal blooms contribute to the decline of seagrass in nutrient-enriched coastal waters. *Journal of Phycology*, 37(4): 453-456.
- Melo-Magalhaes, E.M., Medeiros, P.R.P., Lira, M.C.A., Koenig, M.L. and Moura, A.N., 2009. Determination of eutrophic areas in Mundau/Manguaba lagoons, Alagoas-Brazil, through studies of the

-
- phytoplanktonic community *Brazilian Journal of Biology*, 69(2): 271-280.
- Officer, C.B. and Ryther, J.H., 1980. The possible Importance of Silicon in Marine Eutrophication. *Marine Ecology Progress Series*, 3: 83-91.
- Oliveira, A.M. and Kjerfve, B., 1993. Environmental Responses of a Tropical Coastal Lagoon System to Hydrological Variability: Mundau-Manguaba, Brazil. *Estuarine, Coastal and Shelf Science*, 37(6): 575-591.
- Paerl, H.W. et al., 1999. Rainfall stimulation of primary production in western Atlantic Ocean waters: Roles of different nitrogen sources and co-limiting nutrients. *Marine Ecology Progress Series*, 176: 205-214.
- Piehl, M.F., Twomey, L.J., Hall, N.S. and Paerl, H.W., 2004. Impacts of inorganic nutrient enrichment on phytoplankton community structure and function in Pamlico Sound, NC, USA. *Estuarine, Coastal and Shelf Science*, 61(2): 197-209.
- Quiblier, C., Leboulanger, C., Sane, S. and Dufour, P., 2008. Phytoplankton growth control and risk of cyanobacterial blooms in the lower Senegal River delta region. *Water Research*, 42(4-5): 1023-1034.
- Rabalais, N. et al., 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. *Estuaries and Coasts*, 19(2): 386-407.
- Rahm, L., Conley, D., Sandén, P., Wulff, F. and Stalnacke, P., 1996. Time series analysis of nutrient inputs to the Baltic Sea and changing DSi:DIN ratios. *Marine Ecology Progress Series*, 130: 221-228.
- Reimann, B.E.F., Lewin, J.M.C. and Guillard, R.R.L., 1963. *Cyclotella cryptica*: a new brackish-water diatom species. *Phycologia*, 3: 75-84.
- Rhee, G.Y., 1978. Effects of N:P Atomic Ratios and Nitrate Limitation on Algal Growth, Cell Composition, and Nitrate Uptake. *Limnology and Oceanography*, 23(1): 10-25.
- Rocha, O. and Duncan, A., 1985. The relationship between cell carbon and cell volume in freshwater algal species used in zooplankton studies. *Journal of Plankton Research*, 7: 279-294.

- Rodriguez, S.A., Avila-Perez, P. and Barcelo-Quintal, I., 1998. Bioaccumulation of chemical elements by water hyacinth (*Eichhornia crassipes*) found in "Jose Antonio Alzate" dam samples in the State of Mexico, Mexico. *Journal of Radioanalytical and Nuclear Chemistry*, 238(1): 91-95.
- Roelke, D., Eldridge, P. and Cifuentes, L., 1999. A model of phytoplankton competition for limiting and nonlimiting nutrients: Implications for development of estuarine and nearshore management schemes. *Estuaries and Coasts*, 22(1): 92-104.
- Savant, N.K., Korndörfer, G.H., Datnoff, L.E. and Snyder, G.H., 1999. Silicon nutrition and sugarcane production: A review. *Journal of Plant Nutrition*, 22(12): 1853 - 1903.
- Scheffer, F. and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde*. Spektrum Akademischer Verlag GbmH, Heidelberg.
- Schindler, D.W., 1974. Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management. *Science*, 184(4139): 897-899.
- Smith, V.H., 2006. Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. *Limnology and Oceanography*, 51(1): 377-384.
- Sommer, U., Stibor, H., Katchakis, A., Sommer, F. and Hansen, T., 2002. Pelagic food web configurations at different levels of nutrient richness and their implications for the ratio fish production:primary production. *Hydrobiologia*, 484(1): 11-20.
- Souza, M.F., Kjerfve, B., Knoppers, B., Landim de Souza, W.F. and Damasceno, R.N., 2003. Nutrient budgets and trophic state in a hypersaline coastal lagoon: Lagoa de Araruama, Brazil. *Estuarine, Coastal and Shelf Science*, 57(5-6): 843-858.
- Sutcliffe, D.W. and Jones, J.G., 1992. *Eutrophication: Research and Application to Water Supply*. Freshwater biological association, Ambleside (UK)
- Talling, J.F. and Lemoalle, J., 1998. *Ecological Dynamics of Tropical Inland Waters*. Cambridge University Press, Cambridge, 451 pp.
- Tamminen, T. and Andersen, T., 2007. Seasonal phytoplankton nutrient limitation patterns as revealed by bioassays over Baltic

- Seagradients of salinity and eutrophication. *Mar. Ecol. Prog. Ser.*, 240: 121–138.
- Taylor, D.I. et al., 1995. Responses of coastal lagoon plant communities to different forms of nutrient enrichment -- a mesocosm experiment. *Aquatic Botany*, 52(1-2): 19-34.
- Tilman, D., Kilham, S.S. and Kilham, P., 1982. Phytoplankton Community Ecology: The Role of Limiting Nutrients. *Annual Review of Ecology and Systematics*, 13: 349-372.
- Tomasky, G. et al., 1999. Nutrient limitation of phytoplankton growth in Waquoit Bay, Massachusetts, USA: a nutrient enrichment study. *Aquatic Ecology*, 33(2): 147-155.
- Turner, R.E. et al., 1998. Fluctuating Silicate:Nitrate Ratios and Coastal Plankton Food Webs. *Proceedings of the National Academy of Sciences of the United States of America*, 95(22): 13048-13051.
- Turner, R.E. and Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi river delta. *Nature*, 368: 619-621.
- Turner, R.E. and Rabalais, N.N., 2003. Linking Landscape and Water Quality in the Mississippi River Basin for 200 Years. *Bioscience*, 53(6): 563-572.
- UNICA, 2001. *Energia da Cana-de-Açúcar e Redução do Efeito Estufa.*, São Paulo.
- Utermöhl, H., 1958. Zur Vervollkommnung der quantitativen Phytoplanktonmethodik. *Mitt. Verein.Theor. Angew. Limnol.*, 9: 1-38.
- Vuorio, K., Lagus, A., Lehtimaeki, J.M., Suomela, J. and Helminen, H., 2005. Phytoplankton community responses to nutrient and iron enrichment under different nitrogen to phosphorus ratios in the northern Baltic Sea. *Journal of Experimental Marine Biology and Ecology*, 322(1): 39-52.
- Wehr, J.D. and Descy, J.P., 1998. Use of phytoplankton in large river management. *Journal of Phycology*, 34(5): 741-749.
- Wu, J. and Chou, T., 2003. Silicate as the limiting nutrient for phytoplankton in a subtropical eutrophic estuary of Taiwan. *Estuarine, Coastal and Shelf Science*, 58(1): 155-162.

Zhang, J. et al., 2010 Natural and human-induced hypoxia and consequences for coastal areas: Synthesis and future development. *Biogeosciences*, 7 1443-1467.

CHAPTER II

Phytoplankton dynamics
along a salinity and nutrient gradient
in a sugar cane impacted
tropical lagoon in northeast Brazil

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn,
Svenja Beilfuss, Enaide Melo-Magalhães,
Paulo Petter, Bastiaan Knoppers

In preparation



**Phytoplankton dynamics along a salinity
and nutrient gradient in a sugar cane impacted
tropical lagoon in northeast Brazil**

Gertrud Spörl, Herwig Stibor, Tim Jennerjahn, Svenja Beilfuss, Enaide
Melo-Magalhães, Paulo Petter, Bastiaan Knoppers

ABSTRACT

Phytoplankton community composition and diversity are highly variable in coastal lagoons due to fast changing environmental factors such as nutrients and salinity. We investigated the Mundau Manguaba Lagoon in northeast Brazil which is characterized by nutrient input from sugar cane cultivation and strong temporal changes in tidal intrusion. This affects salinity and nutrient availability and thereby consequently also phytoplankton communities.

During samplings in September 2007, February 2008 and October 2008 highest phytoplankton diversity could be detected in the incoming rivers dominated by typical freshwater species. Cyanobacteria showed an advantage under high temperature and partly under high salinity conditions in combination with low nutrient concentrations. High nutrient availability favoured more for diatoms. The estimation of fast changing environmental

conditions and thereby phytoplankton community composition provide support to characterize water quality and ecosystem conditions.

KEYWORDS

Phytoplankton diversity, salinity, nutrients, tropical lagoon, sugar cane, Brazil

INTRODUCTION

Coastal lagoon systems are transitional zones which are often associated with rapid changes in environmental variables such as salinity, temperature and light. The diversified abiotic conditions, in addition to changing nutrient availability, influence the phytoplankton composition and the species diversity in these areas (Hecky and Kilham, 1988). Marine organisms are used to saline water where nutrients are generally diluted, whereas freshwater species are adapted to usually higher nutrient concentrations. Estuaries and coastal lagoons are special environments because of permanently changing nutrient and salinity conditions. These changes in salinity lead to osmotic stress and play a major role in algae growth and structuring phytoplankton communities in the ecosystems (Kirst, 1989; Rijstenbil, 1988).

Some marine and freshwater species have developed strategies to tolerate salinity fluctuations and survive in brackish water environments. But it is also known that a salinity of approximately 5 forms a lethal barrier for most

phytoplankton species and their diversity is lowest at around this value (Redden and Rukminasari, 2008; Rijstenbil, 1988). Along an estuarine gradient, the distribution of phytoplankton species shows usually a tendency for cyanobacteria and chlorophytes in brakish waters and dinoflagellates and diatoms in more saline waters (Kies, 1997; Muylaert and Sabbe, 1999).

Phytoplankton dynamics and nutrient availability are tightly coupled and systems in transitional zones are also quite complex in nutrient dynamics due to changing freshwater and tidal input (Alpine and Cloern, 1992; Gao and Song, 2005). A distinct increase of anthropogenic impacts such as growing population density, industrial development and intensive agriculture has further contributed to increasing nutrient loads into coastal lagoons. Hence, phytoplankton composition is often used as a parameter for water quality and phytoplankton plays an important role in biogeochemical and ecosystem processes such as the transformation and cycling of key elements with direct and indirect impacts on food webs (Sherrard et al., 2006). However the question arises, whether phytoplankton diversity, which is often used as a predictor of environmental change and water quality, can be easily used for that purpose in such highly diverse and fluctuating environments.

Mundau Manguaba Lagoon in northeast Brazil represents an important coastal ecosystem which is under agricultural and industrial pressure. During the last decades, sugar cane cultivation increased considerably and therefore also the sugar cane industry (FAO, 2004). Raised nutrient loads

(in particular nitrogen and phosphate) are transported in Brazilian rivers and can result in spatial and seasonal differences in nutrient concentrations in the systems (Martinelli and Filoso, 2008). Consequently, changes in element cycling, phytoplankton species composition and food chain structure in these systems have to be expected. An experimental enrichment study with surface water of the Manguaba lagoon has already suggested important shifts in phytoplankton composition from cyanobacteria to diatoms with enhanced concentrations of nitrogen and phosphate. Diatom growth was favored in the lagoon because of very high silicate amounts from soil leaching in the surrounding area and the hinterland (Spörl et al, submit.).

In this study we investigated seasonal and spatial variations of phytoplankton diversity and community composition and their relation to environmental parameters in two lagoons along a gradient from freshwater to marine waters. The regulating factors for phytoplankton composition and seasonal succession are important key parameters to understand the dynamics of tropical lagoon ecosystems in more detail (Gallegos and Jordan, 1997; Pennock and Sharp, 1994). To predict and characterize responses of these ecosystems to further environmental changes it is necessary to know how the heterogeneity in environmental conditions transfers into heterogeneity of phytoplankton composition.

STUDY AREA

Two shallow lagoons build the Mundau Manguaba Lagoon in northeast Brazil, in the state of Alagoas (latitudes 9°35' and 9°36'S, longitudes 35°44' and 35°58'W). A narrow channel system connects these lagoons which each other and with the ocean (Fig. 1).

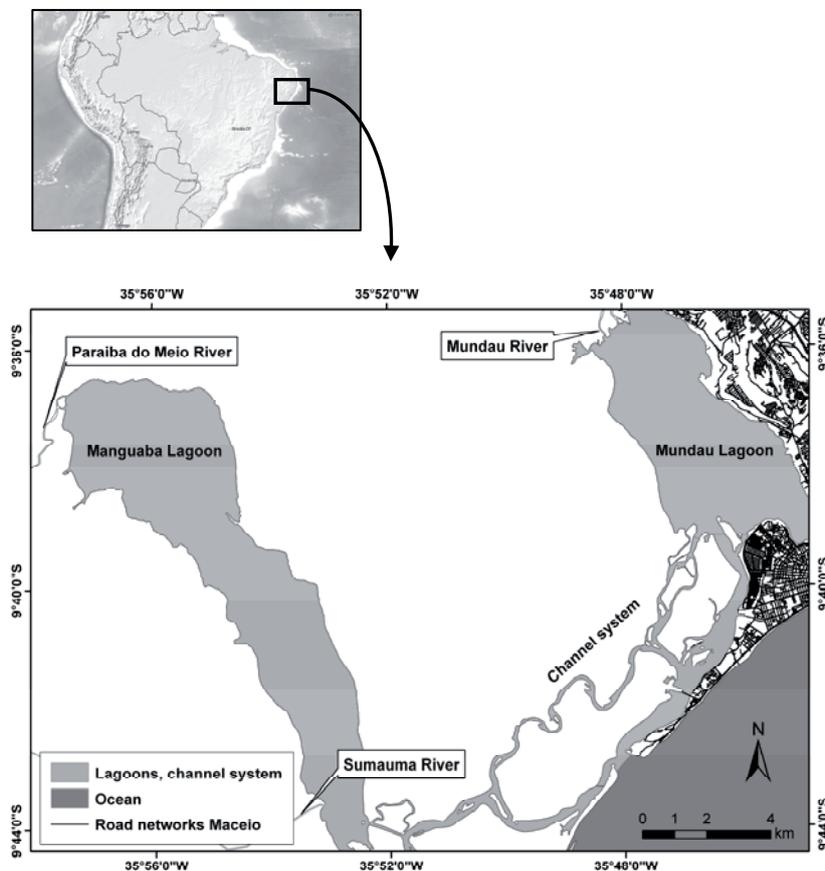


Figure 1: Map of the Mundau Manguaba Lagoon, in northeast Brazil.

The mangrove fringed channels have a joint outlet which leads into the Atlantic Ocean. The Manguaba Lagoon covers an area of 43 km² and is surrounded by sugar cane fields while the 24 km² Mundau Lagoon is

additionally influenced by effluents from the city of Maceio which has 900,000 inhabitants (Oliveira and Kjerfve, 1993). The system has a total dimension of 79 km² with an average depth of 2 m.

The dry season of the tropical climate is from November to March and the rainy season from May to August with an average annual precipitation of 1654 mm (Fig. 2). Mundau River discharges annually an average of 33.5 m³s⁻¹ into the Mundau Lagoon, Paraiba do Meio and Sumauma River 17.6 m³s⁻¹ and 5 m³s⁻¹, respectively, into the Manguaba Lagoon (Oliveira and Kjerfve, 1993; Souza et al., 2003). Most of the tidal energy from semi-diurnal tides dissipates in the connecting channels between the ocean and the lagoons. The different sizes of the lagoons and the channels cause an average residence time of around 1-2 weeks for Mundau Lagoon and 5-7 weeks for Manguaba Lagoon, respectively (Oliveira and Kjerfve, 1993).

The northeast of Brazil is the second largest sugar cane production area in the country. During the last decades sugar cane cultivation increased enormously because of its use as bio fuel for the automobile industry (FIAN and GTZ, 2002). Consequently the consumption of fertilizers like nitrogen, phosphate and potassium as well as organic fertilizers has risen substantially (FAO, 2004).

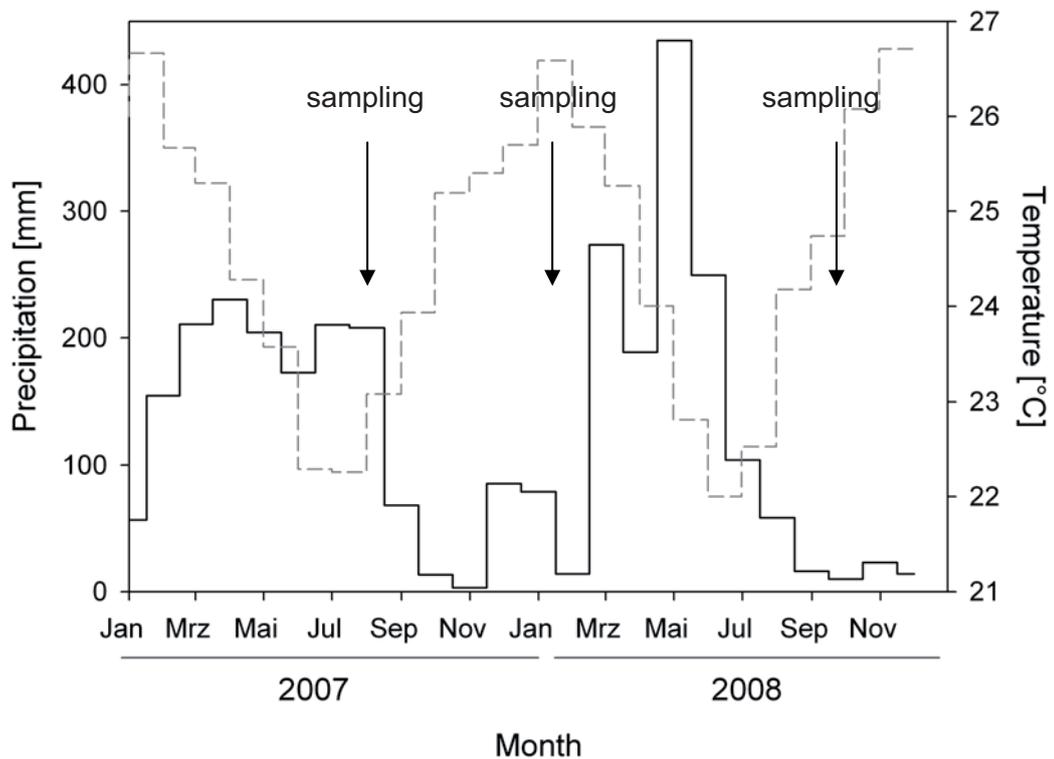


Figure 2: Average monthly precipitation (continuous line) and temperature (dashed line) during the investigated period 2007 – 2008.

MATERIAL AND METHODS

Sampling and analyses

Water samples were taken along a salinity gradient from marine water to freshwater in September 2007 (Sep 07), February 2008 (Feb 08) and October 2008 (Oct 08). Hydrodynamic and geographical characteristics divide the lagoon into three units: the channels (estuary), the lagoons and the rivers (freshwater).

Salinity and temperature of the surface water were measured directly with a *WTW MultiLine* multiparameter sensor. Water samples for dissolved

inorganic nutrients, chlorophyll a and phytoplankton were collected in both lagoons with a Niskin bottle near surface (~ 0.5 m depth). Water samples for nutrient analysis (nitrite, nitrate, ammonium, silicate and phosphate) were filtered through single use membrane filters (0.45 μm pore size) into prewashed PE bottles and stored frozen until the analysis according to Grasshoff et al. (1999). For the determination of chlorophyll a, water was filtered through *Whatmann* GF/F filters and stored frozen until the analysis. Chlorophyll a concentrations were determined following the method of Jeffrey and Humpfrey (1975).

Phytoplankton samples were taken in Sep 07 and Feb 08 by using a 20 μm plankton net and in Oct 08 by sampling surface water directly with brown glass bottles. The phytoplankton samples were fixed with Lugol's iodine and kept in darkness. Phytoplankton was identified and counted with an inverted *Zeiss Axiovert 200* microscope according to Utermöhl (1958). Where possible, at least 400 cells were counted to keep a counting precision of $\pm 10\%$, when cells were randomly distributed (Lund et al., 1958). Biomass was estimated as volume of the species cells by using geometric configurations (Hillebrand et al., 1999) and converted into biomass and cell carbon content (Cc) according to Rocha and Ducan (1985).

Biological diversity (H') (Shannon-Wiener index) and evenness (J) were calculated according to the following equation:

$$H' = \sum_{i=1}^S Pi \ln Pi; (Pi = Ni / N)$$

$$J = H' / \ln S$$

where N is the total amount of phytoplankton biomass, N_i is the individual amount of species biomass and S is the total number of species.

Percentage similarity between single close-by stations was determined by using the equation of Krebs (1989).

Statistics

The Bray-Curtis coefficient was used to produce a similarity matrix of species biomass between seasons and sampling sites (Coph. corr. = 0.9). Thereby average biomass values were used for the Mundau and Manguaba lagoon and the channels, whereas only single station were taken for the rivers. Multivariate statistical analysis was conducted in PAST Version 2.04 (Hammer et al., 2001).

RESULTS

Physico-chemical water parameters in the lagoons

Water level in the lagoons varied greatly (0.6 – 7.1 m) and average depth was between 2.1 and 3.5 m during the different sampling seasons in the lagoons (Tab. 1). Average temperature was highest during the sampling in Feb 08 with values of 30.4 and 30.3 °C in the Manguaba lagoon and the Mundau lagoon, respectively.

Average pH was similar at the sampling sites during the seasons but showed strongest variations in Sep 07 in the Manguaba lagoon. A minimum pH value of 5.7 was detected in the Manguaba channel in Sep 07; the pH reached values up to 9.2 inside the lagoon.

Dissolved oxygen concentrations were only measured in Oct 08 and varied from 4.7 mg l⁻¹ to 12.2 mg l⁻¹ (59.7 – 156.7% oxygen saturation) in the system. The highest oxygen amounts in the Manguaba were detected at

Table 1: Minimum, maximum and average values with standard deviation for physico-chemical parameter and chlorophyll a measured in Mundau Manguaba Lagoon system in Sep 07, Feb 08, Oct 08.

		Sep 07		Feb 08		Oct 08	
		Manguaba	Mundau	Manguaba	Mundau	Manguaba	Mundau
Temperature (°C)	Min	26,7	26,7	29,3	28,8	23,3	27,3
	Max	28,8	31,0	31,1	31,0	28,8	28,0
	AVG (± STDEV)	27.7 (± 0.6)	28.5 (± 1.7)	30.4 (± 0.6)	30.3 (± 0.7)	27.2 (± 1.9)	27.7 (± 0.3)
Depth (m)	Min	0,6	2,2	0,9	0,6	0,9	0,9
	Max	3,8	7,1	3,1	6,8	4,6	6,8
	AVG (± STDEV)	2.3 (± 1.0)	3.5 (± 1.7)	2.1 (± 0.8)	3.1 (± 2.0)	2.6 (± 1.2)	3.2 (± 1.0)
pH	Min	5,7	7,5	6,9	7,0	7,5	7,0
	Max	9,2	8,9	9,2	8,3	9,0	8,5
	AVG (± STDEV)	8.2 (± 0.8)	8.5 (± 0.5)	8.3 (± 0.8)	7.8 (± 0.5)	8.1 (± 0.5)	8.0 (± 0.6)
Oxygen (mg l ⁻¹)	Min	-	-	-	-	5,7	4,7
	Max	-	-	-	-	12,2	11,1
	AVG (± STDEV)					9.2 (± 2.1)	7.8 (± 1.9)
Chlorophyll a (µg l ⁻¹)	Min	-	-	7,0	0,2	2,9	2,6
	Max	-	-	60,1	26,5	47,0	12,4
	AVG (± STDEV)			25.9 (± 22.2)	11.3 (± 11.0)	23.5 (± 14.6)	7.2 (± 3.2)

the transition zone between channel and lagoon whereas the lowest values were measured in the middle of the lagoon. The Mundau lagoon showed a different pattern. While highest oxygen concentrations (~11.1 mg l⁻¹) were

found in the middle of the lagoon, lowest concentrations ($\sim 4.7 \text{ mg l}^{-1}$) were measured in the transitions zone between lagoon and river.

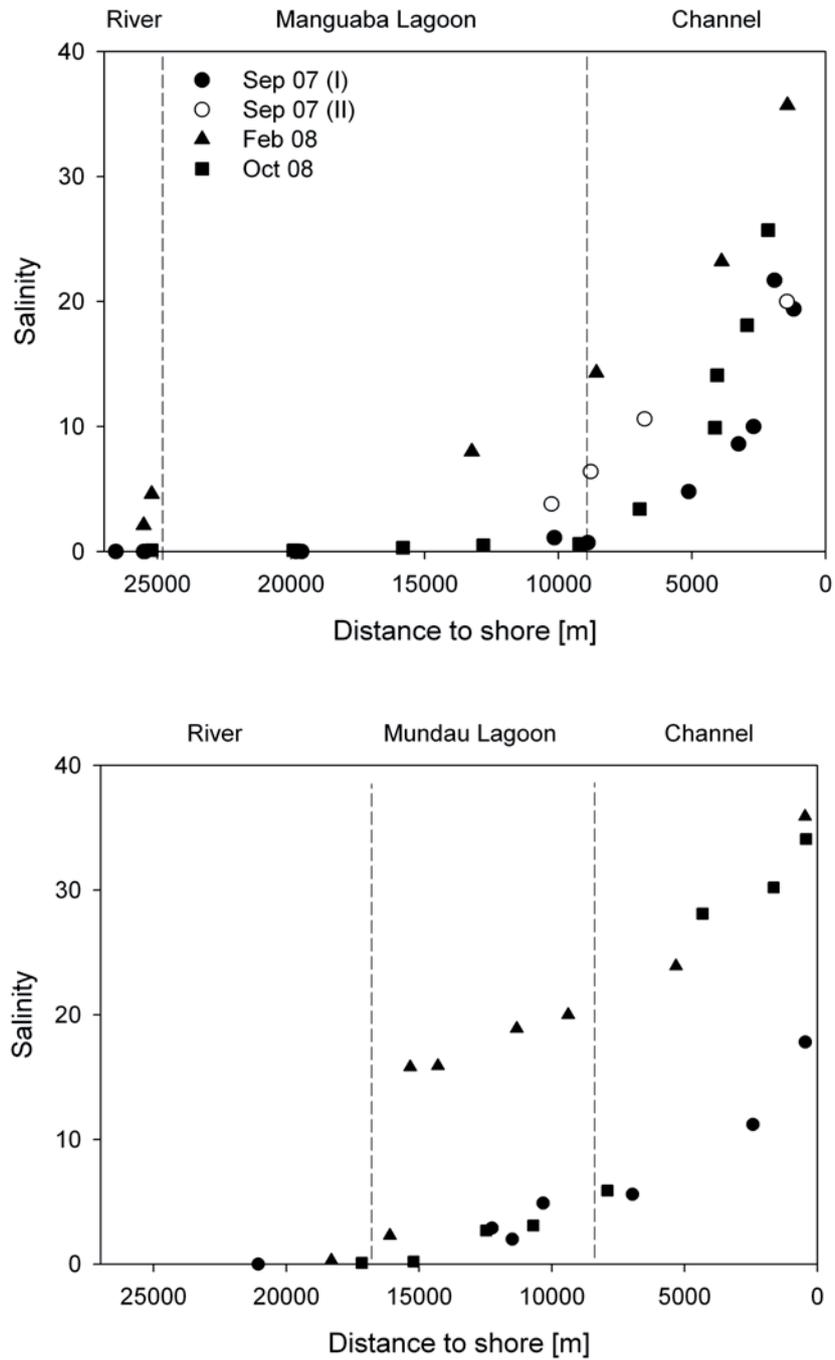


Figure 3: Tidal influence and changes in salinity along the distance in Manguaba and Mundau lagoon in Sep 07, Feb 08 and Oct 08

In Sep 07 lowest salinity values were measured in the lagoons and the channels (Fig. 3). During this season the lagoons were strongly influenced by freshwater input because of high precipitation on single days before the sampling (Fig. 2). Salinity varied on a spatial and temporal scale depending on hydrological changes between evaporation, freshwater and seawater inputs. The Mundau lagoon is generally stronger influenced by saline waters because of a better connection of the lagoon with the ocean and therefore a lower dissipation of tidal energy. Therefore marine water can penetrate up to the northern part of the Mundau lagoon which also results in a short residence time therein.

Spatial and temporal changes in dissolved nutrient concentrations

Dissolved nutrients differed both seasonally and spatially along the gradient from freshwater to the ocean. Dissolved inorganic nitrogen (DIN) concentrations varied between 8.9 and 14.9 μM in Paraiba do Meio and 13.3 and 23.1 μM in Rio Mundau during the different sampling seasons (Fig. 4). During all seasons higher DIN concentrations could be detected in Rio Mundau. Nitrite levels were always $<1 \mu\text{M}$. In Sep 07 and Oct 08 the concentration of nitrate entering the Manguaba lagoon was greater than ammonium (42 and 10%) whereas in Feb 08 ammonium was dominating the DIN with 98%. Nitrogen concentrations in Rio Mundau showed a converse pattern with higher ammonium concentrations in Sep 07 and Oct 08 (67 and 79%) and nitrate as main portion (59%) in Feb 08. Inside the lagoons DIN values generally decreased on the gradient from freshwater to marine water. Nutrient peaks inside the channels could be detected mainly during Sep 07 and Feb 08.

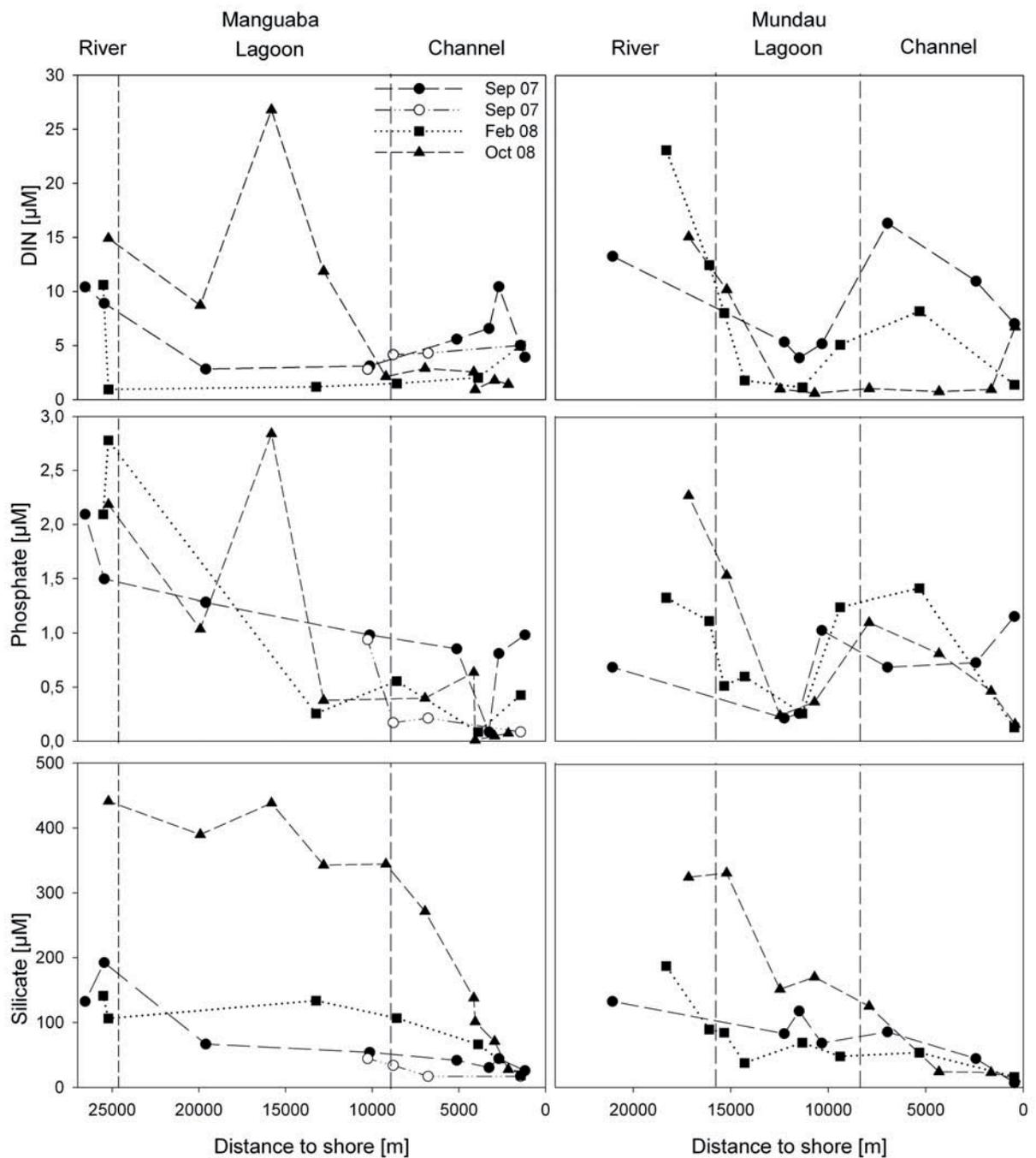


Figure 4: Variation in nutrient concentrations along distance at sampling stations in Manguaba and Mundau lagoon in Sep 07, Feb 08 and Oct 08.

Dissolved phosphate levels ranged from 0.1 to 2.8 μM in the Manguaba lagoon and from 0.1 to 2.3 μM in the Mundau lagoon. The concentrations decrease towards the ocean with little increases in the channels and

reached minimum values of 0.1 μM close to the entrance to the ocean except for Sep 07.

Highest silicate values (440.9 μM) were measured in Oct 08 in the Paraiba do Meio and were twice as high compared to Sep 07 and Feb 08 with maximum values of 199.6 μM and 186.9 μM , respectively (Fig. 4). Silicate levels dropped rapidly inside the lagoons and the channels. In the Mundau lagoon generally lower silicate concentrations were measured; a minimum of 6.9 μM was detected in the Mundau channel in Sep 07.

Phytoplankton distribution, composition and diversity

Chlorophyll a concentrations were only measured in Feb 08 and Oct 08. Average chlorophyll a concentrations measured in Feb 08 were at least twice as high in the Manguaba lagoon ($25.9 \pm 22.2 \mu\text{g l}^{-1}$) compared to the Mundau lagoon ($11.3 \pm 11.0 \mu\text{g l}^{-1}$; Tab. 1). There was a high temporal variation in maximum chlorophyll a values between Feb 08 and Oct 08. Generally highest chlorophyll a values were detected inside the lagoons except for Oct 08. During this sampling chlorophyll a peaks shifted from the Manguaba lagoon into the connecting channel and reached highest values in the transitions zone. Lowest chlorophyll a concentrations were generally measured in the rivers Rio Mundau and Paraiba do Meio in Feb 08 as well as in Oct 08.

Table 2: Phytoplankton cell abundance in the rivers, lagoons and channels of Manguaba and Mundau system in Sep 07, Feb 08 and Oct 08.

	Sep 07			Feb 08			Oct 08		
	Cyanophyta (%)	Diatoms (%)	Chlorophyta Total (* 10 ⁶ cells l ⁻¹)	Cyanophyta (%)	Diatoms (%)	Chlorophyta Total (* 10 ⁶ cells l ⁻¹)	Cyanophyta (%)	Diatoms (%)	Chlorophyta Total (* 10 ⁶ cells l ⁻¹)
Paraiba do Meio	37	53	0,865	78	16	0,610	27	54	0,368
Manguaba Lagoon	73	24	16,200	48	50	6,166	61	33	6,236
Manguaba Channel	9	85	11,849	47	53	8,157	72	23	16,667
Rio Mundau	13	72	0,613	86	13	0,438	19	65	0,386
Mundau Lagoon	72	25	14,731	82	18	6,123	59	36	3,131
Mundau Channel	48	50	2,052	0	100	4,456	64	32	0,852

During the studied period phytoplankton cell density and composition differed between seasons and also between zones. Total cell quantity was generally higher in the Manguaba lagoon than in the Mundau lagoon. Highest cell abundance was recorded in the Manguaba lagoon in Sep 07 with $16.2 * 10^6$ cells l^{-1} mainly composed of Cyanobacteria (73 %) and $11.8 * 10^6$ cells l^{-1} in the channel represented with 85 % by Bacillariophyta (Tab. 2). In Feb 08 total phytoplankton abundance was low compared to Sep 07 and Oct 08. During this season Chlorophyta were present only in a very small number. Cell density in Oct 08 was highest in the Manguaba channel with $16.6 * 10^6$ cells l^{-1} and was dominated by Cyanobacteria.

Highest total cell density in the Mundau lagoon was counted in Sep 07 ($14.7 * 10^6$ cells l^{-1}). Both in Sep 07 and Feb 08 phytoplankton community in the Mundau lagoon was predominantly determined by Cyanobacteria (72% and 82%, respectively). Bacillariophyta determined the total phytoplankton composition in the Mundau channel in Feb 08 (100%). In Oct 08 cell number in the Mundau lagoon and channel was clearly below the number of cells compared to the other sampling seasons.

Diversity of phytoplankton calculated by the Shannon – Wiener diversity index and evenness were in general higher in the Mundau lagoon compared to the Manguaba lagoon (Fig. 5). Lowest average values were calculated for the Manguaba system during the first sampling in Sep 07 within the channel ($H'_{channel} = 0.3$). This low value inside the channel coincided with high phytoplankton abundance, dominated by Bacillariophyta (85%). In Feb 08 maximum diversity and evenness were

found in both systems, although cell abundance was low during this season. During all seasons, the diversity index and evenness were always highest in the rivers with values between 0.9 and 1.9 for diversity and 0.3 and 0.6 for evenness.

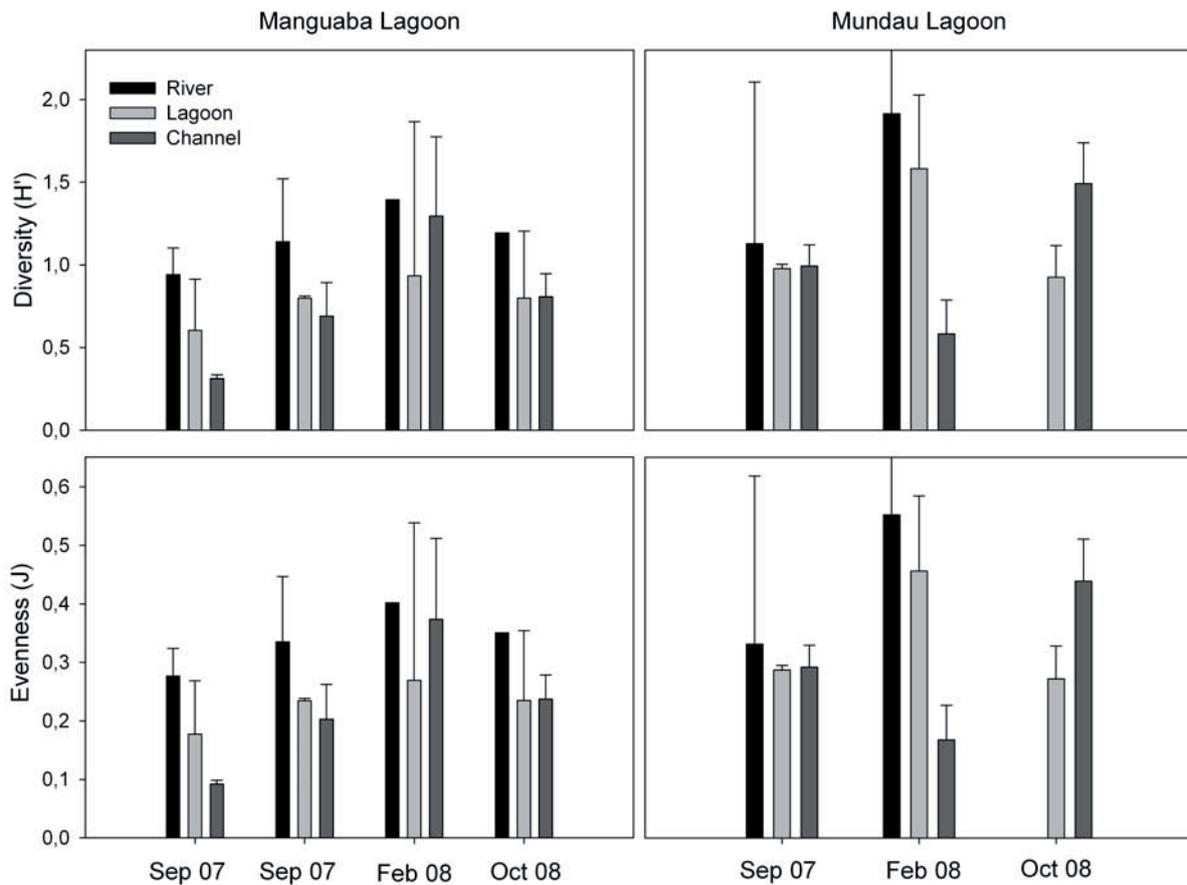


Figure 5: Spatial phytoplankton trends of Shannon – Wiener diversity index (H') and evenness (J) in Manguaba lagoon and Mundau lagoon system during Sep 07, Feb 08 and Oct 08. The lagoon systems are divided in channel, lagoon and river.

Multivariate statistical analysis demonstrated that the grouping pattern of average phytoplankton biomass was primarily determined by sampling season. Study site or salinity spreading seemed to have a minor impact (Figure 6). The biomass at the different zones inside the lagoon system and

the different seasons subdivided the system into three major groups (A - C) on a similarity level of 0.06. Group A was comprised of samples from the rivers and Mundau channel in Oct 08, group B contained samples from the total system during the sampling in Sep 07 and group C included samples

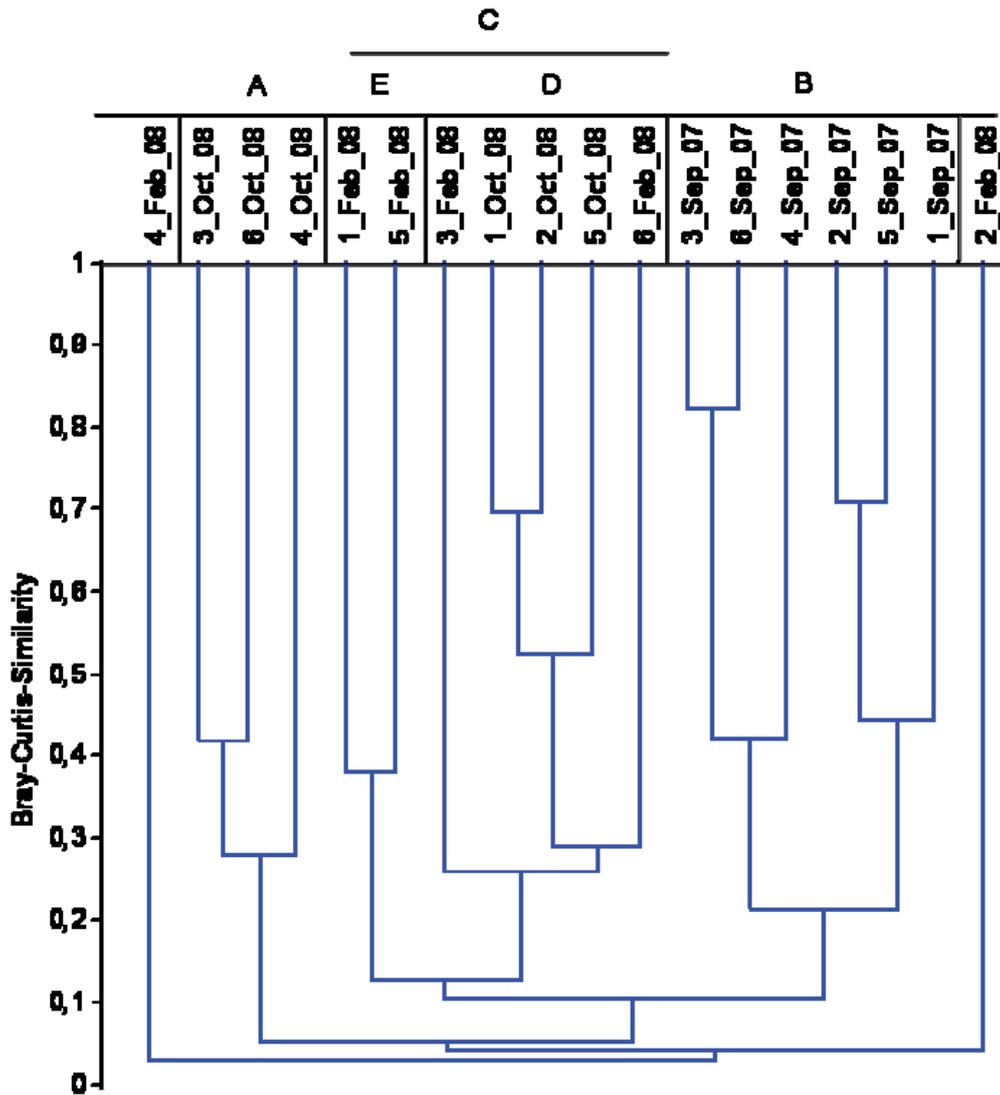


Figure 6: Cluster analysis of average phytoplankton biomass divided into zones in the lagoon system from Sep 07, Feb 08 and Oct 08.

from the sampling in Feb 08 and Oct 08. This group was separated further into group D and E on a similarity level of 0.12 and clustered samples from Oct 08 and from Feb 08. Phytoplankton biomass from Manguaba lagoon and Mundau channel in Feb 08 had a very low similarity to the other groups.

The percentage similarity index for algal communities from nearby stations varied strongly on a temporal and spatial scale. Highest differences between communities of close-by stations were calculated in Manguaba lagoon in Sep 07 whereas lowest values were detected in Feb 08 (Fig. 7). These high fluctuations were usually observed at the transitions zone from the lagoon to the channel or in the area close to the shore line. The change of the diversity index in Feb 08 was accompanied by a community shift from a mainly diatom dominated phytoplankton composition to a community with a high proportion of chlorophytes from the order of *Volvocales* in the transitions zone which alters again to an only diatom represented community close to the ocean. In Sep 07 a transformation in phytoplankton

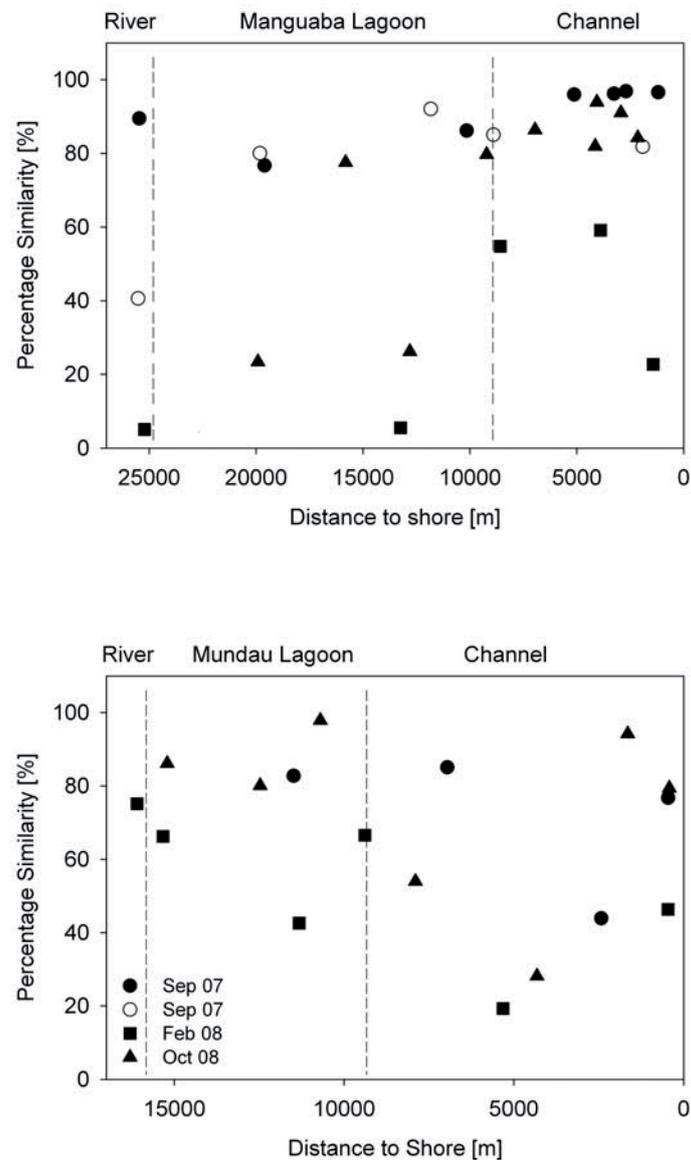


Figure 7: Percentage similarity index in Manguaba lagoon and Mundau lagoon system during Sep 07 (dot), Feb 08 (square) and Oct 08 (triangle). Thereby two transects were sampled during different days in Manguaba lagoon in Sep 07.

community was detected between the river and the lagoon with strongest shifts in the composition of chlorophytes. In Oct 08 percentage similarity index changed inside the lagoon and the channel. A shift from a community with reduced diatom biomass but high abundance of *Anabaena sp.* as only

Cyanobacteria into a community which was mainly dominated by *Coelastrum sp.*, *Scenedesmus sp.* and *Tetraedron sp.* could be observed.

Lowest values of percentage similarity index were detected in the Mundau lagoon in Feb 08. Thereby strong variations in the communities could be observed at the transitions zone between the lagoon and the channel. These patterns showed a shift from a community with 12 % of Cyanobacteria inside the lagoon to a community without Cyanobacteria inside the channel. At the same time a huge proportion of diatoms was detected in the stations in the channel and decreased towards the lagoon from 52% to 0.5%. Similar community composition shifts from diatoms to cynaobacteria were detected in Sep 07 and Oct 08.

DISCUSSION

Salinity related heterogeneity of phytoplankton biomass

Alterations in seasonal and temporal tidal intrusion and changing riverine nutrient loads influence the phytoplankton community structure due to circulation patterns and horizontal or vertical mixing processes (Redden and Rukminasari, 2008). Rapid changes in species composition and abundance between close-by stations could be observed in the Mundau and Manguaba lagoons mainly in the transitions zone between marine and freshwater systems. A replacement of Cyanobacteria by diatoms in the estuaries suggested that most species in the Mundau Manguaba lagoon

occurred within relative narrow salinity ranges with only low signs of adaptation to not species-specific environments.

The Shannon Wiener index showed generally highest phytoplankton diversity in Paraiba do Meio and Rio Mundau where usually no penetration of saline water was measured. However, maximum salinities of 2.1 were detected at the river mouth of Paraiba do Meio in February 2008. According to Telesh (2004) typical plankton diversity and abundance in the Baltic estuary changed on a spatial and temporal scale along a physical, chemical and biological gradient and is most diverse under the salinity level of 5-8.

Salinities within this range can form a lethal barrier for several species which results in reduced phytoplankton diversity because of osmotic stress and lowest diversity could be found in brackish systems, compared with freshwater and marine systems (Schallenberg 2003, Flöder 2004). Brackish water conditions were mainly found in huge parts in the lagoons and the channels, accompanied by low phytoplankton diversity and species abundance.

In February 2008 high salinities (up to 20) were even detected inside the Mundau lagoon which coincided with high phytoplankton diversity in the lagoon and the channels because of optimal conditions for marine species in these areas. However, high salinities which were detected in the channels in October 2008 could also result in disturbances at intermediate intensity and frequency. Strong tidal intrusion influenced the lagoon and

these infrequent short term periodical salinity changes could generally disturb freshwater systems and lead to losses in cell abundance and species diversity.

It has been shown that disturbance by pulsed salinity intervals of a few days into freshwater systems can increase phytoplankton diversity as long as the time between these events exceeds one mean generation time of the community. Furthermore, studies on marine species indicated that salinity can affect phytoplankton growth rate with species-specific salinity demands for the optimal growth rate (Flöder and Burns, 2004 and references therein).

Temporal and spatial distribution of phytoplankton groups

The results of the cluster analysis suggest that phytoplankton biomass in the Mundau Manguaba lagoon varied more on a temporal than on a spatial scale. The composition of phytoplankton biomass from February 2008 differed clearly from September 2007 and October 2008 most probably due to the highest average temperature and maximal salinities in the system in February 2008. It also coincided with high species diversity. Simultaneously the abundance of chlorophytes was scarce. Cyanobacteria abundance in the rivers was much higher during this season compared to September 2007 and October 2008 and dominated by *Merismopedia sp.* in Paraiba do Meio and *Oscillatoria sp.* in Rio Mundau. These cyanobacteria as well as *Anbabaena sp.* are often dominating phytoplankton communities in rivers and lakes (Phlips et al., 2000). Growth under high temperature and low light

intensity benefits Cyanobacteria compared to other algae (Dokulil and Teubner, 2000; Mur et al., 1999).

The water temperature in Mundau Manguaba lagoon varied between 23.3 and 31.0°C and constituted most probably a good environment for cyanobacteria growth. Low nutrient concentrations can also favour for cyanobacteria as it was detected in October 2008 in the Mundau lagoon and channel because of their storage ability of nitrogen and phosphate which can result in the out competition of other algae groups at low nutrient levels (Pettersson et al., 1993). Under the high salinity levels in these environments some Cyanobacteria species can develop because of their halotolerance, but generally these conditions are more favorable for diatoms (Paerl, 1996; Smayda, 1983).

Diatom composition shifted from freshwater to marine water and replaced Cyanobacteria as detected in Feb 08 when Cyanobacteria abundance was scarce in the Mundau channel close to the ocean due to salinities >30. Occurring diatoms in our system like *Cyclotella sp.*, *Skeletonema sp.*, *Chaetoceros sp.* and *Nitzschia sp.* have a huge surface-to-volume ratio and are therefore capable of fast growth, because these species are more abundant and competitive in nutrient depleted environments (Cloern and Dufford, 2005). Big cell sizes coincide with increasing sedimentation rates but at the same time these algae are less vulnerable to grazers.

Mainly at the stations in the channel which are associated with higher tidal intrusion and therefore to stronger dilution of nutrients by ocean water,

large diatoms like *Rhizosolenia sp.* were detected. These algae host symbionts with nitrogen fixing mechanisms to survive under nitrogen limiting conditions (Villareal, 1991). Similar *Rhizosolenia sp.* appearance has been reported from high saline but nutrient depleted surface waters of the Suwannee estuary, the Gulf of California or in the Mediterranean Sea during oligotrophic conditions (Ignatiades, 1969; Kemp et al., 2000; Quinlan and Philips, 2007).

Nutrient effects on phytoplankton communities

Nitrate concentrations measured in Paraiba do Meio River (max. 6.3 μM) and Rio Mundau River (max. 13.1 μM) during the dry season were quite low compared to other regions dominated by sugar cane cultivation. For example in the Paraiba do Sul River, a midsize river in the southeast of Brazil, which is also affected by sugar cane cultivation and industry in its catchment area, nitrate concentrations between 22 to 58 μM were measured during the dry season whereas concentrations were much higher during the rainy season (Silva et al., 2001). Besides the superficial fertilizer runoff from sugar cane fields, an additional source for nitrogen compounds could reach the rivers through the transfer of nitrogen from the atmosphere after the burning of sugar cane (Silva et al., 2001).

Although the concentrations of available dissolved inorganic nutrients (nitrogen, phosphate and silicate) in Paraiba do Meio and Rio Mundau were always greater than the nutrient threshold for algae, phytoplankton cell density detected in the rivers was low. Algal growth is generally said to be limited by dissolved nutrients if the concentrations are below 1.0 μM for

nitrogen, 0.1 μM for phosphate and 2.0 μM for silicate (Egge and Aksnes, 1992; Fisher et al., 1992; Turner et al., 1998). The reduced cell abundance could be the consequence of a high flushing rate and turbidity in the rivers that hamper the production and accumulation of phytoplankton biomass (Cloern, 1996; Knoppers et al., 1991).

Decreased nitrogen and phosphorus values in both lagoons suggested immediate uptake of these nutrients by algae as high cell abundance was detected, except for October 2008 where highest cell abundance was counted in the transition zone from Manguaba lagoon into the channel. Along a gradient from the lagoons to the ocean a decrease in phosphate and DIN was detectable during all seasons. The intrusion of ocean water led to a decline in nutrient concentration mainly in the channel and the southern part of the lagoons because of dilution with nutrient poor marine water, but a distinct relation between nutrient concentration and salinity could not be observed in our system. Single DIN peaks in the channels pointed to resuspension of nutrients from the sediment triggered by strong tidal influence as DIN was mainly composed of ammonium (Eyre and Ferguson, 2002; Trimmer et al., 1998).

The silicate concentrations were high at all stations and decreased seaward. The rapid decrease of silicate values mainly in the channels coincided with elevated Bacillariophyta biomass and pointed to a fast uptake by these algae rather than dilution with ocean water. High silicate concentrations are usually available all year round in most regions of the tropics (Ittekkot et al., 2006). The main source of silicon in our systems

appears to be leaching from latosol soils surrounding the lagoon system and covering the hinterland which are rich in this nutrient (Oliveira and Kjerfve, 1993). An additional source for silicate can also be the recycling of diatom frustules which are available in a huge number in the lagoon system or phytoliths inside the sugar cane tissue which get available after sugar cane burning (Keeping et al., 2009; Le Blond et al., 2010). Nevertheless the recycling of silicate in aquatic systems takes more time than the recycling of nitrogen and phosphate and leads to longer silica retention in sediments (Conley et al., 1993).

The punctual nutrient increase in Manguaba lagoon in October 2008 resulted obviously in strong shifts in phytoplankton composition as shown by the drastic change in the similarity index, accompanied by a rapid increase in biodiversity. Pulsed inflows of nutrient into a system can regulate the phytoplankton diversity therein as it was shown in experimental studies with natural communities in mesocosms (Buyukates and Roelke, 2005; Sommer, 1985). The agricultural runoff from the sugar cane cultivation in the catchment area of Mundau Manguaba lagoon can be considered as a periodical pulse of nutrient effluents from the fields related to precipitation frequency and intensity after fertilizer application. These nutrient supplies can greatly affect phytoplankton diversity by a fast population increase of species capable of utilizing these nutrient pulses which consequently result in community shifts.

The trophic state of aquatic systems is often closely related to species diversity which could be a suitable indicator for eutrophication (Dodson et

al., 2000; Telesh, 2004). Wu (1984) showed a correlation between decreasing diversity index and increasing degree of pollution in Taiwan which was similar to results in the Changjiang Estuary in China, where low diversity indexes corresponded to the appearance of red tide blooms (Gao and Song, 2005).

However our study indicates that in lagoon systems phytoplankton diversity can not be used as only factor to determine ecosystem conditions without the knowledge of the highly fluctuating conditions of nutrients and salinity on a spatial and temporal scale. Salinity and nutrient availability were major variables in Mundau Manguaba lagoon that obviously influenced phytoplankton community structure. The interaction between salinity and nutrient concentration were creating a very heterogeneous environment with strong spatial and temporal effects on phytoplankton abundance and composition. The “good ecological condition” of such a highly dynamic lagoon system can therefore not be estimated by a single quantification of phytoplankton biodiversity. Baselines for estimates of effects of environmental hazards such as fertilizer runoff must include phytoplankton dynamics on a large temporal and spatial resolution.

ACKNOWLEDGEMENTS

We would like to thank our Brazilian partners from the POLCAMAR project for their field assistance during our work in Brazil. We are grateful especially to the staff from UFAL in Maceio for providing information and

facilities. We also thank Matthias Birkicht for his support during nutrient analysis in the lab at ZMT. Financial support by the German Federal Ministry for Education and Research (BMBF) is gratefully acknowledged (Grant No. 03F0455D).

REFERENCES

- Abreu, P.C., Hartmann, C. and Odebrecht, C., 1995. Nutrient-rich saltwater and its influence on the phytoplankton of the patos lagoon estuary, Southern Brazil. *Estuarine, Coastal and Shelf Science*, 40(2): 219-229.
- Alpine, A.E. and Cloern, J.E., 1992. Trophic Interactions and Direct Physical Effects Control Phytoplankton Biomass and Production in an Estuary. *Limnology and Oceanography*, 37(5): 946-955.
- ANA, 2005. *Elaboração do Plano de Ações e Gestão Integrada do Complexo Estuarino-Lagunar Mundaú/Manguaba - CELMM*, Agencia Macopmaö de Aguas; <http://www.ana.gov.br>, Brazil.
- Artemyev, V.E., 1996. *Geochemistry of Organic Matter in River-Sea Systems*. Kluwer Academic Publishers, Dordrecht.
- Barros, G.V., Martinelli, L.A., Oliveira Novais, T.M., Ometto, J.P.H.B. and Zuppi, G.M., 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil). *Science of the Total Environment*, 408(10): 2226-2232.
- Basanta, M.V. et al., 2003. Management effects on nitrogen recovery in a sugarcane crop grown in Brazil. *Geoderma*, 116: 235-248.
- Broadbent, F.E., Rauschkolb, R.S., Lewis, K.A. and Chang, G.Y., 1980. Spatial variability of N-15 and total nitrogen in some virgin and cultivated soils. *Soil Science Society of America Journal*, 44(3): 524-527.

- Budge, S.M. and Parrish, C.C., 1998. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. *Organic Geochemistry*, 29(5-7): 1547-1559.
- Buyukates, Y. and Roelke, D., 2005. Influence of Pulsed Inflows and Nutrient Loading on Zooplankton and Phytoplankton Community Structure and Biomass in Microcosm Experiments Using Estuarine Assemblages. *Hydrobiologia*, 548(1): 233-249.
- Carpenter, E.J. et al., 1999. Extensive bloom of a N₂-fixing diatom/cyanobacterial association in the tropical Atlantic Ocean. *Marine Ecology-Progress Series*, 185: 273-283.
- Carreira, R.S. et al., 2002. Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: an elemental, isotopic and molecular marker approach. *Marine Chemistry*, 79(3-4): 207-227.
- Cifuentes, L.A. et al., 1996. Isotopic and Elemental Variations of Carbon and Nitrogen in a Mangrove Estuary. *Estuarine, Coastal and Shelf Science*, 43: 781-800.
- Cifuentes, L.A., Sharp, J.H. and Fogel, M.L., 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnology and Oceanography*, 33(5): 1102-1115.
- Cline, J.D. and Kaplan, I.R., 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north pacific ocean. *Marine Chemistry*, 3(4): 271-299.
- Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. *Review of Geophysics*, 34(2): 127-168.
- Cloern, J.E. and Dufford, R., 2005. Phytoplankton community ecology: principles applied in San Francisco Bay. *Marine Ecology Progress Series*, 285: 11-28.
- Conley, D.J., Schelske, C.L. and Stoermer, E.F., 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Marine ecology progress series*. Oldendorf, 101(1-2): 179-192.
- Costa, T., Araújo, M., Knoppers, B. and Carreira, R., 2011. Sources and Distribution of Particulate Organic Matter of a Tropical Estuarine-

- Lagoon System from NE Brazil as Indicated by Lipid Biomarkers. *Aquatic Geochemistry*, 17(1): 1-19.
- Dähnke, K., Bahlmann, E. and Emeis, K., 2008. A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary. *Limnology and Oceanography*, 53(4): 1504-1511.
- Dodson, S.I., Arnott, S.E. and Cottingham, K.L., 2000. The relationship in lake communities between primary productivity and species richness. *Ecology*, 81(10): 2662-2679.
- Dokulil, M.T. and Teubner, K., 2000. Cyanobacterial dominance in lakes. *Hydrobiologia*, 438(1): 1-12.
- Domingues, R.B., Barbosa, A. and Galvao, H., 2005. Nutrients, light and phytoplankton succession in a temperate estuary (the Guadiana, south-western Iberia). *Estuarine, Coastal and Shelf Science*, 64(2-3): 249-260.
- Duarte, C.M., Agusti, S. and Agawin, N.S.R., 2000. Response of a Mediterranean phytoplankton community to increased nutrient inputs: A mesocosm experiment. *Marine Ecology Progress Series*, 195: 61-70.
- Egge, J.K. and Aksnes, D.L., 1992. Silicate as regulating nutrient in phytoplankton competition. *Marine ecology progress series*, 83(2-3): 281-289.
- Eyre, B.D. and Ferguson, A.J.P., 2002. Comparison of carbon production and decomposition, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgae and macroalgae-dominated warm-temperate Australian lagoons. *Marine ecology progress series*, 229: 43-59.
- FAO, 2004. Fertilizer use by crop in Brazil. In: F.a.A.O.o.t.U. Nations (Editor). Food and Agriculture Organization of the United Nations, Rome, pp. 1-64.
- Ferreira, J.G., Wolff, W.J., Simas, T.C. and Bricker, S.B., 2005. Does biodiversity of estuarine phytoplankton depend on hydrology? *Ecological Modelling*, 187(4): 513-523.
- FIAN and GTZ, 2002. Economic, social and ecological impacts on Brazil of accelerated liberalisation of the European sugar market. In:

- D.G.f.T.Z. GmbH (Editor). Deutsche Gesellschaft für Technische Zusammenarbeit GmbH, Heidelberg, pp. 1-59.
- Filoso, S. et al., 2003. Land use and nitrogen export in the Piracicaba River basin, Southeast Brazil. *Biogeochemistry*, 65(3): 275-294.
- Fischer, G., 1991. Stable carbon isotope ratios of plankton carbon and sinking organic matter from the Atlantic sector of the Southern Ocean. *Marine Chemistry*, 35(1-4): 581-596.
- Fisher, T.R., Peele, E.R., Ammerman, J.W. and Harding, L.W.J., 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine ecology progress series*, 82(1): 51-63.
- Flöder, S. and Burns, C.W., 2004. Phytoplankton diversity of shallow tidal lakes: influence of periodic salinity changes on diversity and species number of a natural assemblage. *Journal of Phycology*, 40(1): 54-61.
- Gallegos, C.L. and Jordan, T.E., 1997. Seasonal progression of factors limiting phytoplankton pigment biomass in the Rhode River estuary, Maryland (USA). I. Controls on phytoplankton growth. *Marine Ecology-Progress Series*, 161: 185-198.
- Gao, X. and Song, J., 2005. Phytoplankton distributions and their relationship with the environment in the Changjiang Estuary, China. *Marine Pollution Bulletin*, 50(3): 327-335.
- Goldemberg, J., Coelho, S.T. and Guardabassi, P., 2008. The sustainability of ethanol production from sugarcane. *Energy Policy*, 36(6): 2086-2097.
- Grasshoff, K., Kremling, K. and Ehrhardt, M.E., 1999. *Methods of Seawater Analysis*. third ed. Wiley-VCH(Weinheim): 600 pp.
- Grischek, T., Hiscock, K.M., Metschies, T., Dennis, P.F. and Nestler, W., 1998. Factors affecting denitrification during infiltration of river water into a sand and gravel aquifer in Saxony, Germany. *Water Research*, 32(2): 450-460.
- Hammer, Ø., Harper, D.A.T. and Ryan, P.D., 2001. PAST: Paleontological Statistics Software Package for Education and Data Analysis, *Palaeontologia Electronica* 4 (1), Oslo.

-
- Hansson, S. et al., 1997. The Stable Nitrogen Isotope Ratio as a Marker of Food-Web Interactions and Fish Migration. *Ecology*, 78(7): 2249-2257.
- Hecky, R.E. and Kilham, P., 1988. Nutrient Limitation of Phytoplankton in Freshwater and Marine Environments: A Review of Recent Evidence on the Effects of Enrichment. *Limnology and Oceanography*, 33(4): 796-822.
- Hedges, J.I. et al., 1986. Compositions and Fluxes of Particulate Organic Material in the Amazon River. *Limnology and Oceanography*, 31(4): 717-738.
- Heip, C.H.R. et al., 1995. Production and consumption of biological particles in temperate tidal estuaries. In: A.D. Ansell, R.N. Gibson and M. Barnes (Editors), *Oceanography and Marine Biology: an Annual Review*. UCL Press, London, pp. 1-149.
- Hillebrand, H., Duerselen, C.D., Kirschtel, D., Pollinger, U. and Zohary, T., 1999. Biovolume calculation for pelagic and benthic microalgae. *Journal of Phycology*, 35(2): 403-424.
- Hlaili, A., Chikhaoui, M.A., El Grami, B. and Mabrouk, H., 2006. Effects of N and P supply on phytoplankton in Bizerte Lagoon (western Mediterranean). *Journal of Experimental Marine Biology and Ecology*, 333(1): 79-96.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology*, 19: 89-110.
- Hu, J., Peng, P.a., Jia, G., Mai, B. and Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. *Marine Chemistry*, 98(2-4): 274-285.
- Humborg, C., Ittekkot, V., Cociasu, A. and Bodungen, B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature*, 386(6623): 385-388.
- Ignatiades, L., 1969. Annual cycle, species diversity and succession of phytoplankton in lower Saronicos Bay, Aegean Sea. *Marine Biology*, 3(3): 196-200.

- Ittekkot, V., Unger, D., Humborg, C. and Nguyen, T.A., 2006 The Silicon Cycle. Human Perturbations and Impacts on Aquatic Systems SCOPE Island Press, Washington D.C.
- Jassby, A.D., Cloern, J.E. and Powell, T.M., 1993. Organic carbon sources and sinks in San Francisco Bay - variability induced by river flow. *Marine Ecology-Progress Series*, 95(1-2): 39-54.
- Jeffrey, S.W. and Humphrey, G.F., 1975. New spectrophotometric equations for determining chlorophylls a, b, c₁ and c₂ in algae, phytoplankton and higher plants. *Biochem. Physiol. Pflanz.*, 167: 191-194.
- Jennerjahn, T. et al., 2008. Effect of land use on the biogeochemistry of dissolved nutrients and suspended and sedimentary organic matter in the tropical Kallada River and Ashtamudi estuary, Kerala, India. *Biogeochemistry*, 90(1): 29-47.
- Jennerjahn, T.C. et al., 2004. Biogeochemistry of a tropical river affected by human activities in its catchment: Brantas River estuary and coastal waters of Madura Strait, Java, Indonesia. *Estuarine, Coastal and Shelf Science*, 60(3): 503-514.
- Keeping, M.G., Kvedaras, O.L. and Bruton, A.G., 2009. Epidermal silicon in sugarcane: Cultivar differences and role in resistance to sugarcane borer *Eldana saccharina*. *Environmental and Experimental Botany*, 66(1): 54-60.
- Kemp, A.E.S., Pike, J., Pearce, R.B. and Lange, C.B., 2000. The "Fall dump" -- a new perspective on the role of a "shade flora" in the annual cycle of diatom production and export flux. *Deep Sea Research Part II: Topical Studies in Oceanography*, 47(9-11): 2129-2154.
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: C. Kendall and M.J. J. (Editors), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam.
- Kendall, C.S., Steven R.; Kelly, Valerie J., 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large systems across the United States. *Hydrological Processes*, 15: 1301-1346.

-
- Kies, L., 1997. Distribution, biomass and production of planktonic and benthic algae in the Elbe Estuary. *Limnologica*, 27(1): 55-64.
- Kirst, G.O., 1989. Salinity Tolerance of Eukaryotic Marine Algae. *Annual Review of Plant Physiology and Plant Molecular Biology*, 41(1): 21-53.
- Klausmeier, C.A., Litchman, E., Daufresne, T. and Levin, S.A., 2004. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature*, 429(6988): 171-174.
- Knoppers, B., Kjerfve, B. and Carmouze, J.P., 1991. Trophic state and water turn-over time in six choked coastal lagoons in Brazil. *Biogeochemistry*, 14: 149-166.
- Kohl, J.G., Baierova, J. and Dudel, G., 1982. Die Bedeutung der Stickstoff-fixierenden Blaualgen für den Stoffhaushalt stehender und gestauter Binnengewässer. *Acta Hydrochimica et Hydrobiologica*, 10(5): 415-437.
- Krebs, C.J., 1989. Similarity Coefficients and Cluster Analysis. In: S. Pisano (Editor), *Ecological Methodology*. Harper & Row Publishers, New York, pp. 293-323.
- Krusche, A.V. et al., 2002. Composition of particulate and dissolved organic matter in a disturbed watershed of southeast Brazil (Piracicaba River basin). *Water Research*, 36(11): 2743-2752.
- Kudela, R.M. and Dugdale, R.C., 2000. Nutrient regulation of phytoplankton productivity in Monterey Bay, California. *Deep Sea Research Part II: Topical Studies in Oceanography*, 47(5-6): 1023-1053.
- Le Blond, J.S., Horwell, C.J., Williamson, B.J. and Oppenheimer, C., 2010. Generation of crystalline silica from sugarcane burning. *Journal of Environmental Monitoring*, 12(7): 1459-1470.
- Lee, K.S., Bong, Y.S., Lee, D., Kim, Y. and Kim, K., 2008. Tracing the source of nitrate in the Han River watershed in Korea, using delta (15) N-NO₃⁻ and delta (18) O-NO₃⁻ values. *Science of the Total Environment*, 395: 117-124.
- Liu, K.K. and Kaplan, I.R., 1989. The eastern tropical Pacific as a source of delta super(15)N-enriched nitrate in seawater off southern California. *Limnologic Oceanography*, 34(5): 820-830.

- Liu, M. et al., 2006. Organic carbon and nitrogen stable isotopes in the intertidal sediments from the Yangtze Estuary, China. *Marine Pollution Bulletin*, 52(12): 1625-1633.
- Lund, J.W., Kipling, G. and LeCreen, E.D., 1958. The inverted microscope method of estimating algae numbers and the statistical basis of estimation by counting. *Hydrobiologia*, 11: 143-170
- Macedo, I.C., Seabra, J.E.A. and Silva, J.E.A.R., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy*, 32(7): 582-595.
- Martinelli, L.A. and Filoso, S., 2008. Expansion of sugarcane ethanol production in Brazil: environmental and social challenges. *Ecological Applications*, 18(4): 885-898.
- Martinelli, L.A. et al., 1999. Effects of Sewage on the Chemical Composition of Piracicaba River, Brazil. *Water, Air, & Soil Pollution*, 110(1): 67-79.
- McClelland, J.W. and Valiela, I., 1998. Changes in food web structure under the influence of increased anthropogenic nitrogen inputs to estuaries. *Marine Ecology-Progress Series*, 168: 259-271.
- McGlathery, K.J., 2001. Macroalgal blooms contribute to the decline of seagrass in nutrient-enriched coastal waters. *Journal of Phycology*, 37(4): 453-456.
- Melo-Magalhaes, E.M., Medeiros, P.R.P., Lira, M.C.A., Koenig, M.L. and Moura, A.N., 2009. Determination of eutrophic areas in Mundau/Manguaba lagoons, Alagoas-Brazil, through studies of the phytoplanktonic community *Brazilian Journal of Biology*, 69(2): 271-280.
- Middelburg, J.J. and Herman, P.M.J., 2007. Organic matter processing in tidal estuaries. *Marine Chemistry*, 106(1-2): 127-147.
- Middelburg, J.J. and Nieuwenhuize, J., 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. *Marine Chemistry*, 60(3-4): 217-225.
- Mur, L.R., Skulberg, O.M. and Utkilen, H., 1999. Toxic Cyanobacteria in Water: A guide to their public health consequences, monitoring and management. World Health Organization.

-
- Muylaert, K. and Sabbe, K., 1999. Spring phytoplankton assemblages in and around the maximum turbidity zone of the estuaries of the Elbe (Germany), the Schelde (Belgium/The Netherlands) and the Gironde (France). *Journal of Marine Systems*, 22(2-3): 133-149.
- Officer, C.B. and Ryther, J.H., 1980. The possible Importance of Silicon in Marine Eutrophication. *Marine Ecology Progress Series*, 3: 83-91.
- Oliveira, A.M. and Kjerfve, B., 1993. Environmental Responses of a Tropical Coastal Lagoon System to Hydrological Variability: Mundau-Manguaba, Brazil. *Estuarine, Coastal and Shelf Science*, 37(6): 575-591.
- Oliveira, J.I.C.s.M.d. et al., 2000. Nitrogen dynamics in a soil-sugar cane system. *Scientia Agricola*, 57: 467-472.
- Paerl, H.W., 1996. A comparison of cyanobacterial bloom dynamics in freshwater, estuarine and marine environments. *Phycologia*, 35(6S): 25-35.
- Pennock, J.R. and Sharp, J.H., 1994. Temporal alternation between light- and nutrient-limitation of phytoplankton production in a coastal plain estuary. *Marine Ecology Progress Series*, 111: 275-288.
- Peters, K.E., Sweeney, R.E. and Kaplan, I.R., 1978. Correlation of Carbon and Nitrogen Stable Isotope Ratios in Sedimentary Organic Matter. *Limnology and Oceanography*, 23(4): 598-604.
- Pettersson, K., Herlitz, E. and Istvánovics, V., 1993. The role of *Gloeotrichia echinulata* in the transfer of phosphorus from sediments to water in Lake Erken. *Hydrobiologia*, 253(1): 123-129.
- Phlips, E.J. et al., 2000. Light Availability and Variations in Phytoplankton Standing Crops in a Nutrient-Rich Blackwater River. *Limnology and Oceanography*, 45(4): 916-929.
- Piehlner, M.F., Twomey, L.J., Hall, N.S. and Paerl, H.W., 2004. Impacts of inorganic nutrient enrichment on phytoplankton community structure and function in Pamlico Sound, NC, USA. *Estuarine, Coastal and Shelf Science*, 61(2): 197-209.
- Quiblier, C., Leboulanger, C., Sane, S. and Dufour, P., 2008. Phytoplankton growth control and risk of cyanobacterial blooms in the lower Senegal River delta region. *Water Research*, 42(4-5): 1023-1034.

- Quinlan, E.L. and Phlips, E.J., 2007. Phytoplankton assemblages across the marine to low-salinity transition zone in a blackwater dominated estuary. *Journal of Plankton Research*, 29(5): 401-416.
- Rabalais, N. et al., 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. *Estuaries and Coasts*, 19(2): 386-407.
- Rahm, L., Conley, D., Sandén, P., Wulff, F. and Stalnacke, P., 1996. Time series analysis of nutrient inputs to the Baltic Sea and changing DSi:DIN ratios. *Marine Ecology Progress Series*, 130: 221-228.
- Redden, A. and Rukminasari, N., 2008. Effects of increases in salinity on phytoplankton in the Broadwater of the Myall Lakes, NSW, Australia. *Hydrobiologia*, 608(1): 87-97.
- Reimann, B.E.F., Lewin, J.M.C. and Guillard, R.R.L., 1963. *Cyclotella cryptica*: a new brackish-water diatom species. *Phycologia*, 3: 75-84.
- Rhee, G.Y., 1978. Effects of N:P Atomic Ratios and Nitrate Limitation on Algal Growth, Cell Composition, and Nitrate Uptake. *Limnology and Oceanography*, 23(1): 10-25.
- Rijstenbil, J.W., 1988. Selection of phytoplankton species in culture by gradual salinity changes. *Netherlands Journal of Sea Research*, 22(3): 291-300.
- Rocha, O. and Duncan, A., 1985. The relationship between cell carbon and cell volume in freshwater algal species used in zooplankton studies. *Journal of Plankton Research*, 7: 279-294.
- Rodriguez, S.A., Avila-Perez, P. and Barcelo-Quintal, I., 1998. Bioaccumulation of chemical elements by water hyacinth (*Eichhornia crassipes*) found in "Jose Antonio Alzate" dam samples in the State of Mexico, Mexico. *Journal of Radioanalytical and Nuclear Chemistry*, 238(1): 91-95.
- Roelke, D., Eldridge, P. and Cifuentes, L., 1999. A model of phytoplankton competition for limiting and nonlimiting nutrients: Implications for development of estuarine and nearshore management schemes. *Estuaries and Coasts*, 22(1): 92-104.

-
- Savant, N.K., Korndörfer, G.H., Datnoff, L.E. and Snyder, G.H., 1999. Silicon nutrition and sugarcane production: A review. *Journal of Plant Nutrition*, 22(12): 1853 - 1903.
- Schaefer, P. and Ittekkot, V., 1993. Seasonal variability of delta super(15)N in settling particles in the Arabian Sea and its palaeogeochemical significance. *Naturwissenschaften*, 80(11): 511-513.
- Scheffer, F. and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde*. Spektrum Akademischer Verlag GbmH, Heidelberg.
- Schindler, D.W., 1974. Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management. *Science*, 184(4139): 897-899.
- Sherrard, N.J., Nimmo, M. and Llewellyn, C.A., 2006. Combining HPLC pigment markers and ecological similarity indices to assess phytoplankton community structure: An environmental tool for eutrophication? *Science of the Total Environment*, 361(1-3): 97-110.
- Silva, M.n.A.L., Calasans, C.F., Ovalle, A.R.C. and Rezende, C.E., 2001. Dissolved Nitrogen and Phosphorus Dynamics in the Lower Portion of the Paraíba do Sul River, Campos dos Goytacazes, RJ, Brazil. *Brazilian Archives of Biology and Technology*, 44: 365-371.
- Smayda, T.J., 1983. The phytoplankton of estuaries. In: B.H. Ketchum (Editor), *Estuaries and enclosed seas*. *Ecosystems of the World*, pp. 65-102.
- Smith, V.H., 2006. Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. *Limnology and Oceanography*, 51(1): 377-384.
- Sommer, U., 1985. Comparison between steady-state and non-steady state competition - experiments with natural phytoplankton. *Limnology and Oceanography*, 30(2): 335-346.
- Sommer, U., Stibor, H., Katchakis, A., Sommer, F. and Hansen, T., 2002. Pelagic food web configurations at different levels of nutrient richness and their implications for the ratio fish production:primary production. *Hydrobiologia*, 484(1): 11-20.
- Souza, M.F., Kjerfve, B., Knoppers, B., Landim de Souza, W.F. and Damasceno, R.N., 2003. Nutrient budgets and trophic state in a

- hypersaline coastal lagoon: Lagoa de Araruama, Brazil. *Estuarine, Coastal and Shelf Science*, 57(5-6): 843-858.
- Sutcliffe, D.W. and Jones, J.G., 1992. *Eutrophication: Research and Application to Water Supply*. Freshwater biological association, Ambleside (UK)
- Sweeney, R.E. and Kaplan, I.R., 1980. Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry*, 9(2): 81-94.
- Talling, J.F. and Lemoalle, J., 1998. *Ecological Dynamics of Tropical Inland Waters*. Cambridge University Press, Cambridge, 451 pp.
- Tamminen, T. and Andersen, T., 2007. Seasonal phytoplankton nutrient limitation patterns as revealed by bioassays over Baltic Seagradients of salinity and eutrophication. *Mar. Ecol. Prog. Ser.*, 240: 121–138.
- Taylor, D.I. et al., 1995. Responses of coastal lagoon plant communities to different forms of nutrient enrichment -- a mesocosm experiment. *Aquatic Botany*, 52(1-2): 19-34.
- Telesh, I.V., 2004. Plankton of the Baltic estuarine ecosystems with emphasis on Neva Estuary: a review of present knowledge and research perspectives. *Marine Pollution Bulletin*, 49(3): 206-219.
- Tilman, D., Kilham, S.S. and Kilham, P., 1982. Phytoplankton Community Ecology: The Role of Limiting Nutrients. *Annual Review of Ecology and Systematics*, 13: 349-372.
- Tomasky, G. et al., 1999. Nutrient limitation of phytoplankton growth in Waquoit Bay, Massachusetts, USA: a nutrient enrichment study. *Aquatic Ecology*, 33(2): 147-155.
- Townsend-Small, A., Noguera, J.L., McClain, M.E. and Brandes, J.A., 2007. Radiocarbon and stable isotope geochemistry of organic matter in the Amazon headwaters, Peruvian Andes. *Global Biogeochemical Cycles*, 21(2): GB2029.
- Trimmer, M., Nedwell, D.B., Sivyer, D.B. and Malcolm, S.J., 1998. Nitrogen fluxes through the lower estuary of the River Great Ouse, England: The role of the bottom sediments. *Marine Ecology Progress Series*, 163: 109-124.

-
- Turner, R.E. et al., 1998. Fluctuating Silicate:Nitrate Ratios and Coastal Plankton Food Webs. *Proceedings of the National Academy of Sciences of the United States of America*, 95(22): 13048-13051.
- Turner, R.E. and Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi river delta. *Nature*, 368: 619-621.
- Turner, R.E. and Rabalais, N.N., 2003. Linking Landscape and Water Quality in the Mississippi River Basin for 200 Years. *Bioscience*, 53(6): 563-572.
- UNICA, 2001. *Energia da Cana-de-Açúcar e Redução do Efeito Estufa.*, São Paulo.
- Utermöhl, H., 1958. Zur Vervollkommnung der quantitativen Phytoplanktonmethodik. *Mitt. Verein.Theor. Angew. Limnol.*, 9: 1-38.
- Villareal, T.A., 1991. Nitrogen-fixation by the cyanobacterial symbiont of the diatom genus *Hemiaulus*. *Marine ecology progress series*, 76(2): 201-204.
- Voss, M., Dippner, J.W. and Montoya, J.P., 2001. Nitrogen isotope patterns in the oxygen-deficient waters of the Eastern Tropical North Pacific Ocean. *Deep Sea Research Part I: Oceanographic Research Papers*, 48(8): 1905-1921.
- Voss, M. et al., 2005. Riverine discharge into a coastal bay: A stable isotope study in the Gulf of Gdansk, Baltic Sea. *Journal of Marine Systems*, 57(1-2): 127-145.
- Wehr, J.D. and Descy, J.P., 1998. Use of phytoplankton in large river management. *Journal of Phycology*, 34(5): 741-749.
- Wu, J. and Chou, T., 2003. Silicate as the limiting nutrient for phytoplankton in a subtropical eutrophic estuary of Taiwan. *Estuarine, Coastal and Shelf Science*, 58(1): 155-162.
- Wu, J.T., 1984. Phytoplankton as bioindicator for water quality in Taipei. *Bot. Bull. Academica Sinica*, 25: 205-214.
- Zhang, J. et al., 2010. Natural and human-induced hypoxia and consequences for coastal areas: Synthesis and future development. *Biogeosciences*, 7 1443-1467.
- Zhang, J., Wu, Y., Jennerjahn, T.C., Ittekkot, V. and He, Q., 2007. Distribution of organic matter in the Changjiang (Yangtze River)

Estuary and their stable carbon and nitrogen isotopic ratios:
Implications for source discrimination and sedimentary dynamics.
Marine Chemistry, 106(1-2): 111-126.

CHAPTER III

Effect of sugar cane monoculture on
organic matter composition and dynamics
in a tropical coastal lagoon in Brazil

Gertrud Spörl, Carlos E. Veiga de Carvalho,
Bastiaan Knoppers, Tim Jennerjahn

Submitted to Estuarine, Coastal and Shelf Science



**Effect of sugar cane monoculture on
organic matter composition and dynamics
in a tropical coastal lagoon in Brazil**

Gertrud Spörl, Carlos E. Veiga de Carvalho, Bastiaan Knoppers,
Tim Jennerjahn

ABSTRACT

The origin of particulate organic matter in the water column and the sediment in the tropical Mundau Manguaba Lagoon in northeast Brazil was determined by using stable carbon and nitrogen isotopes in combination with C/N ratios. These lagoons are affected by increasing sugar cane cultivation in their catchment area. Water samples were taken along a salinity gradient from the river to the ocean outlet in the dry season in September 2007, February 2008, October 2008 and March 2009 after sugar cane harvest started. The isotopic composition of total suspended matter (TSM) in the lagoons indicated the presence of autochthonous material produced by phytoplankton as well as allochthonous material which originated most probably from sugar cane monoculture in the catchment area ($\delta^{13}\text{C}_{\text{org}}$ -17.1 to -24.6 ‰). $\delta^{15}\text{N}$ values of up to ~ 10 ‰ in the Mundau Lagoon pointed to sewage input from the city of Maceio. Differences in water residence time and tidal intrusion between the lagoons led to higher concentrations of particulate organic carbon (POC) in the Manguaba lagoon which was also reflected in higher phytoplankton

biomass. Similar concentrations and distribution patterns were observed in the surface sediment of the lagoons. High proportions of sugar cane and phytoplankton material accumulated in the Manguaba lagoon where it was also degraded because of a long residence time and a restricted tidal exchange. Strong tidal intrusion and short residence time in the Mundau lagoon suggested an outwelling of sugar cane and sewage organic material into the adjacent coastal waters.

KEYWORDS

Stable carbon and nitrogen isotopes, organic carbon, water column, sediment, tropical lagoon, sugar cane

INTRODUCTION

Coastal lagoons are important transitional zones which link marine and freshwater systems. The distribution and fate of suspended matter in these brackish zones is mainly caused by hydrodynamics, physical and chemical gradients as well as biological processes which are mainly driven by river discharge, changing salinity intrusion and retention time. Depending on these factors material can be modified and stored in the system or exported to the adjacent coastal waters. Allochthonous material from terrestrial sources such as plants, domestic and industrial sewage or agricultural runoff as well as marine sources account for the distribution of particles. But also autochthonous material from primary and secondary production contribute to the organic matter pool and can change according to spatial

and temporal variations in the system (Artemyev, 1996; Heip et al., 1995). Over time considerable portions of organic matter sink through the water column and accumulate in the sediment (Budge and Parrish, 1998).

Several studies described the origin and fate of organic matter in estuaries of temperate zones but little is known about tropical systems (Cifuentes et al., 1996; Jennerjahn et al., 2004; Middelburg and Herman, 2007; Voss et al., 2005). Few studies from Brazil showed mainly an influence of sewage into rivers, but the impact of agricultural intensification on aquatic environments and its consequences are scarce (Barros et al., 2010; Carreira et al., 2002).

Since the end of the last century land use changed heavily in Brazil due to the intensive cultivation of sugar cane and its use as biofuel in the automobile sector which was promoted by the government (FIAN and GTZ, 2002). Nowadays Brazil is the major sugar cane producer in the world with 7 million hectares of cropland which is about 25 % of the global sugar cane area. Actually, the sugar cane industry in Brazil processes about 480 million tones of sugar cane whereof 45 % are turned into sugar production and 55 % into alcohol production with an increasing national and international demand (UNICA, 2001).

The northeast of Brazil is the second largest sugar cane cultivation area and accounts for about 30 % of the country's total production. More than 80 % of agricultural area in this region are covered by sugar cane monoculture (Goldemberg et al., 2008). The annual nitrogen fertilizer

application on Brazilian sugar cane fields is about 80 – 100 kg N ha⁻¹ yr⁻¹ (Martinelli and Filoso, 2008). However, only 20 to 40% of the fertilizer seems to be assimilated by the sugar cane plant, whereas a huge part remains in the soil or is furthermore washed out into adjoining aquatic environments (Basanta et al., 2003; Oliveira et al., 2000). The increasing demand of sugar cane is expected to intensify the impact from the agricultural and industrial processes on the water quality of these aquatic ecosystems.

In complex environments such as coastal lagoons and estuaries, stable nitrogen and carbon isotope composition had already been used to trace the origin and transformation of organic matter in the water and sediments (Barros et al., 2010; Carreira et al., 2002; Cifuentes et al., 1996; Cifuentes et al., 1988; Hu et al., 2006; Jassby et al., 1993; McClelland and Valiela, 1998; Peters et al., 1978; Sweeney and Kaplan, 1980). Marine organic matter has a $\delta^{13}\text{C}_{\text{org}}$ between -22 and -18 ‰ in low latitudes. Terrestrial derived material from C3 plants has values between -30 and -24 ‰ and from C4 plants between -10 to -18 ‰ (Fischer, 1991; Liu et al., 2006). $\delta^{15}\text{N}$ can be affected by inputs from various sources and processes like nitrification or denitrification, the degree of nutrient fractionation in the water column or organic matter diagenesis (Carpenter et al., 1999; Dähnke et al., 2008; Liu and Kaplan, 1989; Schaefer and Ittekkot, 1993; Voss et al. 2001). It can also be used to distinguish between sewage inputs which can have values $>\sim 8$ ‰ and the use of fertilizer and atmospheric fixation by phytoplankton with values $<\sim 2$ ‰ (Hansson et al., 1997; Lee et al., 2008).

In the light of increasing sugar cane cultivation it is necessary to follow its effluents in order to assess their effects and fate in the coastal zone. This study was conducted over a period of two years to obtain information on the sources, the distribution and the accumulation of suspended matter and particulate organic carbon in the Mundau Manguaba Lagoon which is affected by sugar cane monoculture in its catchment area.

MATERIAL AND METHODS

Study Area

The shallow tropical Mundau Manguaba Lagoon (79 km²) in northeast Brazil consists of two shallow coastal lagoons which are connected with a channel system and with the ocean (Fig. 1). The outlet of the lagoons and the channels are lined by mangroves. Manguaba and Mundau lagoon have a dimension of 43 km² and 24 km², respectively, and an average depth of 2 m. (FIAN and GTZ, 2002). The upper catchment area is characterized by a semi arid climate with an annual average precipitation of 800 mm whereas the lower basin close to the coast is tropical humid with an average precipitation of 1654 mm and an annual mean temperature of 25 °C (Fig.2).

During the dry period (November to March) sugar cane is harvested by burning off the sugar cane in the fields and the main production of sugar and alcohol in the factories starts. During the rainy season (May to August), inorganic and organic fertilizers which are applied to the fields and also

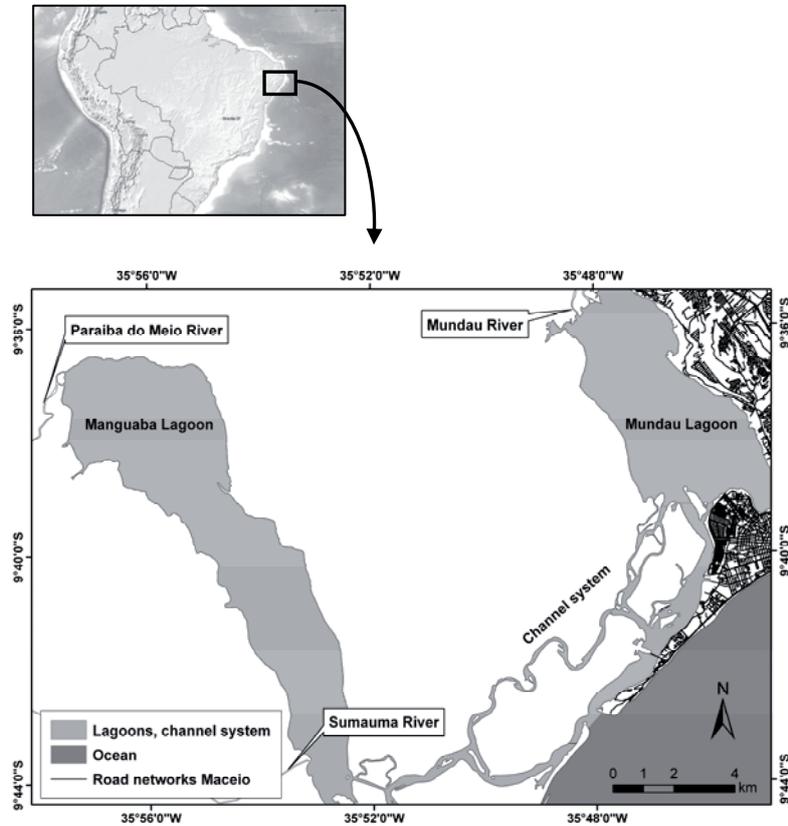


Figure 1: Map of the Mundau Manguaba Lagoon, in northeast Brazil.

organic matter from the soils can be washed into adjoining rivers and transported to the lagoons (Fig. 2). The Mundau lagoon receives additionally effluents from the city of Maceio which has about 900,000 inhabitants (ANA, 2005). The lagoons hydrodynamics are dominated by a semi – diurnal tidal variation, although most of the tidal energy seems to dissipate in the connecting channels between the ocean and the lagoons. The different sizes of the lagoons and the morphology of the channels are responsible for an average water residence time of around 1-2 weeks for

Mundau lagoon and 5-7 weeks for Manguaba lagoon, respectively (Oliveira and Kjerfve, 1993).

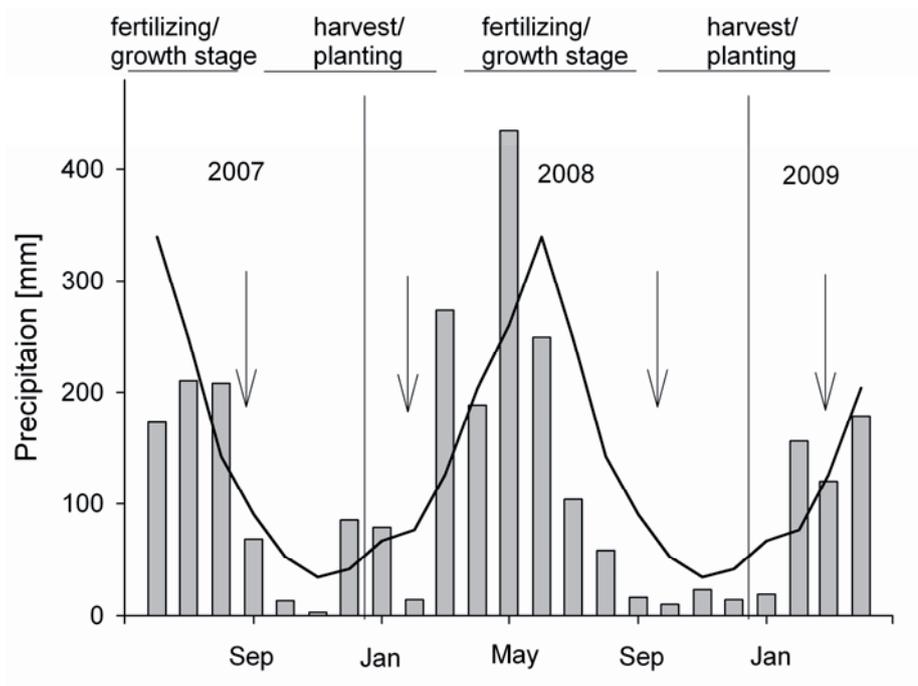


Figure 2: Monthly precipitation in the area of the Mundau Manguaba Lagoon during the investigated period 2007 – 2009. Black line shows the average precipitation over the last 20 years, arrows denote sampling campaigns (source: Laboratório de Agrometeorologia e Radiometria Solar/UFAL, Maceio)

Sampling and sample preparation

Surface water samples were taken with a Niskin bottle along a salinity gradient (salinity of 0.0 – 37.1) in both lagoons in September 2007, February 2008, October 2008 and March 2009 at the beginning and at the end of the dry season. For the determination of total suspended matter (TSM), water samples were taken in PE bottles and stored cool and dark

until the filtration. Samples were filtered through pre-combusted and pre-weight glass fibre filters (Whatman GF/F) and dried at 40 °C.

In March 2007 four sediment cores between 30 and 50 cm length were taken with a hand corer in each lagoon as well as soil and plant samples from the sugar cane fields. Plant material was sampled along the rivers. Sediment cores were subsampled in 2 cm intervals. Sediment, soil and plant samples were dried at 40 °C, ground and homogenized prior to analysis.

Analyses

Total suspended matter, sediment, soil and plant material were analysed for their total carbon and total nitrogen by high temperature combustion using a Carlo Erba NA 2100 elemental analyser. After removal of inorganic carbon by acidification with 1N hydrochloric acid, the samples were dried again at 40 °C and analysed for particulate organic carbon content (C_{org}). Repeated measurements of standard samples gave a precision of 0.1 % for organic carbon and 0.01 % for nitrogen.

The isotopic composition of nitrogen ($\delta^{15}N$) and organic carbon ($\delta^{13}C_{org}$) isotopes was determined with a Finnigan Delta Plus mass spectrometer coupled to a Flash 1112 EA elemental analyser. For the determination of the carbon isotope composition the carbonate in the sample was removed by adding 1N HCl and dried at 40°C. The precision of the method given by an internal standard was 0.2 ‰ for $\delta^{15}N$ and $\delta^{13}C_{org}$.

Statistics

The relationship between particulate organic carbon content and total suspended matter was determined using Pearson correlation. To test differences of carbon and nitrogen isotope ratios of the TSM between years, data were log-transformed and tested by using a one-way ANOVA when data were normally distributed or a Kruskal Wallis test when data were not normally distributed. These differences were tested additionally by post-hoc Tukey's test and Dunn's test, respectively. All tests were carried out in SigmaPlot 11.0.

RESULTS

Total suspended matter composition and distribution in the water column

Average total suspended matter (TSM) of surface water showed temporal and spatial variations during the four sampling periods. TSM was higher in September 2007 in the Manguaba lagoon ($26.9 \pm 8.5 \text{ mg l}^{-1}$; Fig. 3) with highest values inside the lagoon. Lowest concentrations ($13.1 \pm 7.3 \text{ mg l}^{-1}$) were measured in October 2008. TSM concentration generally increased from the Paraiba do Meio River towards the channel. Mundau lagoon also had highest average TSM concentrations in September 2007 and lowest in October 2008 (22.4 ± 14.1 and $16.4 \pm 11.6 \text{ mg l}^{-1}$; Fig. 3).

Table 1: Minimum and maximum values and average C/N ratios of the rivers, the lagoons and the channels in the Mundau Manguaba Lagoon in September 2007, February 2008, October 2008 and February 2009.

		Sep 07	Feb 08	Oct 08	Feb 09
Manguaba		n	n	n	n
River	AVG (± STDEV)	11.7 (± 3.3)	10.4 (± 2.8)	13.8 (± 1.3)	13.7 (± 3.5)
	Min. - Max.	7.3 - 17.7	8.2 - 15.7	3.2 - 28.6	8.6 - 17.9
Lagoon	AVG (± STDEV)	9.7 (± 1.8)	9.8 (± 1.9)	8.4 (± 1.3)	9.8 (± 1.4)
	Min. - Max.	7.4 - 12.9	7.5 - 11.6	6.9 - 9.5	8.3 - 10.9
Channel	AVG (± STDEV)	10.4 (± 2.6)	9.2 (± 1.5)	9.4 (± 1.3)	8.5 (± 1.4)
	Min. - Max.	7.5 - 14.9	8.0 - 12.9	7.1 - 11.6	6.8 - 10.6
Mundau		n	n	n	n
River	AVG (± STDEV)	12.0 (± 8.8)	20.2 (± 23.1)	9.8 (± 1.2)	12.0 (± 0.6)
	Min. - Max.	5.8 - 18.2	5.4 - 46.8	8.6 - 11.0	11.6 - 12.4
Lagoon	AVG (± STDEV)	26.1 (± 18.6)	18.3 (± 7.3)	8.6 (± 1.4)	16.8 (± 1.0)
	Min. - Max.	8.9 - 56.2	11.4 - 25.0	6.5 - 9.6	15.9 - 17.9
Channel	AVG (± STDEV)	22.0 (± 8.1)	26.1 (± 10.9)	9.8 (± 1.7)	21.9 (± 4.0)
	Min. - Max.	14.5 - 34.1	17.6 - 48.4	11.0 - 35.2	17.3 - 24.0

The difference in TSM amounts in the Mundau lagoon between the seasons was smaller than in the Manguaba lagoon. Generally highest average TSM concentrations were measured in the channels, except for September 2007. During that time high average concentrations of 34.4 and 26.1 mg l⁻¹ were detected in the Manguaba and Mundau lagoons, respectively. Very low TSM concentrations were determined in Mundau River and the Mundau Lagoon in October 2008 with average values of 9.8 and 8.6 mg l⁻¹. TSM in Paraiba do Meio was also low in October 2008 and had an average amount of 6.7 mg l⁻¹.

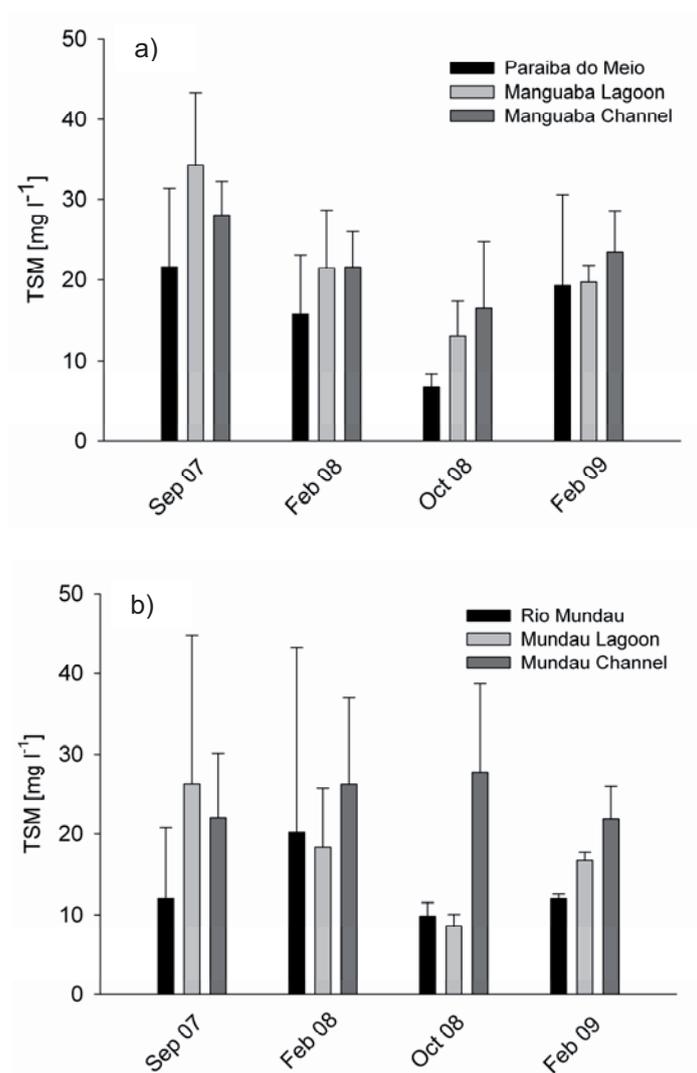


Figure 3: Total suspended matter distribution in the rivers, the lagoons and the channels of the Manguaba (a) and Mundau (b) lagoon system in September 2007, February 2008, October 2008 and February 2009.

C_{org} was positively correlated with TSM in the Manguaba lagoon ($r=0.6$, $p<0.001$, $n=96$) as well as in the Mundau lagoon ($r=0.5$, $p<0.001$, $n=55$).

The highest proportion of organic carbon (6.4 mg l^{-1}) coincided with the highest amount of particulate matter (49.7 mg l^{-1}) in the water column in the Manguaba lagoon in September 2007 (Fig. 4). In October 2008 TSM was low compared to the other sampling seasons and C_{org} values were

$<3 \text{ mg l}^{-1}$. A low average C/N ratio of 8.4 ± 1.3 was determined in the Manguaba lagoon in October 2008. Highest C/N ratios were generally detected in the river ($15.7 - 28.6$). The total nitrogen proportion of TSM was between 0.2 and 3.1 % in the Manguaba lagoon and lower values were detected in the Mundau lagoon ($0.1 - 2.4 \%$; Tab. 4).

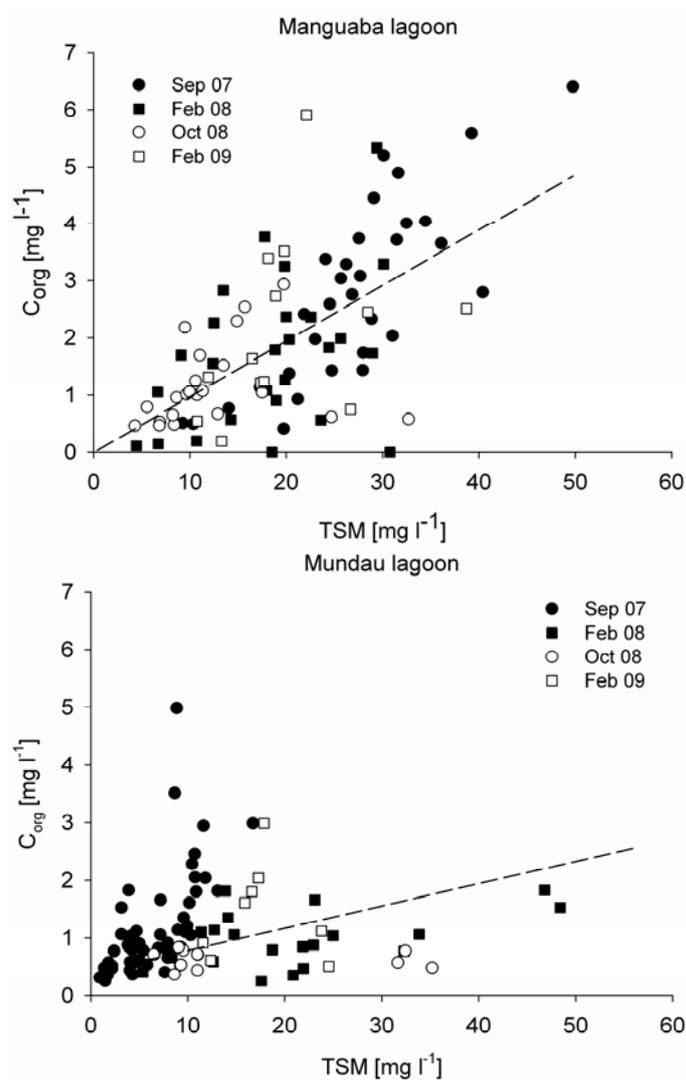


Figure 4: Portion of organic carbon in total suspended matter in the Mundau Manguaba Lagoon during different sampling seasons (September 2007, February 2008, October 2008 and February 2009). Dashed lines denote linear regressions ($r^2 = 0.4$ in Manguaba lagoon and $r^2 = 0.2$ in Mundau lagoon).

The Mundau lagoon (0.9 – 16.7 % C_{org}) showed a different distribution of organic carbon contents which were generally lower than in the Manguaba lagoon (1.5 – 26.7 % C_{org}). Low TSM amounts in the Mundau lagoon coincided with high C_{org} contents in September 2007 whereas in October 2008 high particulate matter concentrations matched with low C_{org} (<1 mg l⁻¹). C/N ratios in the Mundau lagoon were much higher than in the Manguaba lagoon and reached maximum average values of 26.1 inside the lagoon in September 2007 and in the channel in February 2008. During the sampling in October 2008 the average C/N ratios in the Mundau lagoon were much lower than during the other seasons (8.6 ± 1.4, Tab. 1).

Isotopic composition of total suspended matter

$\delta^{13}\text{C}_{\text{org}}$ in the lagoons displayed a wide range from -16.6 to -26.1 ‰ (Fig. 5). In the Manguaba lagoon $\delta^{13}\text{C}_{\text{org}}$ scatter mainly between -18.3 and -20.9 ‰ in September 2007 and were significantly different ($p < 0.05$, Kruskal-Wallis) in October 2008 when $\delta^{13}\text{C}_{\text{org}}$ between -21.1 and -23.3 ‰ was measured. Results from February showed a similar pattern with lower values in 2009 than in 2008 ($p < 0.05$, Kruskal-Wallis). $\delta^{13}\text{C}_{\text{org}}$ in the Mundau lagoon showed no clear pattern in the distribution and scattered between -19.0 and -23.9 ‰.

$\delta^{15}\text{N}$ ranged between 2.0 and 6.5 ‰ in the Manguaba lagoon whereas a wider range was measured in the Mundau lagoon (1.2 – 10.6 ‰). $\delta^{15}\text{N}$ was lower in the Manguaba lagoon in September 2007 and February 2008 than in October 2008 and February 2009 (Fig. 5, $p < 0.03$, ANOVA). $\delta^{15}\text{N}$ in the Mundau lagoon was higher in October 2008 than in September 2007. High

$\delta^{15}\text{N}$ values of ~ 10 ‰ were measured inside the lagoon in February 2008 and 2009 at the end of the dry season. At the beginning of the dry season $\delta^{15}\text{N}$ of ~ 2 ‰ was measured mainly in the Mundau River and in the Mundau channel.

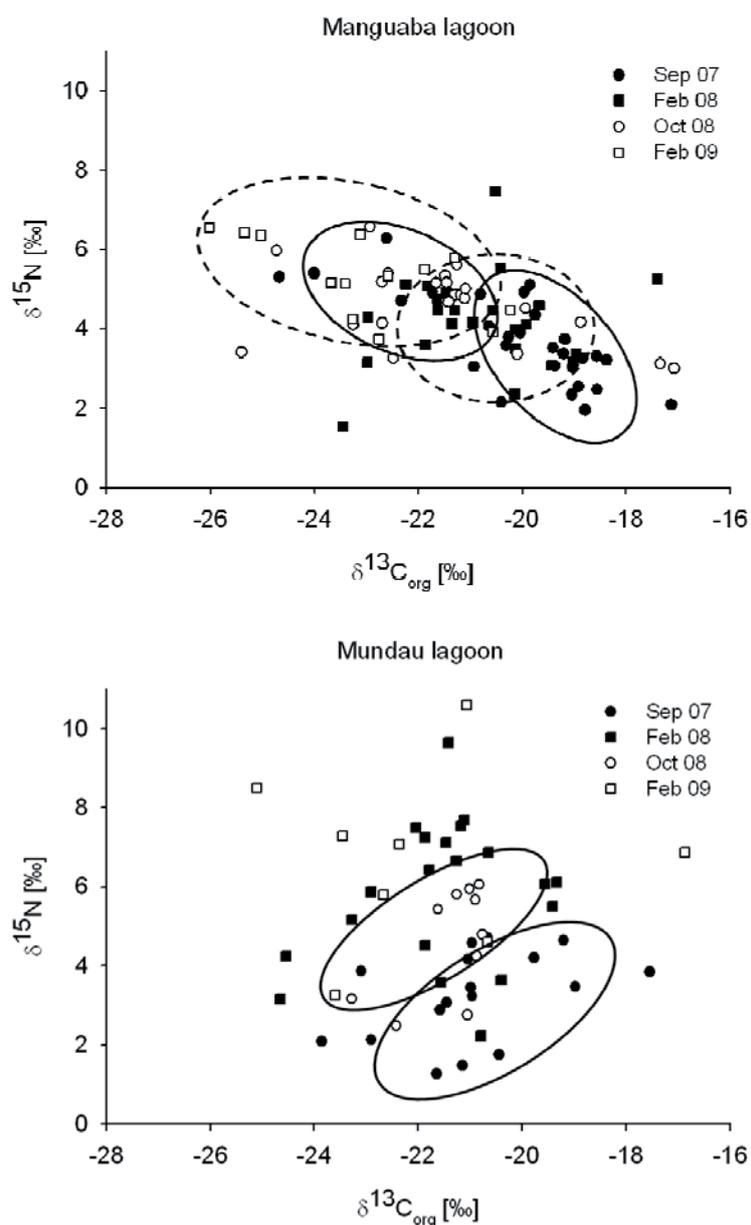


Figure 5: Dual stable isotope composition of total suspended matter in the lagoons in September 2007, February 2008, October 2008 and February 2009. Solid ellipses contain the main distribution of September 2007 and October 2008, dashed ellipses include the one from February 2008 and 2009 which showed statistically significant differences.

End members in the catchment area of the lagoons

Different sources for marine, river and plant and soil derived organic material in the Mundau Manguaba lagoon were determined as end members. Average TSM concentrations in the end members were highest in the Sumauma River with values of $22.6 \pm 14.6 \text{ mg l}^{-1}$. Lowest TSM was measured in the Lago Azul (0.4 mg l^{-1}) but its proportion of C_{org} was high (45.2 %). Lago Azul showed also lowest $\delta^{13}C_{\text{org}}$ (-24.7 ‰) and highest $\delta^{15}N$ (8.2 ‰ ; Tab. 2).

Table 2: Description of organic carbon (C_{org}) and total nitrogen (PN) content of the total suspended matter and its isotope ratio ($\delta^{13}C_{\text{org}}$, $\delta^{15}N$) from the end members in the Mundau Manguaba Lagoon.

Sample	C _{org} [%]	PN [%]	$\delta^{13}C$ [‰]	$\delta^{15}N$ [‰]	C/N	TSM [mg l ⁻¹]	n
Water							
Paraiba do Meio (river end-member)	7.2 ± 4.7	0.5 ± 0.1	-22.9 ± 0.4	4.7 ± 1.3	16.6 ± 8.0	11.1 ± 4.1	4
Sumauma (river end-member)	9.8 ± 5.6	0.8 ± 0.4	-21.2 ± 1.7	4.9 ± 1.3	13.7 ± 1.9	22.6 ± 14.6	4
Rio Mundau (river end-member)	5.4 ± 1.5	0.6 ± 0.3	-21.9 ± 1.0	4.7 ± 1.5	11.2 ± 2.6	11.7 ± 5.3	4
Ocean (marine end-member)	2.0 ± 0.5	0.4 ± 0.2	-20.7 ± 0.0	5.8 ± 1.2	8.2 ± 3.7	8.8 ± 4.0	4
Lago Azul (freshwater end-member)	45,2	1,7	-24,7	8,2	31,3	0,4	1
C4 Plant							
Sugar cane	43,7	1,1	-12,4	8,3	47,7	-	1
Bagasse (smashed sugar cane fibre)	43,0	1,0	-13,7	3,9	49,7	-	1
Reed	43.8 ± 0.4	3.3 ± 0.5	-12.1 ± 0.04	9.9 ± 0.7	15.7 ± 2.4	-	2
C3 Plant							
Mangrove leaf	44.0 ± 0.2	1.0 ± 0.0	-29.8 ± 0.6	4.6 ± 0.3	56,6	-	2
Water hyacinth (Mundau lagoon)	35.0 ± 3.8	1.0 ± 0.0	-27.0 ± 0.5	10.1 ± 1.0	41.7 ± 3.3	-	3
Water hyacinth (Manguaba lagoon)	29.9 ± 9.4	1.0 ± 0.1	-27.7 ± 0.9	7.2 ± 1.4	35.3 ± 12.0	-	3
Soil							
Mangrove	1.5 ± 0.4	0.1 ± 0.0	-	4.1 ± 0.1	19.9 ± 6.6	-	3
Sugar cane field (fresh ploughed)	1.4 ± 0.8	0.1 ± 0.1	-18.3 ± 1.4	5.7 ± 1.3	16.5 ± 4.1	-	2
Sugar cane field (fresh burned)	1.2 ± 0.2	0.1 ± 0.0	-17.3 ± 2.4	5.7 ± 1.9	22.0 ± 1.9	-	2
Sugar cane field (plants ~0.4 - 3m)	1.2 ± 0.3	0.1 ± 0.0	-17.4 ± 2.0	5.5 ± 0.8	20.0 ± 2.6	-	8

Average organic carbon content was very similar for the C4 plants and the mangrove leaf (43.0 to $44.0 \text{ ‰} \pm 0.2$). C_{org} content of the water hyacinth was lower in the Manguaba than in the Mundau lagoon. C4 plants such as

sugar cane and reed had a $\delta^{13}\text{C}_{\text{org}}$ of ~ -13 ‰ and C3 plants like mangroves and water hyacinth of ~ -28 ‰ in the study area (Tab. 2). $\delta^{15}\text{N}$ of the plant material showed a wide range (3.9 – 11.1 ‰) with a remarkable difference in $\delta^{15}\text{N}$ values of the water hyacinths between the lagoons (Mundau lagoon: $10.1 \text{ ‰} \pm 1.0$, Manguaba lagoon: $7.2 \text{ ‰} \pm 1.4$). The $\delta^{15}\text{N}$ of 3.9 ‰ in bagasse, which are the smashed sugar cane fibers after the processing in the factories, was much lower than in fresh sugar cane plants (8.3 ‰).

Soil material showed only small differences in its composition. Especially C/N ratios varied between the different sugar cane soil types and lowest values were calculated for freshly ploughed sugar cane fields without plants. Slight variations were also detected in the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ of the different soils (Tab. 2).

Elemental and isotopic composition of the sediment cores

The data sets of sediment cores from each lagoon displayed no statistically significant differences between locations. Therefore they were considered as replicates and average values used in the following. The only exception was the sediment core in the upper part of the Mundau lagoon which was close to the Rio Mundau and showed differences in the upper 10 cm compared to the other cores. Organic carbon content in the sediment cores varied between 0.7 and 4.9 % (Fig. 6). Average concentrations in the Manguaba lagoon (3.9 ± 0.7 %) were higher than in the Mundau lagoon (2.7 ± 0.4 %; Fig. 6). In both lagoons C_{org} was high and then decreased downcore until ~ 45 cm. The total nitrogen in the sediment cores was

between 0.4 to 0.7 % in the Manguaba lagoon and had lower values between 0.1 and 0.4 % in the Mundau lagoon.

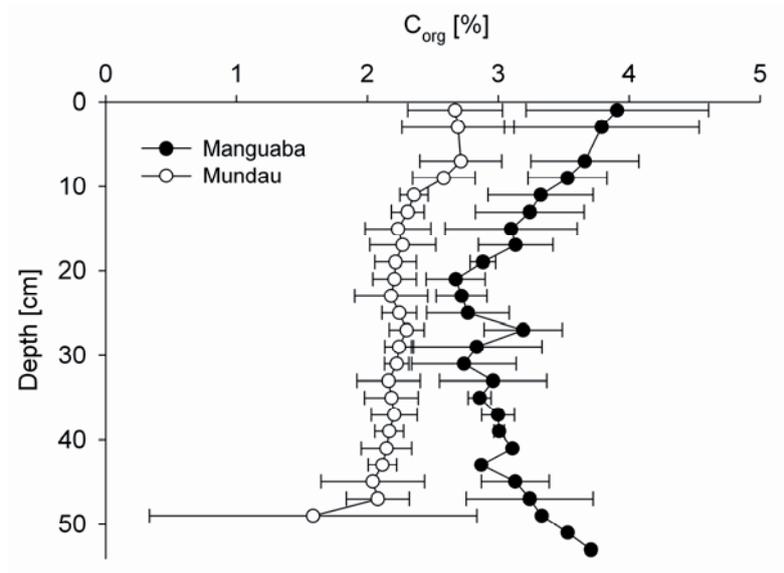


Figure 6: Average organic carbon concentrations with standard deviation in different depths of sediment cores from Manguaba lagoon ($n = 4$) and Mundau lagoon ($n = 4$).

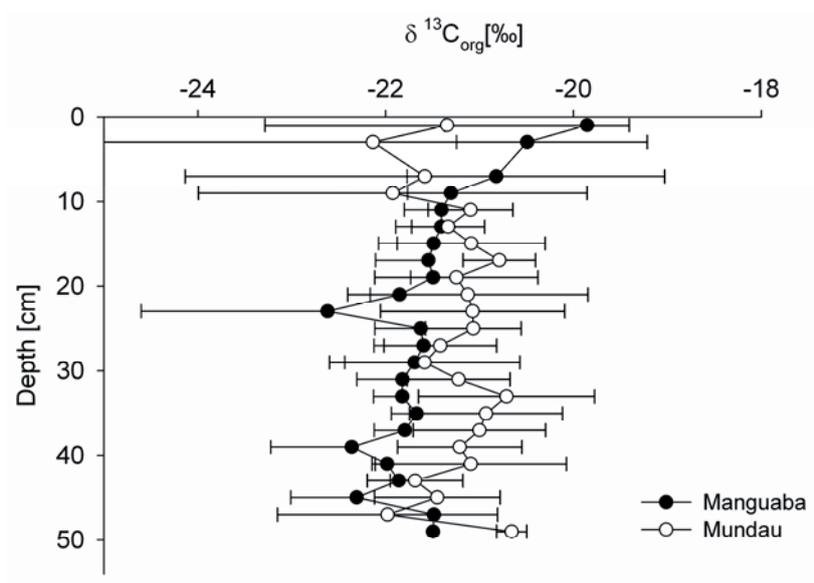


Figure 7: Average $\delta^{13}C_{org}$ with standard deviation in different depths of sediment cores from Manguaba lagoon ($n = 4$) and Mundau lagoon ($n = 4$).

Average $\delta^{13}\text{C}_{\text{org}}$ ranged between -18.3 to -26.5 ‰ and $\delta^{15}\text{N}$ between 2.5 to 7.5 ‰, respectively (Fig. 7, 8). Lower $\delta^{13}\text{C}_{\text{org}}$ values were observed in the upper 10 cm of the sediment in the Mundau lagoon compared to the Manguaba lagoon. $\delta^{13}\text{C}_{\text{org}}$ of the sediment in Manguaba lagoon decreased in the upper 10 cm of the core from -19.9 ± 1.5 ‰ to -21.5 ± 0.6 ‰ whereas the values in Mundau showed no clear trend (Fig. 7).

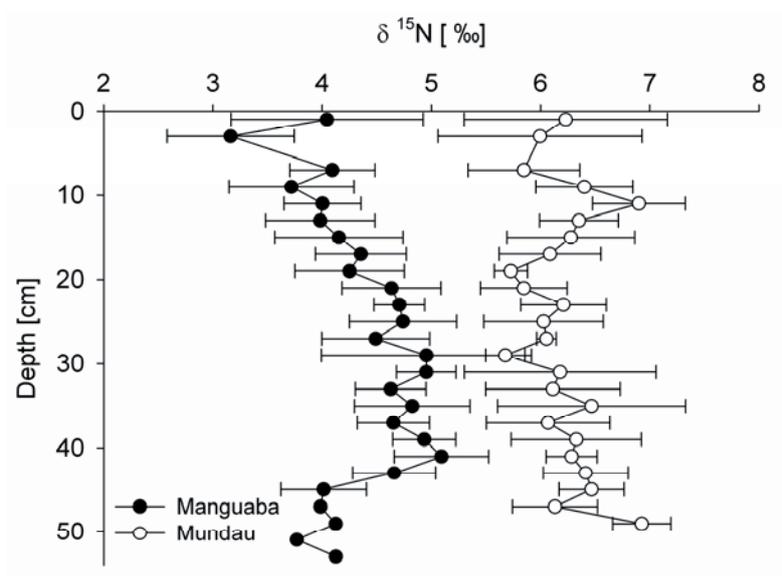


Figure 8: Average $\delta^{15}\text{N}$ with standard deviation in different depths of sediment cores from Manguaba lagoon ($n = 4$) and Mundau lagoon ($n = 4$).

But the core in Mundau lagoon which was close to the entrance of Rio Mundau had a much lower $\delta^{13}\text{C}_{\text{org}}$ (-24.2 to -26.5 ‰) in the upper 10 cm compared to the other cores. Average $\delta^{15}\text{N}$ values in the Mundau lagoon were generally higher than in the Manguaba lagoon (Mundau: 5.0 – 7.5 ‰; Manguaba: 2.5 – 5.7 ‰; Fig. 8). Slight increases were measured with increasing depth in the Manguaba lagoon until ~ 40 cm whereas no clear pattern was observed in the Mundau lagoon.

Table 3: Total nitrogen content (PN) of total suspended matter in the Manguaba and Mundau Lagoon in September 2007, February 2008, October 2008 and February 2009 and total nitrogen content in the sediment cores from March 2007.

	Manguaba Lagoon	Mundau Lagoon
Suspended matter	PN [%]	PN [%]
September 2007	n = 38	n = 17
Minimum	0,3	0,1
Maximum	2,4	1,9
Mean	1,2	1,0
Stdev.	0,6	0,4
February 2008	n = 25	n = 20
Minimum	0,2	0,1
Maximum	3,1	1,6
Mean	1,3	0,8
Stdev.	0,8	0,5
October 2008	n = 23	n = 10
Minimum	0,2	0,2
Maximum	3,0	1,5
Mean	1,2	0,7
Stdev.	0,7	0,5
February 2009	n = 15	n = 8
Minimum	0,4	0,4
Maximum	3,0	2,4
Mean	1,3	1,3
Stdev.	0,9	0,9
Sediment cores		
March 2007	n = 83	n = 89
Minimum	0,4	0,1
Maximum	0,7	0,4
Mean	0,4	0,2
Stdev.	0,1	0,1

DISCUSSION

Sources and distribution of organic matter in the water column of the lagoons

The composition of particulate material contains information about organic matter sources and their modification in aquatic systems. C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ values (-17.1 to -24.6 ‰) in the lagoons indicate that both phytoplankton and terrestrial organic material were part of the suspended matter in September 2007. C/N values >15 are typical for cellulose- and lignin-rich land plants whereas ratios <8 point to marine phytoplankton (Kendall, 2001).

The range of measured $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ values of the TSM samples covered the potential end members which were determined in the Mundau Manguaba Lagoon except for the $\delta^{15}\text{N} < 2.8$ ‰. $\delta^{13}\text{C}_{\text{org}}$ of ~ -17 ‰ and $\delta^{15}\text{N}$ of ~ 3 ‰ in the TSM of the Manguaba lagoon in September 2007 and October 2008 were similar to the isotope values of bagasse (Fig. 5). Bagasse are the smashed sugar cane fibers which are produced during the processing in the sugar cane factories. This organic material is used as fertilizer on the fields and has a higher $\delta^{13}\text{C}_{\text{org}}$ and lower $\delta^{15}\text{N}$ than the fresh sugar cane plant material (Tab. 2). At the beginning of the dry season, after heavy rain showers some days before the sampling, bagasse or material from the remains of burned and harvested plants on the fields seemed to be a main source of organic material that was washed into the rivers and finally transported to the lagoons.

The $\delta^{13}\text{C}_{\text{org}}$ of the freshwater end members in the Mundau Manguaba Lagoon was determined between -20.7 and -24.7 ‰ and pointed to a mixing of sources. But the occurrence of freshwater phytoplankton, which was observed as biomass in the rivers seemed to be a main source at these sampling stations (Spörl et al., submitted.). Additionally, allochthonous organic matter from the sugar cane fields in the catchment area of the rivers were potential sources as no marine influence affected these parts of the rivers. TSM in the Lago Azul end member was very low (0.4 mg l^{-1}). $\delta^{13}\text{C}_{\text{org}}$ (-24.7 ‰) in combination with C/N (31.1) values pointed to macrophytes as origin for organic material in the Lago Azul. C/N ratios of 10 to 30 or even >80 is indicative of old and woody aquatic plants as source which can in parts already be degraded (Kendall, 2001).

The $\delta^{15}\text{N}$ value of 8.2 ‰ in the Lago Azul can be a result of isotopic fractionation in combination with transformation processes which can alter the $\delta^{15}\text{N}$ of nitrate and ammonium in the aquatic environments (Kendall, 2001). $\delta^{15}\text{N}$ of dissolved inorganic nitrogen in the water controls the $\delta^{15}\text{N}$ of the plants which take up dissolved inorganic nitrogen. Plants discriminate against ^{15}N during nutrient uptake which leads to incorporation of relatively more ^{14}N into their biomass. This fractionation could influence the remaining nitrogen pool with higher $\delta^{15}\text{N}$ values that furthermore could be used for primary production by aquatic plants resulting in higher $\delta^{15}\text{N}$ in their tissues. $\delta^{15}\text{N}$ in TSM could also raise due to fractional degradation of organic material because of a faster decomposition of ^{14}N .

High $\delta^{15}\text{N}$ in the TSM ($\sim 10\text{‰}$) of the Mundau lagoon mainly at the end of the dry season points to municipal sewage from the city of Maceio which borders the Mundau lagoon as additional source as the Rio Mundau which discharges into the lagoon showed lighter nitrogen isotope values of $\sim 4.7\text{‰}$. Nitrate derived from waste water (sewage) is usually characterized by $\delta^{15}\text{N}$ values $> 10\text{‰}$ (Grischek et al., 1998; Kendall, 1998). A study on the lipid biomarker composition corroborates our finding that waste water from Maceio city contributed to the particulate matter pool in the Mundau lagoon (Costa et al., 2011).

Potentially high $\delta^{15}\text{N-NO}_3$ from sewage in the Mundau lagoon led to high $\delta^{15}\text{N}$ of TSM and also to high $\delta^{15}\text{N}$ in the water hyacinth tissue compared to the water hyacinth tissue in the Manguaba lagoon as the plants consumed the dissolved nitrogen for their growth. The low $\delta^{15}\text{N}$ values in the lagoons which were mainly detected in the beginning of the dry season indicate high input of atmospheric nitrogen through nitrogen fixation by cyanobacteria as this phytoplankton group was very abundant during this time (Spörl et al., submitted).

The application of mineral fertilizer ($\delta^{15}\text{N}$ of $0 \pm 4\text{‰}$) to agricultural soil could also be an important source which influenced the nitrogen isotopic composition in a system (Kendall, 1998). Broadbent et al. (1980) showed from soil surveys that $\delta^{15}\text{N}$ for cultivated and fertilized soils was $0.7 \pm 2.6\text{‰}$ and $2.7 \pm 3.4\text{‰}$ for uncultivated soils, respectively. $\delta^{15}\text{N}$ values close to 0‰ which point to fertilizer were not detected in cultivated sugar cane fields in the catchment area of the Mundau Manguaba Lagoon most

probably due to the use of the organic bagasse as fertilizer which has a $\delta^{15}\text{N}$ of $\sim 4\text{‰}$ (Tab. 2).

Fate of suspended organic matter in the sediments

Because of a lack of TSM samples from March 2007 when the cores were taken, TSM data from February 2008 and March 2009 may give hints on organic matter production, transformation and decomposition in the water column at the beginning of the dry season. The pattern for average surface sedimentary C_{org} concentrations was very similar to the C_{org} concentrations of the TSM in the lagoons with higher average values in the Manguaba lagoon than in the Mundau lagoon ($3.8 \pm 0.7\%$ and $2.7 \pm 0.4\%$, respectively). But the lagoon sediments contained 3 to 4 times less organic carbon when compared to the TSM. The low C_{org} and N contents in the sediments are probably due to the fast decomposition of organic matter and showed consequently a strong decrease in organic carbon content with increasing depth in the upper layers of the sediment cores in the Manguaba lagoon.

The Manguaba sediment cores had lower average $\delta^{13}C_{\text{org}}$ values in the surface layers compared to Mundau lagoon which is consistent with the range of $\delta^{13}C_{\text{org}}$ observed in TSM. TSM in the lagoons appeared to be mainly derived from particles transported by the rivers which contain sugar cane material and biological production due to high phytoplankton biomass. Over time material can sink through the water column and accumulate in the sediment. Differences in the residence time of the lagoons and the turbidity triggered by the tidal variation seemed to have an important

influence on the fate of the material. $\delta^{13}\text{C}_{\text{org}}$ of ~ -21 ‰ in the surface sediments mainly in the Mundau lagoon is probably indicating strong marine carbon composition in sediments. Intrusion of marine water due to the wide channel in the Mundau lagoon was higher when compared to Manguaba lagoon which is characterized by a restricted tidal exchange and a longer residence time.

Sedimentary $\delta^{15}\text{N}$ of the Mundau lagoon was higher when compared to the Manguaba lagoon. $\delta^{15}\text{N}$ values in the strong marine influenced Mundau lagoon which are in parts in the range of marine nitrate (~ 6 ‰) in combination with high $\delta^{15}\text{N}$ from sewage in TSM of the water column may result in the $\delta^{15}\text{N}$ differences in the lagoons (e.g. Cline and Kaplan, 1975). However, the sediment core in the upper part of the Mundau lagoon which was close to the mouth of the Rio Mundau showed higher terrestrial input. This was most probably the result of lower $\delta^{13}\text{C}_{\text{org}}$ from C3 plants which grew in large amounts along the river bank in this area.

Comparison with other aquatic systems

When comparing the obtained results with other anthropogenic affected regions, the percentage of C_{org} in Mundau Manguaba Lagoon was high compared to other systems (Tab. 4). The Kallada River in India, showed C_{org} values between 2.7 and 3.2 % which seemed to be a result of wash out of organic rich soil mainly from agriculture areas during the monsoon season (Jennerjahn et al., 2008). Similar results were also reported from the Changjiang River in China, where carbon and nitrogen isotope values underlined that soil from the catchment area is probably the main source for

the organic matter composition of the TSM in the estuary (Zhang 2007). In contrast, the high organic carbon contents in the Mundau Manguaba Lagoon are probably due to the long residence time in the lagoons associated with high phytoplankton production and the accumulation of the sugar cane organic material from the catchment area.

Table 4: Composition of C_{org} and PN contents, C/N ratio, $\delta^{13}C_{org}$ and $\delta^{15}N$ of total suspended matter in different tropical and temperate aquatic systems

1. This study
2. Krusche et al., (2002)
3. Martinelli et al., (1999)
4. Hedges et al., (1986)
5. Townsend-Small et al., (2007)
6. Barros et al., (2010)
7. Jennerjahn et al., (2004)
8. Jennerjahn et al., (2008)
9. Zhang et al., (2007)
10. Cifuentes et al., (1988)
11. Middelburg and Nieuwenhuize, (1998)

Location	C_{org} [%]	PN [%]	$\delta^{13}C_{org}$ [‰]	$\delta^{15}N$ [‰]	C/N	Data source
tropical/ subtropical						
Mundau Manguaba Lagoon (Brazil)	0.9 - 26.7	0.1 - 3.1	-16.9 to -26.0	1.3 - 10.6	7.1 - 12.5	1
Piracicaba River (Brazil)	~ 5.7	0.6 - 0.7	-23.8 to -26.2	-	9.2 - 12.1	2, 3
Amazon River (Brazil)	1.0 - 1.2	0.05 - 1.1	-27.0 to -27.8	< 4.0	11.1 - 24.1	4, 5
Babitonga Bay (Brazil)	0.3 - 2.9	0.04 - 0.4	-21.7 to -26.2	-0.1 to 9.3	5.8 - 13.1	6
Brantas River (Indonesia)	0.4 - 1.2	≤ 0.1	-19.6 to -28.9	-2.3 to 10.0	6.4 - 12.7	7
Kallada River (India)	2.7 - 7.9	0.2 - 1.0	-24.2 to -26.9	-2.7 to 5.4	7.1 - 12.7	8
temperate						
Changjiang River (China)	0.8 - 1.4	0.1 - 0.2	-23.0 to -28.2	1.8 - 3.7	3.9 - 13.9	9
Delaware Estuary (USA)	-	-	-16.4 to -25.8	3.7 - 18.7	5 - 18	10
Schelde Estuary (Belgium)			-20.1 to -28.9	9.5 - 12.0	8.9 - 9.1	11

Isotopic composition of organic material in the Brantas River in Indonesia and the Delaware Estuary in USA showed $\delta^{13}\text{C}_{\text{org}}$ ranges of -19.6 to -28.9 ‰ and -16.4 to -25.8 ‰ and $\delta^{15}\text{N}$ ranges of -2.3 to 10.0 ‰ and 3.7 to 18.7-16.9, respectively. Main sources for organic material in the Brantas River were agricultural runoff during the rainy season and phytoplankton production during the dry season (Jennerjahn et al., 2004). The two major pools of organic matter in the Delaware estuary were the in situ phytoplankton growth and a mixture of planktonic and terrestrial detritus (Cifuentes et al., 1988).

The obtained results from Mundau Manguaba system were within similar ranges, except for the low $\delta^{15}\text{N}$ values observed in the Brantas River and the high $\delta^{15}\text{N}$ values described for the Delaware Estuary. Although phytoplankton data from the Mundau Manguaba Lagoon suggested nitrogen fixation by cyanobacteria, the detected $\delta^{15}\text{N}$ were higher than the values in the Brantas River at Wonokromo stations 1 II and 2 II where negative or near to zero $\delta^{15}\text{N}$ of TSM indicated N_2 -fixation as major nitrogen source. This findings were attributed to the dominance of nitrogen fixing cyanobacteria in the phytoplankton community of these stations (Jennerjahn et al., 2004). Cifuentes et al. (1988) suggested that the increase in nitrogen isotope values in the Delaware Estuary was due to extensive nutrient uptake by phytoplankton which became a dominant pool of the organic matter in the system.

Bobitonga Bay in south Brazil which is influenced by heavy industry and urbanization showed $\delta^{15}\text{N}$ up to 9.3 ‰ pointing to contamination by sewage

(Barros et al., 2010). In contrast, $\delta^{15}\text{N}$ of TSM from the Amazon River which is almost a pristine area with no signs of anthropogenic input was ~ 4.0 ‰ (Townsend-Small et al., 2007). Division into coarse and fine fractions of the particulate suspended material in the Amazon River showed that these fractions had almost the same $\delta^{13}\text{C}_{\text{org}}$ ranges but higher C/N ratios in the coarse fraction. Therefore the coarse fraction was considered as less degraded and relatively new material (Hedges et al., 1986).

Similar observations in the Piracicaba River basin which receives urban sewage and industrial effluents suggested that the coarse fraction additionally comprised elevated levels of C4 plant material which was due to sugar cane as new vegetation type in this region. However, $\delta^{13}\text{C}_{\text{org}}$ (> -21.7 ‰) in this sugar cane influenced area was still higher than $\delta^{13}\text{C}_{\text{org}}$ (> -16.9 ‰) of the TSM in the Mundau Manguaba Lagoon (Krusche et al., 2002; Martinelli et al., 1999). These findings pointed to a strong outwash of sugar cane soil and bagasse which was applied as fertilizer to sugar cane fields in the catchment area of the Mundau Manguaba Lagoon.

SUMMARY AND CONCLUSION

Stable isotope analyses have shown that suspended particulate and sedimentary matter has both natural and anthropogenic sources in the Mundau Manguaba lagoon. Impact from sugar cane plants directly or material like bagasse or soil from sugar cane fields could be observed in the lagoons whereas the Mundau lagoon showed also influences from sewage from the city of Maceio. Different water residence times in the

lagoons in combination with tidal export were probably responsible for variations in productivity of autochthonous material. Sedimentary organic matter showed that in the Manguaba lagoon which has a long residence time and a reduced tidal exchange due to a narrow channel sugar cane material is retained and accumulated inside the lagoon. The lower proportion of TSM in the Mundau lagoon and strong tidal intrusion suggest an outwelling of sugar cane and sewage organic material into the adjacent coastal waters.

ACKNOWLEDGEMENTS

We would like to thank our Brazilian partners from POLCAMAR project for their support during our work in Brazil. We especially thank Paulo Petter and the technicians from UFAL in Maceio for their assistance during the expedition and for providing information and facilities. We also thank Dorothee Dasbach for laboratory work at ZMT. Financial support by the German Federal Ministry for Education and Research (BMBF) is gratefully acknowledged (Grant No. 03F0455D). This study is part of the INCT-TMCOcean (www.incttmcocean.com.br) "Continent-Ocean Materials Transfer" project supported by CNPq, Brazil, Process nº 573.601/2008-9.

REFERENCES

- ANA, 2005. *Elaboração do Plano de Ações e Gestão Integrada do Complexo Estuarino-Lagunar Mundaú/Manguaba - CELMM, Agencia Macopmaö de Aguas*; <http://www.ana.gov.br>, Brazil.
- Artemyev, V.E., 1996. *Geochemistry of Organic Matter in River-Sea Systems*. Kluwer Academic Publishers, Dordrecht.
- Barros, G.V., Martinelli, L.A., Oliveira Novais, T.M., Ometto, J.P.H.B. and Zuppi, G.M., 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil). *Science of the Total Environment*, 408(10): 2226-2232.
- Basanta, M.V. et al., 2003. Management effects on nitrogen recovery in a sugarcane crop grown in Brazil. *Geoderma*, 116: 235-248.
- Broadbent, F.E., Rauschkolb, R.S., Lewis, K.A. and Chang, G.Y., 1980. Spatial variability of N-15 and total nitrogen in some virgin and cultivated soils. *Soil Science Society of America Journal*, 44(3): 524-527.
- Budge, S.M. and Parrish, C.C., 1998. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. *Organic Geochemistry*, 29(5-7): 1547-1559.
- Carpenter, E.J. et al., 1999. Extensive bloom of a N-2-fixing diatom/cyanobacterial association in the tropical Atlantic Ocean. *Marine Ecology-Progress Series*, 185: 273-283.
- Carreira, R.S. et al., 2002. Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: an elemental, isotopic and molecular marker approach. *Marine Chemistry*, 79(3-4): 207-227.
- Cifuentes, L.A. et al., 1996. Isotopic and Elemental Variations of Carbon and Nitrogen in a Mangrove Estuary. *Estuarine, Coastal and Shelf Science*, 43: 781-800.
- Cifuentes, L.A., Sharp, J.H. and Fogel, M.L., 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnology and Oceanography*, 33(5): 1102-1115.

- Cline, J.D. and Kaplan, I.R., 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north pacific ocean. *Marine Chemistry*, 3(4): 271-299.
- Costa, T., Araújo, M., Knoppers, B. and Carreira, R., 2011. Sources and Distribution of Particulate Organic Matter of a Tropical Estuarine-Lagoon System from NE Brazil as Indicated by Lipid Biomarkers. *Aquatic Geochemistry*, 17(1): 1-19.
- Dähnke, K., Bahlmann, E. and Emeis, K., 2008. A nitrate sink in estuaries? An assessment by means of stable nitrate isotopes in the Elbe estuary. *Limnology and Oceanography*, 53(4): 1504-1511.
- FIAN and GTZ, 2002. Economic, social and ecological impacts on Brazil of accelerated liberalisation of the European sugar market. In: D.G.f.T.Z. GmbH (Editor). *Deutsche Gesellschaft für Technische Zusammenarbeit GmbH*, Heidelberg, pp. 1-59.
- Fischer, G., 1991. Stable carbon isotope ratios of plankton carbon and sinking organic matter from the Atlantic sector of the Southern Ocean. *Marine Chemistry*, 35(1-4): 581-596.
- Goldemberg, J., Coelho, S.T. and Guardabassi, P., 2008. The sustainability of ethanol production from sugarcane. *Energy Policy*, 36(6): 2086-2097.
- Grischek, T., Hiscock, K.M., Metschies, T., Dennis, P.F. and Nestler, W., 1998. Factors affecting denitrification during infiltration of river water into a sand and gravel aquifer in Saxony, Germany. *Water Research*, 32(2): 450-460.
- Hansson, S. et al., 1997. The Stable Nitrogen Isotope Ratio as a Marker of Food-Web Interactions and Fish Migration. *Ecology*, 78(7): 2249-2257.
- Hedges, J.I. et al., 1986. Compositions and Fluxes of Particulate Organic Material in the Amazon River. *Limnology and Oceanography*, 31(4): 717-738.
- Heip, C.H.R. et al., 1995. Production and consumption of biological particles in temperate tidal estuaries. In: A.D. Ansell, R.N. Gibson and M. Barnes (Editors), *Oceanography and Marine Biology: an Annual Review*. UCL Press, London, pp. 1-149.

-
- Hu, J., Peng, P.a., Jia, G., Mai, B. and Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. *Marine Chemistry*, 98(2-4): 274-285.
- Jassby, A.D., Cloern, J.E. and Powell, T.M., 1993. Organic carbon sources and sinks in San Francisco Bay - variability induced by river flow. *Marine Ecology-Progress Series*, 95(1-2): 39-54.
- Jennerjahn, T. et al., 2008. Effect of land use on the biogeochemistry of dissolved nutrients and suspended and sedimentary organic matter in the tropical Kallada River and Ashtamudi estuary, Kerala, India. *Biogeochemistry*, 90(1): 29-47.
- Jennerjahn, T.C. et al., 2004. Biogeochemistry of a tropical river affected by human activities in its catchment: Brantas River estuary and coastal waters of Madura Strait, Java, Indonesia. *Estuarine, Coastal and Shelf Science*, 60(3): 503-514.
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: C. Kendall and M.J. J. (Editors), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam.
- Kendall, C.S., Steven R.; Kelly, Valerie J., 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large systems across the United States. *Hydrological Processes*, 15: 1301-1346.
- Krusche, A.V. et al., 2002. Composition of particulate and dissolved organic matter in a disturbed watershed of southeast Brazil (Piracicaba River basin). *Water Research*, 36(11): 2743-2752.
- Lee, K.S., Bong, Y.S., Lee, D., Kim, Y. and Kim, K., 2008. Tracing the source of nitrate in the Han River watershed in Korea, using delta (15) N-NO₃⁻ and delta (18) O-NO₃⁻ values. *Science of the Total Environment*, 395: 117-124.
- Liu, K.K. and Kaplan, I.R., 1989. The eastern tropical Pacific as a source of delta super(15)N-enriched nitrate in seawater off southern California. *Limnologic Oceanography*, 34(5): 820-830.
- Liu, M. et al., 2006. Organic carbon and nitrogen stable isotopes in the intertidal sediments from the Yangtze Estuary, China. *Marine Pollution Bulletin*, 52(12): 1625-1633.

- Martinelli, L.A. and Filoso, S., 2008. Expansion of sugarcane ethanol production in Brazil: environmental and social challenges. *Ecological Applications*, 18(4): 885-898.
- Martinelli, L.A. et al., 1999. Effects of Sewage on the Chemical Composition of Piracicaba River, Brazil. *Water, Air, & Soil Pollution*, 110(1): 67-79.
- McClelland, J.W. and Valiela, I., 1998. Changes in food web structure under the influence of increased anthropogenic nitrogen inputs to estuaries. *Marine Ecology-Progress Series*, 168: 259-271.
- Middelburg, J.J. and Herman, P.M.J., 2007. Organic matter processing in tidal estuaries. *Marine Chemistry*, 106(1-2): 127-147.
- Middelburg, J.J. and Nieuwenhuize, J., 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. *Marine Chemistry*, 60(3-4): 217-225.
- Oliveira, A.M. and Kjerfve, B., 1993. Environmental Responses of a Tropical Coastal Lagoon System to Hydrological Variability: Mundau-Manguaba, Brazil. *Estuarine, Coastal and Shelf Science*, 37(6): 575-591.
- Oliveira, J.I.C.s.M.d. et al., 2000. Nitrogen dynamics in a soil-sugar cane system. *Scientia Agricola*, 57: 467-472.
- Peters, K.E., Sweeney, R.E. and Kaplan, I.R., 1978. Correlation of Carbon and Nitrogen Stable Isotope Ratios in Sedimentary Organic Matter. *Limnology and Oceanography*, 23(4): 598-604.
- Schaefer, P. and Ittekkot, V., 1993. Seasonal variability of delta super(15)N in settling particles in the Arabian Sea and its palaeochemical significance. *Naturwissenschaften*, 80(11): 511-513.
- Sweeney, R.E. and Kaplan, I.R., 1980. Natural abundances of 15N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry*, 9(2): 81-94.
- Townsend-Small, A., Noguera, J.L., McClain, M.E. and Brandes, J.A., 2007. Radiocarbon and stable isotope geochemistry of organic matter in the Amazon headwaters, Peruvian Andes. *Global Biogeochemical Cycles*, 21(2): GB2029.
- UNICA, 2001. *Energia da Cana-de-Açúcar e Redução do Efeito Estufa.*, São Paulo.

- Voss, M., Dippner, J.W. and Montoya, J.P., 2001. Nitrogen isotope patterns in the oxygen-deficient waters of the Eastern Tropical North Pacific Ocean. *Deep Sea Research Part I: Oceanographic Research Papers*, 48(8): 1905-1921.
- Voss, M. et al., 2005. Riverine discharge into a coastal bay: A stable isotope study in the Gulf of Gdansk, Baltic Sea. *Journal of Marine Systems*, 57(1-2): 127-145.
- Zhang, J., Wu, Y., Jennerjahn, T.C., Ittekkot, V. and He, Q., 2007. Distribution of organic matter in the Changjiang (Yangtze River) Estuary and their stable carbon and nitrogen isotopic ratios: Implications for source discrimination and sedimentary dynamics. *Marine Chemistry*, 106(1-2): 111-126.

Presentations and Co-author Publications

First author presentations on international conferences

Spörl, G. & T. Jennerjahn: Stable nitrogen and carbon isotope composition of suspended matter and sediments in a coastal lagoon affected by sugar cane monoculture in NE Brazil. ASLO- Aquatic Science Meeting 2009, 25.-30. January 2009, Nice (France).

Co-author presentations on international conferences

Alves, Marina C., **Spörl Gertrud**, Bernardes Marcelo C., Knoppers Bastiaan A.: TRAÇADORES DA MATÉRIA ORGÂNICA NOS SEDIMENTOS DE UM SISTEMA LAGUNAR TROPICAL DO NORDESTE DO BRASIL, Congresso Brasileiro de Geoquímica, Ouro Preto, 22.-25. October 2009

Co-author publications

Michelle P. Araújo, Talitha L.F.Costa, **Gertrud Spörl**, Bastiaan A. Knoppers, Renato S. Carreira: Spatial and temporal changes in the accumulation of organic matter in a tropical Brazilian estuarine-lagoon system as revealed by lipid biomarkers

Submitted to Marine Chemistry

Brockmeyer, B., **Spörl, G.**, Knoppers, B.A., Spitzky, A.: Composition of dissolved, colloidal and particulate organic matter in a sugar cane impacted estuary in northeast Brazil (Manguaba lagoon).

Will be submitted to Biogeochemistry

Acknowledgements

Zuallererst möchte ich mich bei meinem Betreuer PD Tim Jennerjahn bedanken, für die Möglichkeit, meine Doktorarbeit in dem tollen Land Brasilien machen zu können, für die Freiheiten, die er mir während meiner Arbeit zugestand und für all die Diskussionen und Denkanstöße während der letzten Jahre, in denen ich sehr viel lernen konnte.

Vielen herzlichen Dank an Prof. Kai Bischof, der sich sehr kurzfristig bereit erklärt hat, meine Arbeit zu begutachten und Mitglied meiner Prüfungskommission zu sein.

Ein herzliches Dankeschön auch an Prof. Ulrich Saint-Paul für seine Zusage als Prüfer.

Mein ganz besonderer Dank gilt Prof. Herwig Stibor, der mir schon seit meiner Diplomarbeit zur Seite steht und mich während meiner Doktorarbeit immer wieder unterstützt hat. Danke für deinen unermüdlichen Einsatz und dass du die lange Reise aus Frankreich auf dich genommen hast, um an meiner Verteidigung teilzunehmen.

Ganz herzlich möchte ich mich bei meinem brasilianischen Koordinator Prof. Bastiaan Knoppers bedanken, der keine Mühen gescheut hat, uns die besten Arbeitsbedingungen in Brasilien zu schaffen. Vielen Dank für all die Unterstützung.

Very special thanks go to Prof. Carlos Eduardo Veiga de Carvalho for his infinite support during my work in Brazil and also for all his advices. I also would like to thank him to introduce me to the Brazilian culture, the crazy way of living and for making all my visits a wonderful and unforgettable experience. Obrigada!

Mein riesengroßer Dank geht an meine Projekt - Doktorandenkollegen Berit Brockmeyer und Lars Wolff, sowie an Immo Becker, für die gemeinsame

Acknowledgements

Arbeit und das gemeinsame Planen und Diskutieren während meiner Arbeit, aber vor allem für die tolle Zeit in Brasilien.

Furthermore, I would like to thank the Brazilian scientists and technicians Dr. Paulo Petter, Prof. Tereza dos S. Calado, Silvia and Flavio from UFAL, Dr. Nilva Brandini and Dr. Weber Landim de Souza from UFF and Dr. Marco Salomao, Bianca, Fred, Tiago, Wendel, Felipe, Jomar and Pedro from UENF and all other colleagues and students for sharing their knowledge, lab space and support.

Thank you very much to Prof. Carlos Rezende from UENF who gave me the opportunity to do part of my work in his lab and also for all his help and shared knowledge.

Additionally I would like to thank Liliane Tonial for her great assistance and all her effort to make the experiment running. Thanks also for your friendship and the great time in Brazil.

Ein ganz großes Dankeschön an meine HIWIs Svenja Beilfuss, Angela Scharfbillig und Jana Holler für ihren hervorragenden Einsatz und ihre Unterstützung während meiner Arbeit.

Ein ganz besonderer Dank geht an Dr. Ursel Selent für ihre unermüdliche Unterstützung am ZMT. Vielen Dank auch an Prof. Ittekkot und an alle ZMT Kollegen, die mich während meiner Arbeit unterstützt haben, v.a. Dr. Silke Rick und die Techniker Dorothee Dasbach, Matthias Birkicht, Christina Staschok und Dieter Peterke. Ausserdem geht ein ganz herzlicher Dank an Petra Käpnick, Gaby Böhme und Silke Eilemann für ihre tolle organisatorische Unterstützung. Uli Pint war bei Computerproblemen immer sofort zur Stelle - vielen Dank. Und auch ein großes Dankeschön an Christina Fromm für die schnelle Beschaffung von Literatur.

Vielen Dank an Werner Wosniok für seine statistische Beratung.

Meiner Arbeitsgruppe und meinen Freunden am ZMT Anne Baumgart, Claudia Propp, David Kaiser und Dr. Daniela Unger möchte ich besonders für ihre Unterstützung während der letzten Jahre danken. Ein riesengroßer Dank geht vor allem auch an Lucia Herbeck, Ingo Jänen, Dr. Britta Grote, Regine Moll, Shilly David und Dr. Antje Baum für eine tolle und unterhaltsame Zeit mit schönen und entspannenden Kaffeepausen und Ausflügen, aber vor allem auch für ihre Unterstützung am Ende meiner Arbeit.

Vielen Dank an all meine Korrekturleserinnen und an Miri.

Ein ganz besonderer Dank geht an meine Freunde und meine Familie. Allen voran meinen Eltern und meinem Bruder mit seiner Familie, für ihr Verständnis und ihre uneingeschränkte Unterstützung. Vielen Dank an meine Freunde von zu Hause für den Ausgleich, die Abwechslung und all den Spaß, den sie mir neben meiner Arbeit bereitet haben.

Eidesstattliche Erklärung
(Gem. § 6(5) Nr. 1-3 PromO)

Hiermit versichere ich, dass ich die vorliegende Arbeit:

1. ohne unerlaubte Hilfe angefertigt habe.
2. keine anderen, als die von mir im Text angegebenen Quellen und Hilfsmittel benutzt habe.
3. die den Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Bremen, April 2011

Gertrud Spörl