

**ASSESSMENT OF THE ESTUARINE WATERS OF THE STATE OF
PARANÁ (SOUTHERN BRAZIL):
DESCRIPTIVE APPROACH, TROPHIC STATUS AND MONITORING
TECHNIQUES**

Dissertation

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Summary

The coast of Paraná State contains several ecosystems that are under permanent environmental protection, of which Paranaguá and Guaratuba bays stand out due to the great economical and ecological importance. Notwithstanding, the increase of conflicts in this area has been observed in the past years related to the failure and/or lack of appropriate government policies. The main divergences are observed between the urban and harbour development and the conservation of national 'patrimony' areas; between traditional and industrial fishermen; between the aquaculture and the discharge of untreated sewage to the estuaries. In this sense, there is an urgent need of supplying information and strategies for the sustainable environmental development of the area, especially concerning nutrient enrichment and the negative impacts of eutrophication. This work proposes a compilation of approaches to assess the estuarine water quality in the coast of Paraná through descriptive interpretations, definition of the trophic status by indices and the experience of performing long term monitoring for several parameters.

The comprehensive assessment of nutrient sources, loads and dispersion in Paranaguá Bay indicated that the rivers are the main source of dissolved inorganic nitrogen to Paranaguá Bay. The enrichment of dissolved inorganic phosphorus is related to the handling of fertilizers and sewage discharge in the middle section of the bay. The nutrient plumes in this area are rapidly diluted due to the short water residence time and no clear evidence of nutrient enrichment is observed along the main body of the estuary. Information regarding nitrogen and phosphorus organic input, the role of primary production and the rates of nutrients exchange through the water-sediment interface is still required to define the balance of nitrogen and phosphorus in the bay. This is fundamental to evaluate the occurrence and effects of nutrients enrichment in the estuary and further works should focus on these issues. Nonetheless, lack of appropriate sanitation networks clearly requires the implementation of sewage collection and treatment. Still, improved strategies can be implemented in order to diminish the material and financial losses from the harbour activities.

The assessment of Guaratuba Bay provided the definition of three compartments in the system according to the salinity regime. In accordance to eutrophication thresholds, the water quality in the system can be considered intermediate due to higher chlorophyll concentrations and turbidity. Still, oxygen concentrations under the biological stress limit (<5mg/l) and high CO₂ saturation levels are a clear indication of the predominance of heterotrophic metabolism. Overall, the spatial dynamics of water quality seem to be controlled by the material input associated to the freshwater discharge and to the tidal phase fluctuations. Lack of data concerning nutrient inputs must be overcome by an assessment of

the watershed and the discharge of wastewater, as well as the contribution of aquaculture to the oxygen fluctuations and to the nutrient budgets.

The application of trophic indices supplying synthetic information to the administrators and to the public in general is an important tool to the coastal management of the area. The Assessment of Trophic Status (ASSETS) and the Trophic Index (TRIX) methodologies were chosen for their practical features that allow good comparison between systems, keeping in mind the successful application reported to several estuaries and marine areas. Whereas the ASSETS methodology is more comprehensive with the different characteristics of the estuaries in relation to the susceptibility to eutrophication and the negative effects of this process, the TRIX index provides the determination of the trophic status in a finer spatial scale directing the attention to each sampling station. Overall, a shift of the trophic status from 'Moderate' during the rainy season to 'Good' during the dry period was indicated to Paranaguá Bay, while Guaratuba Bay was stated as presenting a permanent 'Poor' trophic status by the ASSETS method. The TRIX indicated that the middle sections of the estuaries, as well as the bottom layers presented worst trophic conditions. The spatial fluctuations of the index were related to variations in the oxygen deviation, the DIN and DIP concentrations, and the seasonality seemed to be more related to the fluctuations of the chlorophyll-*a* concentrations. It is still important to mention that the availability of the data strongly influence the classification; considering that this is a pioneer work in the region, this study presents limitations due to lack of information and restriction of collected data in spatial and temporal scales. This problem might be solved by defining reference conditions through a comprehensive assessment performed through long term monitoring.

In this sense, the FerryBox systems are recommended as a reliable option to overcome the limitation represented by the lack of comprehensive data bases. The monitoring station in Paranaguá Bay and a mobile device (Pocket FerryBox) provided important information concerning the water properties fluctuations. The large variation in salinity, dissolved oxygen, pH, colored dissolved organic matter (CDOM), turbidity and chlorophyll *a* fluorescence at the monitoring station is related to the occurrence of river and tidal creek plumes responsible for the lateral heterogeneities influencing the estuarine dynamics. Higher chlorophyll plumes reaching the station location during low and ebb tides indicated that the primary production is more prominent in the inner regions of the bay. The seasonality, described by the succession of rainy and dry periods, was indicated by higher temperature and freshwater input leading to the enhancement of phytoplankton growth during the "wet" spring/summer. The distribution of the measured parameters along the bay and at the monitoring location is closer to the conservative behavior and more influenced by the tidal variation during the "dry" autumn/winter. Besides the utility of the long term monitoring for the area, the combination of the stationary with the Pocket FerryBox

measurements along the cross section of Paranaguá Bay outlet can be used as input data for hydrodynamic models during high tides. Less variation was observed between the salinity measurements from the station and the ones from the mobile device in high tides, while the lateral heterogeneities caused by plumes and the pattern of tidal intrusion can cause some lags between both measurements during other tidal phases. The experience with the FerryBox systems in Paranaguá Bay demonstrated the applicability and advantages of using both the monitoring and the mobile systems. The monitoring of water properties in Paranaguá Bay should rely on both strategies, providing reliable data on appropriate time and spatial scales.

In summary, the definition of nutrient sources and the distribution of the studied parameters in the bays indicate that management actions should be directed to the subordination of sewage treatment to the Brazilian environmental legislation, as a matter of public health. The diminution of material deposition from the harbour activities can be done through updating the loading mechanisms and collecting the waste, especially in the case of soy and corn that can be used in bio-combustion chambers to produce energy. The determination of the uses and occupation of the land in the hinterlands is an important issue in order to reduce deforestation that is related both to increasing nutrient loads and to the siltation of the navigation channel.

Overall, it is proposed the connection of different approaches that in combination provide a wide and comprehensive assessment of the estuarine waters in relation to nutrient enrichment and eutrophication. This work can be used as a 'general frame' for the development of a monitoring program directed to the water quality in the estuaries of Paraná and Brazil. Still, the success of such environmental management plan depends mainly on the adjustment of the academic efforts in order to provide a better understanding and a simpler judgment to the purposes of governmental agencies and the communities.

Zusammenfassung

Die Küste von des Staates Paraná vereint mehrere, unter Naturschutz stehende Ökosysteme miteinander, von denen sich Paranauá und Guaratuba wegen des hohen ökonomischen und ökologischen Interesses hervorheben. Dennoch nahmen in den letzten Jahren die Konflikte bezüglich fehlender oder ungeeigneter Regierungspolitik zu. Die wichtigsten Konfliktpunkte bestehen zwischen der Stadt- und Hafententwicklung und der Erhaltung der Naturschutzgebiete, zwischen Traditions- und Industriefischerei, sowie zwischen Aquakultur und dem Einleiten unbehandelter Abwässer in die Ästuare. Demzufolge gibt es einen dringenden Bedarf, Informationen und Strategien für ein nachhaltiges Umweltmanagement für diese Region zu erarbeiten. Dies gilt besonders für Nährstoffanreicherungen und deren negativen Folgen.

In dieser Arbeit werden Möglichkeiten zur Bewertung der Wasserqualität im Ästuar von Paraná anhand von anschaulichen Auswertungen, Definitionen der trophischen Zustände durch Indizes sowie die gewonnenen Erfahrungen mit Langzeitmessungen mehrerer Parameter dargestellt.

Durch umfangreiche Studien der Nährstoffquellen, -frachten und -verteilungen konnten für die Bucht von Paranaguá die Flüsse als Hauptquelle für gelösten anorganischen Stickstoff (DIN) betrachtet werden, wohingegen die Anreicherung von gelöstem anorganischem Phosphor (DIP) auf den Umschlag von Düngemitteln, Schüttgutladungen und Abwassereinleitungen im mittleren Bereich der Bucht zurückzuführen ist. Da die Nährstofffrachten in diesem Gebiet schnell verdünnt werden, gibt es keinen klaren Hinweis auf Nährstoffanreicherungen entlang der Hauptachse des Ästuars. Hier verhindert die kurze Aufenthaltszeit des Wassers einen Anstieg der Nährstoffkonzentrationen. Um Bilanzen für Stickstoff und Phosphor in der Bucht aufzustellen, werden Informationen über den Eintrag von organischem Stickstoff und Phosphor, die Rolle der Primärproduktion, sowie Austauschraten von Nährstoffen über die Sediment-Wasser-Grenzschicht benötigt. Dies sind wesentliche Informationen, um das Auftreten und die Effekte von Nährstoffanreicherungen im Ästuar zu bewerten. Daher sollten sich zukünftige Arbeiten auf diese Aufgabe fokussieren. Darüber hinaus sollte das unzureichende Abwassersystem ausgebaut und die Abwässer in Kläranlagen behandelt werden. Weiterhin können verbesserten Strategien eingesetzt werden, um materielle und finanzielle Verluste im Bereich der Hafenaktivitäten zu minimieren.

Die Bewertung der Bucht von Guaratuba ermöglicht anhand der Salzgehaltsverteilung die Unterteilung des Systems in drei Bereiche. Anhand von Eutrophierungsgrenzwerten ergibt sich für dieses System eine mittlere Wasserqualität, die auf erhöhten Chlorophyllkonzentrationen und Trübungswerten beruht.

Sauerstoffkonzentrationen von unterhalb 5 mg/l und hohe CO₂-Sättigungswerte sind ein klares Anzeichen der Vorherrschaft von heterotrophem Metabolismus. Zusammenfassend scheinen die räumlichen Unterschiede der Wasserqualität durch Materialeintrag durch Süßwasser sowie Schwankungen der Tidephase hervorgerufen zu werden. Fehlende Daten bezüglich des Nährstoffeintrags müssen durch die Abschätzung des Einzugsgebietes, der Einleitung von Abwässern, sowie des Beitrages von Aquakulturen zum Nährstoff- und Sauerstoffbudget ersetzt werden.

Die Verwendung von Trophie-Indizes liefert Informationen für Verwaltungen und die Öffentlichkeit und stellt ein wichtiges Hilfsmittel im Küstenzonenmanagement in dieser Region dar. Die beiden Methoden „Bewertung des trophischen Zustandes“ (Assessment of Trophic Status, ASSETS) und „Trophischer Index“ (Trophic Index, TRIX) wurden ausgewählt, da sie eine gute Möglichkeit bieten, Systeme miteinander zu vergleichen, wie die Anwendung für mehrere Ästuare und Seegebiete bereits gezeigt hat. Während die ASSETS Methode umfassende unterschiedliche Charakterisierungen der Ästuare in Bezug auf Anfälligkeit auf erhöhten Nährstoffeintag und dessen negativen Folgen ermöglicht, kann anhand des TRIX Indexes der Gewässerzustand in einer feineren räumlichen Auflösung im Untersuchungsraum bestimmt werden. Insgesamt zeigt ASSETS für die Bucht von Paranaguá einen Wechsel vom mittleren Status während der Regenperiode zu einem guten Zustand während der Trockenzeit, wohingegen die Bucht von Guaratuba einen dauerhaft schlechten Gewässerstatus aufweist. TRIX zeigt, dass sowohl die mittlere Region der Ästuare, wie auch die unteren Wasserschichten, den schlechtesten Zustand aufweisen. Die räumliche Variabilität des Indexes wurde durch die Änderungen der Sauerstoffkonzentration, sowie DIN und DIP Konzentrationen ermittelt, wohingegen die Saisonalitäten eher durch Chlorophyll-*a* bestimmt wurden. Es ist nach wie vor wichtig zu erwähnen, dass die Verfügbarkeit von Daten die Klassifizierung stark beeinflusst. Obwohl dies eine Pionierarbeit in dieser Region ist, konnten die Einschränkungen durch Informationsmangel und begrenzte räumliche und zeitliche Daten gezeigt werden. Diese Probleme könnten durch die Definition von Referenzbedingungen durch eine umfassende Bewertung von Langzeitmessungen gelöst werden.

Das FerryBox System bietet eine zuverlässige Möglichkeit, die Einschränkungen zu umgehen, die durch eine fehlende umfangreiche Datenbasis gegeben sind. Die Messstation in Paranaguá und die mobile Version (Pocket FerryBox) lieferten wichtige Informationen über die Änderungen des Wasserzustandes. Die großen Unterschiede im Salzgehalt, gelöstem Sauerstoff, pH, Gelbstoff (CDOM). Trübung und der Chlorophyll-*a* Fluoreszenz an der Messstation sind an das Auftreten von Fluss- und Prielfahnen gekoppelt, welche laterale Heterogenitäten hervorrufen und somit die Dynamik im Ästuar beeinflussen. Dass höher konzentrierte Chlorophyll-Fahnen an der Messstation während Niedrigwassers gemessen

wurden, weist darauf hin, dass die Primärproduktion im Inneren der Bucht stärker ausgeprägt ist.

Die Saisonalitäten werden durch das Vorherrschen von Regen- und Trockenperioden definiert. Im Frühling/Sommer führen höhere Temperaturen und Süßwassereinträge zu einem Anstieg des Phytoplanktonwachstums. Im Herbst/Winter weisen die gemessenen Parameter entlang der Bucht und an der Messstation ein eher konservatives Verhalten auf, das stärker durch die Tide beeinflusst wird. Neben den Langzeitmessungen können kombinierte Daten der stationären FerryBox mit Messungen der Pocket-FerryBox entlang des Querschnittes der Bucht von Paranaguá als Inputdaten für hydrodynamische Modelle verwendet werden. Während Hochwassers wurden weniger Unterschiede der Salzgehaltmessungen zwischen der festen Station und der Pocket FerryBox festgestellt, wobei während anderer Tidephasen laterale Heterogenitäten durch eindringende Tidefahnen Abweichungen der beiden Messungen voneinander hervorrufen können. Die Erfahrungen mit den FerryBoxen in der Bucht von Paranaguá demonstrierten die Anwendbarkeit und die Vorteile sowohl des festen wie auch des mobilen Systems. Bei der Überwachung der Wasserparameter in der Bucht von Paranaguá sollte man auf die beide Strategien bauen, um verlässliche Daten in angemessener zeitlicher und räumlicher Auflösung zur Verfügung stellen zu können.

Zusammenfassend zeigten die Untersuchungen der Nährstoffquellen und die Verteilung der untersuchten Parameter, dass die Abwasserbehandlung als Thema der öffentlichen Gesundheit der Brasilianischen Umweltgesetzgebung unterstellt werden sollte. Die Reduzierung des Materialeintrages durch die Hafentätigkeiten können durch Erneuerung der Ladevorrichtungen sowie durch Abfallsammlung erreicht werden. Dies gilt besonders für Soja und Getreide, mit dem in Bio-Verbrennungsanlagen Energie gewonnen werden kann. Die Ermittlung der Landnutzung im Hinterland ist wichtig, um Abholzungen zu reduzieren, die wiederum erhöhte Nährstoffeinträge und die Verschlammung der Fahrrinne nach sich ziehen.

Es ist empfehlenswert, die verschiedenen Ansätze miteinander zu verknüpfen, die in ihrer Kombination ein breites Gesamtbild der Ästuare in Bezug auf Nährstoffanreicherungen und Überdüngung liefern. Die hier vorliegende Arbeit kann als „grobe Richtlinie“ genutzt werden, um Überwachungsprogramme bezüglich der Wasserqualität für Paraná und Brasilien zu entwickeln. Weiterhin ist der Erfolg solcher Umweltmanagementvorhaben hauptsächlich abhängig von wissenschaftlichen Bestebungen, für Regierungsbehörden und die Gesellschaft ein besseres Verständnis zu vermitteln und einfachere Beurteilungen bereitzustellen.

CHAPTER I

Introduction
Regional Settings and Pollution Problems
Motivation

INTRODUCTION

The coast of Paraná state, in the south of Brazil, is composed of a complex mosaic of ecosystems interconnected by the waters of the South Atlantic. Inside each of these large estuaries, an intricate net of energy and material transfers occurs through abiotic and biological processes at different time and spatial scales. These dynamics are caused by the general feature of coastal zones where land, atmosphere and oceans interfaces meet (Day et al., 1989). The coupling of these large compartments results in an intense energy exchange, involving directly and indirectly all elements of the coastal ecosystems.

Besides the interactions between the abiotic (such as the water properties and dynamics, the siltation, among others) and the biological processes (such as the production of organic matters, the use of habitats, reproduction and resources competition, grazing and predation), the existence of open and continuous systems must be taken into account. The estuarine systems are under constant influence of the freshwater input and the tidal forcing.

The coastal plain from Paraná state (Fig. 1) has 105 km of coast line and constitutes one of the minor state shorelines of Brazil. In this region, between the coordinates 25°12'44"S-48°01'15"W and 48°35'26"S-48°35'26"W, the rainforest ridge is distant from the coast line, forming a large coastal plain and two estuarine systems. The Paranaguá Estuarine Complex (PEC) is located northwards (25°10'-25°35'S, 48°15'-48°50'W) and comprises two main branches with a total area of around 600 km². This system elongates in the north-south axis forming Laranjeiras Bay, and in the east-west axis constituting Antonina and Paranaguá Bays (see also Fig. 2). In the southern part, Guaratuba Bay (25° 52' S, 48° 38' W) occupies around 50 km².

Overall, the coastal regions and especially estuaries, offer a large multitude of resources explored and exploited by humans. Activities in these environments (such as fisheries, harbour processes, urbanization and tourism) can result in different directions of development. Therefore, the concept of impact depends on the reference point. The urbanization of estuarine systems can alter the functioning of the ecosystems and affect the concentration of nutrients and the magnitude of primary production (White et al., 2004). On the other hand, the development of coastal regions is primordial, considering that more than half of the world population lives in these areas. Still, in regions like the Paraná coast, activities such as fisheries and diverse modalities of extraction (mangrove crabs, oysters, wood) are of great importance for the traditional communities (Lana et al., 2000), even as a cultural identification factor. These activities can be endangered by the development and consequent environmental damage around the bay, even though the existence of a large harbour and cities are also important for these communities.

Paranaguá and Antonina harbours are responsible for important transactions of export and import. Besides bulk carriers, Paranaguá harbour has increased its capacity for containers. Still in Paranaguá harbour area, there are private terminals, such as Catallini for fuel and Fospar that deals with fertilizers processing and transportation. Like any other busy harbour area, the intense traffic of ships in Paranaguá Bay brings impacts as small oil spills, deposition of grains, besides the necessity of frequent dredging activities in the benches and navigation channels.

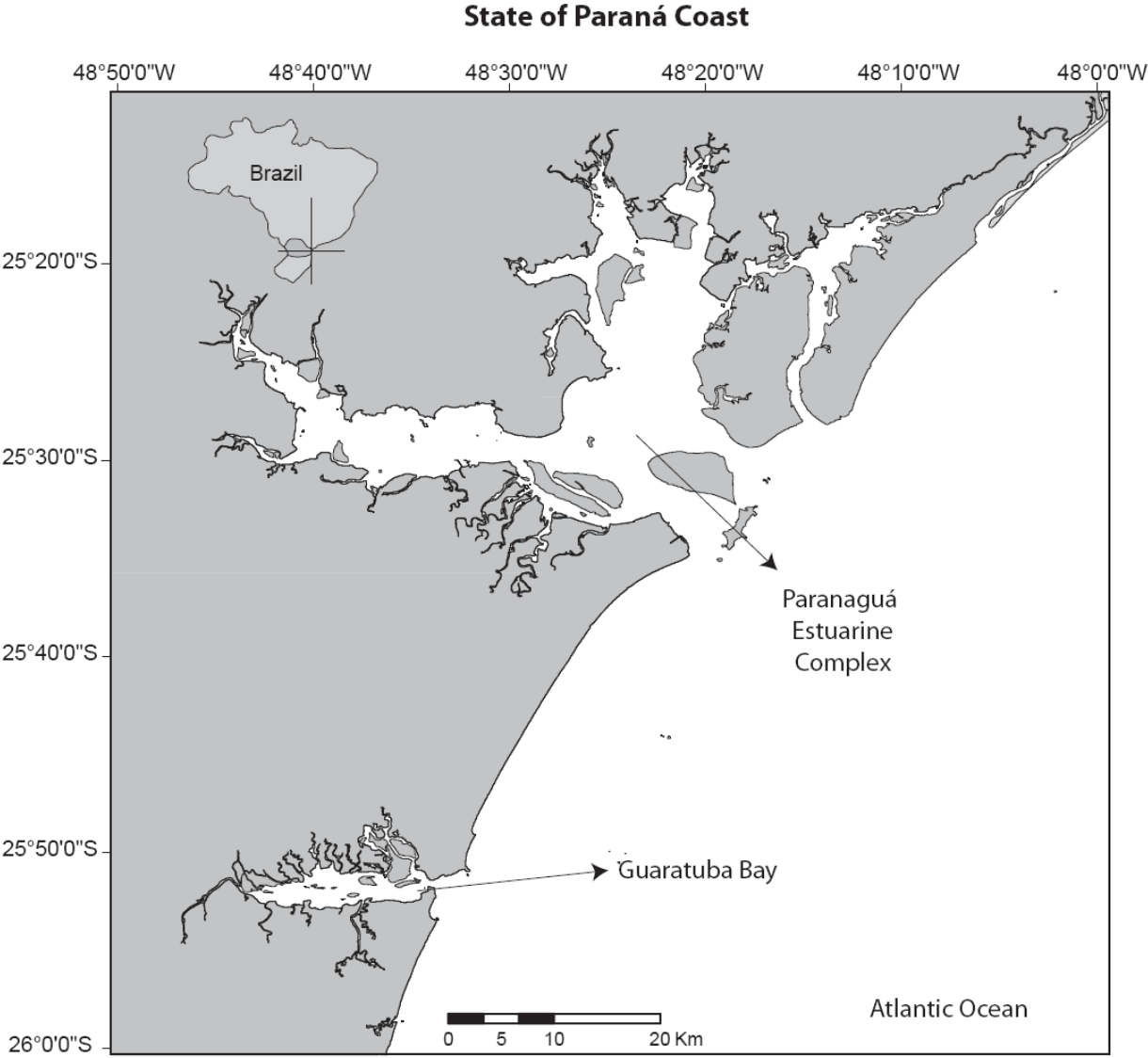


Figure 1: The State of Paraná coast and estuarine systems (Paranaguá Estuarine Complex and Guaratuba Bay).

More conflicts arise from the presence of several environmental conservation areas along the Guaratuba Bay and the Paranaguá Estuarine Complex. These are classified into the categories “full protective” and “sustainable management”, according to the

environmental jurisdiction and allowed activities. In addition, the mangroves and the rainforest are considered as national heritage and thus as permanent protection areas. Any degradation of these ecosystems is summarily prohibited by law; however, the impact on these environments is observed along the bays through illegal settlements and deforestation due to a lack of appropriate surveillance.

The region also counts with its tourism attraction, which can be developed as sport fishing and boating. These activities demand the conservation of the environment and can be prejudiced by the negative consequences of the economic development of the region. As well as the recreation, small scale aquaculture is developed in some areas and depends on the good water quality of the estuary.

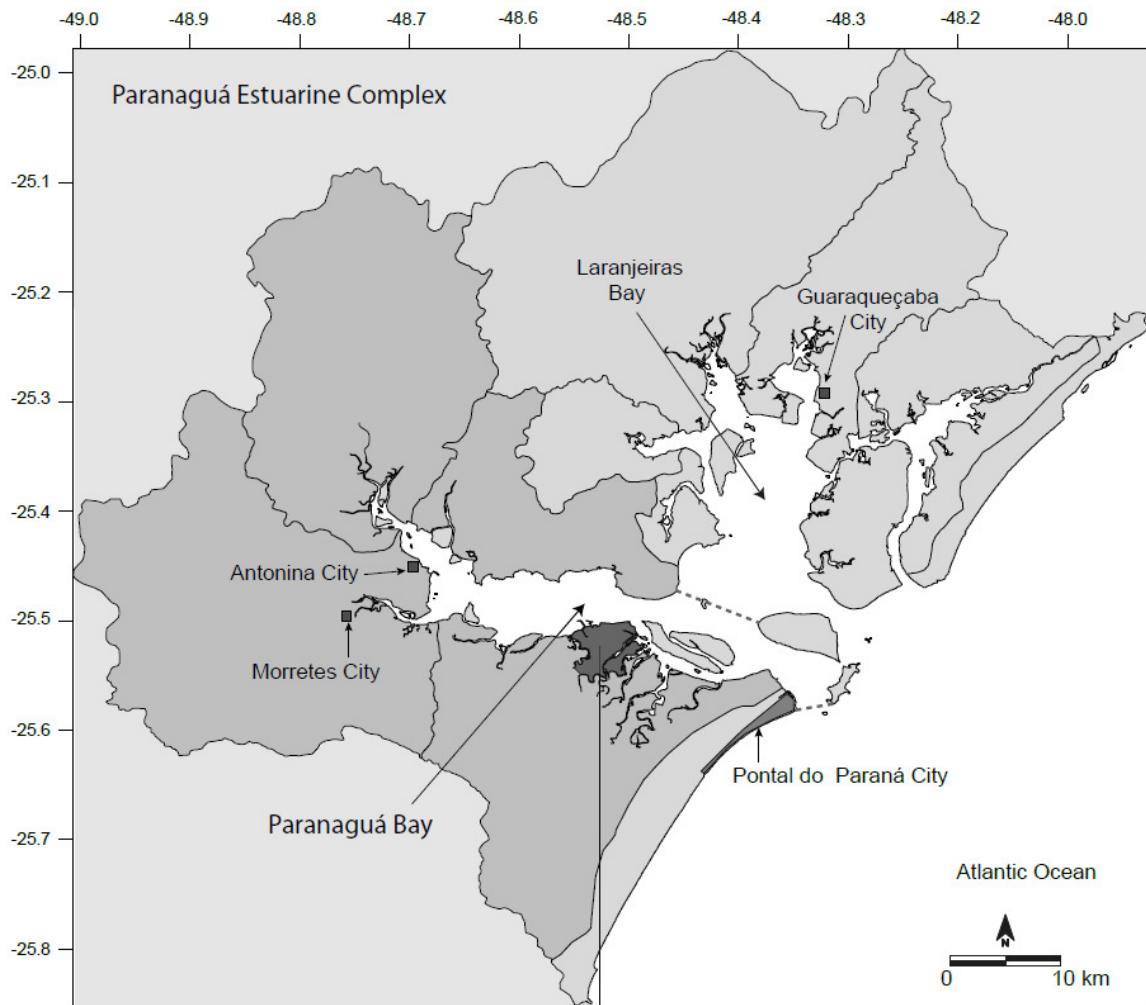
The conservation of coastal regions and natural resources passes by, obligatory, the conflict management generated by the contradictory nature of development and environmental protection. The overlap of the different spheres that makes up the ecosystem implies the requirement for interdisciplinary studies. Thus, it becomes necessary to delineate and characterize the area that comprises this work, presenting various aspects relevant to understand the conflicts regarding the estuary as a natural resource.

Understanding how the coastal systems function also encompasses the concept of “socio-environment” that considers the natural resources and the uses that are made of these. The sensitivity of the coastal environments to anthropogenic impacts constitutes the main issue for the coastal management. This requires the development of interdisciplinary knowledge regarding such systems in order to support the definition of guidelines and standards for the environmental conservation and the regulation of anthropogenic activities.

REGIONAL SETTINGS AND POLLUTION PROBLEMS

Paranaguá Estuarine Complex

The Paranaguá Estuarine Complex is composed of two main branches (Fig. 2). Laranjeiras Bay, along the North-South axis, is considered relatively pristine with large mangrove and rainforest areas. It houses diverse traditional fishermen villages and the city of Guaraqueçaba, which has a low population density and growth. Small scale fisheries and tourism (mainly in summer) are the main activities, with small contribution of harvest (mangrove crabs and oyster) and agriculture.



Paranaguá City and Harbour

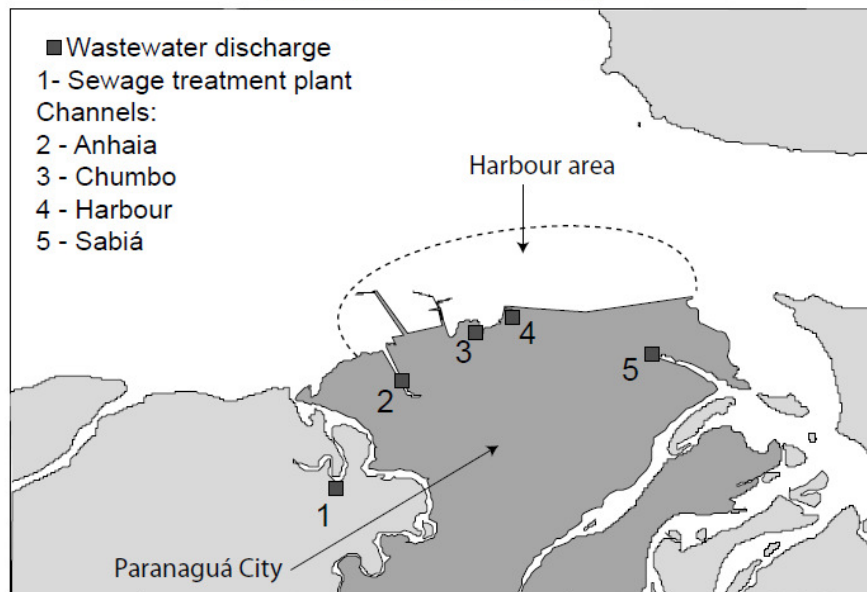


Figure 2: The Paranaguá Estuarine Complex, composed of the Laranjeiras and Paranaguá bays, and the delimitation of the catchment areas. Main cities are indicated by arrows. Paranaguá City and Harbour are zoomed in showing the main waste water discharge sites.

The East-West Axis is composed by Paranaguá Bay (Fig. 2) that houses the harbours called Antonina and Paranaguá. The latter is one of the most important harbours in South America, especially for bulk and container handling. Around 80% of the total population of the PEC is concentrated in Paranaguá City that is located along E-W Axis that still presents dense mangroves and a large portion of the rainforest.

The Paraná coast makes up 3.04% of the total area of the State, represented by a strategic position as exportation corridor through Paranaguá Harbour. It also has an important recreation function due to the tourism in the estuarine area and the beaches in the vicinity, and the historical centers. There are 5 cities sharing the PEC: Antonina, Guaraqueçaba, Morretes, Paranaguá and Pontal do Paraná with a total population of around 160,000 inhabitants. The occupation, dynamics and organizational patterns are related to the harbour activities, tourism, fisheries and services. In this context, the summer activities must be highlighted during which the population can increase up to 400%. Paranaguá is an urban city of medium dimension, while Antonina and Pontal do Paraná present moderate transition to urban societies, and Morretes is a rural city of small dimension. The occupation of the coastal zone is usually disorderly through illegal occupation of the coast line.

Among the agricultural activities, crops of rice, beans, corn and bananas can be highlighted, the latter with the largest acreage. Crop production is associated with extractive activities, such as the manufacture of wood, charcoal and palm. Livestock farming is based on raising of buffaloes, cattle and pigs.

Paranaguá City and harbours

Paranaguá harbour is surrounded by the city with the same name (see Fig. 2), with 90% of its ca. 145,000 inhabitants living in the urban area (IBGE, 2010). It is the center of the coastal region, with its economy based on port activities, tourism, commerce and fishing. It has a developing industrial center, with important chemical (extraction of plant products and fertilizers) and food industries.

The occupation of Paranaguá has occurred along the access routes around the harbor and around the Valadares Island. About 35% of the population is served by the sewage system and around 20% of this sum is effectively treated (Águas de Paranaguá – Paranaguá Waters Company). There is the predominant use of septic tanks or direct discharge into sewers, rivers and tidal channels. Moreover, the use of inappropriate septic tanks for the disposal of sewage can result in groundwater contamination and subsequent damage to water quality from wells of potable water, rivers and beaches. The solid wastes

are disposed in uncontrolled landfills but not all Paranaguá regions are served by a system of regular collection.

The disorderly urban settlement is a factor that promotes the growing inequalities between social classes. The illegal occupation along the margins of tidal creeks and in mangrove areas concentrates the low income population which has less access to appropriate infra-structure. The development of the Paranaguá harbour was a determining factor for the definition of the land use configuration of Paranaguá Bay. The region grew substantially in recent decades and the Paranaguá city and port are established as a harbour pole.

Paranaguá and Antonina harbours are managed by the Administration of the Paranaguá and Antonina Ports (APPA) that provides updated information on cargo handling through its website. The total cargo handled in 2010 accounted for more than 38 million tons among others liquid and solid bulk, vehicles, containers and general cargo (APPA, 2010). Paranaguá Harbour is responsible for the majority share and has increased its capacity by the expansion of the container wharf. Among the bulk cargo, the shipment of sugar, corn, soybean and pellets amounted more than 24 million tons. The fertilizer industry that counts with a private terminal located in the western region of Paranaguá Harbour has handled around 7 million tons of this material in 2010. The development of Paranaguá Harbour in the last years has increased its importance for the trading network of Brazil, reaching the second position among the Brazilian harbours, only behind the port of Santos, with the share of 16% of the total cargo handled in 2010 (ANTAQ, 2010).

Guaratuba Bay

Guaratuba Bay (Fig. 3) is an estuary located in the coastal plain of the Southern coast of Paraná. It is inserted in the city of Guaratuba, with a population of around 32,000 inhabitants (IBGE, 2010). During the summer vacations, especially during New Year's and Carnival, the population in the area can reach a 400% increase. Until 2003, the city presented only 30% of the area covered by a sewage collection net without treatment plant. The untreated sewage is discharged *in natura* direct or through waste water channels. As reported for Paranaguá Bay, a large amount of houses use the septic tank systems, but not all structures are appropriate, which can endanger the groundwater layers.

Besides the city of Guaratuba, considered the most important for this region, at the northern margin of the estuary mouth Caiobá Beach (Matinhos City) is located which has its activities almost totally directed to tourism causing a fluctuating population.

The tourism is enhanced during summer, but there is a constant flux of small boats and fishing platforms along the year in the bay. The estuary mouth is separated by two rocky points around 500 m distant from each other. The crossing between these two points that

represent Caiobá and Guaratuba is made through ferries and represent an important route between Paranaguá harbour and the South of Brazil.

Small scale fisheries are observed inside the estuary, while the large scale is performed in the adjacent shelf especially for shrimp trawling. Due to the decline of fish stocks and the periods of fishery prohibition (reproduction seasons), the development of aquaculture was encouraged as a complementary activity. Due to the good water quality, oyster and shrimp production are performed in few small scale farms inside the bay.

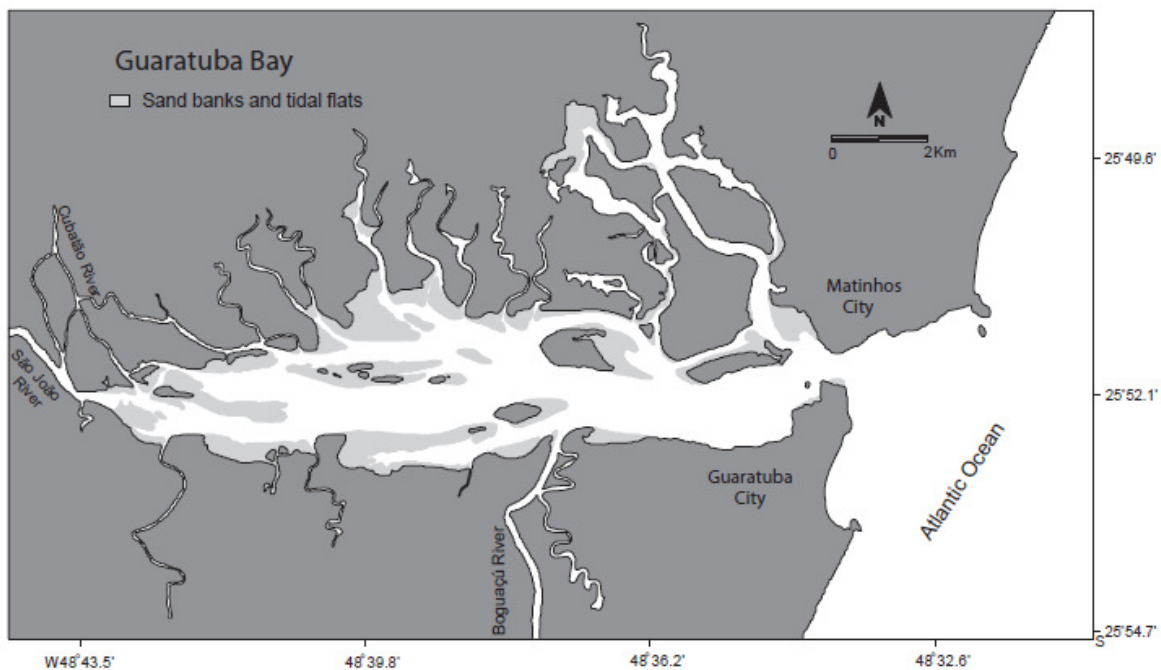


Figure 3: The estuary of Guaratuba Bay and main cities.

In the watershed, several small scale agricultural properties are found, except along the head of the estuary where the intensive cultivation of banana occupies a large extension of acreage.

The estuary is incorporated in the Environmental Protection Area (APA) of Guaratuba that covers 4 cities. This unit has around 200,000 hectares, including the inner waters, the river islands and the largest island of the bay (Saí-Guaçu). The APA aims the protection of the water supply and the lagoon-estuarine complexes that compose Guaratuba area, assuring the rational uses of the natural resources through the coexistence of the diverse activities performed in this region.

In the past 30 years, the estuary mouth has been under increasing pressure due to urban development and the recreational features of the bay. The management of the activities performed in the bay, such the use of inner waters for aquaculture, the possibility of

new hydroelectric power stations in the watershed and the proposals for infra-structure (the construction of the bridge Caiobá-Guaratuba, construction works along the coast line to support the tourism and the containment of erosion), demands a better knowledge of the hydrodynamics and the water quality fluctuation. This information is required for the environmental zoning, which should be based on a diagnose of these activities and the impacts. Overall, the development of Guaratuba Bay depends on the balance between the environmental conservation of protected areas and the sustainable uses of the natural resources, assuring the maintenance of a good water quality.

MOTIVATION

Increasing concern has been addressed to the development of the coastal region of Paraná state in the last decade. Differently from most of other coastal regions of Brazil, urban, industrial and agricultural centers of Paraná are concentrated in the highlands of the Serra do Mar (ridge). Even though the growth of the region followed a different pattern, several environmental problems have already emerged (Lana et al., 2000). Siltation due to increasing sediment load, which is a result of deforestation, demanded more frequent dredging activities. Eutrophication symptoms, such as sporadic harmful algae and macroalgae blooms, were reported in the past by local newspapers leading to financial losses due to prohibition of fisheries and bathing in the estuaries of Paraná State. Still, environmental impacts such as suppression of protected vegetation due to the illegal occupation, water and sediment contamination due to discharge of untreated sewage in the estuaries and accidents in the harbours (such as ship explosion and oil spills) are observed. Several plans for land use have been proposed or established to manage the conflicts between the presence of protected areas and the development in the area but no actions directed to a centralized natural resources management are clearly succeeding to address local problems. Understanding the functioning of the systems and providing comprehensive assessment of the estuarine waters of Paraná State is fundamental for the reduction and remediation of these impacts in the area.

More investigations were performed in the Paranaguá Estuarine Complex than in Guaratuba Bay probably due to the presence of the harbours in PEC. Early investigations presented preliminary information regarding the distribution of nutrients and chlorophyll in the Paranaguá bay (Knoppers et al., 1987; Brandini et al., 1988; Rebello and Brandini, 1990), indicating that the phytoplankton biomass, dominated by diatoms and phytoflagellates (Fernandes et al., 2001; Mafra Junior et al., 2006; Procopiak et al., 2006) is subjected to the conjunction of light availability and nutrient concentration in the water column. The trophic

status in the estuary, indicated by chlorophyll-*a* concentrations, varies from almost oligotrophic in the lower regions during winter to eutrophic in the middle section during summer as a result of interactions between hydrodynamic processes and different mechanisms of nutrients sink and supply, such as the biological uptake, freshwater input, sediment-water interactions and sewage discharge from Paranaguá City (Lana et al., 2000). Estimations of land-ocean fluxes performed through the LOICZ approach indicated that the system exports dissolved inorganic phosphorus to the adjacent coastal area, while net denitrification predominates all over the bay (Marone et al., 2005). Still, no comprehensive assessment was addressed in order to identify and quantify the major sources of nutrients in the bay, as well as to better investigate the fluctuations of the trophic status.

The knowledge of water properties in Guaratuba Bay is even more limited. The hydrodynamics during winter (Marone et al., 2004) and sediment contamination with heavy metals (Sanders et al., 2006) are presented but no information concerning nutrients levels and chlorophyll is available. Considering the increasing pressure of the human activities in the area, it is primordial to define the water quality in the bay, as well as the trophic status of the estuary.

The nutrient enrichment of waterways leading to eutrophication is a worldwide problem that has led to the use of several approaches to study the estuarine systems. The delimitation of a management action regarding hypernutrification and eutrophication necessarily begins with the assessment of basic information regarding the sources of nutrients and the seasonal fluctuations of water quality and the trophic status. Therefore, a comprehensive description of water quality in Paranaguá bay was performed through the quantification of annual nutrient loads from different sources (rivers, atmospheric input, sewage discharge and losses from fertilizers loading in the harbour) and the distribution of nutrients and chlorophyll-*a* concentrations along the estuarine body, covering both rainy and dry seasons (Chapter 2). Moreover, a first assessment of water quality in Guaratuba Bay is presented, providing preliminary information on water properties, nutrients and chlorophyll-*a* levels along the estuary, as well as the seasonal dynamics and the tidal forcing effects (Chapter 3).

The description of water properties by itself supplies important information regarding the functioning of the estuarine systems and the relations between water dynamics and primary production. However, in keeping with the needs for the coastal management, increasing efforts have been directed to develop and simplify the methods to define the trophic status and evaluate the eutrophication process. The determination of primary production through the measurement of carbon fixation or photosynthesis rate (Nixon, 1982) is a direct contribution to the trophic status, but it demands relatively more efforts and the information is not often available. Therefore, several approaches have been developed to

determine the trophic status in a coastal system through synthetic indices using related data sets that are commonly available, such as nutrients concentrations, chlorophyll-*a* and dissolved oxygen. Among the available methodologies, the Assessment of Trophic Status (ASSETS) and the Trophic Index (TRIX) are considered reliable tools to address the eutrophication status in coastal systems, because the methods supply a simple index without losing the comparative power of the analysis. These methodologies provide synthetic classifications, albeit meaningful and representatives, that might ease the establishment of management actions of decision makers.

In order to determine the eutrophication state in these estuarine systems, the ASSETS (Bricker et al., 1999, 2003) and the TRIX (Vollenweider et al., 1998) methodologies were applied (Chapter 4). Besides the synthetic feature of the indices, different spatial scales can be assessed for the comparison of estuaries. While ASSETS is designed to offer a classification for an estuarine body, the TRIX methodology provides a finer spatial scale. The two estuarine systems of the State of Paraná that are the subject of this work were compared to verify regional features of the eutrophication state, supplying information for the coastal management of the areas.

Even though both methodologies are reliable tools, the small data set available for the studied systems can be a limitation for the assessment and the extrapolation of this experience for other estuaries in Brazil. The sampling strategy is based on snapshots due to the limited logistical sampling effort available. Especially in Paranaguá Bay which is a system of relative larger proportions, assessing the water properties fluctuations demands an intensive monitoring program and no attention is given to this issue by the government. All over in Brazil, the monitoring of water properties is limited and the lack of appropriate data bases hampers the assessment of water quality. The available information concerning long term monitoring in the coastal zone is usually restricted to meteorological parameters, bathymetry, currents and the bathing water quality in beaches (fecal coliforms). In other cases, the assessment of estuarine waters is constrained to specific harbour areas and the confidential information is directed to the responsible environmental agency. To overcome the logistical limits of the common sampling strategies, the use of operational systems that couple diverse parameter measurements have been considered a viable option. In this sense, a stationary FerryBox was installed in the outlet of Paranaguá Bay, introducing a new approach of long term monitoring in Brazil (Chapter 5). The measurements from the stationary FerryBox were analyzed in order to verify the fluctuations of water quality, phytoplanktonic dynamics (using *in vivo* fluorescence as a proxy for chlorophyll) in Paranaguá Bay and the effects of events such as the seasonal periods and heavy precipitation events, at long and short time scales.

In addition, a portable version of the FerryBox system was tested in Paranaguá Bay (Chapter 6). This so called Pocket FerryBox is a mobile multi-sensor device that can be used on small survey platforms. Therefore, the information regarding water properties variation in Paranaguá Bay covered both time and spatial scales.

Until present, no assessment of water quality and trophic status of the estuarine waters gathered information in the whole Paraná State coast. The lack of an appropriate data base on water properties hindered the construction of a comprehensive study that aggregates the existing information in order to present a regional management plan concerning the eutrophication. Overall, this work aimed to supply the first overview concerning a wide assessment of the estuarine waters in Paraná State, combining descriptive approaches of evaluation with the definition of trophic status and new techniques for monitoring, leading to a definition of critical activities and zones concerning eutrophication and nutrient enrichment (Chapter 7). The dissertation is compiled in a summary from the results of these chapters in order to deliver an environmental diagnosis and conclusions of the estuarine trophic status of the State of Paraná coast.

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“Sources, loads and dispersion of dissolved inorganic nutrients in Paranaguá Bay”

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Sources, loads and dispersion of dissolved inorganic nutrients in Paranaguá Bay

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Abstract

The present study focuses on the nutrient sources and gradients in Paranaguá Bay (Southern Brazil), where nutrient pollution is related to losses from fertilizer loading in Paranaguá Harbour and the discharge of untreated wastewater. The input of dissolved inorganic nutrients to the bay from the harbour and city as well as from river and atmospheric deposition amounted to $642 \text{ t} \cdot \text{a}^{-1}$ DIN and $92 \text{ t} \cdot \text{a}^{-1}$ DIP. Harbour losses accounted for 6 % of total DIN and 39 % of total DIP loads to the bay, whereas sewage inputs from the city were responsible for 21 % and 22 %, respectively. River inputs made up 68 % of DIN, mainly in the form of nitrate, and 35 % of DIP loads, while atmospheric wet deposition was estimated to be in the order of 5 % of DIN and 4 % of DIP loads. Local maxima in nutrient levels deriving from highly concentrated sewage discharge were observed in front of the harbour and city of Paranaguá, but the plumes are diluted rapidly due to short residence times. DIN concentrations are negatively correlated with salinity, indicating the importance of freshwater input as a main factor controlling nitrogen distribution. Elevated phosphate levels in the stratified middle section of the bay may result both from harbour emissions and phosphate remobilization from sediments. Generally lower DIN and DIP concentrations during the warmer rainy season are supposed to be due to intensified assimilation rates especially in the middle section of the bay where dense phytoplankton blooms are observed. The bay as a whole cannot be classified as being seriously eutrophic, albeit eutrophication symptoms prevail in some restricted locations in front of Paranaguá harbour.

Keywords: Nutrient enrichment, eutrophication, Brazil, river nutrient loads, wet deposition, harbour emissions, sewage discharge

Introduction

The Paranaguá Estuarine Complex (PEC) is among the largest estuaries in Brazil and of great economical as well as ecological importance to the entire southern region of the country. Among the anthropogenic activities around the bay, port industry constitutes a main economic issue in the area, followed by tourism, fisheries, agriculture and aquaculture. On the other hand, large areas of the coastal zone are subject to nature protection by environmental legislation. This holds especially true for the vast mangrove belts bordering the estuary, which serve as nursery and feeding grounds for a variety of fish and shellfish species, as well as for the extended rainforest zone in the hinterland.

The conflicting uses in the area require a sound coastal management policy, implying a profound knowledge of the functioning of the system and the impact of anthropogenic activities on its natural resources. New regulations of CONAMA (Brazilian Council for the Environment) impose severe standards for the assessment of environmental pollution. Especially hypereutrophication may be an issue of concern for the estuary considering its potential sources of nutrient pollution.

Paranaguá harbour is among the most important handling sites for grain and fertilizers in South America. More than 6 million tons of mineral N- and P-fertilizers are handled at the piers each year. The annual export of soybean products accounts for more than 10 million tons, while the total dry bulk handling reached more than 24 million tons in 2010. Spillage from cargo handling during loading operations may be a significant source of nutrient pollution to the bay.

In keeping with the harbour's importance, the city of Paranaguá agglomerates around 80 % of the inhabitants of the PEC, corresponding to a population of about 140,000 inhabitants in 2010 (IBGE, 2010). As it is the case for many cities in Brazil, lack of sanitation constitutes a basic problem in Paranaguá. Only 25 % of the city's population is connected to a public sewage treatment system. A major share of the waste water is thus discharged without any further treatment through a number of small channels entering the bay, creating plumes of high sedimentary fecal steroids concentration in the vicinity of the harbour and city of Paranaguá (Martins et al., 2010). This pathway of nutrient pollution is closely linked to a hygienic problem, manifesting itself in the past in sporadic epidemics caused by *Vibrio cholerae*.

The numerous rivers and streams draining the hinterland of the PEC yield in a high freshwater discharge and may constitute another important source of nutrients to the estuarine system of Paranaguá. Sewage water from villages and small cities located along these streams as well as inputs from agricultural activities in the catchment area, which

mainly rely on small to medium scale banana and rice production and cattle breeding, add to the river nutrient loads. In addition, diffuse sources contribute to the overall budget of nitrogen and phosphorus loads to the bay. Considering the large surface area of the estuary, nutrient input by atmospheric wet deposition may be of due significance, particularly during the rainy season.

Despite the outstanding ecological and economical importance of the PEC, little is known about the specific loads, the dispersion and fate of nutrients in the area. The present paper aims at the discrimination of the most important external nutrient sources, the quantification of the respective nutrient loads and at the investigation of the resulting nutrient gradients in the bay, taking into account seasonal variations. Nutrient data together with information on phytoplankton biomass levels (chlorophyll-*a*) are used to provide a preliminary classification of the status of the area with respect to eutrophication. The nutrient budgets may form a valuable basis for further decisions to be taken in environmental coastal planning of the region.

Material and methods

Study area

The Paranaguá Estuarine Complex is a micro- to mesotidal estuary located in the state of Paraná in Southeastern Brazil. The climate of the region can be characterized as subtropical wet with medium air temperatures exceeding 22°C. The annual precipitation of more than 3000 mm is divided between a rainy season in spring and summer (from October to March) and a dry season in autumn and winter (from April to September).

The PEC covers an area of around 600 km² and is formed by two major embayments defined by its watershed boundaries: (1) Laranjeiras Bay (30 km x 13 km) situated along the North to South axis of the system; and (2) Paranaguá Bay (50 km x 7 km) forming the East to West axis (Fig. 1).

Paranaguá Bay, which is in the focus of the present study, has a mean depth of 5.4 m with a maximum of 33 m. It can be subdivided into an upper, middle and lower section according to the horizontal salinity gradient (Lana *et al.*, 2000; Marone *et al.*, 2005). Table 1 displays the extension of these different sections, their mean depths and average water volume.

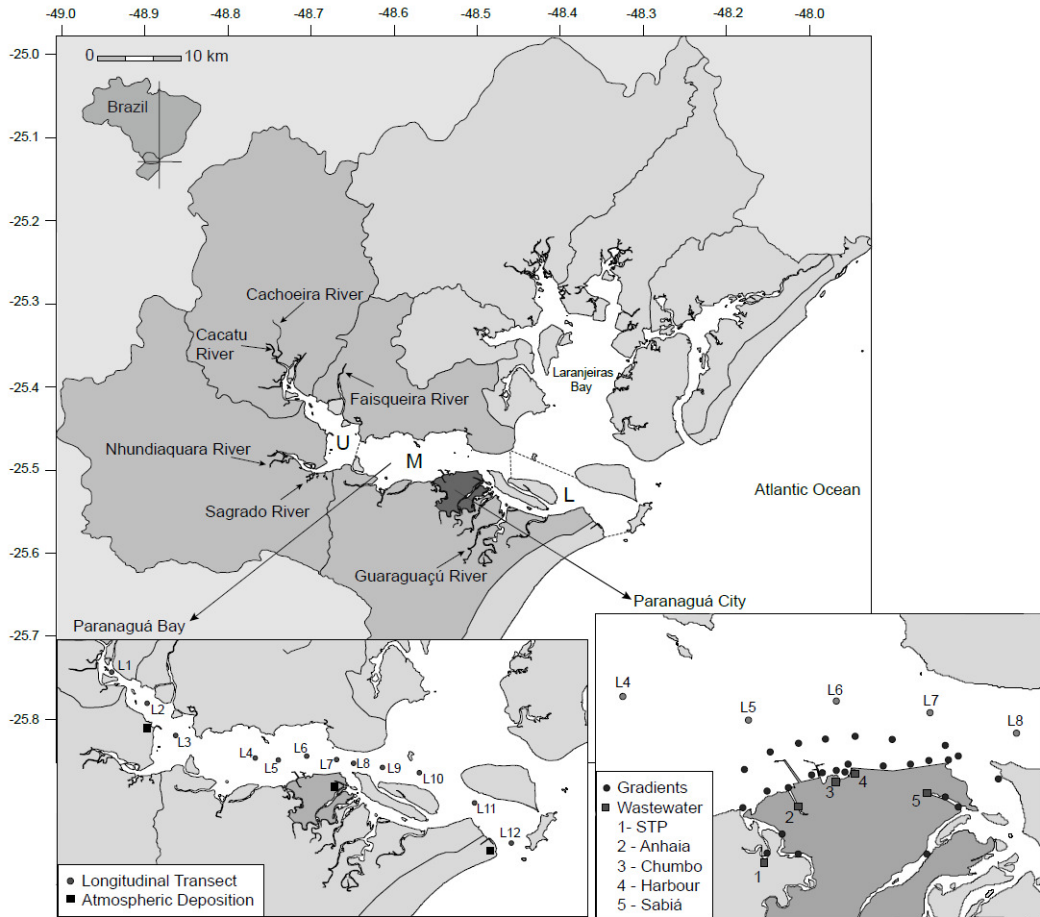


Figure 1: The Paranaguá Estuarine Complex (PEC) includes Laranjeiras Bay (North-South axis) and Paranaguá Bay (East-West axis). Paranaguá Bay is divided into an upper (U), middle (M) and lower (L) section; catchment areas are indicated in dark grey and main rivers by arrows; Zoomed sections right: Locations of sampling stations on the Longitudinal Transect along the main navigation channel of the bay and sites of rainfall sampling; and left: sampling stations around the harbour and city of Paranaguá including the location of the sewage channels and treatment plant.

Table 1: Physical dimensions of the upper, middle and lower section of Paranaguá Bay (Marone et al., 2005).

Section	Area $10^6 [m^2]$	Mean Depth [m]	Volume $10^6 [m^3]$
Upper	50	1.9	95
Middle	93	4.3	400
Lower	187	7.0	1309

Paranaguá Bay is a partially mixed estuary with pronounced lateral heterogeneities especially at the margins of the system resulting from the numerous sites of freshwater discharge and tidal creeks (Tab. 2). Succession of dry and wet periods is a key factor for the understanding of the system's structural dynamics. Mean freshwater input can vary twofold between seasons with a correspondent modification of hydrographic features (Marone et al., 2005). Tides are semidiurnal with spring tidal ranges from 1.7 m at the mouth to 2.7 m in the

inner part of the bay (Marone and Jamiyanaa, 1997). Depending on tidal forcing, wind speed and river discharge, Paranaguá Bay may exhibit both mixed and stratified conditions. Chemical and biological processes in Paranaguá Bay are thus strongly influenced by meteorological factors (Marone and Camargo, 1994; Marone et al., 2005).

Table 2: Hydrographic characteristics of Paranaguá Bay (Marone et al., 2005).

Horizontal salinity gradient (PSU)	<i>Summer</i>	<i>Winter</i>
Mean seasonal gradient	12-29	20-34
Maximum seasonal gradient	0-35	3-35
Horizontal water temperature gradient [°C]	<i>Summer</i>	<i>Winter</i>
Mean seasonal gradient	23-30	18-25
Current velocity [m·s⁻¹]	<i>Ebb</i>	<i>Flood</i>
Maximum	0.85	1.10

The Paranaguá Bay catchment area accounts for around 1,918 km² and is formed by more than 9,000 freshwater streams (de Paula and Cunico, 2007) with a drainage density of up to 1.7 rivers per km² (Noernberg et al., 2004). River discharge to the entire PEC is estimated to account for 200 m³·s⁻¹ in an annual average (Marone et al., 2005). The bulk of it is delivered to the bay through six main rivers (de Paula and Cunico, 2007) on which the sampling strategy was focused.

Sampling strategy

River nutrient loads

In order to account for seasonal variations, dissolved inorganic nutrient concentrations (c) and discharge (Q) of the main rivers entering Paranaguá Bay, i.e. Guaraguaçu, Sagrado, Nhundiaquara, Cacatu, Cachoeira and Faisqueira rivers, were assessed monthly over a period of one year from February 2008 to February 2009 (Fig. 1). In some cases, two tributaries of the main stream were sampled for nutrient analysis and averages were calculated. Direct discharge measurements were available for the Sagrado, Nhundiaquara, Cacatu and Cachoeira rivers (DHID). In case of the Guaraguaçu and Faisqueira river, monthly average discharge data calculated from the catchment area and precipitation rates were taken from a report of a local hydraulic engineering company (RHA, 2008). For all rivers sampled, nutrient loads were calculated as Q·c by multiplying monthly average discharge values (Q) with the corresponding nutrient concentrations (c).

Atmospheric wet deposition

The atmospheric wet deposition was measured at three sampling points in the upper, middle and lower section of the bay (Fig.1). The sampling locations were placed at Antonina harbour (upper section), Paranaguá harbour (middle section) and close to the mouth of the

estuary (lower section). Three subsamples of rainwater at each location were collected for the period of one week per month during the dry season (August, October and November 2007) and the rainy season (January to April 2008), and analyzed for inorganic nutrients. Total atmospheric wet deposition was calculated by multiplying nutrient concentrations by monthly averaged precipitation (DHID) over the different areas of the bay.

Waste water inputs

Samples for inorganic nutrient analysis were taken from the main waste water channels of Paranaguá City (Anhaia, Chumbo, Sabiá and harbour channel) and in the outlet of the sewage plant (Fig. 1) on two occasions during the rainy (February 2008) and dry (September 2008) season. In order to avoid situations of backwater intrusion into the drainage system of the waste water channels during sampling, samples were taken at low tide. Waste water discharge was estimated on the basis of current speed (drifters) and water level measurements, taking into account the individual dimensions of each channel. Nutrient loads were derived for each channel by multiplying nutrient concentrations by discharge. From the single measurements, average loads were calculated and annualized to get an estimate of total yearly nutrient loads. Annual sewage water discharge from the sewage plant of Paranaguá was calculated from data kindly provided by the company Águas de Paranaguá and multiplied with mean nutrient concentrations as an average from the two single measurements in the sewage water outlet.

Harbour emissions

Main pathways of inorganic nutrient inputs from fertilizer spillage in the harbour are dust formation during loading operations with subsequent deposition of fine particles, washing out of matter from the pier during rainfall and direct losses from cargo gears. These diffuse nutrient emissions are extremely difficult to be assessed by direct measurements. Hence, a rough estimation of the fluxes has been done on the basis of indirect calculations.

Losses from fertilizer handling in Paranaguá harbour were estimated by means of throughput data provided by harbour authorities (APPA annual reports, 2010), assuming a total loss rate of 0.01 % (weight based) during the loading procedure (Inros Lackner, 2008). 75 % of the fertilizer losses were supposed to enter the harbour water. Calculation of annual loads of inorganic N and P were based on the molar composition of the fertilizer products.

Nutrient gradients

Water samples for inorganic nutrient analysis were taken with a Niskin bottle from the surface and bottom layer on six longitudinal transects each comprising twelve stations along the main axis of the bay (Fig. 1). Samplings were performed in September and December 2007, February, June and September 2008, and January 2009, starting at the upper end of

the estuary. In addition, vertical profiles of temperature, salinity, turbidity and chlorophyll-*a* concentrations (derived from *in vivo* fluorescence) were performed at each station using a portable water quality measurement device called 'Pocket Ferrybox' with a centrifugal pumping device (Schroeder et al., 2008). On two of the transects (September 2007 and February 2008), vertical CTD and oxygen profiles (Eco-Probe, Sea & Sun Technology GmbH) were obtained.

In order to study the dispersion of nutrients deriving from the harbour and city of Paranaguá in more detail, a narrow sampling grid comprising 27 stations was sampled in front of the harbour and around the city (Fig. 1) both in the dry (September 2007) and rainy season (February 2008). Water samples for further analysis of inorganic nutrient concentration and salinity were taken as described before.

Laboratory analysis

The water samples were stored in PE bottles and cooled until further processing in the lab directly after sampling. For the purpose of dissolved inorganic nitrogen and phosphorus determination, subsamples were filtered through Whatman filters (GF/F) and stored deep frozen until further analysis according to Grasshoff et al. (1999).

Results

Hydrographic pattern

The hydrographic structure of Paranaguá Bay is determined by the inflow of saline and hence denser water from the coastal Southern Atlantic Ocean in the east and the discharge of freshwater from the numerous rivers around the bay. Depending on the tide, the season and the relative importance of river discharge, the interaction of these water bodies may result in a variable thermohaline stratification pattern inside the bay.

A t-test based on data from the six longitudinal transects revealed consistent significant differences in the surface and bottom water characteristics (temperature, salinity) between the seasons and sections of the bay. In the lower section during the dry period, surface water temperatures were significantly higher than at the bottom which is in line with a reduced input of cold freshwater in this season. In the middle section salinities in the bottom water were in both seasons significantly higher than at the surface which reveals the importance of freshwater water inflow at the surface in conjunction with deep saltwater intrusion deriving from the South Atlantic Ocean. The upper section of the bay is dominated by riverine discharge. Due to its reduced water depth, however, vertical mixing usually does not allow any significant physical differences between the surface and bottom water.

There were pronounced salinity difference between the different sections of the bay as well as between the seasons (Fig. 2a). Absolute values ranged from 5.5 to 33.2 during the dry and from 0 to 32.0 during the rainy season. Average salinities in the dry and rainy periods were 17.6 and 9.8 in the upper section, 27.1 and 22.0 in the middle region and 30.4 and 26.8 in the lower area, respectively. By contrast, spatial differences in water temperature (Fig. 2b) were only marginal when compared to the seasonal variation. The average water temperature during the dry season accounted for 20 to 21 °C in all sections of the bay, whereas average temperatures during the rainy season increase by about 5 to 6 °C to around 26 °C, independent from the section of the bay.

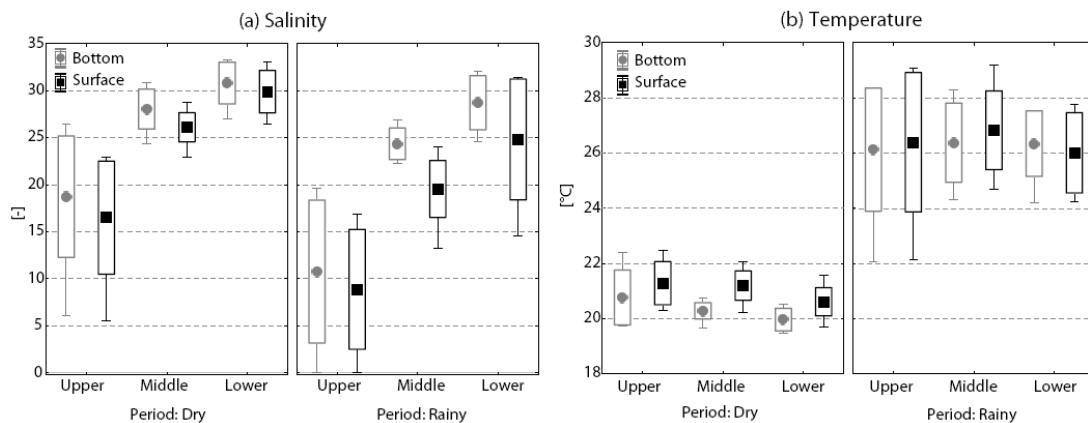


Figure 2: Box plots with mean values, standard deviation (box) and the range (spreads) of (a) salinity and (b) temperature for bottom and surface layers in the three sections of Paranaguá Bay during dry and rainy periods.

Typical vertical profiles of the temperature and salinity pattern along the main axis of the bay are illustrated in figure 3 for two different situations. During flood phase in the dry season (September 2007, Fig. 3 a,b), vertically mixed coastal water with salinities > 29 PSU enters the bay from the east, impeding the development of a pronounced freshwater plume in the inner part of the estuary.

Vertical stratification of the water column is thus much less distinct when compared to the pattern at ebb tide in the rainy season (February 2008, Fig. 3 c,d), which exhibits as a dominant feature a pronounced vertical halocline in the middle section of the bay, i.e. close to the city and harbour of Paranaguá. This is in keeping with a much higher fraction of freshwater inside the bay and a distinctive extension of the riverine plume. Solar heat input to the surface layer amplifies the stratification process especially during the rainy season, with a maximum vertical gradient in the thermocline of about 2 °C.

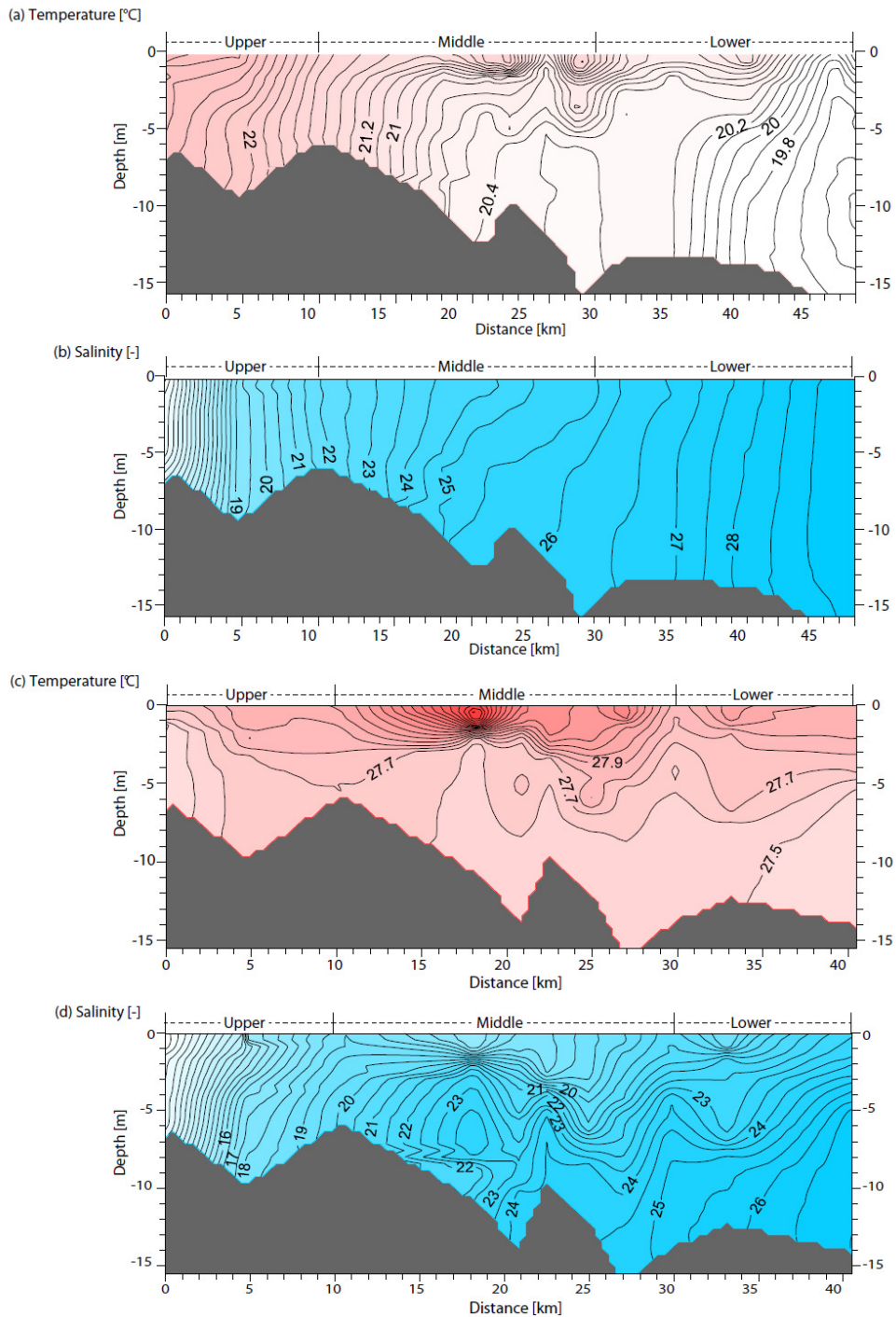


Figure 3: Interpolated vertical temperature and salinity profiles from CTD measurements on a longitudinal transect through the bay of Paranaguá in (a, b) September 2007 (dry season) during flood phase and in (c, d) February 2008 (rainy season) during ebb phase.

Nutrient inputs

River nutrient loads

River nutrient inputs into Paranaguá Bay are dominated by the discharge of 6 main rivers. The Cachoeira river is the most important with respect to freshwater runoff, exhibiting

an average flow of around $40 \text{ m}^3\cdot\text{s}^{-1}$ (Fig. 4a). The average individual discharge of the remaining rivers investigated ranges from $5\text{-}15 \text{ m}^3\cdot\text{s}^{-1}$.

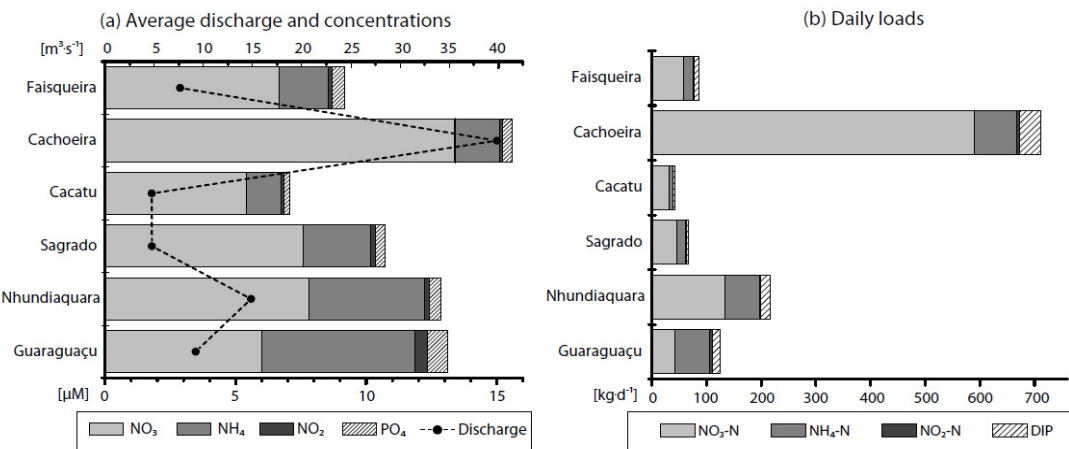


Figure 4: (a) Average discharge, nutrient concentrations and (b) loads of the main rivers entering Paranaguá Bay.

Nutrient concentrations vary considerably in time and between rivers (Tab. 3). The Cachoeira River exhibits the highest average nitrate concentrations exceeding $13 \mu\text{M}$. Highest mean ammonium concentrations of around $6 \mu\text{M}$ were observed in the Guaraguaçu river, followed by the Nhundiaquara river with average NH_4 levels of around $4 \mu\text{M}$. The Guaraguaçu, a coastal plain stream with low hydraulic gradients, also exhibited the highest phosphate levels amounting to around $1 \mu\text{M}$ PO_4 .

No consistent relationship was observed between river discharge and nutrient concentration. A weak but still significant inverse correlation (95% confidence level) between flow and ammonium concentrations was found for the Nhundiaquara River. A similar relationship was observed for the Guaraguaçu with respect to nitrate and DIN.

In general, nutrient loads follow the discharge characteristics of the particular rivers. Due to its high freshwater runoff, the Cachoeira river is the dominant source of nutrient inputs to the bay. In an average, its nitrate load accounts for almost $600 \text{ kg}\cdot\text{d}^{-1}$ $\text{NO}_3\text{-N}$ (Fig. 4b). In comparison, nitrate loads from the other rivers investigated range from $30\text{-}130 \text{ kg}\cdot\text{d}^{-1}$ $\text{NO}_3\text{-N}$. Average ammonium and phosphate inputs from the Cachoeira amount to $76 \text{ kg}\cdot\text{d}^{-1}$ $\text{NH}_4\text{-N}$ and $38 \text{ kg}\cdot\text{d}^{-1}$ DIP, respectively, while individual loads of the remaining rivers range from $8\text{-}64 \text{ kg}\cdot\text{d}^{-1}$ $\text{NH}_4\text{-N}$ and $3\text{-}16 \text{ kg}\cdot\text{d}^{-1}$ DIP. Inputs of nitrite as an intermediate product of nitrification are comparatively low. Maximum nitrite loads of the Cachoeira accounted for ca. $7 \text{ kg}\cdot\text{d}^{-1}$ $\text{NO}_2\text{-N}$.

Table 3: Mean and standard deviation (SD) of dissolved inorganic nutrient concentrations (μM) and of freshwater discharge ($\text{m}^3 \cdot \text{s}^{-1}$) of the main rivers of Paranaguá Bay.

River		Nitrite	Nitrate	Ammonium	DIN	DIP	Discharge
Guaraguaçu	Mean	0.46	5.67	5.67	11.79	0.83	9.84
	SD	0.3	5.7	4.0	7.6	1.3	5.9
Sagrado	Mean	0.19	7.57	2.59	10.35	0.36	4.75
	SD	0.1	3.3	2.1	4.7	0.1	2.9
Nhundiaquara	Mean	0.19	7.25	4.22	11.67	0.44	15.57
	SD	0.1	3.9	2.8	5.6	0.2	8.9
Cacatu	Mean	0.12	5.40	1.33	6.85	0.21	4.74
	SD	0.02	2.9	0.6	3.1	0.1	1.0
Cachoeira	Mean	0.14	13.30	1.49	14.92	0.35	41.83
	SD	0.1	7.6	0.8	7.8	0.1	13.4
Faisqueira	Mean	0.15	6.80	1.75	8.71	0.45	8.27
	SD	0.1	4.1	0.8	4.5	0.1	3.4

In keeping with the seasonal variation in discharge, highest total DIN and DIP loads of all rivers investigated are observed in the rainy season (Fig. 5). Daily maxima occurred in March (ca. 1,700 kg DIN and 130 kg DIP) and November 2008 (ca. 1,800 kg DIN and 160 kg DIP), while the lowest daily nutrient loads were recorded during the dry season exhibiting a minimum in September 2008 (ca. 500 kg DIN and 30 kg DIP). On an annual basis, the total river nutrient input accounted for 32.2 t DIP and 434.6 t DIN, including 339.6 t $\text{NO}_3\text{-N}$, 88 t $\text{NH}_4\text{-N}$ and 7 t $\text{NO}_2\text{-N}$.

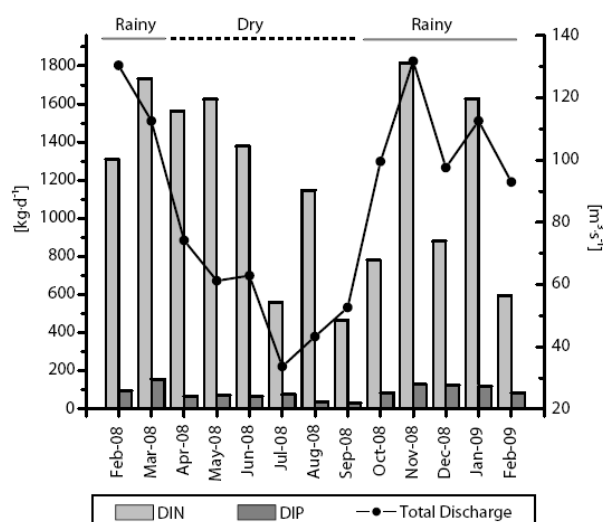


Figure 5: Total river discharge to Paranaguá Bay and dissolved inorganic nitrogen (DIN) and phosphorus (DIP) loads during rainy and dry seasons.

Atmospheric wet deposition

The atmospheric wet deposition of nutrients mainly depends on rainfall, especially in the subtropical wet climate of the area under investigation. Average daily precipitation rates of $11.6 \text{ dm}^3\cdot\text{m}^{-2}$ and $10.6 \text{ dm}^3\cdot\text{m}^{-2}$ were recorded during the rainy season, and $4.1 \text{ dm}^3\cdot\text{m}^{-2}$ and $3.8 \text{ dm}^3\cdot\text{m}^{-2}$ during the dry season for the lower and middle section of Paranaguá Bay, respectively. In comparison, the upper section receives minor daily rainfall, both in the rainy ($5.8 \text{ dm}^3\cdot\text{m}^{-2}$) and in the dry season ($2.0 \text{ dm}^3\cdot\text{m}^{-2}$). In total, the entire Paranaguá Bay was subject to an average precipitation volume of $3.45 \times 10^6 \text{ m}^3\cdot\text{d}^{-1}$ during the rainy and $1.22 \times 10^6 \text{ m}^3\cdot\text{d}^{-1}$ during the dry period (Tab. 4).

Dissolved inorganic nutrient concentrations of rainwater ranged from 0.03-0.49 μM DIP and 2.1-4.7 μM DIN, including 0.5-3.9 μM NH_4 , 0.8-1.8 μM NO_3 and 0.01-0.02 μM NO_2 . In both seasons, precipitation in the middle section exhibited slightly higher ammonium and phosphate levels, while nitrate concentrations are slightly higher in the lower section of the bay.

Table 4: Nutrient loads from atmospheric wet deposition to Paranaguá Bay.¹

Section		Upper	Middle	Lower	TOTAL					
Area dimension [km ²]		50	90	187	327					
Precipitation 10 ⁶ [m ³ ·d ⁻¹]	rainy	0.29	0.99	2.17	3.45					
	dry	0.10	0.35	0.77	1.22		Average	Load		
		[μM]	[kg·d ⁻¹]	[μM]	[kg·d ⁻¹]	[μM]	[kg·d ⁻¹]	[kg·d ⁻¹]	[t·a ⁻¹]	
$\text{NO}_2\text{-N}$	rainy	(0.02)	0.09	0.02	0.32	0.01	0.30	0.71	0.46	0.17
	dry	(0.02)	0.03	0.02	0.11	0.01	0.07	0.21		
$\text{NO}_3\text{-N}$	rainy	(1.15)	4.67	1.15	15.96	1.56	47.54	68.18	44.89	16.38
	dry	(0.79)	1.10	0.79	3.85	1.54	16.65	21.59		
$\text{NH}_4\text{-N}$	rainy	(1.76)	7.14	1.76	24.37	0.51	15.63	47.13	42.98	15.69
	dry	(3.86)	5.41	3.86	18.92	1.34	14.50	38.82		
DIN	rainy	(2.93)	11.91	2.93	40.65	2.09	63.47	116.02	88.32	32.24
	dry	(4.67)	6.54	4.67	22.87	2.90	31.22	60.62		
DIP	rainy	(0.23)	2.07	0.23	7.06	0.03	2.02	11.15	9.83	3.59
	dry	(0.49)	1.52	0.49	5.32	0.07	1.67	8.51		

The daily atmospheric wet deposition of inorganic nitrogen to the entire bay during the rainy period accounts for 116 kg DIN and is almost twice as much as during the dry

¹ Due to a contamination of samples in the upper section of the bay, nutrient concentrations of atmospheric wet deposition are not available for this area. Hence, for the calculation of nutrient loads it was assumed that the upper section exhibits comparable nutrient concentrations of rain water as the middle section.

period (Fig. 6a). The wet deposition of DIP varies less between seasons and accounts for a daily input of 11 kg DIP in the rainy and 8.5 kg DIP in the dry season, respectively. On an annual basis, atmospheric deposition contributes to the bay's total nutrient loads with 32.2 t DIN and 3.6 t DIP per year (Fig. 6b).

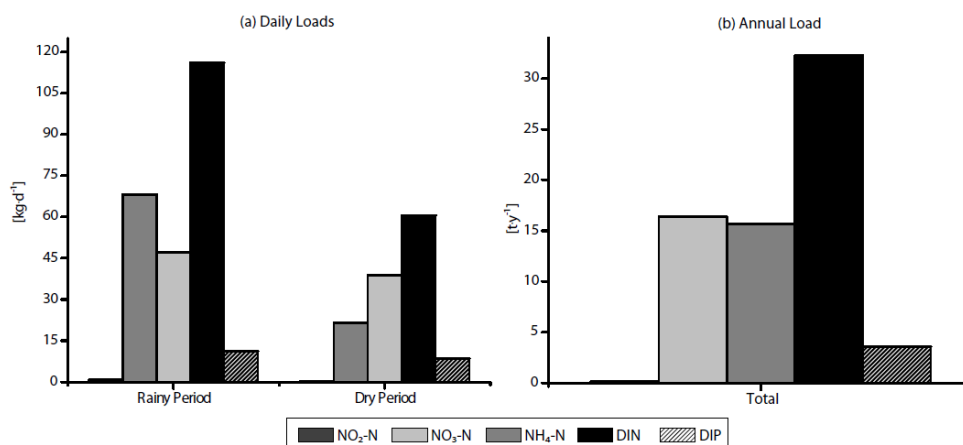


Figure 6: (a) Daily atmospheric wet deposition during rainy and dry seasons and (b) total annual atmospheric wet deposition of dissolved inorganic nitrogen compounds and dissolved inorganic phosphate.

Nutrient inputs from waste water discharge

The sewage plant of Paranaguá City treats about 3.600 m³ of waste water per day (Águas de Paranaguá, 2006). The bulk of domestic waste water from Paranaguá (about 70 %) is discharged untreated through the Anhaia, Chumbo, Sabiá and the Harbour sewage channels directly into the bay. Since these channels also receive a variable portion of storm water during times of heavy rainfall, their nutrient concentrations and loads are highly variable. Independent from rainy or dry seasons, maxima of 3020 μM NH₄, 216 μM NO₂, 300 μM NO₃ and 233 μM DIP were recorded, while minima are occasionally below detection limits for nitrate (Tab. 5).

Table 5: Maxima and minima of nutrient concentrations in waste water (STP: Sewage Treatment Plant).²

Nutrient	Maxima			Minima		
	[μM]	Date	Channel	[μM]	Date	Channel
NH ₄	3020	Sep-08	Sabiá	804	Feb-08	STP
NO ₂	216	Feb-08	Sabiá	2.7	Sep-08	Harbour
NO ₃	300	Feb-08	Chumbo	ND ⁽²⁾	Sep-08	Sabiá
DIN	3129	Sep-08	Sabiá	1109	Feb-08	STP
DIP	233	Sep-08	Harbour	29	Feb-08	STP

² ND = not detectable

Estimations of average daily nutrient loads from waste water input amount to 56 kg DIP and 373 kg DIN, with ammonium making up almost 93 % of inorganic nitrogen inputs. The main source of ammonium is the Anhaia with a mean load of $110 \text{ kg}\cdot\text{d}^{-1} \text{ NH}_4\text{-N}$. In contrast, the Harbour Channel is the most prominent source for phosphate inputs which account for $24 \text{ kg}\cdot\text{d}^{-1} \text{ DIP}$ in an average.

Highest nutrient loads from waste water were observed in September 2008, amounting to $432 \text{ kg}\cdot\text{d}^{-1} \text{ DIN}$ and $79 \text{ kg}\cdot\text{d}^{-1} \text{ DIP}$ (Fig. 7). Calculations of annual dissolved inorganic nutrient loads based on an extrapolation of input data result in 20 t DIP and 136 t DIN per year, including 126 t $\text{NH}_4\text{-N}$, 4 t $\text{NO}_2\text{-N}$ and 6 t $\text{NO}_3\text{-N}$. However, considering the high variability of nutrient concentrations and discharge of waste water and the lack of high-resolution time series these annual loads represent only approximations.

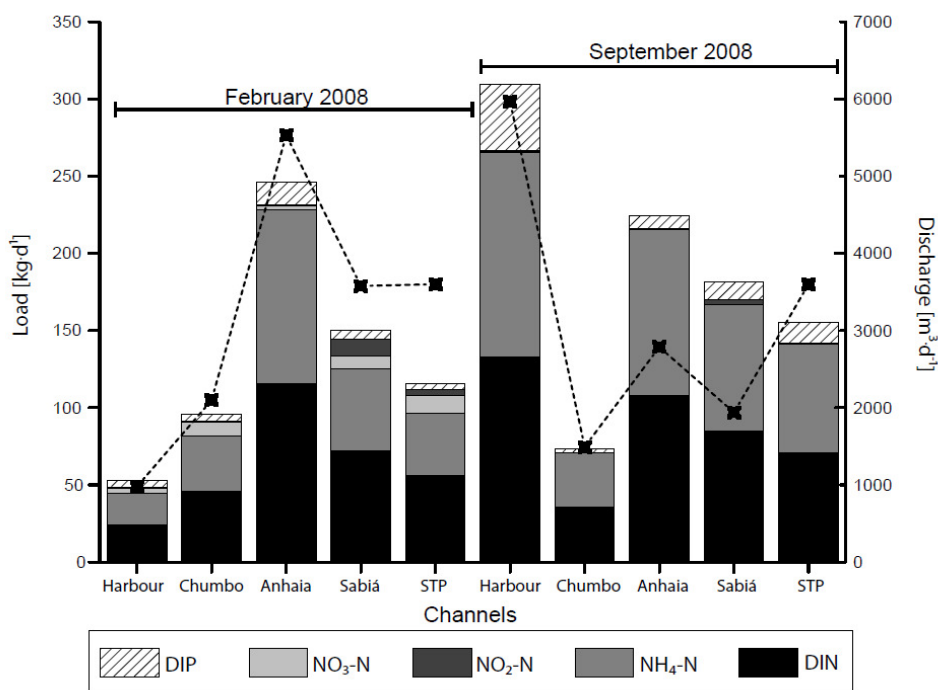


Figure 7: Daily nutrient loads and discharge of the main sewage channels of Paranaguá for February and September 2008.

Estimates of diffuse harbour emissions

In 2007, about $5.3 \cdot 10^6 \text{ t}$ of fertilizers and fertilizer raw material (i.e. phosphate rock) were handled at the port of Paranaguá (APPA, 2008). More than $2.9 \cdot 10^6 \text{ t}$ of these were mineral N- and P-fertilizers which are mainly made up by ammonium, nitrate and/or phosphate in different chemical composition (Tab. 6).

Due to loading and unloading procedures conducted by cranes, semi-enclosed conveyer belts and trucks, part of the fertilizers is lost to the harbour water. On the basis of throughput data for the year 2007 and cargo specific loss rates (see page 6), the annual nutrient loads from fertilizer losses were estimated to 35.4 t DIP, 34.4 t NH₄-N and 4.0 t NO₃-N, equaling an average daily nutrient input to the estuarine environment of 97 kg DIP, 94 kg NH₄-N and 11 kg NO₃-N.

Table 6: Mineral N- and P-fertilizer specification and calculated annual loss rates of ammonium (NH₄-N), nitrate (NO₃-N) and phosphorus (PO₄-P) compounds for Paranaguá harbour in 2007 (Source: APPA, 2008).

<i>Fertilizer</i>	<i>Type</i>	<i>Formula</i>	Loss [t]		
			NH₄-N	NO₃-N	PO₄-P
NITRATO AMONIO	Ammoniumnitrate	NH ₄ NO ₃	4.0	4.0	
SAM STD	Ammoniumsulfate Standard	(NH ₄) ₂ SO ₄	7.2		
MAP GR	Monoammoniumphosphate Granulate	(NH ₄)H ₂ PO ₄	7.1		15.6
DAP GR	Diammoniumphosphate Granulate	(NH ₄) ₂ HPO ₄	6.3		6.9
SAM GR	Ammoniumsulfate Granulate	(NH ₄) ₂ SO ₄	4.4		
TSP	Triplesuperphosphate	(NH ₄ MgPO ₄)	3.7		8.2
TSP GR	Triplesuperphosphate Granulate	(NH ₄ MgPO ₄)	1.3		2.9
MAP PO	Monoammoniumphosphate Powder	(NH ₄)H ₂ PO ₄	0.2		0.4
MAP FAR	Monoammoniumphosphate	(NH ₄)H ₂ PO ₄	0.2		0.4
BIOFOS	Mono-Dicalciumphosphate	Ca(H ₂ PO ₄) ₂			0.1
DYNAFOS	Monocalciumphosphate	Ca(H ₂ PO ₄)			0.1
SSP GR	Singlesuperphosphate Granulate	P ₂ O ₅			0.8
Total			<u>34.4</u>	<u>4.0</u>	35.4
			38.4		

Quantitative comparison of nutrient sources

Estimates of annual dissolved inorganic nutrient loads to Paranaguá Bay from the nutrient sources investigated sum up to 641.5 t DIN and 91.6 t DIP (Tab. 7). About 68 % of dissolved inorganic nitrogen inputs originate from river discharge, mainly in the form of river nitrate, which accounts for 93 % of total annual nitrate loads to the bay. With respect to ammonium inputs, the main contribution (48 %) is from waste water emissions, but still the rivers yield 33 % of total ammonium loads. Fertilizer losses from the harbour activities share 13 % of total ammonium inputs. The anthropogenic activities in the city and harbour of

Paranaguá thus constitute the most important source of ammonium to the bay. This also holds true for dissolved inorganic phosphate. The DIP emissions from Paranaguá share the biggest contribution of total dissolved inorganic phosphorus inputs to the bay. They account for 61 % and mainly derive from inorganic fertilizer handling (39 %), compared to a river DIP input of only 35 %. The atmospheric deposition presents a minor contribution for DIN and DIP loads to Paranaguá Bay, accounting for around 5 % and 4 %, respectively.

Table 7: Annual nutrient loads from different sources.

Nutrient Source	NH_4-N		NO_2-N		NO_3-N		DIN		DIP	
	[ty^{-1}]	[%]	[ty^{-1}]	[%]	[ty^{-1}]	[%]	[ty^{-1}]	[%]	[ty^{-1}]	[%]
Rivers	88.01	33.3	7.00	64.0	339.60	92.7	434.62	67.8	32.20	35.1
Atmosphere	15.69	5.9	0.17	1.6	16.38	4.5	32.24	5.0	3.59	3.9
Waste waters	126.0	47.7	3.76	34.4	6.41	1.7	136.16	21.2	20.42	22.3
Fertilizers	34.40	13.0	-	-	4.04	1.1	38.44	6.0	35.40	38.6
Total	264.09	100	10.93	100	366.43	100	641.46	100	91.61	100

Short-term effects of nutrient inputs to the bay

The potential effects of nutrient inputs to Paranaguá Bay in terms of levels of nitrification and phytoplankton biomass (chlorophyll-a) were studied on repeated longitudinal transects along the main axis of the bay. In addition a snapshot record of the small scale nutrient distribution in the vicinity of the harbour and city of Paranaguá was performed in order to assess the extension of nutrient plumes deriving from the waste water sources and the harbour inputs.

Nutrient gradients along the bay (axis)

In keeping with the dominant influence of river nutrient loads, there was a decreasing trend in dissolved inorganic nutrient concentrations from the upper areas of the bay towards its mouth (Fig. 8). Levels of DIN, nitrate and phosphate in the bay proper were slightly lower during the rainy period. By contrast nitrite concentration in the inner bay were higher during this time of year, whereas ammonium levels did not reveal a clear difference between the seasons. DIN average (rainy and dry seasons) levels ranged from 8.9 to 14.5 μM in the upper area of the bay to 1.1 to 3.5 μM in the lower region. Nitrate follows the DIN distribution especially during the dry season, since it made up the bulk of dissolved inorganic nitrogen in

this period (ca 50%). Nitrate decreased from 5.6 to 11.5 μM NO_3 upstream to about 0.3 to 2 μM NO_3 at the bay's mouth.

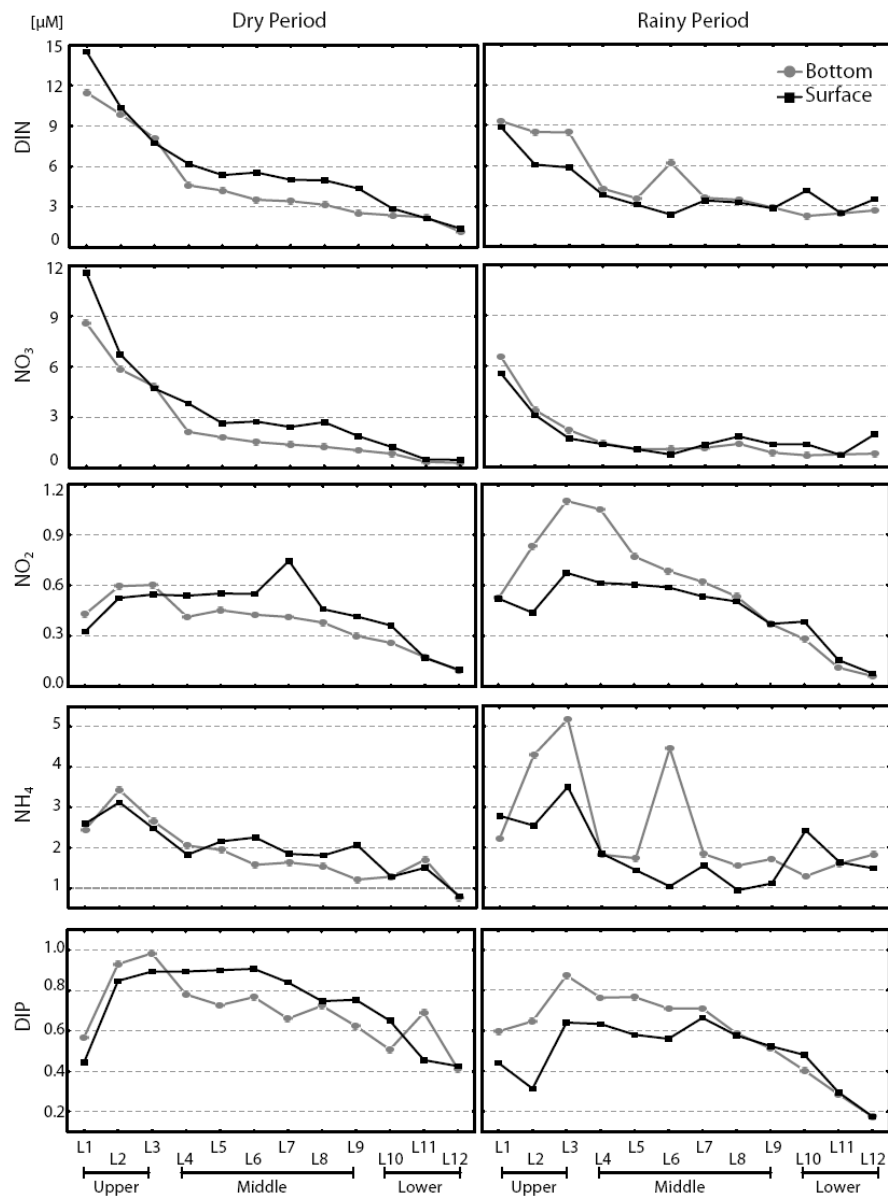


Figure 8: Average dissolved inorganic nitrogen (DIN), nitrate, nitrite, ammonium and dissolved inorganic phosphorus (DIP) concentrations of bottom and surface waters of the inner, middle and lower sections of Paranaguá Bay during dry and rainy seasons.

Nitrite concentrations ranged from 0.06-1.1 μM NO_2 along the estuary with the distinct maximum predominantly in the rainy period close to the mouth of Nhundiaquara River at station L3 (Fig. 8). A similar maximum was observed in ammonium levels (Fig. 8) which peaked during the rainy period to around 5 μM NH_4 in front of the Nhundiaquara. A second peak reaching 4.5 μM NH_4 was located in front of Paranaguá harbour (station L6). Minimum ammonium levels of 0.8 μM were observed during the dry period at the bay's entrance. As it

was the case for nitrite and ammonium, dissolved inorganic phosphorus concentrations were highest at station L3, i.e. close to the mouth of the Nhundiaquara River, culminating in levels of 1 and 0.9 $\mu\text{M PO}_4$ during the rainy and dry period, respectively (Fig. 8). Slightly elevated concentrations were also observed in the vicinity of the harbour and city of Paranaguá around stations L6 and L7 during both periods whereas minimum phosphate concentrations of 0.18 $\mu\text{M PO}_4$ prevailed at the entrance of the bay during the rainy period.

There was a significant inverse correlation between the DIN and nitrate distribution with salinity during both dry and rainy seasons (Tab. 8), whereas ammonium concentrations showed a significant inverse relationship with salinity in the dry period only. This indicates that the dissolved inorganic nitrogen distribution, especially the nitrate concentration in the bay, is largely controlled by freshwater discharge. By contrast, independent from the season phosphate levels do not show any significant relationship to salinity suggesting that other processes than rivers discharge dominate its distribution in the bay.

Table 8: Pearson coefficients (r) for the correlation of dissolved inorganic nutrient compounds and salinity during dry and rainy seasons (bold = significant at 95% confidence level).

<i>Sampling</i>	<i>Period</i>	NH₄	NO₂	NO₃	DIN	DIP	n
<i>Sep-07</i>	<i>dry</i>	-0.612	-0.657	-0.977	-0.964	-0.072	20
<i>Feb-08</i>	<i>rainy</i>	-0.150	-0.235	-0.726	-0.524	0.038	22
<i>Jun-08</i>	<i>dry</i>	-0.451	0.208	-0.906	-0.830	0.170	24
<i>Sep-08</i>	<i>dry</i>	-0.717	-0.492	-0.962	-0.945	-0.296	24
<i>Jan-09</i>	<i>rainy</i>	-0.356	-0.275	-0.487	-0.622	-0.018	24

Nutrient gradients around the city and harbour of Paranaguá

The nutrient input from the city and harbour of Paranaguá results in highly concentrated, albeit localized nutrient plumes along the shoreline (Fig. 9). Close to the mouth of the Anhaia channel, a maximum concentration of 93 $\mu\text{M DIN}$ and 10 $\mu\text{M DIP}$ prevailed. A second hot spot amounting to 46 $\mu\text{M DIN}$ and 10 $\mu\text{M DIP}$ was located at the western part of the harbour close to the Rio Chumbo channel and the western harbour channel outlet. High nutrient levels of 61 $\mu\text{M DIN}$ and 6 $\mu\text{M DIP}$ were also detected at the eastern end of the harbour near the Sabiá channel. In the Emboguacu River creek, which drains the water deriving from the local sewage treatment plant and from several slum areas of the city, maxima of 64 $\mu\text{M DIN}$ and 11 $\mu\text{M DIP}$ were found. Eventually, close to the shore line of Paranaguá, nutrient concentrations were up to 100-times higher than in the middle of the bay.

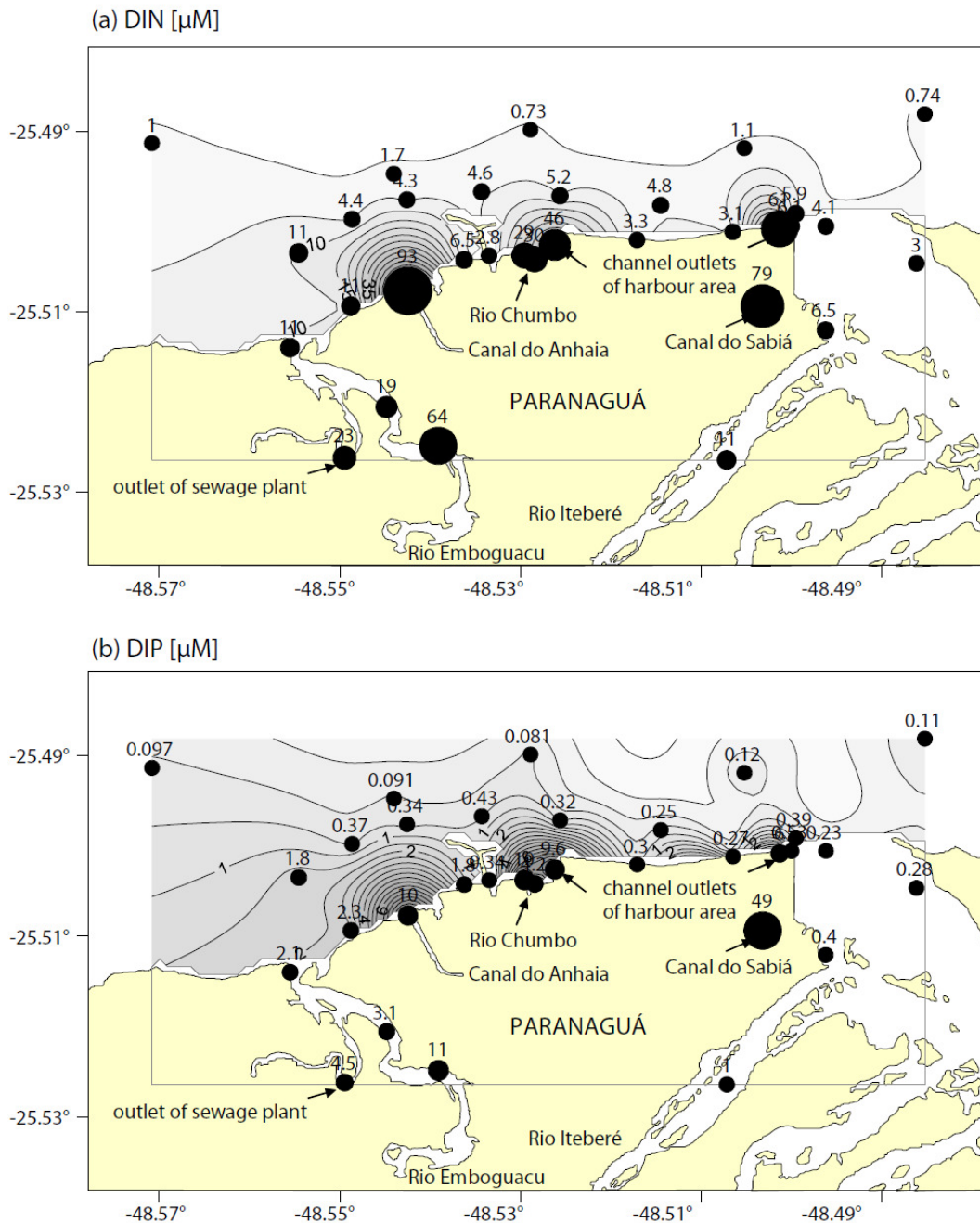


Figure 9: (a) DIN and (b) DIP concentrations [μM] in the vicinity of the city and harbour of Paranaguá in February 2008.

Eutrophication effects

Phytoplankton biomass, measured as chlorophyll-*a* concentration, can be regarded as an indicator for the trophic state of a system. An adequate light and nutrient supply represents the substantial basis for phytoplankton growth and thus for potential subsequent eutrophication effects such as high biomass blooms and oxygen deficiency in the deeper water due to organic matter overload.

Seasonal differences in chlorophyll-*a* concentrations emphasize the importance of light availability even in subtropical regions like Paranaguá Bay (Fig. 10a). During the dry season, i.e. in the southern hemisphere winter when light supply is at minimum, average chlorophyll-*a* concentrations were about $3 \mu\text{g}\cdot\text{dm}^{-3}$ in all sections of the bay. They were significantly lower than during the rainy season, i.e. the southern summer, where average chlorophyll-*a* concentrations of $11 \mu\text{g}\cdot\text{dm}^{-3}$, $17 \mu\text{g}\cdot\text{dm}^{-3}$ and $11 \mu\text{g}\cdot\text{dm}^{-3}$ prevailed in the upper, middle and lower area of the bay, respectively. During this season, despite of higher DIN and comparable DIP concentrations in the upper section (Fig. 11), maximum chlorophyll-*a* levels amounting to $48 \mu\text{g}\cdot\text{dm}^{-3}$ were observed in the middle section of the bay. This is in line with the pronounced vertical stratification observed in this area (see Fig. 3).

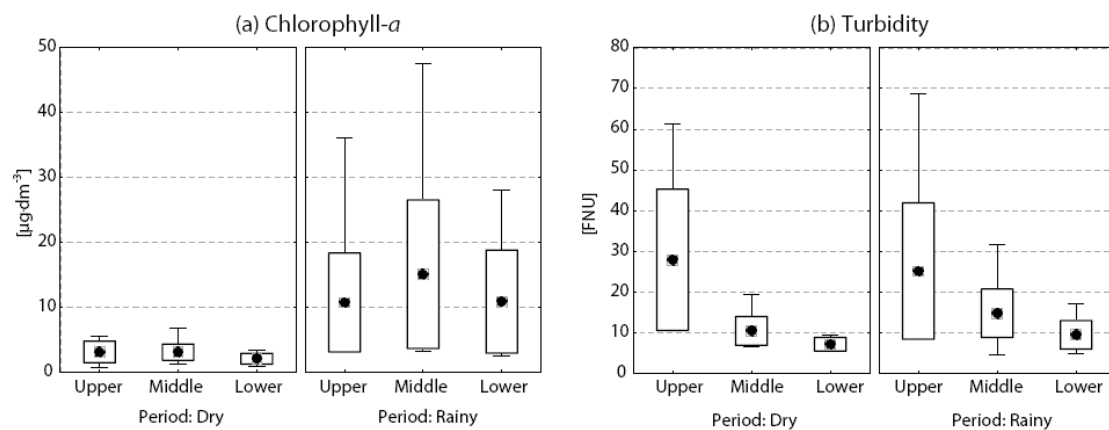


Figure 10: Box-plot of average (a) chlorophyll-*a* concentration and (b) turbidity: Standard deviation (box) and range (maxima and minima in spreads) in the upper, middle and lower sections of Paranaguá Bay in the dry and rainy seasons.

Moreover, in the upper section, light supply is limited by elevated turbidity levels accounting on an average for around 28 NTU in the dry and 25 NTU in the rainy period (Fig. 10b). Average turbidity in the middle and lower sections, however, amounted to only 10-14 NTU and 7-9 NTU for dry and rainy periods, respectively. It seems thus likely that light supply is limiting phytoplankton growth in the upper part of the bay, while in its lower part, where the clearest water prevailed, reduced nutrient availability and a higher mixing intensity is assumed to impede the formation of high phytoplankton stocks.

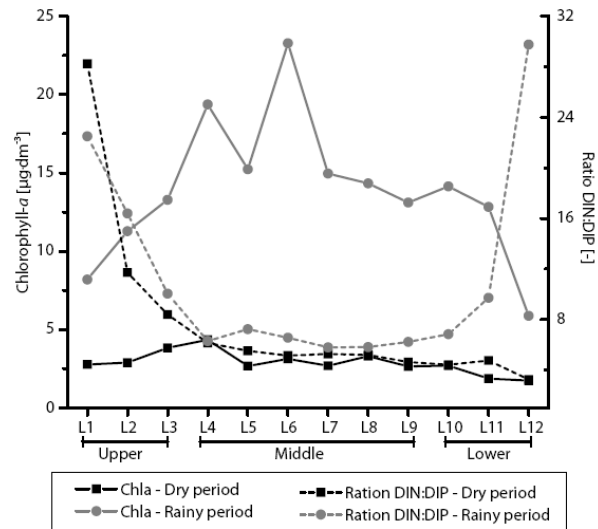


Figure 11: Average chlorophyll-a concentrations and molar ratio of DIN:DIP along a longitudinal transect through Paranaguá Bay during dry and rainy seasons.

Eutrophication classification

In order to assess the trophic status of Paranaguá Bay, published threshold values for eutrophication parameters were compared to measured concentrations. Bricker et al. (2003) recommend an eutrophication assessment scheme based on maximum surface concentrations of DIN, DIP and chlorophyll-a. The scheme is divided into three categories which allow for a classification into low, medium and high susceptibility of the system to develop negative eutrophication symptoms. A rating of the relevant data acquired on the longitudinal transects is presented in Tab. 9, comprising both maximum and mean concentrations. According to this method, most of the observed concentrations of DIN, DIP and chlorophyll-a result in a low to medium susceptibility to eutrophication in all sections and both seasons. Exceptions were due to maximum chlorophyll-a concentrations occurring in all the sections during the rainy season. In this case, the system has to be classified as highly susceptible to develop negative eutrophication symptoms.

Table 9: Classification of the eutrophication status of Paranaguá Bay for the upper, middle and lower section based on DIN-, DIP- and chlorophyll-*a* concentrations in dry and rainy seasons (after Bricker et al., 2003).

Variables	Upper Section		Middle Section		Lower Section		Threshold Limits	
	dry	rainy	dry	rainy	dry	Rainy		
DIN [$\text{mg}\cdot\text{dm}^{-3}$]	Mean	0.15 medium	0.10 medium	0.07 low	0.04 low	0.03 low	0.05 Low	high ≥ 1 1 > medium ≥ 0.1 low < 0.1
	Max.	0.23 medium	0.16 medium	0.12 medium	0.10 medium	0.06 low	0.11 Medium	
DIP [$\text{mg}\cdot\text{dm}^{-3}$]	Mean	0.02 medium	0.01 medium	0.03 medium	0.02 medium	0.02 medium	0.01 Medium	high ≥ 0.1 0.1 > medium ≥ 0.01 low < 0.01
	Max.	0.03 medium	0.03 medium	0.04 medium	0.04 medium	0.03 medium	0.02 Medium	
Chlorophyll- <i>a</i> [$\mu\text{g}\cdot\text{dm}^{-3}$]	Mean	3.3 low	12.5 medium	3.5 low	17.3 medium	2.1 low	10.8 Medium	hypereutrophic > 60 60 \geq high > 20 20 \geq medium > 5 low ≤ 5
	Max.	5.6 medium	36 high	6.9 medium	47.6 high	3.4 low	23.2 High	

Discussion

In the present study some rough assumptions were made to get an idea of the loads of dissolved inorganic nutrients entering the estuarine system of Paranaguá. Nevertheless, this may be justified considering the general difficulties especially in assessing diffuse nutrient inputs and the limitations in resolving the spatial and temporal scales in such a fluctuating estuarine system. It was not possible and not the intention of the authors to assess exhaustively the total nutrient inputs to the bay. Instead, emphasis was on the sources believed to share the main contribution in potentially anthropogenic nutrient loads to the area. Also, investigations were limited to the assessment of the dissolved inorganic fraction of nitrogen and phosphorus only. Information on the particulate nutrient phases as well as on dissolved organic nitrogen and phosphorus compounds are largely missing, even though their contribution to total nutrient inputs may be quite important in the region especially when considering the potential losses from open urea and soy handling in the harbour of Paranaguá. Annual throughput of these products in the harbour amounted to 770,000 tons of urea and more than 10 million tons of soy products in 2010 (APPA). Applying cargo specific losses for the different soy products (soybean flour and pellets) in a similar way as for the calculation of fertilizer losses to the bay, an annual amount of around 900 t of soy is supposed to be lost to the marine environment. An important share of dissolved

inorganic nitrogen and phosphate may come from the decomposition of this particulate organic material and might be restrained to the harbour vicinity.

Results suggest that the anthropogenic nutrient inputs from the city and harbour of Paranaguá, which constitute more than one quarter of total DIN loads (especially as ammonium) and far more than half the total DIP inputs to the estuary, may trigger phytoplankton development in the middle section of the bay. These nutrient inputs are introduced at a site which seems to be more susceptible to eutrophication effects than other parts of the area. The occurrence of a considerable anthropogenic nutrient supply and a strong and shallow thermohaline stratification in the vicinity of Paranaguá during the rainy season lead to the formation of local phytoplankton blooms exhibiting chlorophyll concentrations which clearly exceed eutrophication threshold levels. The prevalence of high phytoplankton stocks in the middle section of the bay seems to be a characteristic feature of the estuarine system of Paranaguá, as evidenced by previous investigations in the region (Knoppers et al., 1987; Brandini et al., 1988; Rebello and Brandini, 1990; Machado et al., 1997). There are several observations on the sporadic occurrence of potentially harmful phytoplankton species in the area, some of which (*Phaeocystis spp.*, *Coscinodiscus wailesii*) attaining high cell densities that can result to an overload of organic matter and decreasing other phytoplankton species and zooplankton abundance (Fernandes et al., 2001; Mafra Junior et al., 2006; Procopiak et al., 2006). Other phytoplanktonic species (*Pseudonitzschia spp.*, *Heterosigma akashiwo*) are related to mussels contamination by algae toxins (Mafra Junior et al., 2006; Procopiak et al., 2006; Fernandes and Brandini, 2010).

However, disregarding the high chlorophyll levels observed during the rainy season in all sections, one may conclude from the classification applied in Table 9 that eutrophication does not constitute a significant problem to the estuary, at least as far as the water column is concerned. Vertical profiles of oxygen levels on the longitudinal transects never revealed saturation values less than 70 % (5 mg O₂/l), with pronounced oversaturation in the surface layer of more than 160 % (11 mg O₂/l) at sites of high phytoplankton biomass in the middle section of the bay. By contrast, anoxic conditions and oxygen deficiency have been observed in the surface sediment layer directly in front of Paranaguá harbour (Liebezeit pers. comm.). They were associated with a high concentration of organic matter and organic phosphorus as well as elevated concentrations of suspended matter in the deep water layers. This is supposed to be mostly due to losses of particulate organic matter from the soy loading activities.

From the findings summarized above it appears that there is a need for mitigation measures in order to achieve and preserve a good ecological status of the estuarine system of Paranaguá. These measures should concentrate predominantly on a reduction of nutrient loads from waste water outfalls and harbour operation. According to the Brazilian

environmental legislation (CONAMA, 2005), the threshold levels for total nitrogen and phosphorus concentrations in waste water discharges account for 740 μM TN and 32 μM TP (10 $\text{mg}\cdot\text{dm}^{-3}$ TN and 1 $\text{mg}\cdot\text{dm}^{-3}$ TP). In the waste water discharge from Paranaguá City inorganic nutrient levels alone by far exceed these threshold limits. Appropriate counter measures may envisage the construction of decentralized sewage treatment units, a consistent separation of precipitation during heavy storms and waste water networks as well as the implementation of an enclosed loading equipment to prevent cargo spillage in the port. The need for these actions is gaining in importance when considering the rapid growth of the harbour and the population of Paranaguá over the past decades.

Apart from these more practical issues, further investigations should be carried out in order to provide a more complete nutrient balance of the estuarine system of Paranaguá, which should focus in particular on the dissolved and particulate organic nutrient fraction, the nutrient transports at the open sea boundaries, the quantification of nutrient sinks in terms of denitrification and phosphate burial as well as on the role of mangroves in the nutrient regime of Paranaguá Bay.

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Abstract

An environmental assessment of the estuarine waters of Guaratuba bay, Paraná State, Brazil, is provided through the analysis of physical-chemical, biological and hydrographic dynamics. Twelve stations with a bi-monthly frequency (from October/2002 until August/2003) were sampled during spring and neap tides for the determination of pH, Secchi depth, CO₂ saturation, dissolved oxygen, chlorophyll, suspended particulate matter and dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate). Based on the evaluation of six parameters (chlorophyll, Secchi depth, CO₂ saturation, dissolved inorganic nitrogen and phosphorus and dissolved oxygen), Guaratuba Bay shows a low to medium trophic status and a predominant heterotrophic metabolism, meaning that respiration overcomes primary production. Horizontal stratification was observed during the rainy season, while during the dry season the system showed more homogeneous conditions. Inorganic and/or organic matter in Guaratuba Bay seem to be controlled mainly by the seasonality of precipitation and/ also by ebb and flood tidal phase variations.

Key-words: water quality, hydrodynamics, nutrients, spatial and temporal variation, Guaratuba Bay.

Resumo

A dinâmica das variáveis físico-químicas, biológicas e hidrográficas, em escalas temporal e espacial, sua variabilidade e tendências, permite avaliar a qualidade ambiental de estuários. Esse trabalho descreve as flutuações da qualidade de água da Baía de Guaratuba, sul do Estado do Paraná. Foram amostrados doze pontos em campanhas bimensais (outubro/2002 a agosto/2003), em situação de sizígia e de quadratura, para a análise das variáveis pH, transparência, saturação de CO₂, oxigênio dissolvido, clorofila-*a*, material particulado em suspensão e nutrientes inorgânicos dissolvidos (nitrato, nitrito, amônio, fosfato e silicato). Considerando as seis variáveis descritoras da qualidade de água (clorofila-*a*, profundidade de Secchi, saturação de CO₂, fósforo e nitrogênio inorgânicos dissolvidos e oxigênio dissolvido), observou-se que a Baía apresentou estado trófico médio

para baixo e que o seu metabolismo é predominantemente heterotrófico, ou seja, os processos de respiração superam os de produção. Foi verificada uma maior estratificação horizontal durante o período chuvoso e características relativamente mais homogêneas durante a estação mais seca. A qualidade da água na baía de Guaratuba parece ser controlada mais pelos aportes de material inorgânico e/ou orgânico associados a pluviosidade e/ou por variações com as fases de maré vazante e enchente.

Palavras-chave: Qualidade de Água, hidrodinâmica, nutrientes, variação espaço-temporal, Baía de Guaratuba.

Introduction

Eutrophication is an important issue that has become a worldwide problem in the last decades (Cloern, 2001; OSPAR, 2001; Bricker et al., 2003). Eutrophication can cause negative impacts to coastal waters, and the evaluation of water quality at appropriate spatial and temporal scales is necessary to understand the complex interactions between non-biological and biological features and the carrying capacity of estuaries.

The State of Paraná, southern Brazil, has two main estuarine systems: the Paranaguá Estuarine System and Guaratuba Bay. Guaratuba Bay (Fig. 1) is a system located at the southern Paraná coast, with around 32,000 inhabitants, and is inserted in the Environmental Protection Area of Guaratuba (APA Guaratuba).

Economic activities are based on tourism, recreation, small scale fisheries and aquaculture. Over the past three decades, Guaratuba Bay has been under increasing urban pressure following the regional development trends but still remains relatively pristine, with extensive mangrove coverage along the margins representing important nursery and feeding environment for several species (Chaves and Bouchereau, 2000). Besides tourism and recreational attractions, activities such as small-scale fisheries, aquaculture and proposals for hydroelectric power plants in the catchment area demand a better understanding of the functioning of the estuarine system and so far no information is available about the nutrient and phytoplanktonic fluctuations in Guaratuba Bay.

The environmental protection and the activities developed in the system can turn into conflicting issues. For example, the population living at the margins of the system can increase up to 300% during summer and sewage treatment plants cover only 30% of the permanent population. Moreover, the quality of shellfish from the aquaculture farms also demands good water quality that can be impacted by sewage pollution. For this purpose, the water quality assessment of Guaratuba Bay was performed in order to investigate spatial-temporal chlorophyll concentrations (as indicator of phytoplanktonic biomass), total phosphorus and nitrogen and inorganic nutrients fluctuations in relation to environmental

descriptors. This information should support the legal guidelines and standards for protection of the environment and regulation of human activities.

Material and Methods

Study Area

Guaratuba Bay (Fig. 1) is located around the coordinates $25^{\circ} 51.8' S$ and $48^{\circ} 38.2' W$ with a surface water area of 50.19 km^2 and an mean depth of 3 m. Around 24% of the bay has shallow waters, while the maximum depth of 27m is observed in the system's mouth (Marone et al., 2004) which is formed by two rocky points that are 500 m distant from each other. From the connection to the Atlantic Ocean, the system widens inwards for 15 km, sheltering many sand banks.

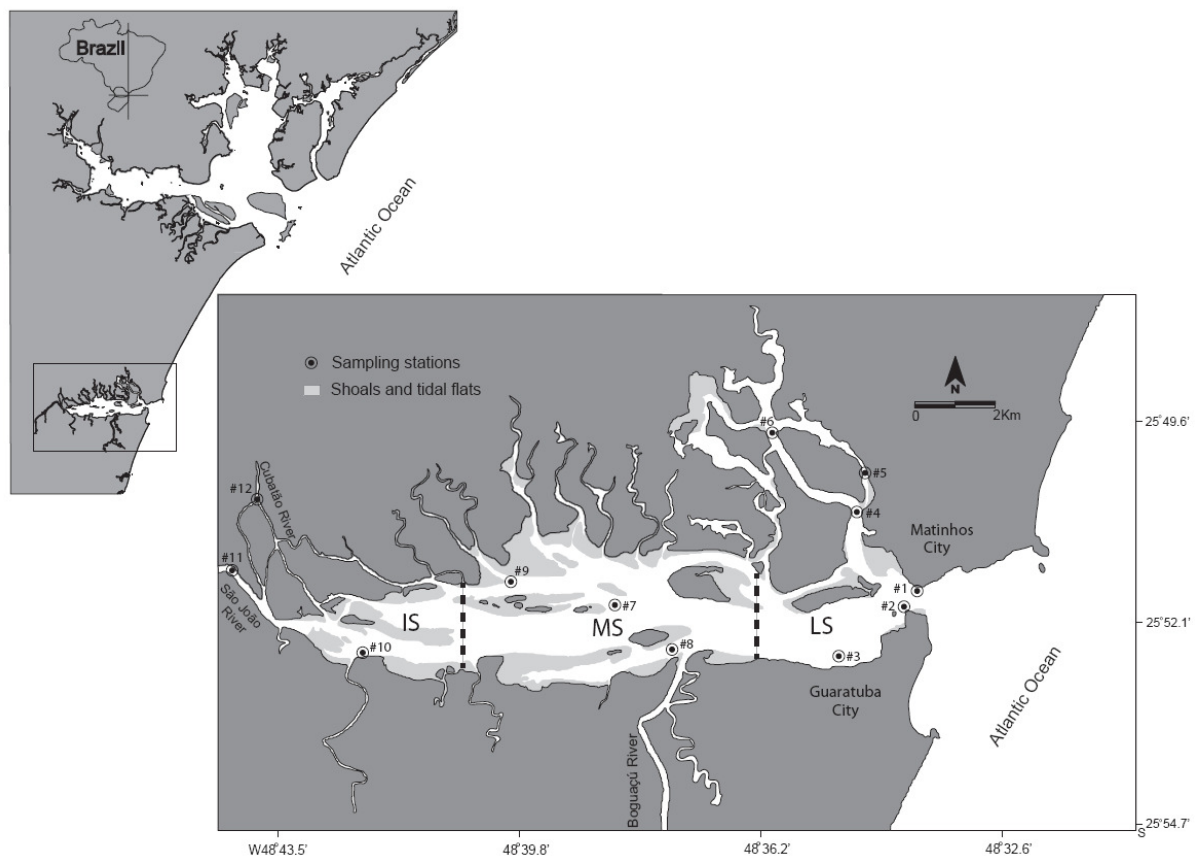


Figure 1: Coast of Paraná State and its two estuarine systems: Paranaguá Estuarine Complex (north) and Guaratuba Bay (south); sampling stations (1 to 12), salinity zones (IS: inner section; MS: middle section, LS: lower section) and main features of Guaratuba Bay are highlighted.

The system receives freshwater discharge mainly from two rivers, Cubatão and São João, which contribute to the majority of the freshwater runoff, reaching up to $80 \text{ m}^3/\text{s}$. The Guaratuba Bay is surrounded by seagrass and mangrove vegetation, which are more

extensive along the northern margin of the estuary, whereas its south margin is largely occupied by urban settlements and agricultural enterprises (Marone et al., 2004).

The hydrodynamic scenario of Guaratuba Bay is presented by Marone et al. (2004). The system has strong currents (more than 2 m s^{-1} at the mouth), and semi-diurnal tides of up to 1.5 m range (0.65 m at neap tide). In a complex tide propagation pattern (progressive, mixed and stationary), up to $75 \cdot 10^6 \text{ m}^3$ of water are transported at spring tidal and $32 \cdot 10^6 \text{ m}^3$ at neap tides. During situations of neap tides and low river runoff, strong vertical stratification is observed due to the intensification of the baroclinic component of the pressure gradient.

The climate in this region is classified as subtropical mesothermic with an average annual temperature of $22 \text{ }^\circ\text{C}$, and a rainy hot summer season (Marone et al., 2004). Data from the Hydrology Department (DHI) indicated that during the studied period mean annual precipitation was around 1800 mm with higher rainfall during the summer time. The annual cycle can be described by the occurrence of a rainy period corresponding to spring and summer, and a dry season with low precipitation during autumn and winter (Marone et al., 2004).

Sampling and analysis

Twelve sampling campaigns were performed between October 2001 and August 2002, in order to determine the Secchi depth and the following variables of bottom and surface waters: temperature, salinity, pH, CO_2 saturation (through alkalinity measurements), dissolved oxygen, chlorophyll-*a*, suspended particulate matter and inorganic dissolved nutrients (nitrate, nitrite, ammonium, phosphate and silicate). Spring and neap tidal situations were sampled each month at twelve stations distributed along the bay. Temperature, salinity and pH were measured *in situ*, while oxygen samples were prepared following the Winkler methodology. The water samples for nutrient, chlorophyll, TN, TP and suspended particulate matter analysis were taken with a Niskin bottle and kept cold until processing and filtration (GF/F fiber glass Whatman filters). Sampling dates and its respective tidal situations are shown in Table 1. Methodologies for analysis and determinations of selected variables are listed in Table 2.

Table 1: Sampling campaigns dates and respective tidal situation.

Spring tide	Neap Tide
October 3 rd , 2001	October 10 th , 2001
December 12 th , 2001	December 20 th , 2001
January 29 th , 2002	February 6 th , 2002
March 27 th , 2002	April 4 th , 2002
May 29 th , 2002	June 6 th , 2002
August 15 th , 2002	August 22 nd , 2002

Table 2: Measured parameters and analysis methods.

Parameter	Method
Inorganic Dissolved Nutrients (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , Si(OH)_4) and Total Phosphorus and Nitrogen (TP and TN)	Grasshoff <i>et al.</i> , 1983
Dissolved Oxygen (DO)	Winkler modified (Grasshoff <i>et al.</i> , 1983)
Chlorophyll- <i>a</i> and Pheopigments	Strickland and Parsons, 1972
Suspended Particulate Matter (SPM)	Strickland and Parsons, 1972
Water transparency	Secchi Disc
pH	pHmeter
Salinity, Temperature	refractometer, Thermometer

Results

Seasonal Periods

Precipitation rates were analyzed in order to investigate the seasonal patterns and the accumulated rainfall in the seven days before the sampling campaigns. They indicated the occurrence of two seasonal periods (Fig. 2), as described also for Paranaguá Bay (Marone *et al.*, 2005). Maximal accumulated precipitation was recorded before the sampling campaigns of October 2001, reaching around 110 mm, while drought periods were observed in June and August 2002.

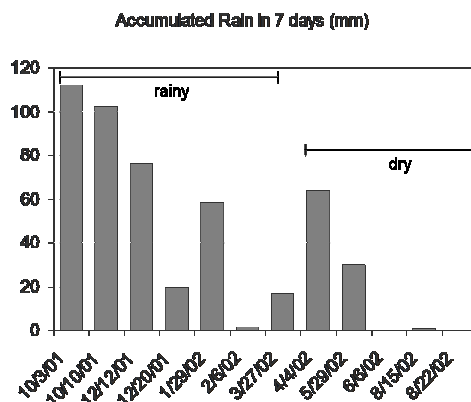


Figure 2: Accumulated rain in 7 days before sampling campaigns.

Seasonality between the rainy and dry periods was analyzed by the *t*-test (Tab. 3) aggregating both bottom and surface layers. The increase of around 3 PSU of salinity due to lower freshwater input in the dry season was followed by the increasing of around 0.5 m of Secchi depth, 0.2 units of pH and 0.8 $\text{mg}\cdot\text{dm}^{-3}$ of dissolved oxygen. Higher average temperatures of 25 °C during the rainy season occurred with an increase of around 30% of CO_2 saturation, and 15% of silicate concentrations. The freshwater discharge is related to overloads of inorganic nutrient loads (Machado *et al.*, 1997; White *et al.*, 2004), but the opposite was observed in Guaratuba Bay. Lower DIN and DIP concentrations during the

rainy season may be a result of higher biological uptake during the period or dilution due to higher freshwater input to the estuary. Although no significant differences were observed in the chlorophyll-*a* concentrations, higher phytoplanktonic biomass was observed in the rainy period. Chlorophyll-*a* data must be taken carefully in this study, because the dry season information could only be taken during April/2002 sampling campaign. All other surveys that correspond to the dry period lack phytoplanktonic data, which may lead to interpretation failures.

Table 3: Averages and *p*-values for the variables (surface and bottom measurements combined) that presented significant difference indicated by the *t*-test between the rainy and dry seasons in Guaratuba Bay.

Variables	Rainy Period	Dry Period	<i>p</i>
Secchi	1.15	1.57	<0.001
Salinity	15.03	18.02	0.024
T. °C	25.19	21.79	<0.001
DO	6.19	6.95	<0.001
pH	7.47	7.68	0.007
Sat%CO ₂	703.72	486.61	0.008
NH ₄ ⁺	1.04	1.87	<0.001
DIN	3.81	5.03	0.014
DIP	0.27	0.32	0.002
Si(OH) ₄	57.62	49.41	0.047

Therefore, the results of the remaining variables were grouped by the seasonal periods and presented as the averages between the measurements performed during the rainy (October to March) and the dry (April to August) season.

Physical setting: Temperature and Salinity

According to the salinity gradients (Fig. 3a), the system was divided spatially into three compartments. Salinity was significantly different (*t*-test, *p*-value<0.05) among compartments that were determined as inner section (IS), middle section (MS) and lower section (LS) (see Fig. 1). Average salinity ranged between 1 during the rainy season and 4 during the dry season in IS, while from 12 to 17 in MS and 23 to 26 in LS, respectively. The stations 11 and 12 were into freshwater zones, once zero salinity was measured at these locations. Moreover, salinity stratification was permanently observed along the middle and lower sections, where bottom salinities were significantly different, and around 4 PSU higher than the values measured in the surface layers.

The inner section presented permanent colder waters, with a mean of 20.9 °C in the dry season, while the maximum average of 25.7°C was observed in the lower section in the rainy period (Fig. 3b). All over the estuary, average temperatures were up to 25°C in the rainy season, while around 22°C in the dry period.

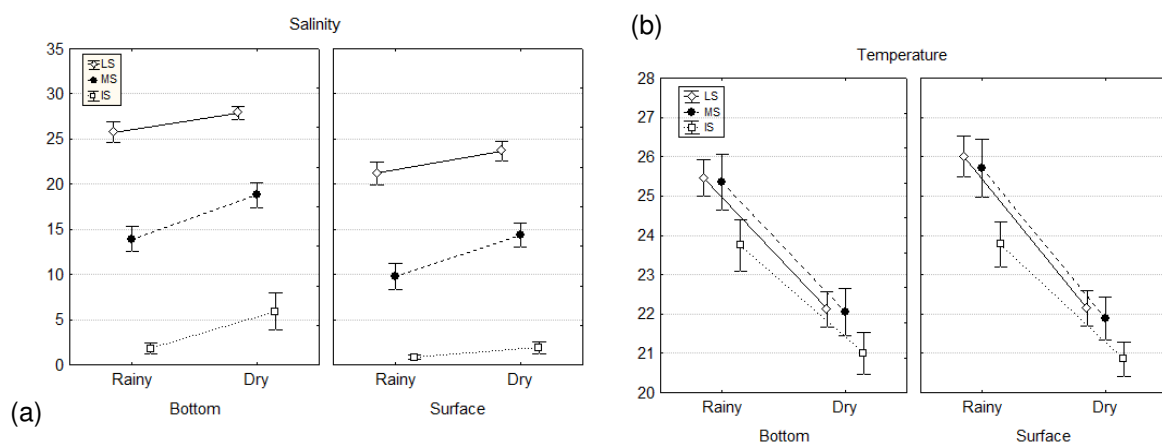


Figure 3: (a) Salinity and (b) water temperature measurements during the rainy and dry seasons for the three compartments (LS, MS and IS) and water layers (bottom and surface) of Guaratuba Bay (average and standard deviation).

Inorganic Nutrients

DIN concentrations (Fig. 4a) were by far higher in the inner section, reaching average concentrations of around 7 and 10 μM in the rainy and dry seasons, respectively, while the average concentrations ranged from around 2 to 4 μM in the middle and lower sections. Nitrate (Fig. 4b) seemed to regulate the fluctuations of dissolved nitrogen because it represented the major share of DIN, especially in the inner section. In this area, around 75% of DIN derived from nitrate, which presented the highest average concentration of around 7.7 $\mu\text{mol}\cdot\text{dm}^{-3}$ during the dry season. Locally depleted patches (nitrate concentrations under the detection limit) were observed at some sampling stations in LS during the rainy season, indicating that primary production was probably limited by nitrogen in this region. Even though the ammonium concentrations (Fig. 4c) were higher than nitrate levels during the dry season at the middle and lower sections, the highest average concentration of 2.7 $\mu\text{mol}\cdot\text{dm}^{-3}$ was also observed in IS during the dry season. Nitrite levels (Fig. 4d) were higher in the inner section, but a decrease of this nitrogen compound was observed in the dry season in this area. Average DIP (Fig. 4e) concentrations ranged between low values of 0.22 to 0.41 $\mu\text{mol}\cdot\text{dm}^{-3}$ in Guaratuba Bay. A pronounced increase of DIP was observed in LS during the dry period that can be a result of the expected lower biological uptake during this season (autumn/winter).

The molar ratio DIN:DIP was higher in the inner section (Fig. 4f) because of permanent higher DIN concentrations. DIN enrichment related to land runoff, especially of nitrate, was reflected in a decreasing seaward gradient of DIN:DIP ratio, with average values of 7.3 to 12.5, 11 to 19.5 and 25.4 to 51.5 in the lower, middle and inner sections,

respectively. This pattern was also verified in Paranaguá and Laranjeiras bays (Machado et al., 1997).

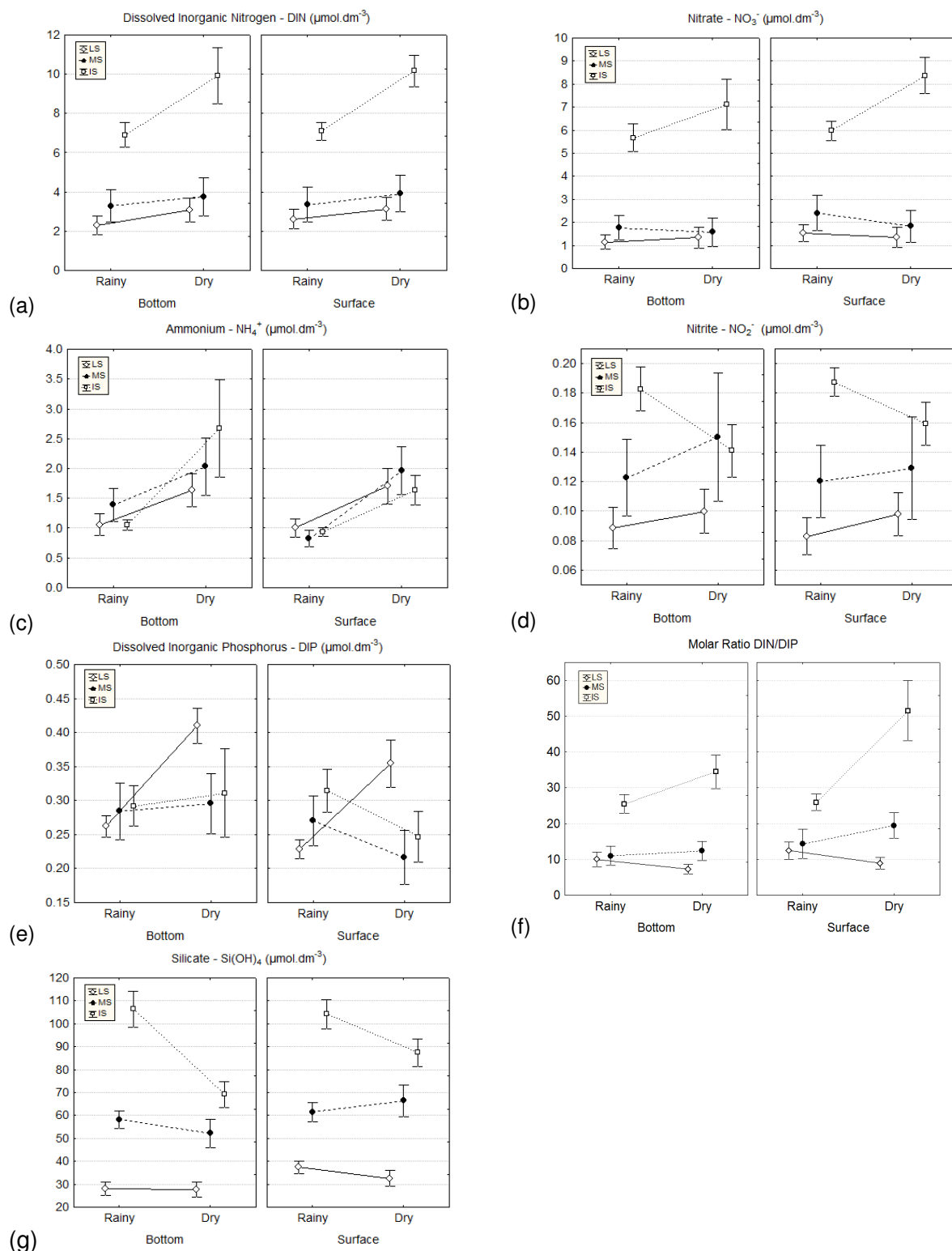


Figure 4: (a) Dissolved inorganic nitrogen - DIN; (b) nitrate; (c) ammonium; (d) nitrite; (e) dissolved inorganic phosphorus - DIP concentrations, (f) molar ratio DIN:DIP and (g) silicate concentrations during the rainy and dry seasons for the three compartments (LS, MS and IS) and water layers (bottom and surface) of Guaratuba Bay (average and standard deviation).

Silicate concentrations (Fig. 4g) varied between 10 and 150 μm along the bay and were considered low as compared to other systems (Knoppers et al., 1999a; 1999b; Souza and Knoppers, 2000). Higher silicate concentrations were observed in the upstream and central region with salinity gradient between 0 and 5, linearly decreasing until the system outlet. The pool of silicate can be incremented by the increase of water residence time and the dissolution of particulate silicate in the water-sediment interface, indicated by higher concentrations in the dry period and during neap tides (Ittekkot et al., 2000).

In general, dissolved inorganic nutrient concentrations were low in comparison with other systems related with eutrophication problems (Ferreira, 2000; Cloern, 2001). These results are not enough for the identification of nutrient enrichment leading to anthropogenic eutrophication. Ammonium concentrations, as an indicator of sewage pollution, were similar all around the bay. Ammonium concentrations were lower than those observed in areas related with anthropogenic pollution in Paranaguá Bay, like around the Harbour and Paranaguá City (Mizerkowski and Machado, 2005).

Biological Interactions: pH, CO₂ saturation, dissolved oxygen, chlorophyll-a, suspended particulate matter and water transparency

A conservative behavior of pH was observed (Fig. 5a). Highest average values in LS reached 8.04, while lowest average of 6.4 was registered in IS. Higher pH was observed in all sections during the dry period together with higher salinities. High CO₂ saturation (Fig. 5b) levels of over 200% were permanently observed in Guaratuba Bay, with maxima over 1500% registered in IS during the rainy season (saturation determined through alkalinity measurements). The relative balance of carbon dioxide species is controlled by pH and allows the identification of autotrophic or heterotrophic conditions (Whitfield and Turner, 1986; Day Jr., 1989; Carmouze, 1994). Guaratuba Bay presented permanent elevated levels of CO₂ saturation during all study period, which indicates the predominance of net heterotrophy, as observed in Paranaguá Bay, located 40 km from the studied site. This pattern differs from Saquarema Lagoon (RJ), where autotrophy was observed during summer and heterotrophy only during winter (Carmouze, 1994).

Dissolved oxygen average levels along Guaratuba bay were over 5.5 $\text{mg}\cdot\text{dm}^{-3}$ (Fig. 5c). Higher levels were recorded in the dry period and in the lower section, which also showed the minima concentration observed. The lowest concentration of 3.70 $\text{mg}\cdot\text{dm}^{-3}$ was measured in the bottom waters of station 6, located in a channel among mangrove margins, while the highest of 10.73 $\text{mg}\cdot\text{dm}^{-3}$ was recorded in the surface layer at station 1. Whereas the lower areas of estuaries have higher oxygenation rates due to waves, winds and

turbulence, the inner areas and the mangrove channels have lower levels related to higher decomposition rates and less water movement, as verified also for Baixada Santista (Braga et al., 2000).

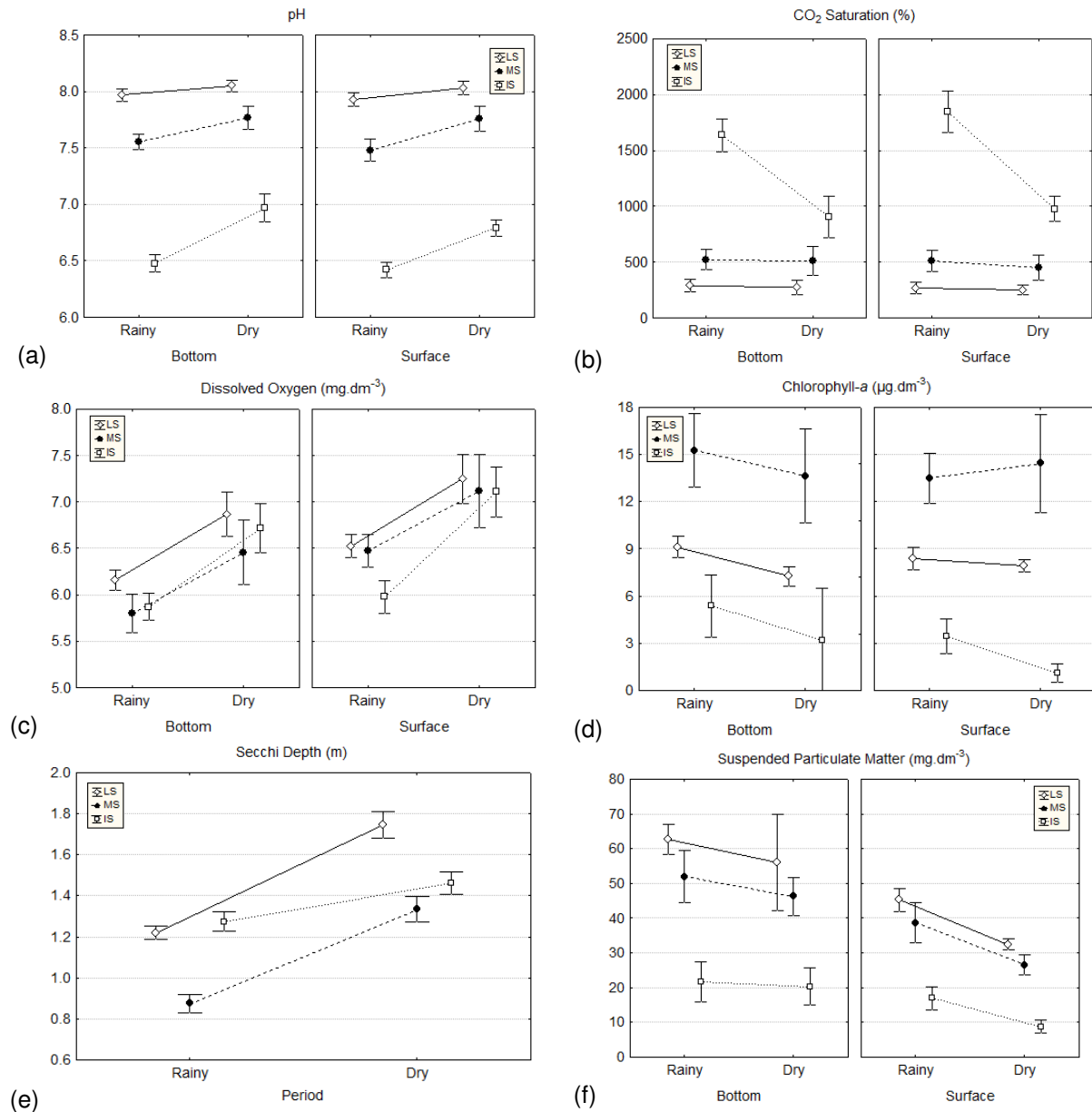


Figure 5: (a) pH, (b) CO₂ saturation, (c) dissolved oxygen, (d) chlorophyll concentration, (e) Secchi depths and (f) suspended particulate matter – SPM during the rainy and dry seasons for the three compartments (LS, MS and IS) and water layers (bottom and surface) of Guaratuba Bay (average and standard deviation).

Chlorophyll-a concentrations (Fig. 5d), considered as phytoplankton biomass indicator, were higher in the bottom layers and in the middle section of the estuary, with the maximal average concentration of 15 µg·dm⁻³ in this area. Lower phytoplanktonic biomass was observed in the lower and inner sections, ranging between 7 and 9 µg·dm⁻³ and 1 and 5

$\mu\text{g}\cdot\text{dm}^{-3}$, respectively. In general, higher phytoplanktonic biomass was observed during the rainy warmer season, except for the surface layers of the middle section where higher chlorophyll-*a* concentrations were observed in the dry period. It is important to emphasize that the lack of appropriate chlorophyll data for the dry season may lead to interpretation misunderstandings.

Along with the higher phytoplanktonic biomass, the middle sections presented less water transparency than the other sections (Fig. 5e), ranging from 1.75 m in LS during the dry season to 0.88 m during the rainy season. The seasonal pattern of increasing water transparency developing with decreasing suspended particulate matter was not observed at the spatial scale because higher Secchi depths detected in the lower section occurred also with the highest suspended particulate matter concentrations (Fig. 5f). This unexpected behavior of higher suspended matter occurring together with high water transparency can be explained by the predominance of suspended coarse particles or simply by analytical errors.

Astronomical Tides

The *t*-test for independent samples was applied and the results for the significant ($p < 0.05$) differences between spring and neap tides are presented in Table 4. It is important to mention that precipitation can influence the interpretation of the effects of the astronomical tides on the fluctuation of the water properties. Even though no significant difference was observed between the accumulated rainfall before the tidal phases, higher precipitation was found before spring tides (55.9 mm) than the levels recorded before neap tides (31.4 mm).

Table 4: Averages and *p*-values for *t*-test between spring and neap tides for the compartments (inner, middle and lower sections) and seasonal periods (rainy and dry).

Variables	Spring Tide	Neap Tide	<i>p</i>
Secchi	1.23	1.42	<0.001
NO ₂ ⁻	0.11	0.14	0.009
NO ₃ ⁻	2.4	3.2	0.04
NH ₄ ⁺	1.19	1.58	0.02
DIN	3.7	4.9	0.01
DIP	0.32	0.26	0.002
Si(OH) ₄	36.5	44.6	0.008
N/P	13.6	19.8	0.003
Chl- <i>a</i>	10.1	7.7	0.02
SPM	34.2	45.1	0.009

Nitrogen and phosphorus concentrations are affected by the tidal phase, as well as the water transparency, the particulate matter and chlorophyll concentrations, with an average difference of around 22% for these parameters between spring and neap tides. The

magnitude of increasing nitrogen content (25%) was similar to the decrease of chlorophyll concentrations (24%) during neap tides. This might indicate that DIN concentrations are regulated by the phytoplanktonic growth. An unexpected pattern was found by the increase of water transparency (1.42 m) and particulate suspended matter ($45 \text{ mg}\cdot\text{dm}^{-3}$) during neap tides, which can be a result of both the predominance of coarse particles or analytical errors. Still, the distribution of DIN and silicate concentration along the Guaratuba Bay indicated that freshwater input is the main source of these compounds, whereas higher DIP concentrations in the lower sections of the bay during the dry season can be related to the input from the ocean. It seems that the system is more dominated by the tidal intrusion during neap tides, while the freshwater plume seems to spread along the bay during spring tides also because of higher accumulated precipitation. Although the observed differences in the salinity were not significant, a slightly lower salinity was observed during spring tides occurring together with the higher precipitation rates.

Trophic Status Thresholds

In order to present a trophic state evaluation of the estuarine waters of Guaratuba Bay, six variables were compared to eutrophication thresholds (Table 5). The CO_2 saturation levels under 100% are considered indicators of predominant autotrophy, while over saturation happens due to the predominance of heterotrophy (Carmouze, 1994). Guaratuba Bay presented a mainly heterotrophic metabolism with very high saturation maxima especially in the inner section of the estuary. Bricker et al. (2003) presents thresholds for the trophic status regarding chlorophyll-*a*, dissolved oxygen and nutrients concentrations, and for water transparency. The methodology considers the maximum values in a precautionary approach, but the mean values are also presented. The mean trophic status in Guaratuba Bay (considering the average values) can be considered intermediate, because of the majority of water turbidity and chlorophyll concentrations fall in the category medium, but low in relation to mean lower nutrients concentrations and no indication for biological stress from oxygen levels under $5 \text{ mg}\cdot\text{dm}^{-3}$. On the other hand, when the maxima are considered, a 'worse' trophic status is indicated. Minimal water transparency indicating the occurrence of 'dark' waters is frequent in Guaratuba Bay, as well as nutrients concentrations around the 'medium' class and the occurrence of biological stress with lower dissolved oxygen levels. Higher chlorophyll concentrations are also found, reaching high levels of around $30 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$.

The predominance of heterotrophy in the estuary may cause the occurrence of low oxygen patches, causing biological stress in extreme situations. Moreover, the pressure of increasing nutrient concentrations can also be related to extreme situations that might not happen simultaneously with increasing chlorophyll-*a*. The increment of primary production,

indicated by the increase of phytoplanktonic biomass occurring during the rainy period, was followed by a decrease in nutrients concentrations, which were however higher during the dry season. Therefore, the susceptibility to eutrophication of Guaratuba Bay, indicated by the variables presented above, can be considered from low to medium because the occurrence of high concentrations of nutrients and low levels of dissolved oxygen take place in the dry period, while higher chlorophyll-a concentrations are observed during the rainy season.

Besides high variation of the measured variables demonstrates that water quality in Guaratuba Bay shows substantial oscillations in short space and time scales. Considering the CONAMA 357/05 resolution (environmental resolution for classifying water bodies related to human use), the values of the variables pH, nitrate, nitrite and ammonium fall within the thresholds for the brackish waters Class 1. This class guarantees the use of water for primary contact recreation (bathing, swimming), protection of water communities, aquaculture and fishery, but demands the measurements of other parameters, such as heavy metals and organic compounds. In conclusion, based on the parameters presented in this study, the water quality in Guaratuba Bay allows the utilization of the estuary for activities such as aquaculture and fisheries, but more information regarding other pollutants is still needed.

Table 5: Mean and maximum values for six variables describing water quality in the three compartments (lower, middle and inner sections) of Guaratuba Bay during rainy and dry seasons compared with trophic status thresholds (after Bricker et al., 2003 and Carmouze, 1994).

		Rainy Season			Dry Season			Thresholds
		LS	MS	IS	LS	MS	IS	
<i>CO₂ Saturation</i> ^{(a)**}	MEAN	269	512	1845	251	452	977	Heterotrophy > 100
	MAX	1790	1502	3614	899	1273	2202	
<i>Turbidity</i> ^{(b)*}	MEAN	1.2 Medium	0.9 High	1.3 Medium	1.7 Medium	1.3 Medium	1.5 Medium	Dark Waters High < 1
	MIN	0.6	0.2	0.8	0.5	0.3	0.3	1 ≤ Medium ≤ 3 Low > 3
<i>Chlorophyll-a</i> ^{(c)**}	MEAN	8.4 Medium	13.5 Medium	3.5 Low	7.9 Medium	14.4 Medium	1.1 Low	Hypereutrophic > 60 60 ≥ High > 20
	MAX	18.2 Medium	29.5 High	16.3 Medium	8.7 Medium	19.0 Medium	2.0 Low	20 ≥ Medium > 5 Low ≤ 5
<i>DIN</i> ^{(d)*}	MEAN	0.04 Low	0.05 Low	0.10 Medium	0.04 Low	0.05 Low	0.14 Medium	High ≥ 1 1 > Medium ≥ 0.1
	MAX	0.16	0.15	0.15	0.16	0.16	0.20	Low < 0.1
<i>DIP</i> ^{(d)*}	MEAN	0.007 Low	0.008 Low	0.010 Medium	0.011 Medium	0.007 Low	0.008 Low	High ≥ 0.1 0.1 > Medium ≥ 0.01
	MAX	0.013	0.022	0.019	0.024	0.018	0.020	Low < 0.01
<i>Dissolved Oxygen</i> ^{(e)*}	MEAN	6.16	5.80	5.87	6.87	6.46	6.71	Anoxia = 0
	MIN	4.30	4.15	4.98	3.70	3.91	3.82	0 < Hypoxia ≤ 2 2 < Biological Stress ≤ 5

^(a) CO₂ saturation in %; ^(b) Secchi Depths in m; ^(c) Surface concentrations in µg·dm⁻³; ^(d) Surface concentrations in mg·dm⁻³; ^(e) Bottom concentrations in mg·dm⁻³.

* After Bricker et al., 2003; ** After Carmouze, 1994.

Discussion

Based on the physical-chemical information, a summary of the main characteristics of the three compartments of Guaratuba Bay can be presented:

1. The inner section is characterized by river influence, presenting shallower depths and lower salinity, pH, chlorophyll and dissolved oxygen concentrations, and elevated CO_2 saturation; Phytoplanktonic growth may be limited by the salinity range and lower DIP concentrations.
2. The middle section is characterized by a mixing zone with higher turbidity and chlorophyll-*a* concentrations, medium concentrations of DIN and dissolved oxygen; Higher primary production can be related to improved conditions of nutrients supply and salinity ranges.
3. The lower section presents mainly a marine influence with greater depths and lower dissolved CO_2 and DIN concentrations. Lower chlorophyll concentrations are observed due to higher hydrodynamics and, possibly, limitation by DIN.

The metabolism of Guaratuba Bay seems to be mostly heterotrophic as a result of presenting CO_2 over saturation, *i.e.* respiration processes outweigh production processes. Excess of CO_2 in riverine freshwater results from interaction between land sources (soil, rocks, riverine processes and gas exchanges), mainly where the runoff of surface soils takes place (Abril et al., 2000). Higher CO_2 saturation levels in the inner section may be a consequence of higher oxygen consumption and, respectively, higher CO_2 production due to anaerobic processes. Moreover, it should be considered that shallow water areas can be enriched with organic matter from land runoff and that nitrification transforms bicarbonate in CO_2 in the same order as oxygen consumption. For that reason, CO_2 saturation in Guaratuba Bay probably results from the interaction between freshwater input, pH, salinity, primary production and mineralization processes, but the quantitative role of the interaction processes are unknown.

Spatial dynamics of water quality seems to be controlled by inorganic and/or organic material input associated with freshwater discharge and/or tidal phase variations (ebb and flood tides), rather than to astronomical tides (spring and neap cycles). Furthermore, lateral input of material from marginal areas seems to be very important for the system dynamics, mostly by tidal intrusion pathways (north margin) and ebb tide flux (south margin). The lowest Secchi depth observed in the middle section can be attributed to this lateral input from mangrove areas especially from the north margin of the system, which is more densely occupied by mangrove swamps than the southern margin. Water circulation system of Guaratuba Bay may be responsible for this geomorphological configuration because tidal intrusion occurs mainly through the northern margin, while ebb tidal currents (together with

river flushing) are stronger in the south margins (Marone et al., 2004). The pattern is corroborated by bottom sediments distribution of Guaratuba estuarine system. The settling rate of fine sediments around the north margin has the same order of magnitude of coarse sedimentation in the south margin (Zem et al., 2005). Lateral input may be an important source of material to the system, influencing light penetration in the water column, and also other physico-chemical variables.

Vertical stratification in Guaratuba Bay is more evident during neap tides and lower river discharge situations, when the baroclinic component of pressure gradient forcing is intensified (Marone et al., 2004). However, during spring and/or higher river discharge, higher turbulent diffusion results in better mixing in the water column. No clear pattern could be identified which enabled a distinction between spring and neap tides and their influence on the measured parameters. In order to perform such a distinction, a fixed sampling point should be applied with high frequency monitoring.

The compartment division in Guaratuba Bay could be better described during the rainy season. Horizontal stratification due to higher freshwater discharge resulted in the river dominance on IS. The other sections seem to be more related to tidal forces and marine input “diluting” riverine inputs. MS differs from LS because of higher influence of drainage material from the margin areas, which can be nutrient enriched and allow better conditions for phytoplanktonic growth. During dry season, horizontal stratification is not so pronounced, which means that tidal forces may be dominant in promoting water mixing. Therefore, continental drainage and the freshwater input may be controlling water quality dynamics during rainy season, while tidal fluctuations may be the hydrodynamic process controlling the studied parameters variation during the dry season.

Considering that the system is used for several small oyster cultivation farms, which are filter feeders (phytoplanktonic feeders), it is recommended that future studies should estimate primary production rates that, coupled with the results presented in this study, would provide information on the carrying capacity of this estuarine system. Moreover, the aquaculture can act in the top-down control of eutrophication as well as supply of organic matter (fecal pellets) that can enhance oxygen consumption due to decomposition. Still, this material can represent an extra source of nutrients due to remineralization.

It is important to highlight that a study about nutrient enrichment processes in coastal ecosystems can be difficult because of diffuse sources of nutrients, such as atmospheric deposition. The sources of the material that compose the system can be far away from the estuary, even on the upper limit of the catchment area of the ecosystem. Thus, assessing the trophic status of the system can be considered an important tool, using information such as water renewal time and quantitative criteria based on different symptoms of eutrophication (Bricker et al., 1999; 2003).

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“Evaluation of the trophic status in estuarine systems of Southern Brazil”

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Article in preparation.

Evaluation of the trophic status in estuarine systems of Southern Brazil

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Abstract

The estuarine systems of Paraná State are inserted in one of the biggest areas of protected rainforest in Brazil, including also large portions of mangrove forests. These estuaries have been under increasing pressure due to the economical development of the area. The intense harbour activities and urban expansion is related to pollution issues and can cause eutrophication problems that hamper the development of the tourism, small scale fisheries and aquaculture in the area. This study focuses on defining the trophic status of Paranaguá and Guaratuba bays which are the main estuaries in Paraná state, applying the ASSETS and the TRIX methodologies in order to supply a comprehensive classification of the systems at temporal and spatial scales. Seasonality, as a succession of rainy and dry seasons, was considered with both methodologies, as well as the water layers only with the TRIX methodology. Whereas Guaratuba Bay presented permanent 'Poor' conditions as stated by the ASSETS methodology, Paranaguá Bay exhibited a shift from 'Moderate' conditions during the rainy season to 'Good' conditions during the dry season. Moreover, the TRIX index indicated substantial differences of the trophic status within the estuarine borders. The lower salinities and freshwater zones, as well as the seawater areas presented lower trophic status, whereas higher status addressed to the middle mixing areas were indicated by the higher phytoplanktonic biomass and oxygen saturation deviation from 100%. The same conditions were observed in the bottom layers that presented higher TRIX indices also due to higher nutrient concentrations. Still, the expression of seasonality differed between the systems. While Paranaguá Bay exhibited lower trophic status during the dry period, the opposite was observed in Guaratuba Bay. Overall, the use of these methodologies are of great importance as a first attempt to classify the trophic status in subtropical estuaries of Brazil, but limitations occur due to the lack of appropriate data sets. In order to allow the expansion of the methodologies to other Brazilian areas and also to

increase the confidence of the analysis, the construction of a comprehensive national data set is strongly recommended, in addition to the review of the reference values.

Key-Words: Eutrophication; water quality; Paranaguá; Guaratuba; ASSETS; TRIX.

Introduction

Estuaries are highly productive systems that account for around 4% of primary production in the world's oceans (Berlinski *et al.*, 2006). They also have key functions as biological filters for material retention and for reproduction, nursery and development of diverse species (Chaves & Bouchereau, 2000; Berlinski *et al.*, 2006). Estuarine and coastal waters are among the most fertilized environments in the world (Nixon *et al.*, 1986; NOAA, 1996), and it is well known that eutrophication is a common problem around the globe (NOAA, 1996; Cloern, 2001; Bricker *et al.*, 1999; Bricker *et al.*, 2003; OSPAR, 2001).

Eutrophication, defined as the elevated accumulation and production of organic matter caused by high nutrient inputs (Nixon, 1982; Bricker *et al.*, 1999; 2003; OSPAR, 2001; Cloern, 2001), can be natural or anthropogenic, enhanced by coastal development (White *et al.*, 2004). The expression of eutrophication can occur in diverse ways, such as decreasing oxygen levels or harmful algae blooms, depending on the ecosystem conditions in relation to hydrodynamics and the configuration of the food web, for instance. In estuaries, the combination of nutrient enriched freshwater and waste water input with a low water renewal time are important factors for the expression of eutrophication symptoms.

Economical activities, such as fisheries and recreation, and the presence of diverse natural protection areas in estuaries of Southeastern and Southern Brazil demand good water quality in the bays. Small scale fishery is very important for the traditional communities, for it is commonly the main source of income for most of them (Diegues, 1998). Considering the decline of fish stocks and seasonal prohibition of fishing during reproduction periods, local populations are motivated to develop shellfish cultures. This activity has been developed in small culture areas, in some cases even large scale productions, but they demand good environmental water quality for the survival of the organisms and their health conditions for consumption. Moreover, the presence of harbors, urbanized and industrial centers generally results in degradation of natural resources in the estuarine systems, requiring the assessment of the environmental quality for the coastal waters.

Several techniques to assess the eutrophication process have been developed to provide appropriate and comprehensive methodologies to be applied in global and regional scales. Among those, the ASSETS (Bricker *et al.*, 1999, 2003) and TRIX methods (Vollenweider *et al.*, 1998) are considered reliable tools for evaluating the trophic conditions in marine areas (Loureiro *et al.*, 2006; Pettine *et al.*, 2007). Defining the trophic status as well

as the causes and indicators of eutrophication is a common term into these methodologies, which seek a simplified but comprehensive classification for a coastal system.

The approach called Assessment of Trophic Status (ASSETS) was developed by a group of specialists following the NOAA's Estuarine Eutrophication Survey (NOAA, 1996; OSPAR, 2001; Bricker et al., 1999; Bricker et al., 2003). In accordance with the method, the eutrophication process is identified with primary and secondary symptoms, such as elevated chlorophyll-*a* and lower dissolved oxygen concentrations, respectively. Primary symptoms have a direct relation to increased nutrient concentrations, while secondary symptoms can be related to other factors that can be both natural and anthropogenic. Other influencing factors, such as the relation between water renewal and freshwater input, are included to determine the susceptibility to eutrophication. Variation in nutrient input due to management actions or increase of loads are also taken into account to describe a future outlook. This methodology has already been applied for diverse USA, Europe and United Kingdom and Asiatic estuaries (NOAA, 1996, Bricker et al., 1999; Bricker et al., 2003; Scavia & Bricker, 2006; Ferreira et al, 2003; Bettencourt et al., 2004; Ferreira et al., 2007).

The trophic index called TRIX and described by Vollenweider et al. (1998), is a synthetic index that is adopted by the Italian Government as a threshold for the classification of the marine waters (Caruso et al., 2010). Chlorophyll, total nitrogen and phosphorus concentrations together with the absolute deviation of oxygen saturation from 100% are used to indicate the primary production levels and intensity, and nutrient enrichment. The technique is also possible using the inorganic dissolved nitrogen and phosphorus. The index is calculated as a linear combination of the logarithms of the four variables (Pettine et al., 2007) leading to a decimal classification into 5 classes of trophic status, from excellent (ultra-oligotrophic) to poor (eutrophic). It was developed for the Adriatic and Tyrrhenian seas, but several other authors presented the efficiency of the methodology to other areas (Damar, 2003; Pettine, et al., 2007; Caruso et al., 2010; Nasrollahzadeh et al., 2008).

The combination of the two methodologies was applied for the coastal systems of southeastern Mexico (Herrera-Silva and Morales-Ojeda, 2009), providing important information regarding the evaluation of the health status of the ecosystems. This is the first attempt to apply the ASSETS and TRIX methodologies in Brazilian estuaries. The methodologies offer a synthetic description of the eutrophication process, and therefore allow the comparison between the systems. The methods are applied to two estuarine systems in Southern Brazil (Guaratuba and Paranaguá bays) to describe the regional features of the eutrophication and to test the representativeness of the methodologies concerning the seasonal periods, in order to provide information for the coastal management in the region.

Material and Methods

Study Site

The study sites are located in the state of Paraná along Southern Brazil (Fig. 1). Paranaguá Bay is located in West-East Axis of the Paranaguá Estuarine System in the central-north region of Paraná coast, while Guaratuba Bay is placed around 40 km southwards. Main features of the systems are presented in Table 1. Paranaguá Bay covers around 55% (330 km²) of the Paranaguá Estuarine Complex surface area (600 km²), while Guaratuba Bay is relatively small with an area of around 50 km². Besides the larger area, Paranaguá bay is deeper (5.4 m average depth) and has more than 10 times the water volume of Guaratuba Bay (average depth 3 m) – around 1800·10⁶ and 140·10⁶ km³, respectively.

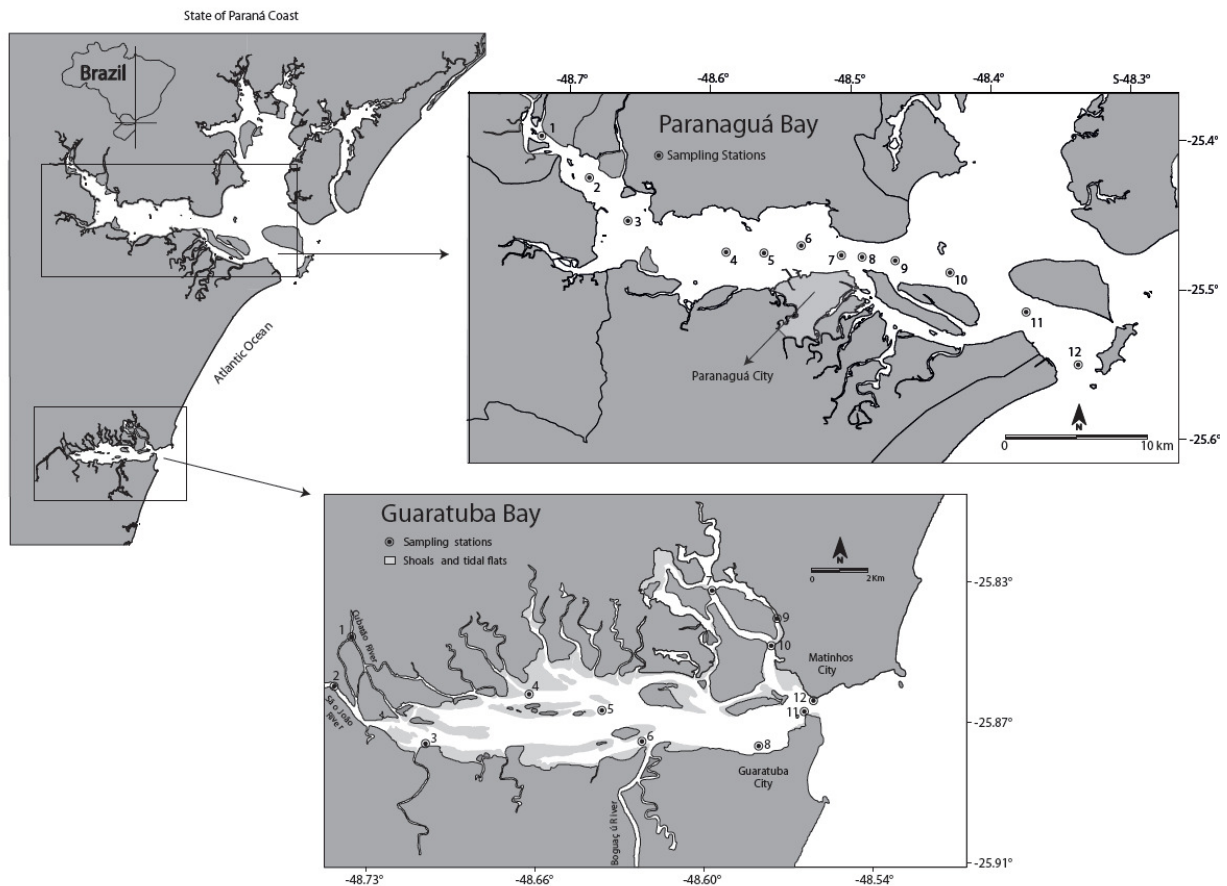


Figure 1: The State of Paraná coast showing the detailed maps of Paranaguá and Guaratuba bays with the applied sampling strategy.

The region is under a semi-diurnal tidal cycle, ranging from an average of 1.5 m in Guaratuba bay to 2.2 m in Paranaguá Bay, with tidal prisms of 75·10⁶ and 580·10⁶. Both systems are partially mixed estuaries with lateral heterogeneities (Marone et al., 2004; 2005).

The region is in a subtropical zone, with warm wet summers and cold dry winters with average air temperature around 23°C. Mean annual rainfall in the region ranges between 2000 and 3000, divided by a rainy season in spring and summer (from October to March) and a dry season in autumn and winter (from April to September). The hydrodynamics and the behavior of water properties in the systems are strongly subjected to the successions of rainy and dry seasons (Lana et al., 2000, Marone et al., 2005). This feature is observed by the discharge values, that ranged in Paranaguá bay from daily averages of 111 m³·s⁻¹ during the rainy season to 51.4 m³·s⁻¹ during the dry season, and in Guaratuba bay from 55.7 m³·s⁻¹ to 34.9 m³·s⁻¹, respectively.

Table 1: Study sites and main estuarine features. Sources of information are presented as numbers in brackets and described below.

<i>Features</i>		Paranaguá	Guaratuba
<i>Location</i>	<i>Lat S</i>	25°30'	25°51'
	<i>Long W</i>	48°30'	48°38'
<i>Surface (km²)</i>		330 ⁽¹⁾	50 ⁽⁴⁾
<i>Volume (10⁶m³)</i>		1804 ⁽¹⁾	140
<i>Average Depth (m)</i>		5.4 ⁽¹⁾	3 ⁽⁴⁾
<i>Maximum Depth (m)</i>		33 ⁽¹⁾	27 ⁽⁴⁾
<i>Tidal Range (m)</i>		2.2 ⁽¹⁾	1.5 ⁽⁵⁾
<i>Tidal Prism (10⁶·m³)</i>		580 ⁽¹⁾	75 ⁽⁶⁾
<i>Average Freshwater discharge (m³·s⁻¹)</i> ⁽²⁾	<i>Rainy Season</i>	111.0 ⁽²⁾	55.7 ⁽⁷⁾
	<i>Dry Season</i>	51.4 ⁽²⁾	34.9 ⁽⁷⁾
<i>Population (in the margins)</i> ⁽³⁾		176,767 ⁽³⁾	27,242 ⁽³⁾

Sources: ⁽¹⁾ Marone et al., 2005 (a); ⁽²⁾ Mizerkowski, et al. In prep.(see Chapter II); ⁽³⁾ IBGE, 2000; ⁽⁴⁾Noernberg et al., 2004; ⁽⁵⁾Angulo and Araújo, 1996; ⁽⁶⁾Marone et al., 2005 (b); ⁽⁷⁾ DHID (values recorded during the sampling periods).

The region is inserted into the largest area of preserved rain forest in Brazil, which led to the establishment of several natural protection and conservation units. Another common feature is the coverage of the estuarine margins by large mangrove forests, which are of great importance as nursing and reproduction areas (Chaves & Bouchereau, 2000; Berlinski et al., 2006), besides providing several resources for the traditional communities that live in the areas (Diegues, 1998).The traditional fisheries communities use the inner estuarine waters for subsistence and commercial capture, and also for small scale aquaculture. Large scale fishery is restrained to the adjacent coastal areas.

Paranaguá bay shelters one of the most important harbors in Brazil that takes its name. Moreover, another small harbor is located in the inner section of Paranaguá Bay (Ponta do Felix harbour). Tourism is also an important activity in all systems and historical

centers are preserved in Paranaguá bay (cities of Paranaguá, Morretes and Antonina). Besides the historical centers, the summer period plays an important role for tourism, during which the population in coastal areas can increase up to 400%, especially between the end of December and February in Guaratuba Bay. Paranaguá, that has its activities mainly related to the harbor, is the largest city of the coast of Paraná with around 140,000 inhabitants.

Data acquisition

In summary, the ASSETS and TRIX methodologies are based on the variables chlorophyll-*a*, dissolved oxygen (concentration or saturation), DIN and DIP concentrations, macroalgae coverage, occurrence of harmful algae blooms (HAB) and loss of submerged aquatic vegetation, as described in the following sections.

The data used are described in Mizerkowski et al., in prep (see Chapter II and III). Twelve stations were sampled in each estuary in different sampling strategies (see Fig. 1) and frequencies (Tab. 2). Water was collected using a Niskin bottle or through a pumping device. Nutrient concentrations were determined through the method described by Grasshoff et al. (1999). Chlorophyll-*a* was analyzed according to Strickland & Parsons (1972) and dissolved oxygen following the Winkler method (Grasshoff et al., 1999) for the samples from Guaratuba Bay. In Paranaguá Bay, a portable device (Pocket FerryBox, Schroeder et al., 2008) provided *in situ* measurements using an *in vivo* fluorescence sensor (Cyclops- Turner Designs) as a proxy for chlorophyll-*a* and a luminescence quenching sensor for oxygen saturation (Optode – AAnderaa). Basic parameters, such as salinity, temperature and pH were determined *in situ*, through CTD or refratometers and pHmeters.

Table 2: Number of samples (n) and frequency of sampling among the five estuarine systems.

Estuary	<i>n</i>	<i>Frequency of sampling</i>
Paranaguá	72	September and December 2007; and February, June and September 2008; January 2009 ⁽¹⁾ .
Guaratuba	91	Fortnightly on March, October and December 2001; January, March, May and August 2002 ⁽²⁾ .

Data sources: ⁽¹⁾ Mizerkowski *in prep.*; ⁽²⁾ Mizerkowski, 2005.

The ASSETS method requires information of the spatial coverage, months and frequency of occurrence for the high chlorophyll concentrations (above 5 µg·dm⁻³) and low oxygen levels (under 5 mg·dm⁻³), which were integrated in the data set. No monitoring actions are directed to assess harmful algae blooms or macroalgae coverage in the systems, thus the presence of these conditions was recovered from published information and local

observations. Not all required information was available, especially concerning loss of submerged aquatic vegetation; although the data was missing for both systems, IT may not be critical in terms of comparison between estuaries. Chlorophyll-*a* concentrations measurements in Guaratuba Bay are available only for one month of the dry period (April 2002) due to problems in analysis. Thresholds for the parameters are presented in Table 3.

Table 3: Parameters and thresholds for the water quality (Adapted from Bricker et al., 2003).

Parameters	Thresholds	Existing Conditions
<i>Chlorophyll-a</i> ($\mu\text{g}\cdot\text{dm}^{-3}$)	hypereutrophic > 60 60 \geq high > 20 20 \geq medium > 5 low \leq 5	Spatial coverage ^(a) , months and frequency of occurrence ^(b)
<i>Dissolved Oxygen</i> ($\text{mg}\cdot\text{dm}^{-3}$)	Anoxia 0 $\text{mg}\cdot\text{dm}^{-3}$ 0 < Hypoxia < 2 $\text{mg}\cdot\text{dm}^{-3}$ 2 < Biological Stress < 5 $\text{mg}\cdot\text{dm}^{-3}$	Minimum average monthly bottom concentrations, spatial coverage ^(a) , frequency of occurrence ^(b)
<i>DIN</i> ($\text{mg}\cdot\text{dm}^{-3}$)	high \geq 1 1 > medium \geq 0.1 low < 0.1	Concentrations, direction of change ^(c)
<i>DIP</i> ($\text{mg}\cdot\text{dm}^{-3}$)	high \geq 0.1 0.1 > medium \geq 0.01 low < 0.01	Concentrations, direction of change ^(c)

^(a) Spatial coverage (% of the salinity zone): high (50-100%), medium (25-50%) low (10-25%), very low (0-10%).
^(b) Frequency of occurrence: episodic (conditions occur randomly), periodic (conditions occur annually or predictably), persistent (conditions occur continually throughout the year).
^(c) Direction of change: increase, decrease, no trend.

Methodology – Assessment of Trophic Status (ASSETS)

The methodology presented by Bricker et al. (1999, 2003) is based on water quality parameters regarding estuarine susceptibility, nitrogen input, primary and secondary symptoms and future forecast in nutrient inputs. The software called ASSETS was released to ease the utilization of the model and can be found under www.eutro.org. Three indexes are considered in ASSETS: Influencing Factors (IF), Eutrophic Condition (EC) and Future Outlook (FO).

Salinity Zones

The definition of salinity zones inside the estuaries followed the proposed by the NOAA National Estuarine Inventory (NOAA, 1999). Three sectors are defined as the freshwater (PSU>0.5), mixing (0.5<PSU<25) and seawater (PSU<25) tidal zones. The salinity was defined as the monthly average along the water column for each sampling station representing a year cycle. The coverage of each zone was defined by interpolating the grouped stations, what supplied a percentage of the system represented by each of

them. Even if not all systems present all the three salinity zones, this classification still allows a better comparison among these highly dynamics systems (Ferreira et al., 2006).

Influencing Factors

IF is calculated through aggregation of the estuarine susceptibility to the nutrient loads. The susceptibility concerns physical and hydrological data to define dilution and flushing capacities. Higher dilution and exportation capacities lead to lower retention time for nutrients, and the opposite situation can lead to enhanced eutrophication. The final classification of susceptibility is a combination of the Dilution and Flushing Potentials (Tab. 4).

Table 4: Determination of Dilution and Flushing potentials and the classification for Susceptibility (adapted from Bricker et al., 1999).

IF vertical stratification:	THEN dilution volume ^(a)	IF dilution value	Dilution Potential	
Homogeneous - All year - Along the estuary	1/VOL _{estuary}	10 ⁻⁶ 10 ⁻⁵	High	
Minor stratification - navigation channels - upper estuary	1/VOL _{estuary}	10 ⁻⁴	Moderate	
Stratified - most of the year - most of the estuary	1/VOL _{freshwater fraction}	10 ⁻³ 10 ⁻²	Low	
Tide Range (m)	Freshwater Inflow ^(b) / Estuary volume ^(a)	Flushing Potential		
macro (>8)	Large, moderate (10 ⁰⁰ -10 ⁻⁰²)	High		
macro (>8)	Small (10 ⁻⁰³ , 10 ⁻⁰⁴)	Moderate		
meso (>1)	Large (10 ⁻⁰⁰ , 10 ⁻⁰¹)	High		
meso (>1)	Moderate (10 ⁻⁰²)	Moderate		
Meso (>1)	Small (10 ⁻⁰³ , 10 ⁻⁰⁴)	Low		
micro (<1)	Large (10 ⁻⁰⁰ , 10 ⁻⁰¹)	High		
micro (<1)	Moderate (10 ⁻⁰²)	Moderate		
micro (<1)	Small (10 ⁻⁰³ , 10 ⁻⁰⁴)	Low		
Dilution Potential				
		High	Moderate	Low
Flushing Potential	High	Low Susceptibility	Low Susceptibility	Moderate Susceptibility
	Moderate	Low Susceptibility	Moderate Susceptibility	High Susceptibility
	Low	Moderate Susceptibility	High Susceptibility	High Susceptibility
^(a) Volume in 10 ⁶ ·m ³ , ^(b) Freshwater Inflow in 10 ⁶ ·m ³ ·d ⁻¹				

The definition of the DIN variation as the nutrient input leading to eutrophication, is based on a simple budget model (“Vollenweider”, Bricker et al., 2003) that defines the variation (in time) of the nitrogen mass in the estuary as a result from difference between the sum of nutrient loading from rivers and anthropogenic sources, and the sum of the nutrient discharge related to advection and exchange with the ocean. The nutrient input, regarded as Human Influence (HI), is defined by the ration between the DIN from the anthropogenic sources (m_h) and the sum of the total DIN inputs, the background concentrations (m_b) plus the anthropogenic DIN leading to the equation:

$$\text{Nutrient Input} = m_h \cdot [m_h + m_b]^{-1}$$

Ferreira et al. (2007) presented an update of the method presented by Bricker et al. (2003) for the expression of m_b and m_h . Considering the hypothetic situation that there is no human input, the background levels (m_b) can be described as:

$$m_b = (\varepsilon \cdot T \cdot m_{sea}) \cdot (\varepsilon \cdot T_p + Q \cdot T)^{-1}$$

where ε is the fraction of water leaving the bay at ebb tides which does not return in the flood (proxy for re-entrainment), T_p is the tidal prism (m^3), m_{sea} is the DIN concentration offshore ($kg \cdot m^{-3}$), Q is the freshwater input ($m^3 \cdot s^{-1}$) and T is the tidal period (s). In addition, the anthropogenic influence (m_h) assumes there is no oceanic input of DIN, only from the river loading and the effluent discharge (M_{ef} in $kg \cdot s^{-1}$) as follows:

$$m_h = (T \cdot [Q \cdot m_{in} + M_{ef}]) \cdot (Q \cdot T + \varepsilon \cdot T_p)^{-1}$$

The nutrient input index is a percentage of the DIN mass that originated from anthropogenic inputs. The results are framed into 5 classes (adapted from Bricker et al., 2003) described as Low (0-0.3), Moderate (0.4-0.6) and High (0.7-1).

The Final classification of the Influencing Factors combines both indices (susceptibility and nutrient input), as shown by Table 5.

Table 5: Determination of the Influencing Factors (IF) through the combination of the estuarine susceptibility and human influence (nutrient input) indices (adapted from Bricker et al., 1999).

		Influencing Factors (IF)		
		Nutrient Input		
Susceptibility		Low	Moderate	High
	High	Moderate	Moderate High	High
	Moderate	Moderate Low	Moderate	Moderate High
	Low	Low	Low	Moderate Low

Eutrophic Conditions

EC is calculated by the combination of the primary and secondary symptoms. The primary symptoms, related directly to the increase of nutrient concentrations, are chlorophyll-*a* concentrations and macro algae. Extreme situations can be the result of several factors influencing the magnitude of the eutrophication processes. Thus, the existing status is described with the maximum values or conditions exhibited by these parameters on a typical annual cycle. The secondary symptoms are also related to the increase of nutrient input, but other factors can influence the expression of the variables. In this phase, dissolved oxygen depletion, toxic or harmful algae blooms (HAB) and loss of submerged aquatic vegetation, (SAV) are considered. Spatial coverage and frequency of occurrence are also taken into account.

A critical limit is determined to each of these variables through the combination of the concentration, frequency of occurrence and spatial coverage according to the thresholds (see Tab. 3) and scores presented in Table 6 and 7.

The resulted value from the logical decision process for the parameters into a salinity zone is aggregated for the estuary level resulting in a final expression value for the symptom in the system, as follows:

$$\sum_{i=1}^n \left(\frac{A_z}{A_t} \right) \cdot \left(\begin{array}{c} \text{Expression} \\ \text{Value} \end{array} \right) = \left(\begin{array}{c} \text{symptom level of expression} \\ \text{value for the estuary} \end{array} \right)$$

where A_z is the surface area of a single zone, A_t the total surface area of estuary and n is the total number of zones in the estuary.

This value of expression is averaged among the primary symptoms, but the highest one is selected among the secondary factors. The higher critical limit is considered instead of

the average of the secondary symptoms in a precautionary approach. Therefore, the estuary that exhibits the critical impacts from only one of the secondary symptoms can be as damaged as the one that presents all these symptoms. Each factor (primary and secondary) is classified into the levels of expression low ($0 \leq \text{value} \leq 0.3$), moderate ($0.3 < \text{value} \leq 0.6$) and high ($> 0.6 \text{ value} \leq 1$), leading to a final classification of the EC (Tab. 8).

Table 6: Determination of the expression level for the primary symptoms (chlorophyll-a and macroalgae). (adapted from Bricker et al., 1999).

<i>IF</i>	<i>AND</i>	<i>AND</i>	<i>THEN</i>	
<u>Chlorophyll-a concentrations</u>	<u>Spatial Coverage</u>	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
Hipereutrophic or High	High / Moderate	Persistent	High	1
	Low / Very Low	Persistent	Moderate	0.5
	High	Periodic	High	1
	Moderate	Periodic	High	1
	Low	Periodic	Moderate	0.5
	Very Low	Periodic	Moderate	0.5
	High	Episodic	High	1
	Moderate	Episodic	Moderate	0.5
	Low / Very Low	Episodic	Low	0.25
	Any coverage	Unknown	Moderate	0.5
Unknown	Any frequency	Moderate	0.5	
Medium	High / Moderate	Persistent	High	1
	Low	Persistent	Moderate	0.5
	Very Low	Persistent	Low	0.25
	High	Periodic	High	1
	Moderate	Periodic	Moderate	0.5
	Low / Very Low	Periodic	Low	0.25
	High	Episodic	Moderate	0.5
	Moderate / Low / Very Low	Episodic	Low	0.25
	Any coverage	Unknown	Moderate	0.5
	Unknown	Any frequency	Moderate	0.5
Low	Any coverage	Any frequency	Low	0.25
<u>Macroalgae Problems</u>	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>	
Observed	Periodic	High	1	
	Episodic	Moderate	0.5	
	Unknown	Moderate	0.5	

Table 7: Determination of the expression level for the secondary symptoms (dissolved oxygen and harmful algae blooms) (adapted from Bricker et al., 1999).

<i>IF</i>	<i>AND</i>	<i>AND</i>	<i>THEN</i>	
<u>Anoxia</u>	<u>Spatial Coverage</u>	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
Observed	High	Periodic	High	1
	Moderate	Periodic	High	1
	Low	Periodic	Moderate	0.5
	Very Low	Periodic	Low	0.25
	High	Episodic	Moderate	0.5
	Moderate / Low / Very Low	Episodic	Low	0.25
	Unknown	Unknown	Low	0.25
<u>Hypoxia</u>	<u>Spatial Coverage</u>	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
Observed	High	Periodic	High	1
	Moderate	Periodic	Moderate	0.5
	Low / Very Low	Periodic	Low	0.25
	High	Episodic	Moderate	0.5
	Moderate / Low / Very Low	Episodic	Low	0.25
	Unknown	Any frequency	Low	0.25
<u>Biological Stress</u>	<u>Spatial Coverage</u>	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
	High	Periodic	Moderate	0.5
	Moderate / Low / Very Low	Periodic	Low	0.25
	Any coverage	Episodic	Low	0.25
	Unknown	Any frequency	Low	0.25
<u>Nuisance Blooms</u>	<u>Duration</u> ^(*)	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
Problem	M, WM, WS, S, PR	Periodic	High	1
	DW, V, W	Periodic	Moderate	0.5
	D	Periodic	Low	0.25
	M, WM, WS, S, PR	Episodic	Moderate	0.5
	DW, V, W	Episodic	Low	0.25
	D	Episodic	Low	0.25
	Unknown	Any Frequency	Low	0.25
<u>Toxic Blooms</u>	<u>Duration</u> ^(*)	<u>Frequency</u>	<u>Expression</u>	<u>Value</u>
Problem	M, WM, WS, S, PR	Periodic	High	1
	DW, V, W	Periodic	Moderate	0.5
	D	Periodic	Low	0.25
	M, WM, WS, S, PR	Episodic	Moderate	0.5
	DW, V, W	Episodic	Low	0.25
	D	Episodic	Low	0.25
	Unknown	Any Frequency	Low	0.25

Table 8: Determination of the Eutrophic Conditions (EC) through the combination of the primary and secondary symptoms indices (adapted from Bricker et al., 1999).

Eutrophic Conditions (EC)				
		Secondary Symptoms		
		Low	Moderate	High
Primary Symptoms	High	Moderate	Moderate High	High
	Moderate	Moderate Low	Moderate	High
	Low	Low	Moderate Low	Moderate High

Future Outlook

The Future Outlook (FO) is an attempt to define the trends for the nutrient input to the estuary in the next 20 years. Population growth trends and management actions are analyzed in order to determine the direction of the changes in the system. The decision can be made simply by determining if the existing conditions are likely to improve or worsen. Otherwise, detailed information can be used, such as the role of population and agriculture (in %), as well as the increase or decrease of pressure from this factors alone combined with the trends for sewage treatment. The final classification (Tab. 9) is provided through the combination of the estuarine susceptibility with the determination of the future changes in nutrient pressures (decrease, no change and increase).

Table 9: Determination of the Future Outlook (FO) through the combination of the estuarine susceptibility and the changes in the future nutrient pressure (adapted from Bricker et al., 1999).

Future Outlook (FO)				
		Future Changes in Nutrient Pressure		
		Decrease	No Change	Increase
Susceptibility	Low	Improve High	No Change	Worsen Low
	Moderate	Improve Low	No Change	Worsen High
	High	Improve Low	No Change	Worsen High

Trophic Status

The final classification comes from the combination of the numerical classification of the three indexes in a matrix of possibilities. Therefore, the systems can be classified as bad,

poor, moderate, good and high (Tab. 10). Several combinations of the indexes were excluded from the matrix considered as improbable or impossible conditions, leading to the “invalid score” result.

Table 10: Matrix of aggregation of the indexes Pressure (Influencing Factors), State (Eutrophic Conditions) and Response (Future Outlook) and final classification for the Assessment of Trophic Status (Source: Bricker et al., 2003).

Grade	5	4	3	2	1																																																																											
Pressure (IF)	Low	Moderate	Moderate	Moderate	High																																																																											
State (EC)	Low	Moderate	Moderate	Moderate	High																																																																											
Response (FO)	Improve High	Improve Low	No Change	Worsen Low	Worsen High																																																																											
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Methodology – Trophic Index (TRIX)

The methodology named Trophic Index (TRIX) was first presented by Vollenweider et al., (1998). Using chlorophyll-*a*, nitrogen, phosphorus and the absolute deviation of dissolved oxygen from saturation (aD%O), this composite aggregates pressure (nutrients), biological response (chlorophyll-*a* as a proxy for phytoplankton biomass) and environmental disturbance in the water quality (oxygen) (Pettine et al., 2007). The first description of the index used the total nitrogen and phosphorus concentrations, but the dissolved inorganic fractions (DIN and DIP) are also considered, once the later are usually strongly correlated to the total concentrations. Vollenweider et al. (1998) suggests that the symbol TRIX (DIN, DIP) is used to distinguish between the different applications. Therefore, the TRIX(DIN, DIP) index is calculated through the following:

$$\text{TRIX} = \left(\frac{k}{n} \right) \sum_{i=1}^n \left[\frac{(\log U - \log L)}{(\log M - \log L)} \right]$$

where the upper (*U*) and lower (*L*) limits of each parameters are used as scale factors. For the definition of these limits, it is recommended to use the mean±standard deviation as boundaries to avoid that extreme values – which occur rarely – lead to large confidence intervals that invalidate the discrimination between different TRIX. For the Adriatic Sea, the basic structure of the trophic index was defined as:

$$\text{TRIX} = \frac{\log [\text{Chla} \cdot \text{aD}\% \text{O} \cdot \text{N} \cdot \text{P}] - [\sum \log L]}{1.2}$$

where a correction constant is determined as the sum of the lower limits logarithms and 1.2 is the scale factor derived from the standardization of the range to 3 log units for each of the four parameters, anchoring the lower, and fixing the number to 10 classes (sum= (3/10·4).

The classification of the estuarine waters using TRIX (Tab. 11) is made through the thresholds values proposed by Penna et al. (2004), applied by by Nasrollahzadeh et al. (2008) and adopted by the Italian Law (Caruso et al., 2010).

Table 11: Determination of the trophic status using the trophic index (TRIX) (adapted from Nasrollahzed et al., 2008).

TRIX	Conditions	Trophic Status
<2	Very poorly productive and very low trophic status	Excellent (Ultra-Oligotrophic)
2-4	Poorly productive and low trophic status	High (Oligotrophic)
4-5	Moderate productive and medium trophic status	Good (Mesotrophic)
5-6	Moderate to highly productive and high trophic status	Moderate (Mesotrophic to Eutrophic)
6-8	Highly productive and highest trophic status	Poor (Eutrophic)

Results

Assessment of Trophic Status - ASSETS

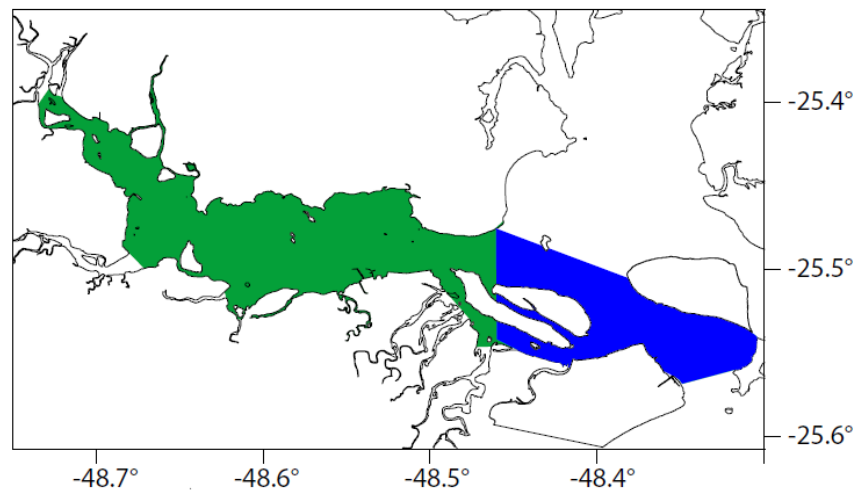
Salinity Zones

The tidal salinity zones and average salinity in the areas in Paranaguá and Guaratuba bays are shown in Figure 2. Around 80% of the surface area of Paranaguá Bay was assessed representing the mixing (mean salinity 18.7) and seawater (mean salinity 27.6) tidal zones and covering 143 and 124.7 km², respectively. The total area of Guaratuba Bay (50.2 km²)

was divided into the freshwater (4.3 km²), mixing (37.6 km²) and seawater (8.4 km²) tidal zones, that presented average salinity of 0.3, 14.1 and 25.1, respectively.

(a) Paranaguá Bay

Zones	Salinity	Area
■ Mixing	18.7	143
■ Seawater	27.6	124.7



(b) Guaratuba Bay

Zones	Salinity	Area
■ Freshwater	0.3	4.3
■ Mixing	14.1	37.6
■ Seawater	25.1	8.4

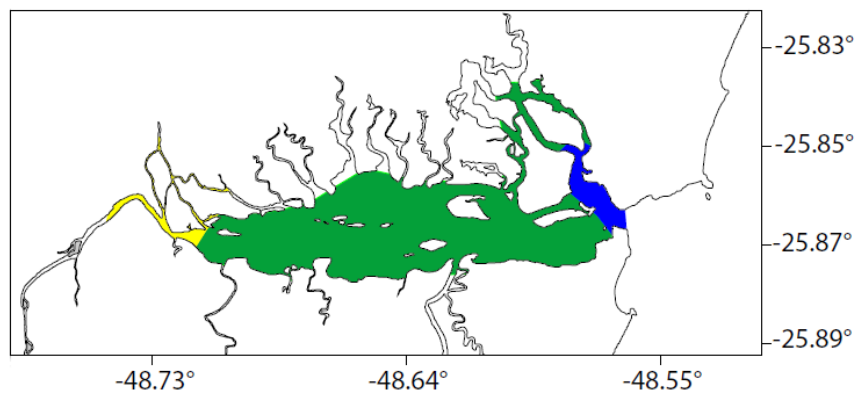


Figure 2: The tidal salinity zones of Paranaguá and Guaratuba bays, average salinity and the areas of the zones (km²).

Susceptibility

The estuarine susceptibility, determined by the combination of the dilution and flushing potentials, is presented in the Table 12. Paranaguá bay is a type B estuary with minor vertical stratification observed along the year (Lana et al., 2000; Marone et al., 2005), whereas Guaratuba bay is mainly vertically stratified (Marone et al., 2004). Considering that the estuarine volume is constant along the year, the dilution potential is moderate in Paranaguá bay and low in Guaratuba bay.

As the estuarine volume, the average tidal range was also considered to be constant along the year in the systems because no information was available concerning the variation in the seasonal periods. The flushing potential of Paranaguá Bay is classified as high during

the rainy period when the freshwater discharge increases more than two times from the dry period, during which the system presents moderate potential. The flushing potential in Guaratuba bay is not affected by the fluctuations in river input, remaining moderate along the seasons. Hence, the estuarine susceptibility is classified as high along the year in Guaratuba bay, whereas in Paranaguá bay varies from low in the rainy season and moderate in the dry season.

Table 12: Determination of the estuarine susceptibility through the dilution and flushing potentials of Paranaguá and Guaratuba bays in the rainy and dry seasons.

	Paranaguá		Guaratuba	
<i>Type</i>	B		B	
<i>Volume (10⁶·m³)</i>	1367		140	
<i>Dilution Volume</i>	7·10 ⁻⁴		7·10 ⁻³	
<i>Dilution Potential</i>	Moderate		Low	
	Rainy Season	Dry Season	Rainy Season	Dry Season
<i>Tide Range</i>	Macro		Meso	
<i>Daily River Input (10⁶·m³)</i>	10	4	5	3
<i>River Input/Estuary Volume</i>	1·10 ⁻²	3·10 ⁻³	3·10 ⁻²	2·10 ⁻²
<i>Exportation Potential</i>	High	Moderate	Moderate	Moderate
<i>Estuarine Susceptibility</i>	Low	Moderate	High	High

Nutrient Input

The determination of ASSETS demands a specific set of data. Information regarding dissolved inorganic nitrogen (DIN) concentrations in the rivers and offshore waters are necessary to define the nutrient input to the systems, together with information on DIN from effluents. The calculations for the nutrient inputs for Paranaguá and Guaratuba Bays are presented in Table 13.

DIN concentrations in the rivers entering Paranaguá Bay were determined as 8.9 µM (1.2·10⁻⁴ kg·m⁻³) in the rainy season and 12.6 µM (1.8·10⁻⁴ kg·m⁻³) during the dry period (Mizerkowski et al. in prep., see Chapter II), while in Guaratuba Bay the averages between the two main rivers (São João and Cubatão rivers) accounted for 10.5 µM (1.5·10⁻⁴ kg·m⁻³) and 11.1 µM (1.6·10⁻⁴ kg·m⁻³) (see Chapter III). Offshore DIN surface concentrations ranged between 0.84 µM (1.2·10⁻⁵ kg·m⁻⁵) in the rainy period and 0.88 µM (1.2·10⁻⁵ kg·m⁻³) in the dry period of the (tire o THE) Paranaguá adjacent coast, while around 0.64 µM (9·10⁻⁶ kg·m⁻³) and 0.58 µM (8.1·10⁻⁶ kg·m⁻³) in Guaratuba area.

DIN anthropogenic input in Paranaguá Bay were projected by Mizerkowski et al. in prep. (see Chapter II) as the sum between waste waters and fertilizers losses during loading

in the harbour. During the rainy season an average of around $411 \text{ kgN}\cdot\text{d}^{-1}$ ($4.8\cdot 10^{-3} \text{ kg}\cdot\text{s}^{-1}$) was determined, while the sum was around $466 \text{ kgN}\cdot\text{d}^{-1}$ ($5.4\cdot 10^{-3} \text{ kg}\cdot\text{s}^{-1}$) during the dry period. DIN effluent discharge to Guaratuba bay was estimated through the combination of average DIN release per capita, considered as 9.04 gN per day (Meybeck and Helmer, 1989; Meybeck *et al.*, 1989), and around 45% of the population of the Guaratuba bay that is not included in the sewage treatment system (SANEPAR, 2003). In the rainy season, it was considered a population increase of around 2 times resulting in a DIN daily input of around $271 \text{ kgN}\cdot\text{d}^{-1}$ ($3.1\cdot 10^{-3} \text{ kg}\cdot\text{s}^{-1}$), while in the dry season the estimation reached $136 \text{ kgN}\cdot\text{d}^{-1}$ ($1.6\cdot 10^{-3} \text{ kg}\cdot\text{s}^{-1}$).

Table 13: Average DIN concentrations in rivers and offshore waters, and estimated loads from anthropogenic effluents to Paranaguá and Guaratuba bays in the rainy and dry seasons and the respective Nutrient Input classification.

	Paranaguá		Guaratuba	
	Rainy Season	Dry Season	Rainy Season	Dry Season
$m_{in}^{(a)}$	$1.2\cdot 10^{-4}$	$1.8\cdot 10^{-4}$	$1.5\cdot 10^{-4}$	$1.6\cdot 10^{-4}$
$m_{sea}^{(a)}$	$1.2\cdot 10^{-5}$	$1.2\cdot 10^{-5}$	$9\cdot 10^{-6}$	$8.1\cdot 10^{-6}$
$M_{ef}^{(b)}$	$4.8\cdot 10^{-3}$	$5.4\cdot 10^{-3}$	$3.1\cdot 10^{-3}$	$1.6\cdot 10^{-3}$
$m_b^{(a)}$	$1.2\cdot 10^{-5}$	$1.2\cdot 10^{-5}$	$7.8\cdot 10^{-6}$	$7.4\cdot 10^{-6}$
$m_h^{(a)}$	$2.5\cdot 10^{-6}$	$1.9\cdot 10^{-6}$	$2.7\cdot 10^{-5}$	$1.7\cdot 10^{-5}$
$m_h/[m_b+ m_h]^{(a)}$	0.2	0.1	0.8	0.7
Nutrient Input	Low	Low	High	High

^(a) in $\text{kg}\cdot\text{m}^{-3}$, ^(b) in $\text{kg}\cdot\text{s}^{-1}$.

According to the ASSETS software, nutrient inputs were calculated using the option coastal equation, that corresponds to the one proposed by Ferreira et al. (2007). The background DIN concentrations (m_b) were constant along the seasons ($1.2\cdot 10^{-5} \text{ kg}\cdot\text{m}^{-3}$) in Paranaguá Bay, while slightly higher levels were observed in Guaratuba bay during the rainy period ($7.8\cdot 10^{-6} \text{ kg}\cdot\text{m}^{-3}$). The input from effluents (m_h) varied in Paranaguá Bay from $2.5\cdot 10^{-6} \text{ kg}\cdot\text{m}^{-3}$ in the rainy period to $1.9\cdot 10^{-6} \text{ kg}\cdot\text{m}^{-3}$ in the dry season, and in Guaratuba Bay from $2.7\cdot 10^{-5} \text{ kg}\cdot\text{m}^{-3}$ to $1.7\cdot 10^{-5} \text{ kg}\cdot\text{m}^{-3}$, respectively. Both systems presented the same classification for the nutrient input in the seasons. Paranaguá bay presents low nutrient loads, whereas the input is high in Guaratuba bay.

Influencing Factors – IF

Susceptibility and nutrient inputs are combined to determine the Influencing Factors (IF) that is presented in Table 14 . The classification for the Influencing Factors in Guaratuba

Bay remains high along the year. In Paranaguá Bay, the variation of the susceptibility from low in the rainy season to moderate in the dry season led to the final classification of IF from low to moderate low, respectively.

Table 14: Influencing Factors (IF) determination using the combination of the estuarine susceptibility and nutrients inputs indices for Guaratuba Bay and for the rainy and dry seasons in Paranaguá Bay.

	Paranaguá Bay		Guaratuba Bay
	Rainy Season	Dry Season	
<i>Susceptibility</i>	Low	Moderate	High
<i>Nutrient Input</i>	Low	Low	High
<i>Influencing Factors</i>	Low	Moderate Low	High

Primary Symptoms

The primary symptoms index, defined by the combination of the classifications for chlorophyll-*a* concentrations and macroalgae problems, is presented in Table 15.

In Paranaguá bay, the increase of primary production occurring during the rainy period reached high chlorophyll-*a* concentrations covering a large area of the estuary, with maxima $47.6 \mu\text{g}\cdot\text{dm}^{-3}$ in the mixing zone and $26.3 \mu\text{g}\cdot\text{dm}^{-3}$ in the seawater zone in February 2008. The occurrence of this condition was considered episodic, because even though higher biomass was observed in the other months of the rainy period, the chlorophyll concentrations observed in February 2008 were in average $18 \mu\text{g}\cdot\text{dm}^{-3}$ higher than in December 2007 and January 2009. Therefore, it is not possible to verify if this is a normal condition for February, when the highest monthly average air temperatures in the year occurs. On the other hand, lower chlorophyll-*a* concentrations were observed in the dry period, with maxima of around $7 \mu\text{g}\cdot\text{dm}^{-3}$ in the mixing zone and $3.5 \mu\text{g}\cdot\text{dm}^{-3}$ in the seawater zone. The coverage of the condition was considered high and the occurrence periodic because concentrations similar to the maxima were observed in several sampling stations of the mixing zone and repeatedly. The final score for chlorophyll-*a* expression in the estuary was 1 for the rainy season and 0.65 for the dry period.

In the past years, the occurrence of macro algae blooms has been a common complaint from local fishermen, interfering in the trawling activities. These blooms are periodic during spring and summer, and remains from the macro algae, especially Rodophytes, are easily found on the shore adjacent to the estuary mouth. Still, patches of green macro algae (speculated to be *Ulva sp.*) are observed around the harbour area and sewage channels outlets from Paranaguá during the rainy season. The periodic occurrence of macroalgae problems in the rainy season is indicated by the maximum symptom level of expression (1), while no problem is observed in the dry season. The final primary symptoms level of expression value in Paranaguá Bay, which is the average between the chlorophyll-*a*

concentrations and macroalgae problems, was determined as 0.75 in the rainy season and 0.33 in the dry season.

Table 15: Determination of the Primary Symptoms level of expression through the combination of chlorophyll-a concentrations and macroalgae coverage in Paranaguá and Guaratuba bays during the rainy and dry periods.

Paranaguá Bay									
		Rainy Season				Dry Season			
		Conditions	Expression	Value	AWV ^(b)	Conditions	Expression	Value	AWV ^(b)
<i>Chl-a</i> ^(a)	Mixing Area Frequency	47.6 High Episodic	High	1	0.53	6.9 High Periodic	High	1	0.53
	Seawater Area Frequency	26.3 High Episodic	High	1	0.47	3.5 Not Applicable	Low	0.25	0.12
<i>Symptom level of expression value for the estuary</i>					1				
<i>Macroalgae</i>	Mixing Area Frequency	Observed Periodic	High	1	0.53	No Problems	-	0	0
	Seawater Area Frequency	Observed Periodic	High	1	0.47	No Problems	-	0	0
<i>Symptom level of expression value for the estuary</i>					1				
Primary symptoms level of expression value					0.75 High	0.33 Moderate			
Guaratuba Bay									
		Rainy Season				Dry Season			
		Conditions	Expression	Value	AWV ^(b)	Conditions	Expression	Value	AWV ^(b)
<i>Chl-a</i> ^(a)	Freshwater Area Frequency	4.3 Not Applicable	Low	0.25	0.02	0.7 Not Applicable	Low	0.25	0.02
	Mixing Area Frequency	29.5 High Periodic	High	1	0.75	19 Moderate Unknown	Moderate	0.5	0.38
	Seawater Area Frequency	15 Moderate Persistent	High	1	0.17	8.7 High Unknown	Moderate	0.5	0.08
<i>Symptom level of expression value</i>					0.94				
<i>Macroalgae</i>			Unknown			Unknown			
<i>Symptom level of expression value</i>					-				
Symptom level of expression value for the estuary					0.94 High	0.48 Moderate			

^(a) Chlorophyll-a surface concentrations in $\mu\text{g}\cdot\text{dm}^{-3}$, ^(b) AWV= area weighted value expression (AWV= [value*zone area]/total area).

In Guaratuba Bay, the freshwater zone presents constant low chlorophyll-a concentrations, with maxima of $4 \mu\text{g}\cdot\text{dm}^{-3}$ in the rainy season and around $1 \mu\text{g}\cdot\text{dm}^{-3}$ in THE dry season, which were determined as low expression and the value of 0.25. High to medium phytoplanktonic biomass was constantly observed along the mixing zone and in one station of the seawater zone in the rainy period, reaching the maxima of around $30 \mu\text{g}\cdot\text{dm}^{-3}$ and $15 \mu\text{g}\cdot\text{dm}^{-3}$, respectively. The combination of high period concentrations in the mixing zone and

medium, but persistent, levels in the seawater zone resulted in a high expression of this symptom in these zones during the rainy season, in which the expression level value for expression chlorophyll in the estuary was determined as 0.94. During the dry period, the biomass was around medium concentrations in the mixing and seawater zones, with maxima of $19 \mu\text{g}\cdot\text{dm}^{-3}$ and around $9 \mu\text{g}\cdot\text{dm}^{-3}$ in, respectively. The coverage of such condition was moderate in the mixing zone, whereas it spread along the seawater zone. The occurrence is unknown because of data availability. This symptom expression of these zones in the dry period was determined as moderate. The final level of chlorophyll expression for the estuary in dry period was 0.48.

Secondary Symptoms

Dissolved oxygen concentrations and occurrence of harmful algae blooms (HAB's) were considered to determine the secondary symptoms expression (Tab. 16). Information regarding harmful algae blooms (HAB's) is often diffuse due to the sporadic occurrence and the lack of appropriate monitoring programs. The estimation of this symptom was more refined for the Paranaguá Bay, which is better known by the authors, indicating that local expert knowledge is an important tool for applying ASSETS.

Fernandes et al. (2001) speculates that the dominant phytoplanktonic specie *C. wailesii* was brought to the system by ballast water to the Paranaguá bay. In PEC, it produces sporadic blooms during which lower zooplankton concentration was observed. These blooms can be considered harmful due to the decrease of light and nutrients availability for other species. Mafra Jr et al. (2006) and Fernandes and Brandini (2010) observed that several harmful microalgae can be found in the phytoplanktonic communities of Paranaguá Bay, such as *Pseudo-nitzschia* spp., *Dinophysis acuminata*, *Prorocentrum minimum*, *Gymnodinium catenatum*, *Phaeocystis* spp., *Chattonella* spp. and *Heterosigma akashiwo* and *Trichodesmium erythraeum*; results also showed occurrence of paralytic and amnesic toxins in mussels and cultivated strains. Although the occurrence and the spatial coverage of the blooms were unknown, the observation of the problem already results in an expression value of 0.25 for this symptom, which was the determination for the final expression value for the secondary symptoms in Paranaguá Bay for both rainy and dry seasons. Information regarding HAB's was not available for Guaratuba Bay, therefore considered as unknown.

Bottom dissolved oxygen levels were constantly over the biological stress ($5 \text{ mg}\cdot\text{dm}^{-3}$) in Paranaguá and Guaratuba bay, with one exception. Oxygen levels under the biological stress limit were observed in a large area of the mixing zone of Guaratuba bay in the dry period, with a minima of $4.2 \text{ mg}\cdot\text{dm}^{-3}$ in April 2002. The occurrence of this condition was

considered periodic, because lower concentrations were already been observed in the previous months, but the monthly average remained over 5 mg·dm⁻³. This situation may occur due to the decrease of primary production indicated by lower chlorophyll-*a* concentrations after the summer, once heterotrophy is predominant in Guaratuba bay according to CO₂ saturation levels (Mizerkowski et al., in prep., see Chapter III). The occurrence of this period event of high spatial coverage in the mixing zone resulted in an expression value of 0.37, that was the final secondary symptoms expression value for Guaratuba Bay in the dry period.

Table 16: Determination of the secondary symptoms level of expression through the combination of dissolved oxygen concentrations and harmful algae blooms (HAB's) occurrence in Paranaguá and Guaratuba bays during the rainy and dry periods.

Paranaguá Bay									
		Rainy Season				Dry Season			
		Conditions	Expression	Value	AWV ^(b)	Conditions	Expression	Value	AWV ^(b)
<i>HAB's</i>	Mixing Duration Frequency	Observed Unknown Unknown	Low	0.25	0.13	Observed Unknown Unknown	Low	0.25	0.13
	Mixing Duration Frequency	Observed Unknown Unknown	Low	0.25	0.12	Observed Unknown Unknown	Low	0.25	0.12
<i>Symptom level of expression value for the estuary</i>					0.25				0.25
<i>Dissolved Oxygen^(a)</i>	Mixing Area Frequency	No Problem	-	0	0	No Problem	-	0	0
	Seawater Area Frequency	No Problem	-	0	0	No Problem	-	0	0
<i>Symptom level of expression value for the estuary</i>					0				0
Primary symptoms level of expression value					0.25 Low				0.25 Low
Guaratuba Bay									
		Rainy Season				Dry Season			
		Conditions	Expression	Value	AWV ^(b)	Conditions	Expression	Value	AWV ^(b)
<i>HAB's</i>		Unknown				Unknown			
<i>Symptom level of expression value</i>					0	<i>Symptom level of expression value</i>			0
<i>Dissolved Oxygen^(a)</i>	Freshwater Area Frequency	No Problem	-	0	0	No Problem	-	0	0
	Mixing Area Frequency	No Problem	-	0	0	4.24 High Periodic	Moderate	0.5	0.37
	Seawater Area Frequency	No Problem	-	0	0	No Problem	-	0	0
<i>Symptom level of expression value</i>					0				0.37
Symptom level of expression value for the estuary					0 Low				0.37 Moderate

^(a) Minimum monthly average bottom concentrations in mg·dm⁻³, ^(b) AWV= area weighted value expression (AWV= [value*zone area]/total area).

Eutrophic Condition – EC

The Eutrophic Condition (EC) is assessed by combining the primary and secondary symptoms expression values (see Tab. 8), and the final classification for Paranaguá and Guaratuba bays is presented in Table 17. The secondary symptoms expression was constant along the year, whereas the primary symptoms shifted from high in the rainy period to moderate in the dry period in Paranaguá Bay, what resulted in the final classification for the EC as moderate to moderate low, respectively. In Guaratuba Bay, EC remained as moderate for both seasons because high primary symptoms and low secondary were observed in the rainy season, while both indices were determined as moderate in the dry season.

Table 17: Determination of the Eutrophic Conditions (EC) by the combination of primary and secondary symptoms indices for Paranaguá and Guaratuba Bays in the rainy and dry seasons.

	Paranaguá Bay		Guaratuba Bay	
	Rainy Season	Dry Season	Rainy Season	Dry Season
Primary Symptoms	High	Moderate	High	Moderate
Secondary Symptoms	Low	Low	Low	Moderate
Eutrophic Conditions	Moderate	Moderate Low	Moderate	Moderate

Future Outlook – FO

The definition of Future Outlook (FO) considers the trends for nutrient inputs concerning increase, decrease or no change in loads. Bricker et al. (1999; 2003) induces the definition based on the opinion of experts, considering the future pressure of population growth and industrial development compared to measures to control nutrients emission, such as sanitation contention and mitigation actions. The definition of Future Outlook to Paranaguá and Guaratuba bays is presented in Table 18.

In Brazil, a program for the acceleration of development (PAC – *Programa de Aceleração do Crescimento*) concerns improvement of sanitation, ensuring funds for all of the cities in the country. This is positive, considering the projection of future conditions, even though other aspects of the program, such as agriculture and industrial development, can result in negative impacts related to deforestation, increase of the use of fertilizers and pollutants discharges. The Sanitation Company of Paraná State (SANEPAR) has made an impressive investment in the coastal zone of the state. The regions where Paranaguá and Guaratuba bays are inserted have received new sewage treatment networks. Still, it is not possible to connect all the houses to the sanitation network due to logistical and financial limitations, and illegal connections to the pluvial network or *in natura* direct discharge can be

easily observed. The input to the groundwater layers should also be considered of great concern, once septic systems are a common feature for all the coastal zones of Brazil. Considering that the estimation of population growth is around 1% for the State of Paraná until 2020, it is expected that nutrients pressure will increase. Moreover, an increase of up to 70% is expected to occur in some coastal regions of the State of Paraná due to new harbours and universities. Furthermore, the balance between population increase and investments in infra-structure might mitigate the environmental degradation due to increasing development of the coastal areas of Paraná State. Considering lack of a consistent analysis on this subject, it was considered that the pressure of nutrient input will remain unchanged for both systems.

Table 18: Determination of the Future Outlook (FO) determined by the combination of the estuarine susceptibility and future nutrients pressure indices in Paranaguá and Guaratuba bays.

	Paranaguá Bay		Guaratuba Bay
	Rainy Season	Dry Season	
Susceptibility	Low	Moderate	High
Change in nutrient pressures	No change	No change	No change
Future Outlook	No change	No change	No change

Assessment of Trophic Status – ASSETS

The determination of the trophic status through the ASSETS methodology for Paranaguá and Guaratuba bays is presented in Table 19. The trophic status of Paranaguá Bay varied from moderate in the rainy period to good in the dry period. Lower susceptibility to develop eutrophic conditions in the rainy period was overcome by the moderate expression of the eutrophic conditions in Paranaguá Bay. Even though lower freshwater discharge and higher nutrient inputs during the dry season lead to an increase of the influencing factors, the eutrophic conditions are better in Paranaguá Bay and the system presents a better trophic status in this period.

Guaratuba Bay presents a poor trophic status along the year resulting for the same conditions regarding the influencing factors and the eutrophic conditions in the rainy and dry periods. The great difference between the two systems is the size and the freshwater input. While Paranaguá Bay presents an average renewal time of around 3 days, in Guaratuba bay the water takes around 9 days to be totally flushed to the coastal adjacent area. Therefore, the estuarine susceptibility is a determining factor for the expression of eutrophic conditions, especially when nutrients inputs are not extremely high (Bricker et al., 1999).

Table 19: Assessment of Trophic Status (ASSETS) for Paranaguá and Guaratuba bays in the rainy and dry period.

	Paranaguá Bay				Guaratuba Bay			
	Rainy Season		Dry Season		Rainy Season		Dry Season	
	Class	Score	Class	Score	Class	Score	Class	Score
<i>Influencing Factors</i>	Low	5	Moderate Low	4	High	1	High	1
<i>Eutrophic Condition</i>	Moderate	3	Moderate Low	4	Moderate	3	Moderate	3
<i>Future Outlook</i>	No Change	3	No Change	3	No Change	3	No Change	3
Trophic Status	Moderate		Good		Poor		Poor	

Trophic Index – TRIX

The TRIX methodology provided a fine spatial scale for the definition of the trophic status along the estuarine systems. The question of setting the right spatial scale concerning the water layer arises when it is necessary to define a grouping factor for determining the trophic status through the TRIX in the estuaries. Vollenweider et al. (1998) used surface concentrations to determine the trophic status of the Baltic Sea, but this approach may represent some LOSS of information in shallow and dynamic estuaries such as Paranaguá and Guaratuba bays. Considering that vertical stratification is observed in Guaratuba bays and in some occasions in Paranaguá Bay, both surface and bottom layers are presented separately.

Correction Constant – $\sum \log(\text{Lower Limits})$

The determination of the sum of the lower limits logarithms depends on the definition of the boundaries. Basic statistics for the parameters are presented in Table 20. Using the minimum of $\text{mean} \pm [2.5 \cdot \text{standard deviation}]$ for the absolute oxygen saturation deviation from 100% (aD%O) and chlorophyll, DIN and DIP concentrations, the value of [-1.4] is suggested as the correction constant for Paranaguá and Guaratuba bays.

Therefore, the TRIX determination for Paranaguá and Guaratuba bays is proposed as:

$$\text{TRIX} = \frac{\log [\text{Chla} \cdot \text{aD\%O} \cdot \text{DIN} \cdot \text{DIP}] - [-1.4]}{1.2}$$

Table 20: Mean, standard deviation, minimum values of the parameters absolute oxygen saturation deviation from 100% (aD%O) and chlorophyll, DIN and DIP concentrations in Paranaguá and Guaratuba bays, with the sum of the lower limits (L) logarithms.

<i>Parameter</i>	Mean	Standard Deviation	n	Lower limit [log]
<i>aD%O</i>	17.6	11.7	425	0.08 [-1.10]
<i>Chlorophyll-a [mg·m⁻³]</i>	8.50	7.83	330	0.14 [-0.85]
<i>DIN [mg·m⁻³]</i>	62.8	54.7	419	3 [0.47]
<i>DIP [mg·m⁻³]</i>	12.6	8.25	419	1.18 [0.07]
			Sum [log L]	[-1.41]

Paranaguá Bay

The water body of Paranaguá Bay was assessed through longitudinal transects along the main navigation channel. To better understand the spatial distribution of the trophic status assessed through TRIX along the estuary body and in the seasons, surface and bottom waters status in the rainy and dry periods are presented in the Figure 3. A decreasing gradient of TRIX from the upper region to the estuary mouth is observed in all situations. Maximum average of over 6 indicating eutrophic conditions was observed in the bottom waters of sampling stations 2 and 3 in the rainy period, while the minimum average under 4 was recorded both in the surface of the stations 11 and 12 in the dry period. Higher TRIX values in the bottom layers during the rainy period were a trend along the bay, except in the station 9. Oppositely, the middle area of the bay (from stations 4 to 8) presented lower trophic status in the bottom layers.

DIN concentrations presented higher contribution to the TRIX determination, except for the bottom layer of station 12 during the dry season when the DIN content was similar to the DIP concentrations and the TRIX index reached average values under 4 (Figure 4). Higher TRIX indices were observed during the rainy period that can be related to higher chlorophyll-*a* concentrations and lower oxygen levels, as observed in the Figure 4, even though higher DIN concentrations were observed during the dry season probably due to the lower biological uptake. During the rainy season, the contribution of the logarithms of the oxygen deviation (aD%O), chlorophyll-*a* and DIP concentrations was similar around the middle area of Paranaguá Bay, especially in the surface waters from the station 4 to 11, whereas the parameters showed a ranking during the dry period. In average, the estuarine waters of Paranaguá Bay presented lower chlorophyll concentrations that were followed by the oxygen deviation, DIP and DIN concentrations during the dry season.

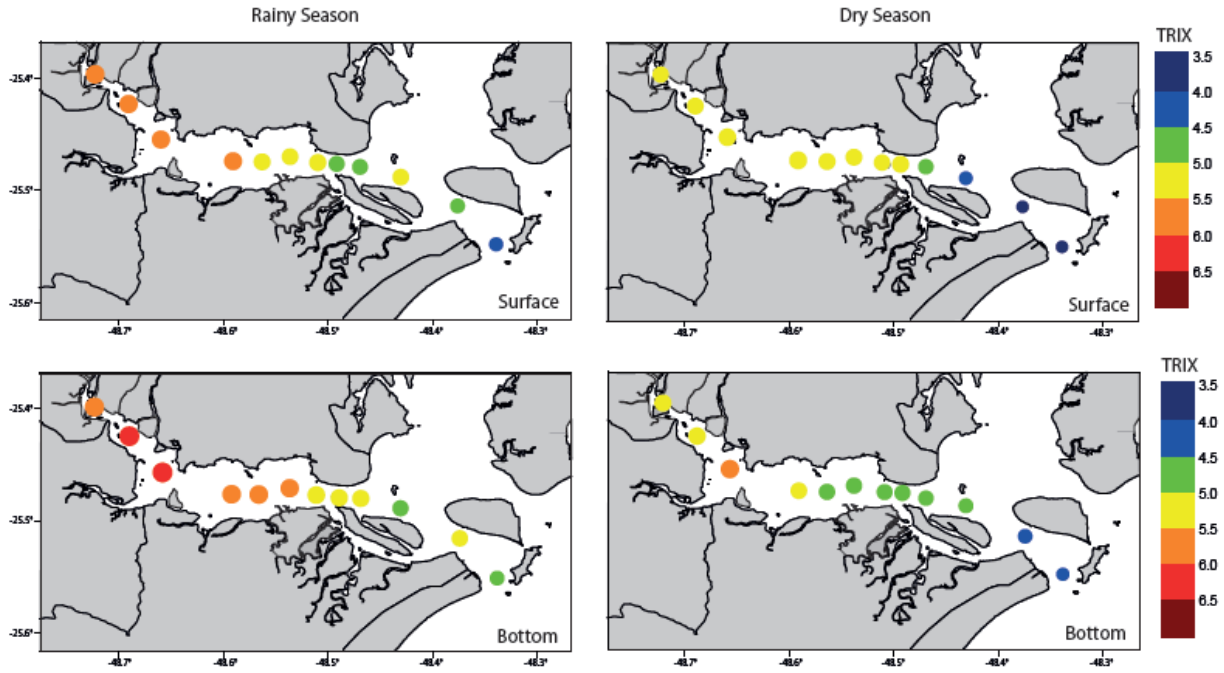


Figure 3: TRIX values for surface and bottom layers during the rainy and dry seasons along the Paranaguá Bay.

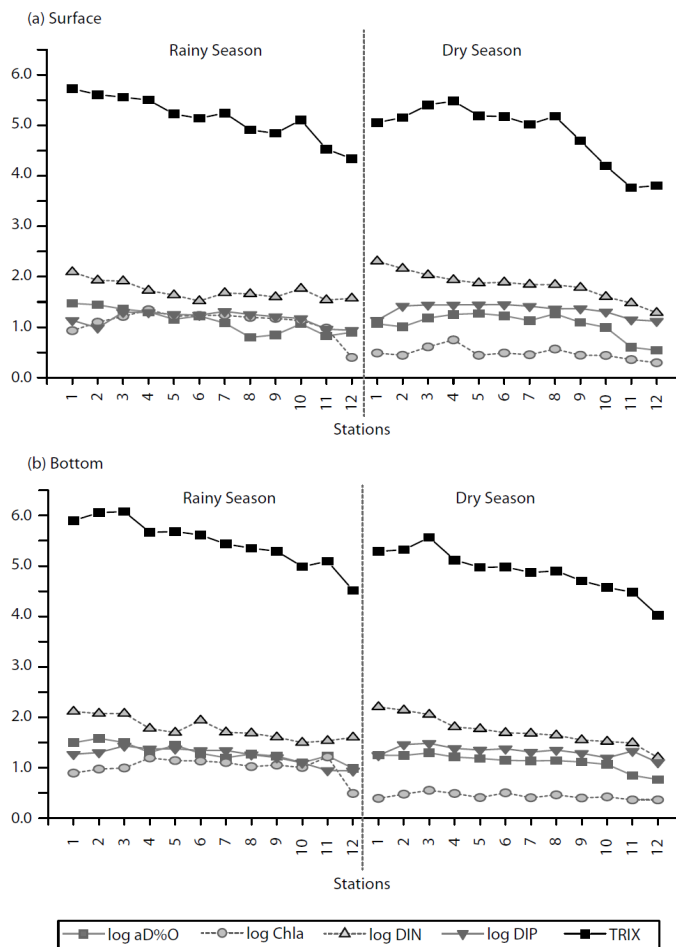


Figure 4: Average logarithms of the oxygen deviation from 100% of saturation (aD%O), chlorophyll-a (Chla), DIN and DIP concentrations and TRIX values of surface and bottom layers during the rainy and dry seasons along Paranaguá Bay.

Moreover, the TRIX indices were mainly higher in the bottom layers, which can be related to lower oxygen levels and higher nutrients concentrations that are probably result of the lower phytoplanktonic biomass, higher decomposition rates and the exchange of nutrients at the water-sediment interface. Overall, the decreasing gradient of the trophic status from the inner areas to the lower section of Paranaguá Bay seemed to follow the DIN pattern, with fluctuations along the estuary that are probable more related to the chlorophyll-*a* and oxygen level variations.

TRIX values were significant ($p < 0.05$) different between the water layers in the rainy season, while the same average corresponding to a good trophic status was observed in the bottom and surface waters in the dry period (Tab. 21). During the rainy period, a slightly better trophic status was addressed to the surface than to the bottom waters, which presented an average along the estuary of around 5.2 and 5.5, respectively. Still, both values classify the estuary with moderate trophic status in this period. Overall, better status classified as 'good' was observed in the dry period that was significant different ($p < 0.05$) from the 'moderate' conditions observed in the rainy season

Table 21: Summary of the Trophic Index (TRIX) averages and classification during the rainy and dry periods for the surface and bottom layers of Paranaguá Bay.

	Rainy Season		Dry Season	
	Surface	Bottom	Surface	Bottom
TRIX	5.2±0.5	5.5±0.5	4.9±0.7	4.9±0.6
Mean	5.4		4.9	
Class	Moderate		Good	

Guaratuba Bay

The spatial distribution of the trophic status in Guaratuba Bay is similar to the one observed in Paranaguá Bay, with a decreasing gradient from the mixing to the seawater salinity zone of the estuary (Fig. 5).

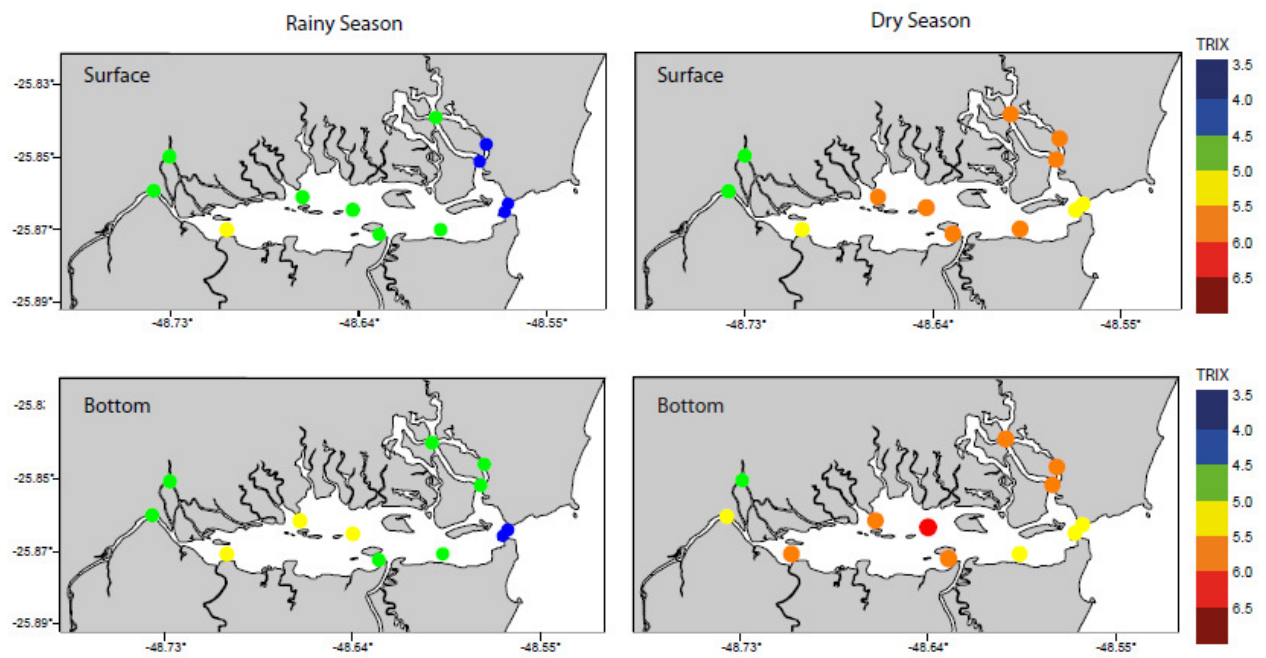


Figure 5: TRIX values for surface and bottom layers during the rainy and dry seasons along the Guaratuba Bay.

Still, the freshwater zone (represented by stations 1 and 2) presented similar conditions along the sampling period, with the predominance of TRIX indices under 5. It is evident the shift to higher trophic status during the dry season in Guaratuba Bay, which was the opposite of what was observed in Paranaguá Bay. During the rainy season, the average TRIX ranged between around 4.8 in the freshwater zone of Guaratuba Bay, whereas between 4.6 and 5.2 in the mixing zone and the lowest TRIX indices around 4.4 were recorded in the seawater zone. The increase of the trophic status during the dry season occurred mainly along the mixing and the seawater zone, with the maximum average of 6.1 in the bottom layers of station 7. The average TRIX gradient ranged from around 5 in the freshwater zone, to 5.7 in the mixing zone and 5.3 in the seawater zone.

Figure 6 shows the variation of the parameters logarithms and the TRIX values for surface and bottom layers during the rainy and dry season in Guaratuba Bay. As observed in Paranaguá Bay, DIN concentrations in Guaratuba Bay seemed to have more contribution to the TRIX determination, with higher values during the dry season. Lower oxygen levels especially in the bottom layers led to higher trophic status, which was more evident during the dry season. Even though the highest DIN concentrations were observed in the freshwater zone, the predominance of oligotrophy and probably heterotrophy in the freshwater zone is indicated by permanent lower chlorophyll-a concentrations that led to the lower TRIX values in this area.

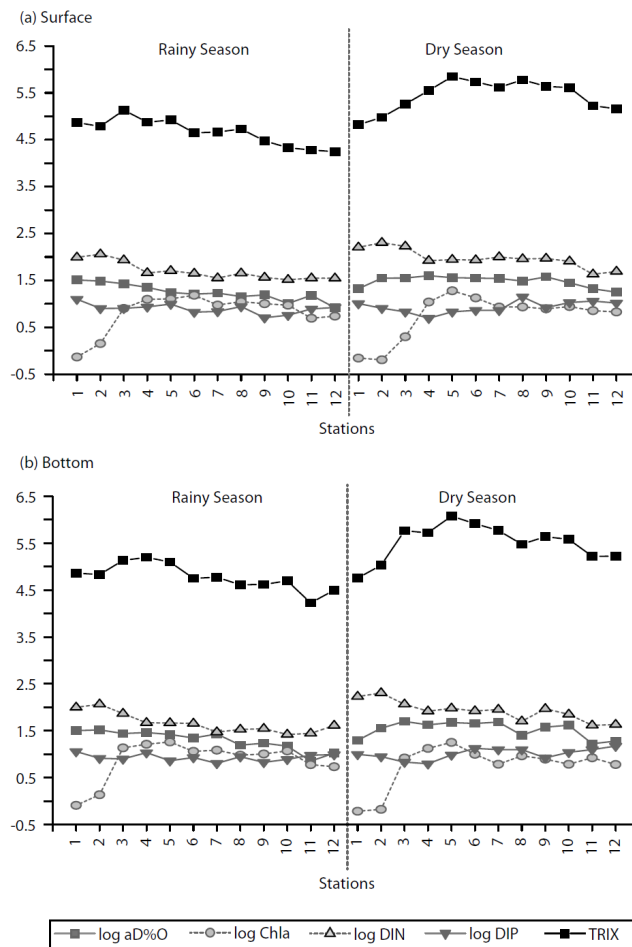


Figure 6: Average logarithms of the oxygen deviation from 100% of saturation (aD%O), chlorophyll-*a* (Chla), DIN and DIP concentrations and TRIX values of surface and bottom layers during the rainy and dry seasons along Guaratuba Bay.

Whereas the ranking of the parameters contribution with lower chlorophyll-*a* concentrations, followed by the DIP concentrations, the oxygen deviation and DIN content was observed in the freshwater zone and at the stations 11 and 12 of the seawater zone, a different pattern is indicated to the middle area of Guaratuba Bay. The increase of the phytoplanktonic biomass in this area mainly overcomes the DIP contribution to the TRIX especially during the rainy season, when it reached logarithms similar to the ones of the oxygen deviation.

Therefore, while the DIN concentrations are of great contribution to the TRIX spatial distribution in Guaratuba Bay, the chlorophyll-*a* concentrations are related to the increase of the trophic status in the middle area of the estuary. Still, the higher trophic status observed during the dry season was related to increasing oxygen deviation, DIP and DIN concentrations whereas similar chlorophyll-*a* concentrations. It is important to mention that the chlorophyll-*a* measurements were performed only once during the dry season in

Guaratuba Bay (April 2002), and this situation may represent a situation of a late summer bloom in the estuary.

Due to the smaller dimension of Guaratuba Bay, it was possible to establish a sampling strategy covering the whole estuarine system. No differences were observed between bottom and surface layers concerning TRIX and the average values (Tab. 22) indicated the predominance of 'good' trophic conditions during the rainy period (mean=4.7) while 'moderate' in the dry season (mean=5.5). Maxima average of 6.1 in the bottom layers of station 5 was observed in the dry season, while the minimum average of 4.2 was in the stations 1 e 2 in the rainy period.

Table 22: Summary of the Trophic Index (TRIX) averages and classification during the rainy and dry periods for the surface and bottom layers of Guaratuba Bay.

	Rainy Season		Dry Season	
	Surface	Bottom	Surface	Bottom
TRIX	4.7±0.6	4.8±0.6	5.4±0.4	5.5±0.3
Mean	4.8		5.5	
Class	Good		Moderate	

Discussion

The ASSETS and the TRIX methodologies indicated that the trophic status of the estuarine systems of the coast of the State of Paraná presented spatial and temporal variations. Through the ASSETS method, a better trophic status was stated to Paranaguá Bay than to Guaratuba Bay even though problems such as harmful algae blooms and macroalgae problems were observed in the northern estuarine system. A larger area and higher freshwater input result in more dynamics observed in Paranaguá Bay that are related to lower susceptibility to negative eutrophication symptoms. Guaratuba Bay with a smaller area and shallow waters has a lower potential to dilute and export the nutrient inputs that are higher due to the estuary proportions, and thus determines the expression of the eutrophication problems. Seasonality is also an important factor to be considered for the application of the ASSETS methodology in subtropical estuaries such as the study areas. A good state was addressed to Paranaguá Bay during the dry season while moderate conditions were indicated during the rainy season due to the problems of phytoplanktonic and macroalgae blooms even though higher freshwater input and low susceptibility is observed during this season. Guaratuba Bay presented a poor state along the year that was mainly determined by the predominance of low dilution and export potentials, high nutrient input and low oxygen levels. Therefore, even though the ASSETS methodology considers

the winter nutrient concentrations, the application of the ASSETS methodologies in subtropical estuaries should consider the seasonality. The first step to apply the method is to test if such periods occur and if the seasonal fluctuations are significant for the estuarine dynamics.

The TRIX methodology indicated that different situations are observed within the estuarine boundaries. In both systems, the middle areas of the bays presented worse trophic conditions than the freshwater and seawater zones. The seasonality was also differently exposed by Paranaguá and Guaratuba Bays. Whereas the increase of DIN concentrations during the dry season was compensated by lower chlorophyll-a concentrations and oxygen deviation in Paranaguá Bay, higher TRIX indices during this period in Guaratuba Bay are related to the increase of the oxygen deviation, DIP concentrations and similar phytoplanktonic biomass.

The TRIX methodology provides a finer spatial scale for the definition of the trophic status within the estuaries, even though it presents more limitation related to estuarine dynamics. The methodology was developed to be applied in marine areas and the susceptibility to develop eutrophication symptoms (e.g. flushing and dilution capacity) is not considered. Moreover, the salinity gradient and the related processes concerning the primary production are also important factors determining the trophic status. This issue is still a critical point for the utilization of the TRIX methodology in estuaries. Still, it can be considered an important tool to define critical areas within the estuarine boundaries and in shorter temporal scale, while the ASSETS methodology provides comparison basis between coastal systems for seasonal/annual cycles.

The utility of TRIX and ASSETS comes from the synthetic classification that eases the establishment of management actions for decision makers. Therefore, it is ideal if the methods supply a simple index without losing the comparison power of the analysis. The combination of surface chlorophyll, DIN and DIP concentrations and bottom oxygen levels for the application of the TRIX methodology (as suggested by the ASSETS method) can be of great reliability to present a better comparison between the two approaches, but whether using only surface or bottom measurements or averages between the water layers should be decided according to the systems dynamics.

The intention of this article was not to compare the ASSETS and the TRIX methodologies but to present a possibility to combine the best features of both. Still, comparing the methods is a valid exercise to observe if the responses are increasing the reliability of the analysis because they are designed to be used in different conditions and use different data sets. Table 23 shows the final classification of the ASSETS methodology together with the TRIX averages for Paranaguá and Guaratuba bays during the rainy and dry seasons. It is observed that the results are the same with both methodologies for Paranaguá

Bay, but different trophic status are indicated for Guaratuba Bay. The ASSETS classified this estuary with a predominant 'poor' trophic status along the year, whereas the TRIX showed a shift from 'good' conditions during the rainy season to 'moderate' during the dry season. The differentiation and the contribution of the salinity zones adopted by the ASSETS can be responsible for a better determination of the trophic status; the TRIX indices for this zone were permanently lower than the indices for the other regions and the average for the system excludes the contribution of this restricted area (around 9% of the estuarine area). Another point to be considered is lack of comprehensive data of chlorophyll concentrations during the dry season in Guaratuba Bay. Increasing the confidence of reference conditions and better investigating the reliability of the TRIX application in estuaries should be further stressed to elucidate these issues.

Table 23: Comparison between ASSETS and TRIX indices during the rainy and dry seasons in Paranaguá and Guaratuba bays.

	Paranaguá Bay		Guaratuba Bay	
	Rainy Season	Dry Season	Rainy Season	Dry Season
ASSETS	Moderate	Good	Poor	Poor
TRIX	Moderate	Good	Good	Moderate

It is important to mention that even though the methodologies count with basic information, not all variables could be assessed for the systems; therefore, the classification is restricted to the availability of data. The contribution of this work is to present a combination of methodologies to determine the trophic state at different scales, showing the importance and utility of using the methods for the costal management of the Brazilian coastal systems. However, considering that this is a pioneer work in the region, this study presents limitations due to lack of information and restriction of collected data at spatial and temporal scales. It is expected that the sensitivity of the methodologies will increase together with the availability of data.

Moreover, the combination of diverse methodologies, such as benthic and pelagic reference conditions as described by the TICOR methodology (Typology and Conditions of Reference - Bettencourt et al., 2004) can expand the coverage and sensitivity of cause-response models. Assessing the data set required for applying ASSETS and TRIX can be a logistical challenge due to the adequacy and acquisition of secondary source information. Unpublished data are difficult to access and depends on personal connections and availability of the responsible researchers. Yet, the trust and integrity of these data can have a great influence on the final classifications due to the lack of standardized and updated records. Therefore, creating a national database with basic information of the water

properties of estuarine systems in Brazil is a primordial step for the application of ASSETS and TRIX methodologies as a coastal management tool.

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“FerryBox Continuous Water Quality Monitoring in Paranaguá Bay”

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FERRYBOX CONTINUOUS WATER QUALITY MONITORING IN PARANAGUÁ BAY

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Abstract

Water quality monitoring is an important requirement for defining impacting activities and the management in estuarine systems, especially where harbour activities occur. The FerryBox is an automated flow-through system that comprises sensors able to conduct continuous monitoring providing online data. It was installed in the southern border of Paranaguá Bay in September 2007 providing a comprehensive data base composed by temperature, salinity, water level, pH, oxygen saturation, turbidity, chlorophyll-a fluorescence and CDOM measurements. Seasonality has been defined by the occurrence of a rainy period, with higher temperature and freshwater input supporting the phytoplankton growth, and a dry season when the parameters presented a closer correlation to the salinity gradient. The monitoring site seems to be under influence of the lateral heterogeneities of the system which is highly dynamic but the monitoring point can be considered as a viable reference point for an environmental impact study for the construction of the new harbour planned in the area. Combined with the mobile Pocket FerryBox performing sampling surveys along the estuary, the FerryBox system has proved to be an important source of information regarding water properties in Paranaguá Bay.

Key-Words: Paranaguá Estuarine Complex, physical-chemical water parameters, monitoring, FerryBox.

Introduction

Monitoring the physical and chemical properties of water can be often impaired by the lack of sampling strategies that allow collection of data on appropriate spatial and temporal scales. In coastal areas, the occurrence of phenomena and events of short duration, such as phytoplankton blooms and effect of storms, requires the development of measuring techniques that overcome the logistical limits of the common survey strategies with a low frequency sampling. The monitoring and supply of reliable data of water properties are normally summarized to oceanographic parameters such as salinity, temperature and

currents. Few types of equipment provide a wide range of basic parameters such as pH, dissolved oxygen, turbidity and chlorophyll-*a* fluorescence all being measured simultaneously. Using operational systems of continuous monitoring has been considered a viable option, leading to the development of autonomous equipment that contains diverse sensors. The FerryBox system combines these characteristics and has been used in several regions and situations, producing data series of high reliability. It has been also applied in combination with remote sensing for the calibration of satellite images for parameters such as temperature and chlorophyll fluorescence (Hydes et al. 2003, 2009; Petersen et al., 2003, 2008; Hartman et al., 2003; Bargerón et al., 2006; Kelly-Gerreyñ et al., 2006, 2007; Garcia-Soto & Pingree, 2009;; Korres et al., 2009).

In Brazil, the monitoring of water properties is limited. Information regarding meteorological and basic oceanographic parameters, such as currents and bathymetry, are a responsibility of the Brazilian Navy and are normally restricted to coastal and harbour areas. Other data on water parameters are related to the fecal coliforms concentration and bathing quality in beaches; or to the monitoring of some specific harbour areas. In this case, the records are usually confidential and presented only to the responsible environmental agency. Chlorophyll concentrations and related environmental parameters in estuaries are not gathered in any data base concerning the eutrophication monitoring, and in several cases are only available in the academic world with very limited temporal and spatial scale.

The Paranaguá Bay is a relatively pristine estuary located in Southern Brazil that houses the Paranaguá Harbour that is one of the most important of South America. There are about 155,000 inhabitants in the area, living in three main cities where the most common economic activities are related to fisheries, tourism and the harbour (Noernberg et al., 2004). Aquaculture, shellfish and mangrove crab harvest are also important to the traditional fishing communities. The estuarine complex has been under increasing pressure from harbour and urban development during the last decades. Paranaguá Harbour reached an important position within the world's trade network, especially for grains and fertilizers. The surrounding occupation of the City of Paranaguá brings common pollution problems related to disorderly occupation and lack of basic sanitation, which are common situations for other occupations in the bay and Brazil. The protected areas of the estuarine system, especially the dense mangrove margins and rainforest coverage, are endangered by the lack of appropriate surveillance and the increasing pressure of population growth over the natural resources. The main problems are related to illegal occupation in these areas, deforestation, discharge of untreated sewage in the bay and pollution related to harbour activities. The assessment of the impact of pollution problems demands descriptive studies of water quality dynamics that can be impaired by lack of appropriate and reliable data sets.

The assessment of water quality in Paranaguá Bay was usually performed randomly, through short term scientific projects and environmental impact reports/studies for new enterprises in the area. There is no data base that group all the information available and no time series has been produced in order to observe long and short fluctuations of the water properties. The use of the FerryBox system, therefore, introduces a new concept for this purpose in the area, because time series of such high resolution are not often produced in Brazil where common strategies are intermittent sampling. The stationary FerryBox is operating in a container near the outlet of Paranaguá Bay since 2007. Additionally, a portable version of the system (The Pocket FerryBox) was first tested in the study area, supplying information of the spatial distribution of water parameters along the estuary (Schroeder et al., 2008).

Data from the FerryBox measurements are analyzed in order to observe the fluctuations of water quality in Paranaguá Bay and the effects of events such as the seasonal periods of heavy precipitation events. The features of water and phytoplankton dynamics are also assessed in high temporal and spatial scales, in order to establish the reliability of the FerryBox information for water modeling and for the environmental management of the system.

Materials and Methods

Study Site: Paranaguá Bay

The Paranaguá Bay (Fig. 1) is located in the east-west axis of the Paranaguá Estuarine Complex (PEC) at Paraná State, southern Brazil (48°25' W, 25°30' S). The region has a subtropical climate, with average annual precipitation over 2000 mm and mean air temperature over 22 °C. An annual seasonal cycle is marked by the occurrence of two periods related to precipitation. The rainy period corresponds to spring and summer, while the dry season occurs during autumn and winter. It is speculated that large atmospheric fronts and the occurrence of El Niño/La Niña events can influence the distribution of rain over the year (Marone and Camargo, 1994).

PEC is a large interconnected subtropical estuarine system, partially mixed with mean tidal range and prism of 2.2 m and $580 \cdot 10^6 \text{ m}^3$, respectively. The tide is semidiurnal and water renewal time is of around 3 days (Marone et al. 2005; Mantovanelli et al., 2004; Noernberg et al., 2004). The Paranaguá Bay has been divided into three compartments along the salinity gradient, named as inner, middle and lower sections (Marone et al, 2005). The areas present different dynamics and water property features. The inner section receives the majority of the freshwater input discharged by the rivers, with lower depths and

salinity. Higher chlorophyll concentrations are observed in the middle mixing section, where the combination of nutrient availability, light penetration and salinity fluctuations allows better conditions for phytoplankton growth in Paranaguá Bay (Knoppers et al., 1987; Brandini et al., 1988; Brandini and Thamm, 1994; Rebello and Brandini, 1990; Machado et al., 1997). The harbour and city of Paranaguá are located in this region, concentrating around 80 % of the population of the bay. The lower section is highly dynamic due to the constant exchange with the coastal adjacent area. Their physical dimensions are presented in Table 1.

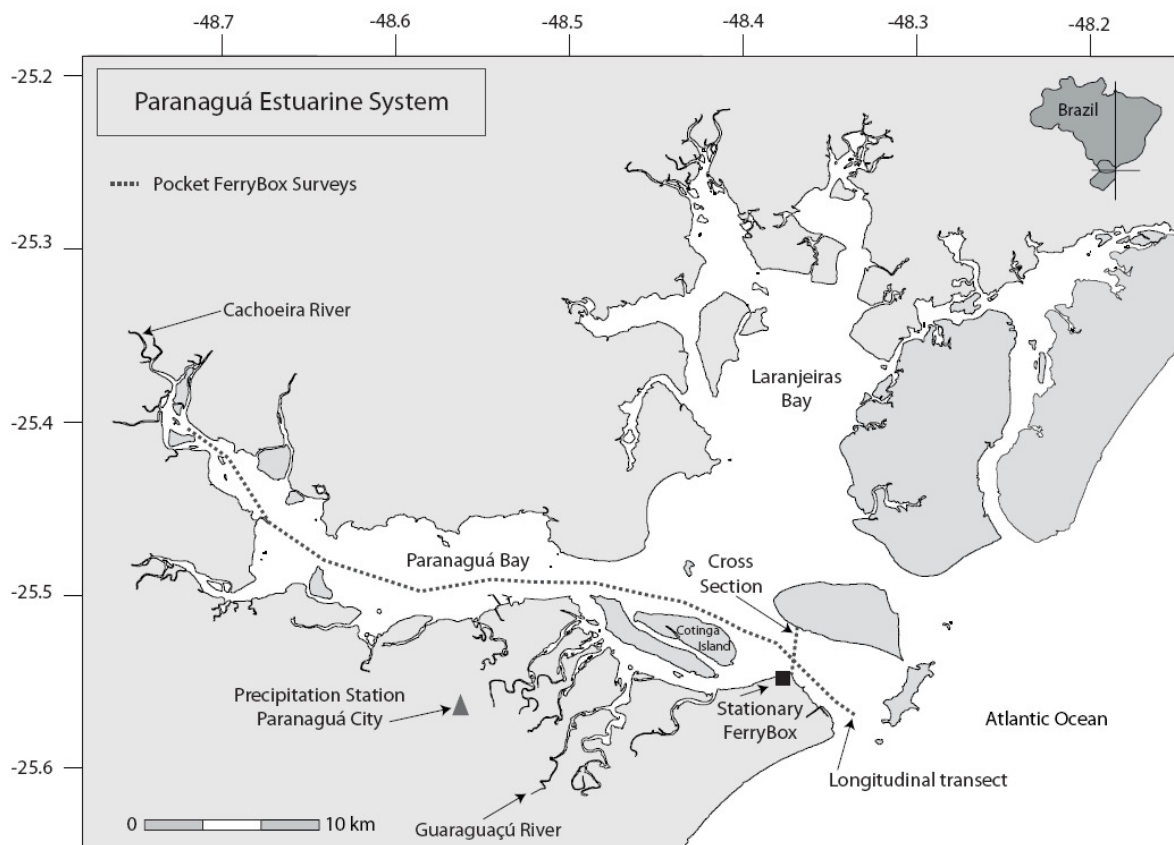


Figure 1: The Paranaguá Estuarine Complex in the Southern Brazil. The location of the Stationary FerryBox, the station for precipitation measurements, Cachoeira and Guaraguaçu rivers are pointed by arrows. The measurements performed with the Pocket FerryBox are shown in dashed lines.

The estuarine system has three main channels of connection with the Atlantic Ocean and the Galheta Channel (indicated by the longitudinal transect presented in Fig. 1) is used as the navigation access for the Paranaguá Harbour. The stationary FerryBox is placed in the south margin of the lower section (25°35'43"S, 48°22'32"W), near the outlet of

Paranaguá Bay and around 600 m from the Galheta Channel. The FerryBox module was built in a pier that enters the water in a depth of around 4 m (Fig. 2).

Table 1: Physical dimensions of the upper, middle and lower section of Paranaguá Bay (Marone et al., 2005).

<i>Section</i>	<i>Area</i> <i>[10⁶ m²]</i>	<i>Mean Depth</i> <i>[m]</i>	<i>Volume</i> <i>[10⁶ m³]</i>
Upper	50	1.9	95
Middle	93	4.3	400
Lower	187	7.0	1309
Total	330	5.4	1800

Description of the FerryBox system: functioning scheme, sensors, data structure and data base

The FerryBox is an autonomous system to measure, record and transmit data that operates continuously with different sensors. The Stationary FerryBox in Paranaguá Bay is placed in a container housing and presents an attached structure to hold the pumps that supply the water to the system, as presented by Fig. 2. Two pumps are placed at the sub-surface (floating at ~0.5 m) and close to the bottom (fixed at ~ 1 m from the bottom), working in alternated cycles of 30 minutes, with coupled sensors for the measurement of water level (tide gauge) and temperature. The water is pumped into the system and enters the main loop through the “debubler” chamber. The later is one of the main features of the Ferrybox, which removes air bubbles that interfere in the optical sensors. The oxygen sensor is placed inside the debubler, from which the water is conducted to the main loop by an internal pump. The basic configuration of the main circulation loop comprises sensors for the measurement of temperature, conductivity, salinity, turbidity, fluorescence (chlorophyll) and pH. The modular concept of the system allows an easily expansion for the installation of other sensors and a CDOM (colored dissolved organic matter) probe was installed later in July, 2008. A description of the main sensors is given in Table 2.

The functioning of the system is controlled by a computer and a series of house keeping parameters. Flow rates and pressure inside the main loop are recorded in order to supervise the circulation of the water. Another important attribute for the autonomy of the system is its self-cleaning feature. It ensures long-term stability and accuracy of the system by preventing biofouling. As a default, once a day the system is flushed with high pressure freshwater, followed by injection of sulfuric acid reaching low pH of around 2.00. Additionally, the inlet tube is flushed back by freshwater in order to prevent blockages. However, biofouling is severe in sub-tropical regions, such as in the study area, requiring further cleaning strategies. The cycle was, therefore, set to have twice a day a complementary

injection of sodium hypochlorite (~pH 9.00). The stationary and the pocket system have been developed with an industrial partner and are commercially available (4H-Jena engineering GmbH, Germany).

Data are logged each minute and sent daily to a regional server through a local connection network (LAN-Intranet). Transfer of data is made automatically to the online data base (<http://TSdata.hzg.de>) where different tools allow the visualization and download of the data.

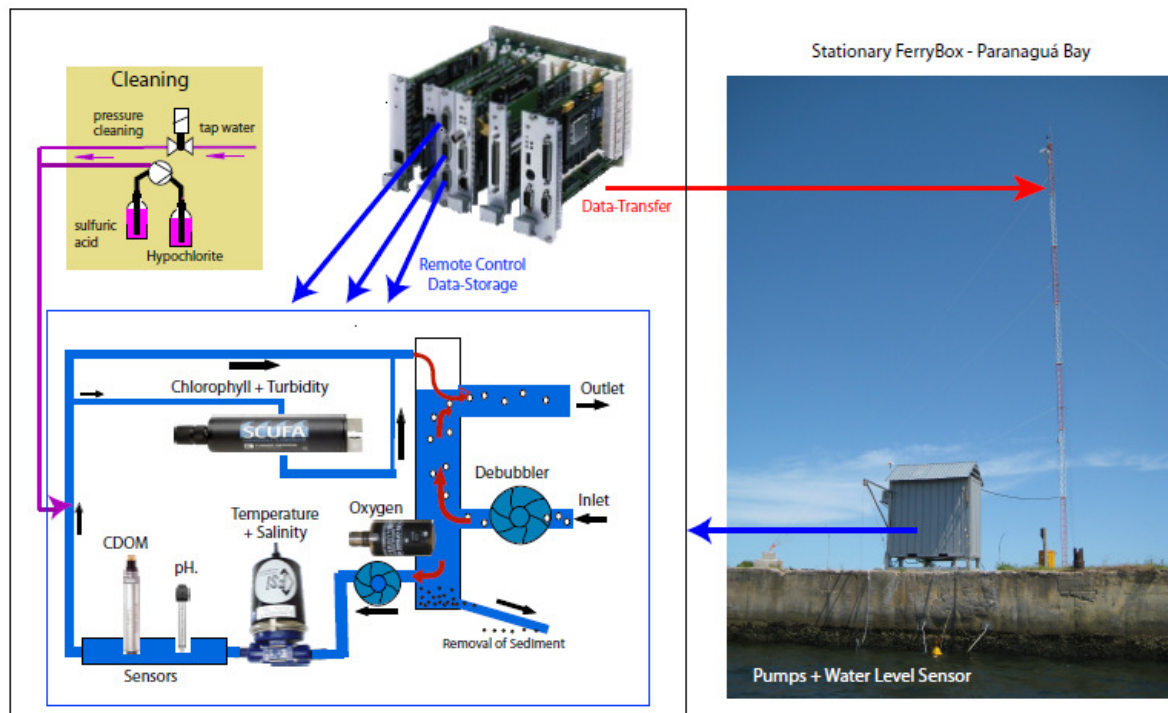


Figure 2: Scheme of the stationary FerryBox from Paranaguá Bay.

Together with the stationary Ferrybox system, a mobile version was tested in Paranaguá Bay. This so called Pocket FerryBox is a compact version of the Stationary one developed in order to perform surveys on small platforms. It was first tested in Paranaguá Bay during sampling surveys along the bay and more detailed information are given by Schroeder et al. (2008). It has also been used to collect comparative data to evaluate the use of Stationary Ferrybox data as real-time input data to hydrodynamic models. The systems were inter-calibrated and several surveys were performed between 2007 and 2009 in order to assess the spatial variation of parameters and applicability of the stationary measurements representing the variability in the outlet. Along the longitudinal transect that followed the main navigation channel (Galheta Channel), continuous measurements in sub-surface (~1 m depth) were performed from the head to the mouth of the estuary starting at

ebb tides. The cross section transects were performed with the Pocket FerryBox as continuous measurements from the vicinity of the Stationary FerryBox until the north margin of the estuary mouth (see Fig. 1), in order to observe the variability of the parameters as the water passes along the main estuarine channel.

Table 2: Main components of the Stationary FerryBox in Paranaguá Bay (see Fig. 2).

Parameter	Range	Unit	Accuracy	Resolution	Uncertainties or bias	Instrument, Manufacturer
water temperature	-10 to 50	°C	0.1	0.01	due to heating up in the tubes (max. 0.5°C)	Excell, Falmouth Scientific Inc., USA
salinity	0 to 50		0.02	0.001		
dissolved oxygen	0 – 150	%	8 or 5%	1		Optode 3830, Aanderaa, Norway
pH	0 to 14	-	0.05	0.01		CPS 11, Endress&Hauser, Germany
chlorophyll-a fluorescence	0.02 to 80	$\mu\text{g}\cdot\text{dm}^{-3}$	5%	0.5	due changing fluorescence yield	SCUFA-II, Turner Design, USA
Turbidity	0.05 to 200	NTU	5%	0.05	offset due to very small bubbles	
CDOM	0.02-2	ppm humic acid	5%	0.02		Cyclops-7, Turner Design, USA

Data Processing

No significant differences were observed between sub-surface and bottom measurements. Therefore, data from both water layers were merged into one single data set. The data from the Stationary FerryBox in Brazil were merged into files providing a long series of records from September 2007 until June 2010. Considering the ‘minute’ measurements, it was expected to access around 1,600,000 measurements for each variable; however, besides the cleaning cycles, and periods with problems in the equipment due to bio-fouling and electrical shut downs, the data were filtered in order to present the most reliable information. Different filters were applied, starting with values of low flow in the main loop. All data measured in periods of insufficient flow (less than $6 \text{ dm}^3\cdot\text{min}^{-1}$) were discarded.

The second step regarded the verification of the variance of the measurements. The sensors perform measurements with different time lags and log the average for each minute of measurements. Therefore, to keep the verification of data quality, the deviation of the measurements per minute was also used to filter the data. A value of 1 % was determined as maximum deviation for measurements of salinity, temperature, pH, dissolved oxygen and CDOM. For fluorescence and turbidity, 5% deviation per minute was assumed to be reliable based on the sensitivity of the sensor and the standard deviation observed.

The CDOM calibration was performed through total carbon concentrations in humic acid solutions (Sigma-Aldrich). Maximum and minimum measured concentrations were

determined as 2 and 0.016 ppm. For the SCUFA sensor, the manufacturer calibration was used with detection limits of 0.02 and 80 $\mu\text{g}\cdot\text{dm}^{-3}$ for chlorophyll-*a* fluorescence and 0.05 to 200 NTU for turbidity; however, the high fluctuation of fluorescence measurements, especially in the period between November 2007 and February 2008, indicated that other approaches were necessary to better sort the records. Therefore, chlorophyll concentrations performed by the classic approach of acetone extraction and fluorometer determination were compared with data to define the maximum observed concentrations. The chlorophyll concentration of 50 $\mu\text{g}\cdot\text{dm}^{-3}$, which has been also reported as the maxima in Paranaguá Bay (Lana et al., 2000) was then assumed as the detection limit for fluorescence.

pH calibration followed the NBS standards (7,00 and 9,00). Also a shift between the pH values measured between September 2007 and May, 2008 and the values measured for the rest of period was observed. The fluctuation of the data seemed similar, with a lag of around 0.7. This behavior seems to be due to a problem in logging the calibration values. Therefore, an analysis of data for the same following period was performed in order to verify if a simple correction of the data would be suitable to match the real values. The difference between the values measured in 2007-2008 differed on average with 0.68 ± 0.09 . The pH data from this period are corrected by this value, keeping in mind that this correction might decrease the confidence of the data.

The filter application resulted in a final data set where gaps of data could be easily found. Another approach was needed in order to allow a better visualization of records. Two approaches were used: hourly and daily averages. Remaining gaps of data were recorded as empty cells. These two approaches were suitable but the hourly records showed the tidal influence on data. In order to analyze the effect of different events, such as storms and blooms, the daily data were used.

Daily precipitation and river discharge levels were provided by the Department of Hydrology of the Paraná Waters Institute (DHID). The rainfall data was analyzed for the measurement station placed at the City of Paranaguá (around 25 km from the FerryBox station) expressing the situation in the middle area of Paranaguá Bay. The river discharge was analyzed also for two locations, one in the head of the estuary and another in the vicinity of the FerryBox station (see Fig. 1). The Cachoeira River, which is the main river in Paranaguá Bay with an average flow of around $40 \text{ m}^3\cdot\text{s}^{-1}$, has three stations measuring the water level. No information was available for the Guaraguaçu River, therefore an estimation based on the catchment area and the discharge of the nearest river with monitoring station was performed according to RHA (2008).

Results

The results are grouped to first present an analysis of the monthly accumulated precipitation and average river discharge to define the seasonality in Paranaguá Bay, followed by the description of the water properties along the estuary body according to the dry and rainy periods. The applicability of the FerryBox monitoring as input data to hydrodynamics models of Paranaguá Bay was tested through measurements of cross sections in the estuary mouth. A description of the long term fluctuations is presented based on the parameters monitored by the Stationary FerryBox from the period between September 2007 and June 2010. The measurements were analyzed in order to assess the influence of the water level, as an indicator of tidal forcing, and the influence of the fluctuations in precipitation and river discharge.

Seasonal Periods: analysis of rainfall and discharge data

It is important to mention that the denotation of a dry season in the subtropical region of Paranaguá Bay is relative, because there is not such a drought period in the area but the precipitation levels and days of rain can be two times higher in the period of summer and spring (Vanhoni and Mendonça, 2008). The seasonality of rainy (spring and summer) and dry seasons (autumn and winter) can be visualized through precipitation and river discharge patterns (Fig. 3). Maxima river discharges were observed in January 2008 and 2010, while the precipitation levels tend to increase during this period but high fluctuations are observed along the year. The highest accumulated precipitation level up 570 mm during a month was observed in January 2008, while the lowest accumulated level of around 14 mm was observed later that year in July.

It seems that no clear definition of the seasonal limits (as a fixed date) can be determined on the basis of the data, although the highest monthly accumulated precipitation and average river discharge are observed in the spring/summer period while the the lowest are registered during autumn/winter. Moreover, a significant positive correlation is observed between the daily levels of rainfall and river discharge (see box in Fig. 3).

Cachoeira river, located in the head of the estuary, presented an average discharge of $45 \text{ m}^3 \cdot \text{s}^{-1}$ whereas Guaraguaçu river discharge was around $10 \text{ m}^3 \cdot \text{s}^{-1}$. Besides of the different contribution in terms of freshwater input to the bay, the location and the main features of both rivers must be taken into account. The catchment area of Cachoeira River (500 km^2) presents a declivity gradient ranging from 0 to more than 47% (de Paula and Cunico, 2007), while Guaraguaçu is a coastal plain river with very low hydraulic gradient. Cachoeira River presents waters with high particulate matter, while Guaraguaçu waters seem to have high concentration of yellow substances in its dark brown waters.

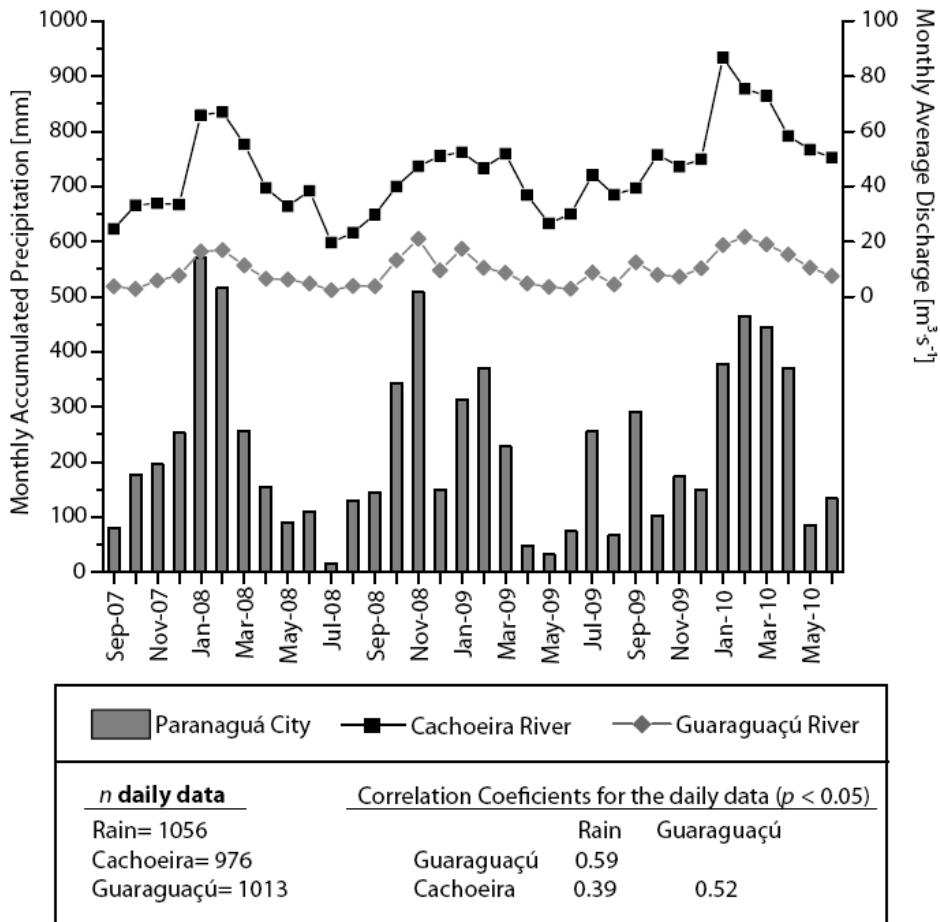


Figure 3: Monthly accumulated precipitation at Paranaguá City and monthly average discharge for Cachoeira and Guaraguaçu rivers from September 2007 to June 2010. Number of daily measurements and correlation coefficients between rain and discharge presented in the table.

Distribution of water properties along the Paranaguá estuary – Pocket FerryBox measurements along the longitudinal transect

Assessing the variability of the water properties along the estuary body is fundamental to understand the parameters fluctuations in the monitoring site, as well as to test the FerryBox representativeness as a descriptor of the overall conditions for the entire system. The distribution of parameters in Paranaguá Bay was assessed through continuous surface measurements along the longitudinal transect (along the main navigation channel, see also Schroeder et al., 2008) performed with the Pocket FerryBox representing the dry (September 2008) and the rainy season (January 2009) (Fig. 4 and 5). A *t*-test indicated that all parameters measured were significantly different ($p < 0.05$) between the two sampling situations, indicating that the seasonality is a major factor influencing the distribution of the

parameters in Paranaguá Bay. Moreover, all parameters presented significant correlation with salinity in both seasons (see boxes in Fig. 4 and 5).

Salinity presents a permanent increasing gradient towards the estuary mouth with a wider range during the rainy period. This is a clear indication of the influence of increasing river discharge during this period when salinity reached 0 PSU in the upper section of the bay. Lower temperatures ranging from 19 to 20 °C were observed in the dry period when it presented high negative correlation with salinity ($r = -0.90$), whereas increasing temperatures up to 30 °C were observed in the middle area of the estuary during the summer with weak correlation with salinity. The conservative pattern of pH, which ranged from the minima of 6.6 at the upper region to the maxima of 8.2 at the outlet of the bay in January, was showed by the permanent strong positive correlation with salinity. The freshwater discharge seems to be the main source of organic and particulate matter to the system, once CDOM and turbidity were negative correlated to salinity and higher averages of 0.7 ppm and 13.1 FNU were observed along the estuary in the summer, respectively.

Oxygen saturation levels in Paranaguá Bay ranged from average of 87 % in September 2008 to 80 % in January. Besides of presenting a positive correlation with salinity, oxygen levels were negatively correlated with chlorophyll-*a* fluorescence ($r = -0.72$) indicating that oxygen consumption is higher than production. The lowest oxygen saturation level of 60.6 % was observed in the vicinity of a zone of higher phytoplanktonic biomass and turbidity in the upper area of the bay during summer. Still, a similar correlation coefficient was observed between oxygen saturation and CDOM ($r = -0.75$). Therefore, primary production seems not to be the major factor controlling the oxygen levels. The combination of high chlorophyll, turbidity and CDOM together with low pH and oxygen levels indicates that heterotrophy predominates in Paranaguá Bay. Therefore, the balance between the input of organic matter enriched waters with high rates of oxygen consumption and the well oxygenated seawater may be controlling oxygen concentrations in Paranaguá bay.

Chlorophyll-*a* fluorescence and turbidity are also positive correlated among each other ($r = 0.57$), which is showed by the distribution of both variables along the estuary and higher values during the rainy season. A patch of higher phytoplankton biomass in January, with chlorophyll-*a* fluorescence maxima of $13.7 \mu\text{g}\cdot\text{dm}^{-3}$, was observed in the upper area of the estuary, together with a large zone of high turbidity reaching values up to 70 FNU. The same pattern of higher fluorescence and turbidity was observed in the upper region during the dry period, but increasing values were also registered for both parameters and CDOM in the lower area of the estuary. This zone was aligned with the Cotinga Island (see Fig. 1) in the vicinity of the Stationary FerryBox, which delimitates a channel were Guaraguaçu River outlet and other large tidal creeks are located.

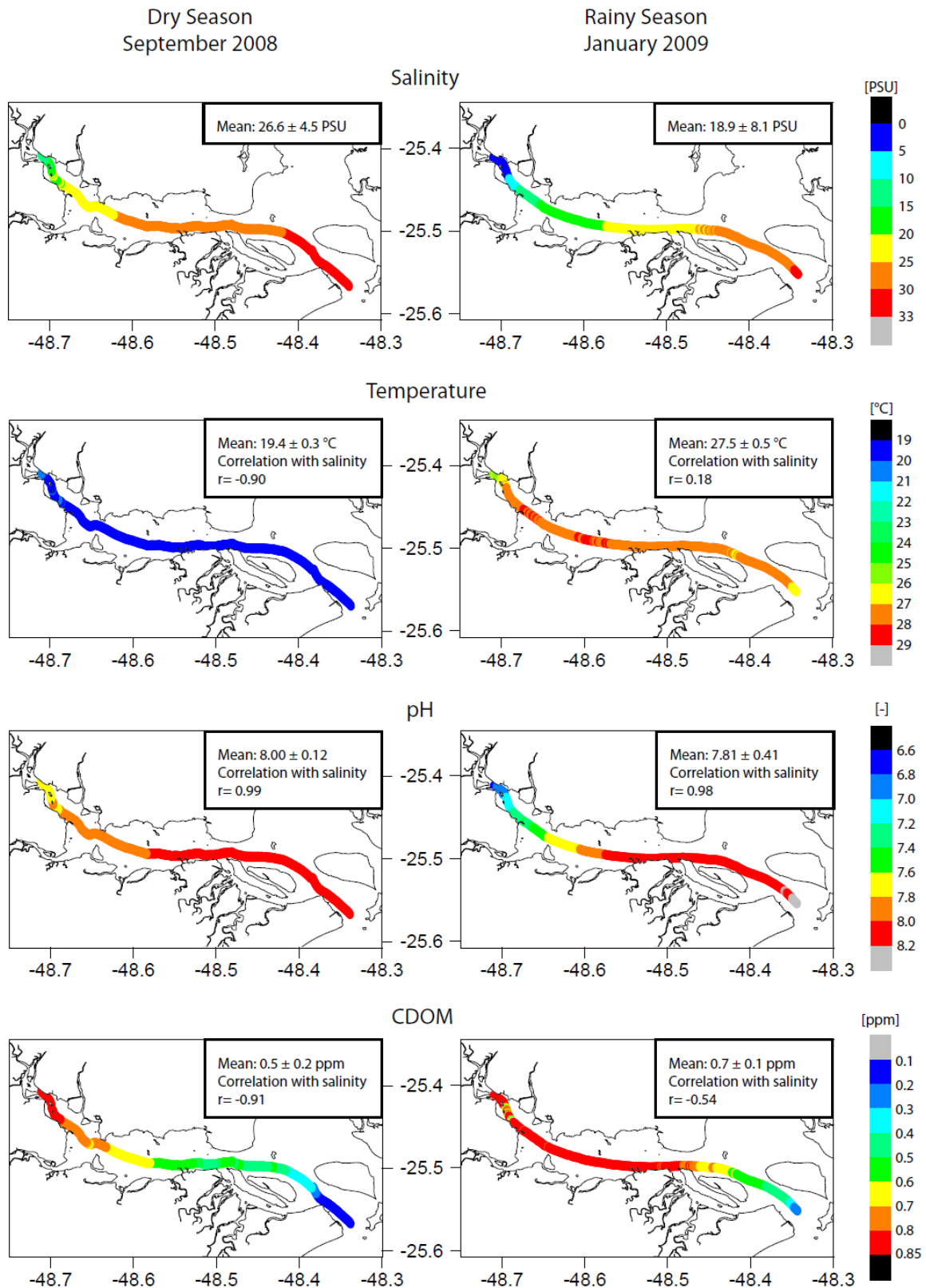


Figure 4: Continuous surface measurements of temperature, salinity, pH and CDOM along the longitudinal transect of Paranaguá Bay during the dry (September 2008) and rainy (January 2009) seasons. Mean and correlation coefficient with salinity are presented in the boxes (all correlations significant with $p < 0.05$, n -September 2008= 867 and n -January 2009= 670).

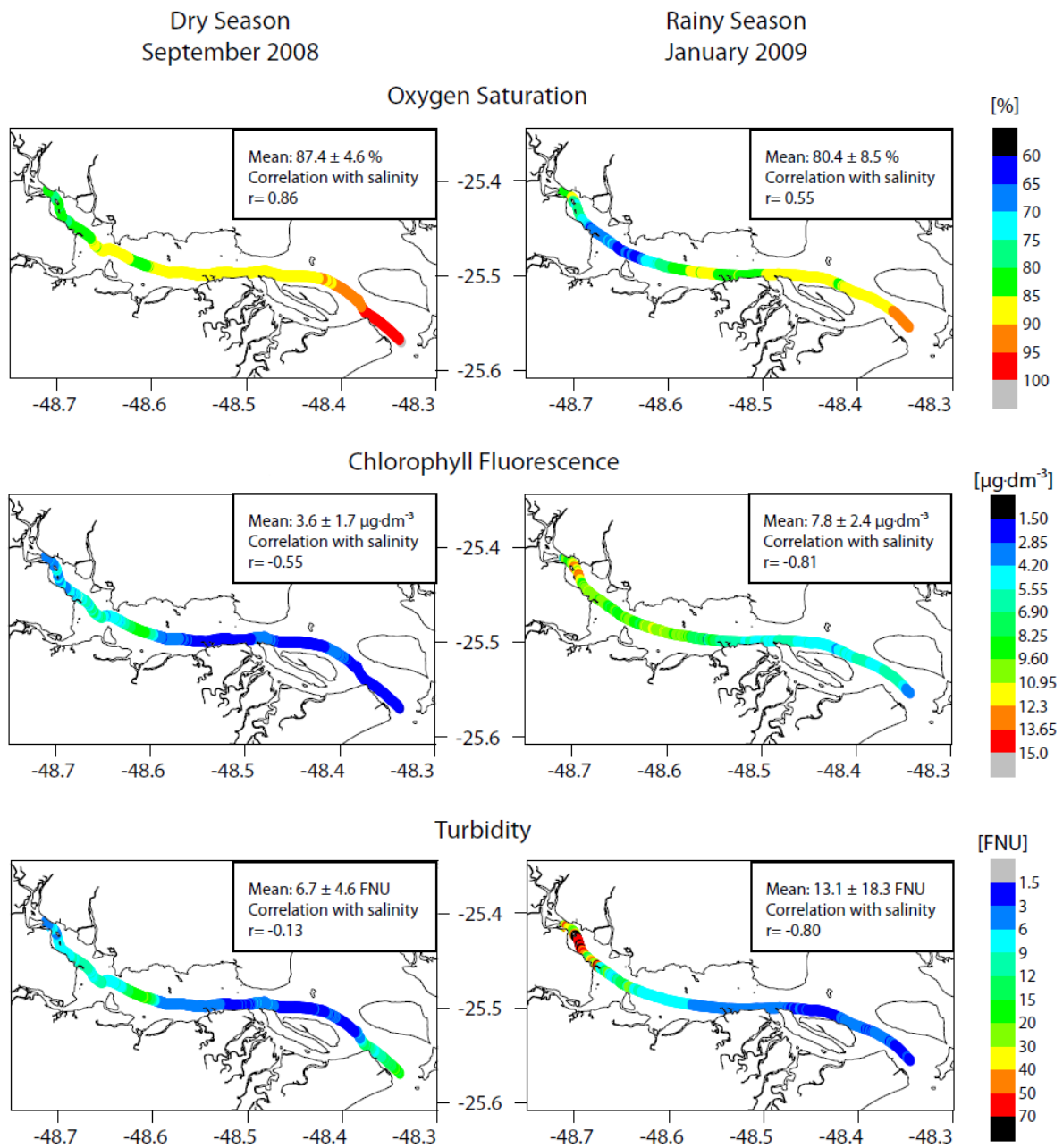


Figure 5: Continuous surface measurements of oxygen saturation, chlorophyll-a fluorescence and turbidity along the longitudinal transect of Paranaguá Bay during the dry (September 2008) and rainy (January 2009) seasons. Mean and correlation coefficient with salinity are presented in the boxes (all correlations significant with $p < 0.05$, n -September 2008= 867 and n -January 2009= 670).

In conclusion, it was observed that oxygen consumption overcomes primary production in Paranaguá Bay, especially around the zone of maximum turbidity. Moreover, the influence of tidal creeks and Guaraguaçu River may impose large influence on the fluctuation of water parameters such chlorophyll-a fluorescence, pH, CDOM and turbidity in the outlet of Paranaguá Bay.

Cross Section in the estuary mouth

The data presented in the previous section showed that Paranaguá Bay is a very dynamic system. The applicability of FerryBox data for hydrodynamic models was tested through joint functioning with Pocket FerryBox and measurements of the cross section that delimitates the south boundary of the estuary to better understand the behavior of water properties in the vicinity of the monitoring site and the coverage that these measurements represented. Salinity and temperature were considered in order to verify the applicability of the FerryBox measurements as input data for hydrodynamic models. The measurements performed during a tidal cycle in February 2008 are presented in the Figure 6, which presents the average of the station records during the time when the pocket Ferrybox measurements were performed across the navigation channel. It is observed a deviation between the stationary measurements and the perpendicular transect, even though the tide signal was clearly followed by both measuring devices.

The temperature measured in the station was in average 0.60 °C higher than the average for the whole cross section. Salinity was often higher along the cross section, and the difference with the values measured in the monitoring station ranged from 0.19 to 5 PSU. The variation of salinity in the station location during the tidal cycle seems to present a shift to the one observed across the channel profile, indicating the response delay due to the intrusion pattern. Nonetheless, the closest similarity between salinity measurements from the monitoring station and the cross section occurred during transects 4 and 13 which are representatives of the high tide period at the location of the stationary FerryBox. At these moments, the salinity is already decreasing across the channel, but it reaches values very close to the ones observed in the station area.

Two detailed perpendicular transects representing a different tidal situations are plotted with the bathymetric profile to present the fluctuations along the cross section (see Fig. 6). The main navigation channel (Galheta Channel) is shown in the center of the bathymetric plot, with maximum depth around 14 m. The following depression, known as the “Ponta do Poço” (“well point”), is characterized by an abrupt increase of depth in a well shape nearby the Stationary FerryBox. Salinity and temperature fluctuations are more expressive along the cross section than in the monitoring site. The influence of the well point is clear during the transect 6, when salinity reached around 33 in this location. In addition, salinity values seem to be constantly lower near the northern margin. During low tide, the decreasing peak of salinity observed over the well point indicates the location of ebb currents. Overall, the representativeness of the Stationary FerryBox seems to be more effective during high tides measured in the monitoring station.

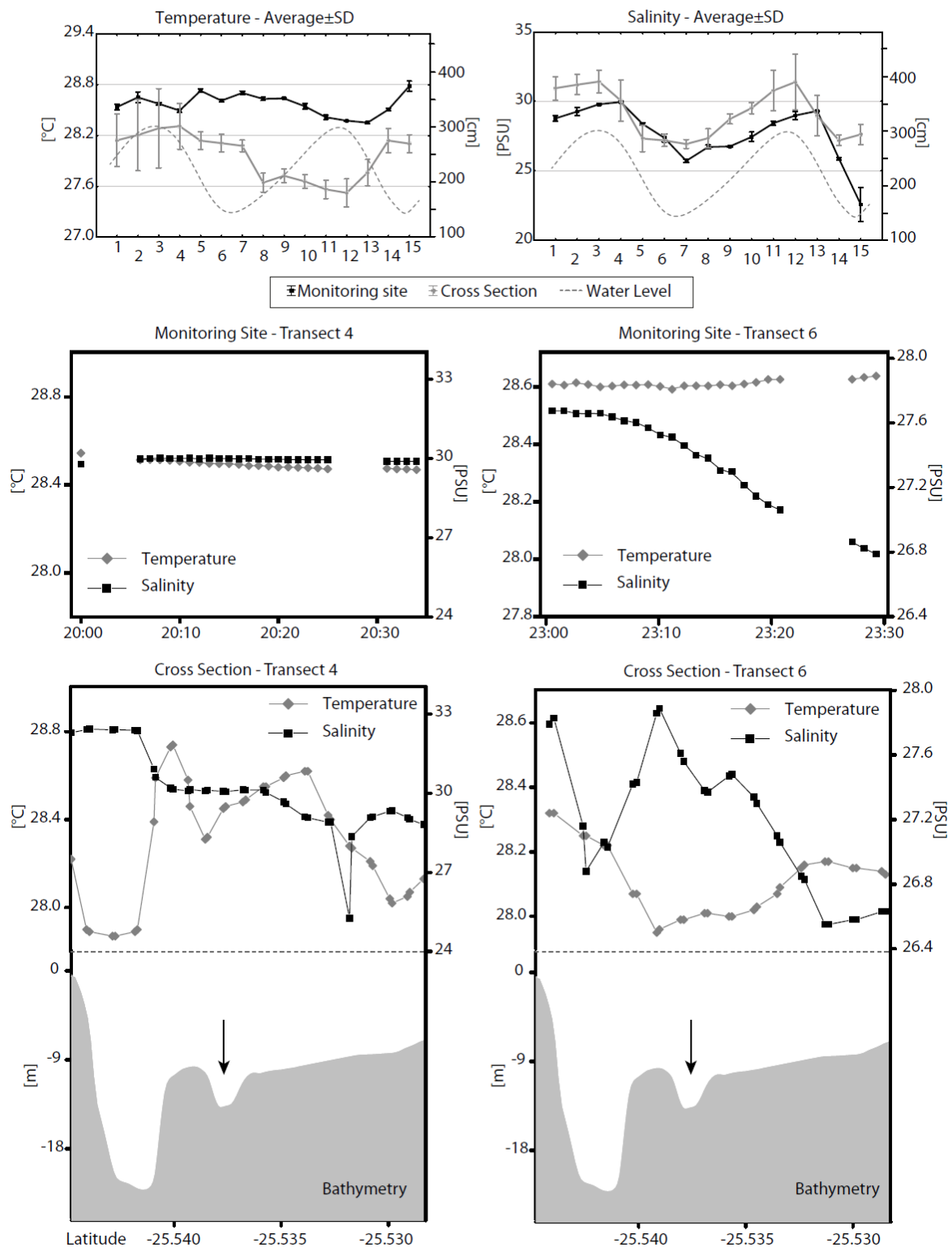


Figure 6: Average measurements of salinity and temperature from the Stationary FerryBox and from the cross section transects performed with the Pocket FerryBox (Average±Standard deviation) for 15 transects during 26 hours sampling. Detailed cross section plots of salinity and temperature measured by the Stationary and the Pocket systems, presented with a bathymetry profile of the cross section (the arrows indicate the location of the Galheta Channel).

Long term scales: description of parameters and trends during seasonal and annual cycles

The monitoring of water properties by the Stationary FerryBox in large temporal scale is presented by the data set of valid measurements for the period between September, 2007 and June 2010. Figures 7 and 8 show the hourly and daily averages presented to show how the processing of data smoothed the measurements to better visualize the fluctuations of the parameters in short and long term during the monitored period.

The subtropical estuary of Paranaguá Bay is a highly dynamic system and high deviation is observed for most of the variables. Considering the normal distribution of the parameters, the values into the 10-90% percentile of occurrence are here defined as the representatives of the general features of the monitoring site, while the extremes are related to special situations such as large freshwater input. The general characteristics of the area are represented by the trimmed mean at 10 % (which considers only the 10-90 % of distribution) presented on Table 3. Mean salinity and water temperature values were around 29 PSU and 25 °C, respectively, while pH values were around the oceanic waters values of 8.2 and mean oxygen saturation is 101 %. Fluorescence, as a proxy for chlorophyll-*a*, can be considered low (Bricker et al., 2003) oscillating around the average of 3.1 $\mu\text{g}\cdot\text{dm}^{-3}$ in the monitoring site, as well as turbidity and CDOM that were in around average values of 2.3 NTU and 0.04 ppm, respectively.

To better understand the relationship between variables, correlation analysis was performed considering the normal distribution of the parameters. Correlation coefficients (r), the number of valid measurements (n of daily averages) and the significance level (p) for the 10-90 % occurrence and for the upper and lower extremes are presented in the Table 5 and 6, respectively.

The seasonality of rainy (spring and summer) and dry seasons (autumn and winter) can be easily visualized through the temperature measurements (Fig. 7), which presented the highest month averages on January and February. No clear seasonality was observed for other parameters, even though some patterns can be highlighted. The general features observed in the monitoring site, described by the 10-90 % percentile of distribution (Tab. 4), indicated that increasing rainfall and river discharge occurred together with the increase of temperature, water level and turbidity, while decreasing salinity and oxygen saturation levels. Moreover, lower salinity waters seemed to be enriched with dissolved organic matter as indicated by the strong negative correlation between salinity and CDOM ($r = -0.52$), as well as slightly higher chlorophyll-*a* fluorescence ($r = -0.16$).

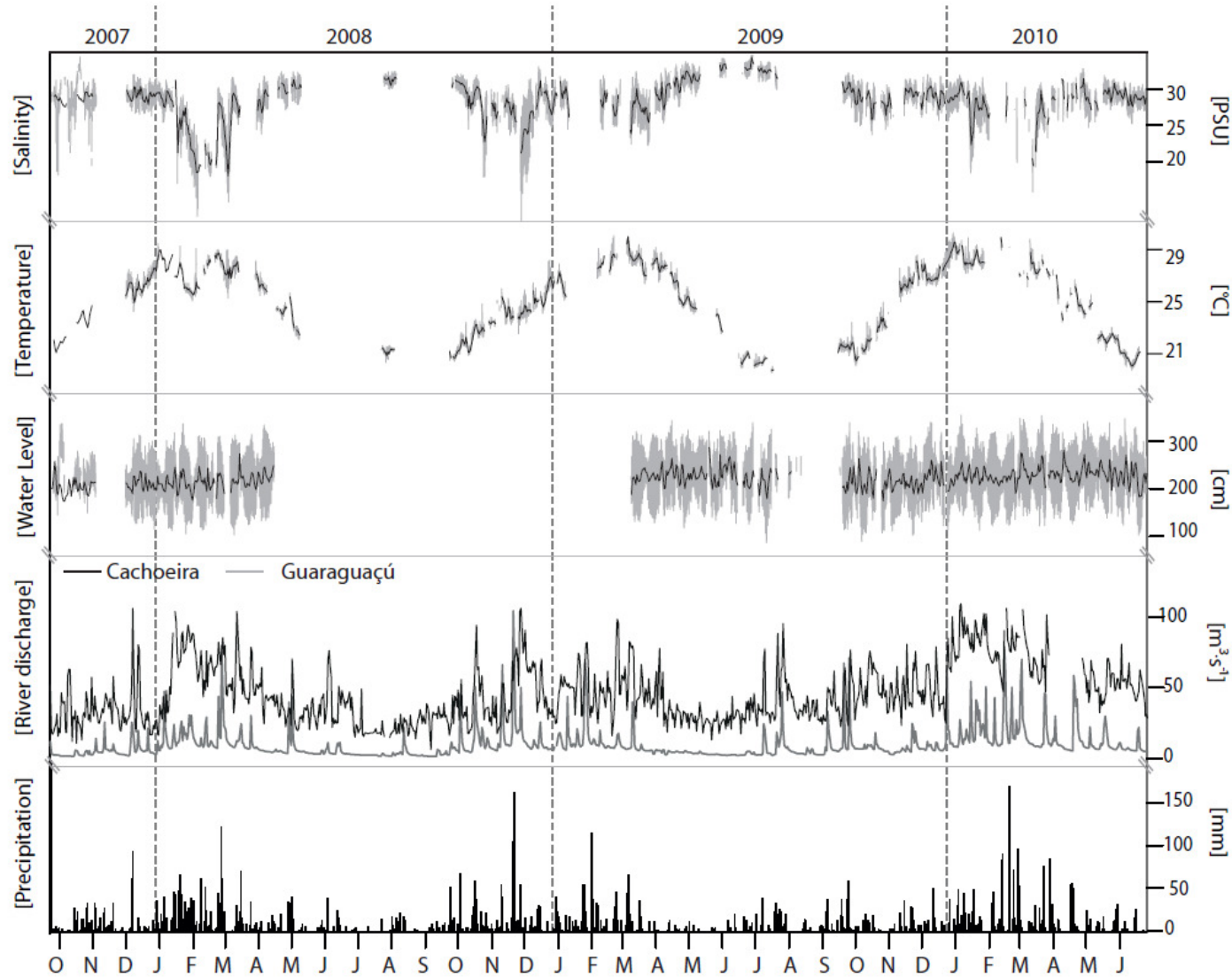


Figure 7: Daily precipitation levels, river discharge and measurements from the Stationary FerryBox for the parameters: water level, temperature and salinity; the FerryBox data is presented as hourly (gray lines) and daily (black lines) averages.

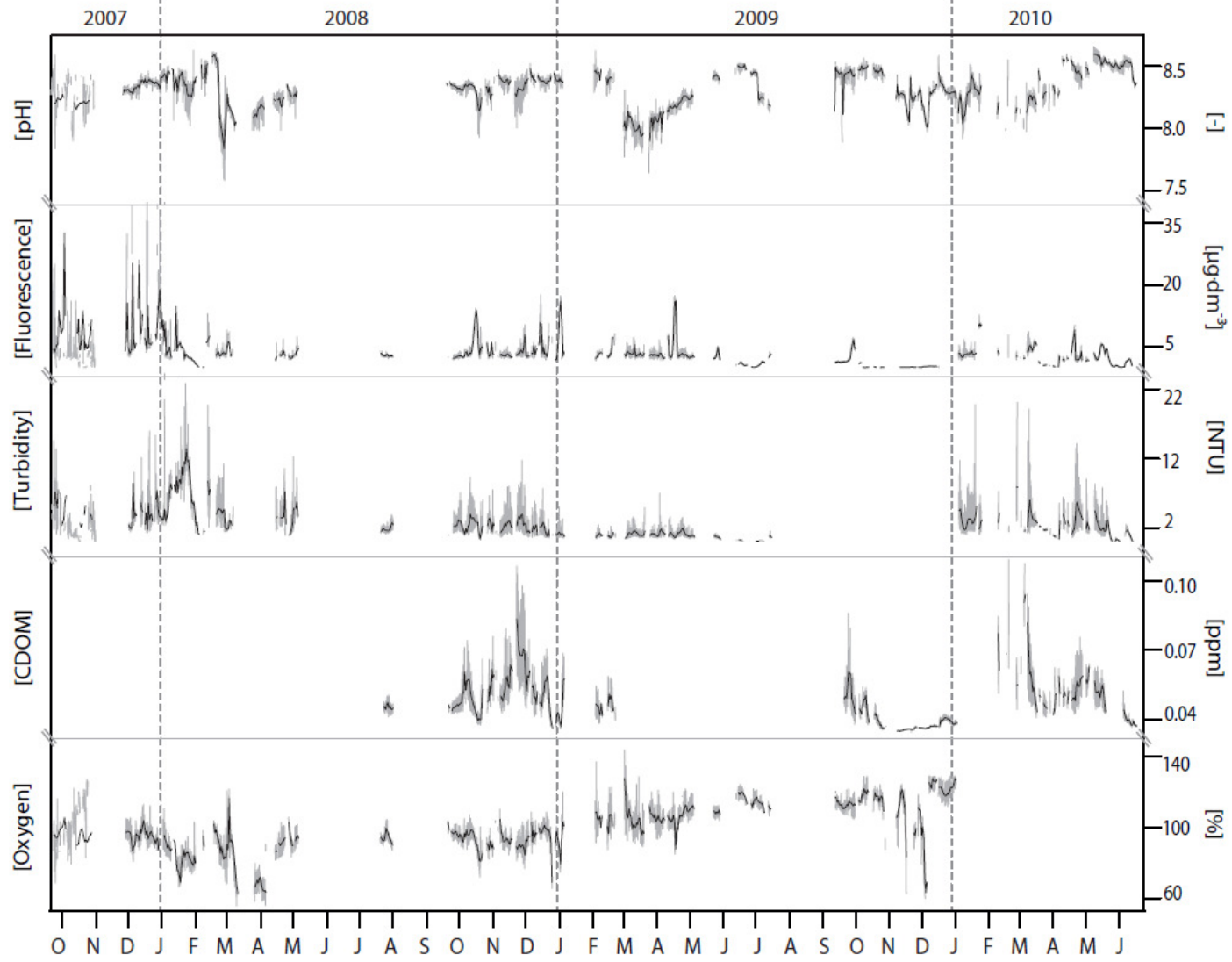


Figure 8: Measurements from the Stationary FerryBox for the parameters oxygen saturation, CDOM, turbidity, chlorophyll fluorescence and pH; the FerryBox data is presented as hourly (gray lines) and daily (black lines) averages.

Considering that the inner areas of the Paranaguá bay presented higher phytoplanktonic biomass (see Fig. 5), the patches of higher chlorophyll-a fluorescence are probably not produced on the site but transported from these areas. Moreover, the negative correlation between fluorescence and oxygen saturation ($r = -0.39$) also indicates that primary production is not the major control of oxygen levels. Still, oxygen fluctuations seem to be a result of the balance between the oxygenated seawater and the waters enriched with oxygen consumption material (organic and particulate matter) because of the negative correlation of oxygen levels with turbidity and CDOM.

When the lower and upper percentiles representing the extreme situations are analyzed (Tab. 5) the relationship between some parameters increased, whereas some new correlations were observed. Extreme situations due to increasing freshwater input are observed when the daily average salinity reached the lower percentiles below 18, which are significantly correlated to the rainfall ($r = -0.31$) and the discharge from Guaraguaçu ($r = -0.52$) and Cachoeira ($r = -0.78$) rivers. Moreover, the increasing rainfall and discharge that occurred together with increasing temperatures are related to higher fluorescence, turbidity and CDOM levels. The extreme values of oxygen are strongly direct correlated to salinity ($r = 0.82$) and pH ($r = 0.92$), whereas reversely to fluorescence ($r = -0.65$) and turbidity ($r = -0.61$). This may represent both the differences between the rainy and dry season, as well as the plumes from the Guaraguaçu River and from the tidal creeks in the vicinity of the monitoring site which may be enriched with organic and particulate matter.

Table 3: Basic statistics of the daily average measurements: valid number of records, mean, trimmed mean (10-90% of distribution), lower percentiles (10%), upper percentiles (90%), minimum and maximum values, variance and standard deviation.

	Valid N	Mean	Std. Dev.	Min.	Max.	Trimmed Mean	Lower Percentile (10%)	Upper Percentile (90%)
<i>Water Level [cm]</i>	488	216.21	19.51	137.80	276.60	215.96	191.94	240.38
<i>Salinity [PSU]</i>	578	28.45	2.63	18.05	34.33	28.73	25.66	31.24
<i>Temperature [°C]</i>	578	24.80	2.70	18.08	29.94	24.90	20.88	28.00
<i>pH</i>	603	8.14	0.35	7.13	8.60	8.17	7.57	8.49
<i>Oxygen Saturation [%]</i>	449	100.35	13.35	60.70	128.66	100.73	85.23	118.60
<i>Chlorophyll-a Fluorescence [$\mu\text{g}\cdot\text{dm}^{-3}$]</i>	521	3.72	3.63	0.03	32.61	3.10	0.24	7.61
<i>Turbidity [NTU]</i>	422	2.63	2.25	0.05	13.17	2.25	0.66	5.53
<i>CDOM [ppm]</i>	326	0.05	0.01	0.03	0.09	0.04	0.04	0.06

The oxygen saturation levels show an increasing trend in 2009. Even though there are no indications that primary production controls the dissolved oxygen fluctuations in the

estuary, one might say that the trophic status of the bay may be increasing leading to higher oxygen saturation. Still, such a trend is also not observed in the fluorescence records. Therefore, it seems that the increase in the oxygen saturation values might be a result of a drift of the oxygen sensor and unfortunately, no control measurements are available.

Table 4: Correlation coefficients (r) and number of data (n) of significant correlations ($p < 0.05$) between parameters for the 10-90 % distribution percentile of the daily averages.

	Rain Paranaguá	Guaraguaçu River Discharge	Cachoeira River Discharge	Water Level	Salinity	Temperature	pH	Oxygen Saturation	Chlorophyll Fluorescence	Turbidity
Water Level	0.12 $n=391$	0.14 $n=391$	0.24 $n=367$							
Salinity		-0.11 $n=462$	-0.23 $n=439$							
Temperature	0.01 $n=464$	0.11 $n=464$	0.32 $n=440$		-0.18 $n=382$					
pH				0.21 $n=226$		-0.27 $n=369$				
Oxygen Saturation	-0.23 $n=359$	-0.23 $n=359$	-0.11 $n=354$				0.40 $n=312$			
Chlorophyll Fluorescence					-0.16 $n=310$	0.13 $n=334$	-0.27 $n=338$	-0.39 $n=272$		
Turbidity	0.16 $n=338$	0.22 $n=338$	0.16 $n=316$			-0.12 $n=290$	-0.30 $n=278$	-0.54 $n=234$	0.14 $n=296$	
CDOM				0.32 $n=55$	-0.52 $n=163$			-0.20 $n=112$		0.24 $n=137$

Table 5: Correlation coefficients (r) and number of data (n) of significant correlations ($p < 0.05$) between parameters for the lower (10 %) and upper (90 %) distribution percentiles for the daily averages.

	Rain Paranaguá	Guaraguaçu River Discharge	Cachoeira River Discharge	Water Level	Salinity	Temperature	pH	Oxygen Saturation	Chlorophyll Fluorescence	Turbidity
Water Level										
Salinity	-0.30 $n=116$	-0.52 $n=116$	-0.80 $n=113$							
Temperature		0.37 $n=114$	0.40 $n=112$		-0.95 $n=34$					
pH				0.49 $n=25$	0.84 $n=13$					
Oxygen Saturation					0.82 $n=24$		0.92 $n=24$			
Chlorophyll Fluorescence	0.27 $n=108$	0.20 $n=108$				0.98 $n=16$	-0.87 $n=20$	-0.65 $n=19$		
Turbidity	0.43 $n=84$	0.54 $n=84$	0.56 $n=81$		-0.78 $n=38$	0.60 $n=31$	-0.73 $n=14$	-0.61 $n=22$	0.75 $n=11$	
CDOM	0.26 $n=129$	0.43 $n=128$	0.47 $n=127$		-0.56 $n=17$	0.43 $n=32$			0.50 $n=41$	

Overall, the fluctuation of the analyzed parameters confirms that Paranaguá Bay is a highly dynamic system, but the extreme situations may show the influence of the major factors controlling the variation of water properties, such as the tidal forcing and the freshwater input. Therefore, to test the relative importance of each of these factors it is important to zoom into the data set and select specific conditions in order to observe the parameters pattern.

Tidal influence on water properties

Even though the daily water level averages presented a direct correlation with the freshwater input, it was assumed that the water level in the region is mainly driven by the tidal forcing during low rainfall and river discharge. The hourly data were used to test the influence of the tidal forcing on the water properties. The fluctuations of water level are clearly observed in the hourly averages for most of the other parameters, with significant albeit weak correlation (Tab. 6) with pH ($r= 0.07$), oxygen saturation ($r= 0.07$), turbidity ($r= -0.03$) and CDOM ($r= -0.10$). The water level is closely tracked by the salinity fluctuations ($r= 0.32$), but stronger correlations are observed between salinity and the other parameters. The strong negative correlation of salinity and CDOM ($r= -0.62$) confirms that the waters with lower salinities are enriched with dissolved organic carbon as well as with particulate matter (turbidity, $r= -0.20$), whereas lower dissolved oxygen levels ($r= 0.32$) and pH ($r= 0.20$).

Table 6: Coefficients and number of data (n) for significant correlation ($p<0.05$) of the hourly averages for the parameters with water level and salinity.

	<i>Salinity</i>	<i>Temperature</i>	<i>pH</i>	<i>Oxygen saturation</i>	<i>Chlorophyll Fluorescence</i>	<i>Turbidity</i>	<i>CDOM</i>
<i>Water Level</i>	0.39 n=8020		0.07 n=8056	0.07 n=5366		-0.03 n=4758	-0.1 n=3364
<i>Salinity</i>		-0.32 n=10908	0.20 n=10644	0.32 n=8254	-0.03 n=9046	-0.20 n=7402	-0.62 n=5567

Even though significant correlation is observed between the parameters and salinity, the large data set and the marked differences observed between the seasons might mask the fluctuations occurring within the tidal period. A period of low river discharge and precipitation, between April 22nd and May 6th, 2009 is presented in Figure 9 to exemplify the fluctuations of the variables in a spring and neap tide. Higher salinity occurred together with higher oxygen saturation and pH, while most of the higher chlorophyll fluorescence and turbidity peaks took place during ebb tides. The monitoring site is mainly oligotrophic

(Knoppers et al., 1987; Machado et al., 1997; Lana et al., 2000) with the occurrence of higher chlorophyll patches that are probably originated from the inner regions of the estuary. In some occasions is not clear whether they were completely transported towards the ocean during a tidal phase or re-entered the system in the next tidal phase. Moreover, less variation is observed during the water level peaks which indicate the better representativeness of the Stationary FerryBox as a monitoring site at high tides.

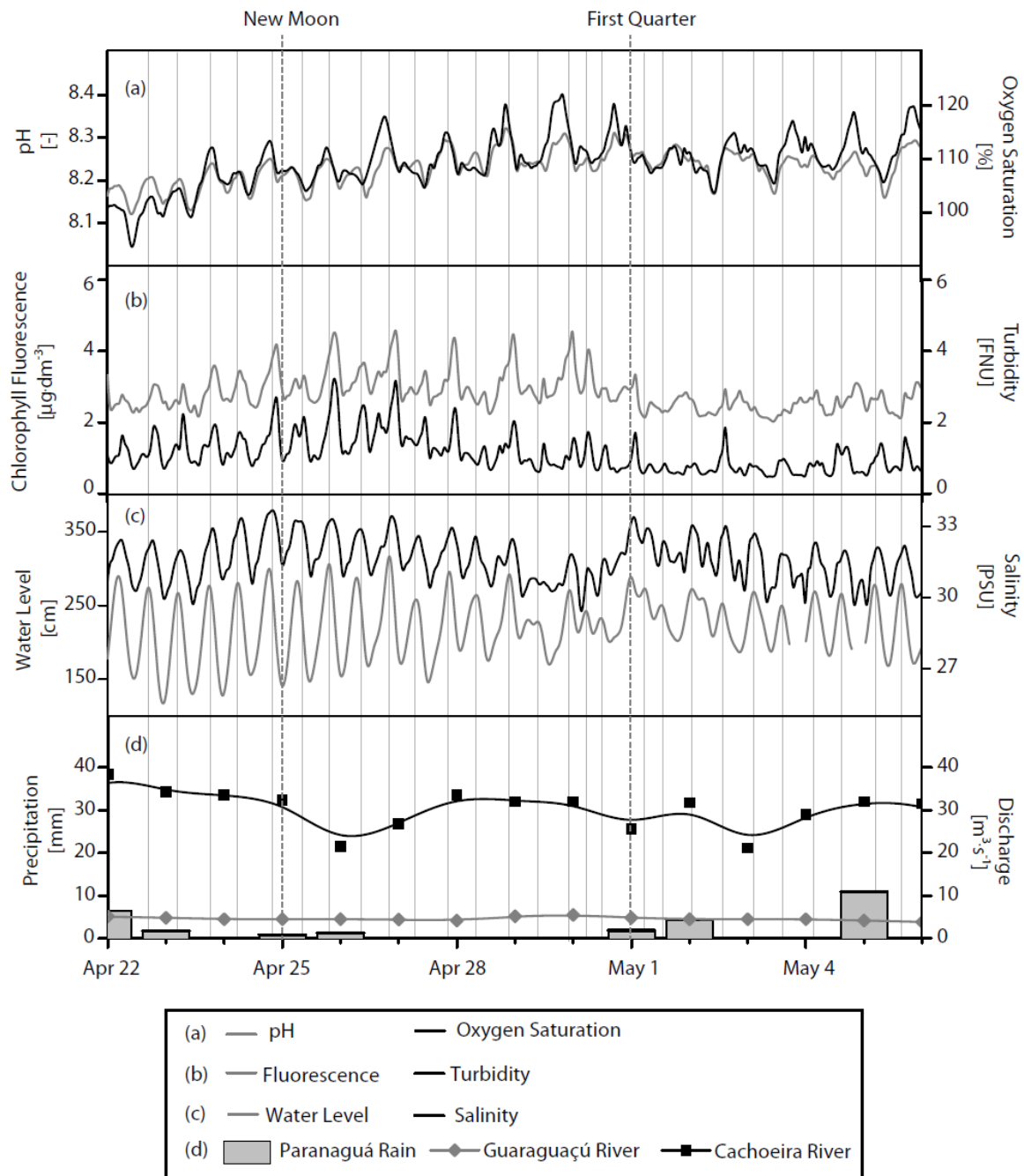


Figure 9: Daily precipitation and river discharge levels and hourly averages for water level (in cm), salinity, chlorophyll fluorescence and turbidity for the period between April 22nd and May 6th, 2009.

Influence of freshwater input on water properties

Succession of the precipitation seasons is a key factor for the understanding of the system's structural dynamics, even though no period can be considered effectively drought (Vanhoni and Mendonça, 2008). Depending on tidal forcing and seasonal differences in wind speed and river discharge, Paranaguá Bay may exhibit both homogeneous and stratified conditions because mean freshwater input can vary twofold between seasons modifying the circulation patterns (Marone et al., 2005). Physical, chemical and biological processes inside Paranaguá Bay are strongly influenced by climatic factors (Machado et al., 1997; Marone et al., 2005) and some periods are highlighted in this to verify how this influence may happen.

Figure 10a shows river discharge, water level and salinity fluctuations in a period within the rainy season from December, 2007 and March, 2008. The increasing discharge in the last fortnight of January, especially from the Cachoeira River with a daily rate that reached around $100 \text{ m}^3 \cdot \text{s}^{-1}$, resulted in a marked decrease in salinity and water level during the next 2 weeks with values around 15 PSU and 130 cm, respectively. The next peak of discharge that occurred in the end of February, when the daily flushing rate of Guaraguaçu River reached around 10 times over the annual average ($79 \text{ m}^3 \cdot \text{s}^{-1}$), resulted in sharp decrease in salinity that lasted for less days than the one occurred in the month before. That is an indication that even though Cachoeira River is responsible for the majority of freshwater input to the estuary, controlling salinity fluctuations especially during the rainy period, the extreme situations of high discharge from Guaraguaçu River also play an important role for the salinity decreases in the outlet of the bay.

The situation presented by the Figure 10b shows the effect of decreasing freshwater input on increasing salinity and water level in the period after summer in 2009. The last peaks of higher discharge between March and the first week of April resulted in decreasing salinity. Still, salinity shows a clear increasing trend following the decrease of the flushing rates of Cachoeira and Guaraguaçu rivers that confirms that the freshwater discharge is a major factor controlling the salinity fluctuation during the rainy period, while the influence of the tidal forcing may overcome the one of the freshwater input during the dry season.

It is clear that the seasonality is determinant on the variation of salinity as well as the distribution of the other parameters monitored by the Stationary Ferrybox are correlated to the salinity fluctuations along the longitudinal transect of Paranaguá Bay. Therefore, to analyze the effect of the freshwater discharge on the monitored site, two situations in the rainy and dry seasons are presented in the next sections.

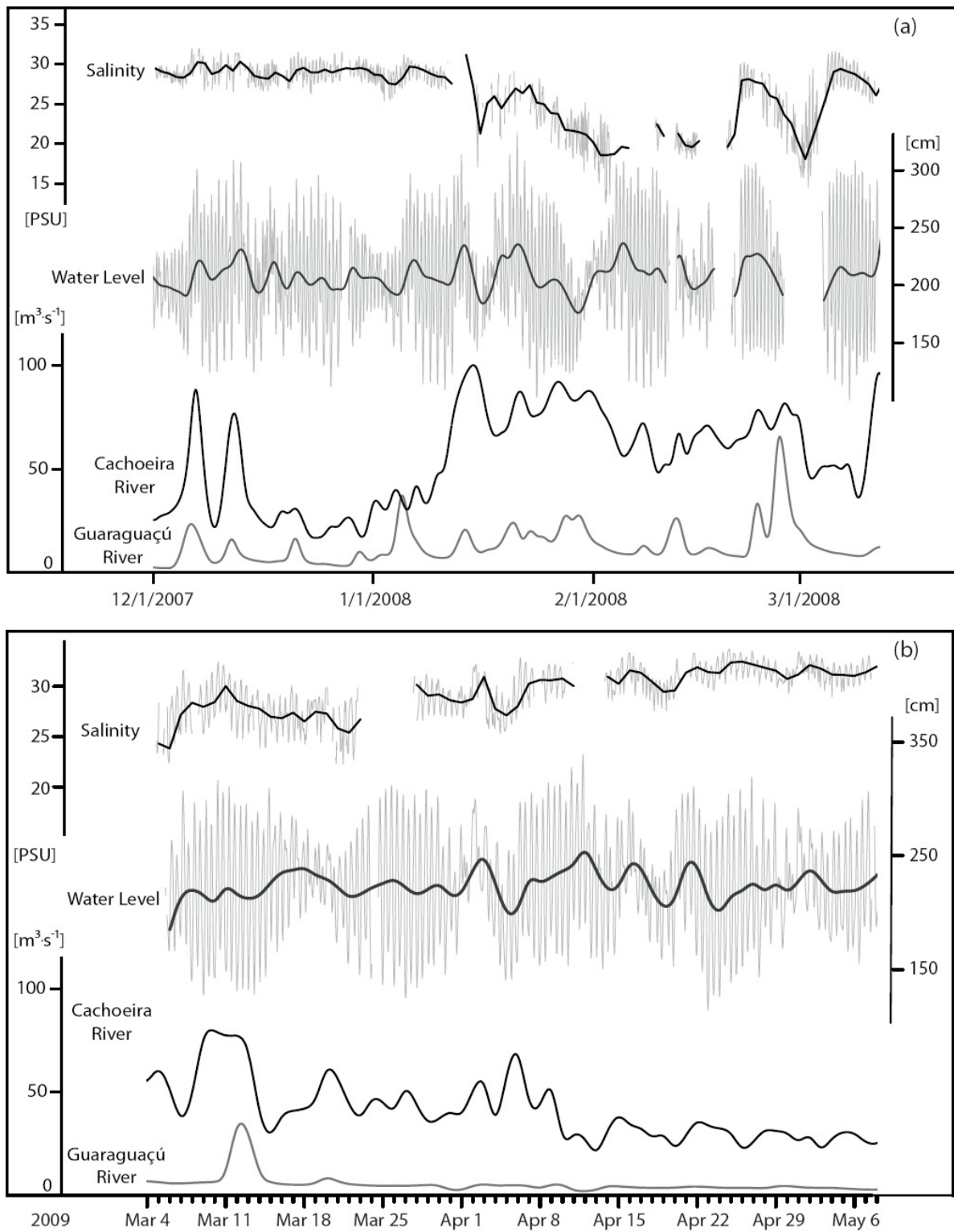


Figure 10: Daily discharge from Cachoeira and Guaraguaçu rivers, water level and salinity measurements from the Stationary FerryBox (hourly averages in gray and daily averages in black) during rainy season in 2008 (a) and beginning of dry season in 2009 (b).

Transition from the dry to the rainy season (2008-2009)

Figure 11 represents the transition to the rainy season between September, 2008 and January, 2009. Temperature shows an increasing pattern, while high fluctuation is observed for the other parameters. The influence of the first peaks of rainfall and river discharge that occurred before October, 5th resulted in a decrease of salinity, pH, turbidity and oxygen saturation while an increase in CDOM; however no influence is observed in the chlorophyll-*a* fluorescence behavior. Such a heavy precipitation event, that accounted for around 70 mm of deposition in a day, represents a diffuse freshwater input of more than $240 \text{ m}^3 \cdot \text{s}^{-1}$ that can be related to short lasting torrential storms. The isolated event, that may have been as well short, can temporally increase the flushing rate of the bay and, therefore, effect the development of the phytoplankton biomass (Ferreira et al., 2005). The next precipitation event that lasted from the 15th to the 21st of October resulted in large increase of river discharge. A sudden decrease in salinity, pH, oxygen, turbidity is observed, while a patch of high chlorophyll-*a* fluorescence, reaching $13 \mu\text{g} \cdot \text{dm}^{-3}$ occurs in a very similar pattern as the one observed by the freshwater input variation. It seems that while dilution might be the major factor during short precipitation events, the estuarine gradient seems to be pushed seawards during higher and longer discharge periods. Salinity and the related variables (pH, oxygen saturation, and CDOM) presented more direct responses to the variations in the freshwater input. Whereas some peaks of chlorophyll-*a* fluorescence are observed together with higher discharge, it is not very clear the influence of increasing rainfall and river input to the pattern of this variable during the following days. Therefore, other factors such as the nutrient availability should be considered when analyzing the phytoplanktonic biomass fluctuations.

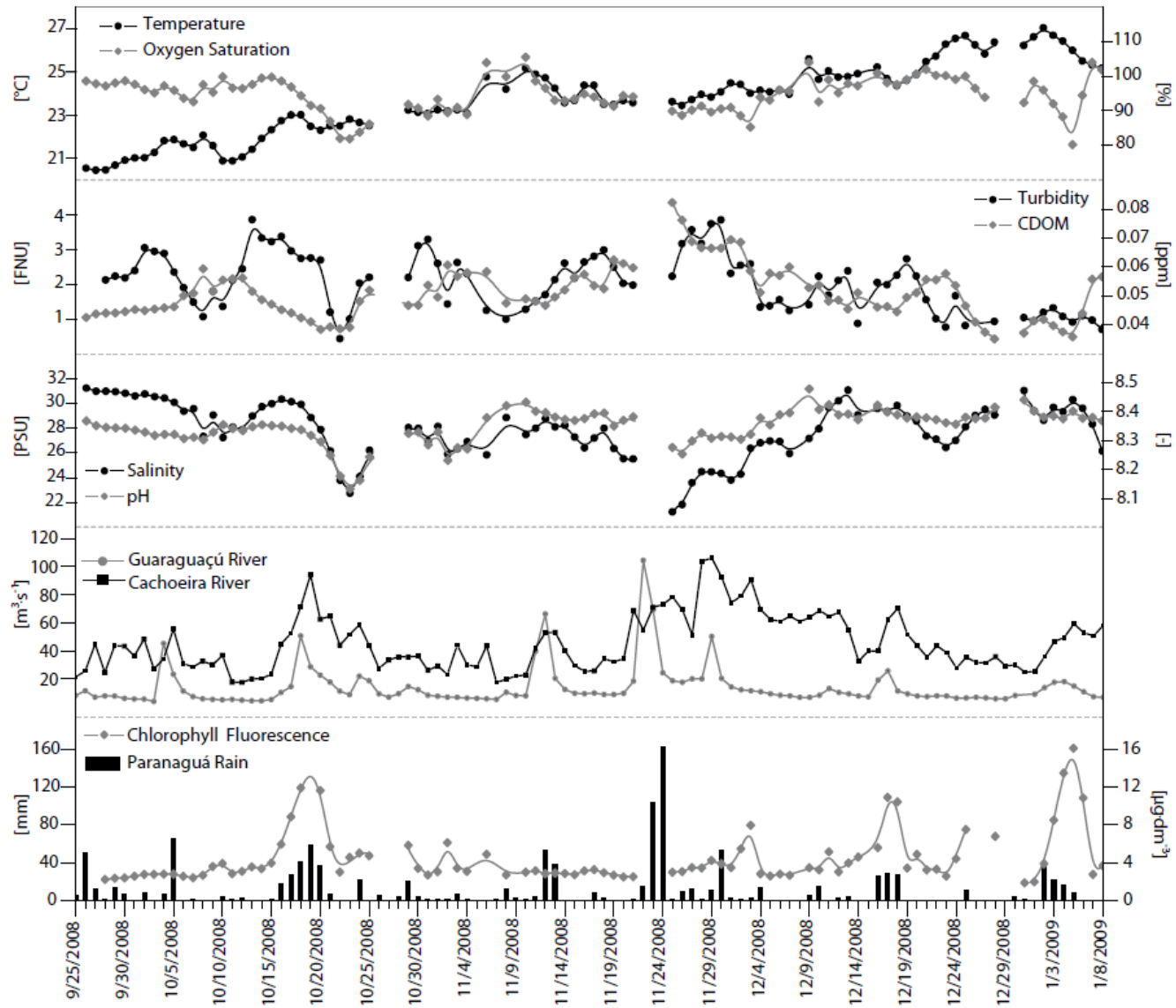


Figure 11: Daily accumulated precipitation, average river discharge and the Stationary FerryBox measurements during spring/summer of 2008-2009.

Transition from the rainy to the dry season (2009)

The period presented by Figure 12 (note that Figure 11 presents different scales than the ones presented in Figure 10) shows the transition between the rainy to the dry season in 2009. As observed in this figure, decreasing freshwater discharge leads to increasing salinity (see also Fig 10b). Moreover, the shift from summer to winter is observed by decreasing temperatures. The close relation of salinity with pH and oxygen saturation is still observed, but unfortunately no CDOM data was available for this period. Still, the fluctuations in river discharge are closely followed by the daily water level averages. The chlorophyll fluorescence is lower than the values measured during spring/summer, with the exception of a phytoplankton biomass peak reaching around $15 \mu\text{g}\cdot\text{dm}^{-3}$ on April 20th. This peak coincided with lower salinity and water level, indicating that it might be a high chlorophyll patch transported from the inner regions of the estuary. Moreover, such a pattern seems to be a late summer bloom but this possibility can only be tested with the information regarding daily fluctuations in nutrient concentrations.

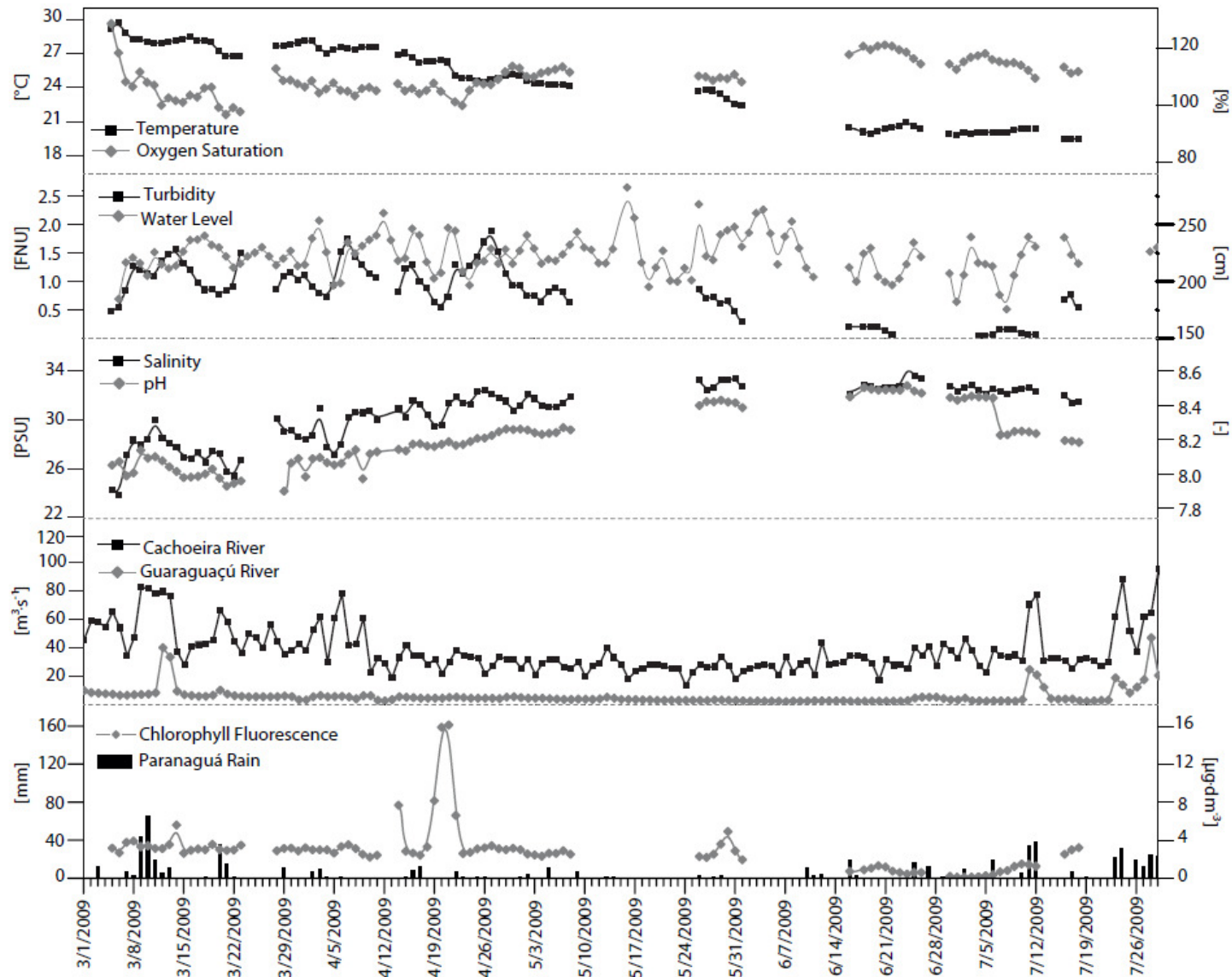


Figure 12: Daily accumulated precipitation, average river discharge and the Stationary FerryBox measurements during summer/winter of 2009.

Discussion

The data base built by applying the FerryBox technology is a great advantage in the monitoring of water properties in Brazil. Such operational systems represent a valuable update to the actual assessment techniques available in the country, providing a wide exchange of knowledge and consistent data set. Problems with severe bio-fouling and the remote operation of the Stationary FerryBox necessitated an optimization that improved the automatization of the system providing reliable information regarding the water dynamics in Paranaguá Bay.

The annual fluctuation is observed by water temperature data. The seasonal signal is not so clear for other parameters, even though specific situations can be highlighted as descriptors of the variations over the year. Abrupt decreases of salinity during high precipitation and river discharge periods, followed by pH and CDOM, especially during high discharge from Guaraguaçu River indicate the occurrence of plumes and fronts in the vicinity of the monitoring station. Therefore, the lateral heterogeneities produced by these plumes are responsible for important seasonal stratification in Paranaguá Bay, especially during the rainy period. Higher chlorophyll fluorescence and CDOM were observed during the warmer and wet periods, as expected due to the increase of temperature and freshwater input. High fluctuations of the precipitation levels and river discharge were observed specially in the transitional periods of 2009 (spring and autumn), but even though the strict determination of the seasonal periods through the FerryBox records is uncertain, the information registered in the almost 3 years of measurements provided a comprehensive overview of the water properties dynamics in the area.

The peaks of chlorophyll-a fluorescence during ebb tides and the negative correlation with salinity indicated that the high chlorophyll plumes are not produced in the measuring location but are produced in the inner regions of the bay and transported to the monitoring site by the tide. Moreover, oxygen consumption seems to dominate over primary production along the estuary, especially at inner areas and higher turbidity regions.

The phytoplankton dynamics are regulated by the combination of temperature and freshwater discharge along the main axis of the bay. During the rainy periods, the decrease of salinity together with the increase of temperature stimulates the development of higher fluorescence plumes, especially in the middle area of the bay. The freshwater input is the main source of dissolved organic matter observed along the main body of the estuary shown by increases of CDOM at lower salinities. In addition, the parameters seem to be closer to conservative behavior in the dry period, in which the tidal exchange might be the major factor

regulating the variation of the water properties. During this period, the distribution of the water properties along the bay shows less variation.

It is possible to use the salinity measurement from the Stationary FerryBox as a descriptor of the outlet of Paranaguá Bay during periods of high tide at the monitoring site. The representativeness of the Stationary FerryBox measurements is hampered by the high dynamics of the system. Paranaguá Bay is a subtropical estuary with high rates of freshwater input leading to an average renewal time of around 3 days. In such highly dynamic systems, it is difficult to define a single sampling point, but the records showed that under defined occasions this extrapolation is possible.

The lateral heterogeneities created by river and tidal creek discharges can have great influence on the water property distribution, as observed by the plumes of lower salinities measured during higher freshwater discharge. Moreover, the indications that tidal currents can be responsible for the horizontal stratification across the navigation channel limit the utilization of the stationary FerryBox measurements as input data for hydrodynamic models; however, the monitoring point can be considered viable as a reference point for an environmental impact study for the construction of the new harbour planned in the area. Nevertheless, the monitoring of water properties in an estuarine system is not likely to be performed by a single measuring point. Considering the presence of mangrove, tidal creeks and several rivers, important information would be lost by this approach. Water properties monitoring in Paranaguá Bay should rely on the combination of strategies, such as the measurements performed at one point in order to observe long term variations and the assessment of a series of parameters along the estuary axis or gradients.

Acknowledgments

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Edson Sakae Nagashima from the Hydrology Department (DHID) from the Direction of Management and Control of Water Uses (DPCA) of the Paraná Waters Institute.

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**“The pocketFerryBox - A New Portable Device for Water Quality Monitoring
in Oceans and Rivers”**

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The pocketFerryBox - A New Portable Device for Water Quality Monitoring in Oceans and Rivers

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Synopsis

A new method called Pocket FerryBox is presented, which improves the monitoring of water quality in coastal waters, estuaries, rivers and lakes. The 'FerryBox' is an automated flow-through system, installed on *Ships of Opportunity* for operational observations. The technology which exists already for some years has been extended for operation on small boats. The system allows a fast survey of water depth, temperature, salinity, turbidity, oxygen, pH, coloured dissolved organic matter (CDOM) and the algal pigments chlorophyll, phycocyanin and phycoerythrin. Results show that with this system water quality parameters can be measured in a reliable and easy way.

Introduction

Monitoring of coastal waters or estuaries requires dense sampling in space and time in order to catch short-term events which might have a strong impact on the coastal ecosystem, such as exceptional phytoplankton blooms or changes caused by storms. Existing observations mostly lack the spatial coverage and temporal resolution required to determine the state of the marine environment and changes therein.

Thus a clear need exists to improve our observational capacities; not only on standard physical parameters such as temperature and salinity, but also on chemical (nutrients) and biological (phytoplankton, zooplankton) parameters. This could be used for the validation and calibration of models and could be linked to observations by satellites or aircrafts (remote sensing), to reveal spatial scales of phenomena. Thus both spatial and temporal scales of marine processes can be better resolved and understood. Most importantly it could provide the detailed, regular, un-aliased data needed to enable assessment of effects of climate change on ocean and coastal environments.

The lack of monitoring systems that provide continuous observations of the marine environment, especially in coastal areas and estuaries is a serious hindrance to the understanding of these systems. Currently, operational monitoring is mainly carried out by manual sampling and analysis during ship cruises. Autonomous measuring systems on buoys

allow measurement of standard oceanographic parameters (temperature, salinity, currents) and in some cases other parameters, e.g., turbidity, oxygen and chlorophyll fluorescence. However, existing observations mostly lack the spatial coverage and temporal resolution required to determine the state of the marine environment and changes within it. Furthermore the automatic systems on buoys etc. are affected by biofouling and the operational costs are high due to ship costs needed for servicing.

To overcome these problems, the use of 'Ships of Opportunity' (SoO) has been introduced since there are many routes for ferryboats and other SoO which run frequently repeated routes.

The 'Continuous Plankton Recorder (CPR)' (Reid et al., 1998) has followed the idea of using scientific equipment on such ships for continuous recording of environmental data. Over the last 60 years it has produced impressive data on plankton abundance and species distribution with time (Vezzuli and Reid, 2003).

Recently, more sophisticated systems have been implemented on ferries which allow precise measurements of temperature, salinity and chlorophyll (Swertz et al., 1999; Harashima and Kunigi, 2000; Rantajärvi, 2003; Hydes et al., 2003; Petersen et al., 2003) and even currents by ADCP (Ridderinkhof et al., 2002).

Applying such a FerryBox system on ferry boats or ships-of-opportunity has several advantages: 1. The system is protected against harsh environment, e.g., waves and currents, 2. Bio-fouling can be more easily prevented, 3. No energy restrictions (in contrast to buoys), 4. Easy maintenance when ferry comes back 'to your doorstep', 5. Lower running costs since the operation costs of the ship do not need to be calculated and 6. Instead of point measurements (buoys) transects yield more information.

There are now several automated systems which are used operationally worldwide.

Even if 'FerryBoxes' have been used during expeditions on research ships (e.g., on RV Polarstern, G. Blöcker, GKSS, pers. comm.), it mostly takes some time and money to install such a system on a ship. The operation of the existing systems on small boats during single field campaigns in an estuary, river or a lake is not feasible.

In order to overcome these restrictions a '*pocketFerryBox*' has been developed with the aim to have a portable, energy-independent system for fast field measurements. Despite these restrictions important oceanographic, chemical and biological should be recorded and stored.

With the new instrument accompanying measurements during sampling in the field shall enable the chemist or biologist to take samples 'more intelligently' according to the

environmental situation. In addition, a survey of important water quality parameters should be possible, covering a large area in a short time interval.

Since the principle of the '*pocketFerryBox*' is similar to the larger '*4H FerryBox* system', (named after the manufacturer) first a description of this system will be given.

Technical Setup of the '*4H FerryBox*'

The '*4H FerryBox*' system' consists of an automated flow-through system with different sensors (temperature and salinity (FSI, USA), *in-vivo* fluorescence as a proxy for chlorophyll-a (SCUFA-II, Turner Design, USA), algal group analyser (AOA, bbe-moldaenke, Germany), turbidity (Turner Design, USA and Endress & Hauser, Germany), oxygen (Aanderra, Norway) and pH (Endress & Hauser, Germany) and automated wet chemical nutrient analysers (APP, ME-Grisard, Germany and Micromac1000, Systea, Italy) for dissolved inorganic nitrate, ammonia, ortho-phosphate and silicate.

The water intake is in front of the ships cooling system at a fixed depth (5 m). The water is pumped continuously along the sensors. Data including time and position (latitude, longitude) are automatically transferred to shore and the system can be remotely operated via mobile phone connection (GSM). On shore all data enter a ORACLE database with access from a public web page (<http://ferrydata.gkss.de>). Water samples for subsequent analysis in the laboratory are taken by an automatic water sampler at predefined positions or according to a measured parameter. The samples were kept refrigerated (4 °C) and in the dark. A more detailed description of the system is reported in Petersen et al. (2003).

For high reliability of the data and long-term stability of a *FerryBox* system the problem of biofouling had to be solved. The biofouling problems can only be avoided by frequent cleaning of the system in particular at times of high biological activity. This can be achieved with an automated self-cleaning system. It prevents biofouling by cleaning specific sensors with tap water under high flow and rinsing the whole system with acidified water after each cruise. This procedure improved the long-term reliability of the data. By these measures the long-term stability of sensors such as salinity could be prolonged up to one year without maintenance and manual cleaning.

The '*4H FerryBox*' system' can not only be used on ships but as well as a 'stationary module' in a container at the shore. Such a module has been installed for time series measurements in different areas. One example is the module in Paranaguá, Brazil (Fig. 1).

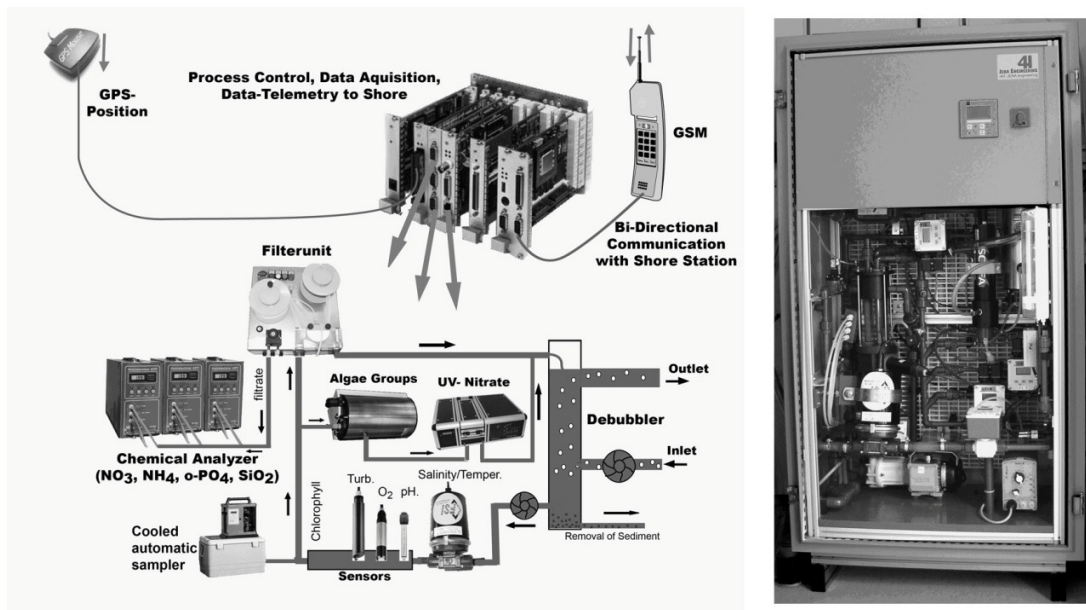


Figure 1: Schematic view of the *FerryBox* flow-through system (left) and a photo of the industrial version, manufactured by the German company 4H Jena Engineering GmbH (right).

Technical Setup of the 'pocketFerryBox'

For the development of the '*pocketFerryBox*' the following problems had to be solved: 1. Reduction of size by optimising the flow-through unit, 2. Choosing small, but reliable sensors for the chemical/biological parameters, 3. Encasing the system in a robust, water-resistant housing and 4. Implementing a software which can be operated easily under severe conditions, e.g., on an open boat with sea spray and rain. Other limits are set by the power supply which should enable to operate the unit from a standard car battery over a period of at least 6-8 hours.

A scheme of the '*pocketFerryBox*' is given in Fig. 2. Water enters the flow-through unit, equipped with sensors by means of a 12 V impeller pump with a flow rate of 3-4 l/min. The flow-through units are identical; up to 6 units can be assembled together. In order to reduce the effective dead volume the water enters the units at the top and leaves at the bottom. Depending on the application different sensors can be selected. The system used during this investigation contained sensors for salinity (7-conductor cell from Sea&Sun, Germany), oxygen (OPTODE from Aanderra, Norway) and 6 CYCLOPS sensors (Turner Design, USA) for turbidity, chlorophyll-fluorescence, coloured dissolved organic matter (CDOM) and for the algal pigments phycocyanin and phycoerythrin (to detect cyanobacteria and special red algae).

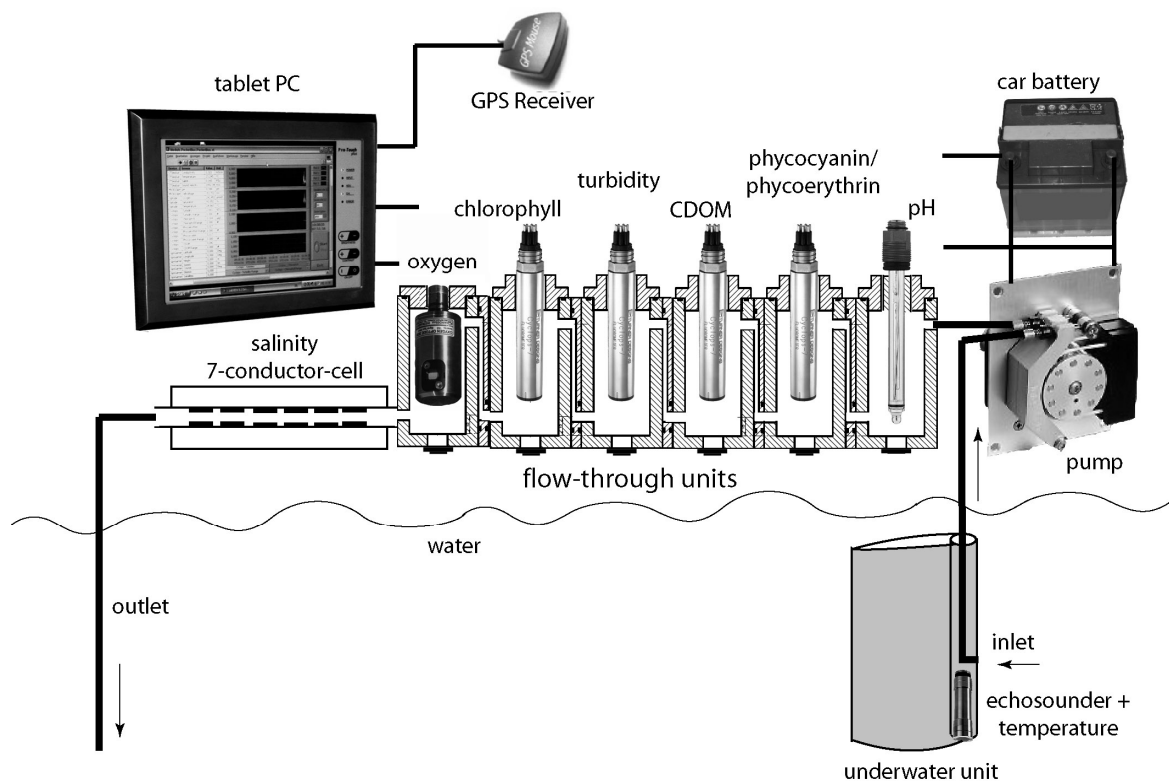


Figure 2: Schematic diagram of the *pocketFerryBox*.

Since one of the aims is to have fast surveys a versatile inlet system has been developed which enables high speed boat velocities. Besides its function as water supply the inlet also contains a temperature sensor and an altimeter (echosounder) that gives information of the water depth with a moderate accuracy of ± 10 cm (in tidal waters this has to be corrected; the resulting accuracy will be less). The position is recorded by a GPS receiver which can be clamped somewhere on the boat.

All data are recorded with a water-proof tablet PC under Windows XT. The program has been written in LabView (National Instruments). All actual data are given in alphanumeric form on the screen. In addition 6 selected parameters can be presented in graphical form as time series. All systems (except the car battery) are installed in a housing ("Zarges®"-box) protected against rain and water spray. For transport the box can be fitted with wheels. The system is suitable for air transport; it weighs about 25 kg. A photo of the *pocketFerryBox* is given in fig 3. On the right the flow-through units are presented.



Figure 3: Photo of the *pocketFerryBox* (left) and of the flow-units (right).

Application of the ‘*pocketFerryBox*’ within a Project in Brazil

Investigation Area

The first mission with the newly build *pocketFerryBox* has been carried out within a project in Brazil. In this project investigations are carried out which will assess the role of the harbour of Paranaguá on the nutrient budget and the growth of phytoplankton in Paranaguá Bay (due to discharges of domestic sewage from the city and fertilizer from the harbour). For this investigation a stationary *4H FerryBox* was installed near the estuary mouth for time series measurements and several field campaigns in the bay should give an overview on the oceanographic and biogeochemical situation during different seasons. In this paper only the results from a field campaign with the *pocketFerryBox* will be given.

In figure 4 a map is given which shows the location of the stationary *4H FerryBox* and the course of a west-east transect with the *pocketFerryBox* from Antonina to the Atlantic Ocean.

Paranaguá Bay can be characterized as an estuarine system comprised of two main water bodies, the Paranaguá Bay (612 km²) and Antonina Bay (260 km²). It is a partially mixed estuary with a mean depth of 5.4 m, a total water volume of 14×10^9 m³ and a residence time of about 4 days. A salinity gradient from freshwater to marine conditions along the east-west and north-south main axes divides the bay into different regions. A lateral gradient originates from the freshwater input of rivers and tidal creeks and creates several ‘micro-estuaries’ in the different sectors of the bay.

The tidal range is between 1.7 m in Antonina and 2.7m at the estuary mouth. It is estimated that the untreated sewage discharged from the city and harbour of Paranaguá is about 48 000 m³ per day with an organic load of 14 000 kg per day.

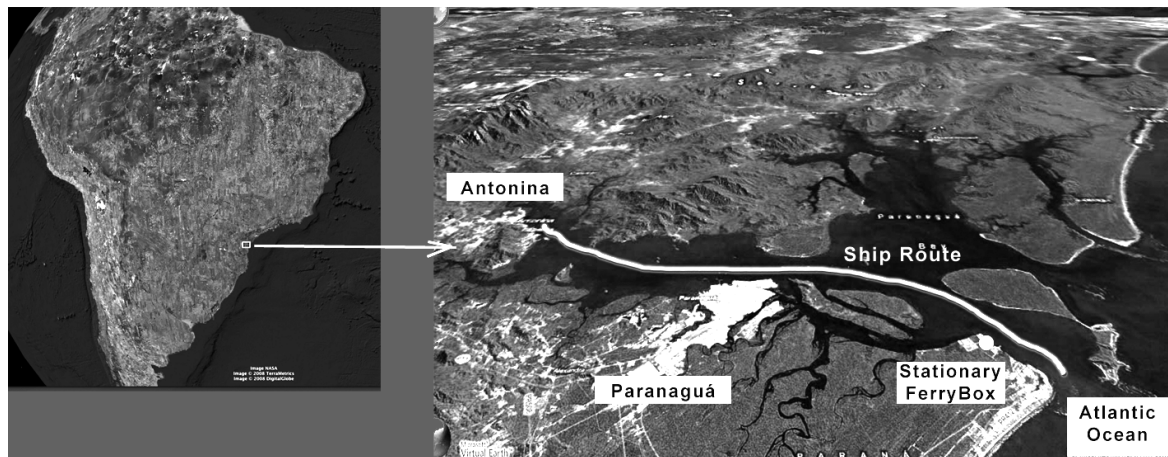


Figure 4: The investigation area of Paranaguá Bay in southern Brazil with a longitudinal transect.

Results and Discussion

Comparison of the pocketFerryBox with the Stationary 4H FerryBox

In order to obtain a consistent data set measurements with the stationary *4H FerryBox* and the *pocketFerryBox* were compared. This was accomplished by installing the *pocketFerryBox* into the same water circuit as the stationary *4H FerryBox*. Since the sensors for salinity, temperature, oxygen and pH were the same type in both systems and had been calibrated together in the laboratory prior to the measurements no results will be shown here. More critical are the parameters *chlorophyll-fluorescence* and *turbidity*: Chlorophyll is measured in the *4H FerryBox* by a SCUFA-Fluorometer (Turner) which has a 90° set-up, whereas in the *pocketFerryBox* a CYCLOPS-Fluorometer (Turner) is used with a 180° set-up. Turbidity is as well measured with the SCUFA (90°, blue light) and with a CYCLOPS (180°, red light) respectively. Since the response of these instruments can depend on the properties of algae and suspended matter a comparison was carried out in February 2008.

The results are shown in figure 5. As can be seen the values for chlorophyll are nearly identical until 5:00 o'clock (UTC) on 14-2-08. At this time the values of the stationary *4H FerryBox* have an offset which occurred due to an operational error in the software, but have nothing to do with sensor response. The comparison of both turbidity recordings are satisfactory with a non-systematic deviation of less than 20%. The values of the *pocketFerryBox* show more noise presumably due to the missing “debubbler” in this system.

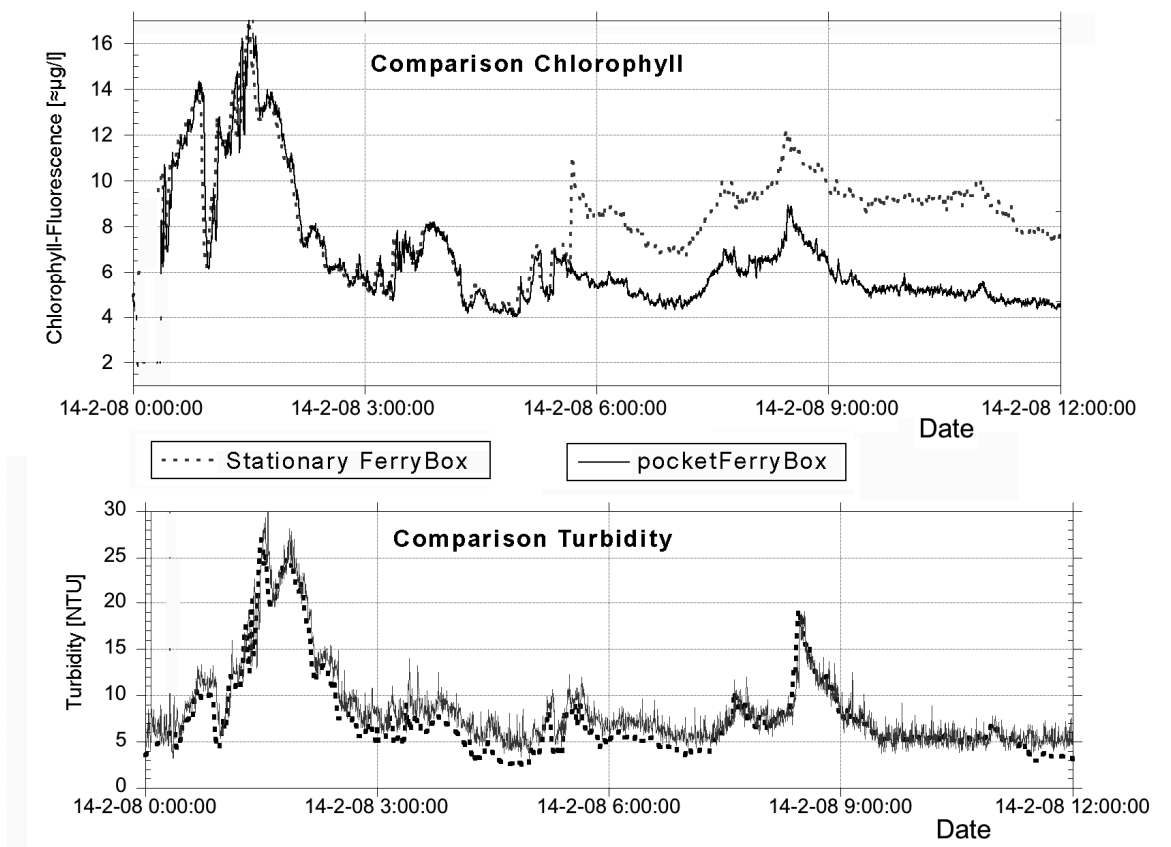


Figure 5: Comparison between measurements with the *pocketFerryBox* (straight line) and the stationary *4H FerryBox* in Pontal (dashed line) in February 2007.

West-East Transect from Antonina to the Estuary Mouth

A west-east transect has been recorded with the *pocketFerryBox* using a small boat (see map in figure 4). During the cruise samples were taken and will be now analyzed in the lab. Results for salinity, water temperature, chlorophyll-a-fluorescence, oxygen saturation, pH and turbidity are depicted in figure 6.

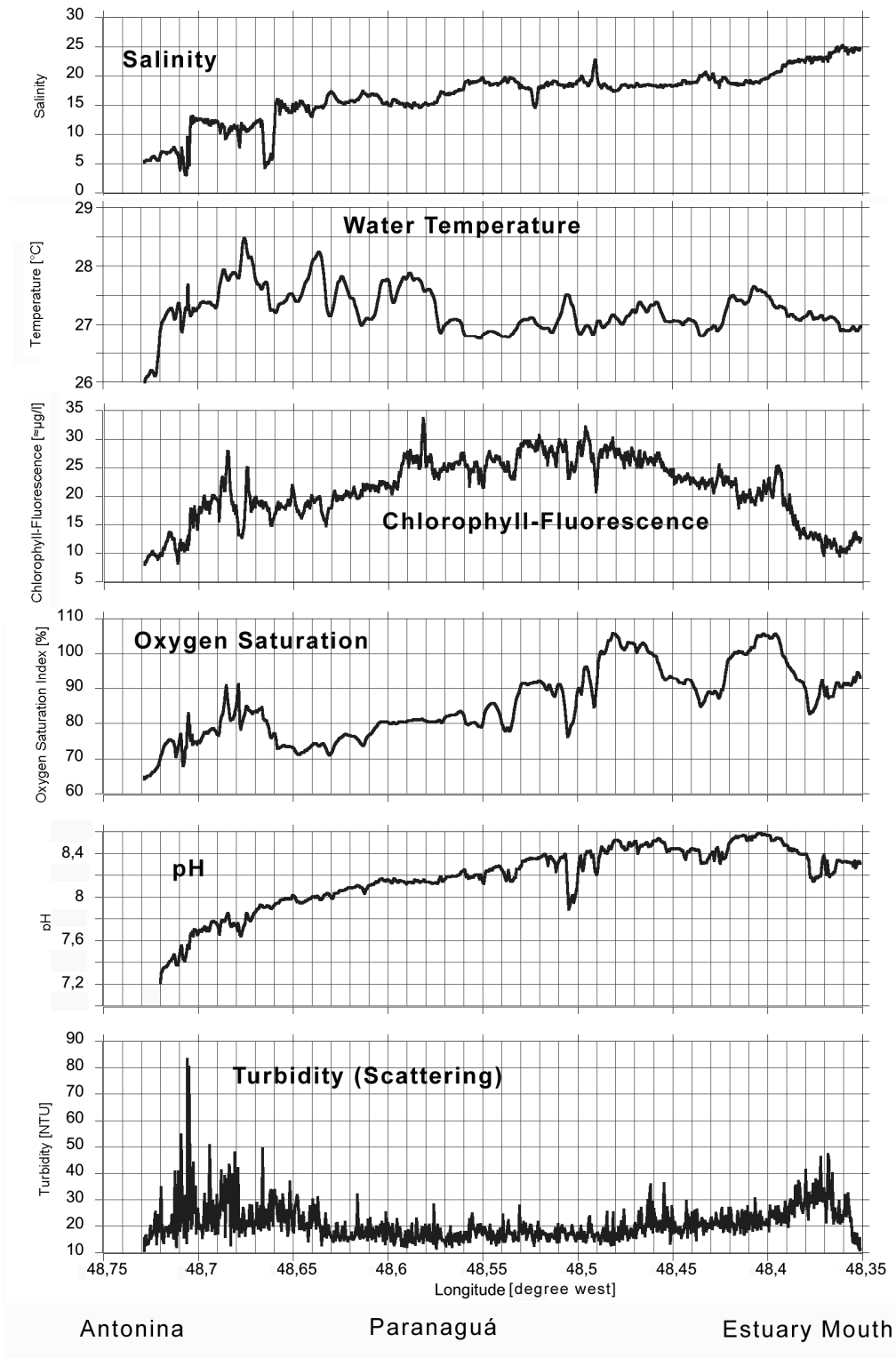


Figure 6: Results from measurements on the West-East transect Antonina- to the Atlantic Ocean (for the course compare map in fig. 4).

As can be seen, salinity, chlorophyll, oxygen and pH show a distinct gradient from Antonina to the estuary mouth. Salinity increases from about 5 to 25 due to the fresh water discharge of several small rivers in the western parts. This is as well reflected in the pH values that change from typical freshwater (Antonina) to marine values.

Turbidity is high in some western areas, low in the navigational channel in the middle parts, slightly enhanced near the estuary mouth and then drops sharply in direction of the open sea.

The chlorophyll transect shows an increase in the middle of the bay with highest values of about 30 µg/l. The reason for this may be the favourable light climate and the availability of nutrients. Whereas the latter will be only clear once the samples have been analysed, the high turbidity near Antonina will prevent algal growth and be responsible for the low chlorophyll values. Towards the estuary mouth the combined effect of enhanced turbidity and lower nutrient concentrations (diluted by salt water) may be the reason for the declining algal growth.

The oxygen concentrations give an overview on the consumption/production processes in the bay: In the western freshwater parts of the bay near Antonina relative large oxygen deficiencies occur with the oxygen saturation being less than 70%. The reason for this will be high consumption of organic material, presumably organic material from the city of Antonina and from rivers. Primary production does not play a significant role due to low chlorophyll concentrations. In the middle of the bay (48.6° to 48.5 °) the oxygen saturation remains relatively low despite high chlorophyll concentrations and good light conditions (low turbidity, sunshine during the campaign). Therefore, the oxygen consumption processes exceed primary production.

This behavior changes towards the estuary mouth: Even with declining chlorophyll concentrations oxygen reaches saturation and in some spots even shows a slight over-saturation. In this area primary production plays a more important role. This is consistent with pH data in this region which there is correlated with oxygen and chlorophyll.

South-North Transect

In order to assess how much the west-east transect were influenced by the large shallow northern parts of Paranaguá Bay, a south-north transect near the estuary mouth was measured, starting from the location of the stationary *4H FerryBox* at the southern shore.

Figure 7 shows a map of the bay with the transect. Due to the shallow water depth of less than 1.5 m in the northern parts only a very small boat could be used.

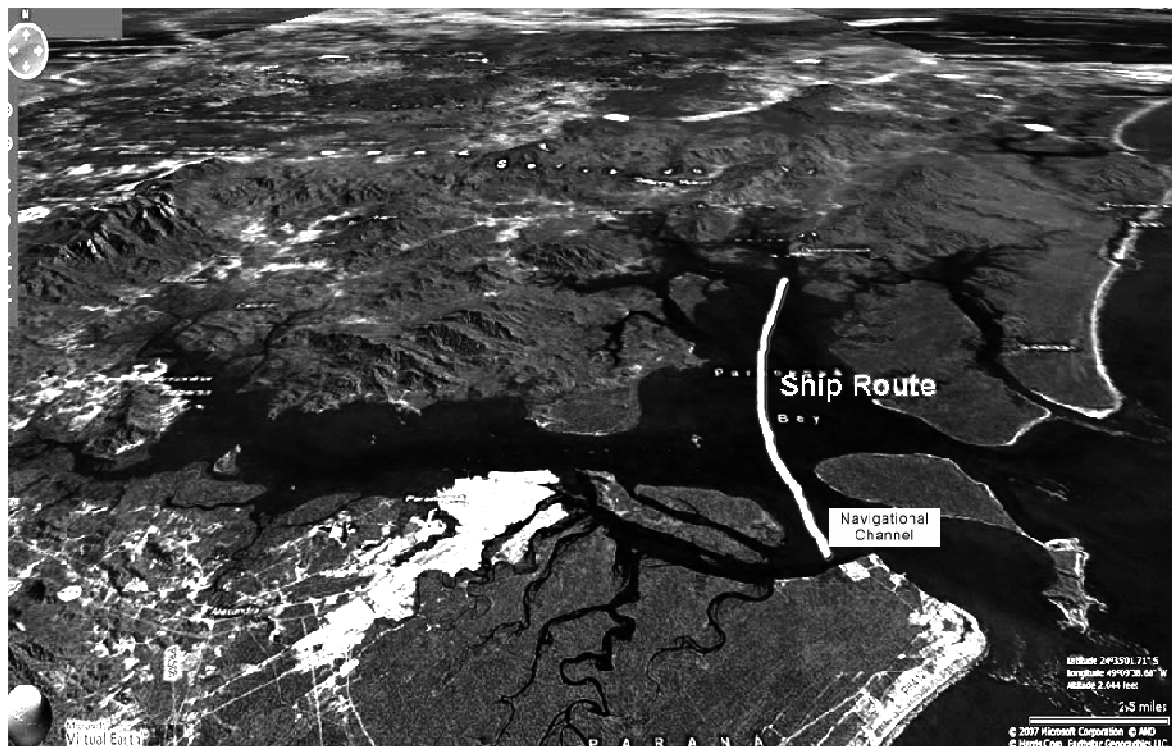


Figure 7: Map of Paranaguá Bay with the South-North Transect.

In figure 8 the results of the south-north transect are depicted. The salinity profile starts with values as are typical in the navigational channel near the estuary mouth (fig. 6) and declines due to the freshwater input from small rivers in the north. However, since the amount of freshwater is smaller than in Antonina that has a larger river, the salinity stays to higher values.

The chlorophyll concentrations increase toward the northern parts. The oxygen saturation stays always around 100% with some fluctuations. Only in the most northern areas it drops below 80% presumably due to consumption processes.

The pH values drop from marine values to 7.8 in the northern parts. Oxygen and pH are correlated and show areas in which primary production slightly exceeds the consumption processes. Turbidity shows a noisy signal with a slight increase towards the north.

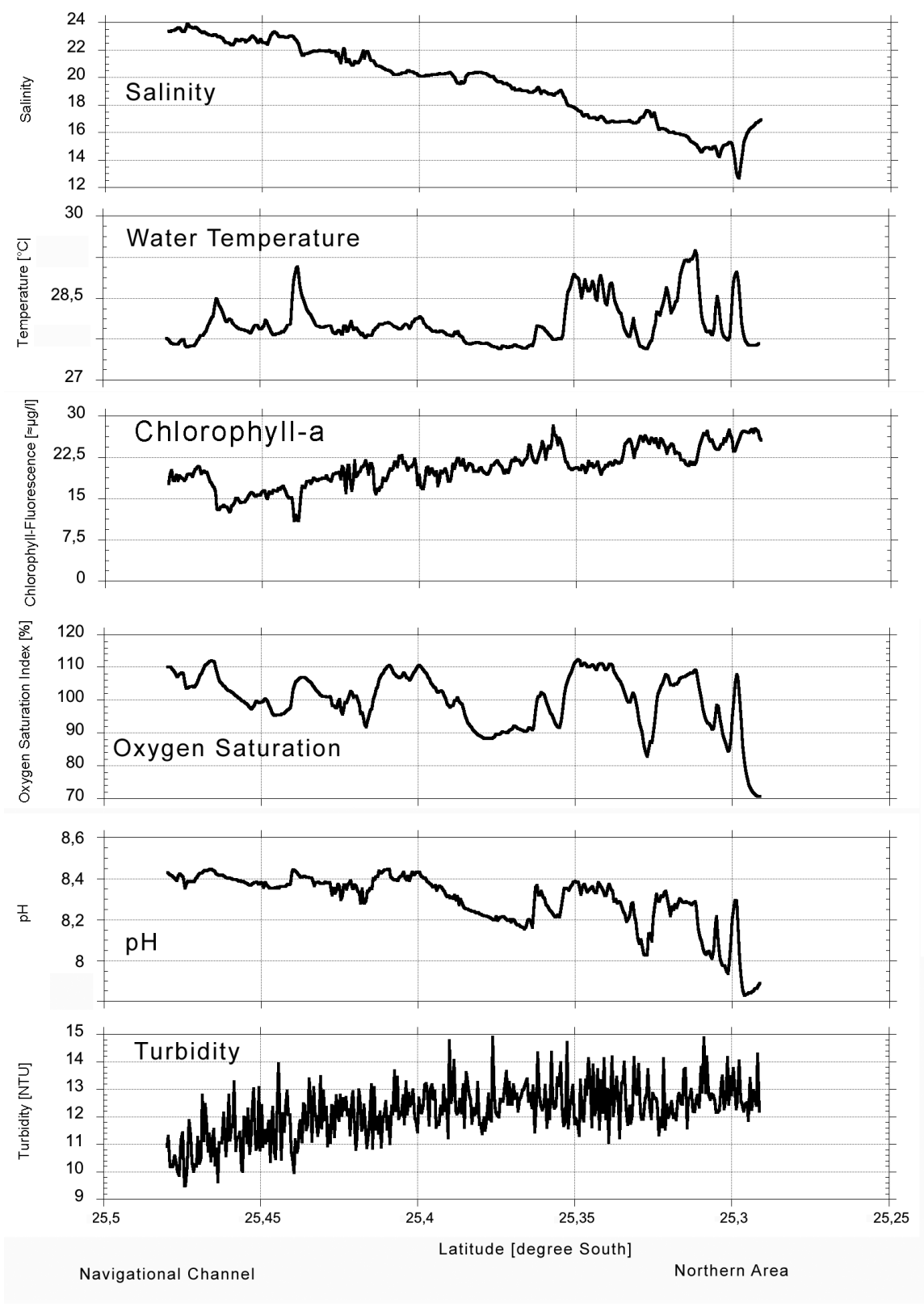


Figure 8: Results from measurements on the South-North transect.

Algal Pigments

Since the sensors for algal pigments phycocyanin and phycoerythrin had not yet been calibrated only relative values are given (Phycoerythrin is a red protein from the light-harvesting phycobiliprotein family, present in freshwater cyanobacteria and red algae; phycocyanin can be found mainly in marine cyanobacteria and some marine red algae).

Whereas the phycocyanin values showed no gradient in the bay, indicating the lack of marine cyanobacteria, some differences could be found with phycoerythrin.

In figure 9 the sensor outputs for phycoerythrin are presented for a west-east and a south-north profile.

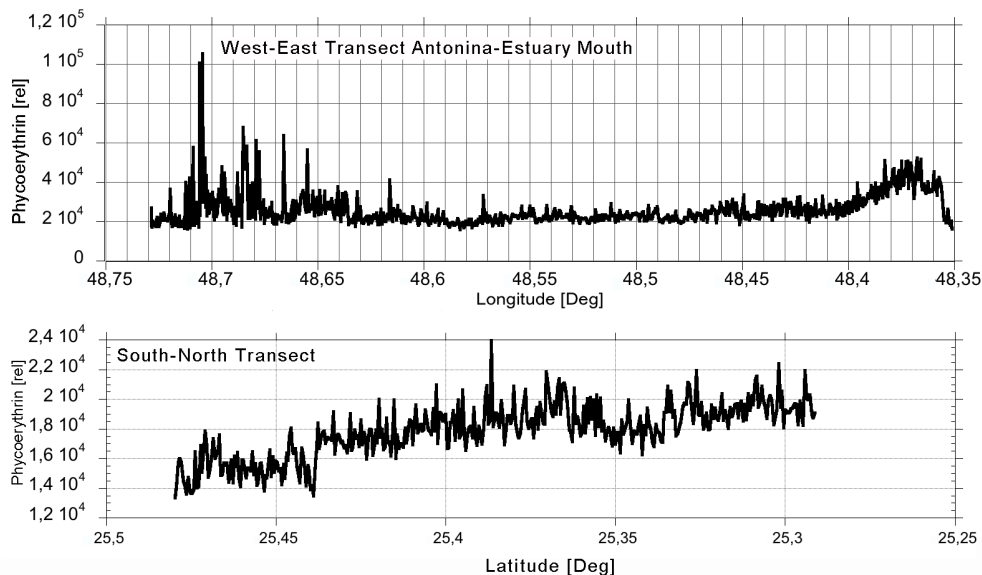


Figure 9: Algal pigment 'phycoerythrin' concentrations on the West-East (upper panel) and South-North (lower panel) transect.

In the west-east transect (upper panel) phycoerythrin concentrations increase in the western freshwater parts of the bay. This would indicate the existence of cyanobacteria which could influence the nutrient budget due to their capacity of nitrogen fixation. However, this has to be confirmed by algae counting in the samples. In the south-north transect an increase of phycoerythrin in the northern, freshwater-influenced parts can be observed as well; though on a smaller level.

Conclusions

Whereas the function and applicability of 'FerryBoxes' for monitoring of estuaries and coastal water has already been demonstrated earlier (Ridderinkhof et al., 2002; Hydes et al., 2003; Petersen et al., 2003, 2005) a suitable instrument for field cruises on small boats was missing. Measurements with the new *pocketFerryBox* within a project in Brazil demonstrated the applicability and usefulness of the new instrument: Within few days a survey in Paranaguá Bay could be carried out by measuring parameters that characterize physics and chemistry of the main water bodies. Since the results were available immediately during the cruise samples could be taken for laboratory analyses more 'intelligently', i.e., especially at areas where the properties of the water bodies changed. The new *pocketFerryBox* will be a useful instrument for fast surveys and accompanying biogeochemical sampling campaigns.

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General Discussion

General Discussion and Conclusions

There is a global trend of increasing nutrient input into the marine and coastal environments during the next decades related to changes in climate, coastal morphology and land use (Tappin, 2002). Understanding how the estuarine systems will respond to these modifications is one of the main issues for the coastal management, demanding the development of knowledge concerning the eutrophication effects on the ecosystem structure and dynamics. In this Chapter, the main features of the estuarine systems of the state of Paraná are compared to provide a comprehensive assessment of water quality related to nutrient enrichment and the response of other related parameters and the trophic status.

Paranaguá and Guaratuba bays, as subtropical estuaries, presented substantial oscillations of the studied variables. One of the main features of the region is the succession of rainy and dry periods that is fundamental for understanding the functioning of the systems. Although the occurrence of an essentially drought season is not observed, the freshwater input through river discharge and precipitation tends to be concentrated from the spring to the summer months, like observed in another subtropical area such as the St. Lucie River Estuary in Florida (Millie et al., 2004). The relation of increasing freshwater input to the nutrients dynamics is not very clear. While there is linearity between higher concentrations and discharge for some of the nutrient species, and in some of the studied rivers of Paranaguá Bay, no relation can be assigned to other situations. In this sense, the need for management actions that encompass the logistical challenge of monitoring such large areas and the diffuse sources is highlighted.

The estimations of nutrient inputs into Paranaguá Bay showed that main sources are related to the river loads, harbour emissions and sewage discharge. The same seems to be true to Guaratuba Bay, with the exception of the port activities that do not take place there. Lack of sanitation, as a common problem in the coastal areas of Brazil, as well as catchment deforestation, increased land drainage, altered patterns of soil erosion, and the development of agrarian and urban/industrial economies have to be better assessed and treated, because these activities produce a marked increase in the terrestrial fluxes of N and P.

Even though high nutrient loads are related to the high freshwater input and the discharge of untreated sewage into Paraná bays, the concentration of nutrients in the estuaries is not alarming according to eutrophication thresholds (Bricker et al., 2003). A similar conclusion can be made about the chlorophyll concentrations (as a proxy for phytoplanktonic biomass), whose maximum values of $46 \mu\text{g}\cdot\text{dm}^{-3}$ in Paranaguá Bay and $29 \mu\text{g}\cdot\text{dm}^{-3}$ in Guaratuba Bay

occurred in isolated events. Although there is a causal relation between increasing nutrients and eutrophication effect, other factors such as the water renewal can act as 'buffer' of the eutrophication process. It has been observed that in some cases high nutrients are not an obligatory symptom of eutrophication, as well as lower nutrients are not excluding the occurrence of the problem (Cloern, 2001; Bricker et al., 2003). This holds true especially for the rainy seasons, when the increase of phytoplanktonic biomass can be related to the consumption of nutrients. On the other hand, increasing nutrients are not followed by high chlorophyll concentrations *per se* during dry seasons. However, the lower freshwater input and water renewal led to lower dissolved oxygen levels under the biological stress limits especially in Guaratuba bay.

The descriptive approach applied to Paranaguá and Guaratuba bays provided important information regarding the dynamics of the systems, although an objective classification of the water bodies was still needed due to lack of appropriate management actions regarding the eutrophication problems in the region. The Brazilian constitution (1988) defines the coastal zone as a national 'patrimony', and a very rigid legislation regarding the protection, conservation and occupation of these areas is stated by national, state and county plans. Still, an intensification of conflicts is observed along the coast of Brazil, related to the failure of the complex legal suite available in the country (Jablonski and Filet, 2008). One of the reasons for this failure can be attributed to the disconnection of governmental actions, communities' participation and the research scope. Providing simple, but comprehensive judgment elements to the administrators and to the public in general is an important issue that has been leading to the development of several synthetic indices to define the trophic status and the level of eutrophication in estuaries.

As used in the Yucatán Peninsula, the combination of ASSETS and TRIX, along with other parameters such as phytoplankton and loss of submerged aquatic vegetation (SAV), was an important advance to the assessment of the ecological condition of this marine coast (Herrera-Silveira and Morales-Ojeda, 2009). In accordance with the ASSETS methodology, Paranaguá Bay presented 'Good' trophic status, while the estuary of Guaratuba exhibits 'Poor' conditions. The susceptibility to develop eutrophication symptoms was determinant for the differences observed between Paraná estuaries. Paranaguá Bay is a large estuary with high freshwater input and water renewal time of around 3 days, whereas Guaratuba Bay presents lower dynamics and seems to be exhibiting serious siltation problems. The main eutrophication symptoms observed in the areas are related to macroalgae accumulations and harmful algae blooms in Paranaguá Bay, while lower oxygen concentrations, combined with relative high nutrient input, are of increasing concern in Guaratuba Bay. The definition of salinity zones

considered by this methodology is an important tool to define the contribution of different areas within the estuaries in relation to the eutrophication problems.

The TRIX methodology applied to each sampling station indicates the areas within the estuarine limits that show worse conditions. Although this index excludes important information about the estuarine susceptibility to eutrophication and other eutrophication symptoms, such as harmful algae blooms and loss of submerged aquatic vegetation (SAV), it is an important approach to specify particularly areas at a finer temporal and spatial scale. Generally, the bottom layers and the mixing areas with salinity between 5 and 25 presented more eutrophic conditions especially due to fluctuations in the oxygen saturation and DIP concentrations, while chlorophyll concentrations were more important to explain the seasonal differences.

The ASSETS methodology seems to be more reliable to assess the trophic status because it considers a wide range of parameters. However, the classification is done to the whole estuarine area and in a year cycle or seasonally, as proposed by this work. In this sense, the TRIX method brings more information in better temporal and spatial resolution but the limitations of applying this methodology in estuaries has to be better understood. The main restraints of using TRIX in estuaries observed in this work are related to the processes regulating the fluctuations of oxygen saturation. For example, consider two areas in the extremes of an estuary with similar nutrients and chlorophyll concentrations: an inner zone with lower salinity and lower oxygen saturation, and a lower region with higher salinity and oxygen supersaturation. The TRIX index will result in a similar value because it considers the absolute oxygen saturation deviation from 100%, but the high input of organic matter in the inner regions of estuaries can bring negative problems due to the consumption of oxygen. The differences in the oxygen balance in estuaries and marine areas have to be inserted in the method. It can be done simply by applying only the deviation from 100% of oxygen saturation, but this is not possible mathematically (logarithms of negative values do not exist). Also, a correction factor by salinity in the classification can be inserted, but this can be ambiguous because the oxygen saturation is already calculated according to the salinity. Therefore, a good option could be that all saturation values over 100% are considered as 1 which result in $\log[1]=0$. In this sense, only under saturation values would be considered indicating alarming situations due to oxygen decrease.

One of the main limitations of both methodologies is related to the lack of appropriate data and reference conditions. Particularly for subtropical systems, it is necessary to make adjustments to thresholds for indicators, like the chlorophyll-*a* concentrations (Xiao et al., 2007). Hence, the combination of the ASSETS and the TRIX methodologies can be recommended for a

Brazilian national monitoring program concerning eutrophication in the coastal zone, keeping in mind the requirements to overcome the limitations through a comprehensive establishment of reference conditions. Herrera-Silveira and Morales-Ojeda (2009) stress that, although 5 years of monitoring data were available for the Yucatán Peninsula, it is expected that higher confidence of the analysis will be achieved with the increase of data availability for reference conditions. In this sense, besides additional research efforts, more attention should be directed to the combination of academic and governmental alliances, in order to implement what the law number 5300 of 2004 stated for the creation and application of environmental monitoring programs for the coastal zone.

Considering the limitations on the availability of data for the coastal systems of Paraná State, the use of the FerryBox system as a water quality monitoring technique is proposed to fulfill the necessities of defining the most important features and phenomena affecting the fluctuations of the phytoplanktonic biomass and other related parameters. The long term monitoring provided by the Stationary FerryBox in Paranaguá Bay indicated that Paranaguá Bay is a very dynamic system and that fluctuations in the ecosystem structure are strongly affected by the seasonality, the lateral input from rivers and mangrove plumes and the tidal forcing. This conclusion was only possible by combining the point monitoring with the spatial sampling with the mobile device (Pocket FerryBox).

Overall, in the same way that no index by itself is able to substitute the original data and the descriptive approaches of assessing water quality in the dynamic subtropical estuaries of the State of Paraná, the water monitoring is not likely to be performed only at one location. There is a clear need to adjust the nutrient inputs to the legislation requirements, especially concerning the waste water discharge, as well as to define clear monitoring programs related to the estuarine status in the state and along the coast of Brazil. More information about the biogeochemical processes affecting nutrients fluctuations is required, such as the determination of the exchange in the water-sediment interface and the nutrient budgets in the studied systems. Future works should be directed to these issues, encompassing the information provided by this work and consistent recommendations for the coastal management of the area.

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Appendix A

Erklärung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertation selbständig angefertigt habe und dabei als Hilfsmittel nur die genannten Quellen benutzt habe. Desweiteren versichere ich, dass die vorliegende Dissertation weder ganz, noch zum Teil bei einer anderen Stelle im Rahmen eines Prüfungsverfahrens vorgelegt wurde.

Kiel, den 28.04.2011


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