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Anthropogenic influences on ecosystem processes in a tropical estuary: Feedback connections and environmental management targets A case study of Dong Ho Estuary, Kien Giang, Vietnam

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Abstract

Estuaries play an invaluable role in the transformation and cycling of materials as they move between land and sea; including anthropogenic materials. Increasingly, human activities are delivering material loads that risk overwhelming the normal functions that these ecosystems provide. In this context, the objective of this study is to assess key biogeochemical processes to understand the influence of anthropogenic activities on ecosystem performance in a tropical estuary. The research presented here focuses on a case study area, Dong Ho estuary in Kien Giang province, Vietnam, which exemplifies the anthropogenic impacts and management issues facing most of the Mekong coastline and other similar areas in Vietnam. Located at the south-western edge of the Mekong delta, the Dong Ho estuary is subject to material inputs from both local and more remote sources; making it vulnerable to degradation and functional loss. Further, as a major food producing area of Southern Vietnam, Kien Giang province and its coastal ecosystems, such as Dong Ho, are under growing pressure from the national government to increase food production (typically rice and prawn aquaculture) but, at the same time, maintain high ecological standard of performance. In addition, the Dong Ho area is witnessing significant increases in population and planned tourism development. Against this backdrop the Dong Ho estuary and its management represent an opportunity to understand the interactions and complexities of anthropogenic activities on ecosystem function and sustainability. In this context, the current study sort to identify the main anthropogenic factors and potential pollutant sources to the ecosystem; define the key physic-chemical and biological factors affecting ecosystem function; identify loads of key materials into the estuary that influence carbon and nutrient stocks in the water column and benthic sediments; measure key biogeochemical processes such as primary production, internal benthic nutrient fluxes, denitrification that underpin ecosystem function; assess if the estuary is retaining materials or simply acting as a pipeline to the sea; and, in view of the new understanding of system behaviour, consider the implications of current inputs and ecosystem function for management and future sustainability of the Dong Ho estuary.

Results from fieldwork and experimental observations showed that the Dong Ho estuary is a strongly heterotrophic ecosystem relying on allochthonous sources of carbon to meet its internal carbon budget. At the same time, the estuary captures carbon, nitrogen and phosphorous annually, although nitrogen tends to be exported to the adjacent Western Sea during the dry season. Further, water column nutrient stocks reflect a strong input of materials from the surrounding catchments during the wet season and dissolved oxygen levels during some periods become very low in bottom waters, indicating a move toward eutrophication and ecosystem dysfunction.

From a management perspective, results from this study highlight the need for strong consideration of current proposals to further alter the hydrodynamics of the estuary through infrastructure development, and the need to develop key wastewater infrastructure and management strategies to mitigate the augmentative impact of urban discharges on the increasing loads from local and remote agriculture and aquaculture activities.

Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Publications during candidature

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Keywords

biogeochemical processes, nutrient cycling, ecosystem performance, tropical estuary

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CHAPTER 1 - INTRODUCTION

1.1. Context to the problem

Coastal ecosystems, particularly coastal estuaries and lagoons, are renowned for high productivity, providing approximately 30% of the total primary production and biodiversity in the world's marine systems (Alongi, 1998). These areas encompass dynamic physical and biological interactions between material inputs from rivers as well as oceans, and these interactions underpin much of their ecological value and function (Hobbie, 2000). Estuaries provide many benefits to society, including providing habitats for key economic species, sources of food, transportation and recreation for humans. Estuaries also play an invaluable role in supporting key biogeochemical cycles, trophic energy flow, and stock recruitment in the marine environment (Wilson, 1988), much of which underpins the ecological services that humans depend upon. However, estuarine ecosystems are under increasing pressure due to human activities, which alters the characteristics, capacities and processes within these ecosystems. Continued rapid growth of human populations in and adjacent to estuarine ecosystems has led to significant impacts including: (1) Nutrient enrichment in rivers and estuaries underpinning harmful algal blooms and oxygen depletion or hypoxia; (2) degradation and loss of coastal habitats such as salt marshes, mangroves, seagrass; (3) alteration of natural hydrological flows due to landscape design or damming of rivers, leading to changes in the magnitude and seasonal patterns of freshwater and sediment inputs into estuaries; (4) declines in fish and wildlife populations due to overexploitation and habitat destruction; (5) pollution by toxic materials including both organic (PCBs & PAHs) and inorganic contaminants (heavy metals) as well as nutrients being discharged into estuaries by industrialisation and agriculture; and (6) biodiversity loss and habitat deterioration by exotic species introduced into estuaries (Bianchi, 2007, Hobbie, 2000).

Government and private sector efforts to better manage estuaries are numerous but they are still in decline and some no longer even resemble the original system (Horton, 2013). For example, in the case of Chesapeake Bay, Horton (2013) argues that the Bay has lost its valuable habitat and its ability to function in the way that nature intended it to. In addition, there has been considerable research into various aspects of the interactions between anthropogenic impacts and estuarine ecosystem performance, and the significance of understanding the key ecological processes in providing an insight into the status of systems performance (Andrew et al., 2009, Hoey and Bellwood, 2009, Edgar et al., 2000). In contrast, little of this research has specifically sought to assess the suitability of particular ecological or biogeochemical processes as indicators of performance within an environmental management context.

Like estuaries elsewhere, tropical estuaries are amongst the most exploited ecosystems in the world, and are facing many conflicts between human activities and maintenance of their ecological functions (Blaber, 2002, Hsieh et al., 2012, Jennerjahn et al., 2004, Pan et al., 2016). However, estuaries in the tropics differ from temperate estuaries in ways which require specific management approaches.

First, it is crucial to understand that tropical estuarine hydrodynamic conditions are strongly affected by tropical climatic conditions which regulate the local rainfall regime and determine the output of freshwater or flow of rivers in regions, as well as presenting high evaporation rates due to consistent high temperatures (Rodríguez, 1975). For example, in a tropical area with rainfall occurring regularly throughout the year, estuaries receive appreciable runoff from rivers and their watershed even during dry season. On the other hand, in the tropical zone with a marked seasonal difference between dry and wet season, such as a typical monsoonal regime, estuaries are influenced by strong seasonal salinity fluctuations which reach a maximum during the dry season drought periods (Rodríguez, 1975).

Second, rates of organic matter and organic detritus discharge into tropical estuaries are considered more significant than in temperate estuaries because tropical rivers usually receive a high volume of runoff and drain heavily forested basins (Rodríguez, 1975). Accordingly, in tropical areas, high quantities of materials supply into estuaries from the river catchments supports the development of abundant populations of phytoplankton, seagrasses and mangroves in estuaries (Osborne, 2000). This is particularly notable given the emerging concept of "cultural eutrophication" in coastal areas (Vollenweider et al., 1992, Jørgensen and Richardson, 1996, Smith, 1998). Eutrophication can occur as a result of natural processes. However, in both popular and scientific literature when referring to eutrophication, it is actually "cultural" eutrophication which is associated with anthropogenic activities through an increase in their nutrient supply into a particular water body. The study of human-induced alteration of ecosystems' nutrient limitation through the "cultural eutrophication" problem has been recognized since the early 1800s. In marine systems, eutrophication has been identified as an environmental threat along the coastlines of Europe, America, India, Australia, Africa, Southeast Asia, China, and Japan, occurring predominantly in areas affected by river inflows but limited by sea water exchanges (Nixon, 1995). In this light, the high organic materials supply from tropical forested basins, associated with increasing organic pollution derived from human activities, exacerbates the "cultural eutrophication" problem of tropical estuaries. Therefore, based on these particular characteristics of tropical estuaries, it is essential to identify an appropriate management and monitoring approach for assessing the impacts of anthropogenic activities on tropical estuaries, and to recommend effective actions for improving the health and viability of these ecosystems.

One major limitation to effective protection and restoration of estuarine performance is being able to undertake monitoring in a way that is useful to management and maximise the cooperation among government, conservationists, scientists and the public (Boesch, 2006, Oxnam and Williams, 2001). This indicates that there is a clear need for innovative and effective monitoring programs and performance assessment technologies. From a holistic systems perspective, little is known of the potential for the use of ecological process behaviour in early warning systems for ecosystem shift from one state to another. For example, it has been shown that increases in nitrogen loading rates may lead to the replacement of seagrasses by phytoplankton and fast-growing macroalgae as the dominant producers in shallow temperate estuaries (Valiela et al., 1997, Duarte, 1995). This type of approach demonstrates the clear value of applying ecosystem process knowledge to support the management of human inputs and behaviour associated with aquatic ecosystems.

As elsewhere, estuaries and the coastal water in Southeast Asia (SE Asia) play important roles in providing some of the world's richest ecosystems, including mangroves, seagrass beds and coral reefs (Chua and Pauly, 1989, Ramesh et al., 2012). These areas also accommodate more than 70% of Southeast Asia's human population and intensive economic development activities, such as fisheries and aquaculture expansion, urbanisation and industrialisation, tourism development and fast growing ports for shipping traffic (Todd et al., 2010). The pressures from human population growth and economic development are the most important drivers influencing the sustainability of estuarine ecosystems in Southeast Asia. Furthermore, the impacts of upstream activities, such as deforestation due to intensive agriculture or logging, mining activities, dam construction for irrigation and hydroelectric power generation purpose, all contribute to the degradation of catchments and estuaries in SE Asian countries (Ramesh et al., 2012). Consequently, estuaries and coastal lagoons in SE Asia, particularly in developing countries, are also confronting the same issues (nutrient enrichment, biodiversity loss and habitat deterioration, pollution by toxic materials), as summarised by Hobbie (2000) and Bianchi (2007). In addition, due to poverty and human capacity issues, the knowledge on how these ecosystems are currently performing and how they might cope with these pressures is very limited and fragmented. This exacerbates the difficulties in implementing regulatory legislation and scientific initiatives with advanced technologies to protect coastal ecosystems while local people in many regions are still struggling to meet their daily nutrition needs whilst seeking to also meet government demands to reach government economic development goals (Blaber, 2002).

Vietnam is a typical example of the situation described above. As a tropical country located in Southeast Asia, Vietnam incorporates 114 small and large rivers that flow to the sea. The two largest rivers are the Mekong River and the Red River, which are also amongst the five largest rivers in Eastern Asia with headwaters that lie beyond Vietnam borders (Tran et al., 2004). Along the 3,260 km Vietnamese shoreline, there is an average of one river mouth each 20km (Cat et al., 2006). Similar to the global and SE Asian situations, Vietnamese estuaries and their functions are now strongly affected by human activities, such as upstream deforestation, mangrove replacement by aquaculture ponds and agriculture, coastal mining, dike and dam building, untreated wastewater from domestic and industrial activities being dumped into rivers and discharged into the coastal zone (Tran et al., 2004).

Against this backdrop, in Vietnam there has been a recent increase in the assessment of ecosystem performance in the broad field of natural resource management and environmental science e.g. (Le et al., 2014, Rochelle-Newall et al., 2011, Wösten et al., 2003). However, the study of specific biogeochemical processes and their significance in estuarine ecosystems performance, or in their management, has been very limited in Vietnam. Any attempts to manage anthropogenic inputs or alterations to coastal ecosystem function have been limited to "best estimates" rather than interventions based on a sound understanding of ecosystem behaviour or performance. This research seeks to address this limitation by characterising key biogeochemical processes currently responding to anthropogenic impacts occurring in Dong Ho estuary, Kien Giang, Vietnam, and assessing the potential use of these processes as indicators to support decision-making and environmental management.

1.2. Estuaries in Vietnam & the specific case of Dong Ho Estuary

❖ *Overview of Vietnamese Estuaries & Biogeochemical Process Studies in these Systems*

As noted above, Vietnams estuaries are under significant human pressure but are poorly understood in terms of their function and sustainability. Anthropogenic activities have caused several problems for Vietnamese estuaries through the dense river and canal networks across the territory, especially in the Mekong delta and Red River delta. The combination of land use changes in the catchment, habitat loss and pollution from human activities leads to the degradation of ecological and biological performance in several estuaries of Vietnam (Le et al., 2015, Luu et al., 2012, Tran et al., 2004).

Given the complexity and dynamic nature of estuaries there have been a range of approaches taken to understanding them at the systems level (Borja et al., 2008, Hamilton and Gehrke, 2005), but this has been very limited in Vietnam. Notably, however, in addition to several agent-based modelling efforts, such as the 2D vertically integrated, coupled hydrodynamic-biogeochemical model, or EcoDynamo modelling software associated with the SWAT model, or hydrodynamic and water quality modelling (Pereira et al., 2004, Duarte et al., 2007, Hoanh et al., 2012), the LOICZ methodology has been the most widely used approach in biogeochemical process study in coastal areas (Crossland et al., 2005, Gordon et al., 1996). Unfortunately, these models have rarely measured keystone processes but, instead, have used best estimates from the literature and other ecosystems. The Land Ocean Interactions in the Coastal Zone program (LOICZ) has focused on the measurement of biogeochemical fluxes and implemented the biogeochemical budget methodology in the coastal zone based on the initial description of Gordon et al. (1996) (Swaney and Giordani, 2011). Amongst more than 200 site-specific budget case studies around the world under this program, seven case studies were undertaken in the Vietnamese coastal zone. They are presented on the LOICZ-Biogeochemical Modelling Node and include Cau Hai lagoon, Thu Bon estuary lagoon, Nha Trang and Van Phong Bay, Phan Thiet Bay and Hau & Tien river estuaries. All these studies followed the LOICZ Biogeochemical Modelling Guidelines to measure water exchange time, salt budgets, net metabolism and modelling of the nutrient budget in these ecosystems (Le, 2006, Nguyen, 2006b, Nguyen, 2006a, Nguyen and Nguyen, 2006, Nguyen et al., 2006, Phan, 2006, Nguyen and Phan, 2006). These are important case studies for understanding the coastal ecosystem metabolism in terms of nutrient budgets and flux estimates at regional scales. However, these studies have not directly measured the biogeochemical processes such as denitrification and nitrification operating under different anthropogenic drivers in coastal ecosystems. The process measurements and nutrient budget modelling described in these Vietnamese case studies were not set in the context of an estuarine ecosystem management framework with the various anthropogenic influences.

As indicated earlier, apart from the LOICZ studies, investigations of biogeochemical processes focusing on nutrient cycling in coastal ecosystems of Vietnam have been limited to a few projects in the Mekong delta and Red River delta. Most of these studies focused on measuring the nutrient dynamics in mangrove areas and plantations associated with aquaculture, such as shrimp and fish ponds (Alongi et al., 1999, Alongi et al., 2000, Wösten et al., 2003). In the Red River estuary, Wösten et al. (2003) also used the LOICZ and CABARET models to demonstrate the C, N, P exchange and fluxes in the estuary due to mangrove biomass growth. However, the calculations are based on average hydrological and nutrient concentration data which are affected by spatial and temporal fluctuations. The studies were formulated under the assumption of a constant nutrient balance that eliminates the errors in the real process measurements but does not take into account the variability of input sources.

Another recent study in the Red River delta by Luu et al. (2012) aimed at quantifying and evaluating the budget of nitrogen, phosphorus and silica fluxes from natural and anthropogenic processes in the basin area before they are delivered to the sea (Luu et al., 2012). A strength of this research is that the calculation of the N, P and Si budgets is based on a combination of various data sources (soil systems and hydro systems) with field measurements to evaluate the impacts of different human activities on the nutrient fluxes through the delta from the upstream watershed to the marine area. However, this study does not refer to the actual nutrient processes that are working inside the estuarine benthic systems, such as nutrient fluxes between sediment and water, or the lack of retention capacity of the ecosystems. Although some studies measured the rates and pathways of benthic decomposition and mineralization in coastal ecosystems, most focused on the impact of fish farming and shrimp ponds on biogeochemical sediment processes, rather than taking into account the various effects of cumulative sources such as land use changes, industrial waste discharge and urbanisation (Alongi et al., 1999, Alongi et al., 2000, Nguyen et al., 2012). In addition to these studies in the two biggest deltas in Vietnam, investigations have also been undertaken on nutrient budgets of water reservoir catchments and nutrient concentration, heavy metal contamination and phytoplankton distribution in coastal estuarine ecosystems in central Vietnam (Giuliani et al., 2011, Le et al., 2014, Rochelle-Newall et al., 2011). However, no research has been undertaken on how the main processes such as denitrification, nitrification and carbon fixation function under the pressures of anthropogenic impacts or their management implications in coastal ecosystems of Vietnam.

❖ *A case study of Dong Ho Estuary*

Dong Ho estuary is located adjacent to Ha Tien town, Kien Giang province, Vietnam (Figure 1.1). The estuary exemplifies the anthropogenic impacts and management issues facing most of the Mekong coastline and other similar areas in Vietnam and Southeast Asia. Dong Ho estuary has all of the key characteristics of a tropical estuarine ecosystem with high biodiversity. Significantly, Dong Ho estuary has complex hydrological conditions that are affected by both the Giang Thanh River inflow from the northeast and tidal exchange with the Southwest Sea, Gulf of Thailand, in the southwest. In addition to this, various canals are directly and indirectly associated with the estuary and provide inputs from local and more remote locations. Importantly, the estuarine hydrology exhibits strong seasonal variability. Fresh water from the Giang Thanh River carries large amounts of sediment into the estuary and dominates water transport as well as water quality in the rainy season (May - November) (Le and Truong, 2011). Conversely, in the dry season (December – April), estuarine waters are dominated by marine influences through tidal flows from the adjacent sea (Thai and Phung, 2009). In addition, the numerous canals, especially the Ha Tien - Rach Gia canal and connecting canals, have a range of implications and complexity for the estuarine hydrology in both seasons. The significance of this strong seasonality for ecosystem performance and the internal biogeochemical cycles of Dong Ho estuary is not known but, given the magnitude of the seasonal changes, they are likely to be highly influential on the ecosystem's performance.

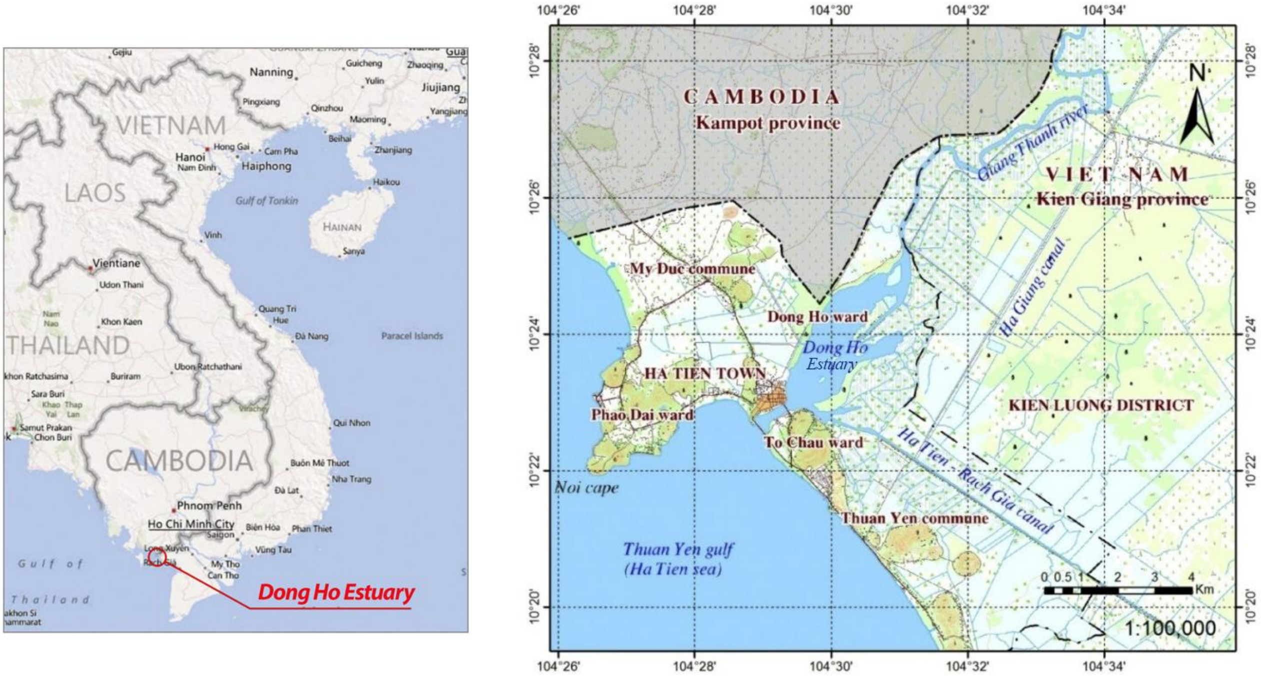


Figure 1.1: Location of Dong Ho estuary and Ha Tien, Kien Giang Province of Vietnam

In 2006, the Dong Ho estuary was identified as a key transition zone in the Kien Giang Biosphere Reserve which was recognised by UNESCO's MAB program (Carter, 2012b). Due to its significant biodiversity values and high potential for tourism development, Dong Ho has attracted great interest from local government and scientists seeking to achieve integrated planning for the conservation and development of this estuary. However, recent studies have shown that pressures from socio-economic development and climate change are altering the ecological, physical and biological conditions of the Dong Ho estuary such that ecosystem processes, specific species and overall biodiversity are being degraded (Phung, 2011, Truong, 2011). Within this context, Dong Ho was selected as a pilot project site in the "Conservation and Development of the Kien Giang Biosphere Reserve (KGBR)" to assess management feasibilities and approaches to assist the KGBR Management Board in establishing sustainable management recommendations for the Provincial Peoples Committee on decision making with regard to development strategies for this area (Carter, 2012b).

Although Dong Ho estuary has high biodiversity and ecosystem values, as well as significant cultural and historical values, this area is currently subject to many environmental problems related to land use changes, intensive food production (rice and prawn aquaculture), and population pressures from urban development and tourism activities. Three major environmental issues have arisen in Dong Ho estuary as a result of these influences: (i) the decline in the total area of the estuary due to the high sediment accumulation rate; (ii) water pollution due to untreated wastewater from domestic sources, the expansion of aquaculture ponds and intensification of agriculture; and, (iii) the degradation of natural resources due to over-fishing, land reclamation and riparian clearance (Truong, 2011). The complexity and potential degradation due to the negative activities occurring in and around Dong Ho were referred to in a recent study of the pesticide and herbicide concentrations in the numerous Mekong canals of Kien Giang and An Giang provinces, and in Dong Ho estuary (Johnstone, 2013). The data shows a significant influence of agricultural production on water quality and ecosystem health in the estuary and the connecting canals. The impacts of key anthropogenic activities on the environmental quality of Dong Ho are discussed in detail in Chapters 2 and 4 of this thesis. The occurrence of these issues is widespread along the Vietnamese coast and Dong Ho estuary provides a good representative ecosystem that can be used as a case study to better understand the ecosystem performance in coastal estuaries under these pressures.

Given the recognition and ongoing management focus, Dong Ho estuary was chosen as a case example to develop a scientific understanding of key biogeochemical processes in a coastal estuary, and to explore the potential use of process measurements in management and decision-making. As previously noted, in view of the socio-economic development and climate change pressures, the Dong Ho ecosystem is representative of a range of similar ecological situations in coastal areas of Vietnam, and so the lessons learned here are expected to provide guidance and a scientific basis for the sustainable development of similar systems elsewhere in Vietnam and the Southeast Asian region.

1.3. Knowledge Gaps & Research Objectives

- *Knowledge gaps & the role of biogeochemical processes in estuarine performance*

The impacts of anthropogenic activities on the nutrient dynamics in coastal areas have been observed and studied in many sites at both small and large scales (Beegle, 2013, Boynton and Kemp, 2008, Elliott and de Jonge, 2002). Numerous studies have investigated the relationship between estuarine ecosystem functions and their ongoing processes, and the significance of the key ecological processes in the management of estuarine performance. For example, many studies have been undertaken in Chesapeake Bay, the largest estuary in the USA, to evaluate the ecological responses to nutrient enrichment over the last centuries in order to develop effective strategies for managing coastal resources (Kemp et al., 2005, Beegle, 2013, Malone et al., 1996, Testa, 2013, Testa et al., 2014). A number of studies by the CRC Coastal in Australia have sought to improve our understanding of the function of tropical estuaries, and the importance of studying coastal nutrient cycles in supporting the management of estuaries and their catchments (Webster et al., 2003, Melzer and Johnson, 2004, Robson et al., 2006). For example, the modelling and nutrient cycling study on the Fitzroy Estuary by Robson et al. (2006) has been used to support the adaptive management framework of the Reef Water Quality Protection Plan by providing estimates for nutrient and sediment loads to the Great Barrier Reef lagoon and associated coastal waters (Robson et al., 2006). Harris et al. (1996)

constructed ecosystem process conceptual models for Port Phillip Bay (Australia) to examine the impacts of increasing sewage discharge, and to investigate the ecosystem responses to nitrogen limitation in Australian coastal waters, with the purpose of understanding the important interactions of ecosystem structure and processes (Harris et al., 1996).

Based on the several examples provided above, it is clear that measuring and monitoring ongoing processes in estuaries provide a useful tool and direct evidence as a basis for management. However, many monitoring programs are focusing on the mix of indicator groups representing elements of the structure and composition of estuarine ecosystems rather than on the ongoing processes which underpin the estuarine ecosystem function and performance. Therefore, an improved way to monitor estuarine environments rather than just stocks of materials is to monitor the ecosystem function and performance relative to both a management goal and comparable system performance levels. Moreover, there is a need to better address the practical aspects of improving the usefulness and effectiveness of any process that we monitor.

Given the present degraded state of many estuaries, biogeochemical process knowledge stands to provide insights that are hard to gain by any other way. As indicated, processes reflect keystone aspects of the overall performance of an ecosystem. There are various examples where people have either shown this or inferred it from their research (Robson et al., 2008b, Valiela et al., 1997, Webster et al., 2003, Harris, 2001, Bianchi, 2007). The overall goal of biogeochemical process measurements is to provide a comprehensive understanding of how process distribution and performance can directly influence management strategies, including how monitoring might be done. For example, the Centre for Coastal Biogeochemistry Research of Southern Cross University, Australia has studied the integration of biogeochemical processes to assess the impact of discharged wastewater on the ecosystem health of the Lower Richmond River, Brunswick River Estuary, Pimpama River Estuary and Emigrant Creek to propose appropriate wastewater treatment methods that meet environmental regulatory requirements for managers (Southern Cross University, 2014). In addition, modelling and managing nutrient losses from agricultural fields to waterways are used for defining water quality under the EU water framework directive (WFD) (Heathwaite et al., 2005). Numerous studies have been undertaken in the U.S, especially in the Chesapeake Bay, to assess the influences of nutrient pollution in coastal waters, based on biogeochemical process measurements and the evaluation of the ecological effects of nutrient cycles in estuarine management (Howarth et al., 2002, Fenn et al., 2003, Kemp et al., 2005). With a better understanding of estuarine and nutrient processes that contribute to eutrophication, much effort has been made in the U.S to enhance the control of agricultural runoff, urban runoff and point sources of N and P flowing into the estuary but there are few comprehensive plans for nutrient enrichment management, particularly from nonpoint sources (Howarth et al., 2002).

Among the key attributes of coastal estuarine system, the keystone biogeochemical processes demonstrate the vital role in balancing and controlling the availability of nutrients as well as oxygen for the ecosystem (Johnstone, 2012, Hanington et al., 2016). Although measuring biogeochemical processes may require more complicated and higher skill levels, this is increasingly becoming more practical and efficient due to the development of technologies such as sensor networks and data collection networks. Moreover, process measurements allow us to improve our predictive capability, especially when integrated into appropriate models and frameworks. The information they provide integrates a range of ecosystem variables including physical, biological and chemical contexts, as well as anthropogenic inputs and regulatory factors.

In conclusion, the potential for using process measurements as indicators for estuarine management has been shown in several of the studies presented above. However, the application of biogeochemical process measurements in the context of Southeast Asia and Vietnam is still questionable and requires more studies to assess the significance of these methods in environmental management. Furthermore, measuring biogeochemical processes can provide a more effective tool and methodology that can then potentially be adopted by developing countries such as the countries in Southeast Asia, which can deliver many of the advantages listed above.

❖ *Research objectives*

The aim of this study is to elucidate the potential use of key biogeochemical processes as indicators for, or evidence to support decision-making and environmental management in the Dong Ho estuary in Ha Tien, Kien Giang, Vietnam. Accordingly, the research has five main objectives:

(i) Identify the main anthropogenic factors and potential pollutant sources to the ecosystem;

(ii) Define the key physic-chemical and biological factors affecting ecosystem function;

(iii) Identify loads of key materials into the estuary that influence carbon and nutrient stocks in the water column and benthic sediments;

(iv) Measure key biogeochemical processes such as primary production, internal benthic nutrient fluxes, denitrification that underpin ecosystem function;

(v) Assess if the estuary is retaining materials or simply acting as a pipeline to the sea; and, in view of the new understanding of system behaviour, consider the implications of current inputs and ecosystem function for management and future sustainability of the Dong Ho estuary.

1.4. Research questions

In view of the overarching research objectives above, the main research questions that the thesis seeks to address are:

How are carbon (C) and nitrogen (N) currently processed within the Dong Ho estuary and what is the potential carrying capacity for these nutrients into the future?

In order to answer this question, there were a number of sub-questions that needed to be addressed:

(1) What are the dominant biogeochemical processes influencing N & C transformation in the Dong Ho estuary?

(2) What is the relative significance of the observed N & C cycling for overall system performance?

(3) What actions might be implemented to enhance the ecosystem and biodiversity resilience of the Dong Ho estuary in the light of current and foreseeable anthropogenic influences?

1.5. Thesis structure

This thesis is comprised of 7 chapters. The first three-chapters include an introduction to the context of the problem in general and in Vietnam (Chapter 1), a description of the study area and the influences acting on the Dong Ho estuary (Chapter 2), and an overview of the research approach taken, and the key methods used (Chapter 3). The ensuing two-chapters (Chapters 4 & 5) present the results from a pilot study undertaken in December 2014 (dry season) and from the three main field campaigns undertaken in August 2015 (wet season), April 2016 (dry season) and November 2016 (wet season). Each of these chapters includes five main sections: an introduction to the chapter, a detailed description of the methods used, the results obtained, and a discussion of the results and key insights gained.

Chapter 4 describes the baseline conditions and stocks of materials in the Dong Ho estuary. This encompasses the bathymetry, benthic habitat types and distributions, key biophysical features, the concentration of dissolved nutrients in the water column, and benthic sediment characteristics.

Chapter 5 focuses on quantifying key processes operating in the estuary, including the rate of benthic and water column primary production, benthic nutrient fluxes and denitrification. This work utilises the three zones of Dong Ho estuary determined from the baseline studies, and aims to describe how these processes influence the ecosystems assimilative capacity for the materials it receives from the different land uses surrounding the estuary.

Chapter 6 utilises the LOICZ modelling methodology to provide a synthesis of the data collected with the aim to summarise the understanding gained, and to allow for comparison with other estuarine system worldwide. It is also used to consider how potential future human impacts might influence the long-term function and sustainability of the Dong Ho estuary.

The last section, Chapter 7 considers the key insights gained from a management perspective and proposes a number of aspects that need consideration as the Dong Ho estuary and its surroundings are developed in the future.

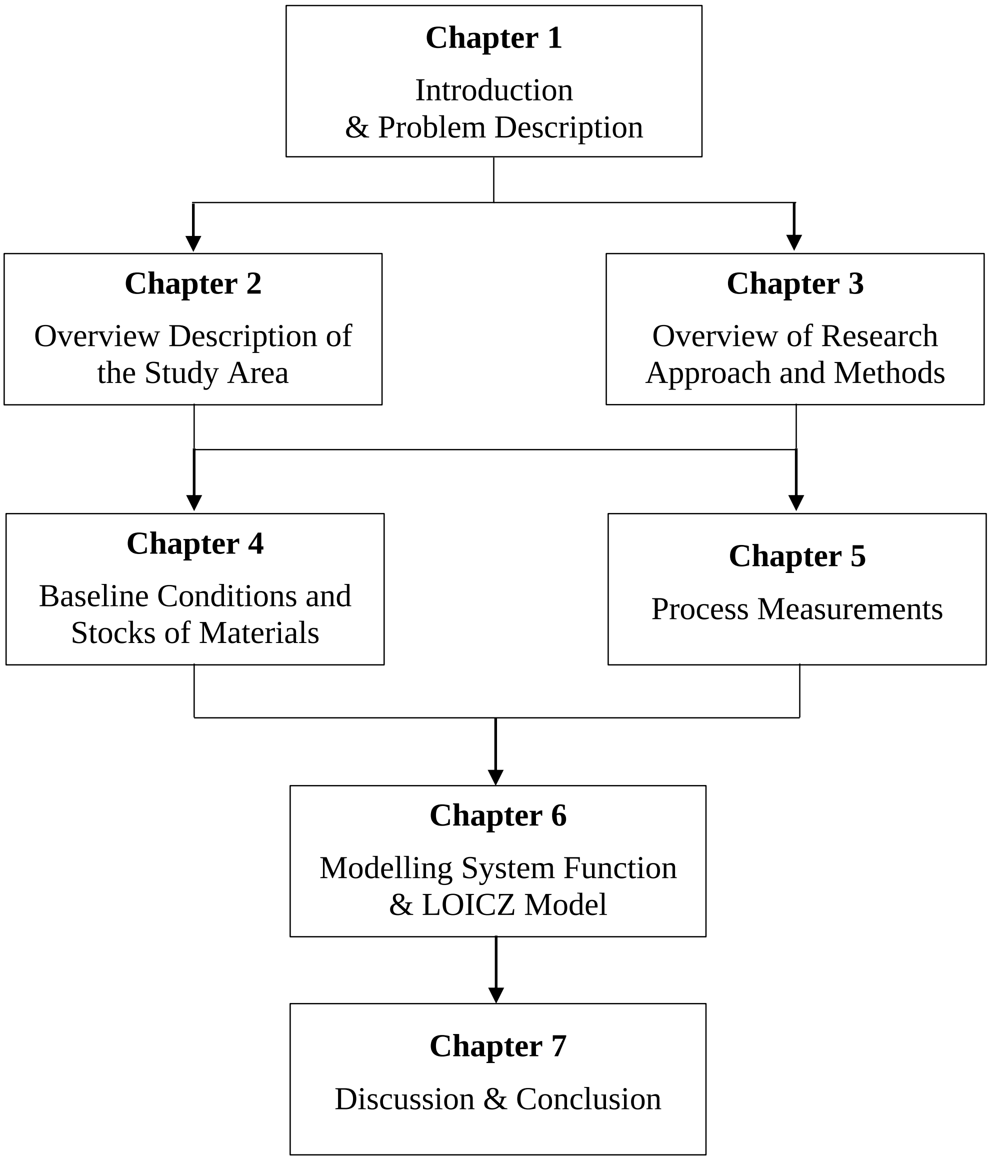


Figure 1.2: Structure of thesis

CHAPTER 2 - OVERVIEW DESCRIPTION OF THE STUDY AREA

Dong Ho estuary is located in the Kien Giang biosphere reserve and is part of the Southern Mekong delta of Vietnam. This study area is called "Đầm Đông Hồ" in Vietnamese by the local people, meaning "Dong Ho lagoon". However, according to geomorphology terms and estuarine classification, Dong Ho lagoon is considered as a 'barrier estuary' and is classified as being at the intermediate state of coastal lagoon evolution due to the level of infilling, its increasing intertidal ranges and elevated turbidity (Roy, 1984, Carter and Woodroffe, 1994, Perillo, 1995). The thesis examines water quality and potential contributions, or exchanges, across the wider estuary out to the boundary depicted in red in Figure 2.1. In order to investigate how the core estuary processed and responded to these materials, the benthic flux, community metabolism and biogeochemical process studies focused in the central estuary as shown in yellow line in Figure 2.1. This central zone is where catchment and oceanic waters all interacted and as discussed later, initial anecdotal evidence suggested this central area to be the zone where most deposition occurred and where the collective influence from Ha Tien town and the catchment was likely to be greatest (Carter, 2012a).

Figure 2.1: Defined boundary of the Dong Ho estuary (red line represents for the whole estuary and yellow line represents for the central estuary)

2.1. Introduction

Dong Ho is an estuary located adjacent to Ha Tien town, Kien Giang province, in the southwest of the Mekong delta region of Vietnam and close to the Vietnam – Cambodian border. The total area of Dong Ho estuary is estimated to be 1,384 ha including 903 ha water surface area, with the rest are mangroves and nipa palm (Carter, 2012a, Nguyen, 2004). The Ha Tien area was formed by alluvial deposition by the Mekong River over the last 6,000 years, and the Dong Ho estuary is "an unusual element" of the delta system (Carter, 2012a, Stattegger et al., 2010). The boundary of the Dong Ho estuary's catchment is poorly defined because this area is a flat coastal plain which has many interconnected canals. There are two main point sources of freshwater into the Dong Ho estuary, these are the Giang Thanh river and Rach Gia – Ha Tien canal. Stream velocity and flushing time of the Giang Thanh river and Rach Gia - Ha Tien canal into Dong Ho estuary are not known but the stream gauging stations are closed once per year in dry season to prevent saltwater intrusion and related effects on agriculture. The closing period of gauging stations varies and depends on the magnitude of salinity intrusion each year. According to Carter et al. (2012) and other studies in this area (Le and Truong, 2011, Truong, 2011), the catchment surrounding Dong Ho is less favourable for agriculture due to the lack of freshwater in the dry season and the presence of acid sulphate soils which exacerbate water quality issues in the dry season.

The hydrodynamic conditions of the Dong Ho estuary are strongly influenced by the humid tropical monsoon climate. Dong Ho has two distinct seasons: the wet season from May to November, and the dry season from December to April. As a result, the peak flood season from July to November contributes up to 75% of mean annual flow to the estuary (Carter, 2012a, Le and Truong, 2011). Flushing is recognized as important and is likely playing a key role in this system during the wet season. This is taken up in more detail in Chapter 6. In the dry season, no freshwater inputs recorded. In the wet season, freshwater flows were estimated to be approximately 1000-1450 m^3/s (DARD, 2014). In the flood season, it was estimated that the freshwater flows into Dong Ho estuary were about half of the flood season flow into the Hau river (Phan, 2006, Wolcke et al, 2016).

In addition to large freshwater flows, Dong Ho estuary also receives large quantities of sediment from the Giang Thanh River in the north as well as inputs from the Ha Tien – Rach Gia flood-control canal in the southeast. Sediment input from the Giang Thanh River has created a bottom silt deposit ranging from 1.3 to 1.5 m thick. The depth and extent of sediment deposits are increasing, reducing the water flows and the total water area (Carter, 2012a, Le and Truong, 2011). The sediment deposition rates vary throughout the estuary, contributing to variation in bathymetry (Truong, 2011, Johnstone, 2012), which is further discussed in Chapter 4.

The Dong Ho ecosystem has high biodiversity including 142 phytoplankton species and 42 zooplankton species in the water phase, and 24 zooplankton species in the benthos (Nguyen and Tong, 2011, Nguyen, 2004, Luong, 2006). In addition, twenty-five mangrove species have been recorded including 327 ha of nipa palm (Nypa fruticans) within 480 ha of wetland forest along the west bank of the estuary (Carter, 2012a, Thai and Phung, 2009). The distribution, structure and species composition of vegetation in the Dong Ho estuary are influenced by tidal exchange (Thai and Thai, 2011).

2.2. Land use and anthropogenic influences on the Dong Ho estuary

The Dong Ho estuary has a long history of landscape changes and represents an important cultural heritage area of the Mekong delta and Vietnam. Since the 1990's, the Dong Ho estuary and its surroundings have been significantly altered due to the influence of human activities (Nguyen, 2011). Perhaps one of the most profound alterations to the Dong Ho estuary system came with the implementation of the flood drainage system feeding to the West Sea under the national government flood management policy in 1997 (Nguyen, 2011). One of the major outcomes of this strategy is the increased flows from the Hau River (Mekong) via the Vinh Te canal and Giang Thanh River into the Dong Ho estuary. This has significantly increased flows and material inputs into the Dong Ho estuary during the wet season (Carter, 2012a, Nguyen, 2011). In addition, the Rach Gia – Ha Tien canal in the southeast of the Dong Ho estuary also contributes substantial freshwater inputs from Long Xuyen Quadrangle as well as high sedimentation rates into the estuary (DARD, 2014). Although the available information on turbidity levels and sediment loads is scant and fragmented, satellite images of Dong Ho between 2005 and 2015 confirm the extensive influence of sediment inputs through the development of large tidal flats inside the estuary over this time period.

In addition to this change in water flow, there have also been significant changes in land use within the catchment feeding the Dong Ho ecosystem (Carter, 2012a). The step changes from low intensity farming to intense rice production along the Vinh Te canal and adjacent areas since 2005 typifies the extent and intensity of changes that are occurring in the Dong Ho system (Carter, 2012a). Moreover, the establishment of the sea dyke in 2003 to build the commercial area of Ha Tien town and the ensuing land reclamation in 2005 in the west sea off Ha Tien, have also strongly affected the coast line of Ha Tien. This includes the hydrological characteristics of the Dong Ho estuary such that water flow from the estuary to the open sea is more constrained (Carter, 2012a). Furthermore, since 2011, land reclamation to the east of Dong Ho for new residential areas has further exacerbated this situation (Carter, 2012a). There have been no empirical studies to date on the impacts of these alterations, however there is strong anecdotal evidence that these changes have strongly influenced the Dong Ho ecosystem.

One other aspect that has been changed in the Dong Ho area is the distribution and abundance of wetland forests which have been increasingly replaced with Nipa palm and aquaculture activities. As illustrated in Figure 2.2, almost 50% of the estuary has been converted to these uses during the last 10 years. This issue is considered to be one of the most influential factors for water quality and the biological function of the Dong Ho estuary (DARD, 2014). In addition to these changes related to food and resource production, the Dong Ho area has also seen rapid population growth and the expansion of urban areas. These changes are due largely to immigration to Ha Tien town and To Chau from rural and other areas. The proposed tourism development in the upcoming years will further alter the land use around Dong Ho and potentially exacerbate existing problems of pollution and nutrient cycling throughout the ecosystem (DARD, 2014).

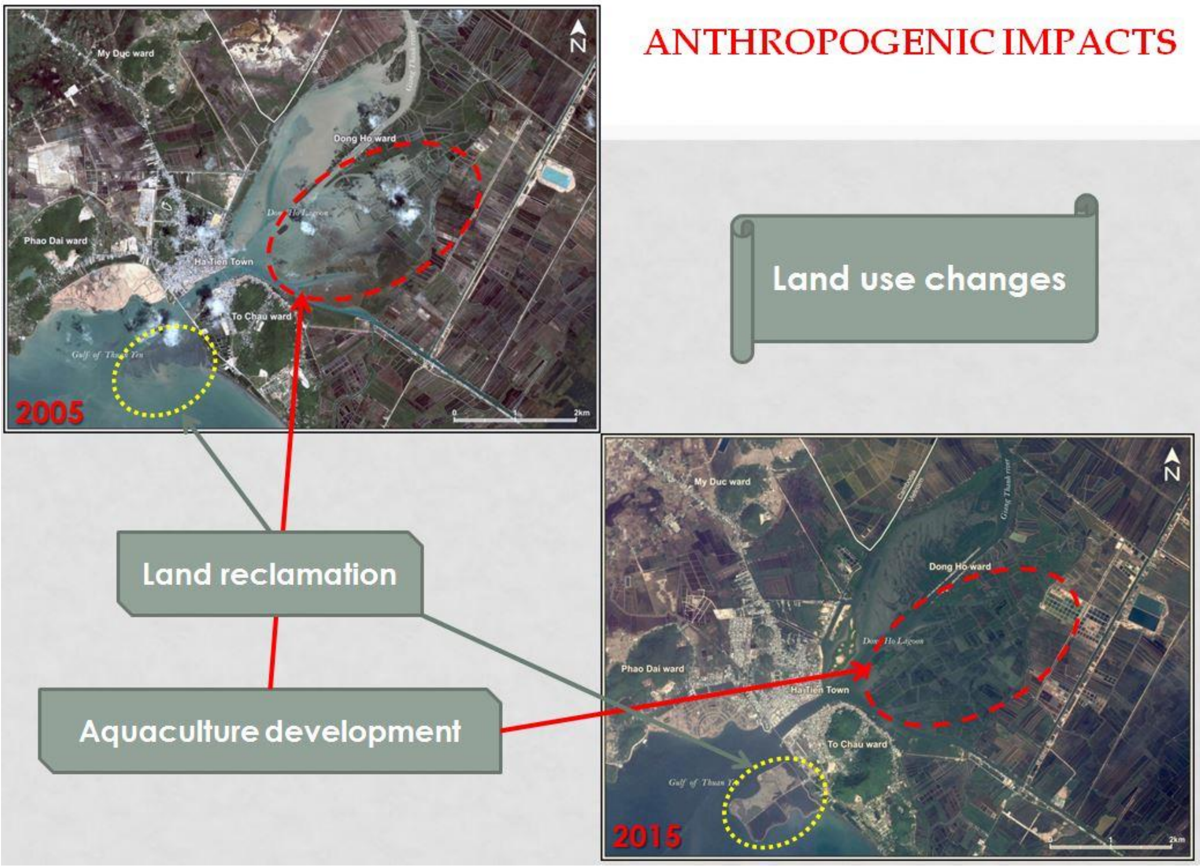


Figure 2.2: Land use changes of the Dong Ho estuary from 2005 to 2015

2.3. Key ecosystem processes operating in Dong Ho

As in similar estuarine ecosystems, the function and sustainability of the Dong Ho estuarine ecosystem are underpinned by key biogeochemical processes including those related to nitrogen, carbon, and phosphorus. Importantly, as elaborated below, alterations to these processes and cycles may potentially have profound impacts on the form and function of the Dong Ho ecosystem. Accordingly, it is crucial to build an understanding of how these nutrient cycles are currently functioning, so that the influence of anthropogenic changes can be more accurately assessed.

2.3.1. Sources of organic carbon and nutrients to the Dong Ho estuary

The Dong Ho estuary receives diverse inputs from both natural processes and human activities. It is not known whether Dong Ho is a sink of materials or not, but anecdotal evidence indicates that more sedimentary and associated organic material reaches the estuary than is exported to the West Sea or adjacent canals (DARD, 2014). The main sources of nutrient inputs into the estuary are summarised in Figure 2.3, this information is based on a review of the literature and field observations from a pilot study. As elsewhere, nutrient loads into Dong Ho can be derived from diffuse sources and point sources. In the case of the Dong Ho estuary, the intimate connection between the different land uses in the catchment and the prolific number of sewer and stormwater drains entering the Dong Ho estuary suggest that significant inputs are received from both agricultural practises as well as urban waste in the immediate surrounds, although, in view of the interconnected canal systems, there is potential for materials to also be drawn from more remote areas. The extent and interconnected nature of the canals related to the Dong Ho estuary are illustrated in Figure 1.1.

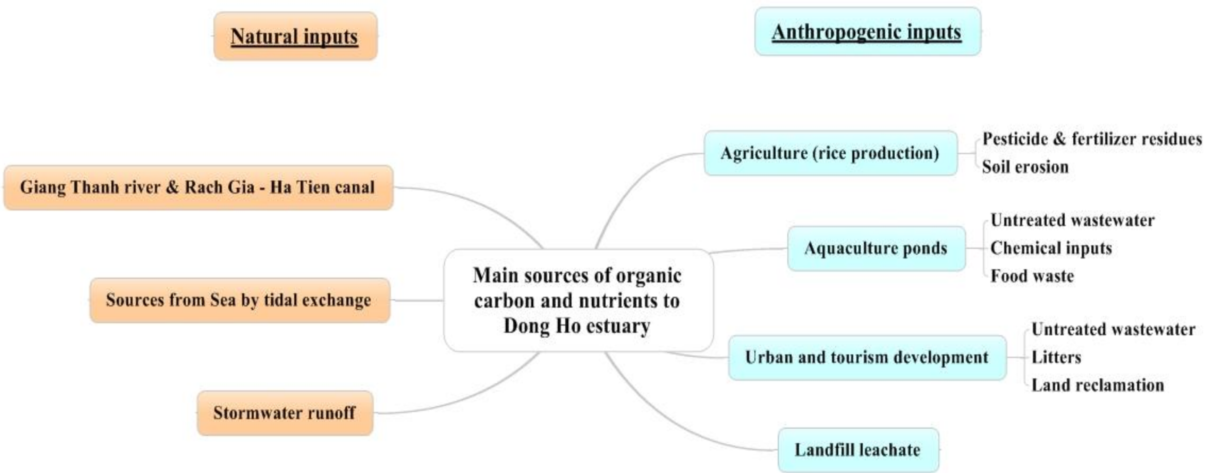


Figure 2.3: Summary of the main sources of organic carbon & nutrient inputs into the Dong Ho estuary, identified from field observations of drains and drainage patterns in the pilot study (2014)

Nutrient delivery into the estuary from external activities related to agriculture, aquaculture, urban population and tourism are likely to have resulted from pollutant impacts on water quality and living organisms in the aquatic system. The increased nutrient loading and accumulation of pollutants and organic matter produced as waste from domestic activities, agriculture, and aquaculture are widespread occurring in the Mekong river delta (Thanh et al., 2004). The residues of fertilizers and pesticides from agriculture and stormwater runoff enter Dong Ho by the Giang Thanh river, Ha Tien – Rach Gia canal and other small canals (DARD, 2014). As a food producing area of Mekong delta, the surrounding areas of Dong Ho have extensive rice paddy fields and aquaculture ponds. The growth of agricultural production with more fertilizer use and aquaculture production with disposal of untreated waste from fish farms leads to increased levels of nitrates and phosphates as well as toxicants into the ecosystem, which causes harmful effects to aquatic life and human health. A recent study in Kien Giang has shown the high level of pesticide concentrations in numerous Mekong canals and the Dong Ho estuary. Diuron is the main pesticide detected in both dry and wet seasons in Dong Ho (Johnstone, 2013). In addition, the soils of the Long Xuyen Quadrangle are typically acid sulphate. Due to unsustainable farming practices and high soil erosion in rice fields as well as dredging of aquaculture ponds, the high iron content associated with low pH values affects the water quality of Dong Ho (Carter, 2012a). Soil washed from agricultural land and from areas of construction activities for urban and tourism development, are another pollutant source in the estuary. The high sediment loads also creates one of major environmental problems for the Dong Ho estuary (Thai and Thai, 2011).

Figure 2.4: Drains for domestic wastewater discharge into the Dong Ho estuary from Ha Tien town (Le Vu - December 2014)

Another important nutrient source for the Dong Ho estuary is the untreated wastewater directly discharged from residential areas of Ha Tien town and the To Chau area. The master plan of Ha Tien town (Decision no.135/2011/NQ-HDND) stated that there would be a wastewater treatment plan for the urban area in 2014. However, since the last fieldwork in November 2016, all domestic wastewater from Ha Tien is directly discharged into Dong Ho without treatment. Field observations have identified eleven large drains discharging wastewater into the estuary along Ha Tien town from the To Chau Bridge to a new construction area near the People's Committee Office.

More importantly, the landfill site to the north of Ha Tien town near the Cambodian border is a possible nutrient and toxin source for the Dong Ho estuary. According to the proposal of planning for conservation and sustainable development in the Dong Ho estuary in 2014 (DARD, 2014), the treatment system for landfill leachate has not been completed and the leachate flows into the estuarine system and groundwater. It is a serious environmental problem for the Dong Ho ecosystem; especially if the urban population and tourism increase, leading to increased dumping into the same landfill site.

2.3.2. Factors influencing biogeochemical processes in Dong Ho estuary

The major factors influencing biogeochemical processes in estuarine ecosystems can be categorised into three main groups: physical factors, biological factors and human factors. Physical factors include benthic topography, physical resuspension and sediment morphology; the internal hydrodynamics include the tidal regime and its effects on residence time; and climatic variables such as light and temperature (Figure 2.5). All of these factors can significantly influence the rate and distribution of key biogeochemical processes in the ecosystem and, in turn, influence overall ecosystem performance. For example, sediment texture affects the diffusive and advective processes in the sediments; therefore bottom topography and current changes may control the fluid transport as well as NH_4^+, NO_x concentrations between the overlying water column and the sediments (Joye and Andersen, 2008, Huettel et al., 1998). It is therefore necessary to clarify the relationships of these factors in different ecosystems to understand the fluctuations or changes in nutrient profiles and process rates.

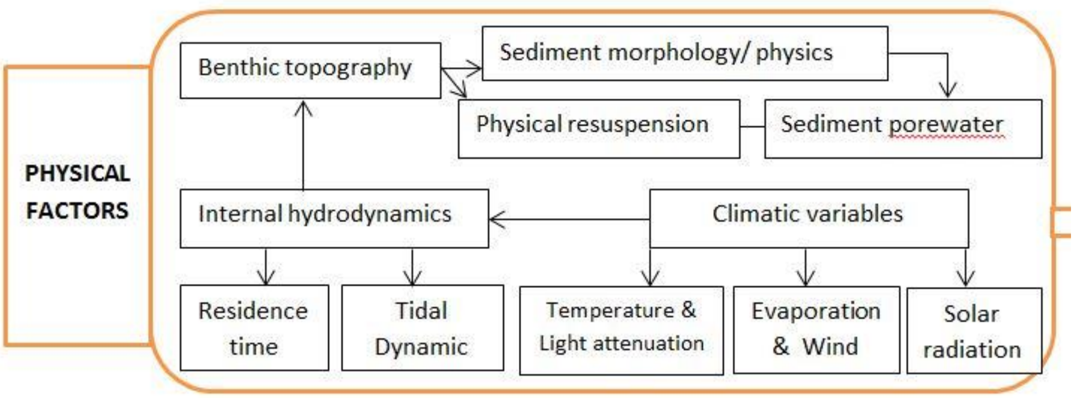


Figure 2.5: Physical factors influencing nutrient cycling in the Dong Ho estuary

Plant communities and benthic fauna are important factors in biogeochemical cycles. In shallow estuarine ecosystems such as Dong Ho, biogeochemical processes within sediments and benthic – pelagic coupling are strongly affected by biological factors including microphytobenthos, benthic macroalgae, macrophyte communities and benthic fauna (Figure 2.6). These factors play important roles in influencing oxygen availability which regulates most nitrogen and phosphorus cycling processes and other biogeochemical processes, such as related to iron and sulfur (Joye and Andersen, 2008). The distribution and concentration of oxygen in sediments are mostly dependent on benthic primary production, rooted benthic macrophytes and bioturbation of infauna. In some shallow coastal estuarine ecosystems with short residence times, benthic primary production can significantly regulate nitrification – denitrification coupling (Joye and Andersen, 2008). Therefore, one of the first tasks in the pilot study is identifying the availability of microphyphobenthos and macrophyte communities in the benthic habitats of the Dong Ho estuary. Depending on the availability of these habitats, the Dong Ho estuary can be divided into different habitat zones for assessing and evaluating the effects of biological factors on nutrient cycles.

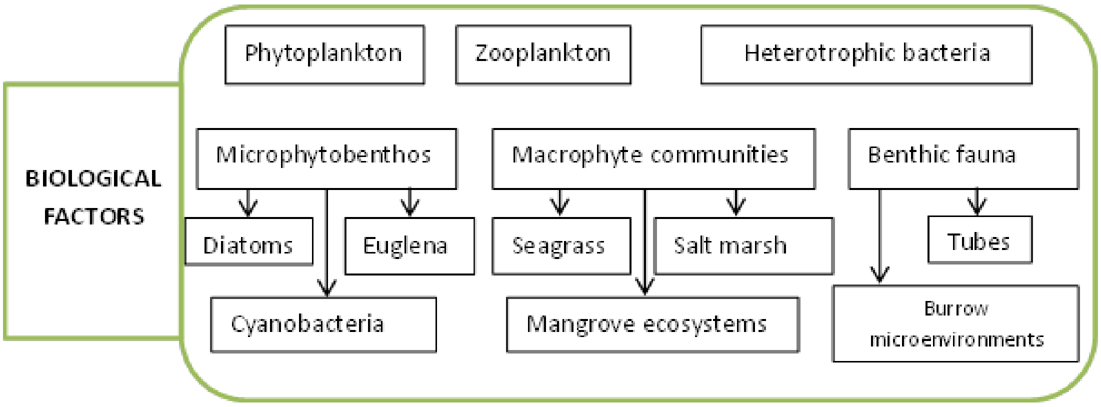


Figure 2.6: Biological factors influencing nutrient cycling in the Dong Ho estuary

In addition to physical and biological factors, human factors are key drivers for changes in nutrient dynamics of the Dong Ho estuary. Human activities are also the factors which can rapidly transform the ecosystem performance and functions. Moreover, human activities, such as land reclamation, land use changes, increasing aquaculture farms or over fishing, will directly alter the characteristics of both physical and biological factors. Therefore, the complexity and links of all three groups of factors need to be addressed to understand how the nutrients are transformed within the estuary.

Figure 2.7 below shows the major factors influencing nutrient cycles such as nitrogen cycling, phosphorus fluxes and carbon fixation in Dong Ho. To understand the interactions between these factors into the Dong Ho estuarine ecosystem functions and performance, it is proposed that key indicators (Figure 2.7) in the water column and sediments, and the nutrient fluxes between them need to be measured and compared with other similar systems. Measuring these key indicators will clarify the ecosystem behaviour and assess how the anthropogenic activities impact on key biogeochemical processes.

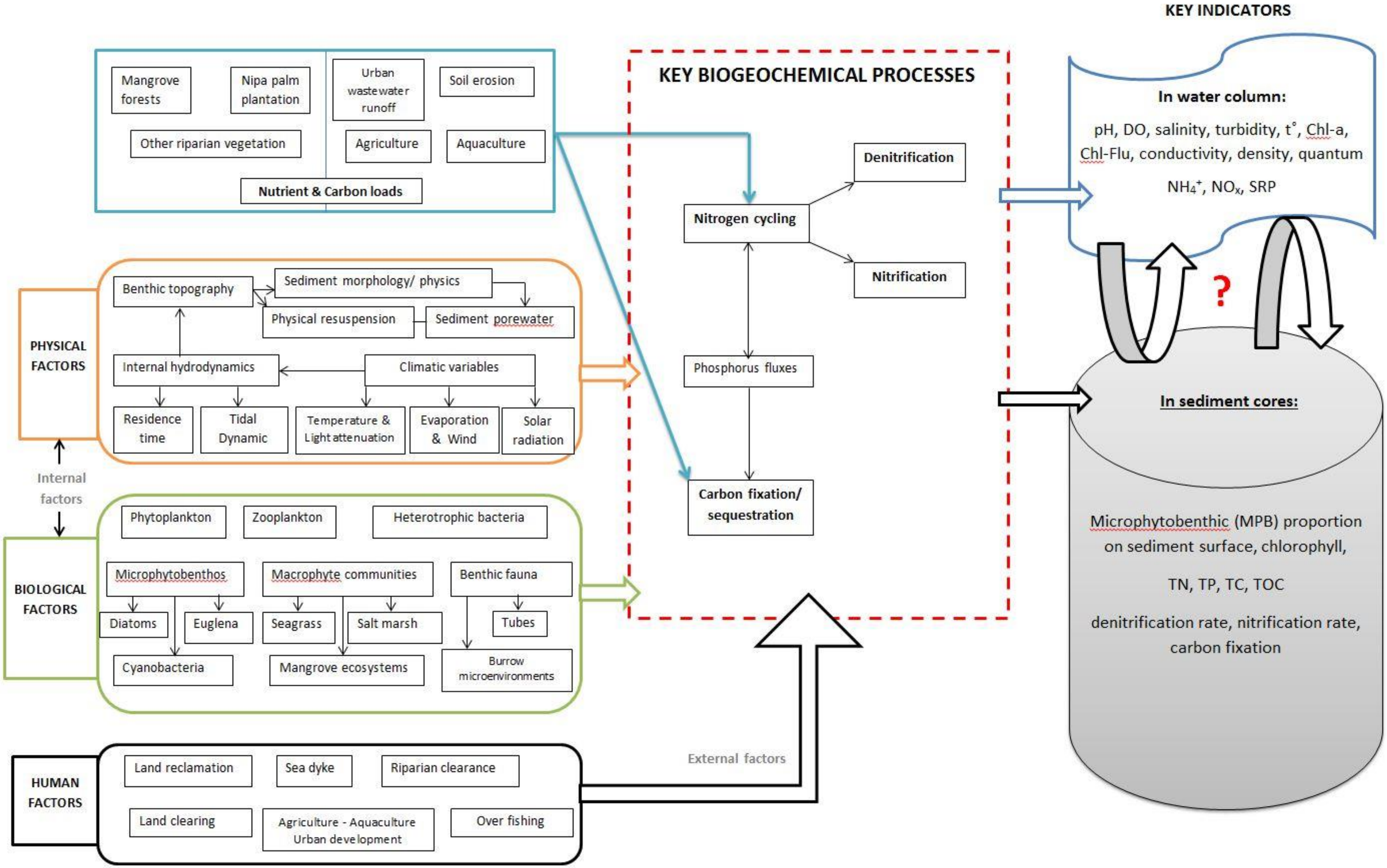


Figure 2.7: Main contributing factors influencing biogeochemical processes in the Dong Ho estuary

CHAPTER 3 - RESEARCH APPROACH AND METHODS

3.1. Introduction

Coastal estuaries are known for being highly productive ecosystems due to the dynamic physical and biological interactions between river inputs and marine exchanges. This unique attribute underpins much of their ecological function and the services they provide (Hobbie, 2000). Despite this, estuaries continue to be degraded in response to a wide range of anthropogenic pressures such that many estuaries can now be considered as no longer reflecting the natural ecosystem they once were in terms of ecosystem services and ecological functions (Kennish and Paerl, 2010). In order to understand the wider ramifications of these vitiating pressures on ecosystem performance, it is crucial to identify the key ecosystem processes operating in the system that may be altered, and the fluxes of materials and pollutants transported or transformed by those processes (Bianchi, 2007). The information gained from such studies provides a fundamental understanding of how these anthropogenic pressures impact on estuarine systems and also elucidates the complexities behind finding management solutions and allocating responsibilities to specific stakeholders or organisations (McComb, 1995).

In addition to understanding the important issues causing estuary degradation, it is also vital that managers are able to undertake effective and ecologically sensible performance monitoring of these ecosystems so that management interventions can be adapted based on tangible evidence. To date, the bulk of monitoring in estuaries has evolved the measurement of water quality and ecosystem health indicators. Whilst such measures have proven useful in many instances, their focus and the information they provide is mostly related to the standing stocks or amounts of materials or species that exist at a given time, rather than the performance of key processes that underpin the delivery of these stocks (Aquatic Ecosystem Health, 2012). For example, it has been well illustrated in a number of studies in Chesapeake Bay and the Gulf of Mexico, that fundamental processes such as denitrification and nitrification underpin the systems overall performance and productivity (Devol, 2015, Nowicki et al., 1997, Kemp et al., 1990, McCarthy et al., 2015).

Biogeochemical processes have the potential to be altered by people in different ways (Alberti, 2008). In this context, by understanding how these processes are currently performing, and then estimating how they may perform in the foreseeable future, we have an opportunity to make informed decisions on the functions of the ecosystem and how we could potentially manage human activities that might alter it. In estuaries and coastal lagoons, an understanding of the biogeochemical processes related to carbon sources, and the nitrogen and phosphorus cycles is crucial if we seek to understand the impacts of anthropogenic activities on ecosystem capacity and performance. Biogeochemical processes, and especially nutrient processes in the coastal zone, have been studied for some time, such that the mechanisms of these processes and their function in aquatic ecosystems is well described (Blackburn and Sorensen, 1988, Jørgensen and Richardson, 1996, Nielsen et al., 2004, Howarth, 1988, Nixon, 1981, Nixon et al., 1986, Capone et al., 2008, Carpenter and Capone, 1983). Aligned with this knowledge, the study of the behaviour of coastal estuarine systems using an ecosystem approach has become more common in order to identify the capacity and attributes of the systems. Some studies, for example, have specifically considered “the consequences of physical, chemical, biological and geological forces on ecological processes” (Alongi, 1998). Accordingly, we now know that the response of ecosystems to human activities can be illustrated through the availability of nutrients and changes in transformation of nutrient cycles (Vitousek et al., 1997, Paerl et al., 2006). Therefore, understanding nutrient fluxes and their regulatory forces is a critical step to being able to sustainably manage the ecosystems facing anthropogenic influences.

Essential nutrients are required for a range of metabolic processes and to underpin primary production. They include nitrogen, phosphorus, organic carbon, silicon, iron, zinc and other trace metals (Smayda, 1983). In particular, nitrogen, phosphorus and organic carbon are considered as the most important elements controlling the primary productivity in shallow coastal estuarine ecosystems (Alongi et al., 1992, Crossland et al., 2005). Several studies showed the influence of dissolved organic carbon (DOC) on primary production (Godwin et al., 2014, Seekell et al., 2015). DOC can attenuate light due to chromophoric molecules, so production is light limited due to DOC content and morphology. In addition, DOC can stimulate primary production by shielding phytoplankton from harmful radiation (Seekell et al., 2015). Thus, in this research, the nitrogen and phosphorus cycles, as well as the carbon fixation in coastal estuarine systems, have been investigated to better understand their significance in controlling ecosystem performance and behaviour, and in relation to sustainable environmental management. These nutrient processes (nitrogen, phosphorus) and carbon fixation are the key features that should be measured in estuarine ecosystem health monitoring programs.

A case study from the Southern Mekong delta of Vietnam has been chosen to illustrate the complexity of estuarine management at the local scale and to assess the potential of using key biogeochemical process measurements in supporting estuarine management strategies. Dong Ho estuary, located in Ha Tien town, Vietnam, exemplifies the anthropogenic impacts and management issues facing most of the Mekong coastline and many other similar areas in Vietnam and Southeast Asia. Dong Ho estuary has all of the key characteristics of a tropical estuarine ecosystem with high biodiversity and complex hydrological conditions that are affected by both the Giang Thanh River inflow from the northeast, the Rach Gia – Ha Tien canal in the southeast, and tidal exchange with the Southwest Sea, Gulf of Thailand, in the southwest. This case study is in response to the urgent need to investigate and provide fundamental scientific evidence to support a sustainable and successful estuarine management strategy. The information from this study may reinforce the potential for the use of process measurements such as nutrient cycling in estuarine management and decision-making, especially for Vietnam and the Southeast Asian region.

3.2. Overview of approach

The aim of this study is to build an understanding of the current function of the Dong Ho estuary in terms of carbon, nitrogen and, to a lesser extent, phosphorous budget. Based on this understanding, the aim is to provide evidence to support decision-making and environmental management in the Dong Ho estuary, as well as potentially identifying key processes that might serve as more effective performance indicators than those currently being used. Therefore, understanding system behaviour and the current performance of key biogeochemical processes driving carbon and nitrogen cycling is crucial. In addition, by translating this knowledge into conceptual models it is hoped that decision-makers will more easily assimilate this new knowledge and apply it in their management processes. The overall approach for this thesis is summarised below in Figure 3.1.

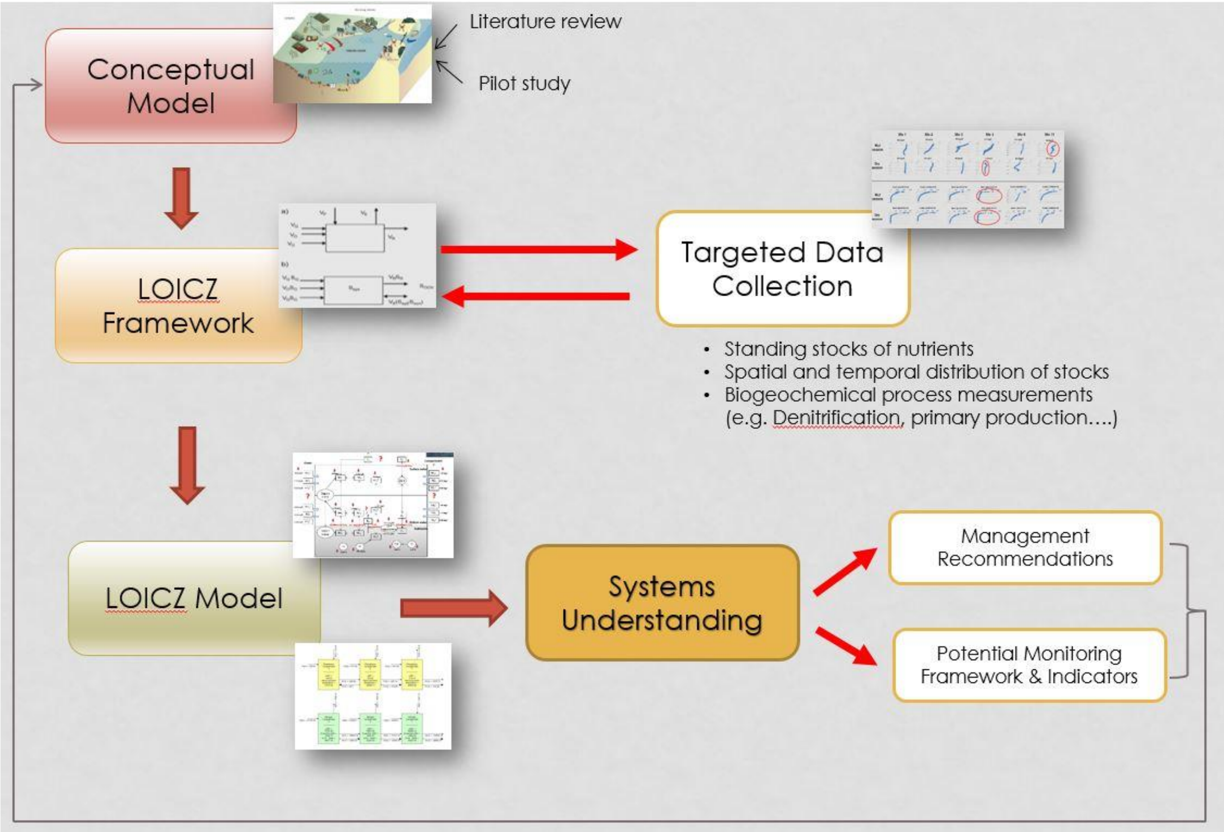


Figure 3.1: General approach used for this thesis

To establish the approach and methodology for the project, an initial conceptual model was built based on a literature review and a pilot study. This provided a basic understanding of Dong Ho estuary's functional components and nutrient processes. As indicated in Figure 3.1, the data collected from field work and process measurements were then collated into a LOICZ estuary model framework to summarise the understanding gained and to allow for a comparison with other estuarine systems worldwide. The LOICZ biogeochemical model (Swaney and Giordani, 2011) is used as a way of setting the research questions and targets. Chapters 4 and 5 provide the data needed to build the LOICZ model. The research focuses on the key nutrients as nitrogen (N) and phosphorus (P); and organic carbon (C) as indicators of ecosystem performance and status. Using a “stocks” and “processes” approach is an effective way to understand how the ecosystem reacts to human impacts and to develop robust budget models of important C, N, P fluxes. The data and results from the LOICZ model are analysed to understand and explore the feedback connections of anthropogenic impacts on important biogeochemical fluxes in the estuary. Finally, more complex conceptual models are built to enable a comparison with the initial project strategy model.

3.3. Structure of research questions

In order to answer the main research question, there are three sub-questions that need to be addressed and each sub-question encompasses two units of analysis for investigation. These units of analysis aim to support and provide more details to answer the sub-questions. Figure 3.2 below is a general conceptual framework that shows the sub-research questions with the data and methods required and the expected outcomes. Each of the three sub-questions is explained in more detail below.

The first sub-question seeks to understand the dominant biogeochemical processes influencing N & C transformation in the Dong Ho estuary. This also provides information regarding seasonal and spatial variations of these processes in the Dong Ho estuary. In addition, the relative levels and extent of the key nitrogen cycle processes of denitrification, and nitrification within the context of available carbon and nutrient processing in the Dong Ho estuary are identified.

The second sub-question focuses on clarifying the relative significance of the observed N & C cycling for overall system performance and its potential capacity to deal with anthropogenic inputs. To answer this sub-question, the main factors influencing ecosystem performance in the Dong Ho estuary are identified in support of the assessment of anthropogenic impacts on key ecosystem processes in the study area.

The third sub-question focuses on defining potential approaches or actions that might be implemented to enhance the Dong Ho ecosystems’ biodiversity and resilience in the light of current and foreseeable anthropogenic influences. The first task to answer this question is identifying the main pathways of influence between anthropogenic impacts and nitrogen and carbon processing in the Dong Ho estuary. Comprehensive analysis of system behaviour associated with anthropogenic influences is a critical step to understand the interactions and complexities of human activities on ecosystem function and sustainability. Accordingly, the main purpose of this sub-question is to assess the effectiveness of measurement of biogeochemical processes as a tool in supporting management strategies for the Dong Ho estuary.

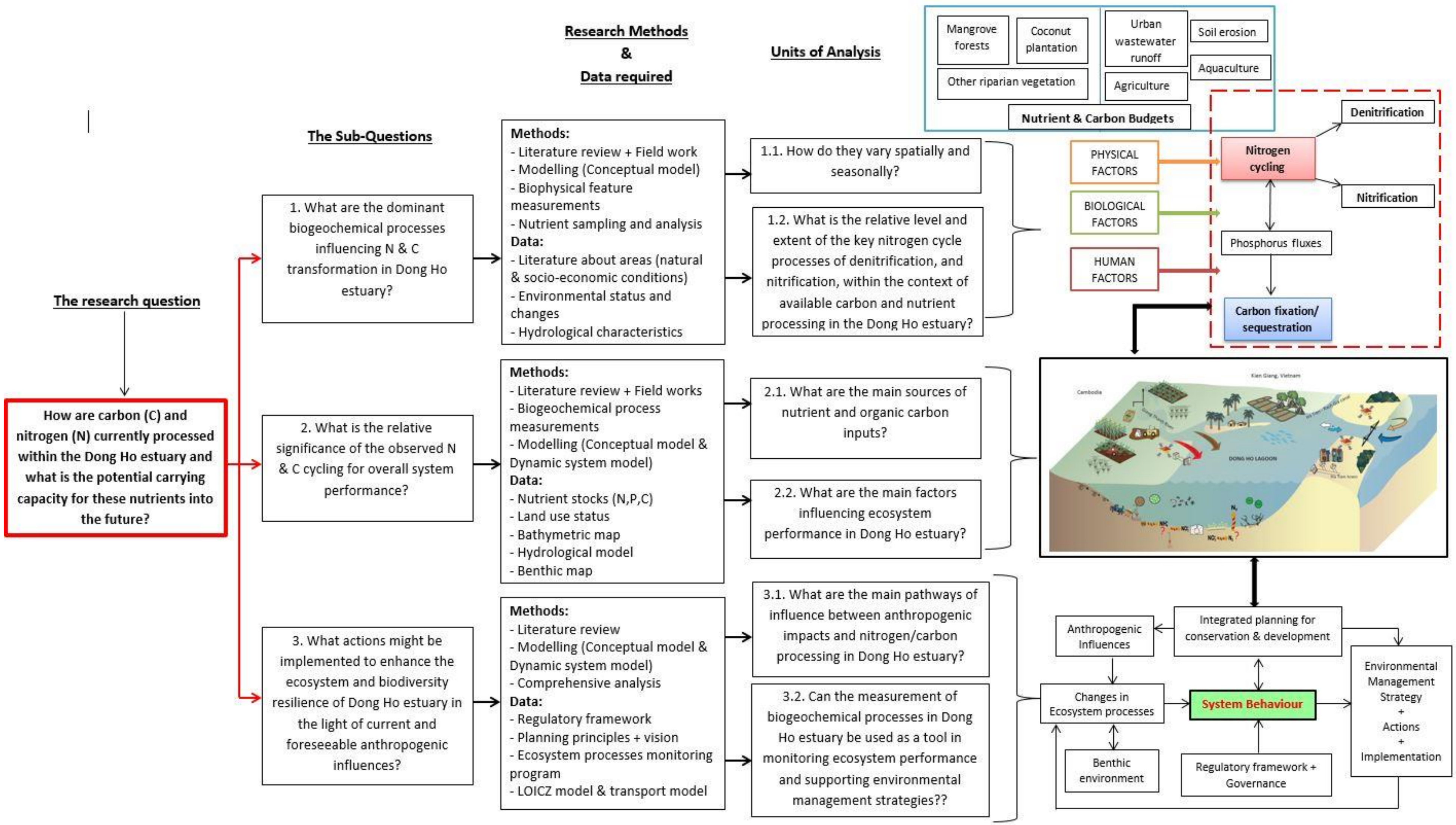


Figure 3.2: General conceptual framework for the research questions

3.4. Overview of Key Methods

This section presents a general overview of the key methods and approaches used in the project to provide a framework for how the respective methodologies were considered and integrated into the relevant sections of the work. A more detailed explanation and description of each method is provided in the relevant sections of the following chapters.

3.4.1. Mapping and Modelling

3.4.1.1. Bathymetric mapping and benthic habitat survey

Bathymetric data and benthic habitats are the foundation for hydrodynamic and ecosystem modelling (León et al., 2005, Lindim et al., 2011, Cogan et al., 2009). Mapping bathymetry and benthic habitats of the Dong Ho estuary can provide wide knowledge underpinning many aspects of management planning and environmental assessment. In addition, bathymetric map and data of benthic habitats of the Dong Ho estuary are benchmarks for selecting sampling sites for measuring biophysical features, nutrient concentrations of the water column and biogeochemical processes of the system. These works are very significant for underpinning the establishment of a zonation map of the system as discussed later in chapter 5 in relation to process measurements. Detailed method descriptions for bathymetric mapping and benthic habitat survey are referred to in sections 4.3.1 and 4.3.2, respectively, in chapter 4.

3.4.1.2. Conceptual models

Modelling approaches are widely used in water quality monitoring, integrated ecosystem assessments and biogeochemical process studies in aquatic ecosystems. Generally, a scientific model can be represented by two major types: mathematical model and conceptual model (Department of Environment and Heritage Protection, 2012). In particular, visual and attractive diagrammatic conceptual models or pictorial conceptual models are powerful tools for science communication (Câmara et al., 1991, Harwell et al., 2010). These conceptual models are effective for describing and illustrating the complex interactions of the real ecosystem under anthropogenic influences into a logical, concise, representative and scientific diagram or framework (Cloern, 2001, Webster et al., 2003).

Given the complexity of the Dong Ho estuary, conceptual models were used to consider the research targets and objectives; and to collate and synthesize key components of ecosystem function related to nutrient cycling and processes as they interact in the Dong Ho system. In addition, conceptual models can synthesize field observations into a framework and understanding for comparison with the results with other estuary systems. Based on the identification of the key biogeochemical processes operating in Dong Ho and the transformation of these processes under anthropogenic changes, conceptual models can be powerful tools to predict potential future changes and then support better sustainability management.

3.4.1.3. LOICZ biogeochemical budget methodology

As noted previously, Dong Ho estuary is comprised of complex and interacting sets of nutrient transformation processes and nutrient stocks. All of which are themselves influenced by physical and chemical conditions. In order to synthesize this information and compare the Dong Ho estuary with other estuaries, the Land-Ocean Interactions in the Coastal Zone (LOICZ) approach is an ideal biogeochemical modelling framework to understand the current performance levels and potential carrying capacity of key biogeochemical processes (N, P, C processes) operating in the Dong Ho estuary. The LOICZ biogeochemical model approach has been widely adopted to support managers and planners in identifying where the nutrients (C, N, P) are going and where management actions need to be targeted to protect the ecosystem health and performance (Wepener, 2007, Ramesh et al., 2015).

The LOICZ methodology uses the fundamental concept of ecology and geochemistry, which is the conservation of mass and a class of mass balance budgets to estimate water-salt-nutrient budgets (Gordon et al., 1996, Wepener, 2007, Swaney, 2011). The mathematical structure of the LOICZ budgeting procedure of C, N and P fluxes in estuaries and coastal waters is described in the guidelines of Gordon et al. (1996) and Swaney (2011). The approach starts with a simple one compartment and well mixed system to construct a mass balance of conservative fluxes: water and salt. For more complex systems, the water-salt-nutrient budget calculations are performed for each compartment and different layers of a stratified system (surface & bottom layer). Regarding nutrient budgets, the approach specifically uses nutrients in the form of dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN) to calculate the net ecosystem metabolism (NEM or [p-r]) and the net balance of nitrogen fixation minus denitrification [nfix-denit] (Smith et al., 2005).

LOICZ budgeting research has also developed a method of flux estimation with secondary data, so primary data collection is not absolutely necessary. However, the current study applies the LOICZ model using primary data collected in the three main field work campaigns. This data set includes DIN, DIP, primary production, net ecosystem metabolism and denitrification, so that all of the major standing stocks and processes are encompassed in the model using local data. Chapters 4 and 5 describe the acquisition of the data necessary to construct the LOICZ model.

3.4.2. Measurements of water quality and sediment characteristics

In order to understand the key biogeochemical processes in the system, it is very important to identify the nutrient stocks or loads of key materials and compounds. Nutrient studies in tropical marine ecosystems such as Dong Ho estuary often have specific requirements due to the limits of available methods and the difficulty in achieving accurate results with regard to sample handling and storage (Johnstone and Preston, 1993). For example, due to the high temperature in tropical systems, the handling and storage of collected samples are big concerns in order to keep the samples in the best condition for analysis. A pilot study of Dong Ho estuary in December 2014 was undertaken to design an appropriate and effective sampling program before undertaking the main field work campaigns in 2015 and 2016. This minimised unforeseen problems and provide a more effective sampling strategy focused on the objectives of the research questions. Furthermore, it is recognised that the samples must be representative to address the spatial variations across the estuary, as well as the variation in tidal exchange and seasons in the Dong Ho estuary system. The sampling covered both high tides and low tides, and dry season and wet season.

3.4.2.1. Determination of water column biophysical features:

As previously noted, the key objective of this study is to understand the system behaviour with regards to nutrient cycling and carbon fixation under anthropogenic influences in Dong Ho. In this context, the field observations are directed at underpinning the definition of nutrient budgets and key physical features in the water column of the Dong Ho estuary. In a shallow system such as Dong Ho, the physical features such as temperature, salinity, conductivity, density, turbidity, light attenuation, DO, and pH correlated to the depth of water column are essential measurements to explain the spatial distribution and stratification of nutrients as well as the changes of biological communities (Twomey et al., 2009, Jorgensen et al., 2005, Zaldivar et al., 2010). Further, biological indicators such as chlorophyll-a and chlorophyll-flu are also essential parameters to demonstrate the primary productivity, trophic relationships and nutrient concentrations in the system. These biological indicators are very useful to indicate the anthropogenic influences on ecosystem health (Phillips et al., 2008, Boesch and Paul, 2001). Both physical and biological indicators in the water column are measured directly by lowering the ALEC Rinko Sonde (model AAQ176) which held the relevant sensors for each parameter. The collected results are vertical profiles of biophysical parameters in the water column of the Dong Ho estuary.

3.4.2.2. Determination of water column nutrient concentrations

Understanding of the available nutrient stocks in the water column is fundamental for describing the nutrient status of any aquatic ecosystem. In the water column, nutrients are taken up by phytoplankton and considered as important indicators relevant to many environmental monitoring guidelines. Nutrients comprise both organic and inorganic forms, and dissolved and particulate forms. The water samples collected in the Dong Ho estuary are analysed using standard techniques for dissolved inorganic nitrogen including ammonium (NH_4^+), nitrate, nitrite (NO_x); and soluble reactive phosphate (PO_4^{3-}) (Ryle et al., 1981, Schaffelke et al., 2003, Parsons et al., 1984). In order to address water nutrient stocks, water samples were collected in both dry and wet seasons, at both high tide and low tide.

3.4.2.3 Determination of benthic sediment characteristics

In shallow water ecosystems, benthic-pelagic coupling has a strong influence on nutrient cycling and thus, sediment analyses are crucial to understanding system function. Sediment samples are collected from the upper 3-5 mm of sediments for measuring solid-phase nutrient levels including total nitrogen, total phosphorus, total carbon and organic carbon. In addition, benthic microalgae also plays a significant role in primary productivity in shallow waters, thus benthic photosynthesis is considered and measured by using spectrophotometric methods (Parsons et al., 1984). In general, sampling processes and sample analysis follow the Practical Guidance for Nutrient Analysis in Tropical Marine Waters of UNESCO 1993 (Johnstone and Preston, 1993) and the Manual of Chemical and Biological Methods for Seawater Analysis (Parsons et al., 1984). In addition, grain size and porosity of sediments are also analysed to better understand how the key biogeochemical processes operating in benthos and the exchange rates with the overlying water.

3.4.3. Biogeochemical process measurements (primary production, nutrient flux, denitrification)

Primary production and nutrient flux measurements are very significant in evaluating the ecosystem performance of coastal estuarine systems (Underwood and Kromkamp, 1999). The response of ecosystems to anthropogenic impacts can be illustrated through the primary productivity and nutrient flux changes. Thus, in order to understand ecosystem functioning better, it is necessary to determine both water column and benthic primary production as well as to estimate the changes in concentration and nutrient ratios of critical nutrient species in the ecosystem (Underwood and Kromkamp, 1999). In addition, given the significance of benthic processes in nutrient cycling, the measurement of denitrification rates and nitrification rates in sediments will support our understanding of system behaviour in terms of nitrogen balance and the potential removal of inorganic nitrogen through conversion to N_2 gas.

3.4.3.1 Primary production and benthic nutrient flux determinations

Primary production and nutrient flux assessment are calculated based on the rate changes of dissolved oxygen and nutrient concentrations, respectively, in the water overlying the sediment core samples (Kemp and Boynton, 1980, Jenkins, 2005, Seeley, 1969, Odum, 1956). Generally, the sediments are collected using a hand corer to obtain approximately 5-10cm of the surface sediment with six replicates in each location. The hand corer is a modified Kajak corer and it is connected with a 45 mm internal diameter acrylic tube 200 mm high, to be used for incubation. The samples are placed in darkness at in-situ temperature. Ambient water samples near the bottom at sampling sites are collected for use in the incubation and kept in darkness at same temperature. At the same time, the water column is measured directly to determine the physical and biological indicators, and surface and bottom water samples are filtered through 0.45µm GF/F filters for subsequent nutrient analysis. The sediment sampling method described above is synthesised from many sources (Valdes-Lozano et al., 2006, Stockenberg, 1998, Conley and Johnstone, 1995, Blomqvist and Abrahamsson, 1985). To reflect the influences of different seasons on nutrient processes, the sediment cores were collected and incubated in both the dry season and wet season.

3.4.3.2. Measurement of denitrification rates

The denitrification process is an important pathway in nitrogen cycling that removes nitrogen from the ecosystem by converting DIN to N_2 gas. Denitrification rates in sediments can be measured by both direct and indirect methods, including the acetylene inhibition technique (Sørensen, 1978); direct N_2 production (Seitzinger et al., 1984); direct N_2 fluxes based on changes in N_2:Ar ratios (Kana et al., 1994); stoichiometric approaches (Redfield, 1958, Nixon, 1981); the calculation of nitrate fluxes into the sediment from pore water profiles (Mengis et al., 1997); mass balance approaches (Wulff et al., 1990, Kamp-Nielsen, 1992, Nixon et al., 1996); and the ^{15}N isotope pairing technique (Nielsen, 1992). Many different studies have analysed and compared these methods to identify the advantages and limitations of each method in different contexts (Eyre et al., 2002, Steingruber et al., 2001, Groffman et al., 2006, Cornwell et al., 1999, Seitzinger et al., 1993). Unfortunately, there is no perfect method and denitrification methodology is still controversial. For differing ecosystems, the physical and biological conditions of the systems, research objectives, availability of equipment and logistical restraints, an appropriate method must be chosen which is suitable for the specific situation and which will provide correct denitrification rates for that system. In this research, the ^{15}N isotope pairing technique was used to measure the denitrification rate in the Dong Ho estuary because this method can identify both the nitrate diffusing from the overlying water column as well as the nitrate produced from the nitrification process within the sediment (Nielsen, 1992). Although this method may underestimate denitrification rates in shallow waters because of the turbulent mixing conditions

(Steingruber et al., 2001), the ^{15}N isotope pairing technique is still valuable and appropriate to the Dong Ho estuarine system conditions. This method assists in providing an understanding of the paired and unpaired denitrification rates, to indicate how important nitrification is in supporting the denitrification process and to allow a comparison with denitrification being driven by remote sources of nitrate.

CHAPTER 4 - BASELINE CONDITIONS AND STOCKS OF MATERIALS

4.1. Introduction

In order to sustainably manage estuarine ecosystems, it is vital to have an understanding of the ecosystems baseline performance and, if possible, its behaviour under various perturbations (Paerl, 2006). This includes an understanding of water quality, benthic sediment characteristics, and the major biota. In addition, an understanding of the physical characteristics of an estuary is also crucial, including the system bathymetry, hydrology and tidal regime. These features are essential to know because of their potential influence on the distribution of nutrient stocks and the biogeochemical processes that might transform them (Roman and Nordstrom, 1996). In this context, this Chapter presents the results of a field campaign aimed at describing the key features of the Dong Ho estuary, including (i) the bathymetry; (ii) major benthic habitats; (iii) the biophysical features of water column; (iv) dissolved nutrient stocks in the water column; and (v) sediment characteristics. The reasoning behind this baseline study and its components is provided below.

The bathymetric condition of an estuary plays a crucial role as it influences ecosystem function and different biophysical and biogeochemical processes (Britton-Simmons et al., 2012, Cogan et al., 2009). For example, bathymetric features can have a large impact on benthic primary production through light attenuation by depth (Gattuso et al., 2006). Prior to the 1980s, few studies considered the role of the benthos from a holistic perspective in many marine and coastal ecosystems and coupling between the water column and sediments in nutrient cycles was similarly neglected (Joye and Andersen, 2008). However, recent studies have shown the importance of benthic primary production for sediment-water fluxes and its role in supporting pelagic primary production (Nixon, 1981, Ferguson and Eyre, 2010, Marinelli and Williams, 2003, Riggs, 2010). In addition, an understanding of estuarine bathymetric features is essential for modelling the system hydrodynamic behaviour, its ecological processes and its nutrient dynamics (Costanza et al., 1998, Costanza and Voinov, 2001).

As noted, in addition to the bathymetry, nutrient dynamics and water quality can be significantly influenced by sediment–water exchanges and, therefore, the biogeochemical processes taking place in the sediment can also be highly important (Larson and Sundback, 2008). Moreover, processes such as nitrogen fixation in sediments can be key to nitrogen regeneration from sediments and play a predominate role in shallow areas (Barnes and Mann, 1991). On the other hand, in estuaries receiving large anthropogenic nutrient loads, the removal of key nutrients like nitrogen, through denitrification, can account for up to 40 - 70% of the total nitrogen entering an estuarine ecosystem (Boynton and Kemp, 2008, Nixon et al., 1996).

Directly linked with these benthic processes, the biota associated with a given benthic area can similarly have an effect on nutrient dynamics and the transformation processes underpinning them (Eyre et al., 2011a). In this context, identifying the presence and distribution of microphytobenthos (MPB) and benthic macrophytes can provide key insights into how the benthic sediments are interacting with the overlying water column. MPB, for example, can often form microalgae mats in the uppermost 1-3 millimetres of the surface sediment layer and can have a profound influence on primary production, mineralization pathways and nutrient fluxes in shallow estuarine systems (Hochard et al., 2010). The presence of MPB can reduce nitrification and denitrification rates because MPB competes with denitrifying and nitrifying bacteria for light and nutrients (nitrate and ammonium). In the same manner, MPB assimilates dissolved inorganic nitrogen in the upper layer of sediment and may thus reduce the nitrogen concentration in overlying waters and surface porewaters in the sediments (Risgaard-Petersen, 2003). In coastal sediments, N assimilation by MPB is often considered to be a major nitrogen sink and can make a greater contributor to N loss than denitrification in some situations (Sundbäck and Miles, 2000). Hochard et al. (2010) have also illustrated that microphytobenthos plays an influential role on exchanges between the water column and sediment with MPB retaining a significant proportion of the available dissolved inorganic nitrogen (DIN) within sediments and may become an important source of organic matter for the water column. In many shallow ecosystems, the biomass of MPB is often higher than the biomass of phytoplankton in the overlying water (Rejilt, 2012, Hochard et al., 2010, Lake and Brush, 2011, Underwood, 2010, De Jonge and Colijn, 1994). In intertidal sediments of estuarine systems, MPB distribution is influenced by tidal cycles and diurnal cycles (Pinckney et al., 1994). In addition, the density of MPB also depends on light availability, sediment grain size and seasonal variations such as sediment temperature and solar radiation (Jerónimo et al., 2013).

In addition to MPB, benthic macrophytes, such as rooted seagrasses and marsh grasses, also contribute a large proportion of primary production in shallow coastal ecosystems (Alongi, 1998). Rooted macrophytes are a sources of both particulate and dissolved organic material for metabolism in benthic communities, and influence benthic fluxes and nutrient transformations (Joye and Andersen, 2008). Further, as highlighted by (Thom et al., 2001) rooted macrophyte systems can be important sources of dissolved organic carbon, CO_2, and CH_4 through benthic microbial processes. Notably, however, much of the detrital materials produced in seagrass communities can be conserved within the community itself and not exported to other areas or communities (Gacia et al., 2002). From this perspective, identifying macrophyte habitats, such as seagrass communities, in Dong Ho estuary provides a better understanding of sediment-water column exchanges that they might modulate in an area.

As a reflection of the summary effect of the other features mentioned above, water quality is often used as an indicator of ecosystem status and performance, as well as manifestation of the biogeochemical cycles operating in an aquatic ecosystem (Howarth et al., 2011, Ittekkot et al., 2000). Further, water quality monitoring in rivers and estuaries provides an understanding of the chemical and biological quality of ecosystems from a remediation standpoint (O'Flynn et al., 2010). In general, the water quality parameters most commonly monitored include physico-chemical parameters such as temperature, salinity, turbidity, light, dissolved oxygen concentration, nutrient concentration such as phosphorus and nitrogen as nitrate, nitrite and ammonia, and pH; biological parameters commonly include phytoplankton (chl-a, chl-flu) (Twomey et al., 2009, Scheltinga et al., 2004).

In estuarine environments, physical variables such as salinity, oxygen and temperature are very important in regulating keystone biogeochemical processes effecting nutrient dynamics. For example, (Capone et al., 2008) demonstrated such influences on nitrification and denitrification rates as the underpinning bacterial communities were sensitive to changes in these conditions. In addition, temperature, light and nutrients are also considered to be key parameters regulating ecosystem production (Kennish and Paerl, 2010). The nutrients nitrogen (N) and phosphorus (P) are essential for plant and animal growth, and they are the most important nutrients associated with eutrophication (Bianchi, 2007). Nitrogen is generally considered as the most important limiting nutrient for phytoplankton in estuaries (Kemp et al., 1990, Nielsen et al., 2002, Boynton et al., 1982, Bianchi, 2007); however, other studies show that phosphorus may limit algal biomass production in brackish areas of estuaries (Smith, 1984, Glibert et al., 1995, Bianchi, 2007). Furthermore, measuring both nitrogen and phosphorus is essential because the biogeochemical cycles of these elements are linked to carbon via stoichiometric relationship or the Redfield ratio, and entrained in the trophodynamics of an ecosystem (Laane and Middelburg, 2011). Recognition of these links and their interactions in ecosystems is fundamental to control the human induced changes in their relative availability, which may affect the resilience and balance of ecosystem functions (Smith et al., 2005). In contrast, when nutrients are abundant in estuarine systems, light ability is generally the dominant limiting factor influencing primary production (Underwood and Kromkamp, 1999). In this situation, increased turbidity increases the light attenuation and reduces the light reaching the bottom water layers as well as the benthic primary producer communities (Miththapala, 2013). In view of these different considerations, the field research presented here examined the key physical parameters, biological parameters and water column nutrient levels in Dong Ho estuary to better understand the potential influences of anthropogenic and natural influences on the ecosystem.

In order to establish a well targeted research strategy for the overall thesis project, an initial pilot study was undertaken in December 2014 to provide an overview of Dong Ho estuary and its baseline conditions. The key objectives of this pilot study were to describe Dong Ho's bathymetry and characterise its benthic habitat type and distribution. Based on the understanding gained from this work, the physico-chemical characteristics of the water column were examined across the estuarine system to assess the spatial and bathymetric variations that might exist in water column structure and quality. The results from the pilot study then directed the selection of sampling sites in the ensuing, more detailed field work campaigns in the wet season (August 2015), and in the dry season (April 2016). In these field campaigns, water quality (biophysical features & nutrient stocks) and sediment characteristics of Dong Ho estuary were also measured and analysed, but were considered within the context of the benthic types and physical dynamics of the different areas within the estuary as defined in the pilot study.

This chapter presents the results of the baseline studies noted above to ascertain the present status of the waters and sediments in Dong Ho estuary. This information was then used to target the ensuing work focussing on biogeochemical processes and particular locations in the Dong Ho estuary (Chapter 5).

4.2. Methods

4.2.1. Bathymetry

In the context of Dong Ho estuary, the bathymetric survey measured water depth at 1,000 locations throughout the estuary at both low and high tide. The data was collected by means of a GARMIN™ D-GPS depth sounder mounted to the survey vessel which captured water depth, position, time of day, and water temperature every 250m along transects along the main longitudinal axis of the estuary, and also along the main canals linked to the estuary. At 750m intervals along the main transects a cross-sectional transect was also run to define the width and profile across the respective channel or section of the body of the estuary. A total of 40 transects were conducted and the information was then plotted using ArcGIS to produce a bathymetric map of the system.

4.2.2. Benthic habitat survey

The benthic habitat survey was undertaken at the start of the project to define the distribution of microphytobenthos and seagrass on the benthos of Dong Ho estuary. The survey utilised a Remote Submersible Video Camera to directly observe the surface of sediment along the transects used for the bathymetric survey. The survey was based on bathymetry map of Dong Ho to ensure representative coverage of the central estuary, the main canal to the sea, and the Rach Gia – Ha Tien canal (Figure 4.6). At each survey location, due to the high turbidity of water column, the camera with attached light system was lowered down to the surface of sediment to capture and film the surrounding benthic habitat.

4.2.3. Measurements of biophysical features in the water column

Water quality surveys of Dong Ho estuary were undertaken four times; in December 2014 (dry season), August 2015 (wet season), April 2016 (dry season) and November 2016 (wet season). The aim of these surveys was to identify the physical and biological features (chlorophyll) of the water column across the system as well as to describe any significant seasonal changes that might occur. A stratified-random sampling plan was used in an attempt to address the spatial variations across the estuary as well as the variation in hydrological and bathymetric conditions in the Dong Ho estuary system (Figure 4.1). The sampling covered both dry season and wet season.

At each location, vertical water quality profiles were obtained for temperature, salinity, conductivity, turbidity, density, quantum (PAR), pH, DO, Chl-a and Chl-Flu. This was achieved by lowering an ALEC Rinko Sonde (Model AAQ176) (Figure 4.2) which held the relevant sensors for each parameter. The sonde was calibrated before each use against certified standards (ALEC manual). Due to the rapid response time of the different sensors, the water quality profiles obtained have a high spatial resolution and it was possible to achieve profiles even in shallow waters (≈ 1m).

Figure 4.1: Locations of main water sampling sites in Dong Ho estuary

Figure 4.2: ALEC Rinko profiler

Figure 4.3: Niskin bottle

4.2.4. Measurement of nutrient stocks in the water column

In order to measure dissolved nutrient levels in the water column, duplicate water samples of both surface water (0.5m depth) and bottom water (0.2m above benthos) were collected at each location (Figure 4.1). The bottom-water samples were collected using a Niskin sampling bottle (Figure 4.3) and surface samples were collected at 0.5m depth using a cleaned and pre-rinsed 1 litre polyethylene sampling bottle. All water samples were immediately filtered through Millipore express PES membrane filter unit 0.45µm using a 50ml syringe to remove particles and microorganisms. Filtered water samples were captured in acid washed and pre-rinsed 20ml HDPE scintillation vials and stored on ice in the field prior to freezing (-40°C) for transport to the laboratory for analysis (Johnstone and Preston, 1993).

All water samples were imported frozen (-20°C) from Vietnam to Australia for analysis in the labs at the University of Queensland and all samples were analysed for ammonium (NH_4^+), nitrate and nitrite (NO_x), and soluble reactive phosphate (PO_4^{3-}). Analysis methods of NH_4^+, NO_x, and PO_4^{3-} followed modified versions from a manual of chemical and biological methods for seawater analysis (Parsons et al., 1984).

4.2.5. Determination of benthic sediment characteristics

Benthic sediments were characterised by measurement of grain size, sediment porosity and the concentrations of solid-phase nutrients (C, N, P). To do this, triplicate sediment samples were collected at each of three sites randomly selected within each of the main bathymetric zones of the estuary (see Figure 5.1). The sediments were collected to a sediment depth of 10cm using a modified version of a piston corer (Conley and Johnstone, 1995) attached to an extendable pole to reach the bottom at ≤8m depth (Figure 4.4). An example of an intact core collected this way is provided in Figure 4.5 set up for sediment incubations (see Section 5.2.1). For sediment analysis the top 3cm of sediment was collected and used to determine water contents, total organic carbon (TOC), total carbon

(TC), total nitrogen (TN) and total phosphorus (TP) (Conley and Johnstone, 1995). An additional set of cores was also collected and the surface sediments (0-5cm) were collected for grain size and porosity determinations. Porosity of sediments was determined by the saturation method (Barnes, 1936, Campbell, 1974). Sediment grain size composition was determined by the sieve-pipette method (Loveland and Whalley, 2000, Gee and Bauder, 1986).

In addition to physical measures, a $5cm^3$ sub-sample of surface sediments (0-1cm) was taken from each core and analysed for chlorophyll content. To do this, the $5cm^3$ sediment sample was placed into a 15 ml falcon tube containing 5ml of chilled 90% acetone and then immediately shaken to extract the chlorophyll. These samples were kept on ice and in the dark to be analysed in the lab within 24 hours of collection. In the lab, the amount of chlorophyll from sediment-acetone samples was determined by spectrophotometric methods (Parsons et al., 1984) using four frequencies; 750, 664, 647, and 630 nm. In addition to providing measures of Chl a, b, and c, the spectrophotometric method also allowed the estimation of phaeo-pigments derived from associated detrital material.

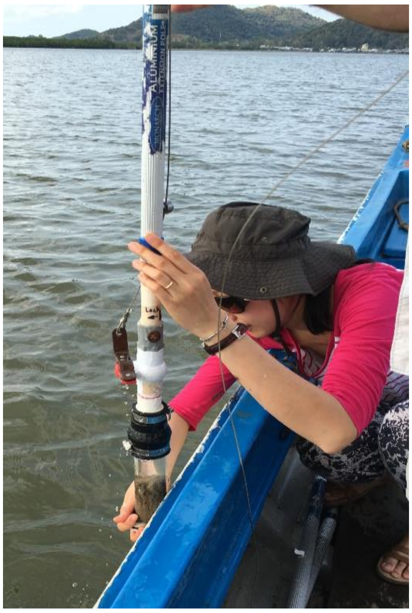


Figure 4.4: Hand corer to capture top intact sediment

Figure 4.5: Sediment core

4.3. Results

4.3.1. Bathymetry

As noted by Truong (2011), sediment deposition rates vary throughout the estuary, contributing to variation in bathymetry. This variation is illustrated in the bathymetric map obtained in this study (Figure 4.6). As discussed later, it also reflects the sediment loads into the estuary. Notably, the map was built from the primary data collection of depth measurements in the 2014 study and showed no difference to a similar data set collected by Johnstone in 2012 suggesting that no significant changes in bathymetry had occurred of that period. The average depth of Dong Ho estuary was approximately 1.5m at low tide and this shallow aspect of the estuary has potential significance for ecosystem processes, as well as for estuarine management strategy (Johnstone, 2012).

As previously noted, the hydrological regime in Dong Ho depends on both the Giang Thanh River and the Ha Tien- Rach Gia Canal, as well as the diurnal tidal characteristics. In the dry season, Dong Ho is strongly affected by tides and sea water intrusion but is often dominated by an overlay of freshwater during the wet season (Truong, 2011). The tidal range for the Dong Ho estuary is approximately 2.5m (Nguyen, 2008) although this can be modified by large freshwater flows during the wet season and periods of flood.

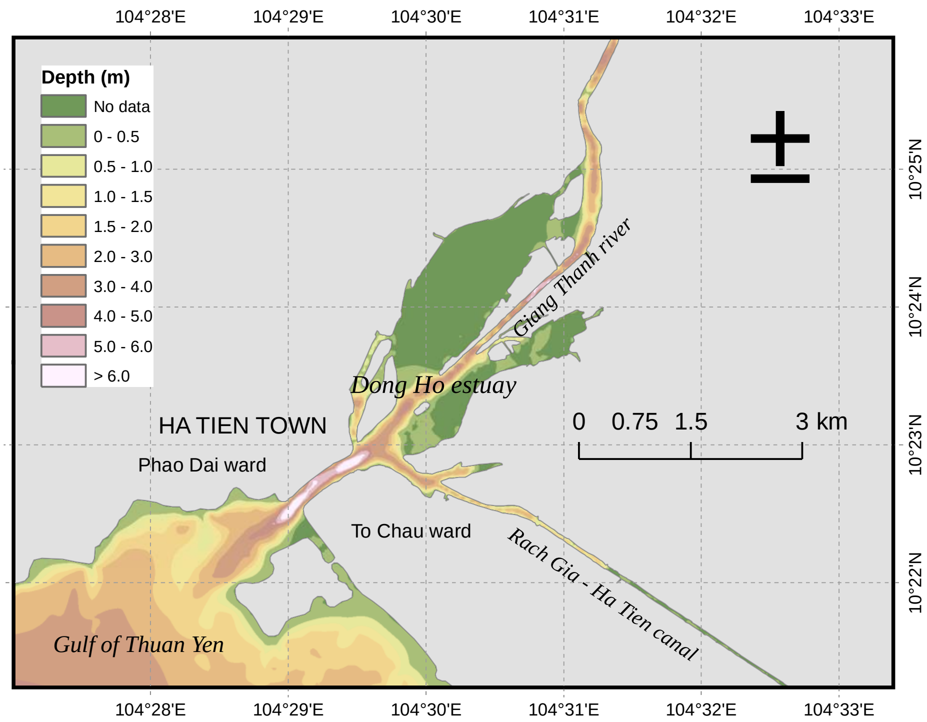


Figure 4.6: Bathymetric map of the Dong Ho estuary

This bathymetric map will be used for zonation in Chapter 5 which reviews key biogeochemical process measurement. More than 75% of Dong Ho estuary is below 4 m and only 8% deeper than 6m. The variation in bathymetry of Dong Ho estuary likely influences the rate of key processes such as primary production (Wendt-Potthoff et al., 2012, Shiozaki et al., 2016, Smith et al., 2016). In Figure 4.6, there are no data in the northwest to southeast of the river due to it is a large intertidal area with the depth below 0.5 m at low tide. It is likely that this large area has many sediment and nutrient processes happening. However, as discussed in chapter 2 and illustrated in Fig. 2.1 (yellow line), the benthic flux, community metabolism and biogeochemical process studies focused in the central estuary to evaluate how the core estuary processed and responded to high inputs of materials and nutrients from the river's catchment. This central area has complex interactions between catchment and oceanic waters, as well as the most deposition and collective influences from the urban area (Ha Tien town) and the catchment were likely to be greatest in this central estuary. Therefore, the bathymetric map focused on showing the depth variations in the central estuary, hence the data was not illustrated in the large area to the NW and SE of the river.

Dong Ho estuary receives large amounts sediment from the Giang Thanh River in the north as well as sediment inputs from the Ha Tien – Rach Gia flood-control canal in the southeast (Carter, 2012a). The depth and extent of sediment deposits are increasing, reducing the water flows and the total area (Le and Truong, 2011). The bathymetric map showed the pocket of deep in the main canal of the gate way to the sea of the estuary while the central estuary is shallower. This bathymetric map is used to support the sampling site selection of water quality survey and zoning different compartments within the estuary for estimating primary production and nutrient fluxes of Dong Ho estuary.

4.3.2. Benthic habitat survey

The benthic habitat of Dong Ho estuary was examined at 13 locations representing for different depths and sections in the estuary (Figure 4.7). Based on this survey, it was observed that the benthic habitats in Dong Ho are quite homogeneous and no seagrass habitats, or individual stands, were detected. Furthermore, the area immediately outside of the estuary (point 121 and 122) in the Gulf of Thuan Yen where seagrasses were previously known to be extensive, were also absent. As discussed later, this is thought to be due to local land reclamation activities. Only one location (point 117 in figure 4.7) showed a distinctly different appearance compared to other locations due to the clear presence of microphytobenthos (MPB) on the sediment surface. Point 117 is also the shallowest location of all measured locations at only 0.7m-depth at low tide.

The survey showed that, based on benthic flora or physical structures such as rocks and different substrata, the benthos across the estuary could not be distinguished into clear areas or sections. Only the shallow area surrounding point 117 reflected a clearly different benthic type with a clearly visible MPB community. This was further assessed as part of the benthic sediment determinations.

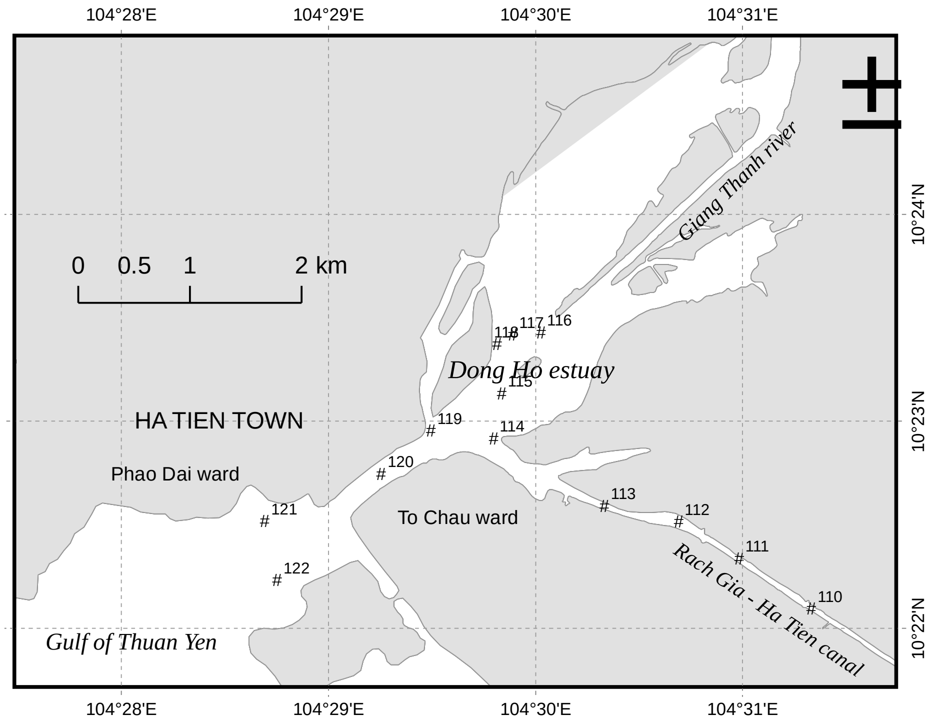


Figure 4.7: Locations of benthic habitat survey in the Dong Ho estuary

4.3.3. Biophysical features in the water column of Dong Ho estuary

Water quality parameters including temperature, salinity, conductivity, turbidity, density, quantum, pH, DO, Chl-a and Chl-Flu, which are measured in-situ at each sampling site correlated by depth. In general, Dong Ho estuary has a complex hydrological condition affected by both Giang Thanh river from the northeast, tidal exchange with the Southwest Sea and the Rach Gia – Ha Tien channel from the east. As described below, the estuarine hydrology exhibits strong seasonal variability.

In this section, temperature, salinity, turbidity, quantum, DO, pH, and chlorophyll-a of water column in Dong Ho estuary are described in details below. These are priority and commonly measured parameters used for water quality monitoring in freshwater and marine systems (Twomey et al., 2009). Also, as discussed later, understanding the dynamics these parameters describe can assist researchers and managers in understanding and predicting natural processes in estuarine ecosystems and help to identify human impacts on these processes.

A total of 14 sampling sites were used for measuring biophysical features in waters of Dong Ho estuary in both dry and wet season (Figure 4.1). However, for ease of comparison and presentation in the text below, 6 sites (1, 2, 3, 5, 8, 12) were selected as representatives of the range of bathymetric and hydrological conditions. The other parameters and sites are included in Appendix 1.

4.3.3.1. Temperature

In general, the average temperature of water column in Dong Ho estuary only showed minor seasonal differences, ranging from 28.5 to 32˚C (Table 4.1). This is a typical characteristic of tropical estuaries which have a consistent and elevated temperature range all year, being classified by wet and dry season rather than by temperature differences (Rodríguez, 1975).

To illustrate the difference between surface and bottom water, six locations below are presented to show the varieties across the Dong Ho estuary at different times of sampling (Figure 4.8). In the dry season, the water temperature was generally homogenous from surface to bottom in most sampling sites with a small point of difference at approximately 0.5m depth. In contrast, in site 5, catchment and river inputs appeared to play a role with surface, less saline, waters had a higher temperature than bottom waters. In the wet season, temperatures in the upper 1.0m of water showed lower temperatures than bottom waters and this was most pronounced in the 2016 wet season. This is thought to be due to the longer period of overcast weather during the 2016 campaign which held air temperatures lower than in the previous sampling period. Also, the 2016 measurements were taken toward the end of wet season (November 2016) when large amount of river flows go into the estuary, and this may have led to the clearer stratification of water temperatures.

Table 4.1: Average temperature of water column (˚C) in Dong Ho estuary

Site	Depth (m)	Dry season (Dec 2014)	Wet season (Aug 2015)	Dry season (Apr 2016)	Wet season (Nov 2016)
1	5	30.41	30.25	31.29	28.88
2	5.3	30.44	30.3	31.25	28.8
3	3.4	30.27	30.49	31.28	28.8
4	3.1	30.48	#	31.18	#
5	6.3	30.52	30.9	31.48	28.89
6	6.1	#	#	31.49	#
7	2.9	#	#	31.99	#
8	1.5	30.34	31.87	31.62	28.58
9	1.8	#	31.34	#	#
10	2.3	#	31.09	#	#
11	4	30.32	31.07	31.53	#
12	4.8	30.56	31.27	31.81	28.52
13	4.2	#	#	31.99	#
14	4	#	#	32.12	#

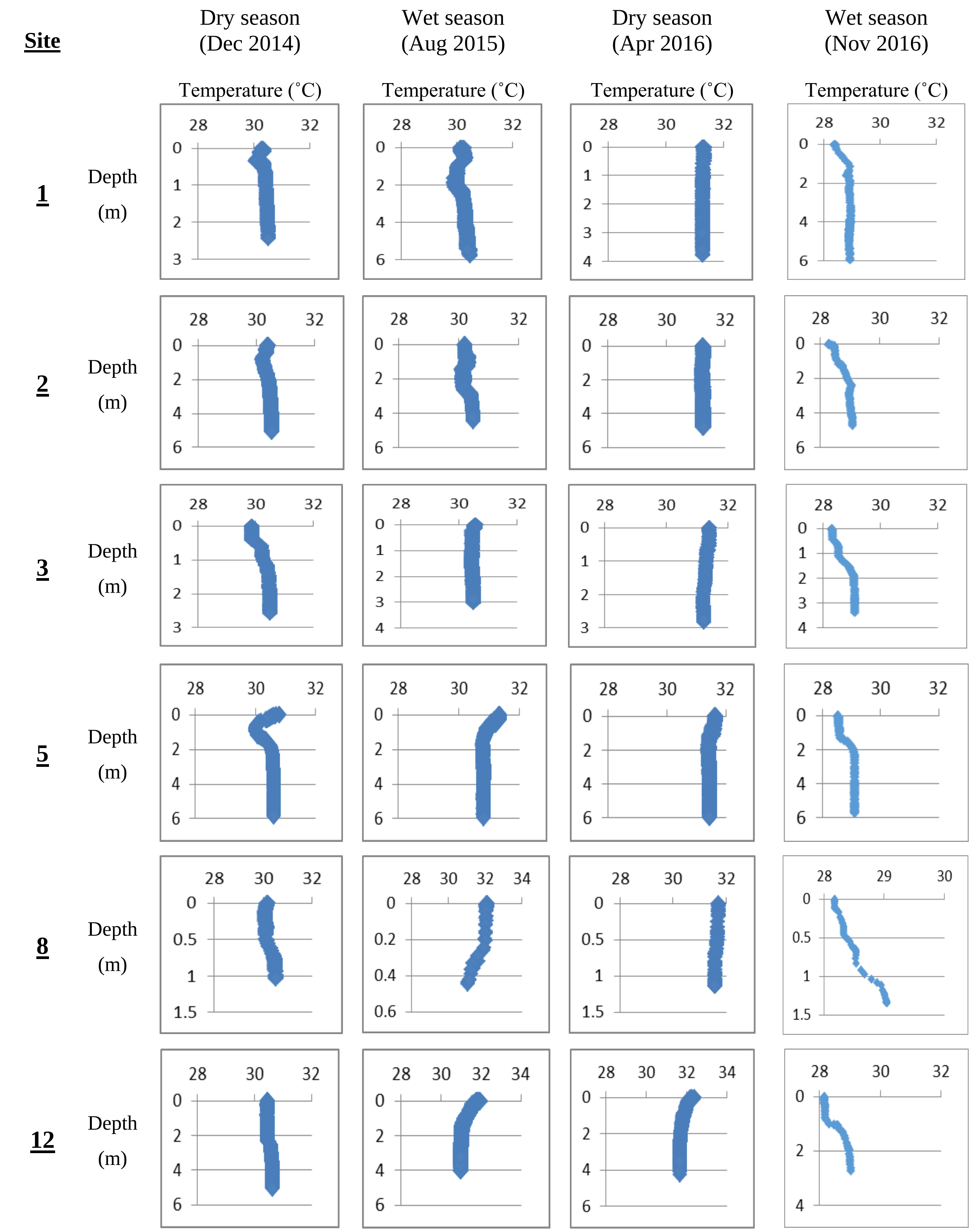


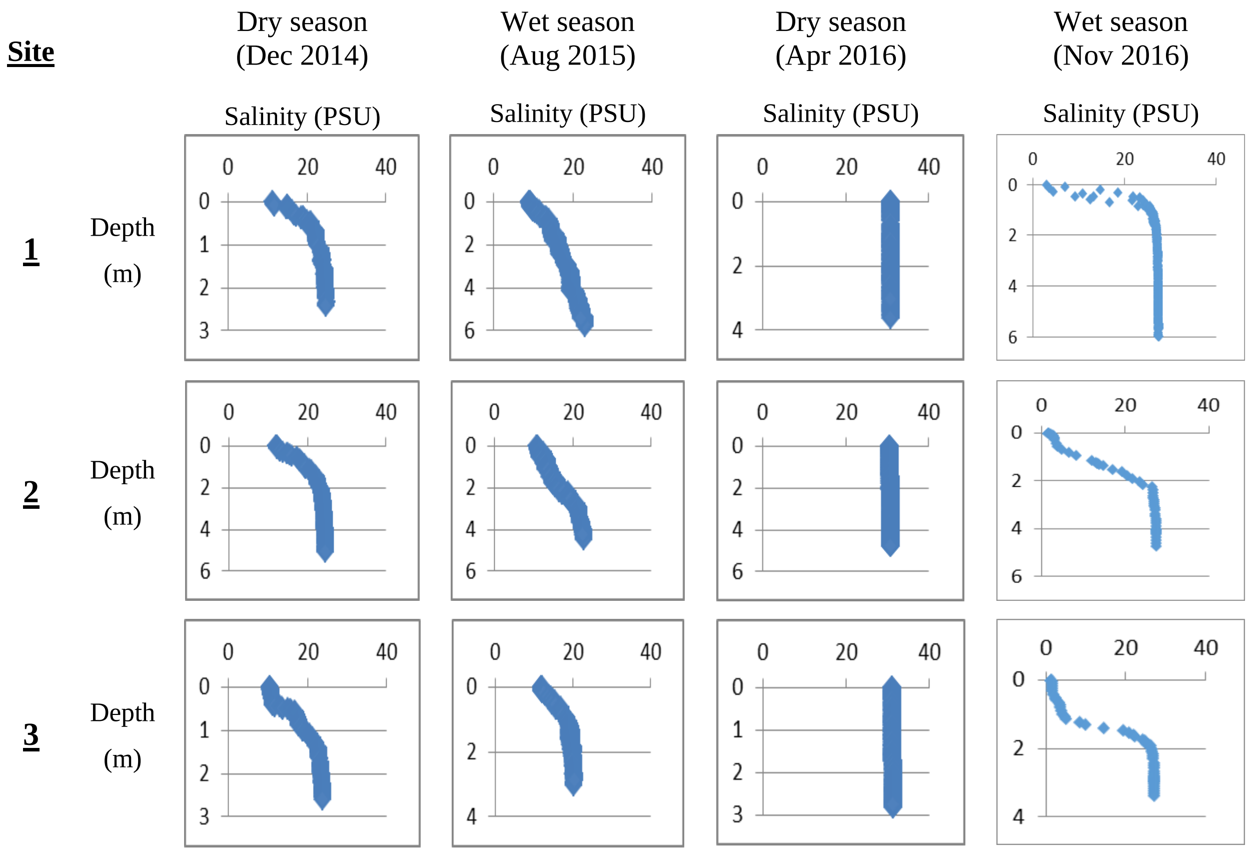
Figure 4.8: Temperature profiles from surface to bottom water in Dong Ho estuary

4.3.3.2. Salinity

The salinity profiles obtained for Dong Ho estuary waters illustrate the interaction between river flows and tidal exchange (Figure 4.9). In addition, there were strong seasonality salinity values between the dry and wet seasons. In the wet season (August and November) and early dry season

(December), salinity is stratified between surface and bottom waters as the estuary receives freshwater from the Giang Thanh river and the Rach Gia – Ha Tien channel. Whilst the upper water layers reflect less dense freshwater from the river, bottom waters had higher salinity values due to the influence of tidal inputs of more dense marine waters.

Results from April 2016, in the final months of the dry season, show that the water column is homogenous for salinity with little to no freshwater inputs from the associated catchment and dominated by marine tidal waters. As illustrated in Figure 4.9, in all sampling sites in April 2016, salinity profiles were consistent around 33 PSU from surface to bottom layer. This salinity regime persisted across all sites including site 7 where the Giang Thanh river enters Dong Ho estuary and at site 14 at the upstream of Rach Gia – Ha Tien channel; both sites most remote to the sea. The observed salinities were not statistically different to those measured in the most marine site outside of the estuary into the Western Sea (See Appendix 1). Importantly, the April 2016 sampling occurred in the final phases of the worst drought in the history of Vietnam’s Southern Mekong Delta, including the Dong Ho area. Conditions were considered so problematic that the local government decided to close the sluice gates to the Western Sea on February 2016 in the upper of Giang Thanh river and main channels to prevent saline intrusion into upstream areas; and to conserve freshwater in these areas. This event may have exacerbated the salinity issue in the estuary by reducing already very low freshwater inputs from the surrounding catchment.



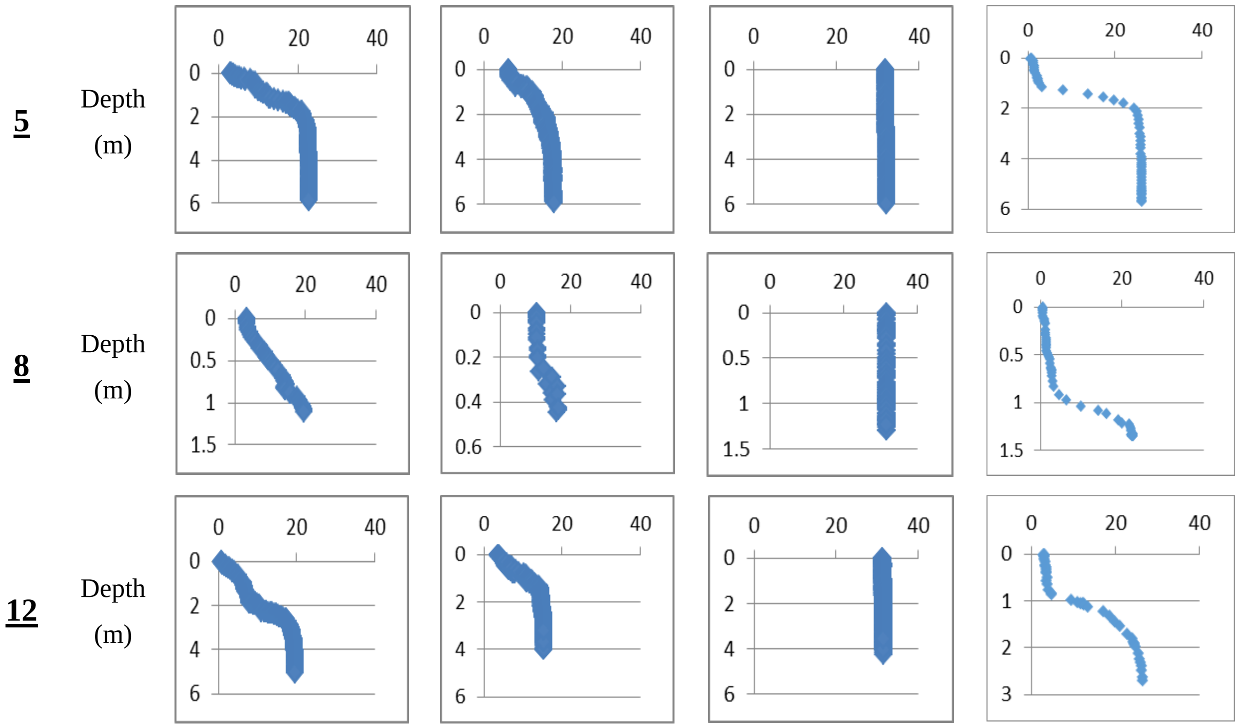


Figure 4.9: Salinity profiles at major sampling sites in Dong Ho estuary

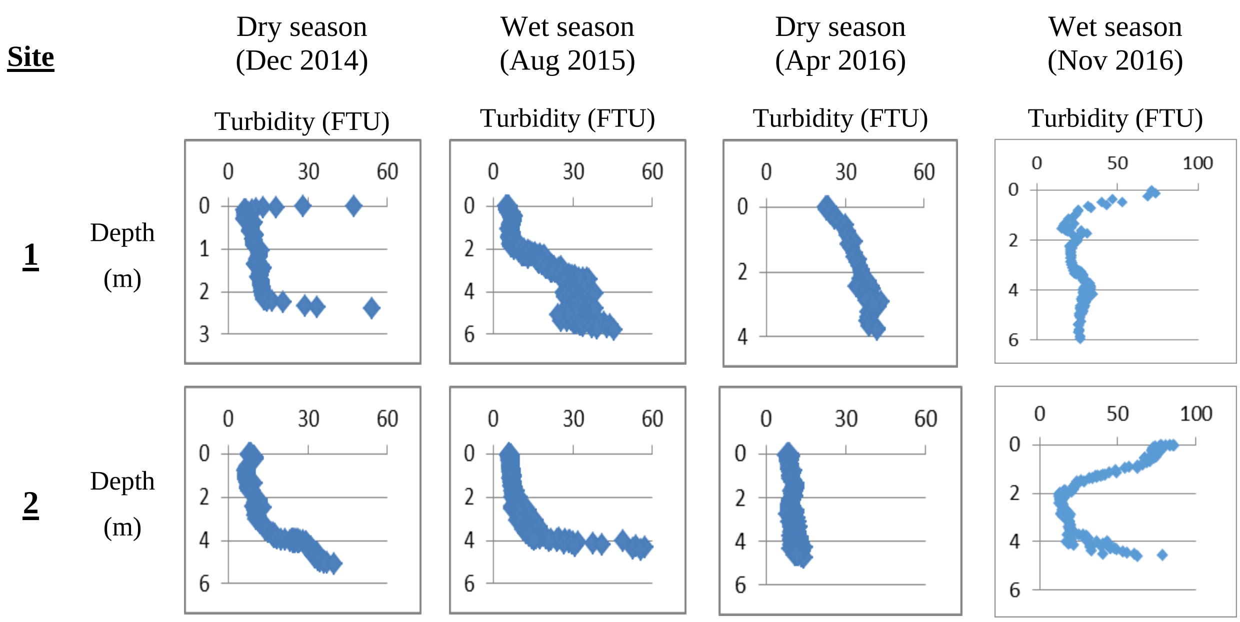
4.3.3.3. Turbidity and light profiles

Dong Ho estuary is known for high turbidity waters considered locally to be due to the influence of freshwater carrying large amounts of sediment from the Giang Thanh river in the north (Carter, 2012a). The observed water column profiles support this notion. Profiles of turbidity in the wet season (November 2016) showed higher turbidity in surface waters compared to bottom waters (Figure 4.10). This does not appear to hold during the wet season sampling event in August 2015, where surface waters showed lower turbidity values than observed in the November 2016 event. The explanation for this may be the different sampling times on the respective occasions. Profile measurements in August 2015 were measured on the flood tide, while in November 2016, turbidity profiles were captured in ebb tide. Tidal exchanges and river flows are the main factors influencing turbidity in Dong Ho estuary and so it is likely that the increased values on the ebb tide reflected a greater input of waters from the upper catchment areas compared to during flood tide when marine waters tend to push catchment waters back into the upper areas; this being most notable when freshwater inputs overall are very low across the system.

In the first month of the dry season in December 2014, the influence of freshwater flows from catchment sources decreased, but was still evident in some locations (e.g. Sites 1 and 5; Figure 4.10). The notably high turbidity in the surface water at site 5 can be explained through its salinity profile which indicates the influence of freshwater from Giang Thanh river.

In the dry season (2016), the sluice gates upstream of Giang Thanh river and Rach Gia – Ha Tien channel were closed, which limited the freshwater carrying sediment flowing into Dong Ho estuary. This may explain the lower turbidity observed in the dry season (2016) and the generally homogeneous turbidity values at different sampling sites inside the estuary. The higher levels observed outside the estuary in the fully marine location may just reflect the more complex inputs from other marine areas adjacent to the sampling site. This would include the influences of tide and sediment run off from land reclamation activities outside the estuary.

As reported elsewhere, high turbidity in the water column leads to rapid light attenuation toward the benthic zone (Kromkamp and Peene, 1995, Krause-Jensen and Sand-Jensen, 1998). In November 2016, the upper 2m of water at all sampling sites had high turbidity to such an extent that light penetration was limited to the upper 2m depth and sometimes to only the upper 0.5m depth. There was generally insufficient light for photosynthesis on the benthos at most sampling sites (except site 8) during this period. As discussed later in page 96, the approximate minimum PAR level (light intensity) required for primary production is around 1 µmol $m^{-2} s^{-1}$ (Peterson et al., 1987, Thompson, 1991). Therefore, light is “sufficient” for primary production if at least 1 µmol $m^{-2} s^{-1}$ of PAR light can penetrate to the benthos or other parts of the water column. However, on the other sampling events, for all sites deeper than 3m, there still had sufficient photosynthetic light on the benthos. Across the study, the most shallow site (Site 8) in all events showed higher photosynthetic light reaching the benthos. This was also the only site where micro-phytobenthos was observed during the benthic habitat survey.



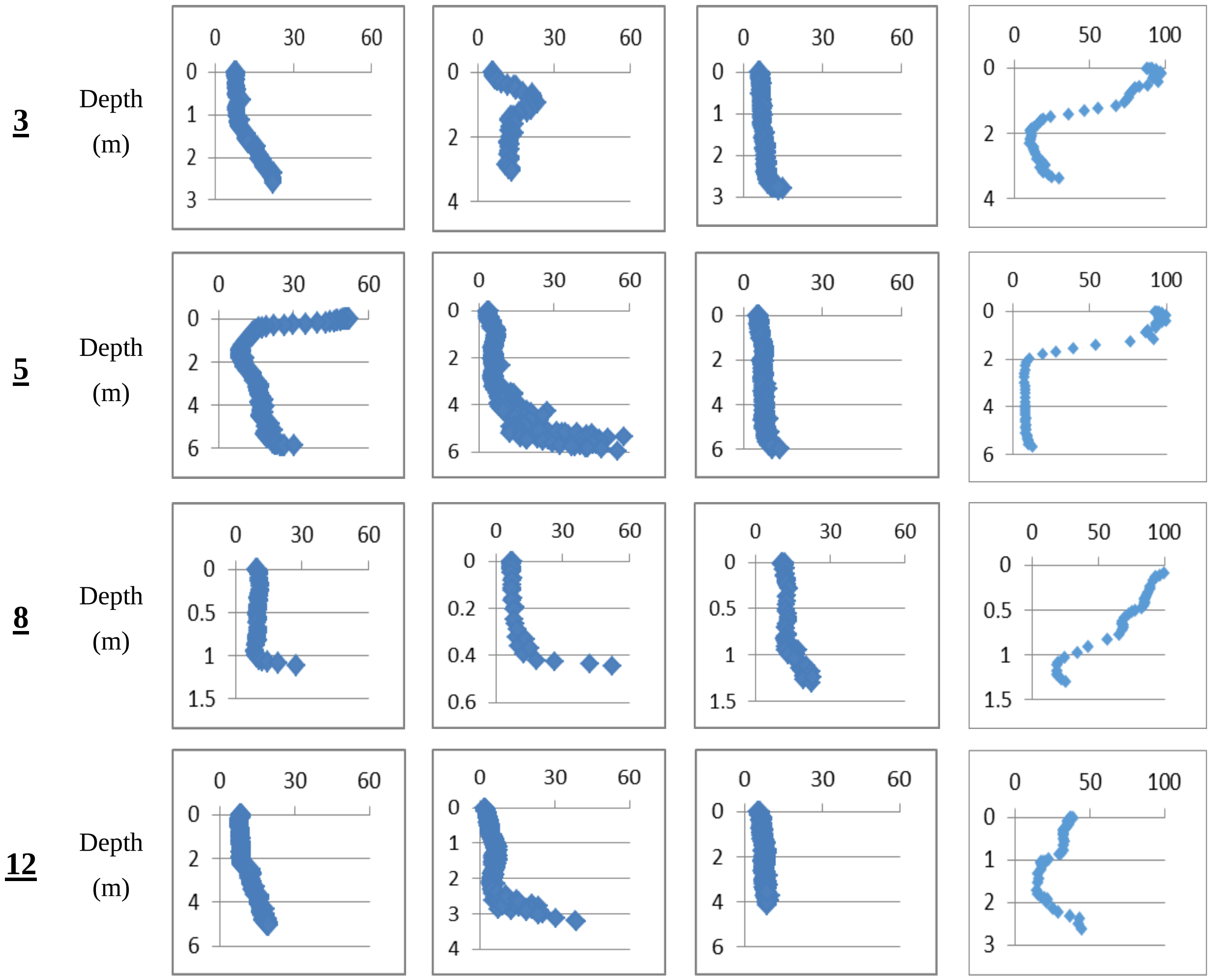
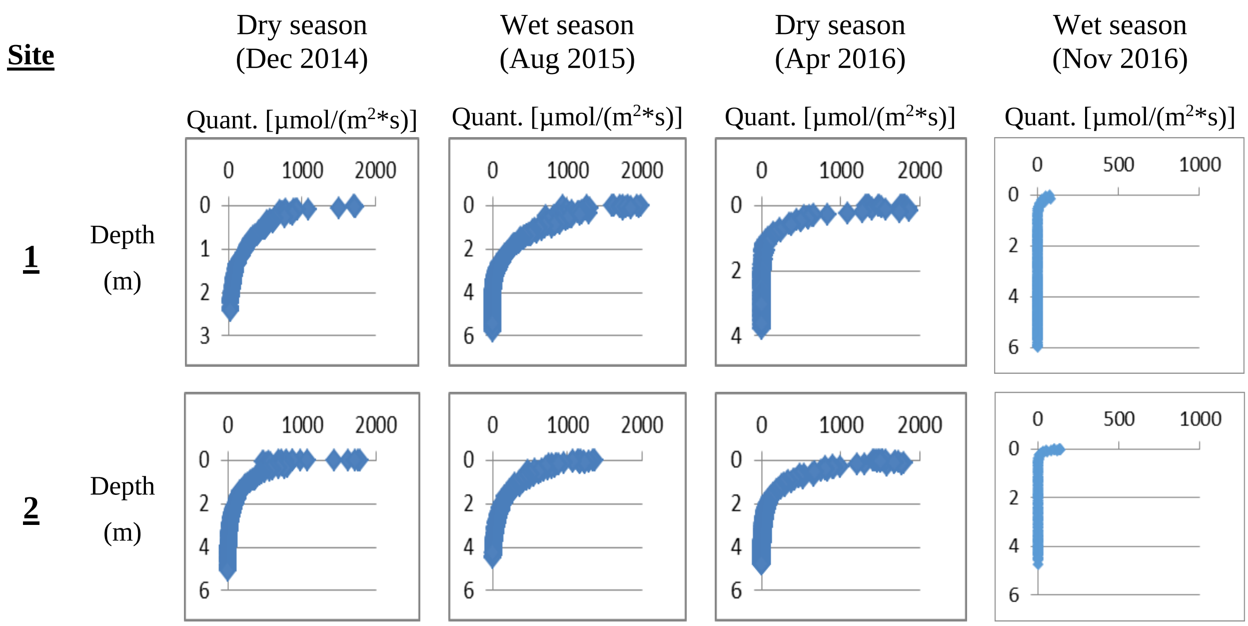


Figure 4.10: Turbidity profiles at major sampling sites in Dong Ho estuary



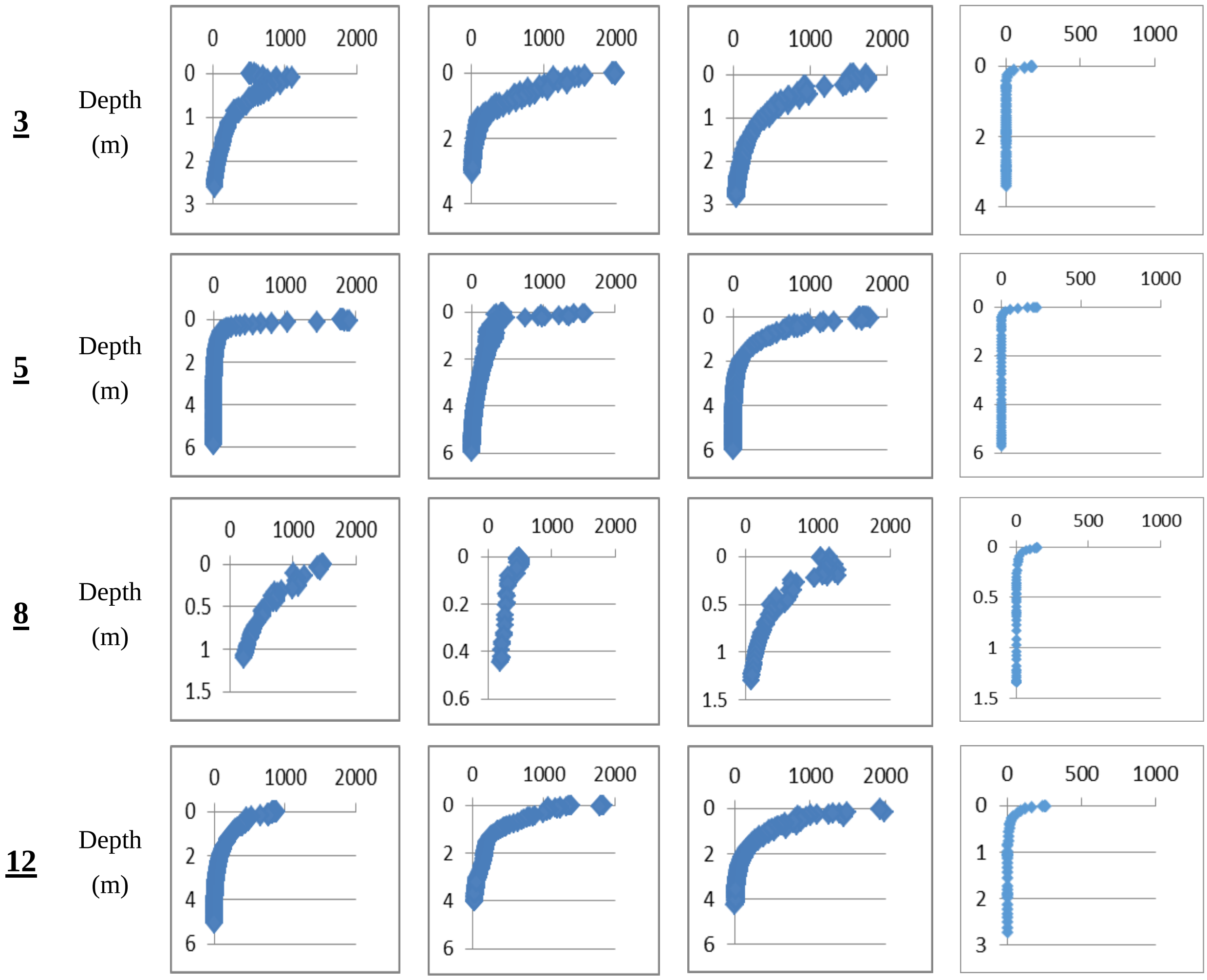


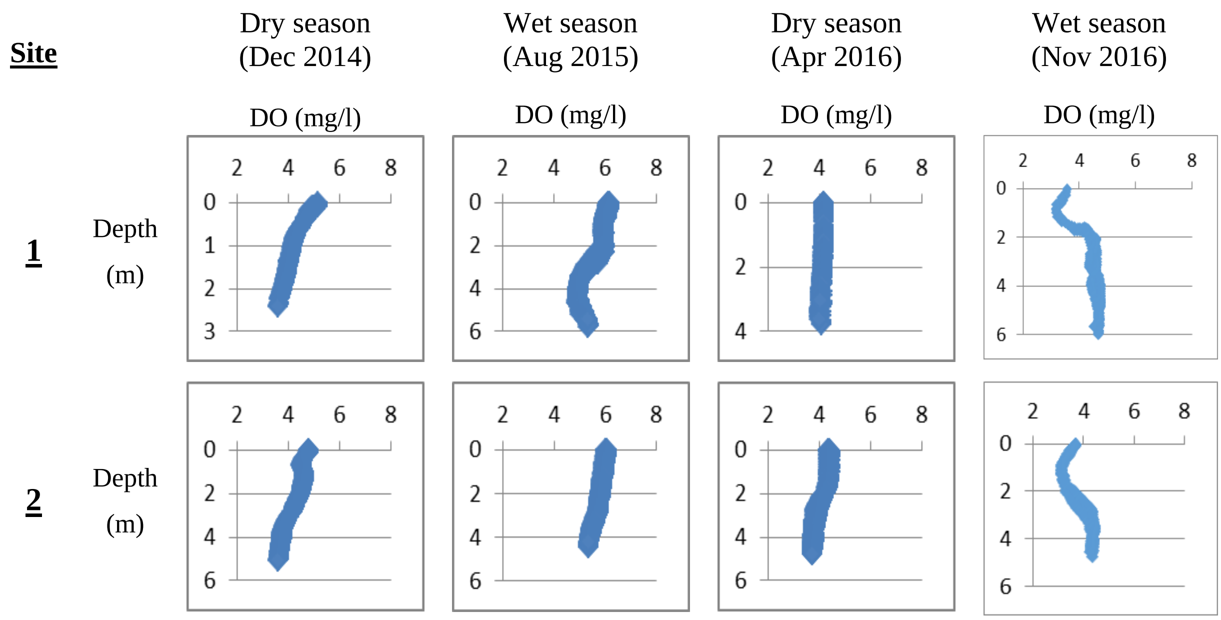
Figure 4.11: Light profiles at major sampling sites in Dong Ho estuary

4.3.3.4. Dissolved oxygen

The level of dissolved oxygen (DO) in the water column of Dong Ho estuary was generally low compared to observations made from other estuaries (Hart et al., 2001, Wilbers et al., 2014). In December 2014 and April 2016 (dry season), most sampling sites showed very low DO with average values ranging between 3-4 mg/l. Notably, at site 5 and site 12, DO levels were below 3mg/l in the bottom water during this sampling event. As discussed later, these low values may have implications for benthic fauna and local fish communities. In contrast, average DO concentrations during the wet season of August 2015 were approximately 5mg/l, which was higher than the average for the wet season in November 2016, and both dry season sampling periods (Figure 4.12). Range in DO concentrations in Dong Ho in different sampling time are presented as: 39-66% DO (Dec 2015); 81-85% (Aug 2015); 46-71% (Apr 2016); 35-71% (Nov 2016). In addition, on some occasions, the low levels of DO observed in bottom waters are crucial to highlight.

In terms of vertical profile of DO levels in the water column, there was a general decrease in DO toward the benthos. At the same time, whilst profiles generally followed a slope toward a minimum value toward the benthos in three of the sampling periods, DO levels showed a distinct minimum at the depth of the fresh-saline water interface at most sites in the November 2016 wet season sampling period. As discussed later, this may reflect the accumulation of organic material at this density interface and the associated higher heterotrophic activity occurring with it. Overall, the levels of organic matter entering the estuary via freshwater runoff is suspected as one of the underlying drivers of heterotrophic processes that lead to the low DO levels across the estuary. This is taken up in the discussion below. In addition, DO levels are also influenced by temperature and salinity. Accordingly, the variations in water temperature and salinity also influence the observed DO levels in Dong Ho estuary water (Gilbert et al., 2005). In this context, the lowest DO levels in bottom waters were measured in the last month of the dry season (April 2016) when temperatures and salinity were highest.

DO levels decreased in bottom waters due to planktonic algae die which enhance microbial respiration of organic matter (Diaz and Rosenberg, 2008). In the case of Dong Ho estuary, the percentage of phaeo-pigments found in sediments dominated compared to active Chl-a. Therefore, low DO concentrations in Dong Ho estuary, especially in bottom waters, was probably augmented strongly by the deposition of dead and degrading plant materials. Hypoxia has not yet occurred in Dong Ho estuary despite the high levels of nutrient concentrations measured in water column. DO levels in all seasons are above severe hypoxic levels (Diaz and Rosenberg, 2008). However, declines in oxygen concentrations in a long time associated with increased anthropogenic nutrient inputs can potentially cause hypoxia or periodic hypoxic events in Dong Ho estuary.



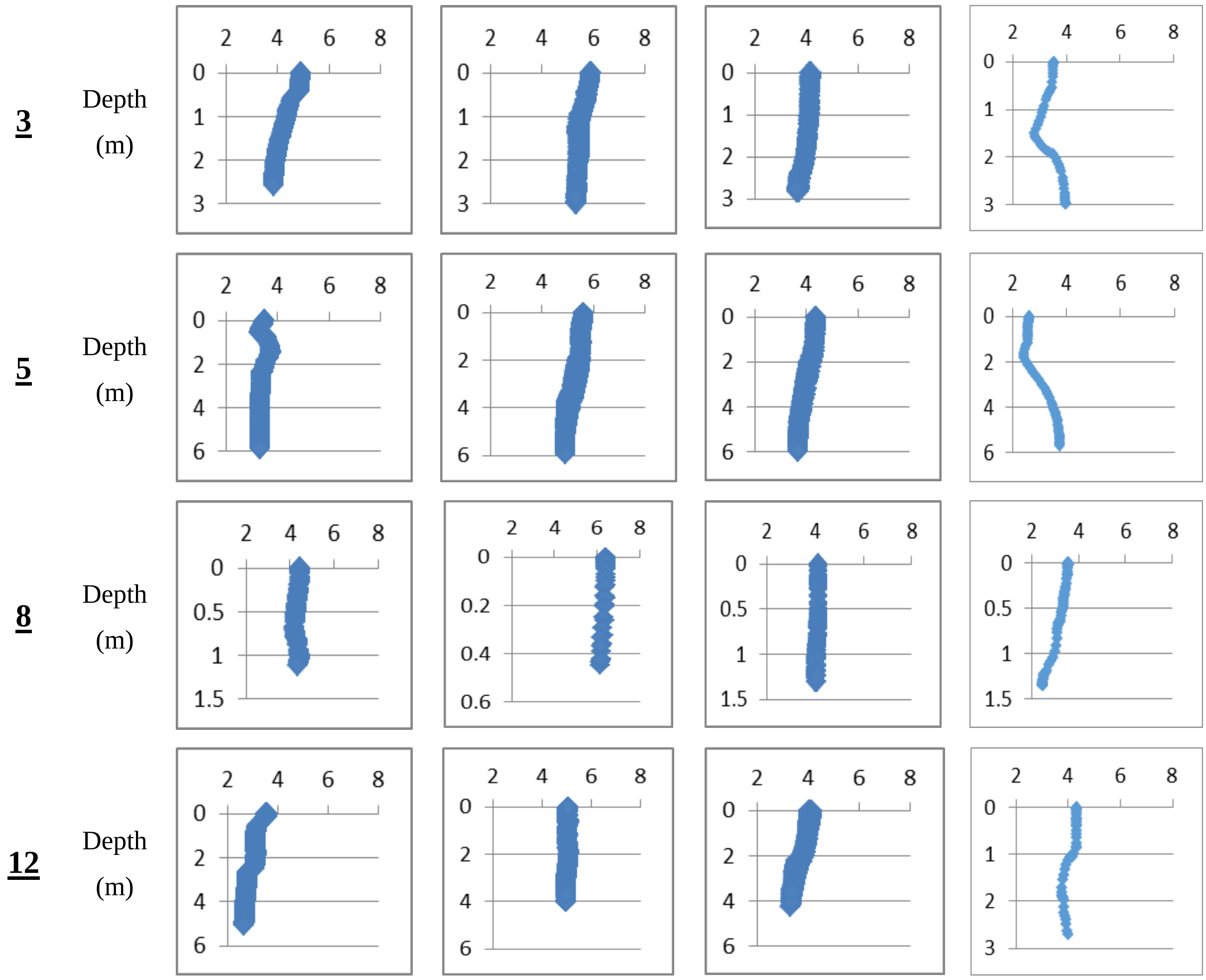


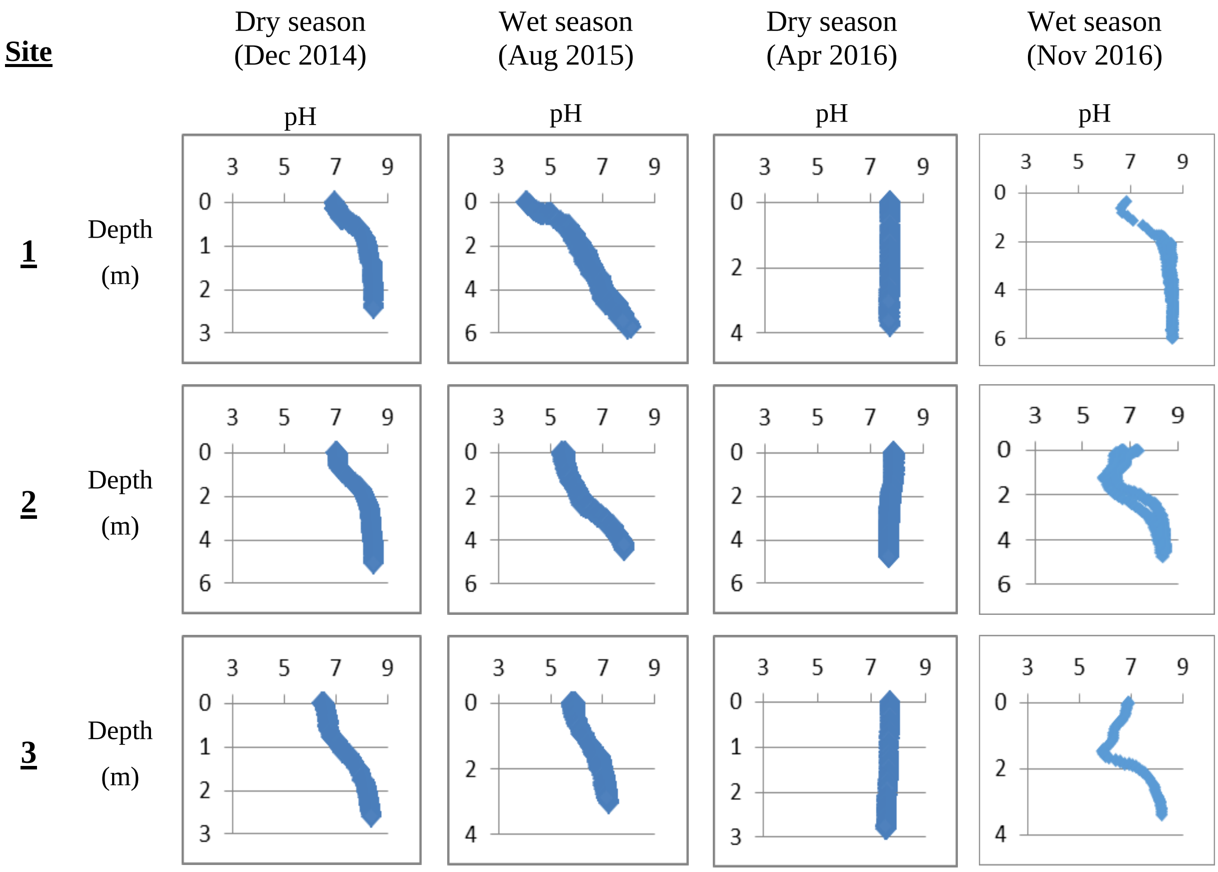
Figure 4.12: Dissolved oxygen vertical profiles at major sampling sites in Dong Ho estuary

4.3.3.5. pH

The difference between dry season and wet season in Dong Ho is also demonstrated through pH data across the estuary. In the dry season, the average pH values observed ranged between 7 and 8. The values showed a slight vertical stratification in April 2016 and in December 2014 between surface and bottom waters (Figure 4.13). By Comparison, in the wet season of August 2015, there was a clear stratification in pH values from surface water to bottom water with average pH values between 3-4 in the surface and 6-7 in the bottom waters. This was most pronounced in the surface water in Rach Gia – Ha Tien canal (site 12), which showed pH values as low as 2 to 4 in surface waters in August 2015. The low values of pH in wet season could be the result of water from acid sulphate soils due to the draining of surrounding swamps for agriculture and aquaculture practices. In this light, all of the sampling sites, including sites 5, 11, and 12, receiving fresh water from Giang Thanh river and Rach Gia – Ha Tien canal, showed low pH (around 2 to 4) and low DO (around 5 – 5.5 mg/l) in the surface water in wet season (August 2015). In all seasons, site 12 in Rach Gia- Ha Tien canal consistently showed the lowest pH value in the surface water. This may be due to the location as it coincides with a focal point where water from agricultural and aquaculture lands enter the canal system and then exchange with waters from the Rach Gia canal and the Dong Ho estuary.

Dong Ho estuary receives freshwater runoff from its catchment in the Southwest of Mekong delta and from Long Xuyen Quadrangle area where are mainly characterised by acid sulphate soils. Low pH measured in the wet season (around 2-4) is not only recorded in Dong Ho estuary but also reflect values reported in the surface water of other areas in the Mekong delta (Carter, 2012). Low pH values clearly demonstrated the high influence of catchment inputs from remote areas into water quality of the Dong Ho estuary.

The pH profiles in the wet season in November 2016 are quite different to those measured in the wet season in August 2015, but they are similar to profiles in December 2014. The surface waters show lower pH values than the bottom water and the average value of pH in November 2016 is around 8; which is much higher than those observed in August 2015. This might be explained by November being the last month of wet season and so the water flowing through the acid sulphate soils in the surrounding agriculture and aquaculture lands may have already flushed out the body of acidic sulphates during the preceding wet period; thus, leading to a reduced impact on water pH values at the end of the wet season.



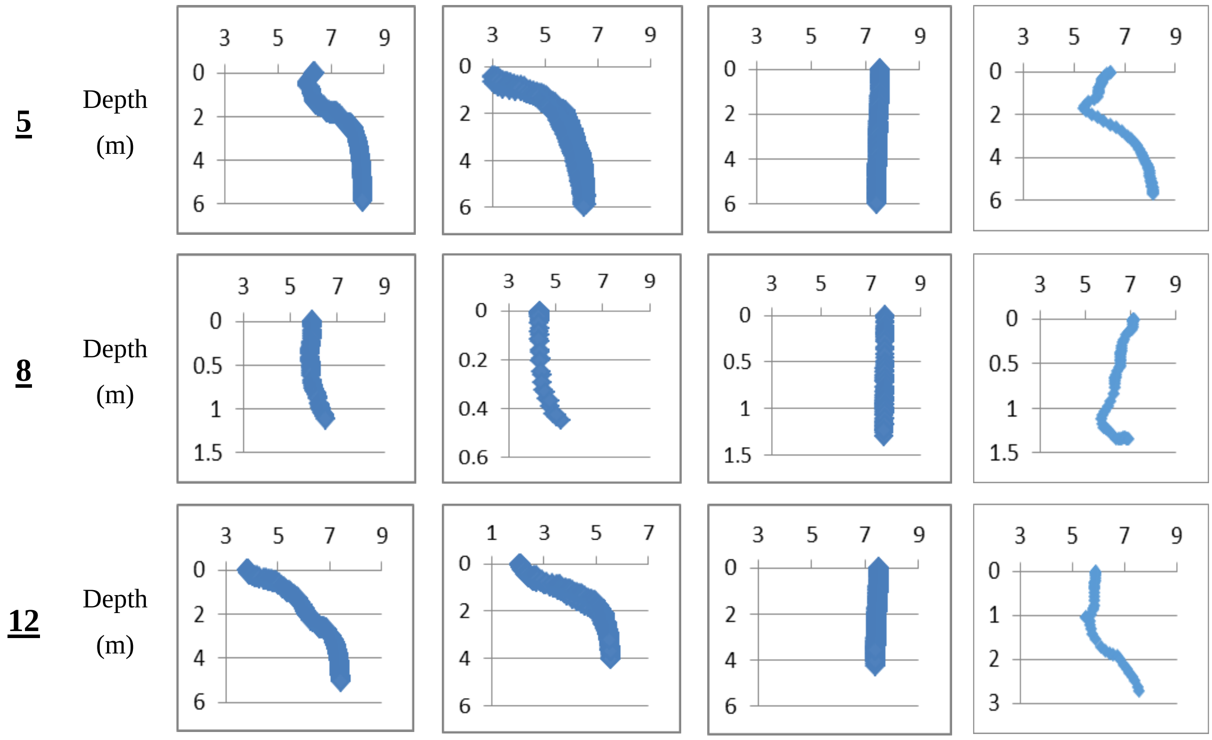


Figure 4.13: Vertical profiles of pH in water column at major sampling sites in Dong Ho estuary

4.3.3.6. Chlorophylls

Water column Chlorophyll-a concentrations were measured in all sampling sites in both seasons to assess the total levels but also to record seasonal variation that might occur. In the dry season, the average Chl-a is 3-4µg/l and most of sampling sites showed a slight vertical stratification in values at some sites between the surface and bottom water (Figure 4.14).

In the wet season, stratification in Chl-a values was more obvious in some sites with values observed in the wet season of November 2016 being different to all other sampling periods (Figure 4.14). In the wet season of August 2015, the Chl-a values were higher in the bottom water than those in the surface water, while in November 2016, the opposite was true with surface water values higher than in the bottom water. As previously noted, the wet season in November 2016 showed significant layering of waters as the larger flows of freshwater dominated the surface of the estuary. Although this lead to low light penetration, it may have delivered phytoplankton from other reaches of the catchment as it drained into the estuary. Further study is required to elucidate this as mentioned later.

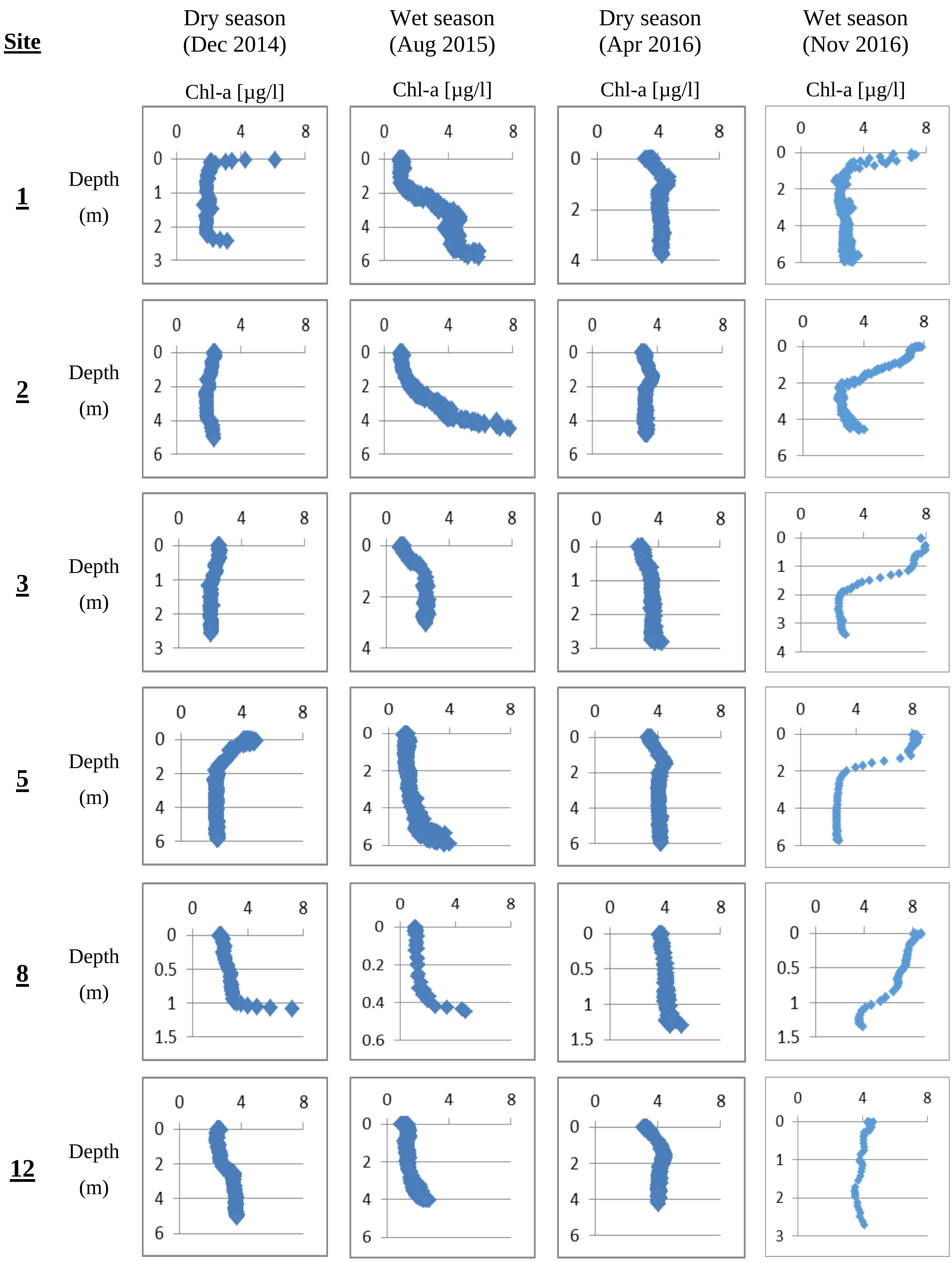


Figure 4.14: Vertical profiles of Chl-a in water column at major sampling sites in Dong Ho estuary

4.3.4. Nutrient stocks in the water column of Dong Ho estuary

At each sampling site, NH_4^+, NO_x and PO_4^{3-} concentrations were determined in the surface water and bottom waters as the first stage of assessing the overall nutrient dynamics in Dong Ho estuary. The nutrient sampling included both flood tide and ebb tide sampling on each field campaign. Sampling followed a transect from outside of Dong Ho estuary in the Gulf of Thuan Yen (Western Sea; site 1) and went upstream to the Giang Thanh river (site 7). A second transect followed the Ha Tien-Rach Gia canal to the north east (Figure 4.1).

In the wet season, the three sites in the west of the estuary (sites 8, 9, & 10) were so shallow (<2m) that surface and bottom water were not separately collected. Instead, the sample was taken at mid depth and considered as surface water relative to the other deeper sites (blue column on graph). In the dry season, more samples in the Giang Thanh river (site 6, 7) and upstream of Ha Tien – Rach Gia canal (site 13,14) were collected and analysed to identify the influences of tidal intrusion on water quality due to more limited freshwater inputs.

Overall, in wet season, the nutrient concentrations observed in Dong Ho estuary were high compared to other estuaries in nearby regions in Vietnam (Vo and Nguyen, 2012, Sebesvari et al., 2012). By comparison, nutrient concentrations in the dry season were similar to other estuaries in the lower Mekong basin (Sebesvari et al., 2012, Chea et al., 2016).There were, however, seasonal differences in nutrient concentrations, and between surface water and bottom water, as well as between high and low tide.

4.3.4.1. Ammonium (NH_4^+)

In the wet season, the average ammonium (NH_4^+) concentration in Dong Ho estuary was around 1.2 - 1.5 mg/l and was higher in the bottom waters compared to the surface. In deeper areas such as sites 1, 2, 3, 5, and 11, NH_4^+ concentrations in bottom waters were twice as high as surface water values on the incoming tide; and three times higher than surface values on the outgoing tide. This was especially so at sites 2, 3, and 5 which are directly influenced by flows from the Giang Thanh River as the tide is going out. The opposite effect was observed in shallow areas (sites 8, 9, and 10) and this is thought to be, in part, due to the influence of nutrient uptake by microphytobenthos coupled to the lower nutrient values at these sites in general. This is discussed further later.

Wet season (August 2015) Dry season (April 2016)

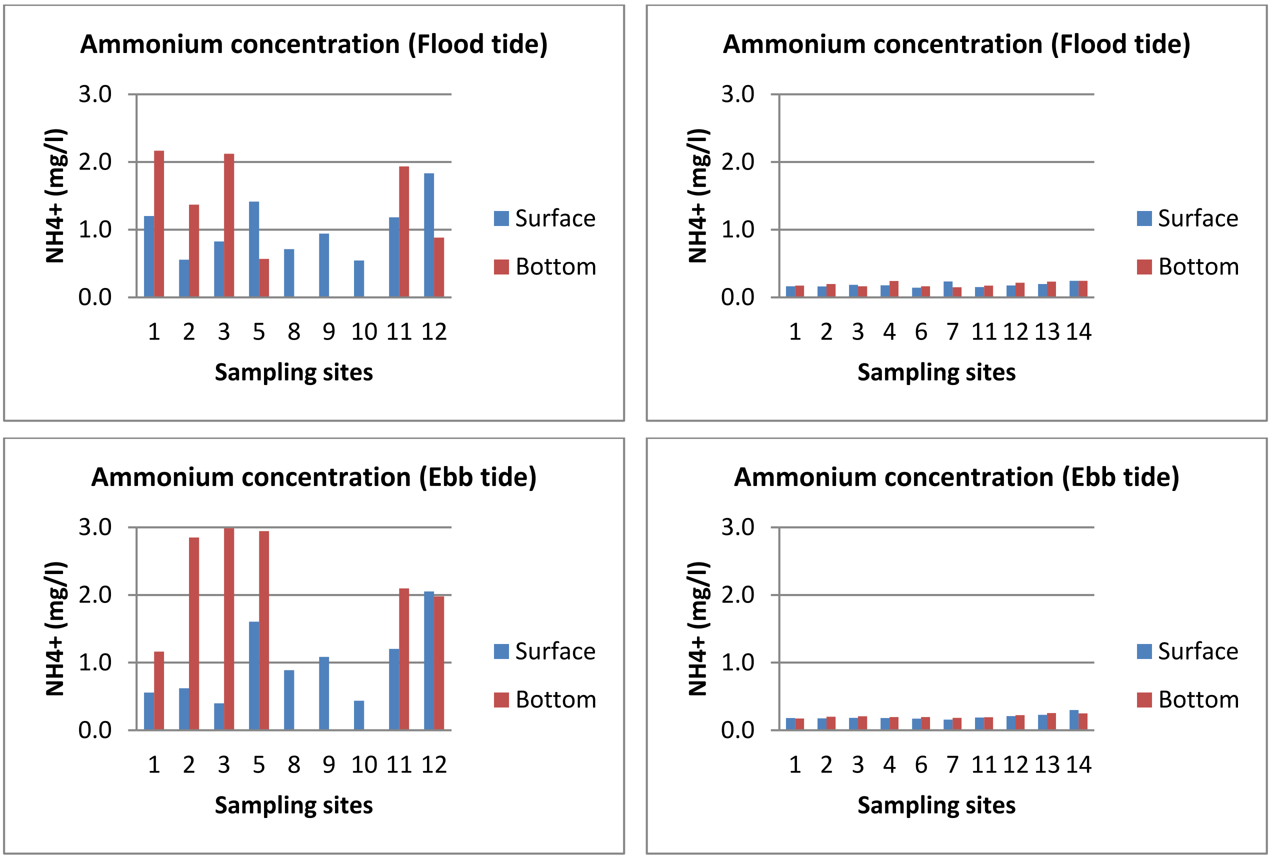


Figure 4.15: Ammonium concentrations in wet and dry season in Dong Ho estuary

In the dry season, the average NH_4^+ concentration in Dong Ho estuary was approximately 0.19 mg/l, which is approximately ten times lower than observed in the wet season. Although in most sampling sites bottom NH_4^+ concentrations were slightly higher than in surface water, however the difference was not significant. These results corresponded with salinity profiles in the estuary during dry season, when most sampling sites were not stratified. The observed average NH_4^+ concentrations were similar and consistent from site 1 to site 7; from outside the estuary to the Giang Thanh river. By comparison, ammonium concentrations in the Rach Gia – Ha Tien canal (from site 11 to 14) were higher than in the central estuary on both flood tide and ebb tides. This may suggest that the main nutrient sources into the estuary during the dry season are derived from the Rach Gia- Ha Tien canal and surrounding connected canals, rather than from the Giang Thanh River. These elevated nutrient levels in the canals of the Mekong are consistent with findings previously reported (Sebesvari et al., 2012).

4.3.4.2. Nitrogen oxides (NO_x)

Measurement of NO_x concentrations in water samples was calculated based on the sum of NO_2^- and NO_3^- concentrations in each sample. As with ammonium concentrations, differences were observed in NO_x concentrations between wet season and dry season, and between flood and ebb tide.

In the wet season, the average NO_x concentration in Dong Ho was approximately 1.2 mg/l (Figure 4.16). In the flood tide, the levels of NO_x in surface waters was lower than in bottom water at most sampling sites while on the ebb tide, the opposite occurred at sites 1 and 2 where surface waters had higher NO_x concentrations than bottom water. The variation of NOx concentrations in sampling sites between flood tide and ebb tide again illustrate the influence of both tidal exchange and freshwater input from the river and canals in the wet season. For example, at site 5, NO_x concentrations were lower compared to site 3 on the incoming tide as opposed to the outgoing tide, when NO_x concentrations were highest amongst all sampling sites.

In the dry season, the average NO_x concentration in the estuary was approximately 0.5mg/l on the flood tide, which was much lower than concentrations observed on the ebb tide (Figure 4.16). Also, on the flood tide, NO_x concentrations in bottom waters was higher than for surface water in most sampling sites, except for site 7 in the Giang Thanh river (Figure 4.16). By comparison, on the ebb tide, the average NO_x concentration was around 1.5mg/l and the highest concentrations (>2mg/l) were observed in the surface water of the central of estuary (site 3 and 4). Except for the sampling sites outside of the estuary and in the Rach Gia- Ha Tien canal, surface water consistently had higher NO_x concentrations than bottom water inside the estuary (sites 2, 3, 4, 6, and 7) on the ebb tide during the dry season. As for other parameters, the big difference in NO_x concentrations between flood tide and ebb tide in the dry season suggests the pronounced influence of tidal exchange in the dry season because freshwater input was so limited.

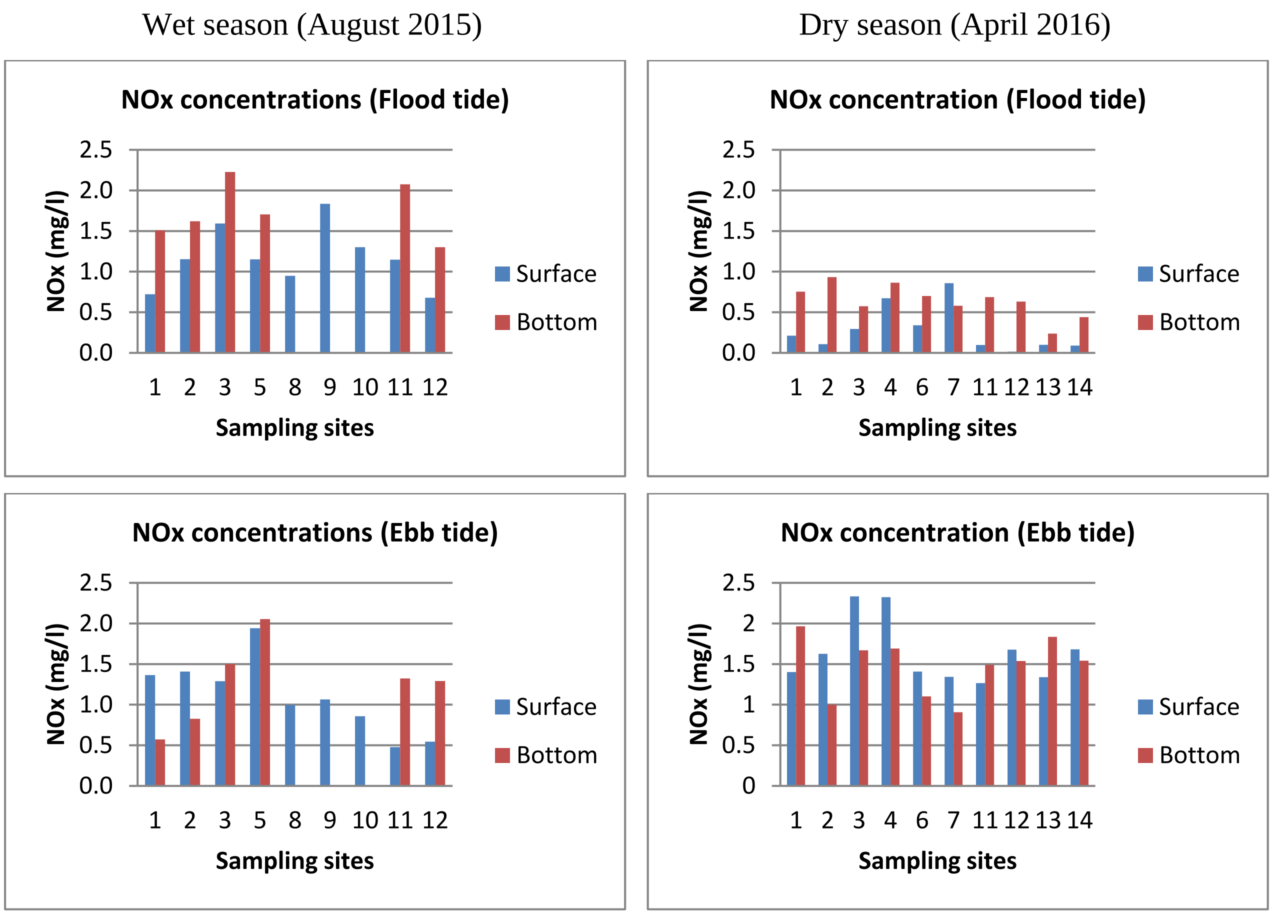


Figure 4.16: NO_x concentration in wet and dry season in Dong Ho estuary

4.3.4.3. Phosphate (PO_4^{3-})

In the Dong Ho estuary, phosphate (PO_4^{3-}) concentrations in the dry season were much lower than in the wet season. The average PO_4^{3-} concentration was approximately 0.1mg/l in the wet season and between 0.01 - 0.02 mg/l in the dry season. In general, in most sampling sites, bottom waters had higher PO_4^{3-} concentrations compared to surface waters. Also, the ebb tide brought higher PO_4^{3-} concentrations than observed on the flood tide (Figure 4.17).

In the wet season, PO_4^{3-} concentrations in the central estuary (site 2, 3, 5) were higher than in Rach Gia – Ha Tien canal on both the flood and ebb tides. In the dry season, PO_4^{3-} concentration in the central estuary were similar to concentrations in Ha Tien-Rach Gia canal on the flood tide, but was slightly higher on the ebb tide (figure 4.17). Due to the limited freshwater input during the dry season, it suggests that the changes in PO_4^{3-} concentration during the dry season in Dong Ho estuary depends on tidal exchange and other local sources such as sewage discharge. Also, although no information exists on groundwater associated with the Dong Ho estuary, groundwater is known to be important for other areas of the Mekong delta (Raksmey et al., 2009, Hoanh et al., 2009).

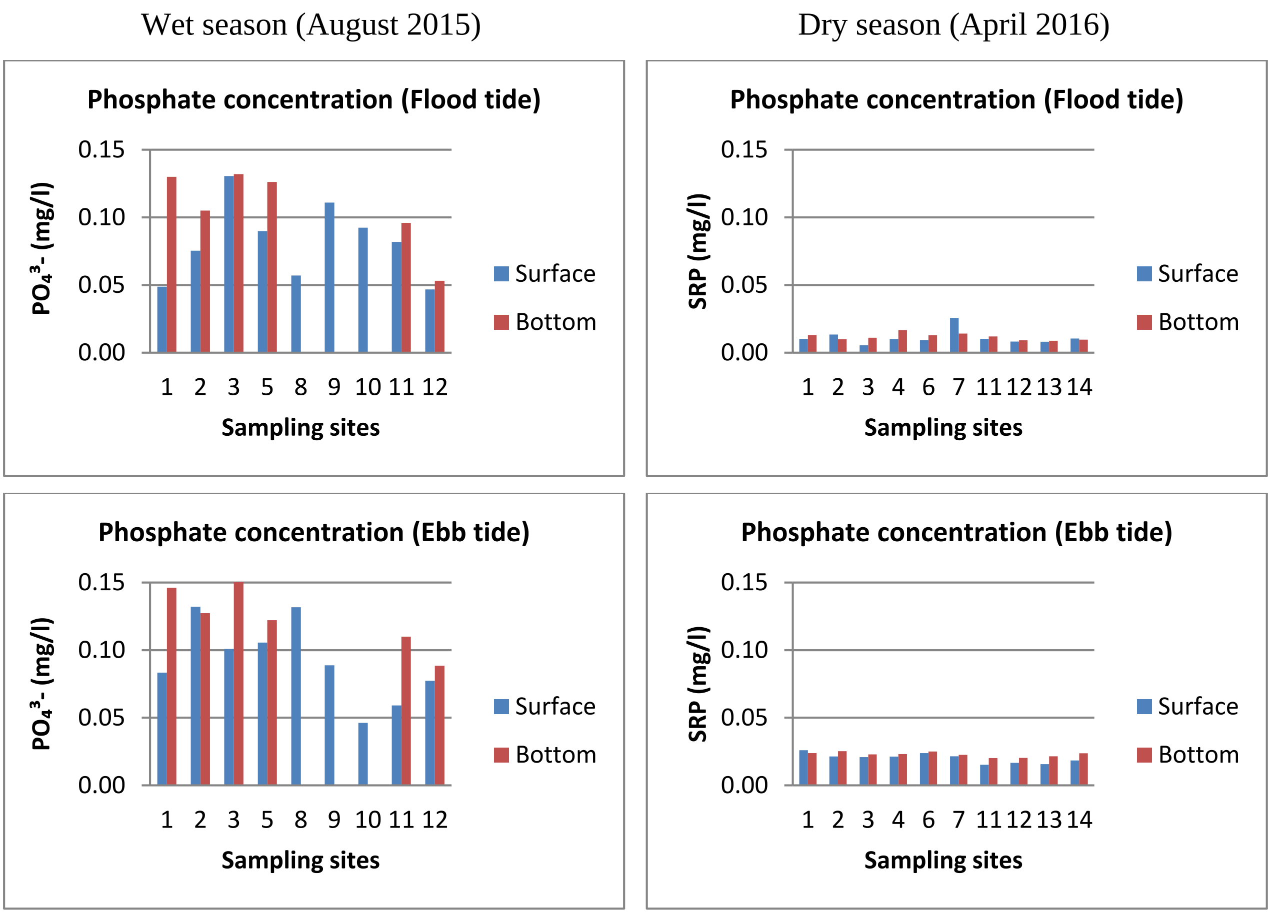


Figure 4.17: PO_4^{3-} concentrations in wet season and dry season in Dong Ho estuary

4.3.5. Benthic sediment characteristics

As described later in Chapter 5, three main zones were identified in the Dong Ho estuary based on bathymetry; these were designated Zone 1, Zone 2, and Zone 3 (Figure 5.1). Zone 1 located at the main gate way from Dong Ho estuary to the sea (Gulf of Thuan Yen), which belongs to the deepest pocket zone (average depth: 5.5m). Zone 2 located in the central of Dong Ho estuary with average depth around 3.4m, where receives all interactions from river, canals and tide. Zone 3 located at the shallowest area of Dong Ho estuary (average depth 1.5m) which is the only zone demonstrating the presence of microphytobenthos.

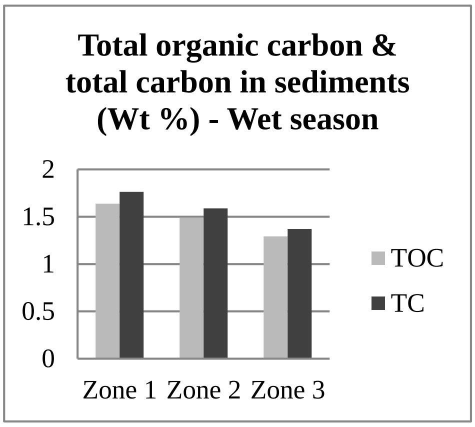
At each sampling site of each zone, solid-phase concentrations of N, C, and P in sediments were determined together with chlorophyll levels, grain size composition and sediment porosity. These were measured in both the wet and dry season.

4.3.5.1. Solid nutrient concentrations in sediments

In all sampling sites and for wet and dry seasons the total carbon content of sediments was dominated by organic carbon (>90%). Figure 4.18 below shows the percentage by weight of total organic carbon (TOC) and total carbon (TC) in sediments from different zones in the wet season and dry season. In both seasons, Zone 1 showed the highest levels of TC and TOC, while zone 3 showed the lowest levels of TC and TOC. These values are in the high ranges reported in other estuaries (Morse et al., 2007, Hanington, 2015).

Wet season

	TOC	TC	TN	TP
	Wt %	Wt %	Wt %	mg/kg
Zone 1	1.637	1.763	0.289	245.52
Zone 2	1.487	1.589	0.294	223.31
Zone 3	1.293	1.371	0.241	300.59



Dry season

	TOC	TC	TN	TP
	Wt %	Wt %	Wt %	mg/kg
Zone 1	1.522	1.646	0.336	269.95
Zone 2	1.424	1.489	0.223	298.93
Zone 3	1.223	1.340	0.208	257.54

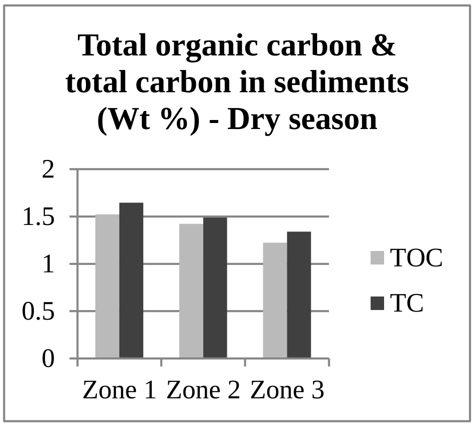


Figure 4.18: Solid nutrient and carbon concentrations in sediments in Dong Ho estuary

In the wet season, total nitrogen (TN) in sediments at zone 1 and zone 2 were higher than zone 3 but total phosphorus (TP) at zone 3 was higher than for other zones. As discussed later, this may be due to the relative differences in materials depositional situations with Zone 1 being the deepest and potentially more depositional than the other two zones. Also, Zone 3 was the shallowest zone with a well-defined micro-phytobenthos which may influence the nutrient standing stocks in the sediments. In contrast, in the dry season, zone 2 had the highest TP in sediments compared to zone 1 and zone 3.

The molecular ratios of C:N:P in sediments in each zone are shown below in table 4.2. Compared to "Redfield ratio" 106:16:1, in the wet season, C:N ratios of zone 2 and zone 3 were close to the Redfield ratio (6.3 and 6.6 respectively) while zone 1 had slightly higher ratio with 7.1. In the dry season, the ratios of C:N in these sampling sites were different compared to wet season results. In the dry season, zone 1 had a lower C:N ratio than Redfield ratio with 5.6 while C:N ratios at zone 2 and zone 3 were 7.6 and 7.4 respectively, which higher than Redfield ratio (6.6). It should be noted that despite small differences in ratios, all of the sediments showed a C:N ratio close to microbial levels rather than those expected from C4 plants or similar sources of detritus (Atkinson and Smith, 1983).

Table 4.2: C:N:P ratios of sediments in three sampling zones in both seasons (molar-based ratios)

	C:N:P ratio in wet season	C:N:P ratio in dry season
Zone 1	185:26:1	158:28:1
Zone 2	184:29:1	129:17:1
Zone 3	118:18:1	134:18:1

4.3.5.2. Sediment chlorophylls

There are two spectrophotometric methods to analyse sediment chlorophylls. The first method identifies the quantity of Chl-a and phaeo pigments, the second method measures Chl-a, Chl-b, and Chl-c (Parsons et al., 1984). Below are the results of chlorophylls measured by both methods in sediments from each of the three zones in Dong Ho estuary. In general, it was observed that surface sediments had higher values of chlorophylls in the wet season compared to the dry season.

Figure 4.19 presents the results for Chl-a and phaeo-pigment values in the three sampling zones. Generally, in both seasons and in all sampling sites, phaeo-pigments values are significantly higher than chlorophyll-a values (Fig. 4.19). This suggests that chlorophyll degradation products dominated in Dong Ho estuarine sediments and may reflect increased phytoplankton growth and/or greater import of these materials from the surrounding catchment during the wet season.

Notably, however, although Zone 1 is located at the deepest site (5-6 m depth) with high turbidity value in the water column, the light profile data showed that there was very low light intensity for photosynthesis in the benthos or for most of the water column; but Chl-a levels measured at zone 1 were the highest of all sampling sites in both seasons. By comparison, zone 3, which was the shallowest zone in the estuary with well-defined microphytobenthos, showed the lowest average levels of Chl-a and phaeo-pigments. These results corresponded with Chl-a measurements in water column for each site (Figure 4.20). Further, in wet season, bottom water Chl-a levels were higher than in the surface water, especially in zone 1, where bottom water contained more than 7µg/l Chl-a. This further suggests that sediment pigment levels are mostly influenced by deposition of dead and degrading plant materials rather than localised production.

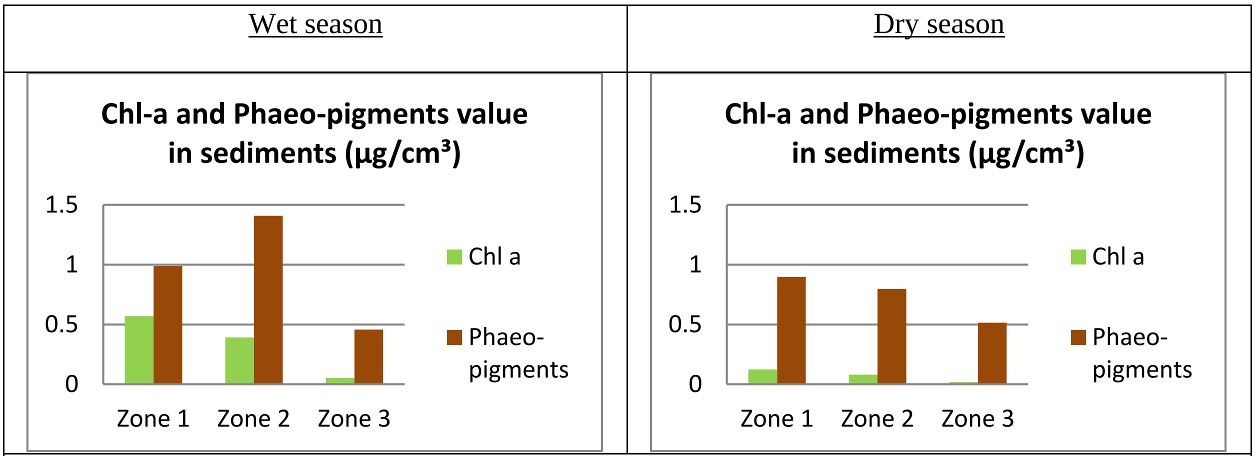


Figure 4.19: Chlorophyll-a and phaeo-pigments value in sediments

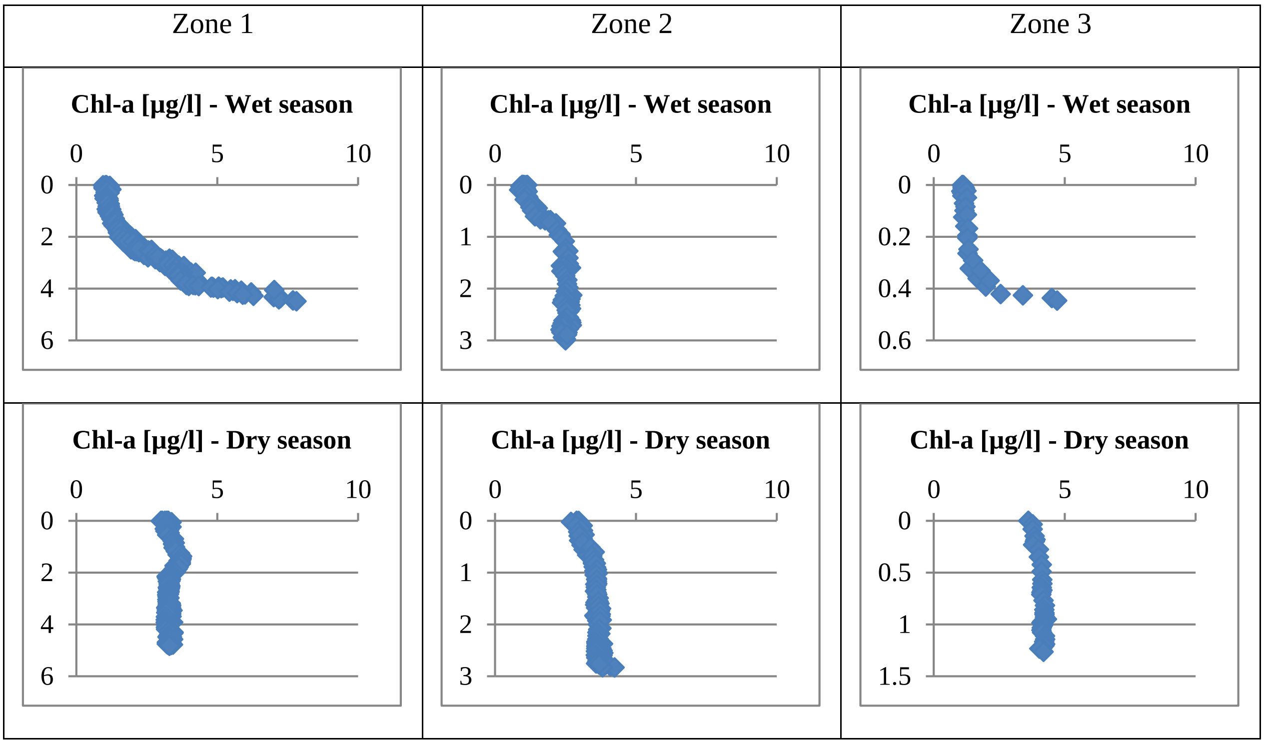
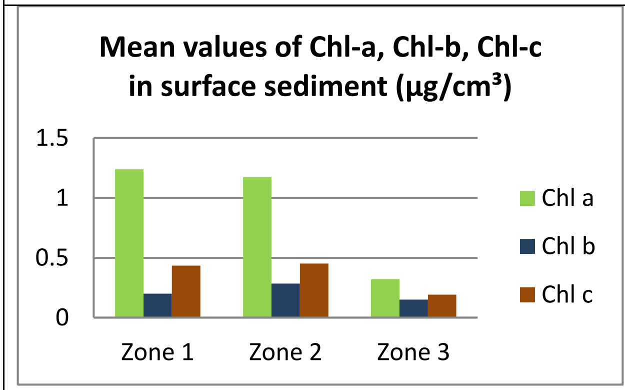


Figure 4.20: Measurements of Chlorophyll-a in water column by depth in 3 zones

The two graphs below (figure 4.21) illustrate the differences between the three types of chlorophylls at each zone (Chl a, Chl b, Chl c). In both seasons and at all sampling sites, Chl-a prevailed and then Chl-c. The quantity of Chl-a in zone 1 was highest and zone 3 had smallest amount of Chl-a in both seasons. High Chl-c value shows that phyto-detritus and potentially viable phytoplankton cells dominated benthic labile organic carbon (Ferguson et al., 2007).

Wet season



Dry season

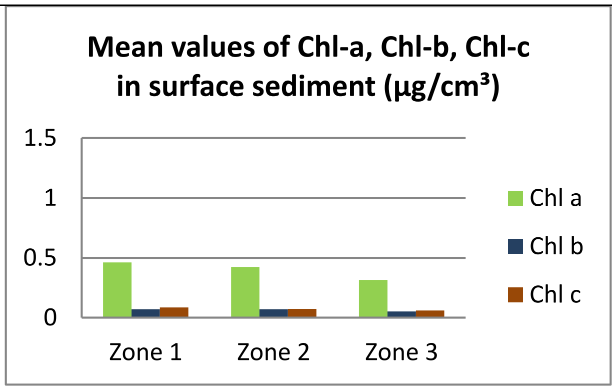


Figure 4.21: Values of Chl-a, Chl-b, Chl-c in surface sediments

In order to justify the spatial distribution of chlorophylls in sediments of Dong Ho estuary, light attenuation coefficient K_d was estimated from vertical profiles of photosynthetically active radiation by the Lambert-Beer equation (Devlin et al., 2008, Brito et al., 2013). Table 4.3 below showed the photosynthetic active radiation (PAR) at the surface water and at the surface sediment, percentage of the surface light reaching the benthos and light attenuation coefficient in different sampling sites in both wet and dry season of Dong Ho estuary. The higher values of light attenuation coefficient (K_d) corresponded to the higher suspended particulate material (SPM) values in estuarine waters (Devlin et al., 2008). These K_d values estimated in each sampling site for each season explained the variations of chl-a levels measured in sediments of Dong Ho estuary. Zone 3 was measured with highest K_d, which means it had highest SPM value and it led to this site had lowest chl-a value in the surface sediments, even this is the shallowest site. In contrast, K_d in zone 1 was smallest and it likely explained why zone 1 had highest chl-a values in both seasons. Comparing between two seasons, light attenuation coefficient in wet season were lower than in dry season, which maybe explained the sediments in wet season was measured with higher chlorophylls than in dry season. In addition, higher light attenuation coefficient values also reflect the higher influence of currents, resuspension of sediments and run-off at sampling sites (Brito et al., 2013). The shallow area (zone 3) was likely to have higher concentrations of suspended particles due to re-suspension of sediments than zone 1 and 2, which led to higher light attenuation coefficient and lower chlorophylls values.

Table 4.3: Light attenuation coefficient in water columns of Dong Ho estuary

Season	**Zone**	**Depth (m)**	**PAR at Surface [µmol/(m2*s)]**	**PAR at Benthos [µmol/(m2*s)]**	**% Light at Benthos**	**Light attenuation coefficient K_d (m^{-1})**
WET	1	4.49	1182.69	5.61	0.47	1.19
	2	4.67	2209.51	1.90	0.09	1.51
	3	0.43	495.03	221.95	44.83	1.88
DRY	1	4.99	407.32	0.27	0.07	1.46
	2	2.92	795.19	8.33	1.05	1.56
	3	1.30	1181.60	78.30	6.63	2.08

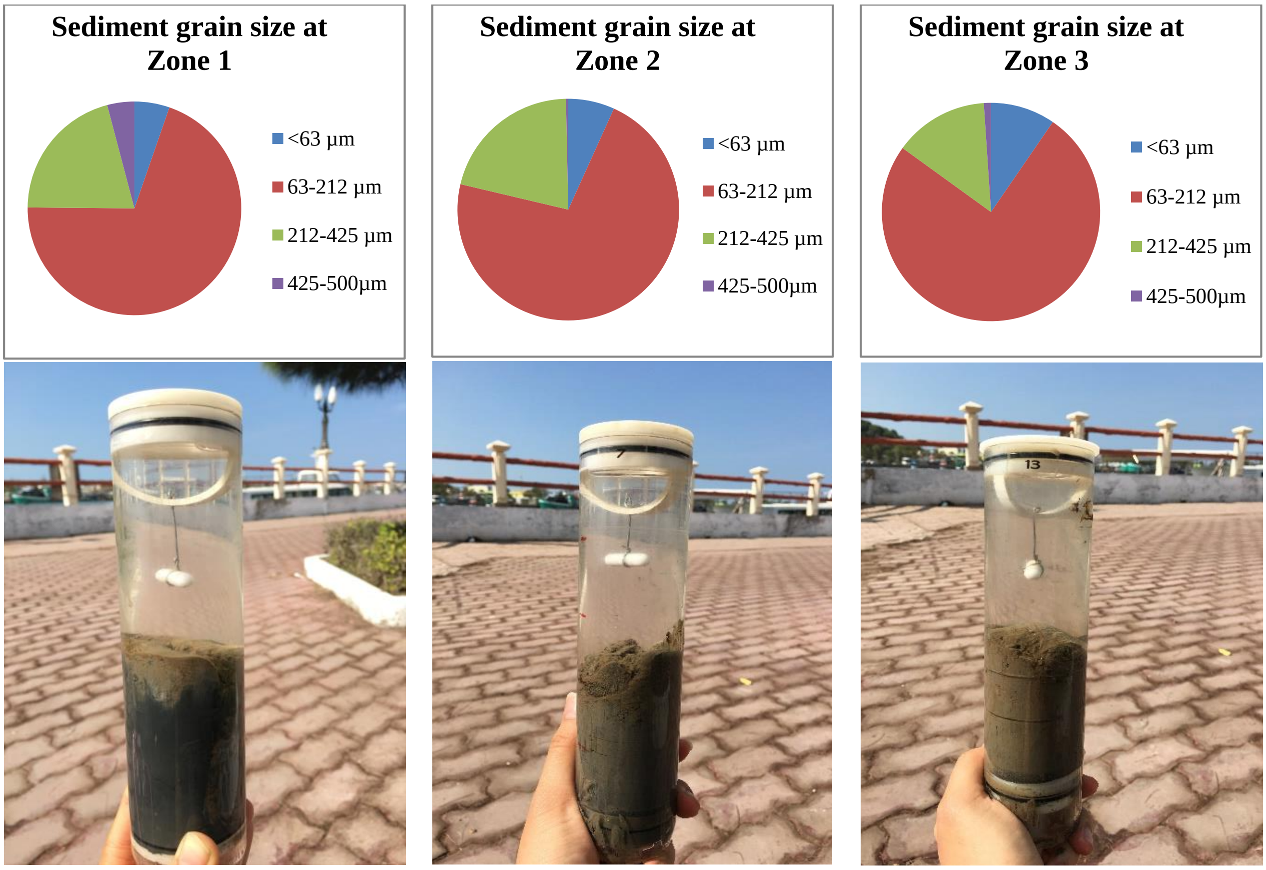
4.3.5.3. Grain size and porosity

Porosity values of ocean and estuarine sediments typically range from Ø= 0.4 nearly to 0.9 (Nafe and Drake, 1961, Tisue et al., 1994). In general, porosity of sediments in Dong Ho estuary ranged at 0.5 and it was similar between different sampling sites (table 4.4).

Table 4.4: Mean values of grain size and porosity of sediments at Dong Ho estuary

Zone	Porosity	Water content	Grain size %			
	%	%	<63 µm	63-212 µm	212-425 µm	425-500µm
1	52.38	3.96	5.31	69.82	20.75	4.11
2	50.16	3.02	6.76	71.93	20.98	0.33
3	54.10	3.75	9.59	75.38	13.98	1.06

Based on sediment grain size classification by the Udden–Wentworth scale, the grain size percentage composition shows sediments in Dong Ho estuary is mostly fine and very fine sand (Switzer, 2013, Wentworth, 1922). Sediments with grain size below 63 µm are silt and zone 3 contains highest silt percentage (nearly 10%) compared to other sites. No clay was detected in surface sediments (5cm depth) at all of the study sites.



Sediment core at zone 1 ***Sediment core at zone 2*** ***Sediment core at zone 3***

Figure 4.22: Percentage of sediment grain size at different sampling sites in Dong Ho estuary with a photograph of a representative sediment core from the respective locations

4.4. Discussion

As indicated in the introduction to the thesis and this chapter, there are key insights that are required in order to best understand how the Dong Ho estuary is currently functioning relative to similar ecosystems, as well as how the estuary is potentially being affected by the associated catchment and land uses. The results obtained in this chapter allow us to now consider the following:

1) Is the Dong Ho estuary highly influenced by catchment inputs?
2) How do the observed levels and concentrations compare to other similar estuaries?
3) Is the system collecting material or simply acting as a pipeline to the sea?
4) In view of the current situation with nutrient levels and potential capture, what do we need to consider in terms of risk and next steps for research?

Each of these aspects is considered below within the context of the results obtained and the insights they provide.

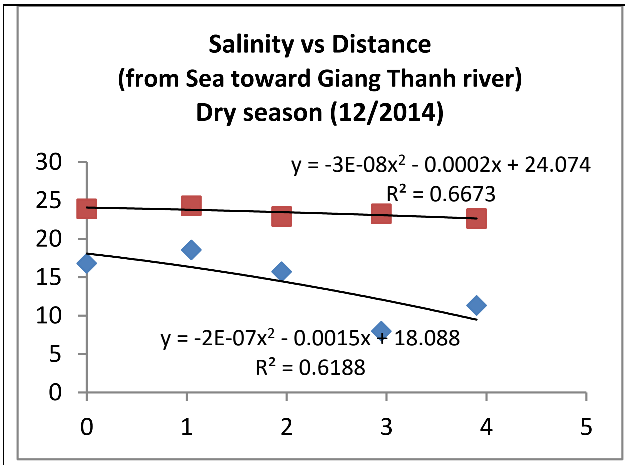
4.4.1. Is the Dong Ho estuary highly influenced by catchment inputs?

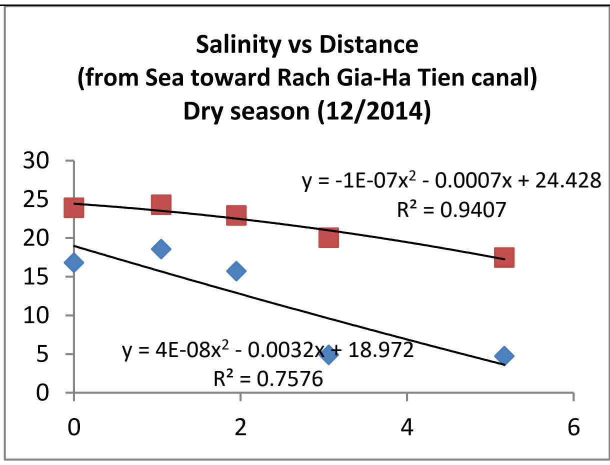
The water quality surveys in Dong Ho estuary were undertaken in December 2014, August 2015, April 2016 and November 2016. In general, biophysical features such as salinity, turbidity, DO, pH and Chl-a in Dong Ho estuary waters showed strong seasonal variations. The influence of the wet season from May to November, with the increased freshwater inputs from the Giang Thanh River and Rach Gia Ha Tien canal, underpin the observed seasonal variations in water quality in the Dong Ho estuary. In the wet season, with an average rainfall of approximately 325.5 mm/month (Kien Giang Statistics Office, 2013), Dong Ho estuary receives large freshwater inputs from its catchment while, in the dry season (April 2016), the estuary receives very limited freshwater input. This is substantiated by the clearly layered water column in the wet season compared to the well mixed and saline dominated waters in the dry season (e.g. see salinity profiles in figure 4.9).

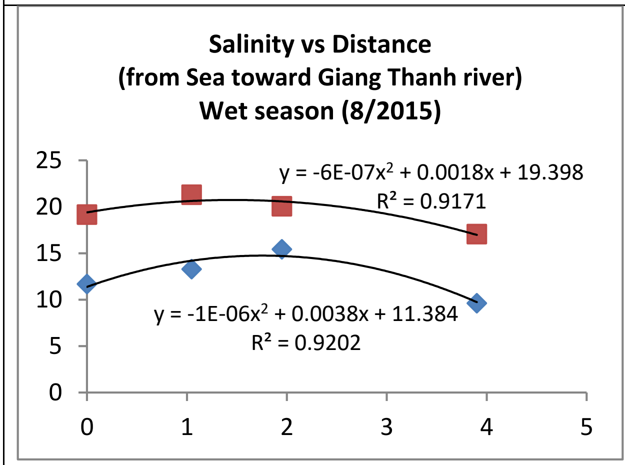
Across the four sampling times in the study, the dry season in April 2016 was most different compared to the others. On this occasion, no vertical layering was observed for any of the parameters measured. Notably, the field observations in April 2016 were at the end of the dry season, whilst the December event was at the start of the dry season. Accordingly, salinity profiles showed a thin upper layer of fresh water as the catchment continued to drain and evaporation rates across the system had probably not reached their peak due to continued, but patchy, cloud cover in this period. In addition, during the April 2016 event, the sluice gates upstream of Giang Thanh river and Rach Gia- Ha Tien canal were closed to prevent saline intrusion further up into the catchment.

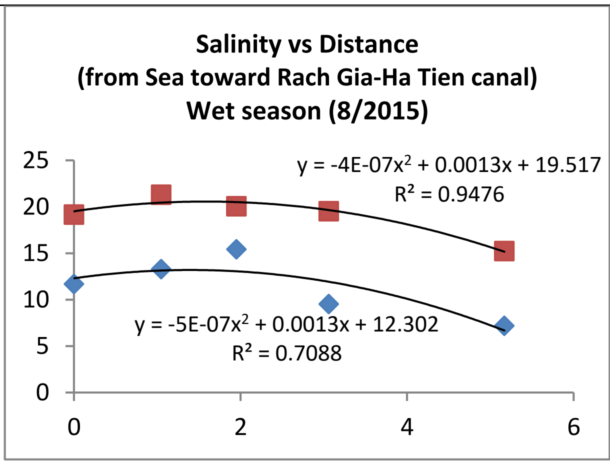
As illustrated in figures 4.10 and 4.13, turbidity levels, and pH values also changed to more reflect the influence of marine waters rather than the fresh water conditions. Due to limited freshwater input in April 2016, Dong Ho estuary had lower turbidity and higher pH values compared to wet season. By comparison, in the wet season, turbidity was higher and the surface water had very low pH values which reflected the low pH values recorded up in the catchment (figures 4.13) (Nhan et al., 2007, Chea et al., 2016). Again, this supports the notion that Dong Ho estuary receives significant sediment inputs from the Giang Thanh river and Rach Gia Ha Tien canal in wet season, and reflects the origins of these waters from areas reported to have issues with acid sulphate soils in remote areas of the Long Xuyen Quadrangle (Carter, 2012a, Le and Truong, 2011). In addition, the different values observed in surface freshwaters in the Dong Ho estuary were very different to the underlying mariner waters and reflect the differential influence that each water body may have; surface freshwater flow into and through the system, versus deeper saline waters confined to the benthos and deeper area of the estuary.

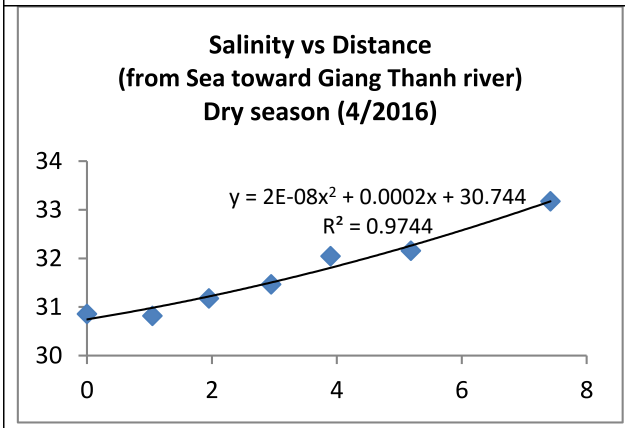
To better describe the influence of tide exchanges and freshwater input in Dong Ho estuary in different seasons, Figure 4.23 below presents the correlations between salinity distribution and distance of sampling sites (by km) from the open sea (site 1), towards Giang Thanh river (site 5), and up along the Rach Gia - HaTien canal (site 12). In the wet seasons (8/2015 &11/2016) and, to a less extent at the start of the dry season (12/2014), surface water and bottom water were separated and the freshwater inputs were well defined with lower salinities observed moving toward the river and canal. By comparison, in the peak of the dry season (4/2016), there was no stratification between surface and bottom waters, and salinity values captured in figure 4.23 at the peak time of this dry season were illustrated by values of mid-water due to mixing of two water layers. Of note, however, salinities observed during 4/2016 were higher toward the river and canal compared to the seaward site (site 1). This is explained by the combined absence of freshwater inputs from the river and canals associated with high evaporation rates in the surface water upstream. This would lead to elevation in salinity relative to the marine inputs through the mouth of the estuary. In the Mekong River Basin within Vietnam, the annual evaporation rate was recorded at between 1500 to 1700mm while mean annual rainfall was only 1300mm (Mekong River Commission, 2005). In periods of no rainfall this level of evaporation is likely to have a strong influence on both aquatic ecosystems, as has been observed. In contrast, in the wet season where freshwater inputs were abundant, salinity levels upstream of Giang Thanh river and Rach Gia Ha Tien canal were lower than for the seaward site (Figure 4.23).

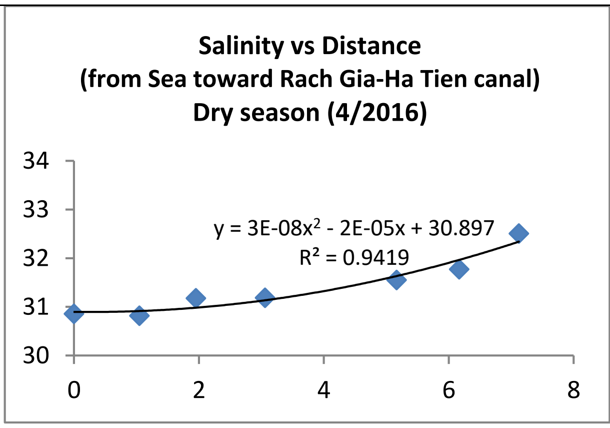

Salinity vs Distance
(from Sea toward Giang Thanh river)
Dry season (12/2014)
y = -3E-08x² - 0.0002x + 24.074
R² = 0.6673
y = -2E-07x² - 0.0015x + 18.088
R² = 0.6188
30
25
20
15
10
5
0
0
1
2
3
4
5

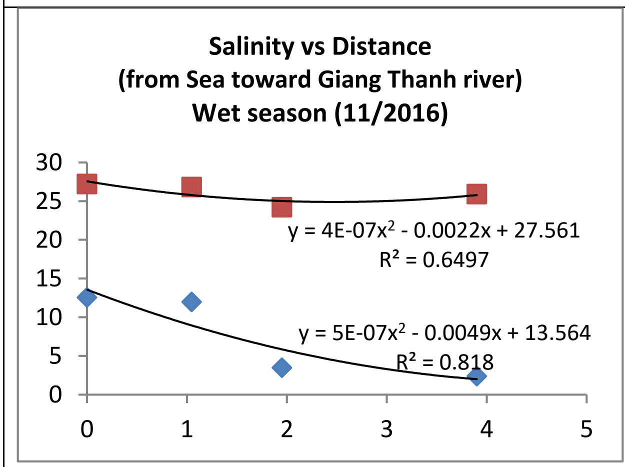

Salinity vs Distance
(from Sea toward Rach Gia-Ha Tien canal)
Dry season (12/2014)
y = -1E-07x² - 0.0007x + 24.428
R² = 0.9407
y = 4E-08x² - 0.0032x + 18.972
R² = 0.7576
30
25
20
15
10
5
0
0
2
4
6


Salinity vs Distance
(from Sea toward Giang Thanh river)
Wet season (8/2015)
y = -6E-07x² + 0.0018x + 19.398
R² = 0.9171
y = -1E-06x² + 0.0038x + 11.384
R² = 0.9202
25
20
15
10
5
0
0
1
2
3
4
5


Salinity vs Distance
(from Sea toward Rach Gia-Ha Tien canal)
Wet season (8/2015)
y = -4E-07x² + 0.0013x + 19.517
R² = 0.9476
y = -5E-07x² + 0.0013x + 12.302
R² = 0.7088
25
20
15
10
5
0
0
2
4
6


Salinity vs Distance
(from Sea toward Giang Thanh river)
Dry season (4/2016)
y = 2E-08x² + 0.0002x + 30.744
R² = 0.9744
34
33
32
31
30
0
2
4
6
8


Salinity vs Distance
(from Sea toward Rach Gia-Ha Tien canal)
Dry season (4/2016)
y = 3E-08x² - 2E-05x + 30.897
R² = 0.9419
34
33
32
31
30
0
2
4
6
8


Salinity vs Distance
(from Sea toward Giang Thanh river)
Wet season (11/2016)
y = 4E-07x² - 0.0022x + 27.561
R² = 0.6497
y = 5E-07x² - 0.0049x + 13.564
R² = 0.818
30
25
20
15
10
5
0
0
1
2
3
4
5

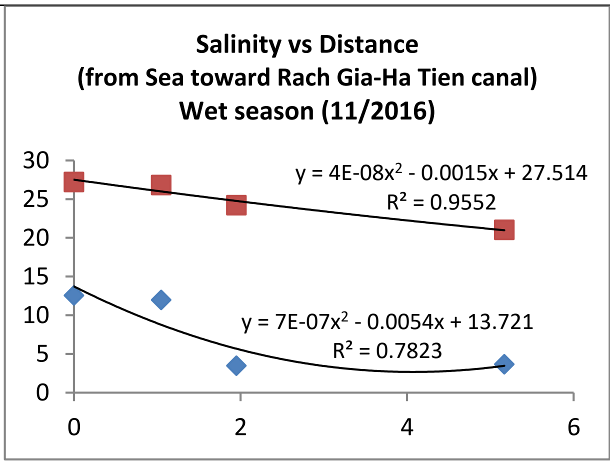
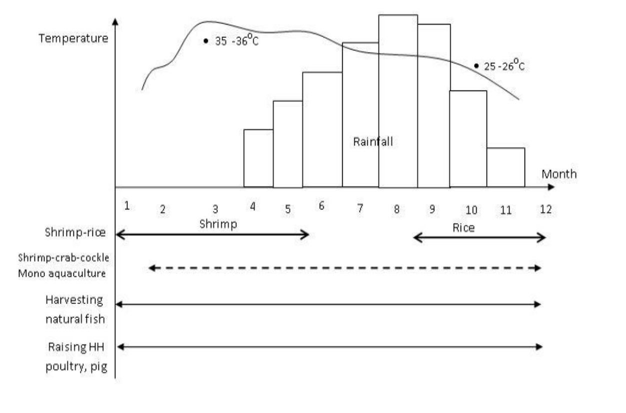

Salinity vs Distance
(from Sea toward Rach Gia-Ha Tien canal)
Wet season (11/2016)
y = 4E-08x² - 0.0015x + 27.514
R² = 0.9552
y = 7E-07x² - 0.0054x + 13.721
R² = 0.7823
30
25
20
15
10
5
0
0
2
4
6

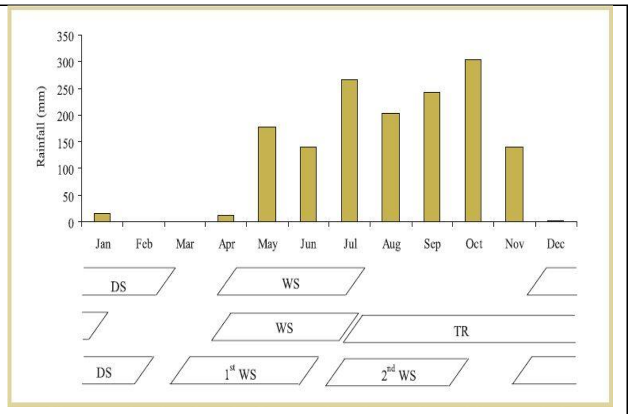
Figure 4.23: Correlations between salinity and distance from the open sea (site 1) towards Giang Thanh river and towards Rach Gia – Ha Tien canal. Blue dots are surface water, red dots are bottom water. Horizontal axis is distance by km, vertical axis is salinity by PSU.

Whilst the salinity data illustrates the impact of catchment freshwater inputs, nutrient concentrations also reflect how catchment sources may be providing significant inputs into the Dong Ho estuary. As with salinity, nutrient levels in the water column varied seasonally and temporally with the highest concentrations observed in the wet season and associated with ebb tide (Figures 4.15, 4.16, 4.17). Whilst some local sources may also play a role (discussed in the next chapter), the major increases in nutrients seen in the wet season highlight the importance of direct inputs from agriculture and aquaculture in the catchment. Concentrations of NH_4^+ and PO_4^{3-} in the wet season (8/2015) were ten times higher than observed in the dry season (4/2016). This can be explained through the combination of high rainfall and the agricultural farming production cycle in the catchment of Dong Ho estuary and the adjacent Mekong Delta (Figure 4.24). As noted previously, measurements made in April 2016, were at peak dry season, and the lack of freshwater was perhaps worse than previous years due to a long drought period; hence there was no record of freshwater inputs into the water column of Dong Ho estuary as seen through salinity profiles. Due to this lack of freshwater and high salt intrusion, rice production in the catchment was not conducted during this period at many locations where it might otherwise have been. Accordingly, in Kien Giang province, shrimp farming practise dominates in the dry season and extended its activity in 2016 due to the drought conditions (figure 4.24-b). However, a shrimp production cycle lasts about 5 months between December and June, and after harvesting, shrimp ponds are flushed into the adjacent estuary or canal waters (Vo and Nguyen, 2012). So, compared to the ongoing water exchange seen with agricultural practises over the wet season and interface period at the start of the dry season, shrimp farming tends to produce a significant pulse of inputs into the estuary over a much shorter and defined time period. This would explain why we did not observe elevated nutrient levels in the dry season despite widespread shrimp farming. As reported in Section 4.3.4, the concentrations of NH_4^+ and PO_4^{3-} were low in the dry season and in the same range as measurements in other estuaries of the Mekong delta, and other estuaries in the world (Vo and Nguyen, 2012, Sebesvari et al., 2012, Fisher et al., 1988, Chea et al., 2016, Thomson et al., 2001). However, PO_4^{3-} concentrations on the ebb tide were twofold higher than in flood tide, in the dry season suggesting that P loading into Dong Ho estuary in dry season comes from local sources such as raw sewage and domestic wastewater produced in Ha Tien town and the To Chau area.

One other aspect of how the catchment waters may influence Dong Ho estuary is through the pH of catchment waters reaching the estuary. The pH of estuarine waters can have large effects on ammonia concentrations. For example, the total ammonia concentration can increase approximately 10-fold when pH values decrease by as little as 1 pH unit (Eddy, 2005). In the context of Dong Ho estuary, the pH of waters in the Dong Ho estuary in the wet season (8/2015) had pH values between 2 to 4 pH units lower than observed in the dry season. This would augment ammonium levels and may partly explain why the concentrations of NH_4^+ in the wet season (8/2015) were ten times higher than in the dry season (4/2016).



a) Rainfall, temperature patterns and the rice-shrimp aquaculture systems and other activities aligned with weather patterns in Thuan Hoa commune, Kien Giang province, Vietnam Mekong delta (Clausen, 2015)



b) Rainfall and double-triple rice farming patterns in Can Tho and Vinh Long: DS (dry season crop), WS (wet season crop) and TR (traditional rice crop) (Nhan et al., 2007)

Figure 4.24: Monthly rainfall and farming patterns in some areas of the Mekong delta (Nhan et al., 2007, Clausen, 2015)

Based on the evidence above, it has been demonstrated that Dong Ho estuary is strongly influenced by catchment inputs from both local and remote areas in the wet season, while in dry season it was influenced mostly by local inputs from sewage and wastewater, as well as the adjacent marine environment. It also substantiates the proposition by Carter (2012) that Dong Ho estuary is a focal point for materials moving out of the agricultural and aquaculture areas of the south-western Mekong area. How much of this material is retained in the system is not clear, but may be important for the estuary's performance and sustainability. The lower dissolved oxygen levels observed in the dry season may, for example, reflect strong heterotrophic activity related to the remineralisation of these materials. This issue is considered more closely through key biogeochemical process measurements (in Chapter 5) and LOICZ modelling (in Chapter 6).

4.4.2. How do the observed levels and concentrations compare to other similar estuaries?

As suggested above, dissolved oxygen can be a key indicator of both primary production but also the relative level of heterotrophy being undertaken in an ecosystem. Dissolved oxygen levels in Dong Ho estuary ranged from 3-6 mg/l and bottom waters consistently had lower DO levels than surface water. DO levels observed in Dong Ho estuary are similar to those reported in inland regions of the Mekong delta, but lower than coastal regions (Wilbers et al., 2014, Hart et al., 2001). Although Dong

Ho estuary is influenced by tidal exchange but it has low DO as inland regions such as Can Tho and Hau Giang where waters receive an accumulation of organic pollutants from urbanized areas and are affected by surrounding aquaculture farms and rice fields. It suggests that despite tidal exchange, dilution rates and turnover rates of Dong Ho estuary are currently not sufficient to refresh the water column. The depletion of DO depends on increasing organic materials and microbial activity and primary production (Hart et al., 2001). Current levels of DO in the Dong Ho Estuary in this study where well under International guidelines for the protection of aquatic life and sustainable water quality these include examples such as the Australian Water Quality Guidelines (ANZECC, 1992) where DO should not be below 6 mg/l, The USEPA recommends DO should be above 4.8 mg/l (USEPA, 2000) and Vietnamese guidelines established for surface water where DO should be above 4 mg/l (QCVN 08: 2008/BTNMT, QCVN 38: 2011/BTNMT). The DO levels measured in the Dong Ho estuary were found to be below these critical levels at many of the sampling sites in the dry season and were often below 4 mg/l in wet season. This would suggest that benthic fauna are under significant pressure for most of the year and unlikely to flourish where they are unable to adjust to these conditions.

Water pH values in the Dong Ho estuary were similar to those reported for many sites across the Lower Mekong basin where pH is considered to be depressed due to stormwater runoff affected by land use in acid sulphate soils (Chea et al., 2016, Van den Bosch et al., 1998). In the Mekong Delta, acid sulphate soils account for 40% of the total agricultural area and at the beginning of the rainy season during May and July, pH in the first-order canals was below 3.5 due to rainwater leaching out and oxidising sulphur compounds, leading to water acidification (Vo and Nguyen, 2012). This situation explains the observations made in the wet season in Dong Ho estuary when it received the increase of acid diluted in freshwater runoff from land practising of the intensive aquaculture farming and the use of chemical fertilizers from agriculture. Sampling sites in Rach Gia - Ha Tien canal in the wet season (8/2015) and the first month of the dry season (12/2014) showed the lowest pH values in the surface water compared to central and upstream of Giang Thanh river (Figures 4.13). The area east and north-north east of the canal is within a known acid sulphate soil zone and pH values along the associated connected canals has been measured at values as low as 2.8 (Johnstone, 2012). Rach Gia - Ha Tien canal connected with various canals from Long Xuyen Quadrangle which is the main source of acid sulphate soils (Buu and Lang, 2004, Vo and Nguyen, 2012). In this context, it is believed that Rach Gia - Ha Tien canal receives more inputs from acid sulfate soil areas than the Giang Thanh river and therefore reflects this in its water quality.

Chl-a profiles were strongly correlated to turbidity profiles in most of sampling sites in Dong Ho estuary, except site 12 with slightly correlated (figure 4.25). Due to high turbidity, is likely to influence the levels of phytoplankton production and potentially restrict it to the upper water column. Turbidity also reflects the level of materials and particles being carried in the water so that, chlorophyll numbers may reflect some local production as well as algal material produced elsewhere but carried to the sites. In general, Chl-a levels in water column of Dong Ho estuary were below the Chl-a standard of other estuaries (White et al., 2015, Loisel et al., 2017, Gitelson et al., 2007). For examples, all sampling sites in Dong Ho estuary in both seasons had Chl-a values below 8 mg/m^3 while water samples collected in turbid, productive estuaries of Chesapeake Bay contained Chl-a from 9 to 77.4 mg/m^3 (Gitelson et al., 2007). Thus, it again suggested that Dong Ho estuary was not productive and primary production rate was likely low compared to other estuaries.

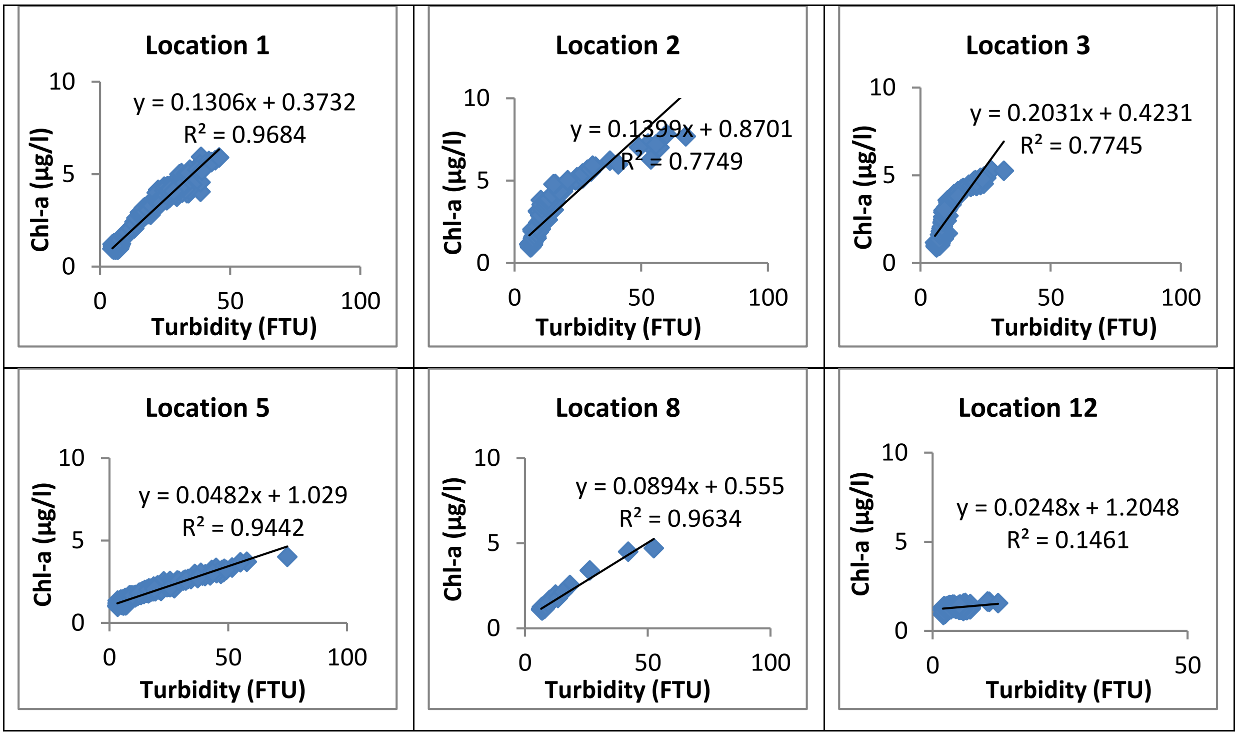


Figure 4.25: Linear regression between Chl-a and turbidity in wet season (8/2015) in Dong Ho estuary

In Europe and North America, agriculture appears to be the major anthropogenic source of nitrogen and phosphorus pollution into rivers and estuaries being derive from agricultural nutrients leaching into aquatic systems from surface runoff, fertilizer use and soil erosion from agricultural land (Sebesvari et al., 2012, Mockler et al., 2017, David and Gentry, 2000). In the context of the Dong Ho estuary, agriculture and aquaculture farming in the catchment are widespread and dominate the landscape with very little or no riparian or other natural systems present that might ameliorate their influence on aquatic ecosystems. As indicated by the nutrient concentrations observed, these land use practises potentially present a significant problem for the future performance of the Dong Ho estuary. Consider, for example, the nutrient concentrations observed in the wet season (8/2015), average NH_4^+ concentrations in the wet season ranged between 1.2 - 1.5 mg/l with concentrations in bottom waters exceeding 2 mg/l, which is higher than the generally accepted levels for freshwater and marine waters in many countries (ANZECC, 1992, Eddy, 2005, PHILMINAQ, 2008). In contrast, PO_4^{3-} concentrations in the wet season were below the Vietnam standard for water quality supporting aquatic life (< 0.2mg/l; QCVN 08:2008/BTNMT) and within the range observed in other estuaries in the Mekong delta (Wilbers et al., 2014, Chea et al., 2016).

Compared to the other dissolved nutrients measured, NO_x concentrations in Dong Ho estuary showed complex seasonal and tidal variations. In the wet season, concentrations of NO_x were much higher on the flood tide than observed in the dry season. In contrast, on the ebb tide, concentrations of NO_x in the wet season were lower than in dry season. Due to shrimp culture in dry season and practising traditionally through frequent tidal water exchanges in extensive farming, the increase of NO_x concentrations in ebb tide could be caused by the shrimp pond effluents (Preston and Clayton, 2003). Therefore, the influence of tidal exchange on nutrient concentrations was more obvious in the dry season. Although average concentrations of NO_x in the Dong Ho estuary were lower than average values reported for other similar estuaries, and below standards of many countries for both freshwater and marine (PHILMINAQ, 2008, Jenkins, 2005, Fisher et al., 1988), they were higher compared to other rivers and estuaries within the Mekong delta (Wilbers et al., 2014, Hart et al., 2001). As mentioned earlier, the extensive farming and aquaculture activities across the catchment and associated with the estuary are likely to contribute DIN and may present a risk for future water quality issues in the estuary (Carter, 2012a).

Based on the Chl-a values and nutrient concentration measurements in the water column, Dong Ho estuary does not fit the classic definition of an eutrophic ecosystem. Despite the high nutrient concentrations in the wet season, Chl-a levels in the water column remain low compared to other eutrophic estuaries (Clement et al., 2001). Similarly, in the dry season TN and TP concentrations in water do not exceed proposed threshold concentrations for eutrophic waters in rivers and estuaries (Yang et al., 2008). Eutrophication leads to increases in the biomass of algae generally reflected through high levels of Chl-a in the water column (Clement et al., 2001, Martinelli and Howarth, 2006) however this was not the case for the Dong Ho estuary over the study period. Notably, however, low DO concentrations and the absence of benthic flora do suggest that the ecosystem is dominated by heterotrophic processes and reflective of a potential outcome from high organic carbon and nutrient inputs (Clement et al., 2001). This warrants serious consideration in view of the proposed future development and anticipated increases in pollution to the Dong Ho estuary as outlined in the 2011 development plan (Carter, 2012a).

4.4.3. Is the system collecting material or simply acting as a pipeline to the sea?

The bathymetric map established in this thesis confirms the findings of with other recent, but less comprehensive bathymetric studies on the Dong Ho estuary (DARD, 2014, Johnstone, 2012). The formation of the current Dong Ho estuary began in 1880 through changes to the ancient Ha Tien port by Renault to re-create the main deep channel in the middle of the estuary linking Giang Thanh river to the Southwest sea (DARD, 2014). This led to the formation of two shallow areas in the west and the east of Cu Dut village, and a larger shallow area in the south of estuary. These areas formed the foundation for the ensuing sedimentation processes occurring in Dong Ho estuary. The continued and recent expansion of these sedimentation areas has been confirmed by means of remote sensing over the period from 1989 to 2011 (Nguyen, 2011, Carter, 2012b). In addition, recent satellite images of the estuary between 2005 and 2015 (figure 2.2) illustrate the transformation in landscape and bathymetry from shallow intertidal areas in the west of Cu Dut village into a mixed mangrove and nipa palm area; and from shallow intertidal areas in the south into extensive aquaculture ponds and mangrove. By 2005, significant land use changes in the northwest of the estuary around Vinh Te canal, the road construction to the west of the estuary, the extension of the central depositional islands, and the seaward reclamation works in the east of the To Chau channel have led to the narrowing of the exit channel from Dong Ho estuary to the Southwest sea. According to Carter (2012b) this has all led to increasing sedimentation in Dong Ho estuary and a shallowing of the system overall. Notably, these processes have led to the formation of larger intertidal zones and a small island near Ha Tien town since 2010 (DARD, 2014). Further, coastal dyke construction and continued land reclamation have probably further altered water flow regimes and exacerbated the infilling of the estuary. Similar estuarine evolution has been reported elsewhere such as in New South Wales, Australia, where a number of estuaries are subject to similar significant land use changes in their associated catchments (Roy, 1984). Based on these observations Dong Ho estuary can be considered to be a depositional site for terrestrial sediments although the level to which nutrients and carbon are trapped in association with this is not yet clear and warrants investigation. The LOICZ modelling in chapter 6 aims to help assess this issue but solid-phase composition of the sediments also provides some insight.

Sediments in Dong Ho estuary are mostly composed of fine and very fine sand, with high organic content in the surface sediments compared to other subtropical - tropical estuaries and coastal marine sediments (Hu et al., 2006, Strady et al., 2017, Ferguson et al., 2003). The levels of organic carbon measured in sediments of Dong Ho are also higher than reported for other sand dominated and shallow sub-tropical estuaries (Morse et al., 2007, Hanington, 2015) but lower than reported for mangrove-dominated estuaries (Costa-Böddeker et al., 2017). Based on these comparisons, the overall levels of TOC in Dong Ho estuary sediments suggests the accumulation of material inputs in the benthos. As noted earlier, high sedimentation loads and anthropogenic inputs from agriculture, aquaculture and urban sewage probably are likely to have contributed to these higher concentrations of TOC in Dong Ho estuary sediments. Zone 1 is the deepest area and had the highest TOC, TC in sediments while zone 3 is the shallowest area had lowest TOC, TC in both seasons. It supposed that zone 1 or the deepest area would have highest accumulation rate. It also indicated that material is being captured in sediments in deeper areas. However, TP levels were highest in zone 3 in wet season and zone 2 in dry season. It suggested that deeper area captured carbon and nitrogen while shallow area retained phosphorus. In addition to organic carbon, high TP values can also be related to domestic sewage, intensive agriculture practices, and phosphate fertilizer residue runoff (Costa-Böddeker et al., 2017).

4.4.4. In view of the current situation with nutrient levels and potential capture, what do we need to consider in terms of risk and next steps for research?

- The current situation with nutrient levels and potential capture:

Overall, based on the physical and biological parameters measured in Dong Ho estuary in both seasons, the first observation is that the water quality is generally quite poor in terms of dissolved oxygen and pH. This makes the waters often unsuitable for fishes and other fauna in the estuary, and of limited use in local aquaculture farms surrounding the estuary. In addition, high levels of suspended sediments in the water column reduced the depth of light penetration and adversely impact on the growth of algae and phytoplankton, leading to reduced benthic primary production and development of the historic seagrass beds that supported fisheries and community livelihoods. The likely source of this high turbidity is the combination of particulate release from agriculture and aquaculture activities as well as soil erosion from the catchment upstream and surrounding agriculture fields. These areas may also act as potential transport vectors for pesticides and fertilizers (primarily phosphorus) via particle absorption in estuary waters. A recent study of the pesticide and herbicide concentrations in the numerous Mekong canals of Kien Giang and An Giang provinces showed significant pesticide and herbicide levels in Dong Ho estuary (Johnstone, 2013). In conjunction with the current study, the presence of herbicides and pesticides in the estuary from remote sources confirms the significance of the associated catchment and land uses for the water quality and status of the Dong Ho estuary.

As elsewhere, including in many Asian countries, estuaries receive sediments from the catchment of rivers and from surface runoff (Miththapala, 2013); Dong Ho estuary receives sediments from both Giang Thanh river, Rach Gia – Ha Tien canal and several connected canals. Accordingly, turbidity profiles in Dong Ho estuary clearly showed the seasonal variation in particulate load with the average turbidity levels in the wet seasons being higher than in the dry season when fresh water input was very limited. Notably, turbidity in surface waters in the wet season was higher than in bottom waters on the outgoing tide due to the less dense freshwater containing suspended sediments move out of the catchment and over the more dense marine waters; this is most obvious in turbidity profiles of November 2016. As indicated earlier, turbidity profiles were negatively correlated with light profiles in Dong Ho estuary; higher turbidity led to lower light levels so that available PAR on the benthos was greatly reduced and only 1 to 5 % of surface levels in the deeper sites (table 4.3). Except the shallow area in site 8 where the light was penetrated near the bottom water with high intensity, other sampling sites with the depth over 3m in both seasons experienced the quantum irradiance values limited at the sediment surface. It suggested that primary production in Dong Ho estuary was likely low compared to other estuaries due to low light intensity.

The replacement of green algae by diatoms seems to happen after the fresh water phytoplankton died or after a strong decrease in biomass (Kromkamp and Peene, 1995). In the case of the Dong Ho estuary, chl-a and c dominated phytoplankton populations in sediments in both seasons. In addition, the phaeo-pigments values were higher than Chl-a values in all sampling sites in both seasons. These results approved that detritus was being degraded in sediment surface and microbial decomposition processes prevailed in benthos of Dong Ho estuary.

Organic carbon to nitrogen ratios (OC/N) in sediments of Dong Ho estuary were in the range reported for benthic marine and estuarine sediments elsewhere (Meyers, 1997, Hu et al., 2006). The OC/N ratios in the Dong Ho sediments ranged from 5.9 to 6.6 in the wet season and from 5.2 to 7.4 in the dry season; although TOC content in sediments was higher in the wet season compared to dry season (figure 4.18). The OC/N ratios are useful indicators of the source of sediment organic matter in estuarine systems (Hu et al., 2006, Andrews et al., 1998). Comparing with the C:N:P ratios of benthic marine plants (Atkinson and Smith, 1983), the low C:N ratio of Dong Ho estuary suggests that the organic matter in Dong Ho sediments are primarily derived from phytoplankton or microbial sources rather than from higher vascular plants such as macroalgae and seagrasses (Meyers, 1994). It also suggests that system was driven by microbial processes. It is also recognised that the degradation of sediment organic matter and benthic processes such as nitrogen fixation and remineralisation can also affect the C/N ratios (Meyers, 1994, Hanington, 2015). In general, however, C/N ratios reflect a combination of organic matter sources, biological degradation process and plankton composition (Thornton and McManus, 1994). In Dong Ho estuary, although organic matter inputs and TOC in sediments are high, the ratios of C/N are low suggesting that benthic processes such as decomposition, remineralisation and nitrogen fixation may play significant roles in the Dong Ho ecosystem.

In summary, the nutrient status of the water column and sediments in Dong Ho estuary indicate significant inputs from the catchment and local sources; although their relative roles vary seasonally.

Also, whilst Dong Ho resembles other highly turbid estuaries elsewhere, the observed nutrient and organic carbon levels, and their propensity to accumulate, do not bode well for the future sustainability of the estuary due to the existing issues with low benthic dissolved oxygen levels and low seasonal pH values. In the wet season, Dong Ho estuary receives higher amount of sediment inputs from Giang Thanh river while Rach Gia Ha Tien canal brings more inputs with high acidity from surrounding acid sulphate soil areas in the catchment. In the dry season, due to limited freshwater inputs from both Giang Thanh river and Rach Gia Ha Tien canal, Dong Ho estuary was dominated by local inputs from Ha Tien town and aquaculture activities inside estuary and it becomes a coastal lagoon rather than an estuary. At the same time, overall sedimentation trends and the plan to further alter water movement is likely to exacerbate these issues as more materials stay within the main estuary and are not flushed into the Western Sea. As taken up in the final chapter, the long-term management of the estuary will therefore require a strategic approach that addresses both local and remote sources of materials, as well as the physical structure of the ecosystem and its ability to pass materials out into the adjacent Western Sea.

- Insights from benthic habitat results:

Visually, the benthic habitats in Dong Ho estuary were areas of homogeneous bare sediment without the presence of seagrass and only the shallow area in the west of the central estuary was observed with green patches of microphytobenthos. Seagrasses are known to impact on benthic carbon cycling and enhance sediment microbial activities which drive benthic remineralisation processes (Hanington et al., 2015, Marbà et al., 2007). For example, the loss of half the seagrass from northern Deception Bay in Queensland Australia was noted to shift ecosystem metabolism from a net heterotrophic seagrass meadow to an autotrophic seagrass patches and bare sediment community (Hanington et al., 2015). In contrast, many studies have demonstrated that vegetated sediments have higher rates of gross and net primary production than bare sediments; and the benthic community can change from net heterotrophic to net autotrophic in invaded bare sediments by seagrass habitats (Pinardi et al., 2009, Eyre et al., 2011c). This highlights the importance of different benthic community types for overall ecosystem function. In the context of Dong Ho estuary, the dominance of bare sediments and highly turbid waters has reduced light penetration leading to lower benthic primary production rates and a lower capacity for removing excess nitrogen from the system through denitrification and capture (Eyre et al., 2011c).

In addition, the number of benthic fauna species identified in Dong Ho estuary are quite low compared to other similar estuaries (24 species: 14 polychaeta, 7 crustacea, and 3 bivalvia - (Carter, 2012a)). Whilst this may be partly due to the seasonal change in salinity from marine in the dry season to strongly freshwater in the wet season (Carter, 2012b), the absence of habitats such as seagrass beds or macroalgal communities may also play a role. In aquatic ecosystems, however, bottom-dwelling animals and invertebrate bioturbation significantly influence microbial activities and nutrient processes in sediments (Mermillod-Blondin and Rosenberg, 2006). In benthic habitats, nitrification occurs in the aerobic sediment layer and denitrification takes place immediately below this layer when oxygen concentration quickly declines. Therefore, the sediment-water interface and the upper few millimetres of surface sediment are very important in studying nitrogen cycling (Nielsen et al., 1990). Most nitrogen transformations occur in the first few millimetres of sediment and it strongly depends on bioturbation through burrowing, constructing tubes, feeding and irrigation activities (McCall and Tevesz, 1982, Aller, 1982). Bioturbation process increases the oxygen availability through increasing the oxic surface sediment layer of burrow walls and transports both particulate and dissolved nutrients into sediments. These activities influence the mineralization and respiration of organic matter as well as nitrogen transformation processes such as nitrification and denitrification. In general, benthic fauna increase both denitrification and nitrification, and the ratio of denitrification to total nitrification can increase or decrease depending on the nitrification rate, and burrow radius, spacing and thickness (Aller, 1988). Therefore, it suggests that the dynamics of biogeochemical processes in Dong Ho estuary are limited due to a very few number of benthic fauna species can survive with the seasonal salinity change.

- Next steps for research:

In view of the preceding results it is appropriate to consider the estuary's capacity to process the nutrient and organic carbon loads entering the benthos and water column. Accordingly, the production of a mass balance model would assist in this and also allow for consideration of how the respective zones in the estuary are processing materials relative to each other and within the context of the overall ecosystem. The low DO, the observed levels of NO_x and ammonium all suggest a very active set of microbial processes driving nutrient, carbon, and oxygen processes. In order to understand how these are underpinning the overall function of the estuary biogeochemically, it is necessary to measure these processes directly and seek to build these into a mass balance model so that their relative significance can be assessed. This work is reported in the following chapters.

CHAPTER 5 - PROCESS MEASUREMENTS

5.1. Introduction

Estuaries have the capacity to assimilate certain levels of anthropogenic pollutants without a significant loss of ecosystem services (Schubel and Kennedy, 1984). However, in many estuaries or some segments of them, human activities have exceeded this capacity and they have suffered persistent ecological damage from estuary to estuary, and also from segment to segment within an estuary (Schubel, 1975). In order to improve the effectiveness of estuarine management and transform scientific predictions to a form usable by managers, estuarine systems are now commonly zoned according to their natural prevailing processes (Schubel, 1975, Howarth et al., 2000). In this context, and based on the bathymetric and other differences observed in the preceding chapters, Dong Ho estuary is also considered here as having three functional zones (Figure 5.1). The first zone is the deepest and is the zone having direct water exchange between the estuary and the open sea. The second zone is the central estuary, and the third one is the shallowest area in the northwest of estuary.

Figure 5.1: Locations of three main zones in the Dong Ho estuary

As is described in detail below, this chapters examines the relative differences in nutrient fluxes within these different zones. The main aim is to assess their respective roles or significances for the overall nutrient dynamics and behaviour of the estuary, as well as to provide the basis for an overall exchange and nutrient budget for the ecosystem. As part of this, the work encompasses potential seasonal influences on nutrient processes and community metabolism within the respective zones and ecosystem.

In addition to understanding the biophysical features and nutrient stocks in the Dong Ho estuarine ecosystem, it is also crucial to understand the key transformation and exchange processes that underpin the ecosystems performance and sustainability. Alterations in the rate of biogeochemical and biological processes in estuaries can lead to altered trophodynamics and assimilative capacity that are relevant to management implications (Hobbie, 2000, Bianchi, 2007, Valiela, 2015). As noted in the preceding chapters, Dong Ho estuary receives significant materials inputs from its associated catchment and appears to retain significant organic carbon and nutrients. In this context, it is then important to understand how these materials may be processed and maintained, or released from the ecosystem. Accordingly, this chapter reports on measurements of biogeochemical processes focused on identifying the rate of primary production, benthic inorganic nutrient fluxes and denitrification in Dong Ho estuary. The intention is to demonstrate the estuary's capacity in the mineralization of organic matter, oxygen utilization, and the associated stoichiometric changes of key biological elements (C, N, & P). Denitrification is also measured as a key process that might remove nitrogen from the ecosystem in addition to physical transport via the observed tidal and riverine flows.

In order to place these measurements in context, it is useful to firstly gain an understanding of the major transformation pathways of these biogeochemical processes. Accordingly, nitrogen, phosphorus and carbon cycling, and primary production in coastal marine systems are briefly discussed below with reflection on their implications for management.

5.1.1. Nitrogen cycling

Although both nitrogen and phosphorus are generally considered limiting nutrients that determine the rate of primary production, nitrogen has generally been regarded as the major limiting element regulating biological productivity in estuaries and coastal marine ecosystems. This conclusion is based on a range of enrichment experiments undertaken in marine waters (Barnes and Mann, 1991, Howarth, 1988, Herbert, 1999), however it is realised that phosphorus may also be a limiting element in some estuarine ecosystems (Sundareshwar et al., 2003, Elser et al., 2007).

As pointed out by some authors, however, nitrogen is widely considered to be the key driver of most eutrophication problems in estuaries and coastal ecosystems (Alberti, 2008, Nixon, 1995). At the same time, nitrogen cycling is likely the most complex and profound set of processes among all biogeochemical cycles in marine and coastal ecosystems with a strong influence on carbon and phosphorus cycles (Gruber, 2008). The major transformation processes of nitrogen cycling comprise ammonification, nitrification, nitrogen fixation, denitrification, and assimilation (Figure 5.1). In terms of the pathways by which nitrogen is lost or added into an estuarine system, denitrification and nitrogen fixation are considered as the most important natural processes (Alongi, 1998) with anthropogenic sources on N playing a varying role in different ecosystems. While nitrification is a process of ammonium oxidation into nitrite and then to nitrate in the nitrogen cycle, denitrification is a key process which transforms nitrate and nitrite to gaseous end-products released to the atmosphere (Devol, 2008, Ward, 2008). Importantly, from a mass balance perspective, denitrification is an active process which can permanently eliminate combined nitrogen from estuary ecosystems and, thus, can partly control or reduce the eutrophication issue (McCarthy et al., 2015).

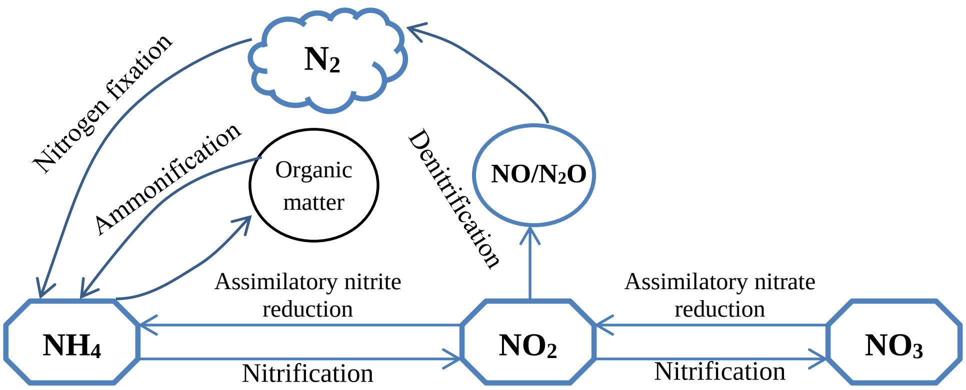


Figure 5.2: Model of the nitrogen cycle and its major transformation processes (Adapted from (Alongi, 1998, Herbert, 1999))

In the nitrogen cycle, denitrification is considered as the most important and predominant natural removal process reducing combined nitrogen to N_2 (Joye and Andersen, 2008, McCarthy et al., 2015). Denitrification is a process mediated by heterotrophic bacteria in anaerobic environments in both the water column and sediment. This process can remove as much as 40-50% of total nitrogen inputs into coastal areas, but it varies depending on environmental control factors (Seitzinger, 1988, Devol, 2015). In general, denitrification occurs when dissolved oxygen concentrations are reduced to, or near, zero; especially near the boundaries of a suboxic zone and the boundary of N-oxides (NO_3^-) (Devol, 2008). Low oxygen concentrations are necessary for the denitrification process in both the water column and the sediment environment, however, especially for the process in the water column, denitrification rates also depend on the oxidization of organic carbon (Devol, 2008). In addition, denitrification rates may also be influenced by environmental factors such as temperature and salinity (Devol, 2008). Based on the nature of the nitrogen cycle, nitrate/nitrite (NO_x) utilised in sediment-based denitrification can be supplied from both the water column and as a by-product of nitrification within the sediment. Accordingly, denitrification in sediment is often coupled with nitrification; particularly in environments with low nitrate concentrations in the water column (Seitzinger and Giblin, 1996). As outlined later, measuring denitrification rates can provide an understanding of the nitrification process in this system and also provide insight into the relative levels of coupling between water column and sediment processes supplying the required NO_x (Joye and Andersen, 2008).

In addition to denitrification as a pathway by which nitrogen can be removed from the ecosystem as gaseous products, anammox (anaerobic ammonium oxidation) is a chemo-autotrophic process that can also transform ammonium to molecular nitrogen (N_2) in anaerobic environments (Devol, 2008). This process involves two reactions: (1) $NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$; or (2) $NH_4^+ + NO_3^- \rightarrow N_2 + H + H_2O$. The anammox process also occurs under conditions of rapid oxygen concentration decline in both the water column and sediments. Compared to many literature reviews about denitrification, only a few studies have focused on the anammox process in the marine environment (Bock et al., 1995, Dalsgaard and Thamdrup, 2002, Dalsgaard et al., 2005, Lotti et al., 2012, Xing et al., 2015). Whilst it was beyond the current study to include measurement of the anammox process, it is realised that the loss of fixed N from the coastal estuarine systems may include both denitrification and anammox.

In terms of new nitrogen entering a marine or estuarine ecosystem, nitrogen fixation is of key importance. Nitrogen fixation is the biological process involving diazotrophic organisms (cyanobacteria) that convert molecular nitrogen (N_2) to cellular nitrogen as ammonium (Dugdale et al., 1961, Mahaffey et al., 2005). Nitrogen fixation is a photo-autotrophic process in the aerobic environment of both the water column and the sediment. In the pelagic zone, pelagic diazotrophs fix atmospheric N_2 gas into ammonium, while nitrogen fixation transforms N_2 in the water column into organic nitrogen in the benthos (Carpenter and Capone, 2008). Numerous factors can limit the extent of nitrogen fixation in an ecosystem including temperature, light, oxygen, turbulence, salinity, trace metals, inorganic nutrients. Nevertheless, oxygen concentration and high energy inputs (such as light) are factors which consistently promote N_2 fixation in both benthic and pelagic habitats. Globally, nitrogen fixation rates measured in the near-surface plankton communities are generally lower than that in the benthos (Capone and Carpenter, 1982). However, compared to other benthic nitrogen cycle processes, N_2 fixation rates are often reduced due to inhibition by high concentrations of dissolved inorganic nitrogen in sediments (Seitzinger and Garber, 1987). In contrast, nitrogen fixation rates can be considerable in benthic environments with high concentrations of dissolved organic matter and active primary producers such as micro-macro phytobenthos (Joye and Andersen, 2008).

In shallow estuarine environments, the benthic remineralization of particulate organic matter largely supports both pelagic and benthic primary production (Nixon, 1981, Ferguson et al., 2003). Often coupled to this organic material, ammonification is a heterotrophic process occurring under both oxic and anoxic conditions to transform particulate organic nitrogen to ammonium (NH_4^+); in many cases, ammonium production has been used to measure organic nitrogen mineralization rates (Aller and Yingst, 1980). Ammonium regenerated in sediments has many pathways in the nitrogen cycle. It can flux from the sediment to the overlying water column, it can be oxidized to nitrite and then nitrate through the nitrification process, or be taken by other biological processes including transformation to N_2 through the anaerobic ammonium oxidation process (Joye and Andersen, 2008). Among these processes, nitrification is a significant photo-autotrophic process in aerobic environments due to its central role in the nitrogen cycle. According to Ward (2008), in oxygenated water columns, nitrification rates are at a maximum near the bottom of the euphotic zone and rapidly decrease when depth increases below this zone. In contrast, due to the inhibition of light and competition for ammonium by phytoplankton and heterotrophic bacteria, nitrification rates near the surface of the water column are often low. In surface sediments, nitrification rates can be higher than from the water column and are often coupled to denitrification (Ward, 2008). Notably, many environmental variables such as temperature, salinity, turbidity, light, inhibitory compounds, and oxygen concentration can affect the nitrification rates and distributions. Therefore, in measuring nitrification rates in specific estuarine environments, it is necessary to carefully consider these regulatory factors as the context to the rates that are observed. Unlike ammonification that can occur in both aerobic and anaerobic environments, nitrification occurs only in oxic conditions and it strongly depends on NH_4^+ concentrations. It has been shown, for example, that the nitrification process terminates at oxygen concentrations from 1.1to 6.2 µM (Henriksen and Kemp, 1988).

To conclude, measuring major transformation processes of the nitrogen cycle is an effective approach for gaining insight on ecosystem capacity and its ability to deal with anthropogenic material inputs. As illustrated by a study of denitrification in the River estuaries of the Northern Baltic Sea, comparing denitrification rates to the local nitrogen loading can provide sound estimates for the nitrogen filtering capacity of these estuaries (Silvennoinen et al., 2007). In addition, nitrification also plays an important role in the consumption of sediment oxygen, and linking organic matter mineralization and nitrogen removal through denitrification (Caffrey et al., 2003). In this context, by also understanding the coupling between nitrification and denitrification, the process and exchange mechanisms influencing nitrogen dynamics in such poorly flushed estuaries becomes much clearer. This significantly strengthens the ability of management to be more targeted in their strategies and potential interventions.

5.1.2. Phosphorus cycling

In coastal estuarine systems, phosphorus (P) enters through rivers, canals, stormwater runoff and marine inputs. Human activities have increased nutrient loads including phosphorus and nitrogen due to the urbanisation, agriculture and aquaculture activities (Mockler et al., 2017). The phosphorus cycle is simpler than the nitrogen cycle due to the fewer oxidation states, and therefore reaction pathways, that P passes through. Accordingly, most of the transformation processes for P are strongly geochemical reactions while the nitrogen cycle is strongly influenced by biological factors with many respiratory and oxidizing reactions (Alongi et al., 1992). The natural processes of mineral weathering and erosion of soil containing inorganic phosphorus in the form of phosphate (PO_4^{3-}) and the mineralisation of organic phosphates, as well as the anthropogenic sources of phosphorus such as fertilizer residues from agriculture production and sewage runoff are the main sources of phosphorus in estuarine systems. Phosphate PO_4^{3-} is the main form of inorganic phosphorus and its availability strongly depends on pH and the ionic state of the waters within which it exists (Baker et al., 2006). In low pH habitats, phosphate readily reacts with soluble iron, manganese and aluminium to form other insoluble compounds (Baker et al., 2006, Chapin et al., 2011).

In the aquatic environment, P is classified into three forms: soluble reactive phosphorus (SRP), soluble unreactive phosphorus (SUP) and particulate phosphorus (PP) (Rigler, 1973). Soluble reactive phosphorus (SRP) is an important indicator of the availability of phosphorus in the form of orthophosphate which is important for algal growth (Mainstone and Parr, 2002). In phosphorus-limited environments, SRP is often low and increasing SRP would affect the relationship of chlorophyll and phosphorus (Carlson and Simpson, 1996). On the other hand, at the whole-of-cycle scale, coastal phosphorus is mainly controlled by fluxes of sediment within and through estuarine ecosystems; thus sediments play a key role in phosphorus dynamics overall (Klotz, 1988). A number of studies have shown that sediments regulate SRP concentrations in the water column through sediment sorption and desorption processes (Lottig and Stanley, 2007, Meyer, 1979).

The physical conditions of coastal estuaries, with mixing of freshwater and saltwater, create a specific chemical habitat for adsorption of inorganic phosphate on particles (Tiessen, 1995). Several studies show the close relationship between phosphorus and iron (Baker et al., 2006, Martins et al., 2014, Zhang et al., 2013). Iron (III) oxides and hydroxides effectively adsorb phosphate under oxic condition and therefore phosphorus enters sediments primarily in particulate form bound to iron (III) hydroxides (Krom and Berner, 1980). Hence, oxygen concentration is also a critical factor controlling the phosphorus cycle in aquatic environments. Another important factor in the regulation of phosphate fluxes from sediments is the sulfate concentration in the overlying water. In marine sediments with high sulfate content, the P fluxes are higher than in freshwater environments (Caraco et al., 1990, Fisher et al., 1995). In estuarine and marine systems, especially where N is in surplus, P can be an important limit to primary production (Wulff et al., 2011).

5.1.3. Carbon cycling

Recently, many studies have shown the significant role of marine and coastal habitats in carbon fixation and sequestration in the global carbon budget (Beaumont et al., 2014, Morris et al., 2012). A high rate of carbon sequestration has been measured in coastal ecosystem components including phytoplankton, benthic microalgae, seagrasses, tidal marshes and mangroves (Thom et al., 2001, Wisniewski and Lugo, 1992). Also, coastal wetlands have been significant targets in studying the global carbon cycle because they can be carbon sinks or sources; potentially releasing substantial amounts of methane and nitrous oxide to the atmosphere (Hansen and Nestlerode, 2014, Morris et al., 2012). However, carbon sequestration in estuarine ecosystems is now strongly influenced by anthropogenic factors; especially by land use changes and sea level rise (Beaumont et al., 2014, Thom et al., 2001). In this context, coastal erosion and sea level rise, as well as land reclamation in coastal areas for urban development, have caused extensive loss of coastal habitats, reducing their capacity to sequester and store CO_2 (Beaumont et al., 2014, Thom et al., 2001). In some cases, increased flooding due to climate change can bring more sediment inputs that carry organic carbon from terrestrial habitats and thus enhance carbon sequestration and fixation (Thom et al., 2001, Reed, 1999). By corollary, an understanding of carbon fixation and sequestration levels in an estuary provides additional insight into the impacts of anthropogenic activities on estuarine processes and ecosystem performance (Sundareshwar et al., 2003).

From a biogeochemical perspective, carbon cycles share many features in common with nitrogen cycles in dominating specialized groups of microorganisms and carrying particular chemical transformations such as photosynthetic fixation or primary production in the euphotic zone (Herbert, 1999). For example, the photosynthetic fixation of carbon is strongly linked to the assimilation of nitrogen by phytoplankton through the process of building living organic tissues (Gruber, 2008). In addition, carbon processing has links to many nitrogen and phosphorus processes. For example, ammonium regeneration is linked to organic carbon oxidation while ammonium mineralization partly depends on the C:N ratio (Joye and Andersen, 2008). In eutrophic systems with high dissolved organic carbon (DOC) concentrations in the sediment, denitrification rates are often higher than in low nutrient systems (Seitzinger, 1988). In addition, a high content of organic carbon in sediment also drives dissimilatory nitrate reduction to ammonia (DNRA) and hence, promotes nitrate assimilation and transformation into organic nitrogen (Buresh and Patrick, 1981, Sgouridis et al., 2011). So, whilst it can be important to consider C, P, and N cycles separately to build understanding, it is essential that their connectedness is not overlooked; especially when evaluating sources and relative significances of organic matter in the estuarine microbial loop (Parker, 2005).

5.1.4. Primary production

Primary production is defined as the photosynthetic formation of energy-rich organic compounds (Nybakken and Bertness, 2005). There are different terms describing associated components of primary production. Gross primary production (GPP) is the total amount of carbon (CO_2) or organic matter fixed by photosynthetic organisms (Howarth and Michaels, 2000). Net primary production (NPP) is the total amount of carbon fixed (GPP) minus the amount of organic matter respired by the primary producers, so NPP is the accumulation rate of new organism biomass supported by nutrient inputs from the river catchment and recycled production of nutrients regenerated within the estuary (Howarth and Michaels, 2000). Net ecosystem production (NEP) or net ecosystem metabolism (NEM) is the difference between GPP and all respiration of both autotrophs and heterotrophs (respiration - R) (Nybakken and Bertness, 2005, Bianchi, 2007, Howarth and Michaels, 2000, Kemp et al., 1997). NEP demonstrates organic carbon in an ecosystem available for storage within the system or loss by export or non-biological oxidation to carbon dioxide (Lovett et al., 2006).

From a nutrient dynamics perspective, primary production is considered as the photosynthetic reduction of CO_2 and uptake of nutrients to produce new algal biomass (Underwood and Kromkamp, 1999). Therefore, in addition to different physical variables in estuaries such as temperature, water hydrodynamics and salinity, there are two major factors influencing primary production or the rate of photosynthesis; nutrients and light limitation. Light attenuation is an important factor controlling primary production of both pelagic and benthic zones in estuaries (Bianchi, 2007). Accordingly, photosynthetically active radiation (PAR) in the water column is often used as an indicator of the potential for the growth of primary producers in aquatic ecosystems (Thompson, 1991). Chlorophylls are indicators measured in the water column and surface of sediments to illustrate the availability of pelagic primary production and benthic primary production, respectively. Nutrient limitation affects primary production by its concentration and ratios of main elements (C, N, P). Most marine systems are nitrogen limited and most freshwater systems are phosphorus limited (Underwood and Kromkamp, 1999), however, some studies have disputed this generalisation (Bianchi, 2007).

In general, it can be said, however, that increased nutrient loading and alterations in nutrient ratios can control phytoplankton and microphytobenthos abundance, which are important sources of primary production (Underwood and Kromkamp, 1999). At the same time, excess primary production caused by accelerated nutrient inputs or eutrophication is a significant environmental problem in coastal marine ecosystems (Howarth, 1988, Elliott and de Jonge, 2002). By corollary, the estimation of primary production rates is a critical aspect in understanding the functioning of these ecosystems (Howarth and Michaels, 2000). Moreover, understanding the variability of primary production by phytoplankton and microphytobenthos in estuaries is a key to understanding the variability in ecosystem metabolism and respiration, as well as nutrient cycling and carbon fixation (Underwood and Kromkamp, 1999, Cloern et al., 2014, Caffrey, 2003, Gerbersdorf et al., 2005). It should also be noted here that most assessments of the link between nutrient concentrations and primary production are based on inorganic dissolved nutrients (Underwood and Kromkamp, 1999), however more recent studies are beginning to highlight the potential role of dissolved organically bound nutrients in exchanging N and P with these DIN pools (Yates et al., 2016). Whilst it was not possible to determine levels of organic N and P in the current study, its potential role is recognised and warrants future investigation.

Despite this global awareness of the role of primary production in estuarine ecosystems, there have been no measurements or mapping of primary producers in the Dong Ho estuary; microbial or otherwise. Consequently, their relative significance in carbon and nutrient cycling in the estuary is unknown. On this basis, this chapter presents the results of field and laboratory measurements of nutrient fluxes, community respiration and primary production for the different habitat zones identified in the previous sections. The results are considered and assessed within the context of the physico-chemical conditions and the standing stocks of nutrients observed in the respective zones respectively.

In summary, measuring key processes such as denitrification, nitrification, nutrient fluxes, community primary production and respiration can provide many valuable insights into how the Dong Ho estuary is currently performing, and how it might respond to future changes in nutrient and organic carbon loads. This approach provides a better understanding of the wider interacting influences (physical, chemical, biological) and the complex ongoing processes currently occurring. Further, this approach can identify potential pathways of impact of anthropogenic material inputs on ecosystem performance and potential carrying capacity. In this light, it is hoped that the insights gained will assist in highlighting risks to the Dong Ho estuary and aid managers in setting potential limits to inputs to the estuary based on the ecosystem capacity to assimilate these anthropogenic inputs.

5.2. Materials and Methods

Process measurements of primary production, nutrient flux and denitrification were based on incubations of sediment cores collected in each zone defined in Dong Ho estuary (Figure 5.1). Sediment core collection for incubations was described in section 3.4.3 (biogeochemical process measurements). As detailed below, each type of process measurement required different incubation times and some refinement of procedure to provide the most accurate measurements possible in the field. Critical steps and calculation methods of primary production, benthic nutrient fluxes and denitrification are also described in details below.

5.2.1. Primary production and Benthic nutrient fluxes

Primary production and benthic nutrient flux estimations were made using the rate of change in dissolved oxygen (DO) and nutrient concentrations in the water overlying the sediment in sediment core incubations (Howarth and Michaels, 2000, Eyre and McKee, 2002, Seeley, 1969, Odum, 1956, Ferguson et al., 2007, Kemp and Boynton, 1980, Jenkins, 2005, Conley and Johnstone, 1995). Separate sediment cores were incubated in dark and light conditions in a water bath at the field site approximately 4 hours after core collection (see Figure 5.3). All cores were held at the same temperature as the ambient water temperature at each sampling site by means of a temperature controlled water bath surrounding the cores. The water overlying the sediment were added more with non-disturbed bottom water from the same sampling sites before starting the incubation. The aim is to ensure the overlying water are full to the top lid of the core. The overlying waters in each sediment core were mixed at a level approximating *in situ* conditions, by a small rotating magnet attached to the lid of each sediment core which was gently rotated by a central magnet in the middle of the water bath (Figure 5.3). The sediment cores were incubated for 3 hours to measure the change in dissolved oxygen and nutrient concentrations in the overlying water in each sediment core. In addition, cores containing only water from each site were also incubated to determine any differences in primary production and nutrient transformation between water column and sediment. For each type of measurement a total of 6 replicate cores for each zone were used.

Determination of Primary Production Rates

The changes in dissolved oxygen in the overlying water in each sediment core and water-only cores were measured by oxygen electrodes through the lid of the incubation core (YSI-DO probe) at the start of each incubation (time zero) and every hour for the 3 hour duration of the experiment. The oxygen probes were calibrated everyday before use and checked again at the end of each incubation. The slope of the linear regression derived for each data set (from each replicate core) over the 3 hour incubation was used to determine the rate of DO concentration change over time. The DO values were corrected for water salinity as measured in incubation waters using a JFE Rinko salinity probe.

The rate of change in dissolved oxygen (DO) concentrations in the overlying water of sediment cores for both light and dark incubations were used to calculate primary production and respiration in the three zone identified in Dong Ho estuary (Odum, 1956, Howarth and Michaels, 2000, Seeley, 1969, Kemp and Boynton, 1980). The DO changes in the light incubation encompasses gross primary production (GPP) by photosynthetic organisms and respiration by all of the organisms in the sediment cores. The DO changes in the dark incubation reflects the respiration (R) by the primary producer community and heterotrophic organisms; not including respiration by macrofauna which was excluded during sampling. The assumed stoichiometric ratios of O_2/C is 1.3 (photosynthetic quotient) was used to calculate GPP in this study because in general, more moles of O_2 are produced in GPP than the number of moles of organic C that are fixed (Howarth and Michaels, 2000). As has been done for other estuarine systems (Bianchi, 2007, Smith and Hollibaugh, 1993), the primary production to respiration ratio (P/R) was calculated for each data set to access the relative production status for each zone in Dong Ho estuary. This ratio (P/R) is a useful indicator for assessing the relative importance of production between 'new' and 'regenerated' materials in aquatic ecosystems (Quinones and Platt, 1991, Kemp et al., 1997). In addition, the net metabolic balance of an ecosystem can be indicated by the difference between all forms of production (P) and respiration (R) by all organisms (NEM / NEP = P - R). Net ecosystem production (NEP) or net ecosystem metabolism (NEM) is an indicator of the trophic state within estuaries and represents the extent to which an ecosystem is a net source or sink of carbon dioxide and whether autochthonous or allochthonous sources of organic matter dominate (Caffrey, 2003, Hopkinson and Smith, 2005). If NEM or NEP is positive (P>R), the system is autotrophic suggesting that internal production of organic matter dominates and there is a net assimilation of inorganic nutrients and net production of organic matter. If NEM or NEP is negative (P<R), the system is heterotrophic and this system is net importer of organic matter and net exporter of inorganic nutrients (Hopkinson and Smith, 2005, Caffrey, 2003, Kemp et al., 1997).

Determination of Nutrient fluxes

Nutrient flux measurements were made at the same time as DO measurements. Immediately prior to the first DO measurement in each core (time zero), a 10 ml volume of the overlying water in each sediment core was collected and immediately filtered through a pre-rinsed 0.45μm filter into a pre-washed and rinsed 10ml HDPE scintillation vial. Each sample was immediately stored on ice in the field and then frozen (-40^{o}C) to be analysed later in the laboratory. On each sampling occasion the 10 ml of water removed from the core was replaced using ambient bottom water collected at the respective sampling site. Nutrient and DO values were determined for this replacement water and used to later to mathematically compensate for any alteration of concentrations in the incubation waters. After 3 hours of incubation a final 10ml sample was collected as for the initial sampling and treated in the same manner. In the laboratory all water samples were analysed for DIN (NH_4^+, NO_x) and PO_4^{3-} using colorimetric methods (Parsons et al., 1984).

All nutrient concentration results from sediment core incubations were plotted against incubation time under light and dark conditions. A total of 6 replicate sediment cores were collected from each estuary zone so that three cores were incubated under light conditions and three sediment cores under dark incubation. The light levels reaching the enclosed sediment was measured and equivalent to that measured at each site and respective depth. The rate of change in nutrient concentration in each core ($d[x]/dt$ with x=concentration of nutrient and t= time) was used to calculate the uptake or release rate from the sediments. The slope of the linear regression of the concentration change over time represented the rate of flux across the sediment-water interface (Forja and Gomez-Parra, 1998). By comparing the changes in nutrient concentrations over time between sediment incubations and incubations only containing water, it was possible to adjust the benthic flux estimates for any nutrient uptake or release from water column processes.

Figure 5.3: Light incubation (left) and dark incubation (right)

5.2.2. Denitrification

Denitrification rates in Dong Ho estuary sediments were measured using the ^{15}N isotope pairing technique originally established by Nielsen (1992) but widely used in similar sediment studies (Pinardi et al., 2009, Mahommed and Johnstone, 2002). This method has the advantage of identifying the relative contributions to the denitrification process from water column NO_x versus NO_x provided through benthic (coupled) nitrification processes (Nielsen, 1992, Steingruber et al., 2001). The ^{15}N isotope pairing technique is a reliable method for measuring denitrification rates in un-vegetated and not bioturbated sediments (Pinardi et al., 2009). Notably, although no quantitative study was undertaken, both the habitat surveys and random sediment sampling prior to incubation experiments showed there to be little to not macrofauna in the sediments within each estuary zone. On this basis, the ^{15}N isotope pairing technique was well suited to the benthic conditions in the Dong Ho estuary.

To undertake denitrification incubations, four sediment cores were collected randomly from each zone as described above in section 3.4.3. Denitrification rate determinations were only conducted in the dark due to the light limitation observed on the benthos. Accordingly, little to no competition between primary producers, nitrifiers and denitrifiers was likely which can be an issue to consider with the method (Pinardi et al., 2009, Rysgaard et al., 1995); nutrient stock measurement also showed that the system was not nitrogen limited.

Immediately on sediment collection the sediment height within the core sleave was gently adjusted so each sediment core was approximately 6-7 cm in height and with 120-140ml of headwater. Incubations were started by injecting $^{15}NO_3^-$ from a 10mM stock solution of 99.6% $^{15}NO_3^-$ into the overlying water in each core (Nielsen, 1992). Depending on the water column volume in each incubation core, the amount of $^{15}NO_3^-$ added was adjusted to ensure the concentration of nitrate in the overlying water column after addition was at least double the initial concentration prior to addition. After the tracer addition, the sediment cores were capped and sealed (gas tight) with rubber stoppers and left to be incubated for 3.5 hours in the dark to simulate *in situ* conditions. As with other core incubations the cores were held at in situ temperature and the water overlying the sediment was stirred by a small rotating magnet attached to the lid of each core. The nitrate concentration in the overlying water of each core was measured before and after the addition of the tracer to calculate the ^{15}N enrichment. At the end of the incubation period, to stop bacterial activity and denitrification process, the water column and the sediment were shaken to form a slurry and a sample of the slurry was collected using a 12ml Exetainer™ evacuated collection tube containing 250µl of 50% v/v $ZnCl_2$ (Mahommed and Johnstone, 2002). Finally, 4ml of water in each Exetainer™ tube was replaced with 4ml of AR grade He gas to provide a headspace. The samples were shaken for 5 minutes before the headspace was analysed on a Sercon 20-22 isotope ratio mass spectrometer, coupled to an auto sampler and GC column to separate O_2 and N_2, and to determine the ratios $^{29}N_2$ /$^{28}N_2$ and $^{30}N_2$ /$^{28}N_2$ (Nielsen, 1992). This analysis was undertaken by WSC stable isotope laboratory at Monash University, Melbourne, Australia. Rates of denitrification were calculated using a revised version of Nielsen's equations (Nielsen, 1992, Steingruber et al., 2001).

5.3. Results

5.3.1. DO Fluxes and Primary Production Determinations

Measurement of dissolved oxygen (DO) changes in sediment core incubations from each of the three zones in Dong Ho estuary showed DO uptake by sediments and water column in both dark and light conditions at all sites (Figure 5.4). In both the wet and dry season, DO uptake by the water column was higher than by sediments, and zone 1 generally had the highest uptake rates compared to zone 2 and 3. Seasonally, benthic and pelagic DO fluxes in the dry season were higher than benthic and pelagic DO fluxes in the wet season respectively. In the wet season, benthic DO fluxes range from -0.2 to -0.8 mmol $O_2.m^{-2}.h^{-1}$, compared to the dry season, where benthic DO fluxes were slightly higher ranging from -0.2 to -1.1 mmol $O_2.m^{-2}.h^{-1}$. These flux rates will be compared with other estuary measurements in the discussion section.

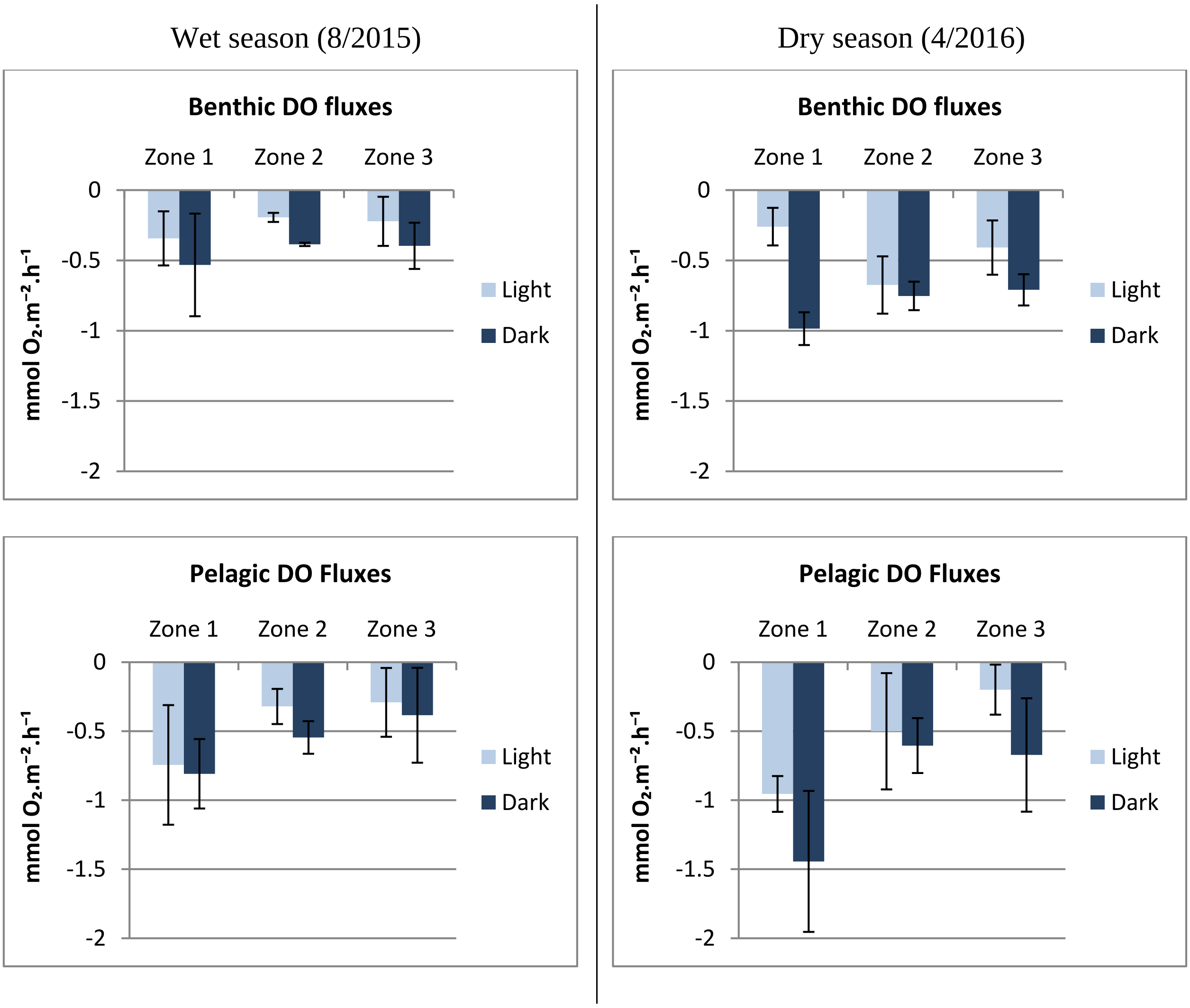


Figure 5.4: Average dissolved oxygen fluxes with standard deviation (mmol.$m^{-2}.h^{-1}$) under light & dark incubations in Dong Ho estuary

The primary production values derived from DO fluxes (as mentioned in method section 5.2.1) showed differences between the different estuary zones and between seasons. Notably, primary production and respiration rates varied between wet and dry seasons (Figure 5.5). In particular, dry season results showed stronger heterotrophy than in the wet season with higher rates of respiration in all sampling sites, and respiration exceeding primary production despite gross primary production also being higher in the dry season than in the wet season. It was further observed that there were larger differences between Gross Primary Production (GPP) in the three zones in the dry season compared to the wet season where GPP values were more similar between sampling sites (Figure

5.5). The mean GPP for combined water and benthos (system GPP) in the wet season was 45.5 ± 2.3 mmolC.m^{-2}.d^{-1}, while in the dry season the combined GPP varied from 19 to 178 mmolC.m^{-2}.d^{-1}, with the highest rate observed in zone 1, and the lowest rate in zone 2 (Figure 5.5).

In terms of pelagic and benthic primary production, respiration rates in the water column were higher than benthic respiration rates in both seasons, whilst GPP was higher in the benthos than in the water column. As discussed later, such high rates of respiration may reflect high levels of organic loading from both allochthonous and autochthonous sources (Gazeau et al., 2005). Of note was the higher value of benthic GPP compared to pelagic GPP in the deepest area of Dong Ho estuary (zone 1) in both seasons where benthic light conditions are very low. The potential reasons for this are discussed below but it is noted that Chl-a values measured in benthic habitats at zone 1 were also highest compared to other sampling sites in the estuary. These results demonstrate that sediments play an important role in primary production of Dong Ho estuary ecosystem and especially in the deep areas such as zone 1.

Although mean GPP of whole system in dry season was two-fold higher than in wet season, but the ratio P/R was similar. In wet season, mean benthic GPP was two-fold higher than mean pelagic GPP. In dry season, mean benthic and pelagic GPP was quite similar.

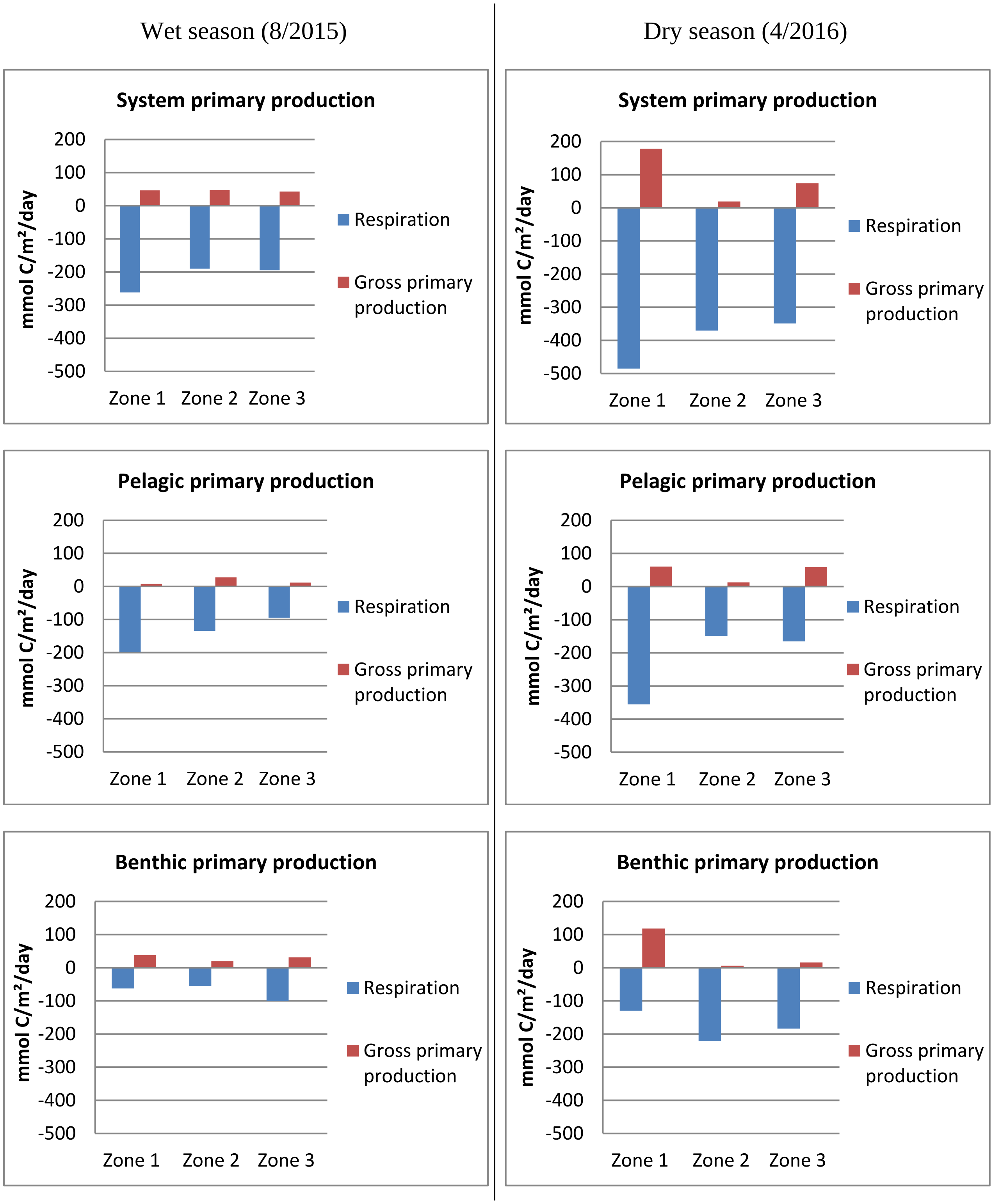


Figure 5.5: Primary production & respiration rates in Dong Ho estuary

Based on primary production and respiration determinations, Dong Ho estuary can be considered as a heterotrophic system due to the net ecosystem production (NEP) being negative and the P/R ratio is <1 (Table 5.1). Whilst a range of factors may contribute to this (see discussion) the attenuation of light in the water column due to high turbidity favours heterotrophic activity; especially if the particulate material is rich in organic carbon (Alongi, 1998). DO levels decreased in all sediment cores during light incubations and water only cores showed strong DO uptake exceeding production and benthic DO uptake (Figure 5.4). As discussed later, this is likely due to high levels of organic matter and heterotrophic activity in the sediment core. Negative NEP also indicates a significant amount of carbon is being respired in Dong Ho estuary.

Table 5.1: Water column and benthic primary production rates in wet and dry season in Dong Ho estuary (mmolC.m^{-2}.d^{-1})

System (mmolC.m^{-2}.d^{-1})	**Wet season**					**Dry season**				
	Zone 1	Zone 2	Zone 3	Mean	Stdev	Zone 1	Zone 2	Zone 3	Mean	Stdev
R	-261.6	-189.9	-194.8	-215.4	40.1	-485.0	-370.5	-349.2	-401.5	73.1
GPP	46.4	47.3	42.9	45.5	2.3	178.6	19.1	74.1	90.6	81.0
NEP	-215.3	-142.6	-151.9	-169.9	39.5	-306.4	-351.3	-275.1	-310.9	38.3
P/R	0.18	0.25	0.22	0.21	0.04	0.37	0.05	0.21	0.23	0.16
Water column (mmolC.m^{-2}.d^{-1})	**Wet season**					**Dry season**				
	Zone 1	Zone 2	Zone 3	Mean	Stdev	Zone 1	Zone 2	Zone 3	Mean	Stdev
R	-199.1	-134.3	-94.7	-142.7	52.7	-355.3	-148.8	-165.5	-223.2	114.7
GPP	7.9	27.7	11.5	15.7	10.5	60.2	12.8	58.2	43.7	26.8
NEP	-191.1	-106.6	-83.2	-127.0	56.8	-295.1	-136.0	-107.3	-179.5	101.2
P/R	0.04	0.21	0.12	0.11	0.08	0.17	0.09	0.35	0.20	0.14
Benthos (mmolC.m^{-2}.d^{-1})	**Wet season**					**Dry season**				
	Zone 1	Zone 2	Zone 3	Mean	Stdev	Zone 1	Zone 2	Zone 3	Mean	Stdev
R	-62.6	-55.5	-100.1	-72.7	24.0	-129.7	-221.7	-183.7	-178.3	46.2
GPP	38.4	19.6	31.4	29.8	9.5	118.4	6.3	15.9	46.9	62.1
NEP	-24.1	-35.9	-68.8	-42.9	23.1	-11.3	-215.3	-167.8	-131.5	106.8
P/R	0.61	0.35	0.31	0.41	0.16	0.91	0.03	0.09	0.26	0.49

The primary productivity in table 5.1 is expressed as the amount of carbon fixed in new organic biomass under a square meter of benthic surface per day (mmol C.m^{-2}.day^{-1}) (Lalli, 1997). A positive number indicates that carbon was fixed and negative number means carbon was respired. In order to compare primary production rates in Dong Ho estuary with other estuaries, water column and benthic primary production per year was calculated based on the combination of the daily rate in the wet and dry season respectively (Table 5.2). By multiplying the average results for wet and dry seasons by the corresponding number of months for each season to calculate the net yearly pelagic and benthic production. The annual gross primary production rate in Dong Ho estuary was 298 g C /m²/year and benthos contributed 56.3%.

Table 5.2: Water column and benthic primary production per year in Dong Ho (g C /m²/year)

	Water column	Benthos	Total	% Benthic
R	-801.32	-549.85	-1351.17	40.69
GPP	130.18	167.92	298.10	56.33
NEP	-671.14	-381.93	-1053.07	36.27

A key piece of the context to the observed DO fluxes and corresponding production rates is likely to be the light attenuation at each site in each season. According to light intensity (PAR) profiles in section 4.3.3.3, PAR is sufficient for primary production by microphytobenthos at all sampling sites except in the wet season (11/2016) where very high turbidity and the resultant light attenuation limits benthic primary production. Also, light attenuation was not consistent between sites and seasons. In the height of the wet season (11/2016), light penetration is limited at all sites to within the upper 0.5m of water (figure 4.11). In periods of low intensity rain during the wet season (8/2015), light was seen to penetrate to the benthos at 1.9 to 5.6 µmol m^{-2} s^{-1} in the deep sites (zone 1 and 2). Notably, the approximate minimum PAR level required for primary production is around 1 µmol m^{-2} s^{-1} (Peterson et al., 1987, Thompson, 1991). This indicates that primary production is only restricted to the surface waters in 11/2016, whilst in other sampling events light intensity is sufficient on the benthos for primary production at each site. This is discussed further later.

5.3.2. Benthic nutrient fluxes

The average values of benthic fluxes of NH_4^+, NO_x, PO_4^{3-} in light and dark incubations in both seasons in Dong Ho estuary are presented in figure 5.6. Error bars represent the standard deviation of three replicate core incubations. Positive flux values represent sediment release of nutrients, and negative value indicates sediment uptake.

Benthic NH_4^+ fluxes were highly variable between zones and seasons. Sediments showed a release of NH_4^+ at zone 1 during both light and dark incubations with mean fluxes ranging from 0.7 (±0.3) to 0.8 (±0.3) mmol.m^{-2}.h^{-1} in wet season, and ranging from 0.03 (±0.03) to 0.07 (±0.05) mmol.m^{-2}.h^{-1} in dry season. Opposite with zone 1, sediments in zone 3 showed an uptake of NH_4^+ during both light and dark incubations with mean fluxes ranging from -0.2 (±0.1) to -0.9 (±0.6) mmol.m^{-2}.h^{-1} in wet season, and ranging from -0.04 (±0.04) to -0.09 (±0.03) mmol.m^{-2}.h^{-1} in dry season. In zone 2, NH_4^+

fluxes varied between light and dark incubations, and showed both uptake and release, with fluxes ranging from -0.2 (±0.1) to 0.1 (±0.4) $mmol.m^{-2}.h^{-1}$ in the wet season, and ranging from -0.006 (±0.02) to -0.05 (±0.02) $mmol.m^{-2}.h^{-1}$ in the dry season.

Benthic NO_x fluxes also showed variability between seasons and zones. In the wet season, sediments of all zones showed an uptake of NO_x during both light and dark incubations, ranging from -0.19 (±0.06) to -0.44 (±0.1) $mmol.m^{-2}.h^{-1}$. In the dry season, sediments in all zones showed an uptake of NO_x during light incubations with mean fluxes ranging from -0.02 (±0.03) to -0.33 (±0.04) $mmol.m^{-2}.h^{-1}$. However, during dark incubations, only sediments in zone 1 showed an uptake of NO_x with a mean flux rate of -0.11 (±0.07) $mmol.m^{-2}.h^{-1}$, and in contrast, sediments in zone 2 and 3 showed a release of NO_x with mean fluxes ranging from 0.03 (±0.04) to 0.06 (±0.02) $mmol.m^{-2}.h^{-1}$.

Benthic PO_4^{3-} fluxes in the wet season were more variable between zones and incubation conditions. In light incubations, sediments in zone 1 and 2 showed an uptake of PO_4^{3-} ranging from -0.005 (±0.001) to -0.016 (±0.002) $mmol.m^{-2}.h^{-1}$ while sediments in zone 3 showed a release of PO_4^{3-} with a mean flux of 0.007 (±0.002) $mmol.m^{-2}.h^{-1}$. In contrast, in dark incubations, sediments in zone 1 and 2 showed a release of PO_4^{3-} ranging from 0.002 (±0.001) to 0.008 (±0.006) $mmol.m^{-2}.h^{-1}$ while zone 3 showed an uptake of PO_4^{3-} with mean flux was -0.001 (±0.003) $mmol.m^{-2}.h^{-1}$.

Overall, benthic PO_4^{3-} fluxes in the dry season were more consistent between zones and incubation conditions than in the wet season showing a release of PO_4^{3-} ranging from 0.0003 (±0.0006) to 0.0015 (±0.0008) $mmol.m^{-2}.h^{-1}$. The exception to this were the sediments in zone 1 under dark incubation, which showed an uptake of PO_4^{3-} at -0.0004 (±0.0004) $mmol.m^{-2}.h^{-1}$.

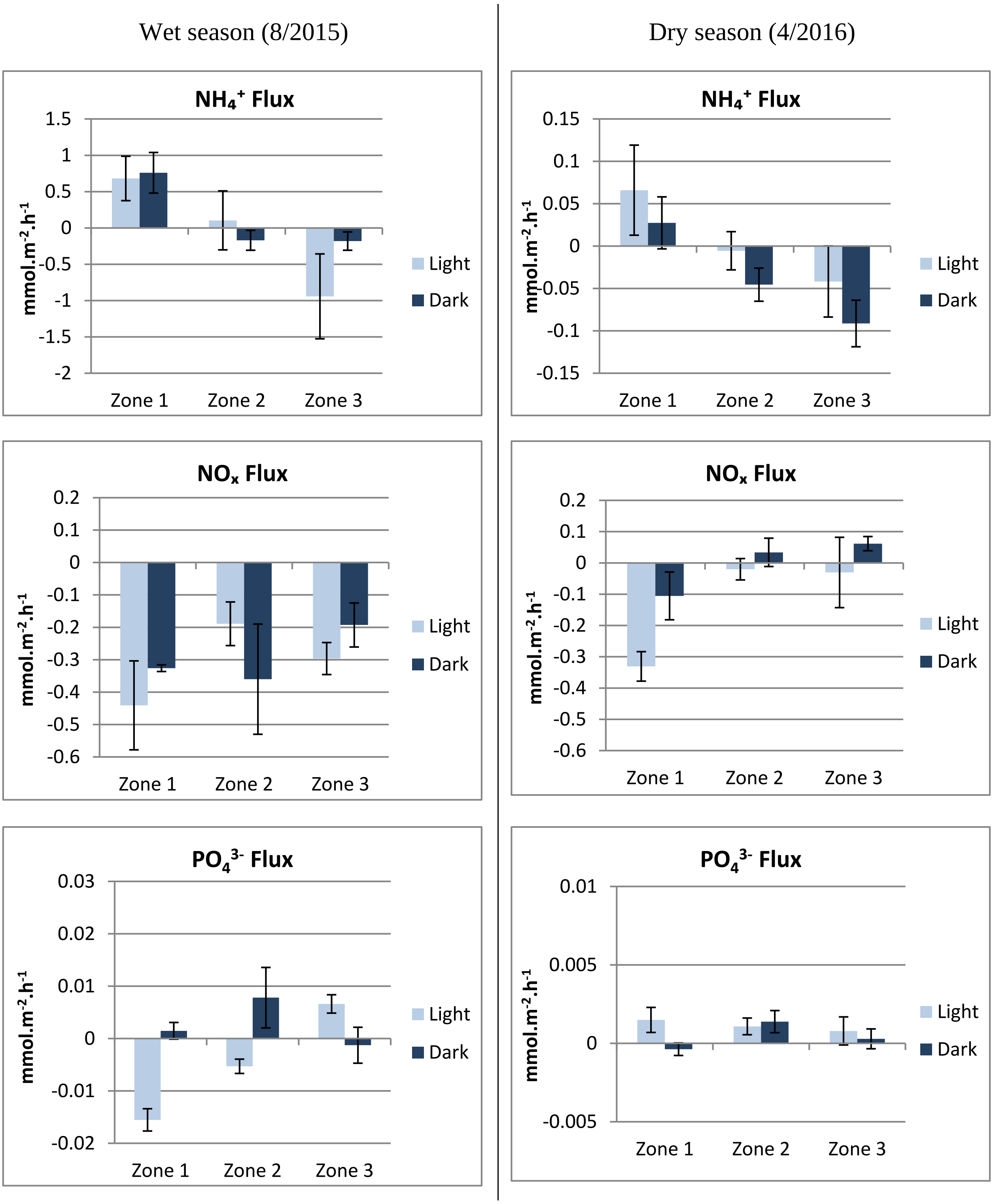


Figure 5.6: Benthic fluxes of NH_4^+, NO_x, PO_4^{3-} under light and dark conditions on sediment cores sampled in wet and dry season in Dong Ho estuary

For the sake of comparisons and for use in developing the LOICZ model in the next chapter, hourly flux rates were converted to daily flux rates for the respective zones in Dong Ho estuary (Figure 5.7). This integrates 12 hours of light flux rates with 12 hours of dark flux rates since the daylight split in Dong Ho is approximately even due to its location near the equator. In general, sediments in Dong

Ho estuary showed an uptake of dissolved oxygen in both wet and dry season, with higher fluxes recorded in the dry season ranging from -13.4 (±3.6) to -17.1 (±3.7) $mmol.m^{-2}.d^{-1}$.

Daily benthic NH_4^+ fluxes were variable between zones and seasons. In zone 1, NH_4^+ fluxes were released from sediments with flux rates ranging from 1.12 (±1.01) in the dry season to 17.3 (±7.0) $mmol.m^{-2}.d^{-1}$ in the wet season. In contrast, sediments showed an uptake of NH_4^+ in zone 3 with flux rates from -13.5 (±8.5) to -1.59 (±0.83) $mmol.m^{-2}.d^{-1}$. In zone 2, NH_4^+ fluxes varied between wet and dry season: NH_4^+ fluxes varied in wet season with the rate of -0.8±6.5 $mmol.m^{-2}.d^{-1}$ and were taken by sediments in dry season (-0.61±0.51 $mmol.m^{-2}.d^{-1}$).

Daily benthic NO_x fluxes also varied between seasons and zones. In the wet season, sediments of all sampling sites showed an uptake of NO_x with mean fluxes from -5.9 (±1.4) to -9.2 (±1.8) $mmol.m^{-2}.d^{-1}$. In dry season, only zone 1 showed an uptake of NO_x at -5.2 (±1.5) $mmol.m^{-2}.d^{-1}$ while in zone 2 and zone 3 sediments released NO_x with mean fluxes ranging from 0.2 (±0.9) to 0.4 (±1.6) $mmol.m^{-2}.d^{-1}$.

As with dissolved inorganic nitrogen fluxes, daily benthic PO_4^{3-} fluxes showed variability between seasons and zones. In the wet season, PO_4^{3-} fluxes was taken up by sediments in zone 1 at -0.17 (±0.04) $mmol.m^{-2}.d^{-1}$ while in zone 2 and zone 3 sediments released PO_4^{3-} ranging from 0.03 (±0.08) to 0.06(±0.06) $mmol.m^{-2}.d^{-1}$. In dry season, PO_4^{3-} fluxes were released from sediments in all zones ranging from 0.013 (±0.014) to 0.029 (±0.015) $mmol.m^{-2}.d^{-1}$.

In general, a comparison with other estuarine and marine studies suggests that the benthic nutrient flux rates in Dong Ho estuary were in the highest range in wet season and in the normal range in dry season (Jenkins, 2005, Hanington et al., 2016, Burford et al., 2008). In wet season, NH_4^+, NO_x fluxes in Dong Ho estuary were similar to other estuaries and coastal lagoons where are heavily impacted by anthropogenic activities (Jenkins, 2005, Burford et al., 2008, Pérez-Villalona et al., 2015). However, PO_4^{3-} fluxes in Dong Ho estuary was lower compared to those systems.

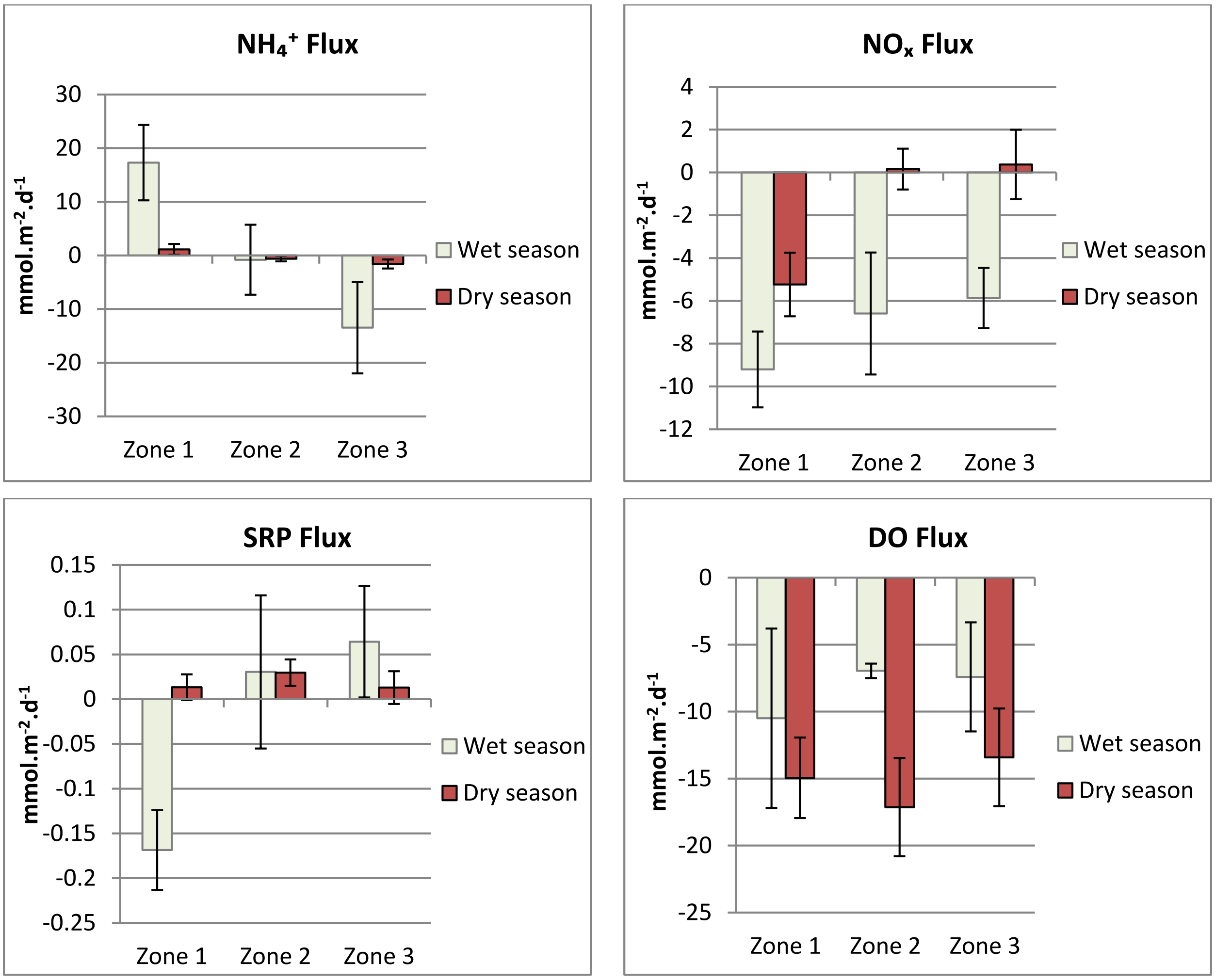


Figure 5.7: Benthic fluxes of NH_4^+, NO_x, PO_4^{3-}, DO per day in wet & dry season in Dong Ho estuary

5.3.3. Denitrification

Results from denitrification rate measurements across the Dong Ho estuary are summarised in Figure 5.8. Generally, the denitrification rates in the sediments of Dong Ho estuary showed variations between seasons and zones. Dry season tends to have higher denitrification rates compared to the wet season, and shallower areas (zone 2 and 3) had higher total (D_n + D_w) denitrification rates than observed in the deepest area (zone 1). In both seasons, coupled denitrification (Dn) was much higher than Dw (denitrification utilising nitrate from the water column). This suggests that denitrification coupled to benthic nitrification was most significant in Dong Ho estuary and, highlights the significance of both the nitrification process as well as the oxic conditions necessary to support the nitrification process. Although nitrification rates were not directly measured in this study, the nutrient fluxes and denitrification rates give a good indication of the significance of this process in Dong Ho estuary.

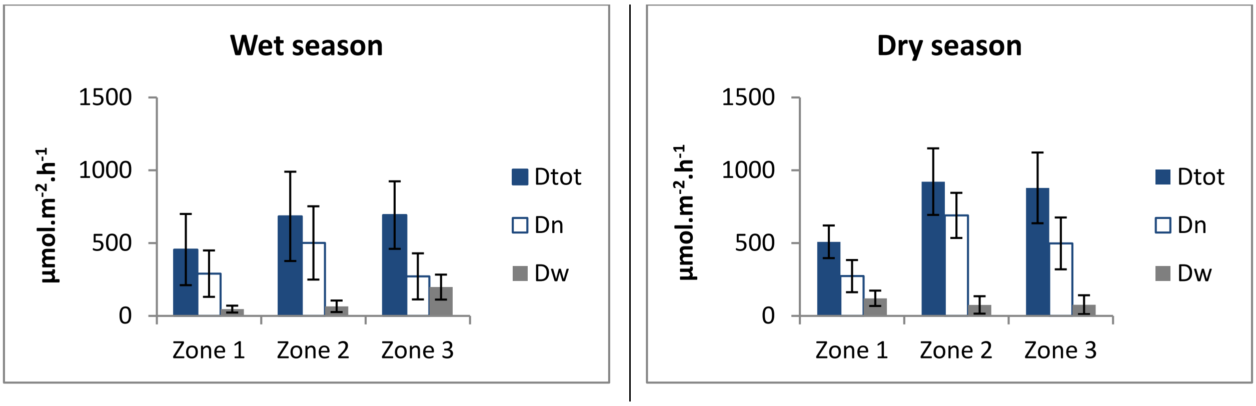


Figure 5.8: Denitrification rates in the wet and dry season in Dong Ho estuary. Dtot is the total denitrification rate in the sediment, Dw is the denitrification of nitrate from the water column, Dn is denitrification coupled to nitrification. Each column is the average value ± sd (n=3)

To better understand the denitrification process in each zone and season, the benthic nutrient fluxes of each zone were converted to the same units as shown below in figure 5.9.

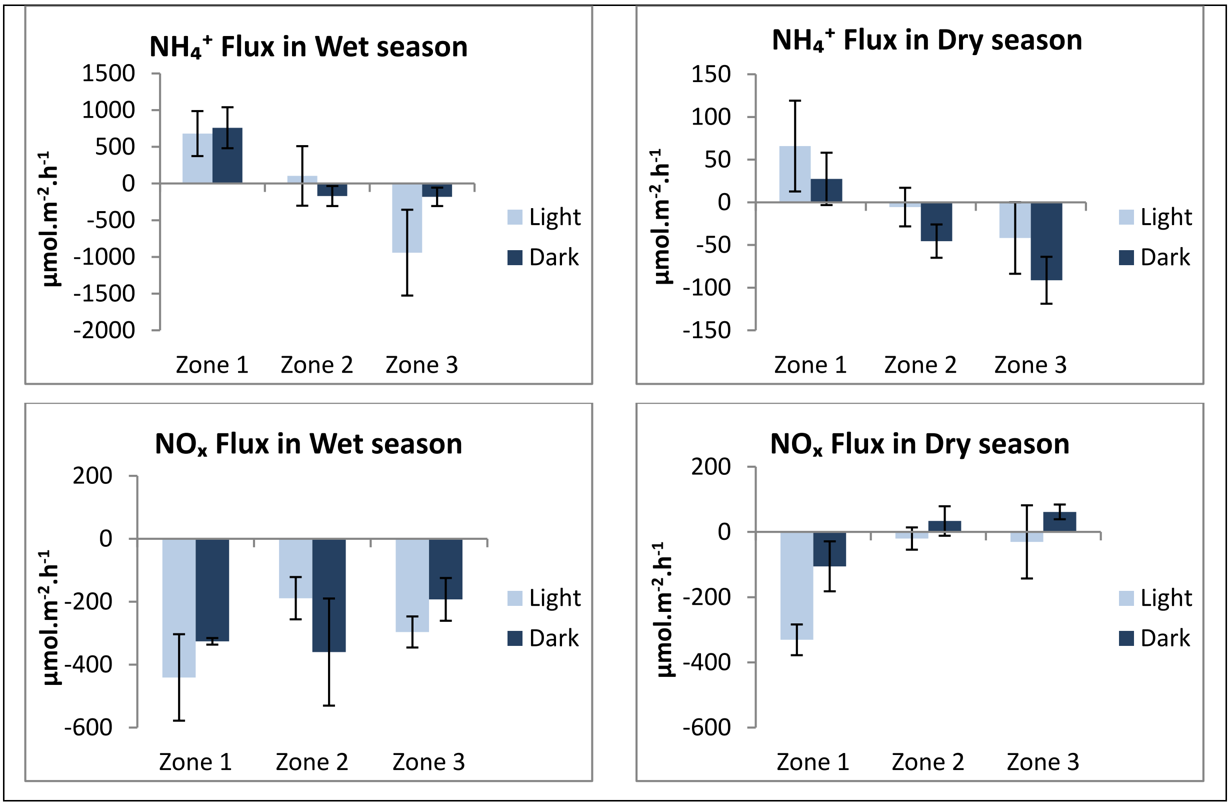


Figure 5.9: Benthic fluxes of NH_4^+, NO_x in Dong Ho estuary

As can be seen in Figure 5.9, denitrification rates were not apparently linked to NO_x or NH_4^+ fluxes in each zone or season. For example, in zone 1, NO_x fluxes showed the highest uptake rates compared to other zones in both seasons but the denitrification rate in zone 1 was lowest. This suggests that the uptake of NO_x is influenced by other processes such as, potentially, dissimilatory nitrate reduction to ammonium (DNRA), and consumption by microphytobenthos. As shown, benthic MPB production is low, but could account for an amount of this nitrogen. In addition, the consistent efflux of NH_4^+ from the same sediments would indicate that NH_4^+ production is consistently strong and could therefore include DNRA processes. Denitrification is widely considered as the dominant dissimilatory NO_3^- sink in sediments but recent studies have also illustrated the importance of DNRA in converting NO_3^- to NH_4^+ in the sediment nitrogen cycle (Joye and Andersen, 2008, Gardner et al., 2006). Clarification of the different denitrification rates in each zone in Dong Ho estuary is discussed in more detail in the discussion section (5.4.3) and the ensuing LOICZ chapter..

5.4. Discussion

5.4.1. Primary production

Despite being recognised as one of the most productive marine ecosystems in the world, and despite their continued modification by human activities, the nutrient dynamics and biogeochemical function of tropical and subtropical estuaries has still not received the level of attention that these aspects might warrant (Chaudhuri et al., 2012, Underwood and Kromkamp, 1999, Cloern et al., 2014). In a recent report on phytoplankton primary production in the world's estuarine ecosystems, it was noted that there continues to be little published information on this aspect for tropical-subtropical ecosystems (Cloern et al., 2014). As indicated by Cloern *et al.* (2014) such a knowledge baseline is essential in order for meaningful and comprehensive comparisons to be made, and research strategies developed. In the context of this thesis, the absence of a baseline for Dong Ho estuary, and the limited global baseline underpin the need for more information and a more comprehensive assessment of biogeochemical processes and keystone components such as primary production.

Table 5.3 below summarises values derived for gross primary production (GPP), ecosystem respiration (R) and net ecosystem production (NEP) (or net ecosystem metabolism (NEM)) in a range of estuaries around the world (Table 5.3). The table includes tropical and subtropical estuaries; these are used later as comparative references for consideration of primary production measurements in Dong Ho estuary. As shown in table 5.3, Dong Ho estuary has a primary production at the lower end of the range compared to other subtropical and tropical estuaries. For example, two tropical estuaries in India (Zuari estuary and Mandovi estuary) are similar to Dong Ho estuary in that they both receive high loads of organic material from anthropogenic activities in the catchment and both demonstrate net heterotrophy and reduced primary production (Ram et al., 2003). Notably, the respiration rates observed for Dong Ho are even higher than in the Indian examples making it more strongly heterotrophic. This would suggest that Dong Ho is receiving greater allochthonous inputs of organic carbon as suggested for the Godavari estuary by Sarma et al. (2009).

The functioning and maintenance of most estuarine ecosystems relies on the photosynthetic production of organic matter. Importantly, phytoplankton primary production is influenced by nutrient loading and light penetration in the water column (Chaudhuri et al., 2012); both of which can vary depending on local conditions. As noted in the results section, despite higher nutrient concentrations in the water column in the wet season compared to the dry season, GPP was higher in the dry season by approximately 50% on average.

Table 5.3: Summary of GPP, R and NEP or NEM in a range of estuaries

Site	Primary production (g C/m²/year)	GPP (mmolC/m²/d)	Respiration (mmolC/m²/d)	NEP/ NEM (mmolC/m²/d)	P/R	References
Dong Ho estuary, VN (Tropics)	298	19 - 178	190 - 485	-143 to -351	0.05-0.37	In this thesis
Apalachicola Bay, FL, US (Subtropics)	401	200 - 250	220 to 300			(Caffrey et al., 2014)
Grand Bay, MS, US (Subtropics)	377	130 - 160	150 to 170			(Caffrey et al., 2014)
Godavari estuary, India (Tropics)		3 - 186	0.3 to 180	-108 to 124		(Sarma et al., 2009)
Mandovi estuary, India (Tropics)		10.1 - 188.2	36.2 to 159.4	-34 to 54	0.28-2.37	(Ram et al., 2003)
Zuari estuary, India (Tropics)		23.6 - 153.2	21.4 to 148.2	-46 to 49	0.67-2.53	(Ram et al., 2003)
Darwin, Australia * (Tropics)	1644	375.3	180		2.1	(Eyre et al., 2011b)
Hinchinbrook channel * (Tropics)	4692	1071.2	534		2.0	(Eyre et al., 2011b)
Moreton Bay, Australia * (Subtropics)	288	65.8	60.3		1.1	(Eyre et al., 2011b)

* Re-calculated to match unit comparison

The reason for this apparent disconnection between nutrient levels and phytoplankton production is considered here to be linked to the seasonality of catchment inputs to the estuary. As indicated earlier, freshwater inputs to the estuary via the Giang Thanh river and connecting channels are significantly higher in the wet season. Associated with these inputs is a higher level of suspended particular matter, which increases water turbidity and, accordingly, leads to the greater light attenuation observed during the wet season. So, despite higher nutrient levels, it is likely that the high light attenuation constrains phytoplankton production to a level lower than in the dry season when PAR reaches deeper into the water column and to the benthos in some areas. The role of turbidity in controlling phytoplankton biomass and production in tropical estuaries with high nutrient concentrations has been shown elsewhere (Cloern, 1999, Pan et al., 2016).

The net yearly pelagic production in Dong Ho estuary is estimated to be approximately -671 g C /m²/year (table 5.2) and is similar to values for net pelagic production recorded in recent studies from the Scheldt estuary with -692 g C /m²/year (Gazeau et al., 2005, Cloern et al., 2014). The similarities between Dong Ho estuary and the Scheldt estuary may help to explain this. The Scheldt estuary is one of the most eutrophic estuaries in Europe due it receiving drainage from urban wastewater and runoff from agriculture across a large catchment (Gazeau et al., 2005). Turbidity is also high in the Scheldt estuary and phytoplankton is light limited, rather than nutrient limited (Gazeau et al., 2005) leading to a predominantly heterotrophic system as is observed in the case of Dong Ho. In order to understand these processes at a whole-of-system level, the metabolism of the Scheldt estuary was measured using both in-situ incubations and the LOICZ budgeting methodology also has been undertaken in this study. This provides a good reference point for the approach and for comparison of the performance of the respective systems.

Net ecosystem metabolism (NEM) in coastal and estuarine environments is an indicator often used to evaluate whether these ecosystems are sources or sinks of carbon (Smith and Hollibaugh, 1993, Chaudhuri et al., 2012). Where respiration exceeds production, NEM is negative and the system is considered to be heterotrophic (Eyre and McKee, 2002). Accordingly, a negative NEM indicates that a significant amount of carbon is being respired within the estuary and exceeds local (autochthonous) primary production; requiring external sources (allochthonous) to meet community metabolic needs. This allochthonous carbon can be derived from terrestrial organic matter transported via freshwater inputs and stormwater, or from marine organic carbon delivered via tidal processes. As in the case of Dong Ho estuary, and shown elsewhere (Gazeau et al., 2005), where the system is heterotrophic and dependent on allochthonous inputs, the remineralisation of organic matter generally leads to low oxygen concentrations in the water column (section 4.3.3.4). In Dong Ho estuary this situation becomes most pronounced in the dry season where DO levels become very low ranging between 3-4 mg/l (Figures 4.12), and oxygen consumption also increases (Figure 5.4). Thus, it can be concluded that Dong Ho estuary has a stronger heterotrophic status in the dry season compared to the wet season, but is predominantly heterotrophic year round.

As presented by Hopkinson and Smith (2005) the mean annual benthic respiration reported for temperate estuaries is 34 mmol C/m^2/day, and ranges from 3 mmol C/m^2/day to 115 mmol C/m^2/day (Hopkinson and Smith, 2005). In Dong Ho estuary, the mean benthic respiration rate was estimated to be 72.7± 24 mmol C/m^2/day in the wet season and two times higher in the dry season with 178.3±46 mmol C/m^2/day. Both seasons had higher benthic respiration rates than the mean annual benthic respiration reported for temperate regions (Hopkinson and Smith, 2005). According to Hopkinson and Smith (2005), sediment respiration is typically highest where there is an abundant benthic filter feeding community and a good input of allochthonous organic matter; and is lowest in sandy sediments with low organic content (Hopkinson and Smith, 2005). Unfortunately it was beyond this study to accurately describe the benthic faunal assemblages in each zone of the Dong Ho estuary. However, annual benthic respiration was highest in zone 3 which was the shallowest area, and the zone where benthic organisms such as small bivalves were collected in a number of the sampling cores collected in this area. Further, grain size in zone 3 reflected a higher silt content compared to other zones, supporting the notion proposed by Hopkinson and Smith (2005).

The respiration rates of whole estuarine systems in temperate climatic regions ranges from 69 mmol C/m^2/day to 631 mmol C/m^2/day, with an average of 294mmol C/m^2/day (Hopkinson and Smith, 2005). By comparison, the whole-of-system respiration rate determined for Dong Ho estuary was 215.4±40 mmol C/m^2/day in the wet season and 401.5±73 mmol C/m^2/day in the dry season. This highlights the very high respiration rate of Dong Ho in the dry season and the significant change that occurs seasonally. From a water quality management perspective, this suggests that the risk of oxygen depletion and other impacts of eutrophication are likely to be more pronounced in the dry season, although this is underpinned by materials being delivered from the catchment in both seasons, with the wet season loads dominating. Even comparing with some tropical estuaries in India (Godavari estuary, Mandovi estuary) and in Australia (Darwin estuary), the respiration rates observed in Dong Ho estuary in the dry season are very high and indicative of high organic inputs (Ram et al., 2003, Sarma et al., 2009, Eyre et al., 2011b).

5.4.2. Benthic nutrient fluxes

Estuarine and marine ecosystems are highly dynamic and increasingly impacted by anthropogenic activities including urban inputs from sewage, stormwater, industrial developments and agricultural activities. In this context, the ability of these systems to process the materials they receive from these human activities, and the rate at which these processes might occur are key aspects to understanding the potential future function and sustainability of the system of concern. The exchange of nutrients between the benthos and water column is a central component of this understanding, and has been used widely in many studies to indicate and infer the relative status and performance of marine and estuarine ecosystems (Jenkins, 2005, Pérez-Villalona et al., 2015, Hanington et al., 2016).

A comparison of the flux rates measured in this study with other estuarine and marine studies suggests that the benthic nutrient flux rates for some nutrients in Dong Ho estuary are in the highest range reported during the wet season, and within the generally reported range in the dry season. Table 5.4 summarises flux rates from the literature and includes those recorded in the current study. The table includes values from estuaries in temperate, subtropical, and tropical regions.

Table 5.4: Benthic nutrient fluxes reported in other estuarine and marine studies

Location	**NH_4^+ (mmol/m²/h)**	**NO_x (mmol/m²/h)**	**PO_4^{3-} (mmol/m²/h)**	**Source**
Dong Ho estuary- Wet Dry Season *Tropical area*	-0.94 to 0.75 -0.09 to 0.06	-0.44 to -0.19 -0.3 to 0.06	-0.005 to 0.007 -0.0004 to 0.001	In this thesis
Port River Day (Australia) Night *Subtropical area*	-0.67 to 2.75 0 to 3.21	-1.46 to 0.133 -1.46 to 0.089	-0.386 to 0.203 -0.383 to 0.241	(Jenkins, 2005)
Deception Bay Day (Australia) Night *Subtropical area*	-0.01 (±0.01) to -0.06 (±0.06) -0.02 (±0.004) to 0.02 (±0.03)	-0.006 (±0.009) to -0.014 (±0.002) -0.003 (±0.002) to 0.005 (±0.002)	-0.001 to -0.002 -0.0002 to 0.0012	(Hanington et al., 2016)
Escambia Bay (Florida, USA) *Subtropical area*	-0.048 to 0.11	-0.0079 to 0.029	-0.0017 to 0.0033	(Didonato et al., 2006)
Humber Estuary (UK) *Temperate area*	-0.28 to 1.1	-1.8 to 0.63	-0.046 to 0.092	(Mortimer et al., 1999)
Darwin Harbour Day (Australia) Night *Tropical area*	0.84(±0.9) 3.54(±8.72) to 8.2(±15.52)	0.15(±0.46) 0.04(±0.1) to 0.17(±0.56)	0.035(±0.034) 0.05(±0.09) to 0.1(±0.15)	(Burford et al., 2008)
San José Lagoon (Puerto Rico) *Tropical area*	0.77(±0.7)	-0.04(±0.05)	0.167(±0.14)	(Pérez-Villalona et al., 2015)

In the wet season, NH_4^+ and NO_x fluxes in Dong Ho estuary were similar to those reported for Port River and Darwin Harbour (Australia), and San Jose lagoon (Puerto Rico) which are all heavily impacted by anthropogenic activities (Jenkins, 2005, Burford et al., 2008, Pérez-Villalona et al., 2015). By comparison, PO_4^{3-} fluxes in Dong Ho estuary were lower compared to most of the estuaries identified from the literature. Further, the sediments in Dong Ho estuary generally showed a release of PO_4^{3-}. Such PO_4^{3-} efflux often accompanies reduced DO concentrations and can reflect the duration of hypoxic conditions in sediments (Didonato et al., 2006, Cowan and Boynton, 1996). This concurs with the results obtained in the Dong Ho estuary because the PO_4^{3-} efflux observed at all sampling sites in the dry season coincided with a period of lower DO levels in the bottom water (around 3-

4mg/l). In addition, low oxygen concentration and high temperature in sediments may enhance the release of P to water column (Pérez-Villalona et al., 2015) which also concurs with the observations made in Dong Ho estuary when PO_4^{3-} release was highest.

The net daily sediment oxygen fluxes at all sampling sites were negative, indicating that respiration exceeded primary production in all sites in both seasons. However, in some tropical estuaries and coastal lagoons which have higher levels of organic carbon in sediments due to anthropogenic impacts and restricted water circulation, the rates of sediment oxygen consumption in Dong Ho estuary were lower than those estuaries (Valdes-Lozano et al., 2006, Pérez-Villalona et al., 2015). It is believed that the longer water residence time with high water temperature during the dry season increased the demand of oxygen for degradation and thus exacerbates the sediment oxygen deficit in those systems (Valdes-Lozano et al., 2006, Pérez-Villalona et al., 2015). Therefore, due to the large freshwater inputs in the wet season, Dong Ho estuary is likely to have a shorter water residence time compared to those studies such that DO levels are maintained at a higher level than in more static systems despite high DO uptake rates. It is also suggested that the sediment oxygen fluxes observed in Dong Ho in the dry season were higher than in wet season due to higher temperatures and reduced water circulation resulting from limited to no flows from the catchment to augment tidal exchange rates as occurs in the wet season.

As mentioned previously, benthic nutrient fluxes are important indicators of which biogeochemical processes dominate in a particular system or sediments. In turn, this assists in understanding how excess nutrients from human activities might be cycled and internally processed by an ecosystem. In the case of Dong Ho estuary, this perspective is particularly useful when considering nitrogen dynamics and the potential for the estuary to deal with increasing loads from anthropogenic sources. For example, in the wet season, NO_x fluxes at all sampling sites showed an uptake in both dark and light incubations. This suggests that the denitrification process may play an important role in controlling water column dissolved nitrogen levels in Dong Ho estuary. However, as shown in the results obtained, nutrient fluxes were highly variable between zones and seasons, indicating that there may be differences in denitrification and nitrification rates across the estuary and between dry and wet season. This is discussed further below.

5.4.3. Denitrification

The denitrification rates measured in this study are at the higher end of the range previously recorded in other coastal and estuarine sediments in tropical and sub-tropical systems (Joye and Andersen, 2008, Seitzinger, 1990, Steingruber et al., 2001, Pérez-Villalona et al., 2015). The average measures of net N_2 removal via denitrification calculated in Dong Ho estuary range from 210.5 – 1150.1 µmol

N_2-N m^{-2} h^{-1}. This compares with denitrification rates reported in other sub-tropic and tropical estuaries around the world, such as Southern Moreton Bay (Australia) where rates ranged from 38.5 – 206 µmol N_2-N m^{-2} h^{-1} (Eyre et al., 2011c); Mae Klong estuary (Thailand) which ranged from 0-7.4 µmol N_2-N m^{-2} h^{-1} (Dong et al., 2011); and a tropical and highly urbanized San Juan Bay estuary (Puerto Rico) ranged from 18.4 – 937.9 µmol N_2-N m^{-2} h^{-1} (Pérez-Villalona et al., 2015).

Despite the relatively high rates, denitrification may not be the only process utilising dissolved inorganic nitrogen from the sediment in Dong Ho estuary with other processes such as anammox or the dissimilatory nitrate reduction to ammonium (DNRA) also potentially playing a role. As discussed in the results section (5.3.3), in zone 1 in both seasons, the DNRA process may play a dominant role in sediments at this site due to the uptake of NO_x and release of NH_4^+ which suggested the conversion of NO_3^- to NH_4^+ in the sediment and it led to the denitrification rate in zone 1 was lower than other zones. In tropical and subtropical coastal systems, high organic matter content, oxygen deficit, sulfate reduction and high temperatures, may all support DNRA such that it is sometimes considered as potentially predominant over denitrification, and this has been demonstrated by a number of studies (Pérez-Villalona et al., 2015, Gardner et al., 2006, An and Gardner, 2002, Dong et al., 2011). Future work in Dong Ho estuary needs to target this process more directly so that this process can be more accurately integrated into our understanding of N dynamics in the system.

In regard to denitrification, in both seasons, denitrification coupled to sediment nitrification (Dn) predominated over denitrification based on nitrate from the water column (Dw). The contribution of Dn to total denitrification was higher in the dry season, and zone 2 demonstrated the highest contribution of Dn (70%) to total denitrification. This suggests that the removal of nitrogen via N_2 may be influenced by benthic oxygen levels and fluxes necessary to support nitrification in sediments. This interpretation is supported by the dissolved oxygen uptake by benthos in the dry season which was higher than in the wet season, and benthic respiration rates in zone 2 in the dry season were also highest. The strong correlation between total denitrification and benthic DO fluxes in the dry season (r^2=0.94) and in the wet season (r^2=0.99) also suggests the potentially significant role of nitrification coupled to denitrification in Dong Ho estuary (Figure 5.10).

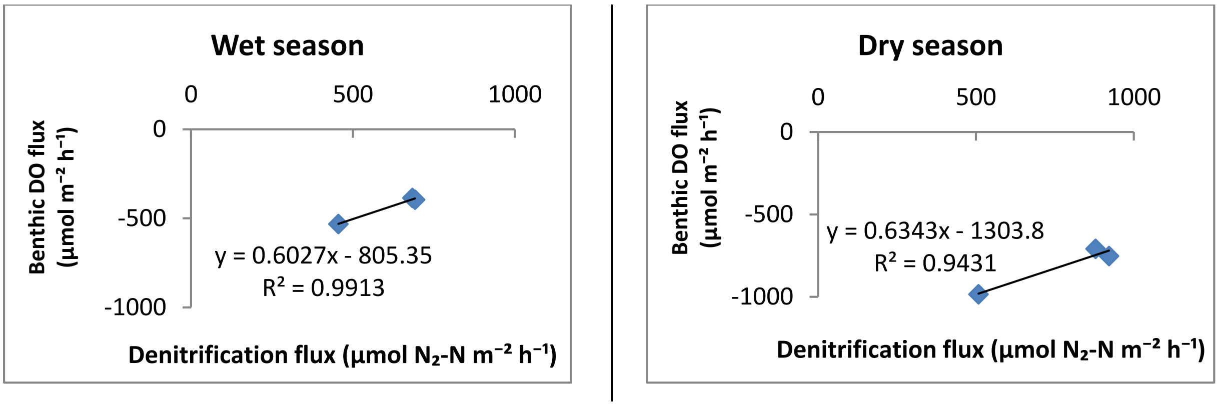


Figure 5.10: Relationship between total denitrification and benthic DO flux in Dong Ho estuary

In addition to DO concentrations and NO_x supply, the amount and quality of organic carbon in sediments may also control denitrification (Seitzinger, 1988, Murray and Parslow, 1999, Arango et al., 2007, Myrstener et al., 2016, Dodla et al., 2008). The denitrification rate and its relationship with benthic organic carbon may vary depending on nitrate concentrations, sediment respiration rates and whether the system is strongly influenced by anthropogenic inputs or it is a pristine system. In an aquatic system receiving a significant amount of organic matter and with elevated nitrate concentrations in Illinois and Michigan (USA) showed that benthic organic carbon may stimulate denitrification when nitrate concentrations are high (Arango et al., 2007). However, in a pristine system with low organic carbon sediments, adding organic carbon did not affect denitrification rates in the surface sediment (Seitzinger, 1988). In addition, high organic carbon content may enhance the DNRA process which can compete nitrate used for denitrification (Seitzinger, 1988, Tiedje et al., 1983, Giblin et al., 2013). On the other hand, a study in Port Phillip Bay (Australia) indicated that increasing the current nitrogen load by double increased the total denitrification flux, but increasing the nitrogen loading by 2.5 times current loads rapidly decreased denitrification (Murray and Parslow, 1999). Moreover, this study also showed that denitrification efficiency declines as sediment respiration rate increases (Murray and Parslow, 1999). Therefore, from a management point of view, in order to maintain an effective denitrification process to remove nitrogen, water management strategy need to address the organic carbon and nutrient loads from external sources such as sewage or agriculture production.

In the context of Dong Ho estuary, in the wet season, denitrification showed a strong correlation with total organic carbon (TOC) in sediments, while in the dry season, denitrification had a strong correlation with total nitrogen (TN) in sediments (Figure 5.11). As discussed and illustrated in chapter 4, Dong Ho estuary receives higher organic matter loading in the wet season. Thus, it appears that such organic matter inputs to the benthos may be an important environmental regulator of denitrification in the wet season. The correlation between TOC and denitrification in the wet season suggested that higher organic carbon in sediments reduced denitrification rates in Dong Ho estuary.

Meanwhile, in the dry season, denitrification rates appear to be influenced by the level of total nitrogen in sediments. As mentioned above, elevated levels of available nitrogen have been shown to influence denitrification rates elsewhere and, thus, may play a significant role in the seasonal changes observed here.

In figure 5.11, the negative slope of sediment TN concentration vs denitrification showed that higher TN in sediments reduced denitrification rates in Dong Ho estuary. As illustrated in literature review, a study in Port Phillip Bay (Australia) indicated that increasing the current nitrogen load twofold increased the total denitrification flux, but increasing the nitrogen loading by 2.5 times current loads rapidly decreased denitrification (Murray and Parslow, 1999). In this light, it is suggested that Dong Ho estuary received enough nitrogen loading and accumulated total nitrogen in the sediments to a point where may be reducing the denitrification rates. Similarly, high organic carbon content may enhance the DNRA process which can compete nitrate used for denitrification (Seitzinger, 1988, Tiedje et al., 1983, Giblin et al., 2013). Consequently, negative correlation between TOC and denitrification suggested that higher organic carbon in sediments reduced denitrification rates in Dong Ho estuary.

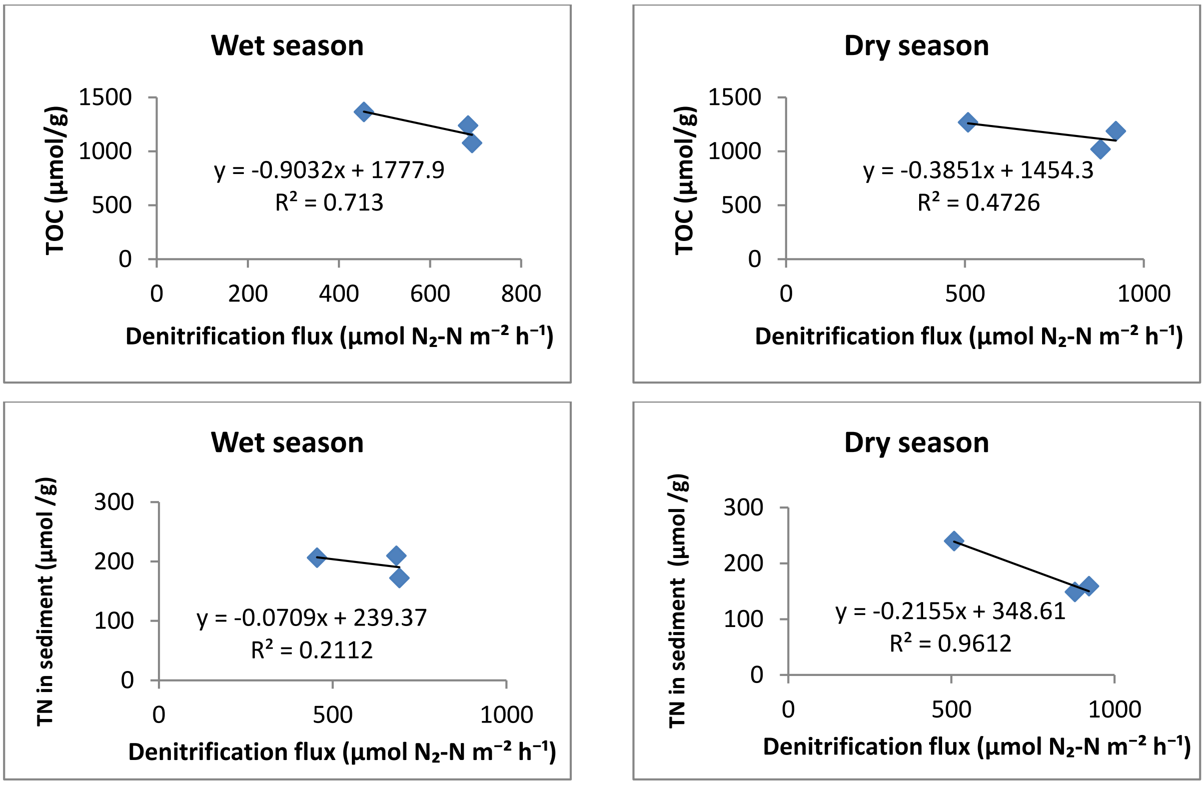


Figure 5.11: Correlations between organic carbon (TOC) and total nitrogen (TN) in sediments and total denitrification

As reported in the habitat survey of Dong Ho estuary, microphytobenthos (MPB) was observed in zone 3, the shallowest zone. The presence of MPB can reduce nitrification and denitrification rates because MPB competes for light and nutrients with denitrifying and nitrifying bacteria (Risgaard-Petersen, 2003, Sundbäck et al., 2000). However, zone 3 exhibited high denitrification rates despite the presence of MPB indicating denitrifying and nitrifying bacteria predominated over MPB in this case.

In conclusion, it is suggested that nitrogen cycling in Dong Ho estuary is very dynamic and the system is currently functioning at its highest capacity in removing allochtonous excess nitrogen. This statement is based on the denitrification rates measured in Dong Ho estuary. The denitrification rates measured in Dong Ho estuary are in the highest ranges compared to other estuarine systems, thus it suggested that Dong Ho estuary has likely reached its highest capacity in removing excess nitrogen. The increase of organic carbon and DIN loading expected to enter the estuary in the future development plans (DARD, 2014) may therefore significantly influence the performance and sustainability of the system by reducing the effective of nitrogen removal via denitrification. As further discussed in the later chapters, the results here add further insights to the key background and management concerns listed in chapter 4. These results reconfirmed that Dong Ho estuary is highly influenced by organic carbon and nutrient loads from its catchment as well as the system seems to retain materials rather than export to the sea. In view of denitrification, the Dong Ho estuary does provide some removal of N and thus contribute to the sink term for this nutrient. However, the ability to assimilate the increase inputs of organic carbon and nutrients is reducing, and the removal of nitrogen via denitrification is less efficient. The carrying capacity and performance of the Dong Ho estuary will be discussed further in the next chapter.

CHAPTER 6 - MODELLING SYSTEM FUNCTION AND LOICZ MODEL

6.1. Introduction

Biogeochemical budgets have been used for many years to provide insights on nutrient fluxes and processes in estuaries, and to evaluate the impacts of human activities on these processes (Swaney, 2011). In particular, a nutrient budget can provide a fundamental framework for identifying and assessing the importance of various nutrient sources or sinks within an estuarine system. Amongst scientific budget methodology programs, the Land-Ocean Interactions in the Coastal Zone (LOICZ) biogeochemical budget program (Gordon et al., 1996, Swaney and Giordani, 2011) was probably the best known in constructing quantitative nutrient budgets for coastal and marine waters (Swaney, 2011). The original aim of LOICZ program focuses on understanding the role and contributions of the coastal zone to the global carbon and nutrient cycles (Swaney, 2011, Smith et al., 2005). However, in the second phase of LOICZ (2004-2014), increased concerns with implications of human activities and the potential use of simple nutrient budgeting approaches in management of coastal ecosystems seeks attention from many scientists and managers. In view of this situation, the LOICZ biogeochemical modelling framework was developed for estimating biogeochemical processes related to the net metabolism of estuaries and coastal marine ecosystems and to infer carbon sources and sinks. The LOICZ methodology has since been applied at different temporal and spatial scales in more than 200 locations to develop site-specific budgets (Swaney and Giordani, 2011).

As implied above, LOICZ nutrient budgets derived in the modelling framework are a useful tool for understanding how coastal ecosystems respond to pressures of increasing nutrient inputs from human activities (Newton and Icely, 2008). The LOICZ approach achieves this because it develops carbon and nutrient budgets based on inputs via tributary and river discharge, precipitation, residual flow and exchange flow (Flynn, 2008, Smith, 2001); all of which reflect the collective influence of human activities in the corresponding catchments for the estuary of interest. Results from the application of the LOICZ biogeochemical models in a large number of coastal systems worldwide has shown that estuaries play a very significant role in the delivery of nutrients from land to the coastal zone, and have highlighted how potential changes in land use can affect nutrient cycling of these coastal ecosystems (Flynn, 2008, Giordani et al., 2008, Wepener, 2007, Buzzelli et al., 2013, Wösten et al., 2003). Moreover, application of the LOICZ model methodology has also provided robust estimates of the fluxes in shallow coastal waters and can be useful for representing the wide range of trophic conditions associated with these shallow coastal ecosystems (Giordani et al., 2008).

As indicated in earlier sections, one of the core aims of the current project was to provide insights and management support information based on research data, or evidence, of ecosystem function and performance. Key concerns of the local government in Kien Giang province revolve around whether the level of nutrients and other materials entering the estuary are being processed within the ecosystem and, therefore, whether the estuary can be sustainably managed (Carter, 2012a). As noted in Chapter 4, this requires consideration of aspects including:

1) Is the Dong Ho estuary highly influenced by catchment inputs?
2) How do the observed levels and concentrations compare to other similar estuaries?
3) Is the system collecting material or simply acting as a pipeline to the sea?
4) In view of the current situation with nutrient levels and potential capture, what do we need to consider in terms of risk and next steps for research?

Notably, the LOICZ modelling methodology provides a proven and widely comparable tool suited to addressing points 3 and 4 above: i.e. is the system collecting material or simply acting as a pipeline to the sea; and, in view of the current situation with nutrient levels and potential capture, what do we need to consider in terms of risk and next steps for research?

Consequently, in view of the global reputation and application of the LOICZ biogeochemical modelling methodology, the framework was applied to Dong Ho estuary to estimate the exchange of mass between each zone in the estuary and to provide important insight into how potential changes in land use might affect these areas. The LOICZ approach is an ideal model for the Dong Ho estuary situation where hydrodynamic data for Dong Ho estuary is limited. This approach attempts to use a minimum of data which typically might be found in developing countries (Swaney and Giordani, 2011). In addition, the advantage of the LOICZ approach is that it reduces the complexity in developing models of fluxes, but with limited data availability this approach can illustrate a comprehensive understanding of underlying biogeochemical processes and system behaviour (Wepener, 2007). Furthermore, by applying a widely applicable, uniform methodology to provide estimates on carbon (C), nitrogen (N) and phosphorus (P) fluxes in estuaries, biogeochemical performance of Dong Ho estuary can be compared with LOICZ models built in other estuarine and coastal areas for a better understanding of the role of the coastal zone as a source or sink for the key elements C, N, and P. Information from LOICZ biogeochemical model can predict the locations where management actions should be targeted including reduction of nutrient loads into the systems or preventing nutrient release from the sediments (Wepener, 2007).

6.2. Methods

As indicated in the introduction to the thesis, there is a high level of concern among local, provincial, and national agencies over the long-term sustainability of the Dong Ho estuary (Carter, 2012a).

Central to this is the issue of water quality and the ability of the estuary to cope with current and foreseeable anthropogenic inputs and loads. In this context, there are a number of considerations made by local government which this project aims to assist in addressing. Specifically, they are four points as mentioned in discussion section of chapter 4 and again noted in the introduction of this chapter. Whilst previous chapters have addressed one or more of these considerations, it remains necessary to build a system's level understanding so that aspects such as points 2 and 3 above can be further elucidated. Also, to support wider management strategies for the estuary, it is necessary to consider the ecosystems performance at locally relevant scales, capturing its particular components and processes, as well as at the whole-of-system scale so that pertinent risks can be identified for the purposes of management intervention.

Against this backdrop, this chapter uses the Land Ocean Interactions in the Coastal Zone (LOICZ) budget modelling methodology to address these issues and needs. Since its inception LOICZ has focused on the measurement of biogeochemical fluxes in coastal and estuarine ecosystems with the aim to better characterise the nutrient budgets and processes in these ecosystems, as well as to better highlight the crucial role these ecosystems play locally and globally in providing fundamental environmental services and resources. Accordingly, LOICZ has implemented the biogeochemical budget methodology in a wide range of coastal ecosystems including estuaries and has evolved the methodology from the initial approach by Gordon et al. (1996) (Swaney and Giordani, 2011). The LOICZ model is a steady state box model based on the stoichiometric relationships between water, salt and nutrient budgets (Gordon et al., 1996). Within defined water bodies, salt budgets and water volume dynamics are used to estimate water exchange between each defined ecosystem compartments. Dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets are calculated using water budgets and the respective nutrient concentration data. Non-conservative fluxes of DIP are attributed to net ecosystem metabolism (NEM) while non-conservative fluxes of DIN are attributed to the net balance of nitrogen fixation minus denitrification [nfix-denit] (Smith et al., 2005).

As described earlier, Chapter 5 (Figure 5.1), Dong Ho estuary was divided into 3 main compartments or zones based on the physico-chemical characteristics that prevailed in each. Based on the LOICZ modelling guidelines (Gordon et al., 1996), and the basic box model approach of sources, sinks and fluxes of nutrients, each compartment was modelled individually and then integrated into a whole-of-estuary model. This allowed for the identification of particular performance and process attributes in each zone, as well as the consideration of how these zones each contribute to overall estuary function. Also, it allows for assessment of the key processes and functions at different scales relevant to the identification of potential risks that management may need to address.

On this basis, each zone in the estuary is described in a box model using the associated flux and water quality data sets from previous chapters. The data used for the wet season was collected in August 2015, and the data presented for dry season was collected in April 2016 since these most represent the range of conditions that Dong Ho estuary demonstrated over the project. The model boundary definition is presented in the table 6.1 below.

Table 6.1: Boundary definition of three compartments in Dong Ho estuary

	System area (10^3 m^2)	System average depth (m)
Compartment 1 (Zone 1)	210	5.5
Compartment 2 (Zone 2)	537	3.4
Compartment 3 (zone 3)	367	1.4

Each zone or compartment comprises one or two layers depending on seasonal variations and the stratification of the water column where it occurred. In the dry season, Dong Ho estuary was not stratified and strongly dominated by sea waters due to restricted freshwater inputs from the river and surrounding canals. In this case the LOICZ model contains three compartments with a single layer in each. In the wet season, two scenarios were examined encompassing the conditions existing in the beginning and end of the wet season where flood conditions lead to significant changes in vertical stratification of the water column (section 4.3.3.2). In the early wet season with non-flood conditions (August 2015), Dong Ho estuary is strongly stratified due to the high volumes of freshwater it receives from the river and associated canals. For this scenario the LOICZ model contains three compartments with two-layers in each compartment for both zone 1 and zone 2 (the middle and most seaward compartments), and a single layer for zone 3 (the non-stratified inner most compartment) which is the shallowest area. Under this condition, river discharge (V_Q) for the Giang Thanh river and other freshwater flows (V_O) from surrounding canals and stormwater were estimated to be approximately 1000 – 1450 m^3/s (DARD, 2014). In the flood period of the wet season, it was estimated that the flows of V_Q and V_O into Dong Ho estuary were about half of the flood season flow into the Hau river (Phan, 2006, Wölcke et al., 2016) due to the connection between Rach Gia – Ha Tien canal and connecting canals into Dong Ho estuary. This is considered as one of the main flood pathways into the West Sea from the Hau river through canals in the Mekong delta (DARD, 2014). The precipitation (V_P) in Dong Ho estuary is about 325.5mm/month in the wet season (August) and 0.5mm/month in the dry season (April) according to monthly rainfall data obtained at the local Rach Gia meteorology station in Kien Giang (Kien Giang Statistics Office, 2013). The evaporation rate (V_E) varies between 180-220mm/month in the dry season and between 100-150mm in the wet season (Alliance, 2011). Unfortunately, groundwater data was not available and has not been measured in Dong Ho estuary.

The salinity values used were taken from the vertical profiles obtained for each compartment both wet and dry seasons as reported in Chapter 4.

DIN & DIP fluxes were estimated using the mass balance approach employed by the LOICZ budget methodology and utilising the water column nutrient concentration data collected in each compartment during the wet and dry seasons accordingly. Due to a lack of data on specific nutrient loads and their sources, it was assumed that all nutrient loads were accounted for and delivered by the river runoff which was sampled upstream in site 4, 5, 6, 7 (See Chapter 4, section 4.3.4). Further, the transport of dissolved inorganic nutrients into and out of different compartments of Dong Ho estuary were assumed to follow that same general flows and mixing processes described for water and salt. It is recognised that the LOICZ model only focuses on the influences in terms of exchanges and processes.

6.3. Results

In this section, the metabolic status and ecosystem performance of Dong Ho estuary are reported and analysed based on *in situ* incubation measurements and the LOICZ budgeting procedure. As the initial step to formulating the LOICZ box models conceptual models were developed based on the field data to examine the links between the observed stocks and process rates measured using *in situ* incubations in each zone of the system in both wet and dry season (Figures 6.1, 6.2, 6.3). This also assisted in performing checks and balances on the values obtained, relative to other similar systems, and how they would be integrated into the LOICZ framework. Using the insights and checks gained from the conceptual models, the LOICZ biogeochemical modelling methodology was then applied to each of the respective zones to understand how each of them functioned relative to each other, and compared to other similar estuary ecosystems.

Finally, the respective box models were integrated into a whole-of-system LOICZ model for the estuary to consider whole system metabolism and the interactions of the estuary with the Western Sea and adjacent canals. This also assisted in addressing a key management consideration on whether the Dong Ho estuary was a point of net accumulation or export for nutrients (nitrogen and phosphorus) and carbon to the sea.

6.3.1. Conceptual Models based on field data

As presented below, a total of six conceptual box models were developed encompassing the nutrient budgets and biogeochemical processes occurring in each of the three defined zones in Dong Ho estuary in the wet and dry season. In each box model three fundamental compartments are described; surface water, bottom water and the sediments. The respective stocks are presented for each compartment (NH_4^+, NO_x, PO_4^{3-} in waters and Ch-a, TN, TP, TOC, TC in sediments), and flux rates of nutrients, dissolved oxygen and N_2 are also included. Numbers in black represent the amounts or stocks of the respective elements, while numbers in red represent the flux rates (mmol/m^2/day) between the sediment and water column. In terms of nutrient fluxes, a positive number indicates nutrient release and a negative number illustrates nutrient uptake.

6.3.1.1. Zone 1

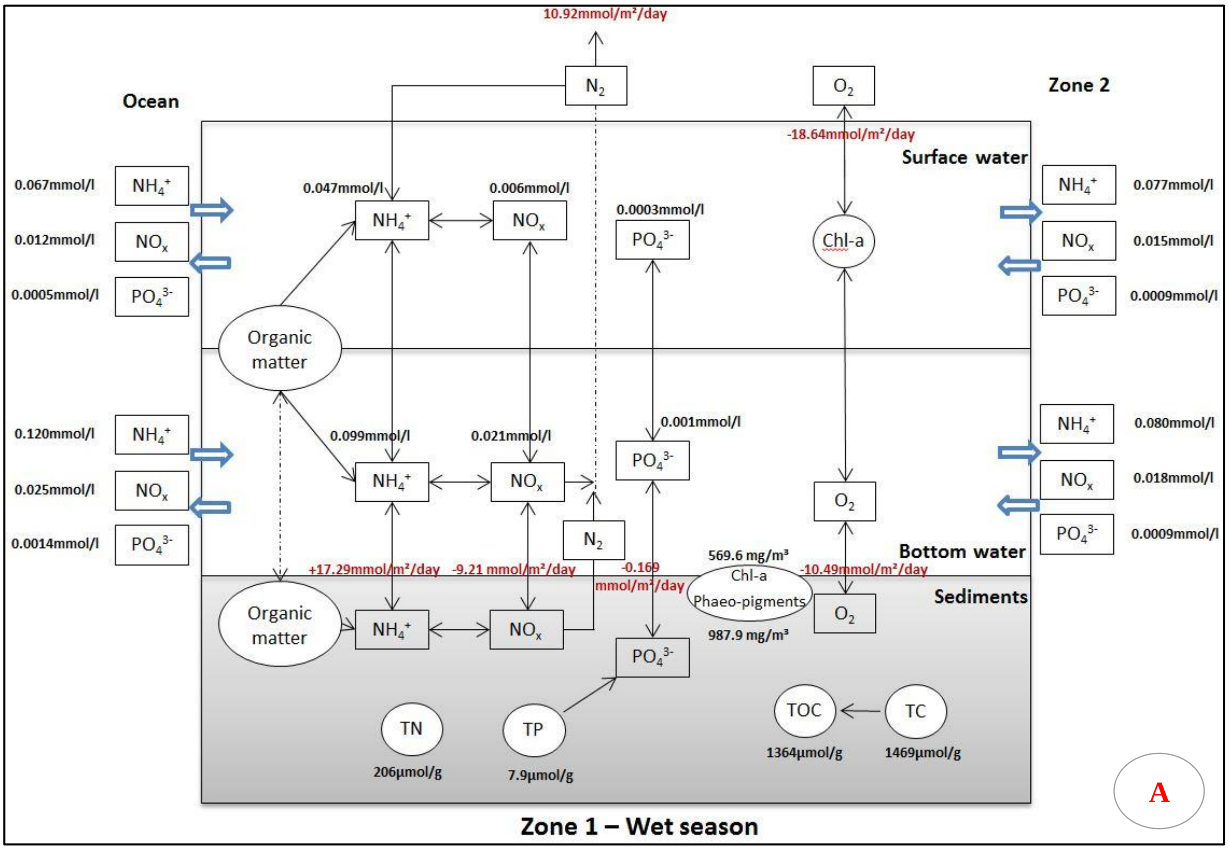
Zone 1 is the deepest area in Dong Ho estuary with an average depth of 5.5m but reaching 7.5 meters in some parts. This is the main channel of flow from the estuary into the ocean and vice versa. In addition, this compartment also directly receives domestic wastewater discharge from Ha Tien town and the To Chau area along the banks of the zone.

In the wet season, due to the strong influence of freshwater inputs from Giang Thanh river and Rach Gia - Ha Tien canal, there is a strong stratification in the water column as illustrated by salinity and nutrient profile data (described in site 2 in section 4.3.3.2 and 4.3.4). As reflected in the field data there is a clear difference in nutrient concentrations in surface and bottom waters (section 4.3.4). In general, bottom water contained higher DIN concentrations than surface water and this is augmented by DIN released from the sediments (Figure 6.1A). In contrast, DIP concentrations in surface waters were higher than in bottom water, coinciding with an uptake of DIP by the benthos (Figure 6.1A). When comparing nutrient concentrations in zone 1 to concentrations outside of the box (zone 2 and the ocean), the conceptual model suggests that nutrients were potentially consumed in the upper water layers in zone 1 or exported from zone 1 to the ocean. Notably, the overall respiration rate of zone 1 was the highest compared to the other zones in the wet season.

As indicated previously, there was no stratification in the water column in the dry season and thus, nutrient concentrations between surface and bottom water were comparable. A significant uptake of NO_x was observed into the sediments (-5.23 mmol/m^2/day) but this was partially offset by a release of NH_4^+ (+1.12 mmol/m^2/day), corresponding to approximately 21% of the total DIN exchange between sediments and the water column. In stark comparison to wet season conditions where DIP was taken up by the benthos, DIP was released from sediments into the water column in the dry season. Comparing water column DIN and DIP concentrations in zone 1 to outside of the zone showed that DIP concentrations were similar to those in the adjacent ocean waters, but DIN was potentially subject to import due to higher concentrations in oceanic waters than observed in zone 1. As mentioned later, the dominance of tidal flows and the absence of riverine flows may influence this situation such that estuary waters are not fully flushed away from the estuary mouth and so concentration values reflect estuarine processes rather than oceanic processes and inputs.

Regarding nitrogen (N_2) removal from the system via denitrification in zone 1, the dry season showed a higher denitrification rate compared to the wet season. Notably, in the wet season the total amount of N lost via denitrification was almost equal to the amount of N entering the sediments via NO_x uptake (Figure 6.1A) and there was a simultaneous release of ammonium into the water column. This conflicts with the observation that denitrification at this site was driven mostly by NO_x derived from coupled nitrification in the sediments as indicated by the N^{15} denitrification measurements (Figure 5.8). In view of the concomitant and substantial release of ammonium from the same sediments, it may be that, in addition to nitrification in the sediments, that other processes may be utilising NO_x entering the sediments. For example, the dissimilatory nitrate reduction to ammonium (DNRA) has been observed in similar coastal sediments and can be significant in the ammonium production budget (An and Gardner, 2002, Gardner et al., 2006). Also, whilst NO_x is energetically not the preferred source of N for many primary producing organisms (Gottschalk, 2012), the chlorophyll levels observed in sediments at this site (Figure 4.21) might indicate some level of NO_x uptake by benthic primary producers.

In the dry season the situation changed. Whilst the total amount of N being removed by denitrification only increased by approximately 9%, the potential contribution from water column NO_x dropped to approximately 43% of the total N_2 release compared to the potential contribution of approximately 84% seen in the wet season. Interestingly, the results of N^{15} denitrification measurements indicate that the relative contribution from water column NO_x increases in this period, although coupled NO_x supply within the sediments still predominates (Figure 5.8). In this case, and in view of the concomitant uptake of NH_4^+, sediment nitrification persists but other processes such as DNRA may have decreased.



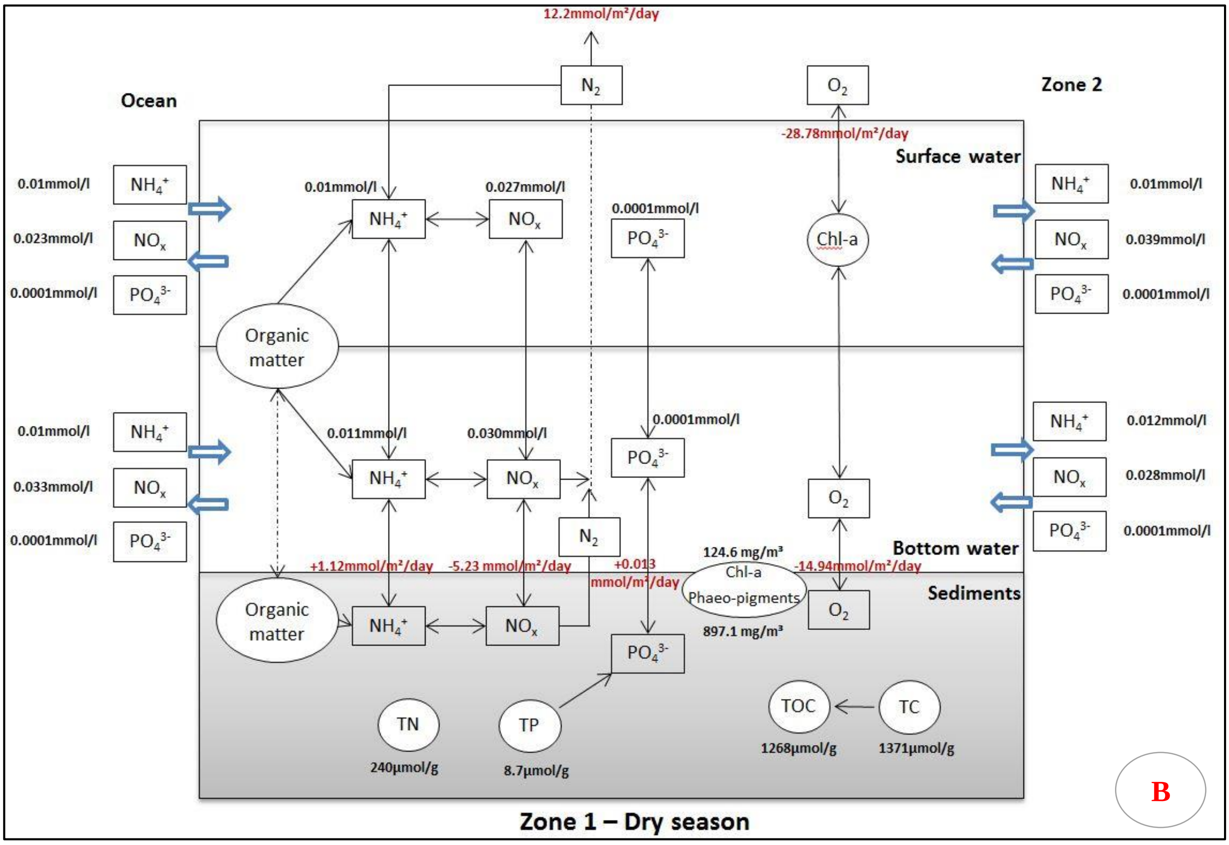


Figure 6.1: Conceptual models summarising the stocks and processes measured in situ in Zone 1. All values are expressed as mmol of N or P as contained in the respective nutrient species.

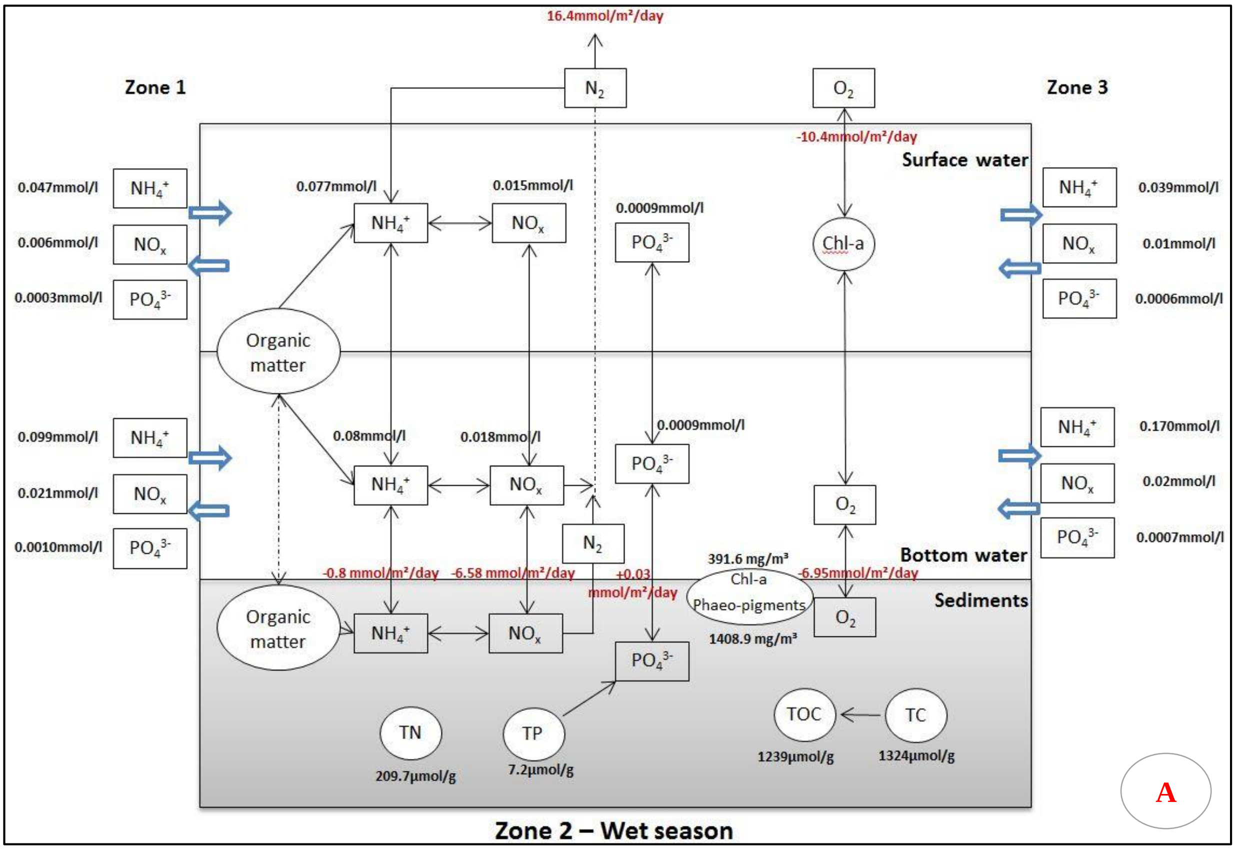
6.3.1.2. Zone 2

Zone 2 is the central area of the estuary where flows from the Giang Thanh river, Ha Tien – Rach Gia canal and tidal exchanges from the Southwest Sea all interact. The average depth of this compartment is approximately 3.4m at low tide with the deepest patches reaching approximately 4m. It is shallower than the most seaward compartment (zone 1) and directly receives the discharged water from the nearby extensive shrimp ponds in the northeast of Dong Ho estuary. As seen in zone 1, nutrient budgets and fluxes in zone 2 also showed a seasonal variation.

As mentioned previously, the water column in zone 2 was stratified in the wet season, with the surface waters in zone 2 containing higher nutrient concentrations than surface waters in both zone 1 and zone 3. In contrast, to zone 1, there was a net uptake of DIN by sediments in this zone (-7.38 mmol/m^2/day) with no release of either NO_x or NH_4^+. Regarding, DIP concentrations in the bottom water were in the same order as for the other zones and received a contribution from DIP release from the benthos (Figure 6.2 A). The higher nutrient concentrations observed in surface waters in zone 2 confirmed the influence of freshwater inputs into Dong Ho estuary and verified the direct nutrient loading from Giang Thanh river, Rach Gia -Ha Tien canal and the nearby shrimp ponds.

In the dry season, there were no significant differences between surface and bottom water due to the absence of detectable freshwater inputs as shown in vertical water column salinity profiles (Chapter 4). DIP concentrations were conservative between inside this zone and the adjacent zones even though there was a release of DIP from sediments. In contrast, despite an observed uptake of -0.45 mmol/m^2/day DIN by sediments in zone 2, DIN concentrations in the water column in zone 2 were higher than observed in both zone 1 and zone 3. This highlights the contribution received from nearby domestic and aquaculture sources, as well as potential inputs from the adjacent zones.

In terms of system metabolism in zone 2, the zone was heterotrophic in both seasons with respiration exceeding the gross primary production on both occasions. In terms of N_2 removal from the system, total denitrification was lower in the wet season being approximately 75% of the dry season rate (Figure 6.2A,B) and is consistent with the observations from the other zones. In the wet season the total amount of N removed by denitrification is approximately 30% higher than observed in zone 1 but approximately the same as the rate observed in the upstream zone 3. Notably the potential contribution from sediment NH_4^+ and NO_x uptake equates to approximately 45% of the total N released via denitrification. This suggests that benthic processes dominate the supply of DIN to this process and this is substantiated by the dominance of coupled nitrification observed in the N^{15} denitrification measurements for this site and season (Figure 5.8). In contrast, a release of NO_x was observed from sediments in this zone in the dry season indicating an excess of NO_x relative to demand by denitrification and other sediment processes. At the same time, the contribution of sediment NO_x to denitrification from coupled nitrification increases in the dry season so that it is almost equal to the total amount of N released via denitrification (Figure 5.8).



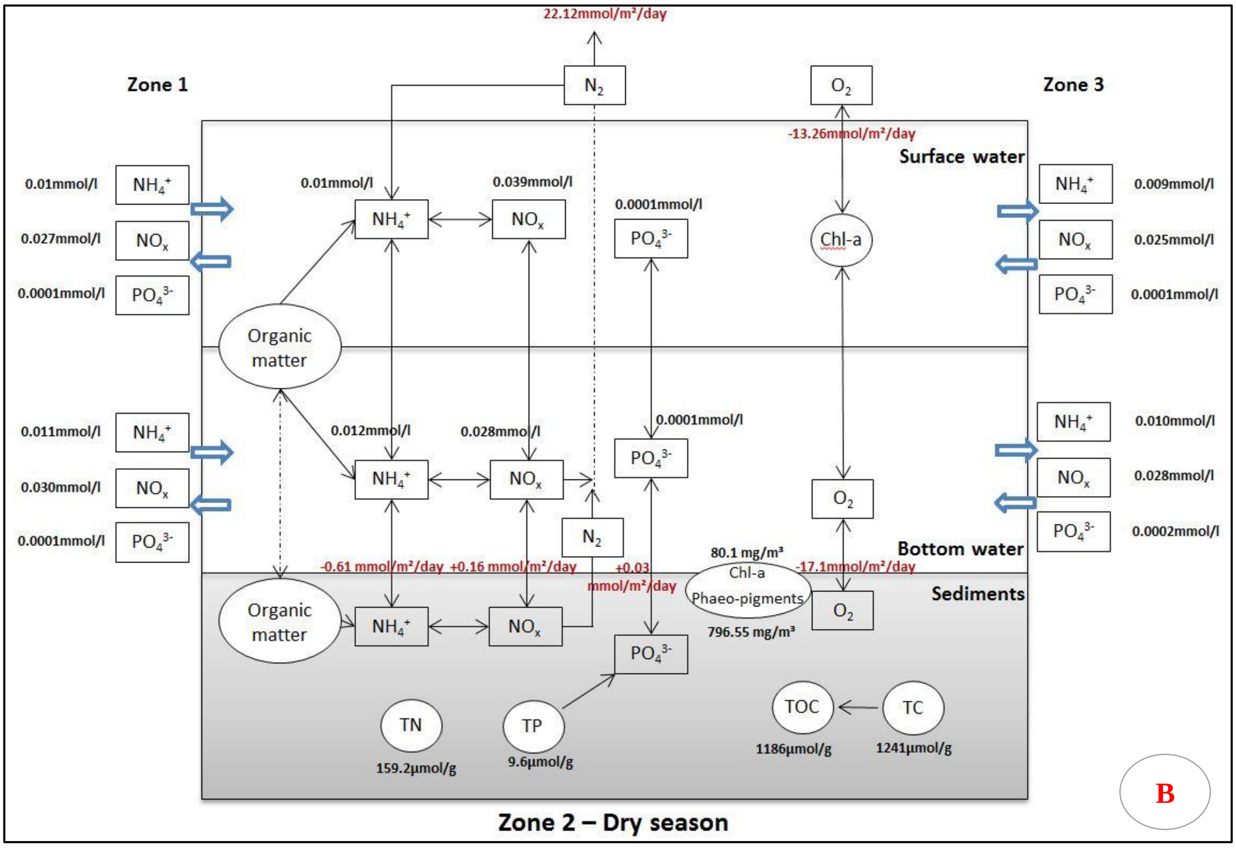


Figure 6.2: Conceptual models summarising the stocks and processes measured in situ in Zone 2. All values are expressed as mmol of N or P as contained in the respective nutrient species.

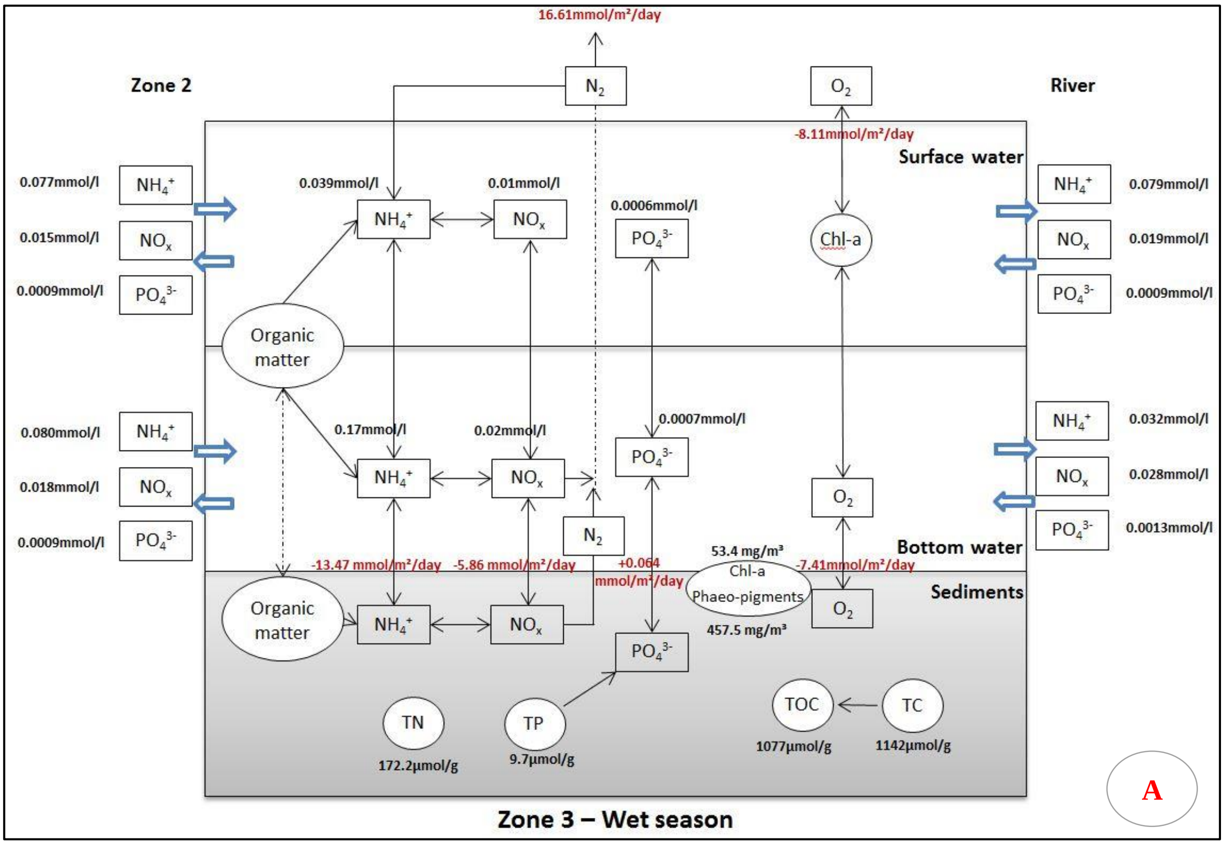
6.3.1.3. Zone 3

Zone 3 is the shallowest area in the northwest of Dong Ho estuary with average depth around 1.4m at low tide reaching ≤ 2.0m in some few patches. This compartment is considered as a transitional area between the intertidal and mangrove area in the north of Dong Ho estuary, and zone 2 in the central estuary. This area receives flows from the river and some small canals in the west of the estuary draining from a mixture of domestic and agricultural areas. Nutrient concentrations measured in some of the small canals in the west of the estuary (site 9, 10) in the wet season were similar to the nutrient concentrations measured in zone 3 suggesting that these small canals may be directly influencing zone 3. In both seasons, nutrient concentrations in the water column in zone 3 were lower than zone 2 and in the upstream river sites. Whilst this may be due to a number of influences, it is notable that this site had the only obvious microphytobenthic communities identified in the benthic surveys (Chapter 4), so that there may be significant uptake of nutrients in this zone by these communities. Further, water entering this zone from the river mostly pass through the mangroves and intertidal zones in the north of zone 3, which may reduce nutrient inputs into this compartment.

Zone 3 showed a difference in N removal via denitrification processes between seasons with total denitrification being higher in the dry season at 21.09 mmol/m^2/day, compared to 16.01 mmol/m^2/day in the wet season (Figure 6.3A & B). In conjunction with this, the total uptake of DIN into the sediments in the wet season was approximately the same as the amount of N lost via denitrification with rates of uptake averaging 19.33mmol/m^2/day compared to an average total denitrification rate of 16.61mmol/m^2/day. Aligned with this, the N^{15} denitrification estimations showed that the contributions from water column (Dw) and coupled sediment (Dn) NOx sources were not statistically different (Figure 5.8).

By comparison, in the dry season, when total denitrification rates were higher, the apparent contribution from water column DIN pools could only conceivably provide 7.5% of the total, compared to the 100% potential contribution from these pools in the wet season (Figure 6.3A & B). This observation concurs with the results from the N^{15} denitrification determinations which show a marked decrease in the Dw contribution to total denitrification from approximately 42% in the wet season to approximately 13% in the dry season. This shift from significant utilisation of water column stocks of NO_x in denitrification in the wet season to increased reliance on coupled sediment-based nitrification for NO_x in the dry season does not appear to be due to the level of available NO_x in the water column as these are approximately the same for both seasons (Figure 6.3A & B). Rather, in view of the small release of NO_x from sediments and the increased uptake of dissolved oxygen measured in the dry season (Figure 5.4), it appears that nitrification processes increase in the dry season at this site so that water column stocks of NO_x are not required to meet the demands of denitrification.

In contrast to DIN, DIP showed an overall decrease in both water column standing stocks and sediment fluxes between the wet and dry seasons (Figure 6.3A & B). Notably, however, DIP fluxes were consistently out of the benthos with no benthic uptake observed in either season.



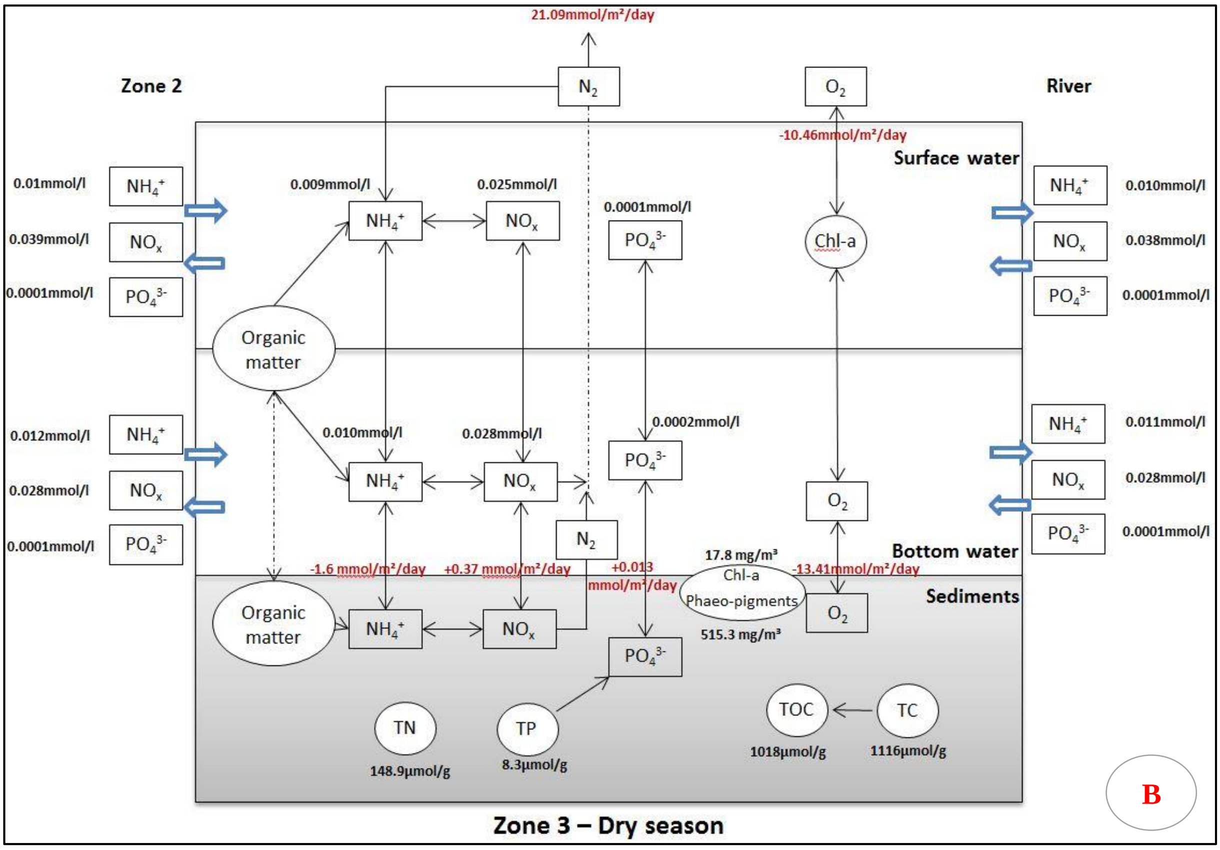


Figure 6.3: Conceptual models summarising the stocks and processes measured in situ in Zone 3. All values are expressed as mmol of N or P as contained in the respective nutrient species.

6.3.2. Results from LOICZ Modelling

The main aim of this section of the thesis is to describe the relative roles and significance of each zone in the estuary in terms of nutrient cycling and materials transfer. At the same time, it is intended to provide a method for understanding Dong Ho estuary at the whole-of-system level to assist managers when considering the possible future and sustainability of the Dong Ho estuarine system through the assessment of inputs, outputs, and processing of nutrients. It also allows the comparison between Dong Ho estuary and other similar ecosystems in Vietnam, Southeast Asia and globally.

As described previously, Dong Ho estuary has two distinct seasons. In the wet season, the middle and most seaward compartments are clearly two layered as the freshwater from the catchment flows over the lower oceanic saline water. In addition to building a mass balance summarising these two layers, this study also seeks to describe the relative differences in what each layer contributes. Therefore, in the wet season, zone 1 and zone 2 are separated into two-layer systems in the LOICZ model. Due to the more homogenous water column observed in zone 3, this was modelled as a one layer box model.

In comparison, in the dry season, especially in April 2016, freshwater inputs were not discernible and vertical profiles of salinity in all zones showed that the water column was a well mixed single layer of water. Accordingly, dry season box models for all zones used only a single water layer.

For each season, water column salt budgets and nutrient budgets (DIN, DIP) are presented in box model budget diagrams for all zones. As per the LOICZ methodology, the units used in the diagrams are: area ($10^3.m^2$), volume ($10^3.m^3$), depth (m), time (day), water flux ($10^3.m^3.d^{-1}$), salinity flux (10^3 psu.$m^3.d^{-1}$), nutrient flux ($mol.d^{-1}$), metabolism ($mol.C.d^{-1}$).

6.3.2.1. Dry season models

In the dry season, especially in April 2016, salinity profiles across the estuary showed that freshwater inputs including riverine and groundwater inputs were very low or non-existent due to sluice gates upstream of the river and canals were closed to prevent salt intrusion. Concurrently, evaporation rates in the area were high, so that salinity levels were influence more by evaporation in some sites than by freshwater inputs (see section 4.4.1). Thus, in the LOICZ model, freshwater discharge was assumed to be subtracted and Dong Ho estuary was strongly influenced by tidal exchange. Water and salt budget diagrams for Dong Ho estuary in the dry season are presented in Figure 6.4. Due to the high evaporation (V_p) compared to very low precipitation (V_e), and no other detectable freshwater inputs, the upper reach of the system became hypersaline compared to incoming tidal waters. Also, based on the calculation from the LOICZ model, the water exchange time (residence time) in the Dong Ho estuary was determined to be approximately 9 days in the dry season. Within the estuary, zones 2 and 3 had the longest water residence times (3 days and 4 days respectively) while zone 1 had the shortest water residence time (2 days). The longer residence times in the inner estuary zones would increase the deposition of materials in these areas and supports the observations made earlier that the estuary was increasingly shallow in these zones (see Chapter 4, bathymetry section 4.3.1).

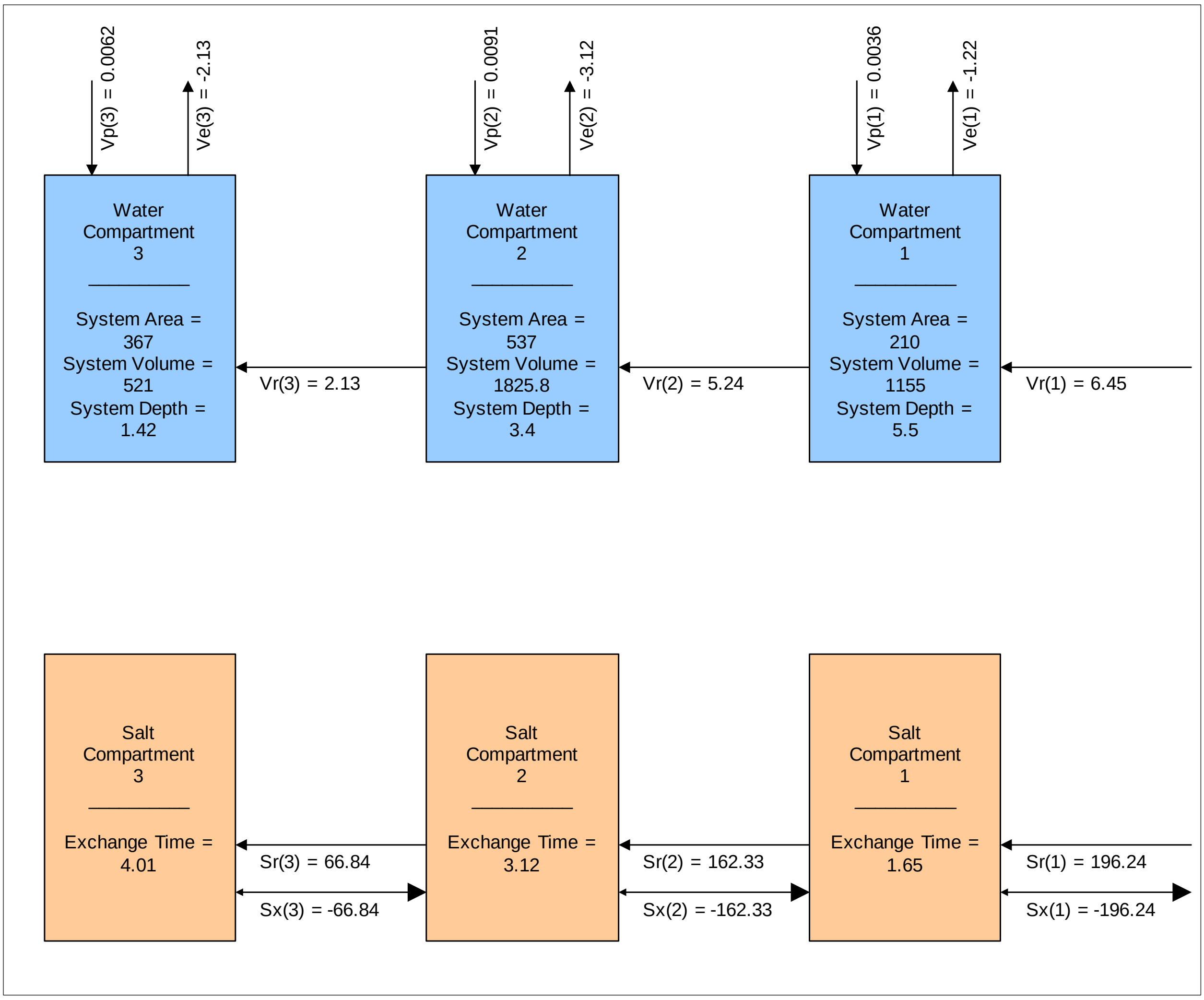


Figure 6.4: Water and salt budget diagrams for Dong Ho estuary in the dry season

Phosphorus and nitrogen budget box models for Dong Ho estuary in the dry season are presented in Figure 6.5. In terms of the overall estuary in the dry season, the central zone in Dong Ho estuary is a net source of DIN to waters up toward the catchment and to the adjacent sea via the seaward zone 1 (Figure 6.5). Concomitantly, the same central zone is a sink for DIP, receiving input from upstream areas as well as from the sea via zone 1 (Figure 6.5). Using the LOICZ methodology, the estuary exported approximately 1587.03 mol.d^{-1} DIN (22.22kg.d^{-1}), and accumulated approximately 27.95 mol.d^{-1} DIP (0.87 kg.d^{-1}). The benthic sediments played an important role in the observed exchanges and ecosystem metabolism in the dry season because they accounted for 82% of the DIP accumulated in the estuary and provided approximately 98% of the DIN exported from the system.

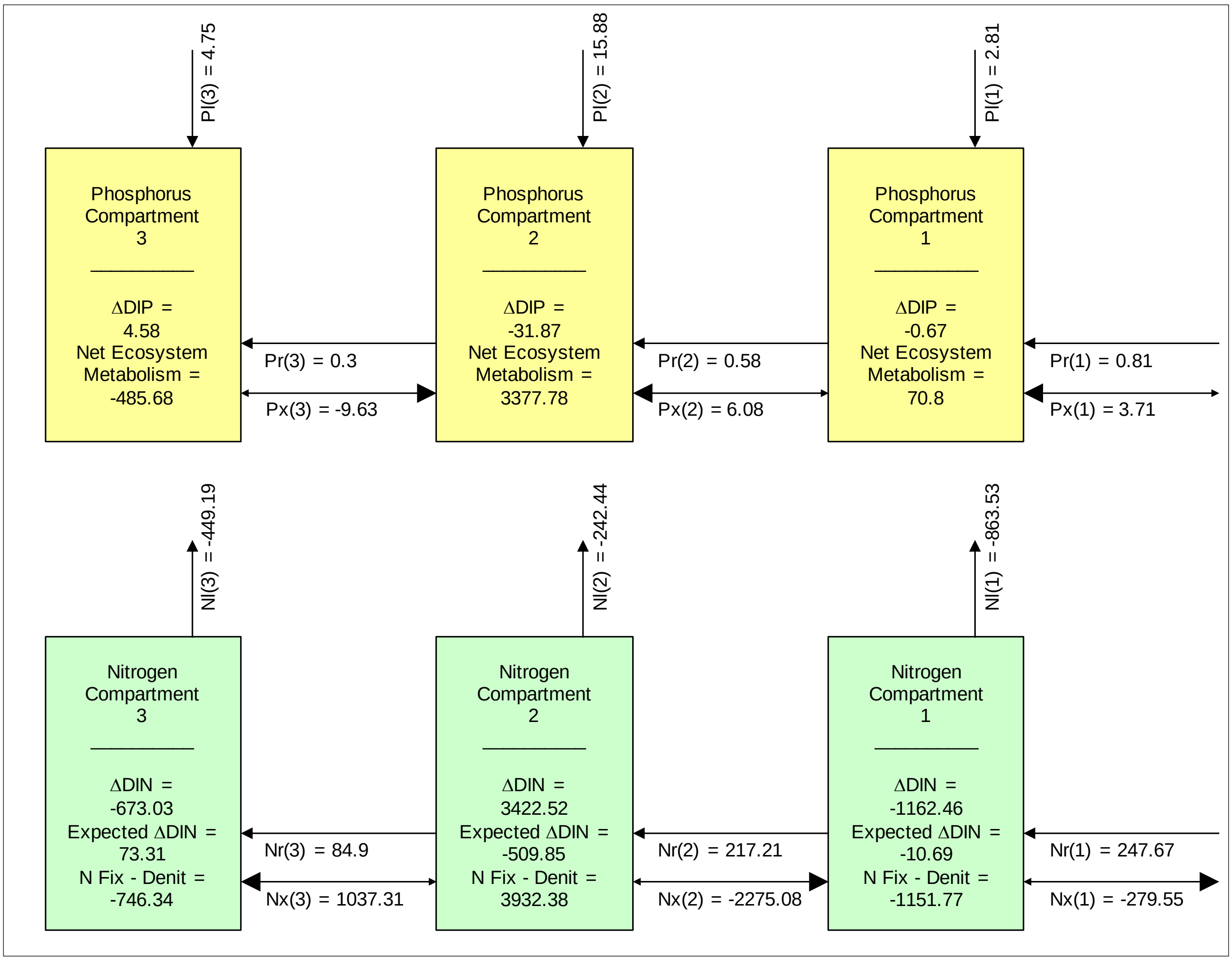


Figure 6.5: Phosphorus and nitrogen budget diagrams for Dong Ho estuary in the dry season

As summarised in Figure 6.5, zone 2, the central estuary, also played a significant role in the overall estuarine metabolism with the highest net ecosystem metabolism (NEM). This zone also had a higher nitrogen fixation rate than denitrification which underpins its apparent ability to export DIN to other zones in the ecosystem. In comparison, the other zones had higher denitrification rates than n-fixation such that they relied on inputs from zone 2 to balance their N budget.

In contrast to DIN dynamics, the water column in zone 2 requires DIP input from both the associated benthos, and from zones 3 and 1 to balance its DIP budget. In this context, zone 2 and the benthos within it were keystone to the DIP and DIN budgets for the Dong Ho estuary overall during the dry season underpinning the supply of DIN to other zones, and capturing the DIP being exported from these other zones.

6.3.2.2. Wet season

As noted previously, in the wet season, Dong Ho estuary receives freshwater inputs from Giang Thanh river and Rach Gia Ha Tien canal. The most inner compartment, zone 3, was assumed to receive approximately 30% of Giang Thanh river flow based on the estimation of hydrodynamic data in the estuary (DARD, 2014). The middle compartment, zone 2, receives flows from both the Giang Thanh river (V_q) and Rach Gia – Ha Tien canal (V_o), but the flow from the canal represents approximately 10% of the combined input including the Giang Thanh river (DARD, 2014). Water and salt budget models for the wet season conditions in the Dong Ho are presented in figure 6.6. In contrast to the dry season situation, the water input from precipitation (V_p) in the wet season is approximately double the volume lost via evaporation (V_e). The average water exchange time (residence time) for the whole system was determined to be approximately 4 days under average wet season conditions of rainfall. Compartment 3 and 2 have the longer water exchange time (1.5-2 days) while compartment 1 has the stronger vertical exchange and the residence time is only 1 day.

Phosphorus and nitrogen box models for Dong Ho estuary in wet season are presented in Figure 6.7. As noted previously, flows from the Giang Than river dominates water inputs to the Dong Ho estuary during the wet season. Despite these higher flows the models indicate that Dong Ho estuary is a net sink for both DIN and DIP in the wet season. Overall, the collective system accumulated 127,025.69 mol.d^{-1} DIN (1,778.36 kg d^{-1}) and 2011.54 mol d^{-1} DIP (62.30 kg.d^{-1}). This level of nutrient retention has been reported elsewhere and suggest that the Dong Ho estuary captures a significant portion of the total wet season load entering the ecosystem from the associated catchment and other local sources. This capture also helps to explain the elevated concentrations of DIN and DIP observed in the water column in Dong Ho estuary during the wet season.

Notably, the exchange between each zone in wet season is more complicated than in the dry season due to the structure of the water column and the vertical exchange between upper and lower layers in zones 1 and 2. In general, it can be seen that the lower water layer retains more DIN and DIP compared to the upper layer and the most seaward area, zone 1, played the most important role in accumulating DIN and DIP in the system. This zone accounted for approximately 88% of the DIP and 95% of the DIN captured within the Dong Ho estuary in the wet season. In regard to nitrogen dynamics and budget balance, the zones behaved differently than observed in the dry season. Only zone 3, the most inner and shallow zone, had a higher nitrogen fixation rate than denitrification, whilst zones 1 and 2 showed the opposite situation with higher denitrification rates than nitrogen fixation. Consequently, whilst zone 2 was the main source of mobile DIN in the dry season, zone 3 took this role in the wet season delivering DIN to the adjacent zone 2.

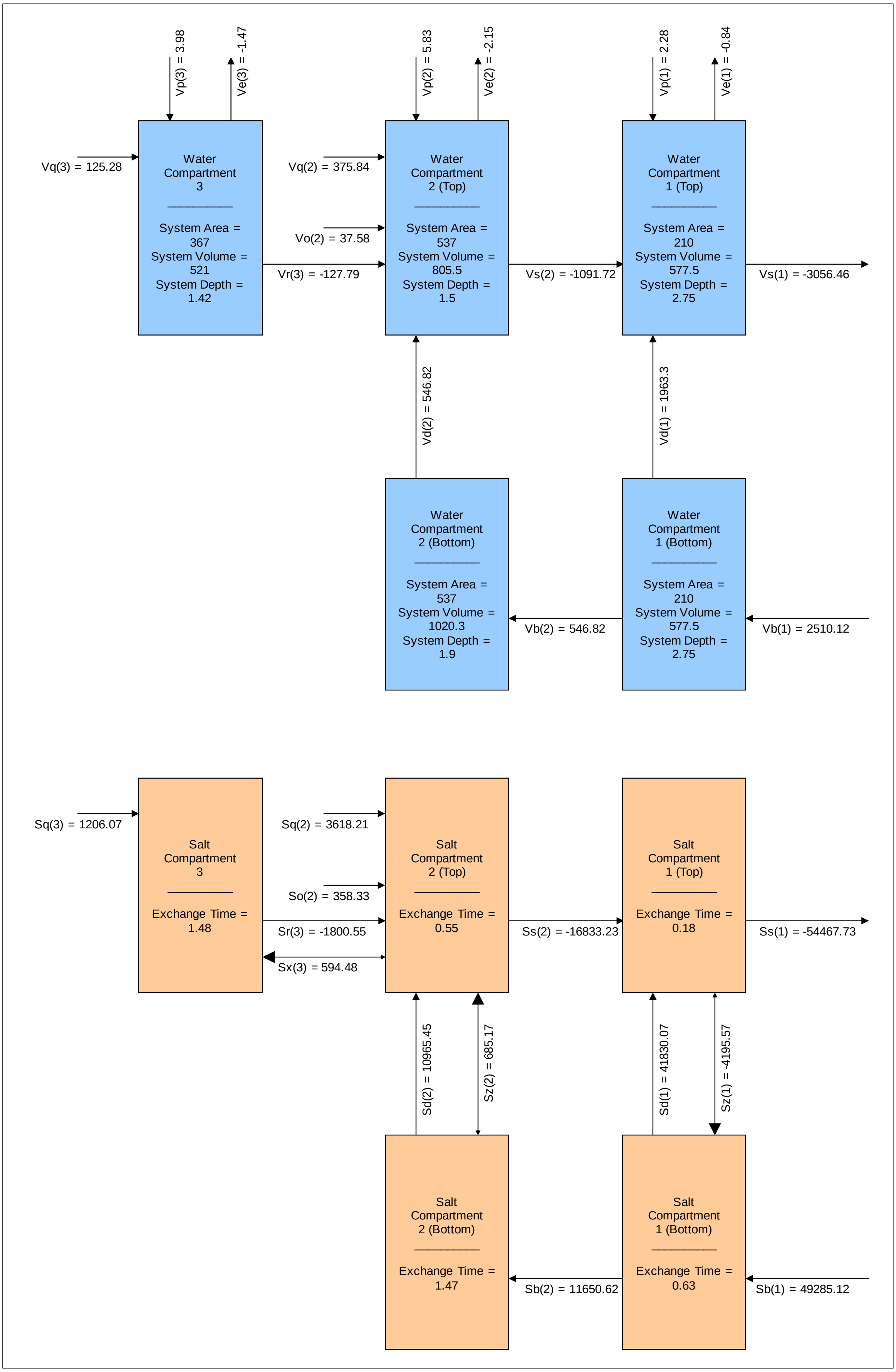


Figure 6.6: Water and salt budget diagrams for Dong Ho estuary in the wet season including box models for the two water layers identified by field measurements.

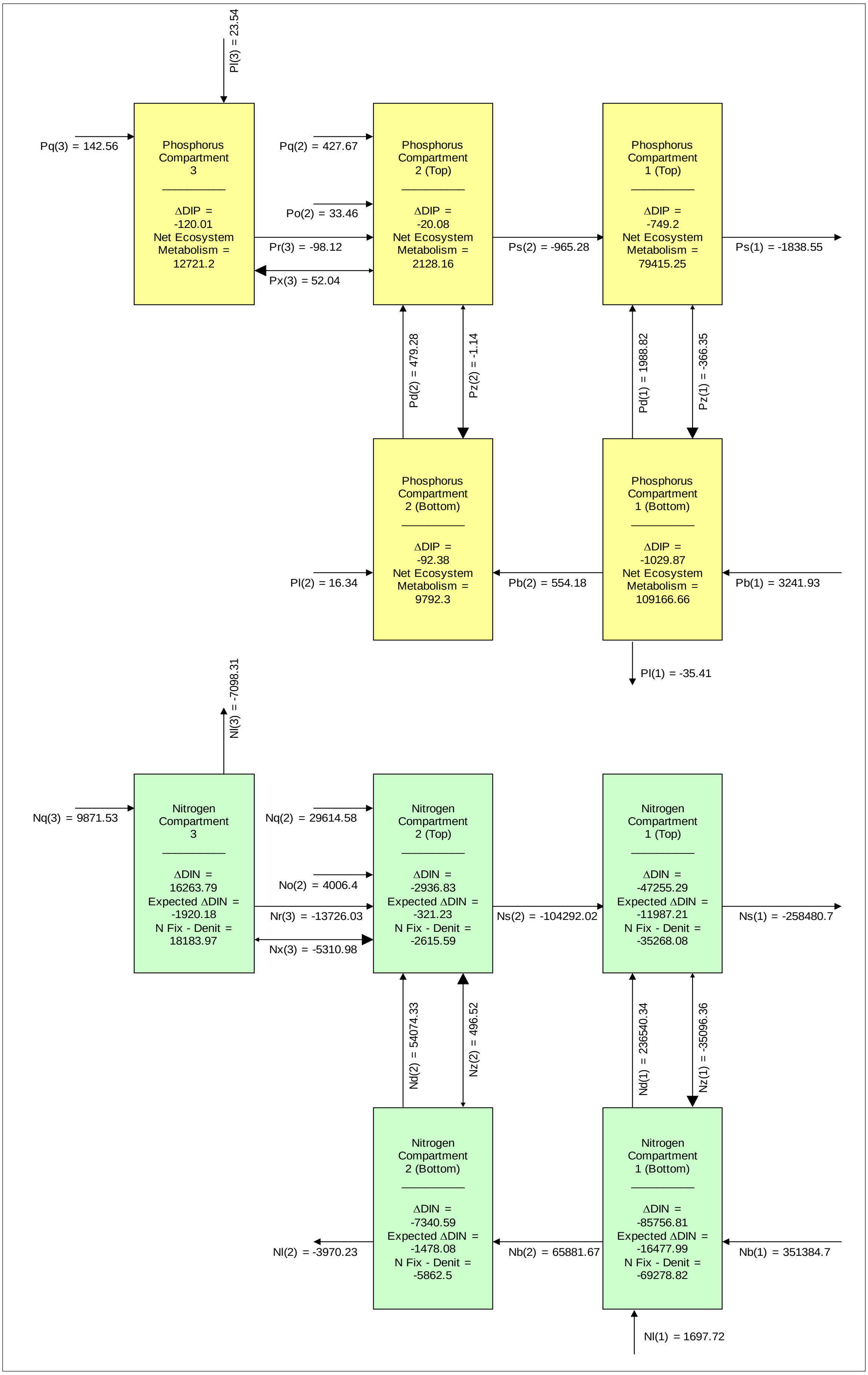


Figure 6.7: Phosphorus and nitrogen budget diagrams for Dong Ho estuary in the wet season

6.4. Discussion

6.4.1. General Observations

According to LOICZ models describing the wet and dry season, net ecosystem metabolism (NEM=p-r) calculated for the whole system in Dong Ho estuary is positive in both seasons, suggesting that the estuary is marginally autotrophic. However, as described in Chapter 5 (section 5.3.1), net ecosystem determinations based on *in situ* measurements show that heterotrophy dominates in both seasons with p:r ratios below 1. This disparity has been reported elsewhere such as in the Scheldt estuary (Gazeau et al., 2005). Like the Dong Ho estuary, the Scheldt estuary receives high inputs of allochtonous organic matter and generally has high turbidity. As reported by Gazeau et al., (2005) the LOICZ approach using DIP fluxes to calculate NEM may over estimate primary production and under estimate the role of DIP exchange with particles comprising the turbidity in these ecosystems (Gazeau et al., 2005). In view of this, the results obtained using the LOICZ method in Dong Ho estuary may similarly over estimated water column primary production but, given the dominant role of benthic sediments in both DIN and DIP budgets, this disparity may indicate that the sediments in the Dong Ho estuary are even more significant than the LOICZ modelling indicates here. Accordingly, the influence of water column primary production on estimations of nutrient exchange between zones in this study is likely to be less than suggested by the derived box models.

In both seasons, DIP fluxes in Dong Ho estuary were in the range reported for similar estuaries in the Mekong Delta, but DIN fluxes were slightly higher compared to nutrient fluxes calculated in LOICZ models for the Tien and Hau River estuaries, the biggest estuaries in the Mekong delta (Phan, 2006, Nguyen and Phan, 2006). In terms of nutrient export or import, both the Hau and Tien River estuaries are reported to export DIN and DIP to the sea in both the dry and wet season. In contrast, the Dong Ho estuary is a net sink of for both DIN and DIP in the wet season, and it is a net source of DIN and a net sink of DIP in the dry season. However, it should be noted that the rate of DIN and DIP fluxes in the dry season were very low compared to the flux rates in the wet season. Importantly, the Dong Ho estuary is subject to significant restrictions in water exchange and net flows over a lot of the years due to the extensive use of dykes and sluice gates to control salt water movement throughout the associated waterways. Whilst such infrastructure also exists in areas associated with the Tien and Hau Rivers, it is not as restrictive of flows as occurs in the Dong Ho situation (DARD, 2014). Consequently, on an annual scale, Dong Ho estuary can be considered as a sink of both nitrogen and phosphorus; especially for nitrogen.

In light of the preceding observations, heterotrophic estuaries have been shown to act as a source of dissolved inorganic nutrients (Smith and Hollibaugh, 1993). However several studies have also shown that estuaries can act as a net sink for land-derived nutrient discharges, capturing significant amounts of material and nutrients derived from land-based sources (Hung and Kuo, 2002, Hung and Huang, 2005, Robson et al., 2008a). According to the LOICZ model in this study, the Dong Ho estuary acts as a nutrient sink with an annual average of 31.6% of the incoming nitrogen and 52.1% of the incoming phosphorus retained within the estuary; with wet season deposition playing a critical role in this capture. The mean ratio of DIN:DIP entering the estuary was calculated in this study to be approximately 101:1, while the ratio of DIN:DIP remaining in the system was approximately 62:1. In both cases these ratios suggest that the ecosystem is phosphorous limited rather than nitrogen limited compared to the generally accepted Redfield ratios expected in these ecosystems (Magnien et al., 1992). Whilst a number of studies have suggested that nitrogen is the main limiting nutrient in coastal and marine ecosystems (Nixon, 1995, Alberti, 2008), recent reports have demonstrated that phosphorous may also be the limiting nutrient in some estuaries (Wulff et al., 2011, Hanington et al., 2016). So, compared to Redfield ratios (16:1) Dong Ho estuary (62:1) can be considered as P limited, which, as discussed in the final chapter, has strong implications for water quality management strategies. In addition, in view of the levels of dissolved inorganic N and P there is a weak correlation between GPP and SRP availability but no correlation with DIN. This supports the notion that there is a potential for phosphorus limitation rather than nitrogen limitation of primary production in the Dong Ho estuary.

In the context of water quality management, the ability of the estuary to process and potentially remove excess nitrogen is also important to consider. As noted earlier, the efficiency of denitrification in removing nitrogen in Dong Ho estuary was different in each zone and varied seasonally (Table 6.2). The relative efficiency of denitrification removal of DIN in the estuary was calculated based on the net balance of nitrogen fixation minus denitrification [nfix-denit] derived in the LOICZ model; DIN fluxes between sediments and water column; fluxes between zones; and denitrification rates measured by *in-situ* incubations. As presented in Table 6.2 below, the estimations show that denitrification processes were more effective in the dry season compared to the wet season, and zone 3 played the most significant role in removing nitrogen from the estuary overall. It has been demonstrated elsewhere that an ecosystem with longer exchange times can retain materials longer and, thus, is likely to process accumulating materials over a longer time frame leading to increased rates in processes such as denitrification (Smith et al., 2005, Joye and Andersen, 2008). This concurs with the estimates for denitrification efficiency in Dong Ho estuary. Whilst deposition is highest in the estuary during the wet season, water residence times are much longer in the dry season allowing for extended process times. Further, as demonstrated by the results from zone 3, areas with the highest residence times show the highest levels of process effect (Table 6.2).

Despite the above observations however, the percentage of nitrogen removed by denitrification in the Dong Ho estuary was quite low compared to other estuarine systems (Joye and Andersen, 2008, Saunders and Kalff, 2001). As discussed in the previous chapter, there are a number of factors influencing the denitrification process including organic carbon supply and quality, the availability of NO_x and processes supplying it, and suitable Redox conditions that allow denitrification to occur. As shown in Chapter 5 the levels of available organic carbon and DIN are sufficient to support denitrification but decreasing levels of dissolved oxygen in the water column in some zones may indicate that sediment Redox conditions may not be adequate for maximum denitrification rates to be achieved; and may play a role in the different denitrification rates observed. It is noted that denitrification rates in some zones in Dong Ho estuary were in the higher range compared to other estuarine systems, but the collective efficiency of denitrification across zones was low.

Table 6.2: The efficiency of denitrification in removing nitrogen in Dong Ho estuary (%)

	Compartment 1 (Zone 1)	Compartment 2 (Zone 2)	Compartment 3 (Zone 3)	Whole system
Wet season	1.75	4.76	8.69	5.29
Dry season	5.49	12.81	28.39	16.43

6.4.2. Considering different scenarios using LOICZ models

6.4.2.1. Flood conditions

As mentioned previously, the Dong Ho estuary can be subject to flood events when freshwater inputs totally dominate the estuary beyond the more typical rainfall and input conditions that commonly predominate in the wet season. In order to understand the systems performance in terms of nutrient fluxes under such flood conditions, the LOICZ modelling approach was used to consider the implications of these increased flows into the system. To do this, the model used the salinity, DIN, DIP data collected in the stronger of the wet seasons observed during the study period (August 2015) and adjusted river flows according to estimates made by DARD (DARD, 2014). In view of the information provided by local managers and agencies (DARD, 2014), it was assumed that due to the larger volumes of freshwater entering the estuary that the water column would be mixed and, thus, the LOICZ models should be comprised of a single water layer. In flood condition, the exchange time was estimated from LOICZ models to be approximately 1.5 days in Dong Ho estuary.

Taking this approach, the LOICZ box models for the flood period showed that DIP was again accumulated at 180.21 mol per day (5.58 kg d^{-1}) in the system but at a much lower rate; presumably due to the flushing effect of the higher flows. Further, DIN was also exported to the sea at 90399.95 mol per day (1265.60 kg d^{-1}). This contrasts with the net accumulation of DIN and DIP in the estuary determined for the average wet season conditions as modelled above. Interestingly, in the flood scenario model Dong Ho estuary retains less DIP and transports more DIN to the Western Sea which would further exacerbate the limitation on productivity due to low DIP stocks in the system.

It should also be restated that Dong Ho estuary is one of many flood pathways into the Western Sea from the Hau River and associated canals in the Mekong delta; the Hau River receiving significant water flows from the main Mekong River. At the same time, it is currently proposed that eleven hydropower dams be instated in the Mekong Delta in Thailand, Lao and such that flows to the Mekong and into Hau River will be substantially altered (Wölcke et al., 2016). In this light, flood events that might flush the Dong Ho estuary are likely to decrease and the level of materials accumulation increase as flows are reduced. In addition, the positive aspects derived from floods of the Mekong Delta in terms of generally improving water quality by flushing acid sulfate soils and agricultural pesticides may also be lost (Wölcke et al., 2016).

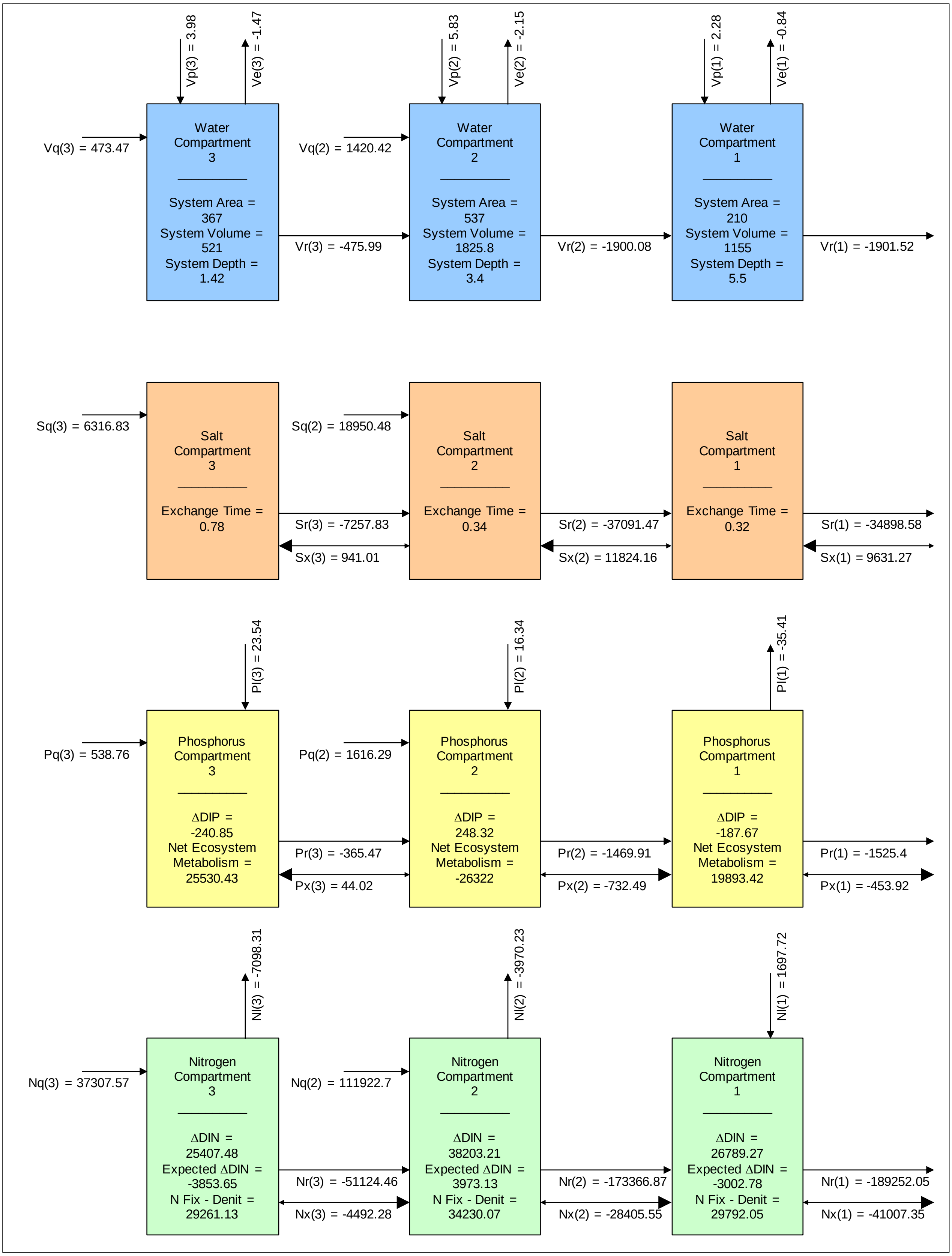


Figure 6.8: LOICZ box models for water and salt budgets, N and P budgets under a flood scenario for Dong Ho estuary

6.4.2.2. Estuary Development Scenario

According to the most recent development strategy for Dong Ho estuary and adjacent land use (DARD, 2014), it is expected that the population of Ha Tien town and the surrounding area will increase due to urban growth and tourism development. Simultaneously, provincial and national government strategies are working to increase the intensity of agriculture and aquaculture production in the catchment of the estuary to meet national goals for food production (Carter, 2012a, DARD, 2014). As a result, increasing population living along the estuary is likely to cause an increase in untreated domestic wastewater being discharged directly into the estuary ecosystem. The field observation of drains and drainage patterns in pilot study and field work campaigns showed that eleven large drains currently discharge untreated sewage into the estuary along Ha Tien town, and smaller communities along the estuary dump their waste water directly into the waterways. In addition, it is already recognised by government that existing rice farming and aquaculture in the catchment supplying Dong Ho estuary across both Kien Giang and An Giang provinces already deliver nutrients and materials to the estuary. Consequently, any increase in the intensity of these activities is likely to deliver higher inputs of nutrients and other materials than currently occurs.

In this context, based on the changes proposed in the current development plan for the area (DARD, 2014), this study modelled a scenario for the development plan in Dong Ho estuary to examine the potential ramifications of increased N and P loading into the system. Based on the predictions for Dong Ho's catchment development strategy (Carter, 2012a, DARD, 2014), a conservative increase of 25% is proposed for N and P entering the estuary annually over the next 5 years. Using this, the LOICZ model used the model conditions as for the baseline models developed at the start of this chapter and drawn from results of field work (section 4.3.4 and 6.3.2). Based on the initial modelling and field observations, it was concluded that the highest loading of materials occurred in the wet season and the highest potential of direct removal, flushing of these inputs would also occur at this time. Therefore, a scenario of increasing N & P loading in wet season was modelled to illustrate the maximum condition that Dong Ho estuarine ecosystem could be subject to in the foreseeable future.

Potential P and N budgets for Dong Ho estuary in the wet season under a development scenario are presented in figure 6.9. The model suggests that under the conditions described above, Dong Ho estuary would behave as a sink of DIN and DIP with 160919.16 mol d^{-1} DIN (2252.87 kg d^{-1}) and 2515.35 mol d^{-1} DIP (77.90 kg d^{-1}) being retained in the system. In this scenario, the denitrification efficiency in removing the increased nitrogen load into the system is likely to be reduced to only 4.52% (with 1.4% in compartment 1, 4.7% in compartment 2, 7.1% in compartment 3) if denitrification rates were maintained at the same levels as observed in the current study. As suggested earlier, aspects such as organic carbon loads and DIN stocks can significantly influence denitrification rates and so enhanced organic inputs may have a negative or positive effect on this process depending on other concomitant influences (Seitzinger, 1988, Murray and Parslow, 1999, Arango et al., 2007, Myrstener et al., 2016, Dodla et al., 2008). Further study is necessary to understand what is most likely for the Dong Ho estuary situation.

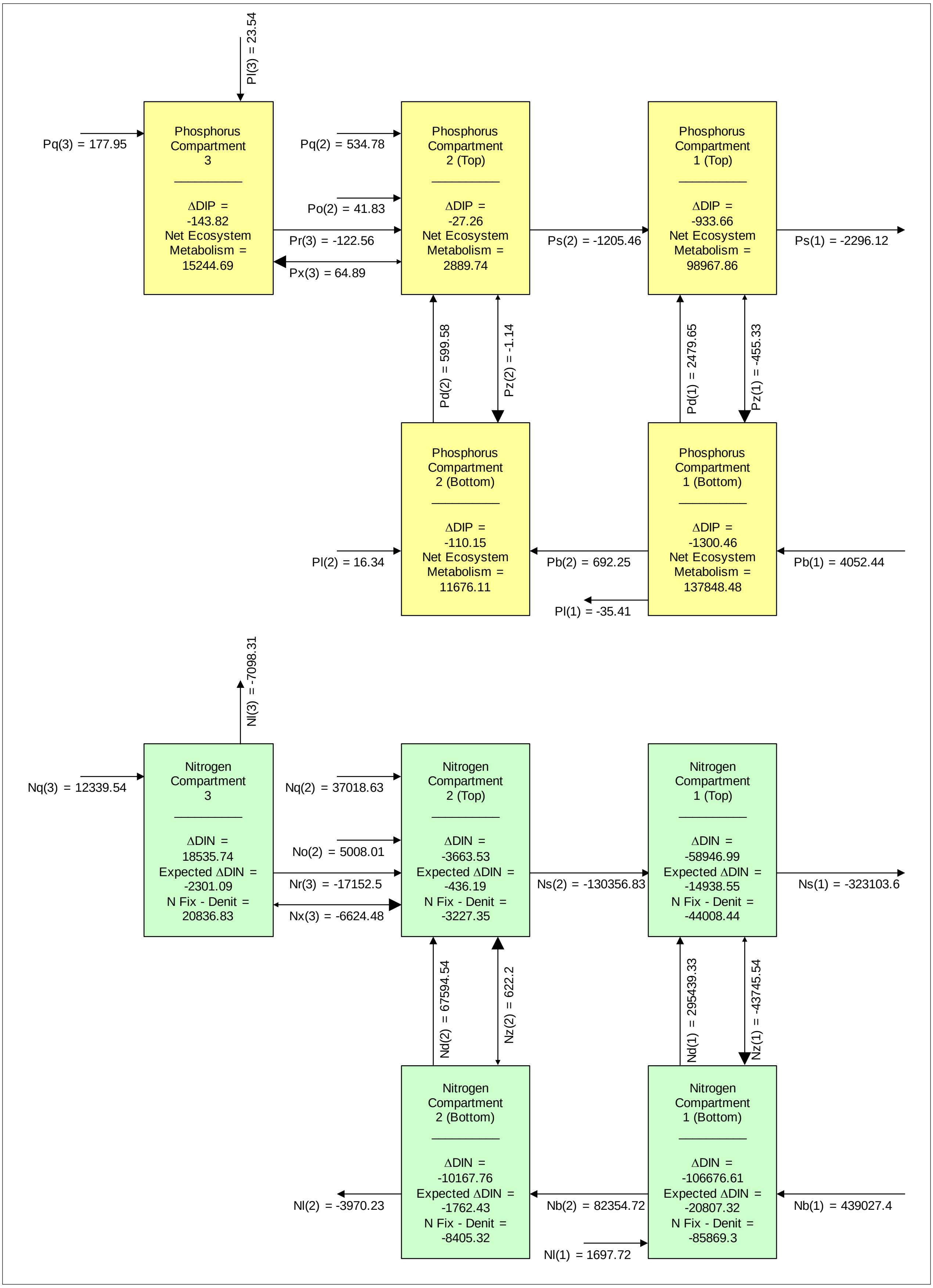


Figure 6.9: Potential P and N budgets scenario for the Dong Ho estuary in the wet season as proposed plan in the future

6.4.3. Implications for management and monitoring

6.4.3.1. Implications for management

The nutrient budgets from the LOICZ modelling estimated the quantity of nutrient inputs, exports and internal stores in Dong Ho estuary. Accordingly, they provide critical information relevant for the management of human activities that may influence ecosystem performance and also suggests potential indicators for assessment of impacts from anthropogenic nutrient discharges from adjacent land use. The relative importance of various anthropogenic nutrient inputs varies seasonally; especially with regard to the intensity of agriculture, aquaculture. Population increase is also occurring and is further likely to exacerbate issues with nutrient loads to the estuary. As shown earlier, freshwater inputs in the dry season are very limited and Dong Ho estuary accumulates 0.01 kg/ha/day phosphorus and exports 0.2 kg/ha/day nitrogen to the sea. By comparison, in the wet season, nutrient loading into Dong Ho is much higher and the system accumulated both phosphorus and nitrogen at the higher rates of 0.56 kg/ha/day and 15.96 kg/ha/day respectively. Further, scenario modelling indicates that during flood events, despite large freshwater flows from the estuary into the Western Sea, only nitrogen was exported by 11.36 kg/ha/day but phosphorus was still retained at 0.05 kg/ha/day. Consequently, estuarine management strategies should include seasonal variations and the different roles that estuary plays in nutrient budgets relative to aspects such as timing of discharges, total loads permitted into the system, and the potential ramifications of aspects such as the treatment and quality of waste waters entering the estuary. Moreover, in view of the Redfield ratios of materials deposited and held in the estuary the system appears to be P limited. This makes it crucial for managers to address both N and P in any discharges to the estuary to avoid eutrophication and potential algal blooms in the future (Didonato et al., 2006).

In the dry season, water exchange in Dong Ho estuary was mostly influenced by tidal exchange due to limitation of freshwater inputs from riverine flows. Nutrient concentrations and nutrient budgets in Dong Ho estuary in the dry season were in the range and similar to other estuaries in the Mekong delta and other tropical estuaries (Nguyen and Phan, 2006, Phan, 2006, Hung and Huang, 2005). Model outcomes suggest that the Dong Ho estuary ecosystems carrying capacity for N & P is currently sufficient to address loads in the dry season. However, regarding ecosystem metabolism status as measured by *in situ* incubations in the dry season, respiration rates in the system were high and in the higher end of the range compared to other estuaries globally as described in Chapter 5. This confirmed that a significant amount of carbon is being respired in Dong Ho estuary in the dry season but also raises the possible issue of oxygen depletion in bottom waters if organic carbon loads and potentially elevate respiration rates further when salinities and water residence times are high during this season.

In contrast, in the wet season, due to the large amount of freshwater inputs from the catchment and surrounding land uses, nutrient budgets in Dong Ho estuary reflected was very high stocks compared to other estuaries (Vo and Nguyen, 2012, Sebesvari et al., 2012). Further, the LOICZ model in the wet season also identified that Dong Ho estuary system retained significant amount of nitrogen and phosphorus loads into the system. Moreover, the efficiency of denitrification in the wet season was quite low with only 5.3% of total nitrogen inputs removed via this process. As a result, Dong Ho estuary can be said to have a limited capacity to remove key nutrients (N & P) in the wet season. In opposite to the wet season, as suggested by scenario LOICZ modelling, in flood events, Dong Ho estuary probably has a capacity to flush nitrogen from the system; but current infrastructure planning may limit this.

In terms of the potential influence of local development planning on ecosystem performance in Dong Ho estuary, the planning scenario model showed that locally, the system can expect increased loads from population growth, with possible seasonal peaks due to increased resident tourism. This is likely to be strongly augmented by increases in both aquaculture and rice production in the adjacent land areas surrounding the estuary. More importantly, Ha Tien is located at one of the main focal outlets of waters from the wider south-western Mekong area. As such, it receives inputs from upstream provinces such as An Giang province which is also working to increase food production. Increases in nutrient and pollutant loading caused by anthropogenic activities from remote areas will potentially significant affect Dong Ho estuarine ecosystem behaviour. The importance of an appropriate design of the floodway from An Giang province to Kien Giang province through the Vinh Te canal which directly flows into Dong Ho estuary is specifically recognised in the water management strategy of the upper Mekong delta (Alliance, 2011, Wölcke et al., 2016). Therefore, planning for conservation and development of Dong Ho estuary should be integrated and revised based on the flood and water management strategy in the upper Mekong delta in order to forecast the changes and impacts of potential nutrient loading into the Dong Ho system.

In term of the relative roles and significance of each zone or compartment, zone 3 or compartment 3 played an important role in nutrient exchange and contributed the highest nitrogen removal efficiency by denitrification process in Dong Ho estuary. However, the development plan of small entertainment island inside Dong Ho estuary which is adjacent to zone 3 and zone 2 will probably affect the hydrodynamic conditions of the estuary as well as nutrient exchange between compartments inside the estuary. It was proposed that the entertainment complex would be constructed in that small intertidal island should be reconsidered and cancelled in the master plan of Ha Tien town and Dong Ho area (DARD, 2014).

6.4.3.2. Implications for monitoring

Nutrient budgets have proven to be especially useful as evidence in identifying differences in the magnitude of various inputs in a catchment and indicating the increased nutrient loading from the land to coastal waters due to human activities over past decades (Allan and Castillo, 2007). The LOICZ model developed in this study suggested that nutrient budgets in Dong Ho estuary varied seasonally and spatially across the different zones and, accordingly, each zone functioned differently in terms of its ability to process and transform materials it received. Therefore, monitoring the ecosystem performance of Dong Ho estuary in the light of current and foreseeable anthropogenic influences requires long term data collection of nutrient budgets at the local scale as well as at larger scales across the associated catchment. For example, zone 1 played the most important role in accumulating DIN and DIP, which accounted for approximately 88% of DIP and 95% of DIN accumulation in Dong Ho estuary in the wet season. Thus, seasonal field data needs to be obtained at spatial scales and a resolution that allows managers to identify the scale at which anthropogenic loads may be having a significant effect on ecosystem performance. This becomes especially important with the pending construction of two land reclamations adjacent the mouth of Dong Ho estuary which will likely alter the hydrodynamic characteristics and nutrient exchanges inside and outside the central estuary. The sampling sites used in this study, illustrated in figure 6.10, may provide a good starting point from which a long-term monitoring program can be developed.

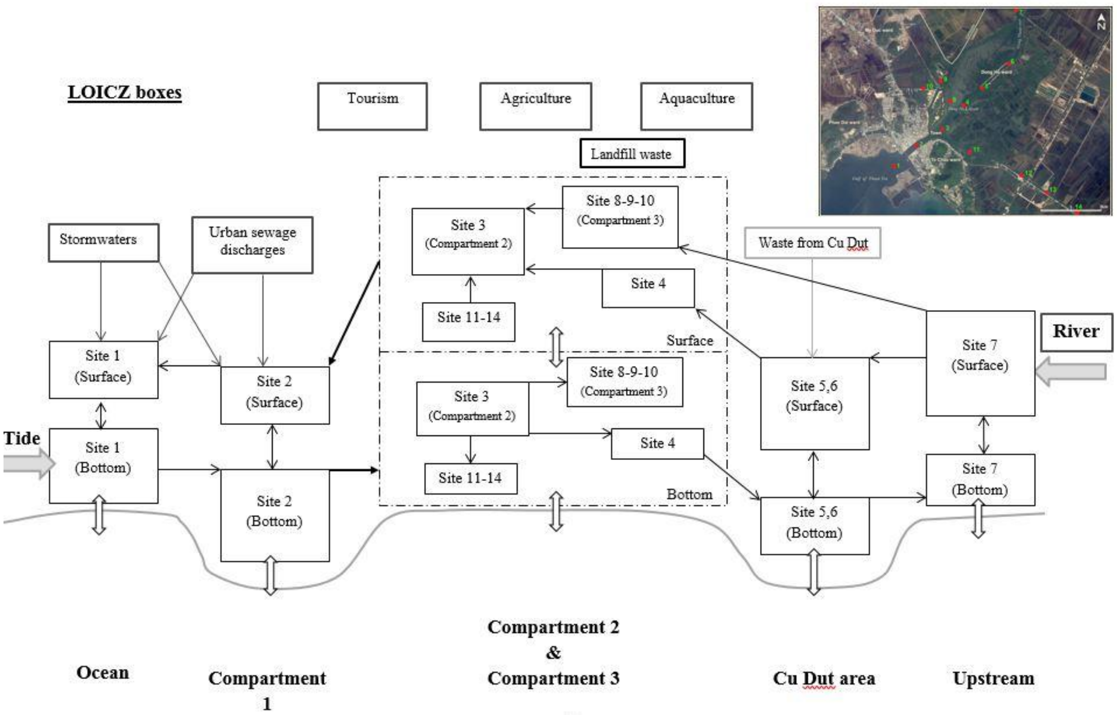


Figure 6.10: Conceptual diagram of sampling sites and main compartments in Dong Ho estuary

Agricultural activities are frequently considered the most important N inputs into rivers and coastal waters (Allan and Castillo, 2007), and a considerable organic load from the intensification of coastal aquaculture activities in Southeast Asia has created negative impacts to estuarine and coastal water ecosystem (Chua and Pauly, 1989, White et al., 2013). In the context of Dong Ho estuary, nutrient budget monitoring program needs to based on timeframe of rice and shrimp production cycles in the surrounding areas and in the wider catchment of south-western Mekong region. In addition, the effects of cumulative impact of nutrient enrichment in the system can be reduced by the implementation of regular water quality monitoring in the outputs of aquaculture and agriculture farms or adjacent canals directly received the discharge from that farms.

As discussed previously, the ecosystem metabolism of Dong Ho estuary calculated from LOICZ modelling based on DIP fluxes cannot be applied in this turbid system. Consequently, measurement of ecosystem primary production in Dong Ho estuary should be undertaken by using in situ incubations as described in Chapter 5. Furthermore, more nutrient accumulated in the system leads to higher nutrient concentrations stored in benthic sediments. The significance of sediments in internal processes and nutrient storage capacity needs to be assessed through measurements of benthic nutrient fluxes and denitrification process by in situ incubations as described in Chapter 5. The results collected from these field measurements associated with LOICZ models can provide a comprehensive understanding of ecosystem performance of Dong Ho estuary. Therefore, monitoring program should include the measurements of key biogeochemical processes including primary production, benthic nutrient fluxes and denitrification. In addition, developing a time series of rate measurements and understanding simulation model calibration and verification will support the future monitoring strategy.

6.5. Key insights

LOICZ modelling approach is a useful method for understanding Dong Ho estuary at the system level as a sink or source of nutrient. The knowledge gained from LOICZ models allow managers consider the possible future and sustainability of Dong Ho estuarine system based on the assessment of inputs and outputs of nutrients. Although it is not suitable to calculate metabolism status based on DIP fluxes due to high turbidity, LOICZ model is still valuable in term of research aim in understanding system behaviour and the current performance of key biogeochemical processes driving phosphorus and nitrogen cycling. According to LOICZ model, the Dong Ho estuary acted as a nutrient sink with an annually average of 31.6% of incoming nitrogen and 52.1% of incoming phosphorus retained within the estuary, especially the wet season significantly contributed to these amounts. In addition, higher N:P ratios relative to Redfield proportions suggested a greater overall potential for phosphorus limitation rather than nitrogen limitation of phytoplankton in Dong Ho estuarine system. Although denitrification rates in Dong Ho estuary were in the higher range compared to other estuarine system but the efficiency of denitrification was low with maximum 16.4% nitrogen removed in the total nitrogen loading in dry season and only 5.3 % removed in wet season.

Regarding to implications for management and monitoring, Dong Ho estuary behaves as a capture point for materials and nutrients from local and remote sources. Within the context of potential influence of development plan on ecosystem performance in the near future, Dong Ho estuary showed a limited capacity to remove key nutrients as nitrogen and phosphorus to the ocean or by internal denitrification process. It suggests that monitoring strategy need to cover spatial and seasonal variation to understand the whole system performance. Furthermore, planning for conservation and development of Dong Ho estuary should be integrated and revised based on the flood and water management strategy in the upper Mekong delta in order to predict the changes and impacts of potential nutrient loading from remote sources into the Dong Ho system.

CHAPTER 7 - SYNTHESIS AND CONCLUSION

7.1. Background

In Southeast Asia, the impact of anthropogenic activities on estuaries includes both increased nutrient discharges and a reduced assimilation capacity for these nutrients of these ecosystems (Ramesh et al., 2012). With lower assimilation and increased discharges from sources including agricultural activities, human waste disposal, and aquaculture, anthropogenic influences are now considered to be key drivers for nitrogen and phosphorus loading in Southeast Asian coastal waters (Smith et al., 2005). In this context, Dong Ho estuary was chosen as a case study located at the south-western edge of the Mekong delta in Vietnam because it exemplifies the anthropogenic impacts and management issues facing most of the Mekong coastline and other similar areas in Vietnam. The core aim of this study was to build an understanding of the current performance of the Dong Ho estuary in terms of carbon, nitrogen and phosphorus budgets in order to better define the processes and components that might be integrated into better management strategies for Dong Ho and similar estuaries. These insights would then provide an improved basis for decision-making and environmental management under the current and foreseeable anthropogenic influences acting on these coastal ecosystems. In addition, this study also aims at potentially identifying key biogeochemical processes that might serve as more effective performance indicators.

As noted in chapter 2, Dong Ho estuary and its surrounds have been significantly influenced by the implementation of the flood drainage system to the Western Sea, and the changes in land use which include the intensification of rice production and aquaculture activities, the expansion of urban areas and tourism, and expanded land reclamation since 2005 (Nguyen, 2011, Carter, 2012a, DARD, 2014). Collectively, these activities have significantly increased the transport of materials into Dong Ho estuary from its catchment, especially during the wet season (Carter, 2012a, Nguyen, 2011). The intimate connection between the different land uses in the catchment and the Dong Ho estuary through various canals, and the number of sewer and stormwater drains along the Ha Tien town highlight both the extent of the connectivity, as well as the complexity associated with the many direct and indirect pathways through which materials enter the Dong Ho ecosystem. This connectivity virtually assures the movement of sedimentary and associated organic materials from agriculture, aquaculture, and expanding urban populations from across the south western delta area into the Dong Ho estuary, thus making it a focal point for these loads before it can potentially move outward into the Western Sea. Once entering the estuary, these external inputs are augmented by the input of domestic wastewater from Ha Tien town and To Chau area, all of which is untreated and directly discharged into the estuary (DARD, 2014).

The conceptual model presented in Figure 7.1 is an attempt to collate and summarise the various elements interacting and influencing the status and function of the Dong Ho ecosystem. This conceptual model is based on the field observations made in this study combined with insights from the literature review of Dong Ho estuary and uses the IAN symbol libraries by Courtesy of the Integration and Application Network, University of Maryland, Center for Environmental Science (University of Maryland). In addition to helping to synthesise the work conducted in this thesis, it is hoped that the model will also assist in communicating to managers the complexity associated with the interactions between Dong Ho estuary and its surrounds, as well as how important it is to take a multi-scale and multidisciplinary approach to its investigation and future management.

As discussed in the introduction and overview of the study area, this study focuses on assessing the ability of the Dong Ho estuary ecosystem to cope with some of these anthropogenic influences from the view of how this might affect the ecosystems future sustainability and performance. In this context, the main areas of investigation undertaken are reflected on the conceptual model (Figure 7.1) to demonstrate how the activities align with the issues at hand. Accordingly, the different aspects are addressed in specific sections of the thesis: (A) identifying anthropogenic factors and potential pollutant sources to the ecosystem (Chapter 2); (B) physical factors, biological factors affecting ecosystem function (Chapter 4); (C) loads of key materials into the estuary that influence carbon and nutrient stocks in the water column and benthic sediments (Chapter 4); (D) measurement of key biogeochemical processes such as primary production, internal benthic nutrient fluxes, denitrification (Chapter 5); (E) clarify if the estuary is retaining materials or simply acting as a pipeline to the sea (Chapter 6); and, (F), in view of the new understanding of system behaviour, implications for management and monitoring are suggested for environmental management strategy development and integrated planning with the aim of enhancing both human welfare and ecosystem resilience in the Dong Ho estuary (Chapter 6 and 7).

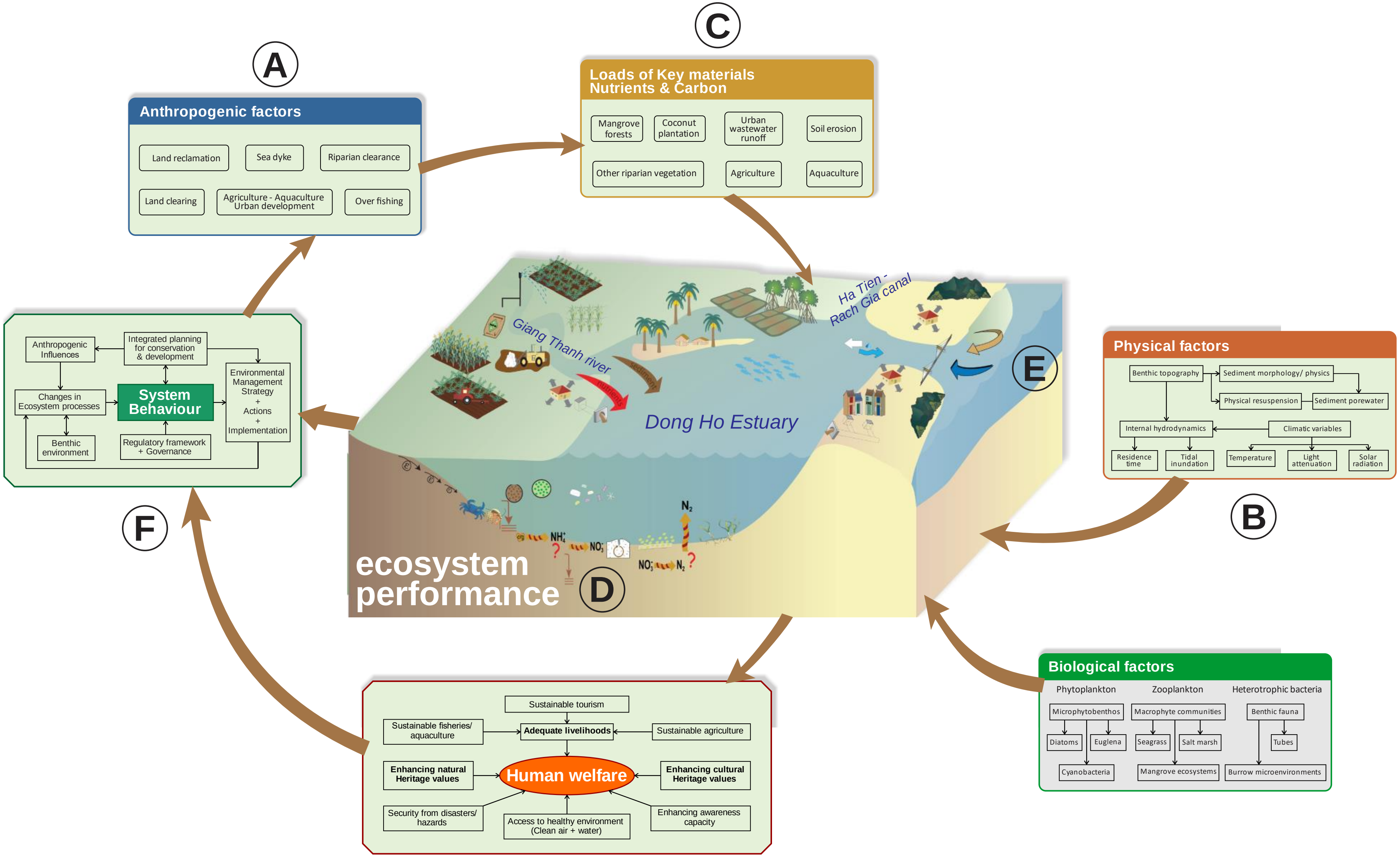


Figure 7.1: Conceptual model describing the various factors influencing ecosystem performance of the Dong Ho estuary

7.2. Synthesis and key findings

Using the broader conceptual model developed above (Figure 7.1) the thesis then worked to specify the particular target elements in each of the main areas of interest in order to produce the most appropriate and useful information relevant to management and decision-making by local agencies and stakeholders.

As noted in figure 2.7 (Chapter 2) and displayed again below, a strong emphasis of the thesis has been to build an improved understanding of ecosystem performance for Dong Ho estuary through the examination of key biogeochemical processes such as nitrogen cycling, phosphorus fluxes and carbon fixation; all of this within the context of the anthropogenic influences and the physical, chemical and biological factors acting in the ecosystem and associated waters. The structure of the approach taken was summarised initially in Figure 2.7. As indicated in Figure 7.2 below the study has achieved its primary data collection goals across the key areas identified at the outset.

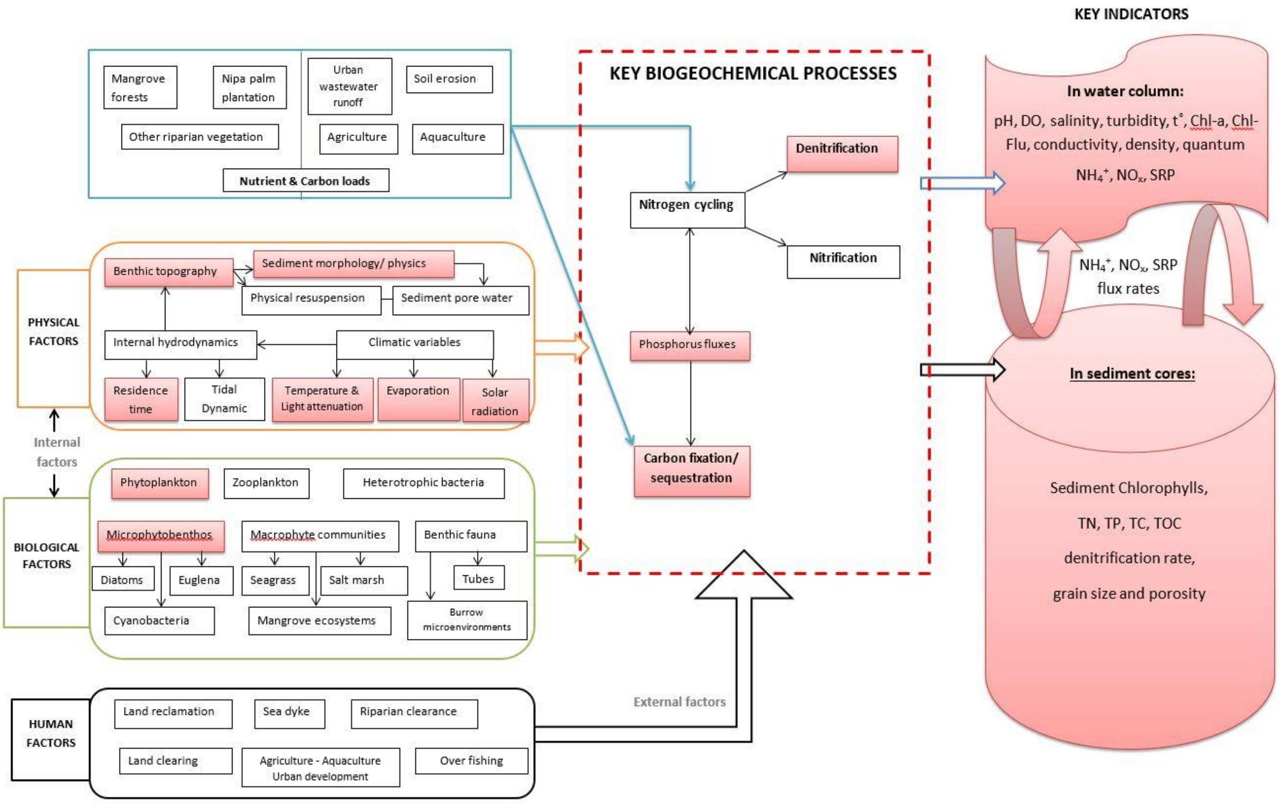


Figure 7.2: Main contributing factors influencing biogeochemical processes in Dong Ho estuary (Boxes are highlighted in red to represent components where data and information were generated as part of the thesis work)

Aligned with the logic and overall approach presented in Figures 7.1 and 7.2, the key findings of this study are presented and discussed in terms of the thesis research questions listed in Chapter 1.

7.2.1. What are the dominant biogeochemical processes influencing N & C transformation in Dong Ho estuary?

In order to identify how carbon and nitrogen are currently processed within the Dong Ho estuary, this study has quantified, for the first time, primary production rates, benthic nutrient fluxes and denitrification rates in Dong Ho estuary (Chapter 5). Due to a lack of information about baseline conditions and stocks of materials in this system, it was necessary to clarify and assess the bathymetric conditions, benthic habitats, biophysical features and nutrient stocks in the water column, as well as sediment characteristics (Chapter 4). All of these elements are central to building an ecosystem-level understanding of the estuary. This work indicated that there were spatial variations in the bathymetry and benthic characteristics of the estuary, as well as strong seasonal and spatial variations in the biophysical features and dissolved nutrient stocks in the water column.

The spatial variations in bathymetric characteristics and benthic habitats allowed for the classification of Dong Ho estuary into three representative zones for use in focusing on key biogeochemical process measurements (Figure 5.1). The area encompassing the main canal from the central estuary out to the Western sea (Zone 1) was the deepest zone (average depth of 5.5m) in the Dong Ho estuary and this directly receives sewage discharged from Ha Tien town and the urbanised To Chau area. The interaction between river flow and tidal exchange was clearly observed in this zone due to strong freshwater flows over the incoming marine waters on tidal exchanges during the wet season. Zone 2 represents the central area of Dong Ho estuary with an average depth of 3.4m and comprises as the largest area compared to other zones. This zone is subject to complex interactions between the flows of Giang Thanh river and Rach Gia - Ha Tien canal, flows from the large tidal flats in the northwest, and the tidal exchange emanating via Zone 1. The third zone, Zone 3, was the shallowest area with an average depth of 1.4m and included the largest tidal flat in the northwest of the estuary. This zone was the only zone microphytobenthos was observed. With the exception of this zone, benthic habitats in Dong Ho estuary were homogeneous bare sediment without the presence of seagrass or any macro-algal assemblages.

To assist in the zonation process and to describe the scope of the estuary, measurements of biophysical features and nutrient stocks in the water column were undertaken across the whole estuary (Figure 4.1) from Giang Thanh river, Rach Gia Ha Tien canal and outside of the estuary in the open sea. In general, biophysical features and nutrient stocks in the water column of Dong Ho estuary demonstrated strong seasonal variations. The important influence of large freshwater inputs in the wet season and the predominance of marine waters in the dry season are fundamental to this variation. In the wet season, the water column was clearly stratified with two bodies of water as freshwater from the river flowed over the more saline water which was exchanged by tidal flows. This was starkly different to conditions in the dry season; especially in the final months when sluice gates were closed in the upper of Giang Thanh river and main channels to prevent saline intrusion. In this period Dong Ho estuary becomes a hypersaline coastal lagoon with little to no freshwater inputs from the associated catchment and is dominated by marine tidal waters. This seasonal difference in stratification of the water column was demonstrated by vertical profiles of salinity in the wet and dry season (section 4.3.3.2). This seasonal variation strongly influenced the nitrogen and phosphorus exchange in Dong Ho estuary, which will be discussed later.

Primary production rates were measured by using *in situ* incubations of sediment cores to estimate rates of dissolved oxygen (DO) flux within the water column and between the benthos and water column. This showed that benthic and pelagic DO fluxes were negative with the sediments and water column taking up DO in both dark and light condition in all zones. Thus, high respiration rates in the water column and benthos exceeded gross primary production, which indicated that Dong Ho estuary is a predominantly heterotrophic ecosystem. In a heterotrophic system, organic matter consumption exceeds primary production and can lead to low oxygen concentrations in the water column (Gazeau et al., 2005). Notably, the level of DO in the water column of Dong Ho estuary was generally low compared to other estuaries, especially in the dry season (Hart et al., 2001, Wilbers et al., 2014). Most sampling sites in the dry season showed very low DO toward the benthos with average values ranging between 3-4 mg/l (section 4.3.3.4). Also, despite high nutrient concentrations in the water column, Dong Ho estuary had lower primary production compared to other tropical and temperate estuaries (section 5.4.1) (Eyre et al., 2011b, Caffrey et al., 2014). The annual gross primary production (GPP) rate in Dong Ho estuary was 298 g C /m^2/year and the benthos contributed 56.3%.

As presented in Chapter 4, in Dong Ho estuary, water column nutrient concentrations in the wet season were quite high while in the dry season they were similar to other estuaries in lower Mekong basin (Sebesvari et al., 2012, Chea et al., 2016). Nutrient concentrations varied seasonally and temporally with the highest concentrations observed in the wet season and associated with ebb tide; indicating the influence of nutrient enriched waters entering from upstream of the estuary. Shrimp and rice farming production cycles in the catchment of Dong Ho estuary and Mekong Delta have been identified elsewhere as suppliers of nutrients and other pollutants in the Mekong delta system (Clausen, 2015, Nhan et al., 2007, Vo and Nguyen, 2012), so the observed nutrient levels support this suggestion. In the wet season, nutrient inputs from Giang Thanh river and Rach Gia Ha Tien canal dominated water quality in Dong Ho estuary and led to the concentrations of NH_4^+ and PO_4^{3-} in the wet season being ten times higher than observed in the dry season (section 4.3.4). This further supports the conclusion that nutrient loads are much higher in the wet season and are likely driven by catchment inputs from both local and remote areas. By comparison, in the dry season when catchment inputs are essentially zero, local inputs from Ha Tien town and adjacent land uses play a more important role in influencing nutrient stocks in Dong Ho estuary.

In view of the nutrient stocks observed in the water column and sediments (section 4.3.4 and 4.3.5), the exchange of nutrients between the benthos and water column was then assessed using core incubations (section 5.3.2). A comparison with other estuarine and marine studies suggests that the benthic nutrient flux rates in Dong Ho estuary were in the highest range in the wet season and in the mid range in the dry season (Jenkins, 2005, Hanington et al., 2016, Burford et al., 2008). In the wet season, NH_4^+, NO_x fluxes in Dong Ho estuary were similar to those reported for other estuaries and coastal lagoons heavily impacted by anthropogenic activities (Jenkins, 2005, Burford et al., 2008, Pérez-Villalona et al., 2015). However, PO_4^{3-} fluxes in Dong Ho estuary were lower compared to those systems and may indicate that P is a limiting nutrient in the Dong Ho ecosystem. In view of the high fluxes of DIN observed and the similarity to other impacted estuaries, it is suggested that the internal nitrogen processing in Dong Ho estuary are currently nearing its assimilation capacity while the system is likely to be P limited.

Benthic nutrient fluxes are important pathways to understand which biogeochemical processes dominate in sediments. These measurements are particular importance for the management of excess nutrients and internal nutrient cycling in the ecosystem. In the wet season, NO_x fluxes in all sampling sites showed an uptake by the benthos in both dark and light incubations. This suggested that denitrification process were potentially high in the estuary but the observed variability in fluxes between sites and seasons suggested that denitrification and nitrification rates across the estuary may similarly vary with site and season.

The average measures of net N_2 release via denitrification calculated in Dong Ho estuary range from 210.5 - 1150.1 µmol N_2-N.m^{-2}.h^{-1}, which are at the higher end of the range previously recorded in other coastal and estuarine sediments in both tropical and sub-tropical systems (Joye and Andersen, 2008, Seitzinger, 1990, Steingruber et al., 2001, Pérez-Villalona et al., 2015). In both seasons, denitrification coupled to nitrification (Dn) was predominant compared to denitrification based on nitrate from water column (Dw). This indicates the significance of benthic processes and conditions in underpinning the relative performance and distribution of the denitrification process. From a management perspective, this means that inputs to the benthos, such as organic carbon and bound nutrients from sewage or other waste waters, must be considered relative to how it might effect this key process.

Despite the relatively high rates of denitrification, the dynamics of the observed levels of NO_x also suggest that other processes such as the dissimilatory nitrate reduction to ammonium (DNRA) may also be acting on the DIN stocks. Zone 2 and zone 3 in Dong Ho estuary showed different stories compared to zone 1 in terms of biogeochemical processes influencing DIN stocks. For example, based on the benthic nutrient flux rates, it suggested that in zone 1, in both seasons, DNRA process were significant in sediments due to an uptake of NO_x beyond that processed through denitrification, and a substantial release of NH_4^+. The denitrification rate in zone 1 was also the lowest compared to other zones. By comparison, in the dry season, although NO_x was released from sediments in zone 2 and zone 3, denitrification rates were higher than zone 1 which showed the higher influx of NO_x into sediments. In view of these observations, it is proposed that the nitrification process in sediments was very significant in zone 2 and zone 3 and generated enough NO_x to supply for denitrification process. This suggestion is further supported by a high rate of NH_4^+ flux into sediments at the same sites which would supply the observed nitrification in both zones. On the other aspect, processes such as DNRA and anammox have been shown elsewhere to play varying roles in controlling benthic DIN fluxes and processing (Dalsgaard et al., 2005, Devol, 2008, Dong et al., 2011). Whilst their role in Dong Ho estuary is still unclear, the observed DIN processing warrants an investigation of their respective roles. It will require future study about another processes of nitrogen cycling such as DNRA, anammox and nitrification to fully understand the nitrogen dynamics in Dong Ho estuary.

7.2.2. The relative significance of the observed N & C cycling for overall system performance in Dong Ho estuary

Based on the biogeochemical process measurements (Chapter 5) and the LOICZ modelling approach (Chapter 6), several insights for overall system performance in the Dong Ho estuary were gained.

First, system metabolism and performance of Dong Ho estuary varied seasonally and spatially across the different zones. Primary production and respiration rates varied between the wet and dry seasons. The mean GPP of the overall ecosystem in the wet season was 45.5 ± 2.3 mmolC/m^2/day while in the dry season, overall ecosystem GPP was 90.6 ± 81 mmolC/m^2/day. Primary production in Dong Ho estuary was likely light limited due to high turbidity, particularly in the peak of wet season when high loads of suspended particular matter in freshwater flows from Giang Thanh river and connecting canals discharged into the estuary. The net pelagic production in Dong Ho estuary was estimated in this study to be -671 g C /m^2/year and is similar to the lowest range of net pelagic production recorded in recent estuarine studies (Gazeau et al., 2005, Cloern et al., 2014). This negative net ecosystem metabolism indicates that a significant amount of carbon is being respired within the Dong Ho estuary and effectively removed from the ecosystem. This view is reinforced by the results from the baseline study that indicated that the Dong Ho estuary receives high levels of organic matter from allochthonous sources in its catchment. In view of the negative ecosystem metabolism observed, the Dong Ho estuary would require this external input to meet its carbon budget.

Second, based on the data obtained, Dong Ho estuary acts as a nutrient sink with an annual average of 31.6% of incoming nitrogen and 52.1% of incoming phosphorus retained within the estuary; with the wet season significantly contributing to these amounts. In addition, higher N:P ratios relative to Redfield proportions suggests a greater overall potential for phosphorus limitation rather than nitrogen limitation to production in the Dong Ho estuary ecosystem. Therefore, based on all data collected, this study suggested both light and P limitation can be limiting factors of primary production in Dong Ho estuary. Whilst each one plays a role, the combination of both of them is important, especially given the seasonality in the system.

Third, while denitrification rates in Dong Ho estuary were in the higher range compared to other estuarine systems, the efficiency of denitrification was low with a maximum of 16.4% of the total nitrogen loading in dry season being removed, and only 5.3 % being removed in the wet season. Due to the high loads of materials suggested as entering the ecosystem, it was initially considered that denitrification might not play a significant role in mitigating the impact of excess nitrogen entering the system this way. As discussed in the previous chapter, however, the observed denitrification rates and the level of nutrient retention estimated for the estuary may suggest that this process is already being limited by prevailing conditions of higher organic carbon and total nitrogen inputs to sediments. This warrants further targeted study.

In conclusion, measurements of key biogeochemical processes such as primary production, benthic nutrient fluxes and denitrification, and modelling biogeochemical budgets by LOICZ framework demonstrated some evidence for the current ecosystem performance and carrying capacity of Dong Ho estuary. The results proved that the Dong Ho estuary is highly influenced by anthropogenic inputs from its catchment due to the materials accumulated in the system which required high DO demand for metabolism and turned the system into heterotrophic with high amount of carbon is being respired. In term of N:P, although Dong Ho estuary is being capable of removing N via denitrification but P seems to stay in the system with higher ratio. As noted that P is considering as potential limit for primary production in estuary (Wulff et al., 2011), especially it can stimulate the algal bloom and turn the system to eutrophication (Hanington et al., 2016). These scientific evidence can support the managers and decision makers in monitoring the ecosystem behaviour as well as establishing environmental management strategy to enhance ecosystem resilience of Dong Ho estuary.

7.3. Implications of the research for the Dong Ho Estuary

In terms of the information needed for modelling and management of coastal ecosystems, Turner (2000) suggests four types of database: (i) Estimations of biogeochemical fluxes in the system; (ii) simulations of dynamic processes to explore the consequences of environmental changes and forecast the future fluxes; (iii) an understanding of anthropogenic activities or effects of socio-economic changes on fluxes of nutrients and toxics and sediments; (iv) an assessment of the impacts of changes in processes and functions on human welfare (Turner, 2000). All of these information types can be supported by studying and quantifying key biogeochemical processes in coastal systems. Moreover, understanding the interactions between the coastal ecosystem processes and anthropogenic activities cannot be accomplished by only field observational studies (Turner, 2000). To be able to capture the current status and future priorities of coastal estuarine systems, monitoring of key ecosystem processes is proved by this study to supply basic information for management strategy.

In this context, this research sort to elucidate how the Dong Ho estuary is currently functioning and how the estuary is potentially being affected by the associated catchment and land uses through: (1) characterising the baseline conditions of bathymetry and benthic habitats, biophysical features of water column, current nutrient levels in water column and benthic sediment characteristics; (2) estimations of primary production rates, benthic dissolved inorganic nutrient fluxes, denitrification rates; (3) modelling nutrient fluxes in LOICZ framework.

The key findings of this research have highlighted actions that might be implemented to enhance the ecosystem and biodiversity resilience of Dong Ho estuary as follows:

7.3.1. Implications for management

Reconciling the conflicts between conservation, protection and arising of the use of the estuary is the goal of management (Wilson, 1988). In the case of Dong Ho estuary, in the light of current and foreseeable anthropogenic influences, management actions need to be considered at both local level and catchment level.

At the catchment level:

(1) Control of sediment and nutrient loading into the estuary:

As the system is retaining material inputs from its catchment such as sediments and nutrients, it is crucial to control sediment and nutrient loads into the Dong Ho estuary. One of the greatest concerns of local government at the moment is the sediment accumulation decreasing water depth and transforming Dong Ho estuary into a shallow lake (DARD, 2014). Understanding the current bathymetric conditions (see section 4.3.1) and previous studies about estuarine evolution progress (Roy, 1984, Wolanski, 2006) will provide evidence for the management strategy of sedimentation in the Dong Ho estuary in the future. In view of the foreseen sedimentation rates due to increased anthropogenic activities, and the limited freshwater inputs in the dry season, the capacity of the estuary to delivery materials into the sea is increasingly limited and will exacerbate the current situation of Dong Ho estuary. It is important to take note of this issue and potentially improve our understanding of how the changing hydrodynamics of the ecosystem will act on its ability to process the concomitant loads arriving from the catchment.

The sediment loading is also associated with increased turbidity and nutrients in the water column. The turbidity values and nutrient concentrations measured in the water column in the wet season are higher than in the dry season (Chapter 4) confirmed the significant influence of freshwater inputs from catchment. Reducing sediment loads from river inputs and stormwaters will not only decrease the turbidity and nutrients discharged but also limit the excess pesticide and fertilisers runoff from agriculture and aquaculture production. However, it is noted that with reduced turbidity can enhance the algal production due to improved light attenuation associated with high nutrient concentration. Therefore, the combined strategy needs to be considered to control both turbidity and nutrient loading into the waters of Dong Ho estuary.

Being located at one of the main focal outlets of flood waters from the wider south-western Mekong area, the Dong Ho estuary receives dissolved and particulate materials from a catchment extending into adjacent provinces such as An Giang province. In view of the current situation with nutrient processing, materials retention levels and transport through Dong Ho estuary, this connection with remote catchment demands a management strategy integrated with the flood and water management strategy for the upper Mekong delta. Accordingly, in view of the interconnected canal systems, it is essential to address the cooperation between Kien Giang province and other provinces such as An Giang in controlling sediment and nutrient loading into the Dong Ho estuary.

(2) Management strategy for seasonal variations

The key biophysical features and nutrient stocks in the water column of Dong Ho estuary highlight a pronounced difference between the dry and wet seasons (Chapter 4). These seasonal variations are also demonstrated through the results of biogeochemical process measurements (Chapter 5) which reflected the seasonal differences in ecosystem carrying capacity for nutrient and organic carbon inputs into Dong Ho estuary. For example, as illustrated in the LOICZ modelling conducted in this study, Dong Ho estuary is a net sink of nutrients in the wet season due to it is receiving large amounts of material from its catchment during high rainfall and flood events. Therefore, from a management point of view, managers need to consider appropriate management strategies for different periods to promote the water quality and ecosystem carrying capacity. Such actions might include the timing of discharges and total loads permitted into the system at different periods as well as the recognition that peak tourism populations may coincide with the period when the need for reduction in nutrient loads to the estuary are highest.

Local level considerations:

(1) Risk management for eutrophication

The Chl-a values and nutrient concentrations in the water column suggest that Dong Ho estuary is not currently within the ranges indicating it to be clearly eutrophic (Chapter 4). However, low DO concentrations and the absence of benthic flora do suggest that the ecosystem is dominated by heterotrophic processes and reflective of a potential outcome from high organic carbon and nutrient inputs (Clement et al., 2001). This requires serious consideration in view of the proposed future development and anticipated increases in pollution to the Dong Ho estuary as outlined in the 2011 development plan (Carter, 2012a). In addition, the system appears to be P limited. This makes it crucial for managers to address both N and P in any discharges to the estuary to avoid eutrophication and potential algal blooms in the future.

More importantly, extensive and intensive shrimp ponds inside and adjunct to Dong Ho estuary are strongly dependent on the water quality of the estuary for their own success. Therefore, in order to meet the demand of increasing food production from the national government (typically rice and prawn aquaculture), it is important to ensure that water quality targets used by industry and government agencies consider the threshold nutrient concentrations as well as turbidity levels entering the system from sewage or stormwater discharged. Currently, domestic wastewater and stormwater from Ha Tien town and To Chau area are discharging into Dong Ho estuary without treatment. The urgent need to build and implement the wastewater treatment plan in the area as proposed in the master plan of Ha Tien town in 2014 (DARD, 2014) and results from this study highlight the urgency with which this needs to be pursued to completion.

(2) Management strategy for different zones in the estuary

Bathymetry and benthic characteristics classified Dong Ho estuary into some main areas. The pocket of deep in the main canal from the central estuary to the Southwest sea (Zone 1) showed the highest organic carbon and total nitrogen contents in sediments compared to other areas in Dong Ho estuary indicating retention of these materials in the deeper site. The shallower central estuary (Zone 2) receives multiple inputs from both Giang Thanh river, Rach Gia Ha Tien canal and marine exchanges; which may explain the higher nutrient concentrations observed in the central estuary compared to other areas. The shallowest area (zone 3) encompassing the tidal flat in the west of estuary was the only zone with the presence of microphytobenthos (MPB) in surface sediments; which may, in part, explain why zone 3 had the lowest nutrient concentrations in both water column and sediments. MPB has been shown to influence nutrient exchange in sediments and shallow areas restricted by oscillating tidal currents and freshwater runoff (Kjerfve and Magill, 1989). In addition, zone 3 contributed the highest nitrogen removal efficiency via the denitrification process in Dong Ho estuary. Notably, however, there is a current proposal for government to construct a small island immediately next to zone 3 inside the estuary (DARD, 2014). Given its proposed size and location, the island will likely change the hydrodynamic and bathymetric conditions of the estuary substantially and, subsequently, further alter water flows and depositional processes in the ecosystem. In light of this, managers need to more closely consider the pros and cons of this construction in the context of high sedimentation in the estuary and the longer term issues arising from further reducing freshwater flows and constraining any flushing of the ecosystem in wet season conditions. This recommendation is further supported by the LOICZ models in this study which verified that the system is retaining materials from catchment inputs. So, as with the proposed island construction, the establishment of infrastructure such as land reclamation in the mouth of estuary is very important to evaluate against the ecosystems current function in order to ensure the sufficient water exchange and reduce the sedimentation process of the estuary.

7.3.2. Implications for monitoring

The key findings of this study suggest the need for monitoring ecosystem performance in Dong Ho estuary as follows:

(1) A need for continuous monitoring

Dong Ho estuary is considered and planned as an important area for tourism development of Ha Tien town and Kien Giang province (Carter, 2012b). Thus, the ecosystem performance and good water quality are very essential to attract sustainable tourism. As illustrated in Chapter 4, the biophysical features and nutrient stocks in the water column showed seasonal variations and the influence of anthropogenic activities can be clearly and quickly monitored through common indicators such as salinity, turbidity, DO, pH, chl-a, DIN, DIP concentrations. A monitoring program utilising these indicators needs to be consistent and reflect the demonstrated changes in the ecosystem in different periods including the wet season, the dry season, and flood events. The annual ecosystem health monitoring programs in Moreton Bay and Southeast Queensland’s catchment, Australia (EHMP, 2005, EHMP, 2010) are good examples for the managers of the Dong Ho estuary to consider when establishing a continuous monitoring program. In addition to the methodologies and technical aspects, these programs also provide a good initial method for feeding monitoring information back to management and key stakeholder groups; an essential element of successful monitoring programs.

In addition, regular water quality monitoring of the outputs of aquaculture and agriculture farms and the adjacent canals directly receiving the discharge from these farms is important. Controlling the quality of waste waters entering the Dong Ho estuary is a crucial task to improve the ecosystem performance and sustainability. Moreover, it is essential to advise and engage local farmers and residents living inside the estuary in Cu Dut village about water quality and its management. As primary users of these water resources, their effort in helping to minimise inputs and maximise water quality for their own use would contribute significantly to a successful management model.

(2) A need for key biogeochemical processes monitoring

This thesis aimed at potentially assessing key biogeochemical processes that might serve as indicators of performance within an environmental management context. The results from measurements of primary production, benthic nutrient fluxes and denitrification in Dong Ho estuary demonstrated that understanding these processes can provide good insight into the relative ability of an ecosystem in providing ecological services and to be able to estimate the carrying capacity of the ecosystem for certain material inputs or loads. For example, primary production measurements illustrated that Dong Ho estuary is predominantly heterotrophic year-round and a significant amount of carbon is being respired. This suggested that the system is receiving large amounts allochthonous inputs of organic carbon from its catchment and, thus, a link to sources beyond the immediate estuary. Another example is the implication of denitrification measurements. This study showed that a process like denitrification can help modulate the potential impacts of DIN loads in the system. However, in the case of Dong Ho estuary, although denitrification rates were high and provides some removal of nitrogen, the efficiency of denitrification compared to nitrogen loads is low. As discussed in chapter 5, higher organic carbon and total nitrogen content in sediments can reduce denitrification rates in Dong Ho estuary, it shows that the ecosystem processes for removing excess N may be compromised by factors such as the quality and quantity of wastewater and the materials it contains. Feeding this insight back to management provides weight to the need for water quality management strategies that can specifically target the maintenance of environmental processes that assist in delivering broader sustainability outcomes for the ecosystem and the communities that depend on it. In this light it is proposed that, where possible, processes such as denitrification be included in indicator sets for monitoring so that managers have a clearer understanding of how interventions may, or may not, be assisting the natural ability of the ecosystem to address anthropogenic inputs and outcomes.

7.4. Broader implications of the study and future work

As noted in the literature review, tropical estuaries are amongst the most exploited ecosystems in the world. However, the nutrient dynamics and biogeochemical function of tropical estuaries has not received the corresponding level of attention this might warrant, so that there continues to be limited published information on this aspect of tropical-subtropical estuarine ecosystems. In this light, the understanding of biogeochemical processes and ecosystem function developed here for the Dong Ho estuary adds to the multiscale perspective necessary for the future management of Dong Ho and similar tropical estuaries. This is especially significant in the regional context of Southeast Asian countries which are also seeking to meet the demand for greater agricultural and aquaculture production in their coastal areas, but simultaneously working to maintain critical ecosystem services and resources in these areas.

From a management perspective, this study demonstrated the importance of addressing the different land use activities in the broader catchments upstream of the coastal zone if sustainable management outcomes are to be achieved. As illustrated in the case of Dong Ho estuary, it receives and retains material inputs, such as sediments and nutrients, from local and remote sources in its catchment such that the estuaries sustainability is clearly linked to how these source areas are managed. Accordingly, as demonstrated in a number of developed country cases (Hutchings et al., 2005, Collins et al., 2007), it is crucial that management strategies reflect the multi-scale connections between sources and retention zones, as well as the human activities and policies that underpin ecosystem function across the appropriate scales and keystone locations. The ecosystem health management strategy for Moreton Bay (Australia) is a good example of this approach (EHMP, 2010), as is the Great Barrier Reef Water Quality strategy (Authority, 2010); both of which deliberately seek to address diffuse and point sources of impact on the estuary through a multi-scale and integrated set of strategies.

From an assessment and modelling perspective, this study confirmed that LOICZ modelling framework is a useful approach for understanding an estuary at the system level and allows stakeholders to estimate sink or source terms for key nutrients and materials. However, as discussed in Chapter 6, this method is not suitable for calculating ecosystem metabolism status based on DIP fluxes where an estuary is highly turbid. This observation confirms the suggestion by Gazeau et al., (2005) who also suggested this might be the case in a study on the Scheldt estuary which was similarly very turbid. In addition, the application of LOICZ modelling in this study has highlighted its limitation when applied in a system where the water column is strongly stratified such that the waters reflect two different water bodies or model compartments within sections of the estuary. In the LOICZ toolbox, only the most seaward compartment of the model allows for two layers, whilst other compartments only allow for a single layer. Accordingly, in the case of the Dong Ho estuary in the wet season, and in similar stratified estuaries containing more than one area with two water layers, further calculations are necessary in order to more accurately reflect the complexity of all of the associated salinity values and other corresponding flows when constructing mass balance estimations for water, salinity and nutrients.

Further Research

In addition to the results and insights gained in the present study, a number of aspects arose that warrant further study in order to make our understanding of the Dong Ho estuary and similar ecosystems more complete and accurate.

Nutrient Processes

As previously discussed (Chapter 5), nitrification and DNRA processes may also play a significant role in nitrogen cycling in Dong Ho estuary. Whilst knowledge on their respective involvement may not significantly alter the estimates of N mass balance in the ecosystem, studies in cold and temperate coastal ecosystems (An and Gardner, 2002, Gardner et al., 2006, Giblin et al., 2013) indicate that, in some cases, these processes can play crucial roles in mediating nitrogen availability to biological processes. Accordingly, an improved understanding of these processes in the Dong Ho nitrogen budget would augment our understanding of the pathways through which the N budget and transformations may be influenced by human inputs. In addition, the current study focused on dissolved inorganic nutrients and was logistically unable to investigate dissolved organic matter (DOM) and the associated dissolved organic forms of N and P that may play a role in the respective nutrient budgets. Again, the role of organically associated N and P has been shown to be significant in some coastal ecosystems (McGuirk Flynn, 2008), so may be an important factor in the Dong Ho ecosystem. For example, DOM concentrations can dominate the nitrogen and phosphorus pools (Torres-Valdés et al., 2009), and both dissolved organic and inorganic nutrients are important factors in primary production in estuaries (Seitzinger and Sanders, 1999, McGuirk Flynn, 2008). Consequently, the inclusion of additional measurements of concentrations and fluxes of dissolved organic nutrients would further bolster our understanding of transformation pathways and critical nutrient pools that anthropogenic inputs may be influencing. In this context, the other extension to the current knowledge set is an understanding of sediment pore water nutrient pools and their dynamics. Field conditions in the current study prevented the accurate determination of nutrient concentrations in sediment pore waters, however other studies highlight how an understanding of pore water nutrient stocks is important when assessing benthic nutrient fluxes and can reflect the influence of anthropogenic inputs on sediment biogeochemical processes (Caffrey et al., 2002, Eyre and Ferguson, 2002).

Ecosystem Modelling

In addition to the mass balance insights gained though the LOICZ modelling toolkit, other forms of modelling would also greatly assist in developing a more comprehensive understanding of Dong Ho estuaries' performance, sustainability and risks to its function. There are many types of models designed to assess nutrients and biogeochemical processes in rivers, estuaries and coastal zones (Booty, 2001). In the context of Dong Ho estuarine system, the nutrient fluxes and biogeochemical processes characterised in the current study could be further considered and used as inputs to one or more modelling approaches depending on access to tidal and hydrodynamic data. These modelling approaches could include Mike 21/3 Ecological modelling (DHI Water & Environment, 2004) or STELLA modelling package (Johnstone, 2006). The Mike 21/3 Ecological modelling platform is a numerical tool for developing 2D and 3D models to stimulate the spatial distribution of biological, physical and chemical transformation processes in coastal areas, lakes and estuaries. In the case of Dong Ho, the Mike 21/3 Eco Lab FM would be a very useful tool for evaluating the transport fate and potential influences of discharging pollutants or nutrients into the ecosystem, and would greatly improve the identification of target sources and areas of high risk in terms of ecological impact. In addition, Mike 21/3 Eco Lab can be used as a forecast system to predict the water quality and changes of the system behaviour (DHI Water & Environment, 2004) which would bolster management decision making across a range of aspects such as periods of human health risk from contaminants, and areas likely to receive different loads under various water flow and discharge scenarios. On the other hand, an understanding of the feedback processes acting within the ecosystem could also be useful to understand, so a dynamic systems modelling approach may also be advantageous to develop. One package that is widely used for this purpose is the STELLA modelling software, and this has been used in other studies to describe the dynamics of nutrient fluxes and biogeochemical processes in coastal aquatic ecosystems (Costanza and Voinov, 2001, Costanza et al., 1998, Arquitt and Johnstone, 2004).

Climate Change

In the context of climate change, Dong Ho estuary is highly vulnerable to the impacts of sea level rise and altered flood water regimes (Carter, 2012b). Assessing the feedback connections of anthropogenic impacts on ecosystem performance in Dong Ho estuary in the future needs to be developed with these potential impacts in mind. Furthermore, as noted in this study, water exchange of the Dong Ho estuary with the Western Sea is currently reduced due to limited freshwater inputs in the dry season, land reclamation in the mouth of estuary, and proposed construction plan within the estuary. Therefore, the increased use of dykes to address sea level rise in the future may further worsen this problem. Subsequently a hydrodynamic model specific to the needs of the Dong Ho estuary may help to investigate natural mechanisms to improve flush within the system.

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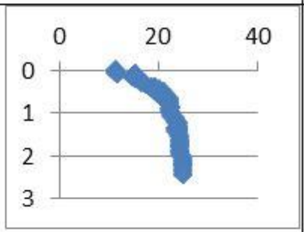
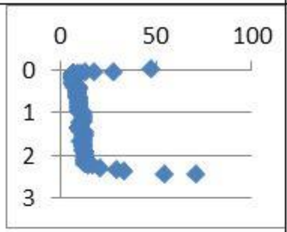
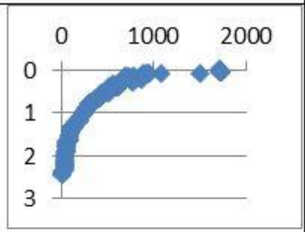
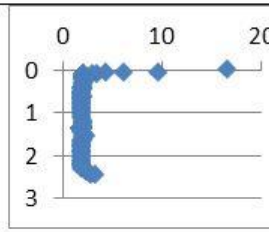
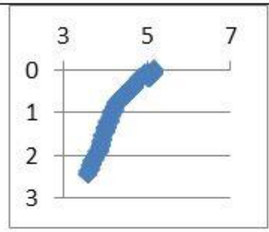
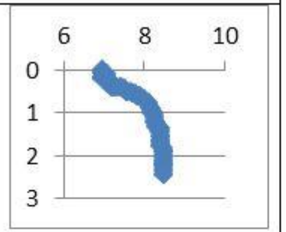
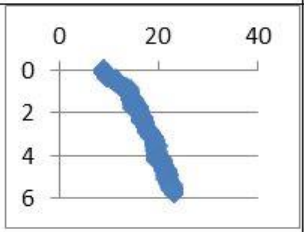
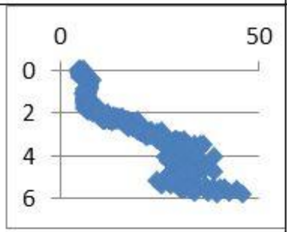
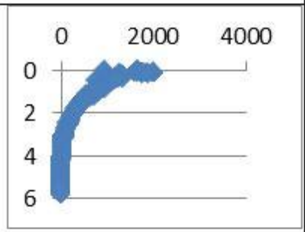
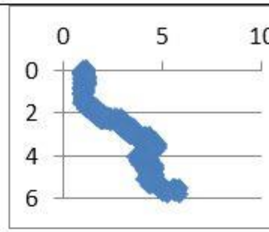
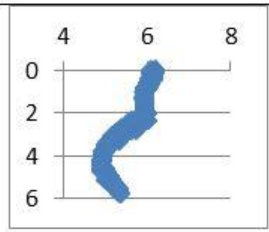
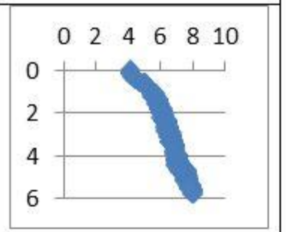
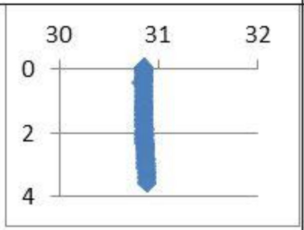
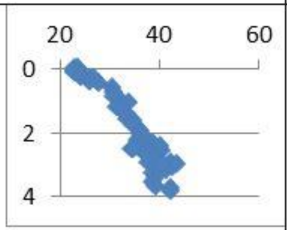
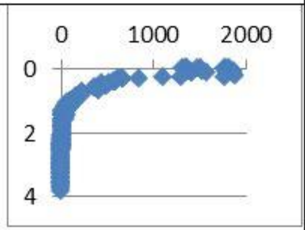
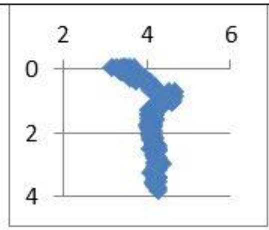
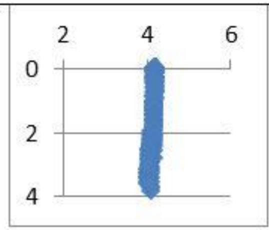
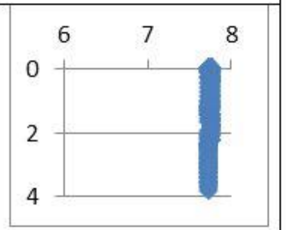
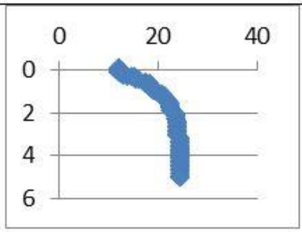
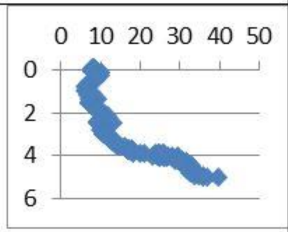
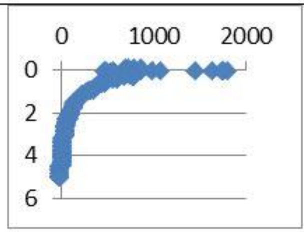
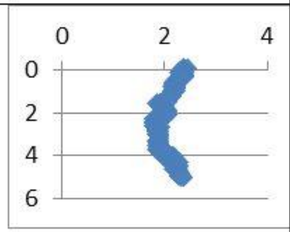
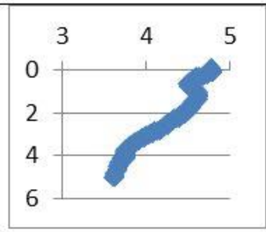
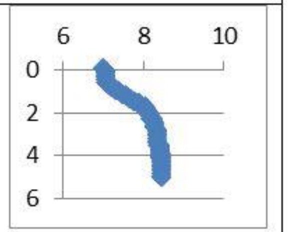
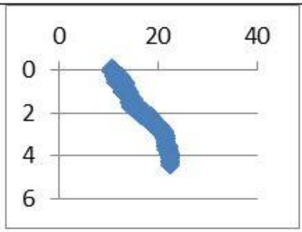
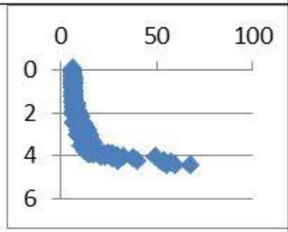
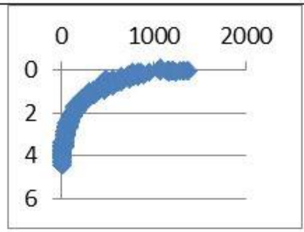
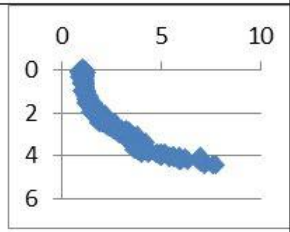
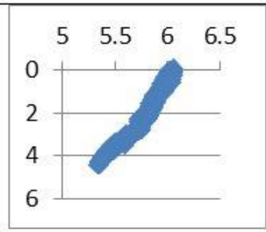
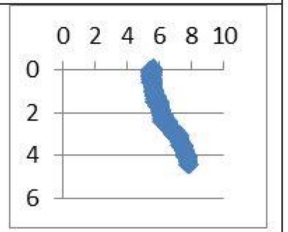
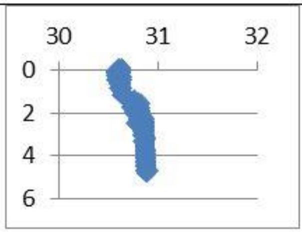
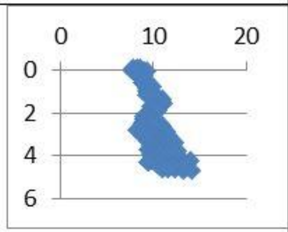
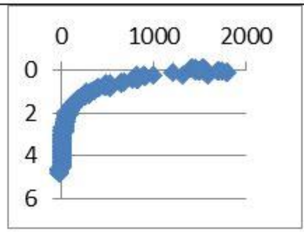
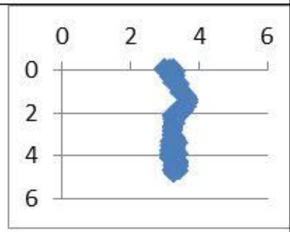
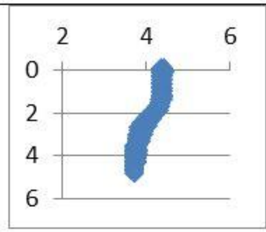
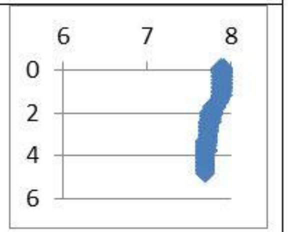
APPENDIX 1

Water quality measurements at different sampling times:

December 2014 – August 2015 – April 2016

Location 1	**Salinity (PSU)**	**Turbidity (FTU)**	**Quant. [µmol/(m2*s)]**	**Chl-a [µg/l]**	**DO (mg/l)**	**pH**
12/2014						
8/2015						
4/2016						

Location 2	**Salinity (PSU)**	**Turbidity (FTU)**	**Quant. [µmol/(m2*s)]**	**Chl-a [µg/l]**	**DO (mg/l)**	**pH**
12/2014						
8/2015						
4/2016						

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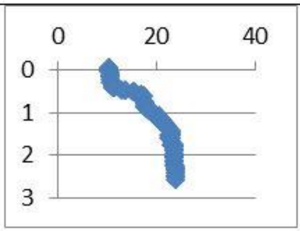
<td>
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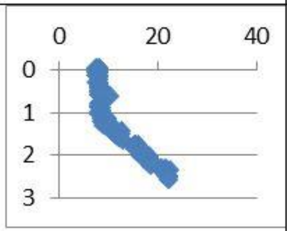
<td>
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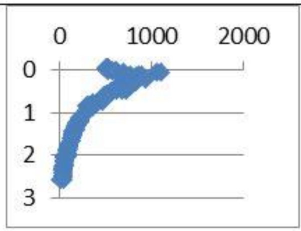
<td>
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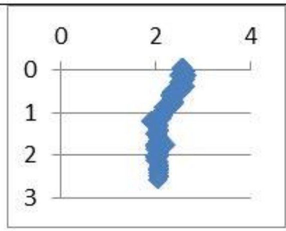
<td>
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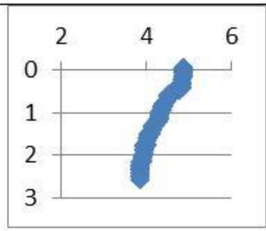
<td>
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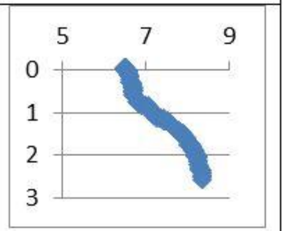
<td>
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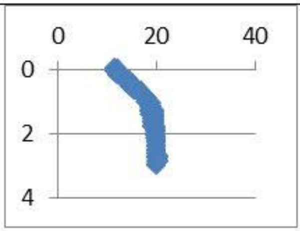
<td>
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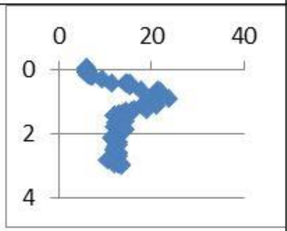
<td>
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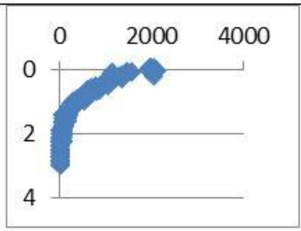
<td>
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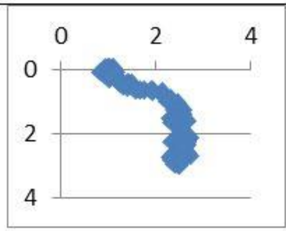
<td>
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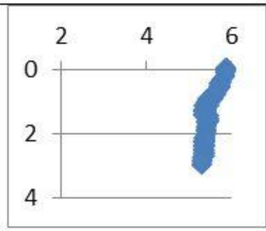
<td>
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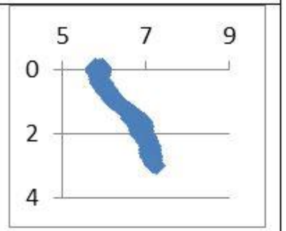
<td>
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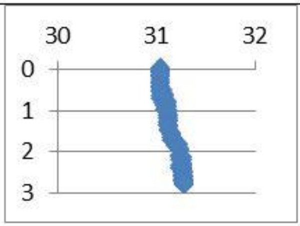
<td>
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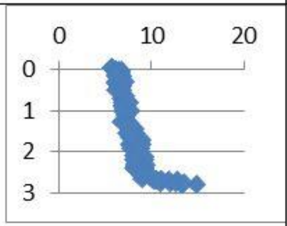
<td>
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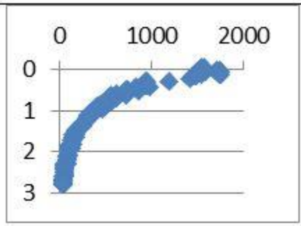
<td>
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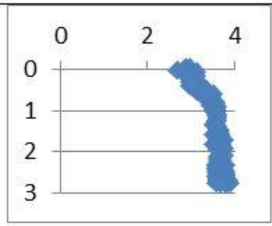
<td>
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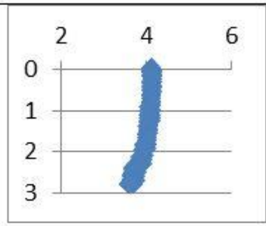
<td>
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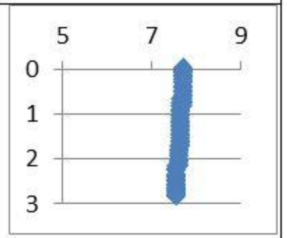
<td>
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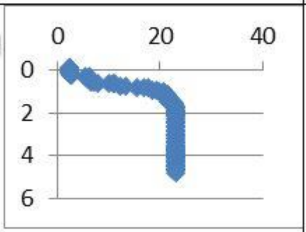
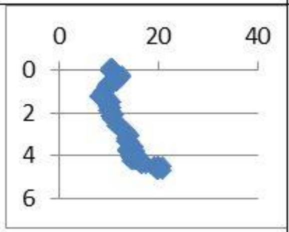
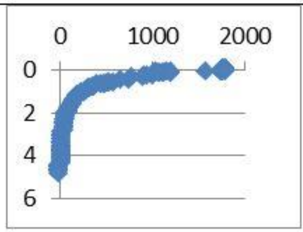
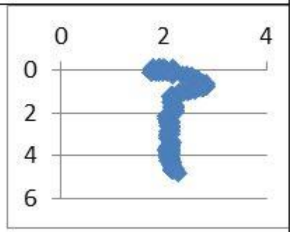
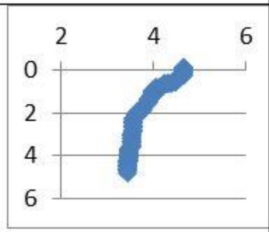
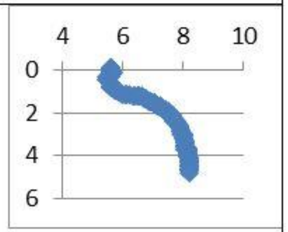
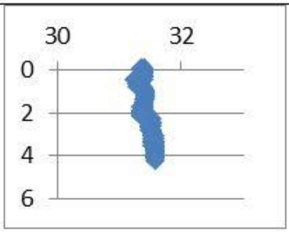
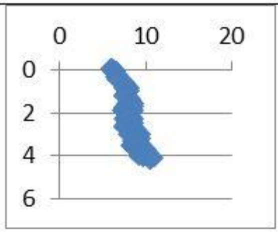
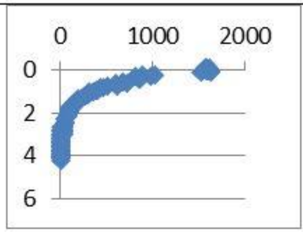
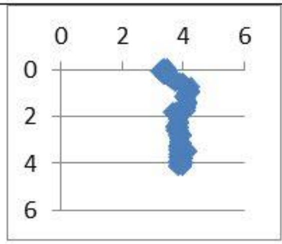
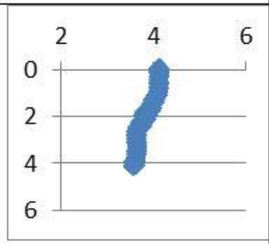
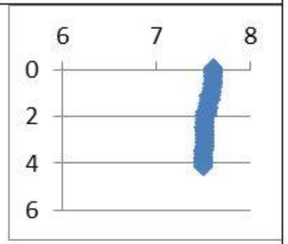
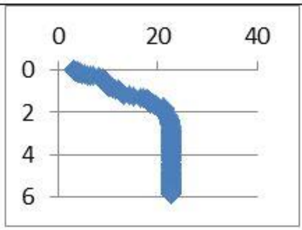
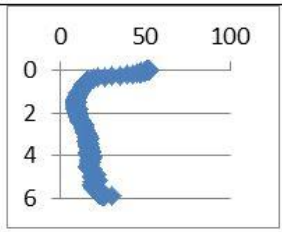
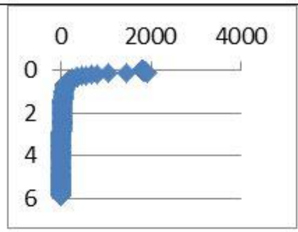
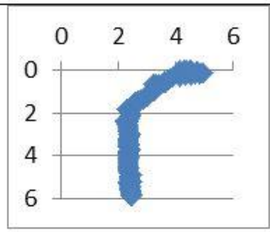
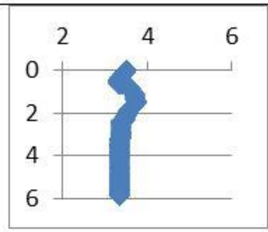
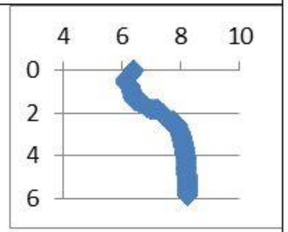
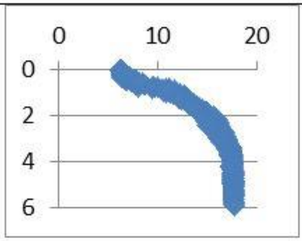
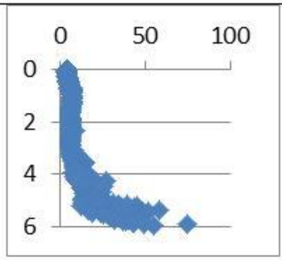
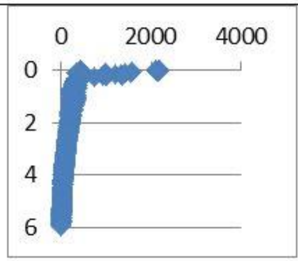
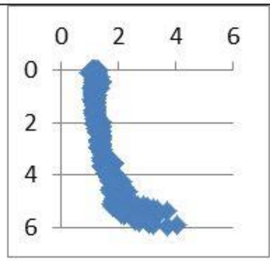
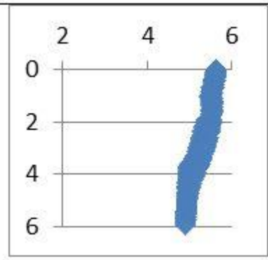
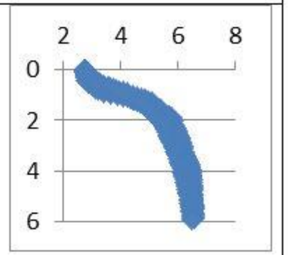
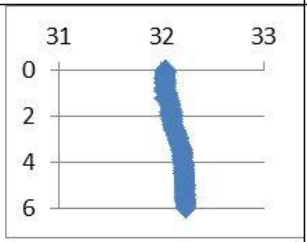
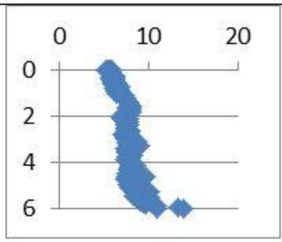
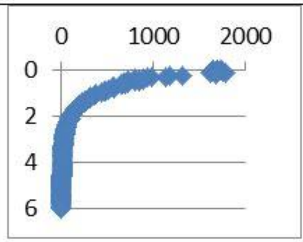
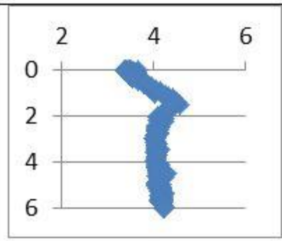
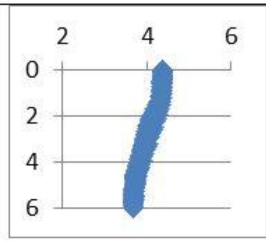
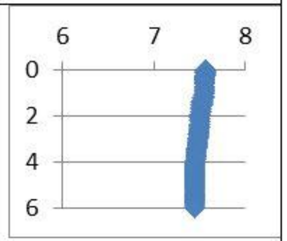
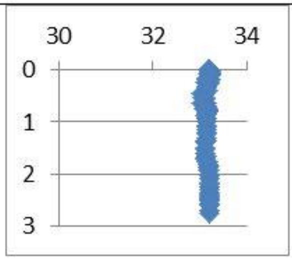
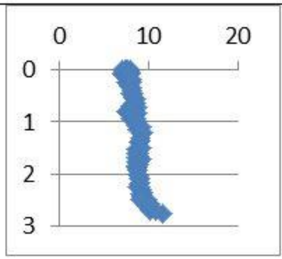
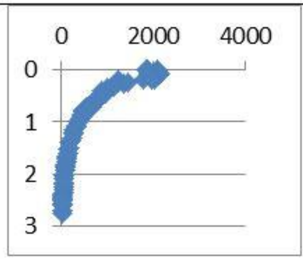
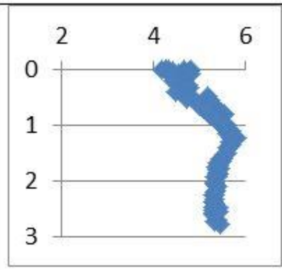
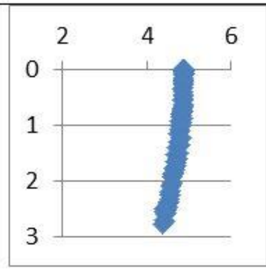
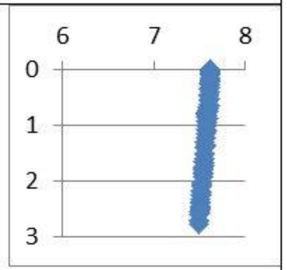
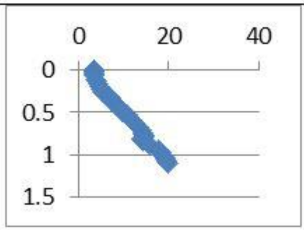
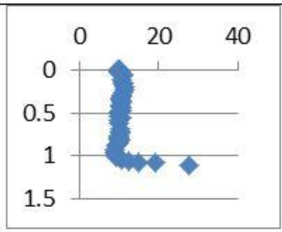
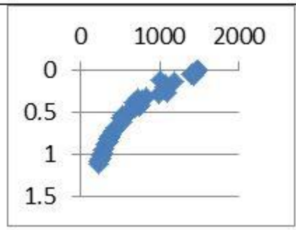
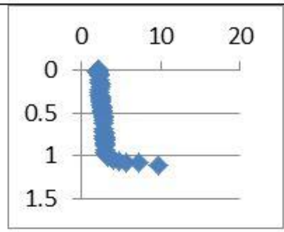
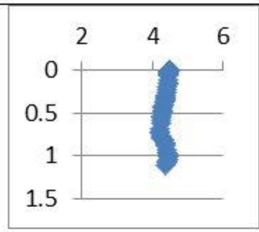
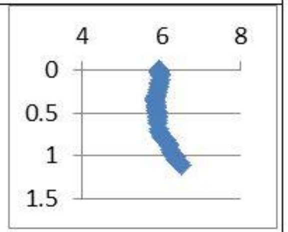
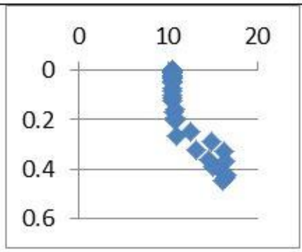
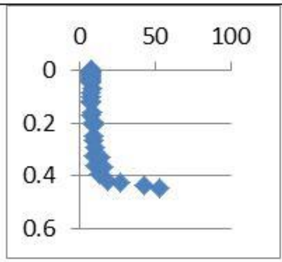
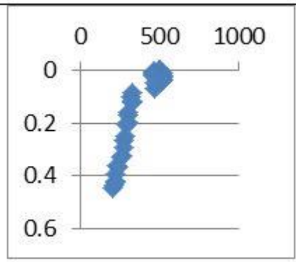
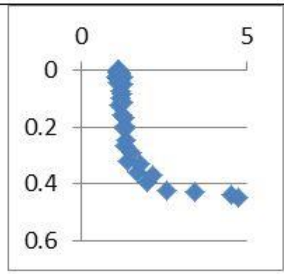
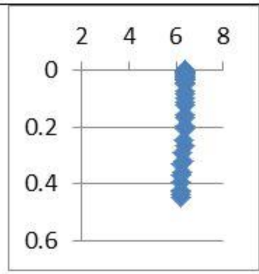
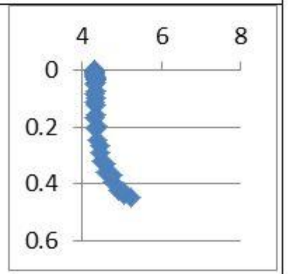
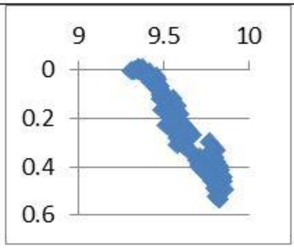
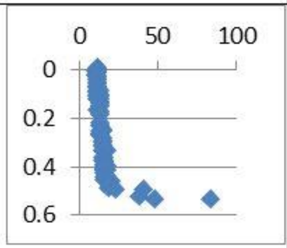
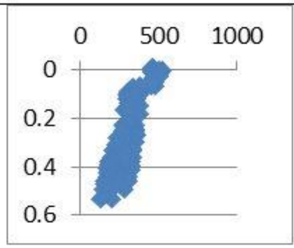
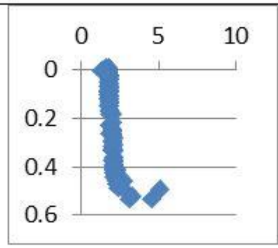
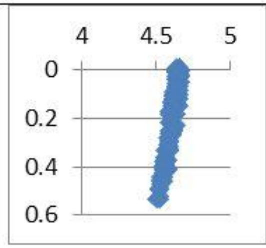
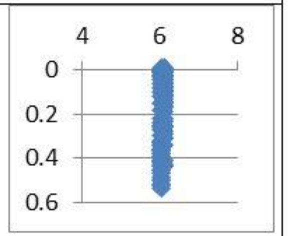
Location 4	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
12/2014						
4/2016						

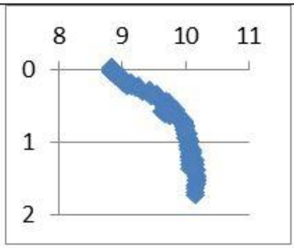
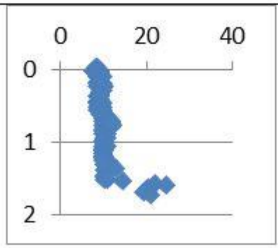
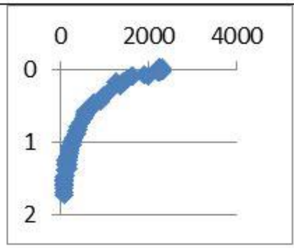
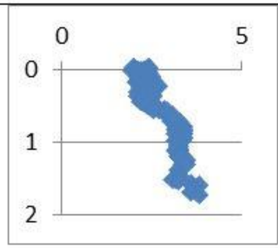
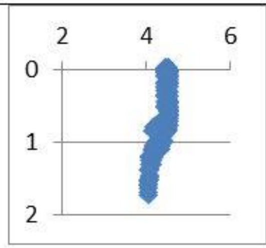
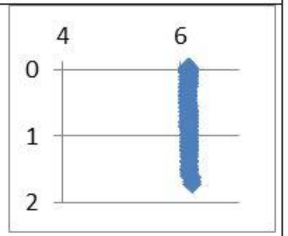
Location 5	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
12/2014						
8/2015						

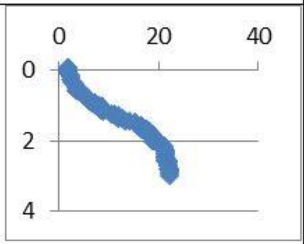
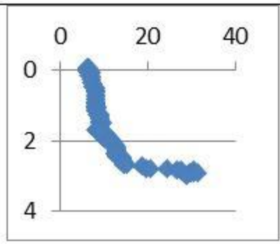
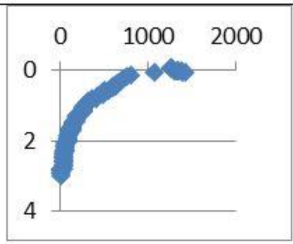
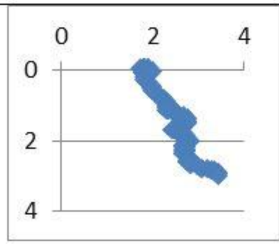
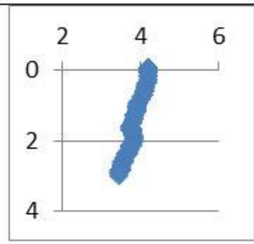
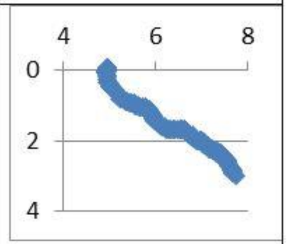
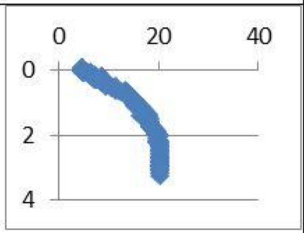
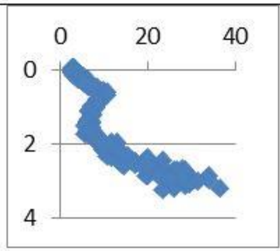
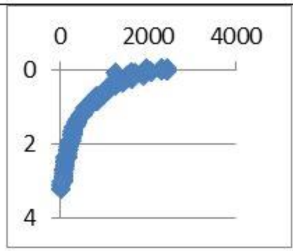
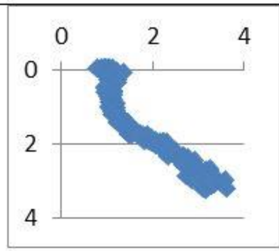
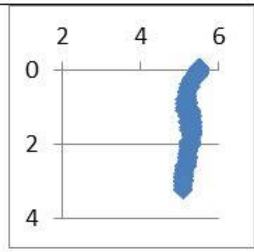
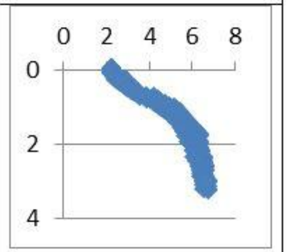
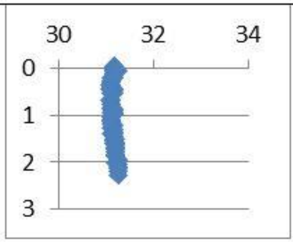
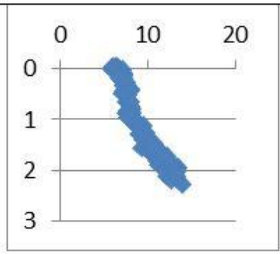
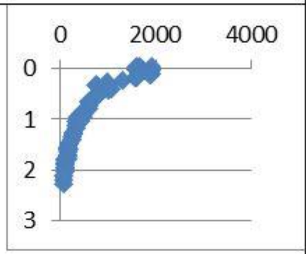
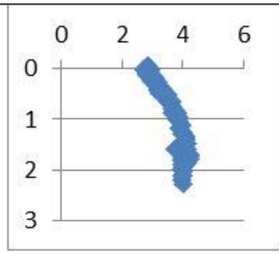
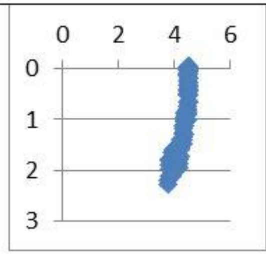
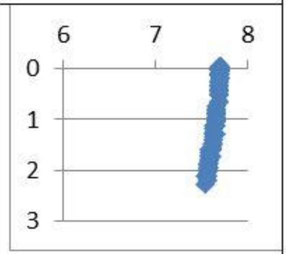
Location 6	**Salinity (PSU)**	**Turbidity (FTU)**	**Quant. [μmol/(m2*s)]**	**Chl-a [μg/l]**	**DO (mg/l)**	**pH**
4/2016						

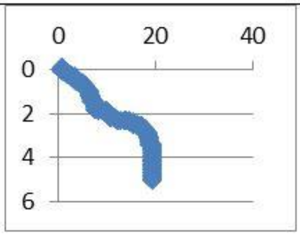
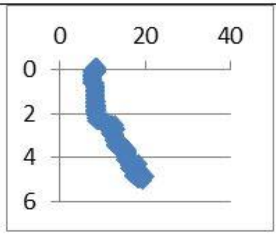
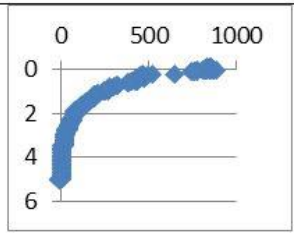
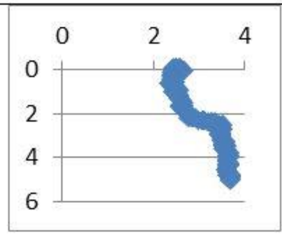
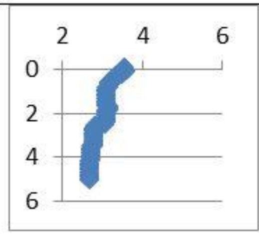
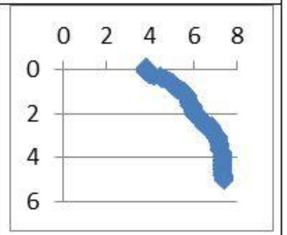
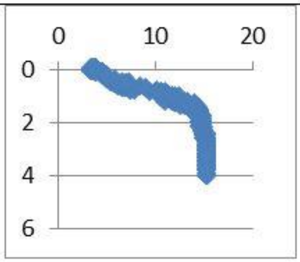
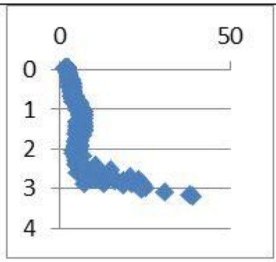
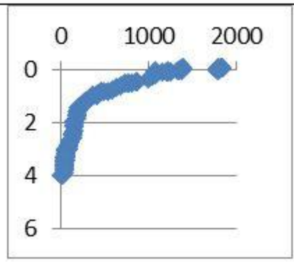
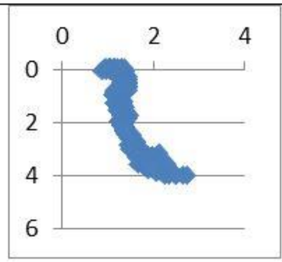
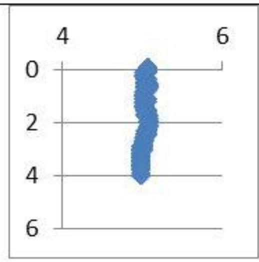
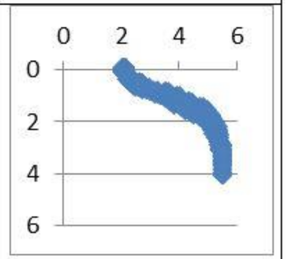
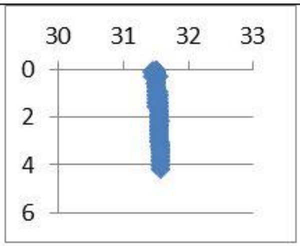
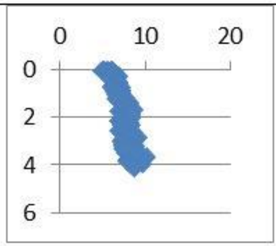
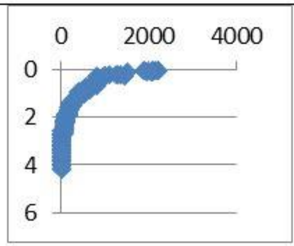
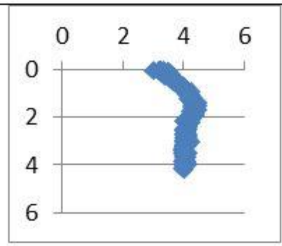
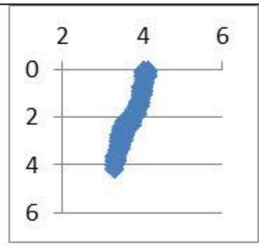
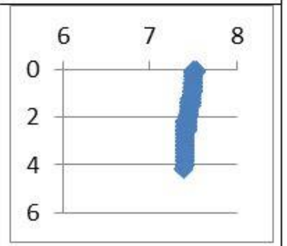
Location 7	**Salinity (PSU)**	**Turbidity (FTU)**	**Quant. [μmol/(m2*s)]**	**Chl-a [μg/l]**	**DO (mg/l)**	**pH**
4/2016						

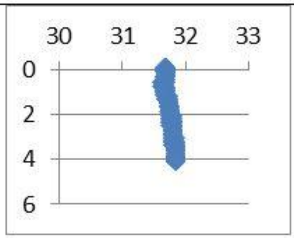
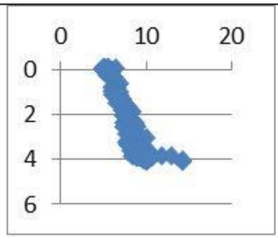
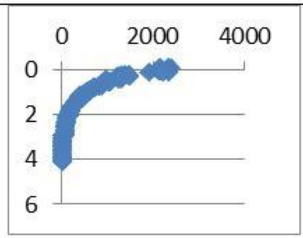
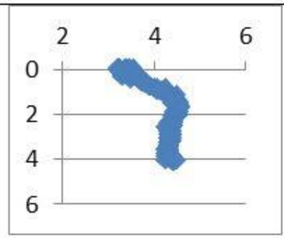
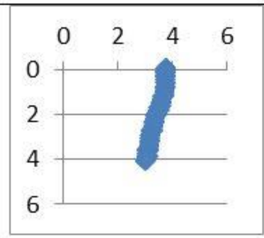
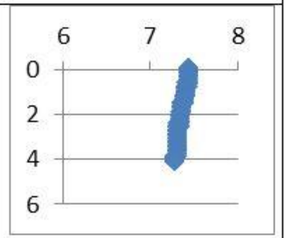
Location 8	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
12/2014						
8/2015						

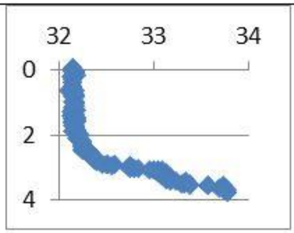
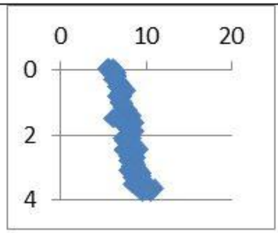
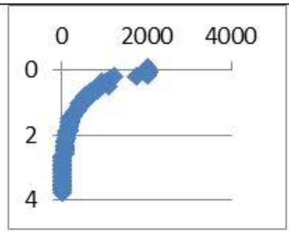
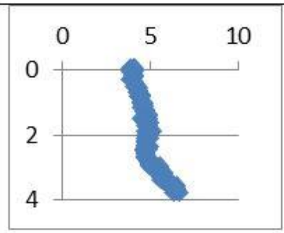
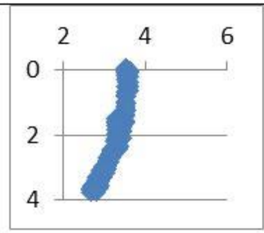
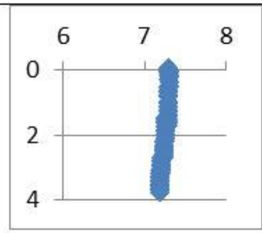
Location 9 Chart Area	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
8/2015						

Location 10	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
8/2015						

Location 11	**Salinity (PSU)**	**Turbidity (FTU)**	**Quant. [µmol/(m2*s)]**	**Chl-a [µg/l]**	**DO (mg/l)**	**pH**
12/2014						
8/2015						
4/2016						

Location 12	Salinity (PSU)	Turbidity (FTU)	Quant. [µmol/(m2*s)]	Chl-a [µg/l]	DO (mg/l)	pH
12/2014						
8/2015						
4/2016						

Location 13	Salinity (PSU)	Turbidity (FTU)	Quant. [μmol/(m2*s)]	Chl-a [μg/l]	DO (mg/l)	pH
4/2016						

Location 14	Salinity (PSU)	Turbidity (FTU)	Quant. [μmol/(m2*s)]	Chl-a [μg/l]	DO (mg/l)	pH
4/2016						

APPENDIX 2

Data from the mass balance models (nutrient concentrations, nutrient fluxes and denitrification rates in Dong Ho estuary)

				Concentrations (mmol/l)						Fluxes (mmol/m2/day)					Denitrification	
		Temp.	Salinity	NH_4^+		NO_x		PO_4^{3-}		NH_4^+	NO_x	PO_4^{3-}	DO benthic	DO pelagic	Total	Dn
				Surface	Bottom	Surface	Bottom	Surface	Bottom						**mmol/m2/day**	
Wet season (August 2015)	Zone 1	30.3	17.298	0.047	0.099	0.006	0.021	0.000	0.001	17.287	-9.202	-0.169	-10.494	-18.637	10.917	6.948
	Zone 2	30.49	17.736	0.077	0.080	0.015	0.018	0.001	0.001	-0.803	-6.591	0.030	-6.951	-10.399	16.403	12.015
	Zone 3	31.87	12.7625	0.039	0.170	0.010	0.020	0.001	0.001	-13.472	-5.869	0.064	-7.407	-8.111	16.610	6.511
Dry season (April 2016)	Zone 1	31.25	30.818	0.010	0.011	0.027	0.030	0.000	0.000	1.121	-5.234	0.013	-14.938	-28.778	12.200	6.551
	Zone 2	31.28	31.177	0.010	0.012	0.039	0.028	0.000	0.000	-0.612	0.160	0.030	-17.128	-13.260	22.118	16.556
	Zone 3	31.62	31.701	0.009	0.010	0.025	0.028	0.000	0.000	-1.597	0.373	0.013	-13.411	-10.461	21.088	11.942

APPENDIX 3

The water residence times in Dong Ho estuary

		The water residence times (day)
Wet season (August 2015)	Zone 1	0.81
	Zone 2	2.02
	Zone 3	1.48
Dry season (April 2016)	Zone 1	1.65
	Zone 2	3.12
	Zone 3	4.01