ESTIMATION OF THE CONTRIBUTION OF ATMOSPHERIC DEPOSITION TO COASTAL WATER EUTROPHICATION

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ABSTRACT

Human activities often lead to increased inputs of nutrients from point and/or distributed sources into the coastal environment, causing eutrophication. The pollution load from point sources such as domestic sewage outflows and industrial discharge can be quantified and controlled directly. However, the pollution load due to distributed sources such as atmospheric deposition (AD) and runoff cannot be easily be quantified since they are diffuse and highly variable in time and space. Recent research has suggested that atmospheric deposition can be a major source of nutrients to aquatic ecosystems where these nutrient species can play a critical role in major biogeochemical cycles. The role of atmospheric deposition of nutrients in the coastal zone pollution over Southeast Asia (SEA) is least understood due to the paucity of observational data pertaining to nitrogen (N) and phosphorus (P) species and they have not been investigated in a systematic manner. The atmospheric fallout of airborne particles through dry atmospheric deposition (DAD) and wet atmospheric deposition (WAD) to the ocean surface is thought to be an important source of nutrients in SEA in a view of recurring forest and peat fires and the abundant rainfall in this tropical region.

The quantification of individual species is critically important since N and P species play an important role in causing coastal eutrophication and altering biogeochemical cycles. Moreover, there is a strong need for development of numerical models to simulate various biochemical processes and to explore various possible scenarios concerning the atmospheric deposition of nutrients. Hence, both field-based investigations and modeling work are addressed in the present research

work. Specifically, this work investigates the atmospheric deposition of nutrients through periodical field monitoring of airborne particles and the chemistry of rainwater, laboratory measurements of nutrients, estimation of atmospheric deposition of nutrient fluxes and their possible impacts on aquatic ecosystems using a three dimensional (3-D) numerical eutrophication model “NEUTRO”.

The atmospheric sampling of nutrients was carried out in Singapore, and the concentration levels of N and P species in both airborne particulates and precipitation (rainwater) were determined using validated laboratory analytical techniques. The N species include ammonium (NH_4), nitrate (NO_3), nitrite (NO_2), total nitrogen (TN) and organic nitrogen (ON) while P species include phosphate (PO_4), total phosphorous (TP) and organic phosphorous (OP); the charges of ions are not included for the sake of simplicity. The measured concentration levels of nutrients show that atmospheric deposition is an important contributor to nutrient loading in coastal zones of Singapore and its surrounding region, in particular during smoke haze episodes caused by uncontrolled forest and peat fires.

NEUTRO is a dynamic biochemical model that takes into consideration time-variable chemical transport and fate of nutrients, and plankton and dissolved oxygen in the water column due to nutrient loadings from point and distributed sources. For the present study, NEUTRO is enhanced in its capability to investigate the fate of atmospherically deposited nutrients. There are two steps involved in the application of the model. In the first step, data on atmospheric nutrient fluxes and baseline concentration of diluted nutrients in the water column are utilized to explore possible scenarios allowing qualitative and quantitative understanding of the relative importance of atmospheric and ocean nutrient fluxes in this region. In the second step, the model is used to study spatial and temporal variability of eutrophication rate

in the Singapore Strait due to changes in nutrient fluxes from atmospheric deposition in the model domain. The motivation for applying this numerical modeling approach is to quantify water quality variability due to the transfer of atmospherically-derived nutrients into coastal water and to predict the resultant nutrient and phytoplankton dynamics in this region. Model computations show that atmospheric fluxes might account for considerable percentage of total nitrogen mass found in the water column of the Singapore Strait. This finding is significant for regional eutrophication under nutrient-depleted conditions. The relative importance of regional episodic smoke haze episodes vs background local air quality to coastal eutrophication in Singapore in terms of atmospheric nutrient deposition is also investigated.

Overall, this research study provides valuable data on nutrient (N and P) species derived from airborne particles and rainwater and also insights into their possible impacts on aquatic ecosystem resulting from atmospheric deposition of nutrients onto the coastal water. The results obtained from the modeling study could be used for gaining a better understanding of the energy flow through the marine food web, exploring various possible scenarios concerning the atmospheric deposition of nutrients onto the coastal zone and studying their impacts on water quality.

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LIST OF SYMBOLS

B_j	Concentration of j-th pollutant at computational boundaries
C	Total concentration of pollutants
C_j	Concentration of j-th pollutant
C_j^0	Initial concentration of j-th pollutant in the water
C_j^B	Baseline concentration of j-th pollutant in the water
C_t	Concentration of pollutant at time t
C_0	Initial concentration of pollutant
P_r	Annual rainfall or precipitation rate
CBOD	Carbonaceous biological oxygen demand
D_p	Particle diameter
DO	Dissolved oxygen
E_x, E_y, E_z	Turbulent diffusion coefficients
F	Flux
HABs	Harmful algal blooms
IM	Inter-monsoon
I	Total number of chemical species
N	Nitrogen
NEM	Northeast monsoon
NO_2^-	Nitrite
NO_3^-	Nitrate
NH_4^+	Ammonium
P	Phosphorus
PO_4^{3-}	Phosphate
Q	Discharge of the source
R_j	Physical-chemical reaction terms
Si	Silica
S_j	Concentration of j-th pollutant at the source
S_{jWD}	atmospheric wet deposition
SWM	Southwest monsoon
t	Time
ρ	Density
Tg	Teragrams = 10^{12} g
TSS	Total suspended solids
U	Tidal current in x- direction
V	Tidal current in y- direction
W	Tidal current in z- direction
W_j	Settling velocity of j-th pollutant
Δx	Computational grid-cell sizes in x- direction
Δy	Computational grid-cell sizes in y- direction
Δz	Computational grid-cell sizes in z- direction
Δh	Thickness of water layer affected with initial dilution

LIST OF ABBREVIATIONS

AD	Atmospheric deposition
ADB	Asian Development Bank
AD-N	Atmospherically deposited nitrogen
AOGS	Asia Oceania Geosciences Society
APHA	American Public Health Association
ASEAN	Association of Southeast Asian Nations
ASTM	American Society for Testing and Materials
DAD	Dry atmospheric deposition
DHI	DHI Water Environment and Health
DON	Dissolved Organic Nitrogen
ENSO	El Niño Southern Oscillation
EPA	Environmental Protection Agency
ERA	Environmental Resource Associates
GESAMP	Group of Experts on Scientific Aspects of Marine Environmental Protection
HVAS	High volume air sampler
HTCO	High Temperature Catalytic Oxidation
IC	Ion chromatography
IN	Inorganic Nitrogen
N	Nitrogen
NIST	National Institute of Standards and Technology
NRC	National Research Council
NUS	National University of Singapore
ON	Organic Nitrogen
OP	Organic Phosphorus
PM	Particulate matter
$PM_{2.5}$	Particulate matter less than 2.5 μm in aerodynamic diameter
PM_{10}	Particulate matter less than 10 μm in aerodynamic diameter
P	Phosphorus
PUB	Public Utilities Board
QA	Quality assurance
QC	Quality control
RH	Relative humidity
SRM	Standard reference material
TN	Total nitrogen
TP	Total phosphorus
TSP	Total suspended particulate
U.K.	United Kingdom
UNESCAP	Economic and Social Commission for Asia and the Pacific
UNEP	United Nations Environment Programme
U.S.A.	United States of America
U.S. EPA	United States Environmental Protection Agency
WAD	Wet atmospheric deposition
WASP	Water Quality Analysis Simulation Program

WDOE	State of Wasington Department of Environment
WHO	World Health Organization
WHRC	Woods Hole Research Center
WS	Water soluble
0-D	Zero dimension
1-D	One dimension
2-D	Two dimensions
3-D	Three dimensions

CHAPTER 1: INTRODUCTION

Over past few decades, eutrophication has become one of the leading causes of water quality impairment at a global level (Selman et al., 2008). Eutrophication is defined as the process which changes the nutritional status of a given water body due to discharge of the nutrient resources, resulting in increased algal biomass (Nixon, 1995; Jorgensen and Richardson, 1996). Eutrophication of coastal water is recognized as a major environmental problem and a threat to the health of marine ecosystems all around the world (NRC, 2000; Cloern, 2001; Seitzinger et al., 2005; Selman et al., 2008). Even though marine water has assimilation capacity towards pollution load, the combined effect of additional pollutants with the nutrients load may cause outbreak of harmful algal bloom. Among different pollutants that are being released into the coastal environment, excess concentrations of two nutrients such as nitrogen (N) and phosphorus (P) are the main reasons for eutrophication. The major effects of eutrophication include an increase in nutrient concentrations, changes in N:P ratio, accelerated phytoplankton primary production and biomass, malfunctioning of marine ecosystems and reduction of biodiversity, increase in sedimentation and light reduction, depletion of oxygen concentration as well as downstream effects on economy and human health implications. Various factors such a climate change, changes in land use pattern and coastal geomorphology also influence the rate of eutrophication.

Both point and distributed sources contribute to the increase in the concentration of nutrients. The pollution from point sources such as domestic sewage outflows and industrial discharge can be quantified and controlled directly. But the pollution due to distributed sources such as atmospheric deposition and runoff is difficult to be quantified since they are diffuse, and highly variable in strength due to changes in the frequency of occurrences of precipitation events and smoke haze episodes (caused by forest fires) on a seasonal basis. Atmospheric deposition is an important source of nutrients to the ocean that may deposit the pollutants/nutrients directly onto water bodies and contribute indirectly to terrestrial loads. Atmospheric inputs potentially stimulate primary production, but their relative effect on coastal eutrophication remains undetermined to a large extent.

Atmospheric nutrients have recently gained attention as a significant additional source of new N and P loading to the ocean. Transport via the atmosphere has been recognized as an important pathway for the transfer of particles and nutrients to surface water through wet and dry deposition in addition to that caused by riverine outflow, direct wastewater discharge and terrestrial runoff. These sources together increase eutrophication problems near the coastal areas (e.g. Spokes et al., 1993; Paerl et al., 2000; De Leeuw et al., 2003). At some places, atmospherically deposited nutrients have been reported to have a tenfold increase in their concentrations in recent decades due to a diverse array of industrial human activities and forest fires (Jickells, 1998; Smith, 2003). The global projected ratio of the estimated deposition of oxidized nitrogen in 2020 to the values for 1980 is between 1.5 and 3 and in some limited areas up to 4 (Galloway et al., 1994; Watson, 1997). Figure 1.1 shows the spatial patterns of total inorganic nitrogen (TN) deposition across the globe estimated in (a) 1860, (b) early 1990s, and (c) 2050.

The global distribution of the atmospheric total phosphorus (TP) deposition shows higher concentrations over land, especially in areas influenced by the North African dust and smaller concentrations in more remote marine environments (Figure 1.2). In 1860, N deposition > 750 mgN/m^2/yr occurred over a very small area of southern Asia while significant regions received > 1000 mgN/m^2/yr in 1990. For the first time, most of the regions of South and East Asia have been projected to receive > 5000 mgN/m^2/yr in 2050

(Figure 1.1). Estimates of the atmospheric fluxes of nutrients to the coastal and pelagic oceans suggest that the atmosphere can be a major source in terms of mass of N and P species and plays a major role in the oceanic biogeochemical cycling. The effect of atmospheric N and/or P on marine productivity depends on the biological availability of both inorganic and organic N and/or P forms that are present in the aquatic ecosystems.

Eutrophication due to nutrient pollution from various sources is a global issue, and has greater impacts in the developing regions of the world. For illustration, Southeast Asia (SEA), the Singapore Strait in particular, is focused in this work. Although considerable progress has been made in reducing the amount of pollutants discharged from various sources over SEA, environmental contaminants generated by dispersed sources (such as runoff or atmospheric depositions) remain poorly characterized due to the paucity of comprehensive observational data over SEA. The air in Singapore and the SEA region is episodically polluted by the transboundary smoke haze from the land and prolonged forest fires in Indonesia and neighboring countries (Balasubramanian et al., 2003). The pollutants released in the atmosphere are spread much wider by prevailing winds and are transported and deposited onto terrestrial or aquatic ecosystems through wet or dry deposition. Because of recurring forest fires, burning of fossil fuels, industrial emissions over SEA on a large scale and the abundant rainfall in this tropical region, the atmospheric fallout of particles (dry deposition) and wet deposition of nutrients to the aquatic systems are thought to be significant. However, till date, no detailed studies have been reported on nutrient composition in aerosol particles and precipitation in this region.

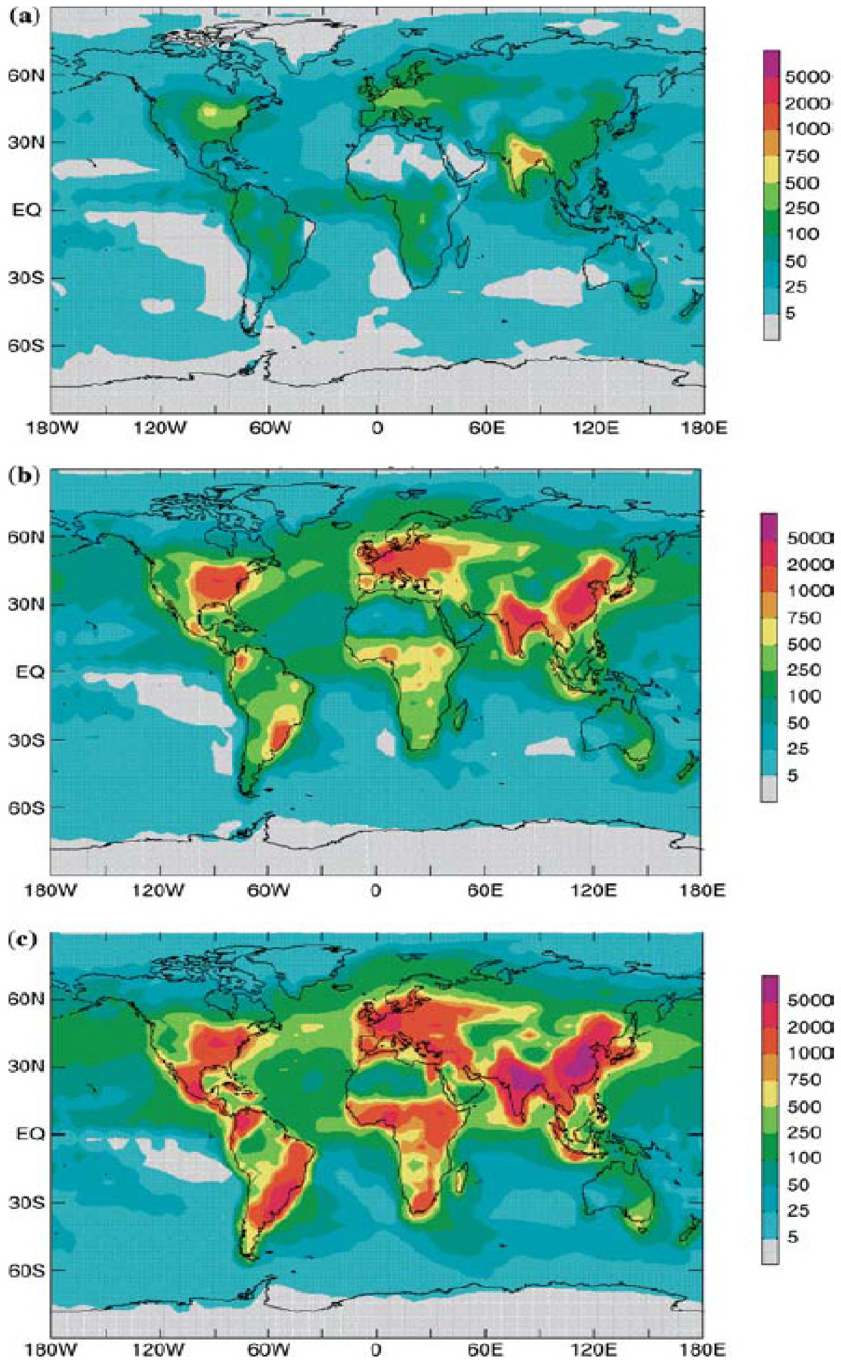

Figure 1.1 Spatial patterns of total inorganic nitrogen (TN) deposition across the globe estimated in (a) 1860, (b) early 1990s, and (c) 2050. Units for the values shown in the color legend are mgN/m^2/yr (Adapted from Galloway et al., 2004).

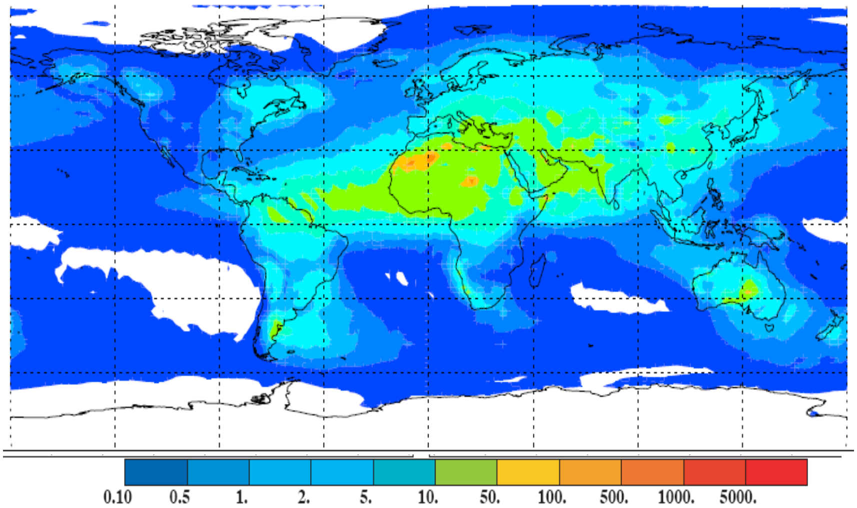

Figure 1.2 Spatial patterns of total phosphorus (TP) deposition (mg/m^2/yr) across the globe (Mahowald et al., 2008).

The main objectives of the present study are:

1. To fill the existing knowledge gaps in the studies related to the atmospheric monitoring, assessment and impacts of dry and wet atmospheric depositions of nutrients (N and P species) over the Singapore Strait and surrounding regions;
2. To establish a long-term field monitoring station for dry atmospheric deposition and wet atmospheric deposition sampling and to develop laboratory methods for speciation of nutrients in aerosol particles and precipitation;
3. To estimate fluxes of atmospherically-derived nutrients (N and P species) onto coastal environments of Singapore and surrounding regions;
4. To investigate the responses of aquatic ecosystems to atmospheric nutrient deposition/loading by means of a numerical modelling approach.

The central hypothesis is that the atmospheric input is an important external source of nutrients to the marine environment that accounts for a considerable fraction of excessive primary productivity. The present study is intended to identify and quantify the atmospheric deposition of nutrients, and to develop an eutrophication model to estimate the contribution of atmospheric nutrient deposition to coastal water eutrophication. The laboratory methodology is developed to derive speciation and of nutrients and determine their corresponding concentrations in aerosol particles for dry atmospheric deposition (DAD) and in precipitation for wet atmospheric deposition (WAD). The atmospheric deposition of inorganic and organic nitrogen (N) fluxes, inorganic and organic phosphorous (P) fluxes onto the water surface in the Singapore Strait and the surrounding region are calculated. Using the measured data on atmospheric nutrient fluxes, baseline concentration of diluted nutrients in the water column, the numerical eutrophication model (NEUTRO) is applied to run different scenarios allowing quantification of relative contribution of atmospheric and ocean fluxes in the Singapore Strait.

"NEUTRO" is a 3-D eutrophication model. It is a dynamic biochemical model that simulates time-variable transport and fate of nutrients, plankton and dissolved oxygen in the water column. NEUTRO is an enhanced model that can be applied to distributed source (atmospheric deposition) and to determine the water quality changes from seawater baseline due to nutrients from atmospheric deposition. The effects of atmospheric nitrogen deposition on surface water nutrients and marine phytoplankton concentration are also quantified using this model. NEUTRO is applied to explore three exploratory scenarios in the Singapore Strait by taking into consideration: (a) flux of nutrients from lateral ocean boundaries only; (b) atmospheric fluxes only; and (c) combination of fluxes from the ocean and the atmosphere. This approach allowed a qualitative as well as a quantitative understanding of the relative importance of atmospheric nutrient fluxes in the region. Later, the enhanced model is used to study spatial and temporal variability of eutrophication rate in the Singapore Strait due to atmospheric deposition in the domain. The importance of regional smoke episodes, hazy days and non-hazy days, to atmospheric nutrient deposition on the biological responses in the coastal water of the Singapore region are also investigated. The direct measurement of energy flow in the system of atmosphere-coastal zone is so complicated that even assessment of percentage contribution of atmospheric nutrients relative to fluxes through “open” horizontal boundaries of water column could be highly beneficial for the source characterization/apportionment in the studied domain. The modelling study suggested in this work (Chapter 5) offers an alternative way to quantify nutrients balance in the system.

As the present work is focused on studying atmospheric nutrient deposition and examining its impacts on water quality by eutrophication modelling, it is necessary to provide a thorough review of earlier studies reported in the literature pertaining to this subject. Chapter 2 reviews the current status of knowledge in the area of atmospheric deposition of nutrients. The overall structure of the thesis is briefly explained below.

1.1 Structure of thesis

The thesis is organized in 6 Chapters. Chapter 1 deals with an introduction to atmospheric deposition in general, and its contribution to coastal water eutrophication in particular and also sets up the rationale for the research described in this thesis. Chapter 2 reviews the relevant literature pertaining to atmospheric deposition pathways, fate and transport, field measurement and laboratory analysis of atmospheric nutrients, as well as eutrophication modelling. A detailed description of the experimental methods employed in this study is provided in Chapter 3. In this chapter, the rationale behind the various experimental approaches and analytical tools and eutrophication modelling are also discussed. Chapter 4 discusses the results obtained on field measurements and flux estimations of atmospheric deposition of nutrients, whereas the results and discussions with reference to model development, validation and application to understand the effect of atmospheric nutrient loading in Singapore coastal water are presented in Chapter 5. An insight into the interaction of eutrophication and atmospheric deposition of nutrients and its impact on coastal water are also provided. General conclusions drawn from a series of investigations undertaken in this thesis work together with some recommendations for further research in this field of emerging interest are given in Chapter 6.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

In recent years, atmospheric nitrogen deposition onto surface water has received considerable attention, particularly in the context of eutrophication of aquatic systems. Global industrialization and increased vehicular emissions are the major contributors to the cultural modification of atmospheric nitrogen cycle (Galloway et al., 1995; Vitousek et al., 1997; Smil, 1999). Till now, most of atmospheric research pertaining to nitrogen budgets has focused mainly on inorganic nitrogen in terms of identifying its sources and understanding its deposition patterns (Asman et al., 1998; Rejesus and Hornbaker, 1999; Cornell et al., 2001, 2003). However, the environmental implications of atmospheric organic nitrogen and other N and P compounds are relatively less well understood (Seitzinger and Sanders, 1999; Cape et al., 2001; Neff et al., 2002; Herut et al., 2002; Cornell et al., 2003).

In recent decades, nutrient (nitrogen and phosphorous species) loads and concentrations in some lakes, rivers, estuaries, coastal water and the open sea have shown a 10–20 fold increase (Jickells, 1998; Smith, 2003). The sources of nutrients to the aquatic ecosystem vary from site to site and from region to region. For some aquatic systems, industrial emissions and municipal effluents are the largest single input. For most aquatic systems, however, distributed sources of nutrients are now of a greater importance, because of improved point source treatment and control (particularly for P), and due to an increase in the total magnitude of distributed sources (particularly for N) over the past three decades. The inputs of nutrients from distributed sources are difficult to measure and regulate since they are derived from activities dispersed over wide areas of land and are variable in time due to weather condition. Atmospheric inputs are now recognized as an important input to the coastal ocean (Moore et al., 1984; Duce et al., 1991), although delivered as a diffuse flux in contrast to localized river inputs. SEA now suffers from greatly increased fluxes of nutrients in aquatic ecosystems due to both point and distributed sources (UNESCAP and ADB, 2000). A significant fraction of the total nitrogen entering coastal and estuarine ecosystems along coastal water arises from atmospheric deposition; however, the exact role of atmospherically derived nitrogen in the decline of the quality of coastal, estuarine, and inland water is still uncertain. In the open sea, the contribution of atmospheric deposition (AD) of nitrogen is relatively large (Example, 40–50 % of the total load, Cornell et al., 1995). Galloway and Cowling (2002) showed that anthropogenic nitrogen fixation will increase by ~ 60 % by 2020 and most of N increase will be in Asia (Galloway et al., 1995).

2.2 Atmospheric deposition

2.2.1 Pathways and chemical composition of nutrients from atmosphere

The atmosphere is considered as an important pollutant transportation route by which nutrients and particles are delivered to the sea surface. Several activities such as man-made or natural sources contribute to nutrient loadings in the atmosphere and their transport can occur in very large spatial scales from air mass trajectories. The man-made sources include agricultural, industrial and construction activities, transportations, municipal incinerators, pesticide applications, combustion of fossil fuels and vehicle exhaust; and natural sources can be volcanic eruptions, gases and particles from mineral aerosols, aerosols from the ocean, windblown gases spray, primary biogenic particle and biomass burning (forest and grass fires) emissions. A significant and increasing source of nutrients to freshwater and marine ecosystems is atmospheric deposition either as “wet deposition” or as “dry deposition” of particles (Figure 2.1). Three steps are involved in wet deposition: (i) the pollutants need to come into contact with condensed water in the atmosphere, (ii) the pollutants must be scavenged by the droplets and (iii) it then has to start raining before the condensed water evaporates back into water vapor, thereby releasing the pollutants back into the air (Seinfeld and Pandis, 2006). Dry deposition can be conceptualized as a three-step process: (1) the gas or particle is moved toward the surface by thermally or mechanically driven eddies, (2) it is transferred by diffusion across a thin layer close to the surface where turbulence is absent and (3) the gas or particle is captured by the surface (Seinfeld and Pandis, 2006). Dry Atmospheric Deposition is composed of small particulates that fall from air or collected from aerosol, while Wet Atmospheric Deposition involves dissolved chemical compounds that occur in rainfall. In general, WAD is more important than DAD for components associated with small particles, which are mainly those produced by gas to particle conversion. Wet deposition of nutrients occurs when gaseous, or particulate N or P is transferred from the air onto an underlying surface via precipitation.

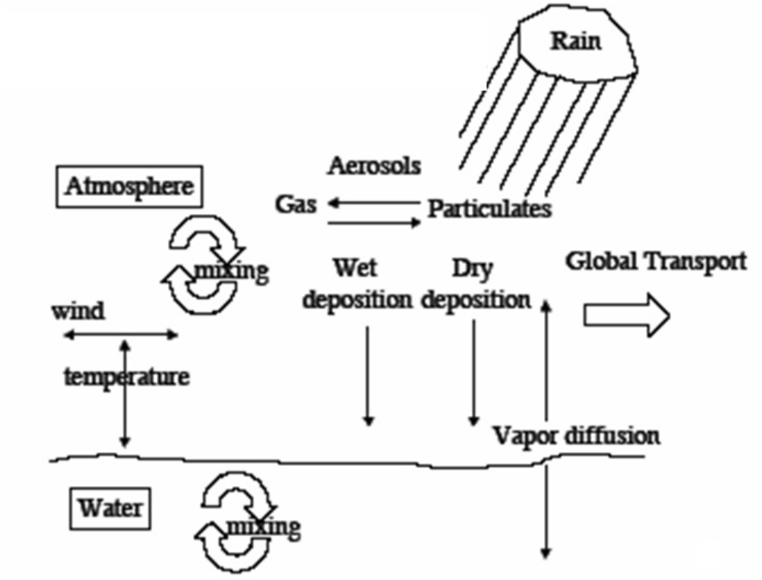

Figure 2.1 Schematic diagram of atmospheric deposition occurrence onto aquatic ecosystem

The first step in determining the quality of ambient air is to measure its total suspended particulate matter (TSP). The urban air TSP is an aggregate of direct emissions from different sources and those formed through condensation and transformation. TSP refers to all particles suspended in the air, while airborne particulate matter (PM) PM_{10} and $PM_{2.5}$ are particulate matter having diameter equal to or less than 10 and 2.5 µm, respectively. At least, one of these three parameters acts as ambient air quality standards in most countries around the world. Nutrients play an important role in the health and functioning of aquatic ecosystems and are present naturally in the environment. However, human activity has increased the supply of biologically reactive forms of nutrients, particularly N and P species. The general forms of nitrogen such as ammonium (Ammonium-N: NH_4-N), nitrate (Nitrate-N: NO_3-N) and nitrite (Nitrite-N: NO_2-N)) are commonly referred to as dissolved inorganic nitrogen (DIN) (Sharp, 1983; Janet, 1998; Guildford and Hecky, 2000; Erisman et al., 2001). While phosphorus is available to primary production in a dissolved inorganic phase as phosphate (PO_4-P), nitrogen is supplied to aquatic plants mostly as DIN. Airborne biologically available N compounds include inorganic reduced forms (ammonia and ammonium), inorganic oxidized forms (nitrogen oxides, nitrate and nitrite) and organic forms (urea, amino acids, and unknown compounds). Phosphorus is an essential element for growth of algae (Daniel et al., 1998; Haugarth and Jarvis, 1999; McDowell et al., 2001). Atmospherically deposited nitrogen can reach N-sensitive waterways via direct deposition to the water surface, or by deposition to land surface and subsequent runoff (indirect deposition). Phosphorus (Phosphate, total phosphorous and organic phosphorous) is a component of atmospheric deposition. Airborne phosphorous is transported to surface water by particles derived from soil, dust, pollen, insects, bird excrement, fertilizers, ashes, some pesticides, and aerosols from the ocean. This is especially true in regions where wet deposition exceeds dry deposition, since P is usually bound to particles such as dust and windblown soils. Accordingly, in agricultural regions where P is applied as a fertilizer, or in arid regions where soil is readily transported by wind, atmospheric deposition tends to be most highly enriched with P (Herut et al., 1999). The airborne P typically accounts for 10 to 20 percent of total phosphorus loadings to water bodies from all sources (Swackhamer et al., 2004).

2.2.2 Biomass burning

Biomass burning is a primary source of many trace substances that are important in atmospheric chemistry (Crutzen et al., 1979; 1985; Andreae et al., 1988; Crutzen and Andreae, 1990; Lobert et al., 1990). The regional smoke haze in SEA is caused by a high concentration of airborne particulate matter (PM), predominately of very fine particles with a diameter of less than 10 μm, that is directly emitted from biomass burning together with those from other sources such as industries, on-road vehicles, road dust, as well as PM formed from gaseous pollutants in the atmosphere. These particles often grow in size as humidity increases, further impairing visibility. The worst haze episodes in SEA occurred in 1997 and 1998, but forest fires during 1998 in Mexico and the southern United States (Qadri, 2001; In et al., 2007) caused a similar regional haze episode in Central America. During the 1997–1998 periods, forest fires were also reported in Brazil, Spain, Greece, Australia, Mongolia and Russia. Haze can become “transboundary” pollution when it is dense at sources, extends to thousands of kilometers away from the source and remains at measurable levels after crossing into another country's air space at remote locations (Figure 2.2). While coarse particles fall out from the atmosphere within several hours up to a day, fine particles have the longest residence time (up to weeks) in the atmosphere and travel extensive distances (hundreds to thousands of kilometers). In view of the growing incidence of forest fires and the resulting haze throughout the world, there is need for a greater understanding of the various aspects of these phenomena, including their chemistry. It was first recognized in the late 1970s that tropical vegetation burning is a major global source of trace gases, such as CO_2, CO, NO_x, NH_3 and aerosols, with significant impacts on regional and global climate, atmospheric chemistry and hydrological cycles (Crutzen et al., 1979; 1985; Crutzen and Andreae, 1990; Lobert et al, 1990; Andreae, 1991; Crutzen and Carmichael, 1993; Yokelson et al., 1999). Although these pollutants are harmful to health and ecosystems, the full environmental impact assessment of the haze requires considerably more detailed chemical characterization.

The emission production and characteristics from vegetation fires strongly depend on the combustion stage (basically flaming and smouldering combustion), the combustion efficiency and the physico-chemical properties of vegetation burnt (Lobert and Warnatz, 1993). The most significant reactive nitrogen (NO_x) is emitted during the flaming stage of fires while most other nitrogen containing compounds are emitted during smouldering stage of fires. Large diameter or densely packed necromass (such as logs, peats) and large diameter live vegetation (trunks) are usually partially consumed resulting in smouldering combustion (Stocks and Kaufman, 1997; Yokelson et al., 1997). Characteristically, for low efficiency combustion processes, smouldering combustion emits larger amounts of incompletely oxidized compounds including CO, CH_4, NH_3, other nitrogen containing compounds and fine particles than flaming combustion per unit amount of biomass consumed by a fire. Biomass fires are inversely related to precipitation; they generally occur during dry periods when precipitation amounts are very low or non-existent since heavy rains tend to extinguish fire. Ultimately, removal of trace gases from the atmosphere is mainly by oxidation processes. Most deposition in the tropics takes place during the wet season when precipitation amounts are exceedingly large, and it is the deposition rate that should be related to ecological impacts.

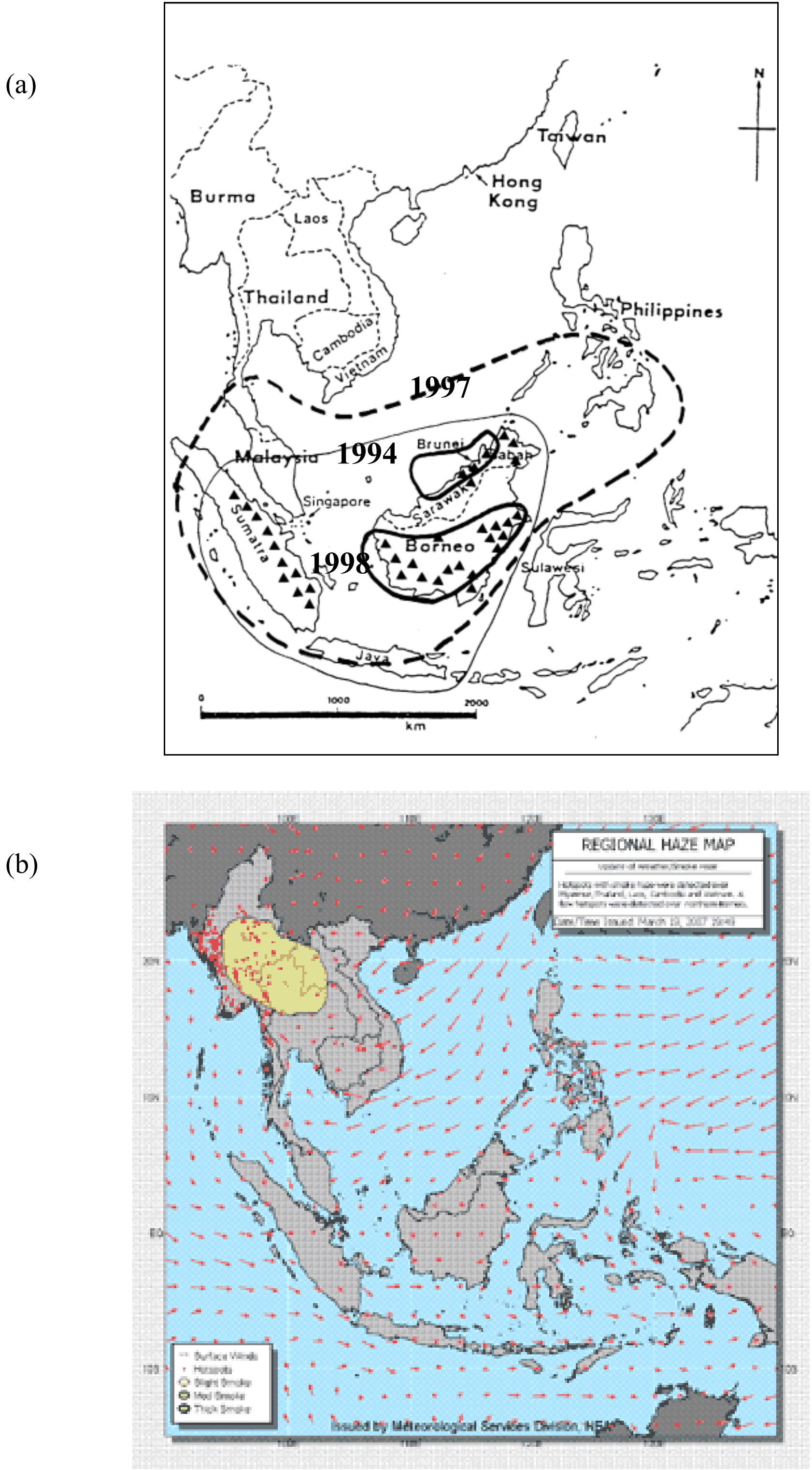

Figure 2.2 (a) Approximate location of forest fire hot-spots and area affected by regional haze in SEA; (—) August-October 1994, (----) July-October 1997, (▬) February-April 1998. (▲) Site of forest fires (Adapted from Radojevic and Tan, 2000); (b) Extent of the haze in SEA during March 2007; red dots - Site of forest fires (Adapted from NEA, Singapore).

Biomass burning is found to be a major source of reactive nitrogen (Kondo et al., 2004; UNEP and WHRC, 2007) and phosphorous (Mahowald et al., 2005; Baker et al., 2006). The emission rates of NO_X due to biomass burning were responsible for ~ 9–20 % of the estimated global rate of terrestrial nitrogen fixation (Lobert et al., 1990). Budgets of global NO_x and NH_3 emissions by biomass burning source are about 3–13 teragram (Tg)N/yr (Watson et al., 1992) and 1–9 TgN/yr (Schlesinger and Hartley, 1992), respectively. Mahowald et al. (2005) reported that biomass burning emissions and human disturbance were responsible for ~ 23 % of the phosphorus flux in the Amazon and the global source of atmospheric phosphorus (< 10 μm) is 1.39 TgP/yr, of which, 4.8 % is anthropogenic (Mahowald et al., 2008). Reid et al. (2005) reported that the fresh smoke particle mass has density around 1.8–2.2 g/cm^3 and that of the dry smoke particles has density varying in range of 1.2–1.4 g/cm^3. The forest fires produce a variety of coarse mode particles (typically 2.5–15 μm diameter, dp) while lower in mass fraction than accumulation mode particles (10 %); in addition to coarse mode ash particles (2 < dp < 20 μm), giant ash particles having diameters of up to a millimeter or more can be generated by very intense fires (these have even been tracked by weather radar) (Reid et al., 2005). Rising levels of atmospheric deposition lend urgency to understand the fate and impacts of ‘new’ N. Nutrients increase due to biomass burning may thus strongly impact terrestrial and oceanic biogeochemistry (Galloway et al., 2008).

Recurring incidence of air pollution phenomenon on an unprecedented scale due to land and forest fires has been a feature of SEA’s ecology since the Pleistocene Age (Qadri, 2001). The forest fires in Indonesia were the main sources of extensive SEA haze events during 1990 (Nichol, 1997, 1998; Radojevic, 1997, 1998, 2003; Fujiwara et al., 1999; Radojevic and Hassan, 1999). During the 1990s, six separate haze episodes (1983, 1990, 1991, 1994, 1997 and 1998) occurred in Southeast Asia (Radojevic and Hassan

1999, Muraleedharan et al. 2000). The forest fires that hit the Association of Southeast Asian Nations (ASEAN) region in 1997–1998 caused the most environmental damage recorded in history (UNEP, 1999). The regional haze episode in SEA is usually associated with dry weather and droughts modulated by the El Niño Southern Oscillation (ENSO), an ocean-atmosphere-climate phenomenon that is linked to the periodic warming of water across the central and eastern tropical Pacific Ocean. The severity of the fires episodes was linked to the occurrence of ENSO creating conditions ripe for fires. The smoke haze occurrence was due to advection of biomass burning impacted air masses from the Indonesian provinces, Sumatra and Kalimantan (Borneo), where extensive forest fires took place (Balasubramanian et al, 1999). These islands are situated around Singapore from southeast (SE) to southwest (SW). The areas of forest fires ranged from several hundred kilometers to about 2000 km from Singapore.

Despite the existing in-depth knowledge on fires and their underlying causes in SE Asian ecosystems (Goldammer et al. 1996), little research has been done on the implications of vegetation burning in this region on atmospheric chemistry, public health and aquatic ecosystem (Nichol, 1997, 1998; WHO, 1998; Balasubramanian et al., 1999; Balasubramanian and Qian, 2004). The fate of the initial fire emissions depends strongly on both their composition and the regional state of the atmosphere. Once airborne, the particles begin to grow slightly in size as they age through condensation and coagulation. In addition, new fine particles are created by nucleation of gaseous fire emissions such as the conversion of NO_x to nitrates (Jänike, 1993). Particles are removed from the atmosphere by gravitational settling, precipitation and cloud scavenging. Because gravitational settling velocity increases with particle diameter, larger particles (diameter > 10 μm) are lost from the plume faster than smaller ones. Wet removal thus dominates the atmospheric lifetime of the pyrogenic particles, which is therefore largely controlled by meteorology (Garstang et al., 1997).

The environmental effects of the more recent 2006 smoke haze episodes remain poorly understood. The United States Environmental Protection Agency (US EPA) developed PSI (Pollutant Standards Index) value, which is adopted by the National Environment Agency (NEA) in Singapore, gives an indication of the prevailing air quality and potential health effects. The PSI is developed to provide the public with information about daily pollution levels (i.e. good, moderate, unhealthy, very unhealthy and hazardous) and to enable authorities to decide on appropriate action to protect the public and to ameliorate the situation. The highest PSI value is reported after the concentrations of CO, SO_2, NO_2, O_3 and PM_{10} are measured and are available through the internet at http://app.nea.gov.sg/psi/. During haze episodes the PSI is invariably based on PM_{10} measurements because this pollutant far exceeds the concentrations of other pollutants.

2.2.3 Review of global and regional atmospheric deposition

Atmospheric deposition is a significant and potent source of nutrients that can accelerate eutrophication and its associated environmental consequences in freshwater, estuarine, and coastal ecosystems (Duce et al., 2008, Galloway et al., 2008). Both airborne N and P species are derived from natural and anthropogenic (point and distributed) sources and transported to surface water. It has been reported that about 20–40 % of new N inputs into coastal water are of atmospheric origin (Duce, 1986; Paerl, 1995; see Table 2.1) and atmospheric deposition alone contributes from 300 to over 1000 $mgN/m^2/yr$ in coastal water (Duce et al, 1991). At some places such as Europe, America and Asia, the atmospherically deposited nutrients have been reported to have increased tenfold in recent decades due to a diverse array of industrial human activities and forest fires (Galloway et al., 1995; Galloway et al., 2004). For Danish marine water, atmospheric nitrogen deposition has been estimated to be equal to river runoff (Skjøth et al., 2002). The atmospheric contribution to the nitrogen load of the German Bight during 1989–1992 was estimated to be about 30 % (Beddig et al., 1997), and estimates for the Baltic Sea points at a 50 % contribution from atmospheric deposition (Rosenberg et al., 1990). Table 2.1 gives the estimated contribution of atmospherically derived N (AD-N) to the total new N inputs in estuarine, coastal and open ocean water.

Table 2.1 Estimated contribution of atmospherically derived N (AD-N) to the total new N inputs in estuarine, coastal and open ocean water

Receiving water	**New N (%) as AD-N**	**sources and forms**	**References**
Baltic Sea	> 25	W+D, I	1, 2
North Sea (coastal)	20–40	W+D, I	3
Western Mediterranean Sea	10–60	W, I	4
Sargasso Sea (surface water)	~ 25	W, I	5
Narragansett Bay	12	W, I+O	6
New York Bight	10–40	W, I	7
Rhode River, Maryland	40	W, I+O	8
Neuse River-Pamlico Sound, North Carolina	38	W+D, I	9

Note:W-wet; D-dry; I-inorganic; O-organic

References: (1) Rodhe et al., 1980; (2) Ambio, 1990; (3) GESAMP, 1989; (4) Martin et al., 1989; (5) Prospero and Savoie, 1989; (6) Nixon, 1995; (7) Valigura et al., 1996, 2000 (8) Correll and Ford, 1982; (9) Paerl and Fogel, 1994.

The nutrient composition in rainwater indicated a dominant anthropogenic source for N species and a continental, natural and anthropogenic source for P species (Herut et al., 1999). Atmospheric deposition of P, typically occurs at lesser concentrations than nitrogen, which is soluble P in seawater has been estimated to be significantly lower between 1–2 x 10^{10} molP/yr (Duce, 1986) which is especially true in regions where wet depositions exceed dry, since P is usually bound to particles such as dust and windblown soils. The flux of P to the marine environment resulting from dissolution from eolian dust has been estimated to be 3 x 10^{9} molP/yr which represents about 10 % of river fluxes to the ocean (Delaney, 1998). Globally averaged anthropogenic sources (assuming biomass burning which produces 0.025 (TgP/yr) of TP and 0.012 (TgP/yr) of PO_4 is 90 % anthropogenic) are ~ 5 % of total TP and ~ 15 % of PO_4 (Mahowald et al., 2008). Table 2.2 summarizes recent measurements on wet deposition of phosphorus reported in the literature by other researchers.

Table 2.2 Summary of literature on phosphorus concentrations from atmospheric deposition

Location	**Aerosol P (ng/m^3)**	**Rainfall P (mgP/l)**	**Wet deposition ($mgP/m^2/yr$)**	**Dry deposition ($mgP/m^2/yr$)**	**References**
Amazon	17				1
Amazon			4	7	2
Corsica	10–20		10–20	5–10	3
Chesapeake Bay		16–36			4
New Zealand	4	6	9	1.4	5
Connecticut	10		4	0.25	6
Southern France		2–140	5		7
Long Island Sound			3.6	0.14	8
Israel			9.0		9
Amazonia, Brazil	58.6			16.1	10

References: 1. Artaxo and Hansson, 1995; 2. Swap et al., 1992; 3. Bergametti et al., 1992; 4. Boynton et al., 1995; 5. Chen et al., 1985; 6. Yang et al., 1996; 7. Migon and Sandroni, 1999; 8. Hu et al., 1998; 9. Herut et al., 1999; 10. Mahowald et al., 2005.

Qualitative and quantitative assessment of atmospheric depositions of nutrient are essential for understanding its regional variations for determining the occurance of episodic nutrient loads, and for demonstrating, by analysis of pluriannual trends, the efficiency of emissions reduction policies on the regional scale. Table 2.3 shows the estimates of present-day rates of fixed-nitrogen inputs to the oceans. Over the continents, inorganic nitrogen (IN) species (nitrite + nitrate and ammonium) make up most of the fixed nitrogen in rainwater and in atmospheric aerosol (Spokes et al., 2000).

Table 2.3 Estimates of present-day rates of fixed-nitrogen inputs to the oceans

Source	**Nitrogen flux (10^{12} mol/yr)**	**References**
Dinitrogen fixation	1–3	1, 2
River input: DIN+DON, Natural	1–2.5	3, 4
River input: Anthropogenic	0.5–2.5	
Atmospheric input: DIN, Natural	1–2.5	3, 4
Atmospheric input: DON, Anthropogenic	1–2.5	
Atmospheric input: DON	2–6	5

Note: References: 1. Mackenzie et al., 1993; 2. Capone and Carpenter, 1982; 3. Galloway et al., 1995; 4. Duce et al., 1991; 5. Cornell et al., 1995.

Like the IN ions, organic nitrogen (ON) may be incorporated into rainwater by direct dissolution of gaseous species or by scavenging (in clouds or by falling water droplets) of atmospheric aerosol. The ON containing compounds present in rainwater have not routinely been included in budget assessments, yet they are important components of atmospheric N deposition (Neff et al., 2002). Evidence suggest that water soluble atmospheric ON is principally continental in origin, that these compounds contribute significantly to the total soluble nitrogen flux (Cornell et al., 1995) and that a significant fraction is available to phytoplankton as an N source (Peierls and Paerl, 1997). ON deposition in SEA was about 41 % of total nitrogen (TN) (Cornell et al., 2003). The dissolved organic nitrogen (DON) in Rain at Continental, Coastal and Oceanic Sites is shown in Table 2.4 (Cornell et al., 2001). In the marine atmosphere, these inorganic species decline markedly in concentration with increasing distance from their land-based natural and anthropogenic sources, and ON becomes relatively more important (Cornell et al., 1995). Approximately a third of the dissolved nitrogen in rainwater from continental locations is present in organic forms, while in remote marine rains, there is less data, but ON typically makes up ~ 60 % of TN in bulk rain samples.

Table 2.4 DON in Rain at Continental, Coastal, and Oceanic Sites[a]

Location	**Mean DON Concentration, mol/l**	**DON as Percent of TN**	**References**
Continental Sites			
Amazonia, Brazil	22	22	1
Australia		15	2
Canada	24	38	3, 4, 5, 6
Czech Republic	29	24	7
India	15		3
USA–continental	27	46	3, 8–17
Coastal Sites			
Costa Rica	7	33	18
Ireland	3.3		19
Japan	17	19	20
New Zealand	9	56	21, 21
NE Brazil	3	25	1
North Sea	6.3	6	22
Puerto Rico		33	23
Sweden	3.6	5	24
USA – coastal	22	38	13, 25–30
UK	20	26	1, 19, 31–34
Venezuela		16	35
Oceanic Locations			
NE Atlantic	7	65	1
NW Atlantic	8.3	59	1, 30, 36
Mid Pacific	5.5	63	1, 19, 30

[a] The DON values accepted for inclusion in this comparison are the published mean concentrations in rain, snow, and bulk deposition samples, and have been determined as (Kjeldahl N - NH_3), albuminoid N, or (TN - DIN). The average percent is the mean value of the published averages of ON as a percentage of total nitrogen. References: 1. Cornell et al., 1995; 2. Crockford et al., 1996; 3. Eriksson, 1952; 4. Shaw et al. , 1989; 5. Dillon et al., 1991; 6. Nicholls and Cox, 1978; 7. Kopacek et al., 1997; 8. Bourne, 1976; 9. Butler and Likens, 1995; 10. Grant and Lewis, 1982; 11. Hendry and Brezonik, 1980; 12. Jassby et al., 1994; 13. Prospero et al., 1996; 14. Seitzinger and Sanders, 1999; 15. Shon, 1994; 16. Urban and Eisenreich, 1988; 17. Verry and Timmons, 1982; 18. Eklund et al., 1997; 19. Cornell et al., 1998; 20. Timperley et al., 1985; 21. Wilson, 1959; 22. Rendell et al., 1993; 23. Bowden, 1991; 24. Broberg and Persson, 1984; 25. Peierls and Paerl, 1997; 26. Scudlark et al., 1998; 27. Tarrant et al., 1968; 28. Valiela and Teal, 1979; 29. Valiela et al., 1978; 30. Williams, 1967; 31. Allen et al., 1968; 32. Gore, 1968; 33. Carlisle et al., 1966; 34. Roberts et al., 1984; 35. Lewis, 1981; 36. Knap et al., 1986.

The current paucity of high-quality dry deposition and rainwater composition data from most countries in Asia makes a quantitative survey of dry and wet depositions across the whole region impossible at present (Ayers, 1991). By selecting data from sites well away from the major urban and industrial centres, the Australian results can be taken to define a "baseline" for an unpolluted continental setting (Kato and Akimoto, 1992) when compared to Asian locations. The two salient points drawn by Ayers and Yeung

(1996) were: (i) that very substantial increases in emissions over decadal time scales have already occurred and will go on occurring in Asian countries and (ii) the total regional emissions comprise a large fraction of global emissions. The latter point is underscored by global emissions estimates during 1980 for NO_x from industrial activities/fossil fuel use of 22 TgN/yr (Dignon, 1992). The published relatively unpolluted locations are in Indonesia (at Bukit Koto Tabang and Sumatra by Gillett et al., 2000) and Katherine in Australia (Ayers and Yeung, 1996).

Several research studies have highlighted the importance in addressing the atmospheric deposition onto the surface water over SEA (Balasubramanian et al., 1999; Paerl, 1997; Cornell et al., 1995; Abram et al., 2003). The Indonesian forest fires, which took place in Kalimantan and Sumatra, during the 1997–1998, deteriorated the regional air quality in SEA (Bangkok Post, September 27, 1997; GEO, 2003). Both airborne particulate matter and other air pollutants were spread over Southeast Asian countries (including Indonesia, Malaysia, Singapore, and Brunei, as well as southern parts of Thailand and the Philippines), with peak levels of particulates in Kuala Lumpur, Singapore, and many Indonesian cities far exceeded ambient air quality standards (World Bank, 1997). The Air Pollution Index (API), which is a measure of SO_2, NO_2, CO, ozone and dust particles, reached a critical level of 839 on September 23, 1997 in Malaysia. Worthwhile to mention that API levels of 100–200 are considered "unhealthy"; levels of more than 300 are equivalent to smoking 80 cigarettes a day and are "hazardous." Measurement of NO_2 shows that its concentration was 8.4 ± 5.5 $\mu g/m^3$ at various sites throughout Brunei Darussalam during October 1997 and February 1998 (Radojevic, 1997). Air quality, in terms of PSI (Pollutant Standards Index), measured 101–200 (5 % of days unhealthy) in 1994 and (3 % of days unhealthy) in 1997.

The deterioration in air quality was due to the transboundary smoke haze from the land and forest fires in Indonesia (Yong, 2002). Due to abundant rainfall in SEA region and the recurring forest fires on a large scale, the significant quantities of N species might have been delivered from the land to the ocean via the atmosphere. The emissions from the forest fires cause several environmental impacts on marine ecosystems (Crutzen and Andreae, 1990; Andreae and Crutzen, 1997; Galloway et al., 2008). Burning of crop residues due to the uncontrolled (Indonesian) forest fires seems to be a major source of reactive N in SEA in spring (Kondo et al., 2004). In SEA, the pollutant most consistently elevated in association with biomass smoke during 1997–1998 Southeast Asian biomass burning episodes is particulate matter (Radojevic and Hassan, 1999; Balasubramanian et al., 1999). With the wind generally blowing from the SE/SW direction during southwest monsoon (SWM, June to September) period, the combustion generated gaseous pollutants and fine particles emitted from the biomass burning were transported to Singapore, Malaysia and Thailand (Brauer and Hisham Hashim, 1998). At the end of October, the onset of the northeast monsoon (NEM, November to March) brought a sudden return to PSI levels below 50 and good air quality. The annual mean pH calculated from volume weighted mean concentration of H^+ was 4.20 in Singapore, which is a typical acidic value (Hu et al., 2003). Table 2.5 shows the nominal annual average wet and dry deposition fluxes (μeq/m^2/yr) and concentration of nutrients (N and P components) in some Asian countries including Singapore.

Table 2.5 Nominal annual average wet and dry deposition fluxes (μeq/m^2/yr) and concentration of nutrients (N and P components) in Asian countries

Country	Period	Wet deposition flux			Dry deposition flux
Fluxes		**NH_4^+**	**NO_3^-**	**PO_4^{3-}**	**NO_2^- (gas)**
Malaysia[1]	1993 –1998	39.8	58.2		33.08
Indonesia[5]	1992, 1996	76.7	28.1		45
Australia[4]	1991	4.37	4.97		1.7
HongKong[4]	1988–1991	24.3	37.5		
India[8]	1992–1998	12.5 1.2 (dry)	18.2 11.8 (dry)		
Concentration		**Wet deposition**			**Dry deposition**
Malaysia[2]	1996–1997	13.7 (μmol/l)	19.9 (μmol/l)	0.18 (μmol/l)	
Indonesia[3, 5]	1990, 1992, 1996	26.6 (μeq)	0.88 (mg/l)[3] 12.2 (μeq)[5]		
HongKong	1997[7]; 1988–1991[4]		40.45 (μg/dm^3)[7]		42 (μg/m^3)[4]
India[8] (μeq/l)	1992–1994	25.7 17 (dry)	17.7 24 (dry)		
Singapore[6, 7]	1997–1998; 1999–2000	18.2 (μeq/l)	19.6 (μeq/l)		

Note: References: 1. Ayers et al. (2000); 2. Ayers et al. (2002); 3. Asiati et al. (2001); 4. Ayers and Yeung (1996); 5. Gillett et al. (2000); 6. Hu et al. (2003); 7. Balasubramanian et al. (2001); 7. Tanner and Fai (2000); 8. Pillai et al. (2001).

2.2.4 Impact on aquatic ecosystem

Concerns on rising nutrient loads and their adverse effects on large scale freshwater, estuarine and marine environment have led to a need in extensive research and management of nutrients. Atmospheric nitrogen deposition has been shown to contribute an increasing fraction of the overall nitrogen and phosphorus load. The atmospheric inorganic input is furthermore directly consumable by the algae, which is only true for parts of the river runoff. Pollutants accumulate in the air and can then be advected over marine areas with associated high dry deposition; if rainfall occurs at this time, particularly high depositions can occur (Spokes et al., 1993, 2000). Once the atmospheric nutrients enter surface seawater, the chemical form of the dissolved ion may be altered, thus changing its solubility, retention in the euphotic zone, and bioavailability.

The impact of nutrient-enriched atmospheric inputs is enhanced under oligotrophic conditions. The resulting atmospheric deposition events, while small in overall annual budget terms, may be able to promote phytoplankton blooms under nutrient depleted conditions at surface water because of the atmospheric spreading of nutrients over surface water (Owens et al., 1992; Ridame and Guieu, 2002). Martin et al. (1994) provided strong evidence that the addition of iron to N and P rich water mass can result in marked increases in phytoplankton activity.

Estimates of the atmospheric fluxes of nutrients to the ocean suggest that the atmosphere can be a major source in terms of their mass (Duce et al., 1991; Prospero et al., 1996). Atmospheric inputs by both dry and wet deposition occur at high N:P ratios (Baker et al., 2003; Chen et al., 2007). The dry deposition mode is a significant source of nutrients to surface water at the yearly scale (Migon et al., 2001). However, when nutrient concentrations in surface water are low, nutrients do not accumulate and are immediately consumed by biota (Migon et al., 2001), and new production triggered by the atmospheric nutrients input may not be clearly observable. The rapid exhaustion of atmospheric suspended matter during atmospheric washout by rain/precipitation causes high pulses of nutrients associated with washout events (Buat-Menard and Duce, 1986). Evidence is available that AD significantly modifies oceanic chemistry (GESAMP, 1989, 1990) and biogeochemical processes in estuarine and coastal water before mixing with the ocean in a variety of complex and poorly understood ways (Jickells, 1995; Paerl, 1997). The coastal and oceanic primary production due to atmospherically transported nutrient sources may be promoting the major biological changes that are now apparent in coastal and oceanic water, including the proliferation of harmful algal blooms (HAB) and decline in water quality and fish stock (GESAMP, 1989, 1990; Jickells, 1998; Herut et al., 1999; Markaki et al., 2003). High nutrient conditions favouring coastal HAB have also been associated with some cholera outbreaks (Camargo et al., 2007). Human sickness and death, resulting directly (e.g., ingested nitrates and nitrites from polluted drinking water) or indirectly (e.g., aerosol exposure to algal toxins, consumption of contaminated seafood causing poisoning syndromes) from inorganic nitrogen pollution, can have elevated economic costs (Van Dolah et al., 2001).

Reactive N is now considered to give rise to the biggest pollution problem in coastal water (NRC, 2000; Howarth et al., 2000; Rabalais, 2002). Excessive N loading to surface water is the key cause for accelerating eutrophication and the associated environmental consequences (Nixon, 1995). Since atmospheric inputs do occur all year round, the flux of N from the air may not only trigger blooms, but also contribute to the water column nitrogen standing stock, and hence the magnitudes of the bloom. The increasing amounts of atmospheric anthropogenic N entering the ocean could increase annual new marine biological production by 3.5 %; the excess nitrogen can deplete essential oxygen levels in the water and has significant effects on climate, food production, and ecosystems all over the world (Duce et al., 2008). The wet atmospheric dissolved inorganic nitrogen (DIN) contribution to the primary production rate of the south-east Mediterranean was estimated to be 8 % and that of dissolved inorganic phosphorus (DIP) in the range of 4–11 % (Herut et al., 1999). The main toxic action of NO_3 on aquatic animals like fish and crayfish seems to be the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen. Atmospherically derived dissolved ON has also been shown to stimulate bacterial and algal growth (Peierls and Paerl, 1997). This ON may selectively stimulate growth of facultative heterotrophic algae such as dinoflagellates and cyanobacteria (Antia et al., 1991).

From an ecological perspective, however, P may be of considerable importance since far less P than N is required for balanced plant growth (Redfield, 1958). Some studies have shown evidence that the atmospheric input of P is likely to affect biological productivity in Mediterranean oligotrophic water (Herut et al., 1999; Markaki et al., 2003). The relative degrees of riverine inputs decreased with increasing distance from land, so atmospheric inputs of P played a major role on the biogeochemical processes of some oligotrophic surface seawater (Markaki et al., 2003). Markaki et al. (2003) reported that up to 38 % of new primary production in the eastern Mediterranean was supported by the atmospheric inorganic phosphorus (DIP) dissolved from eolian dusts. Coupling links between the atmospheric and marine environments are of importance when describing the physical and chemical processes giving rise to variations in chlorophyll-a concentration levels and algal blooms (Hasager et al., 2003).

2.2.5 Review of analytical methods

The coastal atmosphere adjacent to large urban areas is strongly affected by the emissions of air pollutants (Gao et al., 1996; Baker et al., 1997; Holsen et al., 1997; Fang et al., 2006). The major airborne pollutants include the ionic species such as nitrite + nitrate, ammonium and phosphate associated with suspended aerosol particles, which may greatly vary in their size, chemical composition and, temporal and spatial variations (USEPA, 1999; Karthikeyan and Balasubramanian, 2006). The chemical composition of particulate matter in the polluted atmosphere and rainwater has received great attention in recent years as high concentrations of ionic species in the aerosol particles in the coastal atmosphere. The particulate matter in the polluted atmosphere could enhance the air-to-sea deposition fluxes to coastal water and affect the quality of the coastal ecosystem (Yang et al., 1996), but also deteriorate air quality and influence human health (Fang et al., 2006). The chemical characterization of the water soluble fraction of particulate matter and dissolved fraction of rainwater is particularly important for achieving a better understanding of many atmospheric processes, including cloud formation, visibility degradation and acidification of clouds, rain and fog (Shaw, 1987; Corner et al., 1991; Seaton et al., 1995; Turnbull and Harrison, 2000). Among the water soluble components of PM, inorganic and organic constituents of nutrients such as N and P species have recently become more important in terms of surface water quality and eutrophication phenomena. A multiplicity of phosphorus forms, including ortho-, pyro-, poly-, meta-, organic, colloidal, and suspended phosphorus, are present in natural waters. Each of these forms can be measured either partially or fully (depending on the reaction conditions) as orthophosphate via hydrolysis.

In recent years, many rapid and simple methods are used for the determination of phosphorus as phosphate in water samples. Spectrophotometric methods are based on the formation of yellow molybdophosphoric acid and its reduction to a blue heteropoly compound, phosphomolybdenum blue (Lyddy-Meaney et al., 2002; Zhang and Chi, 2002; APHA, 2005). Ion Chromatography (IC) is widely used for the measurement of inorganic ions in airborne particles and rainwater since it offers advantages in terms of sensitivity and multiple analyte determination in a single assay. The recent development of improved hydroxide-selective ion-exchange columns and online electrolytic generation of high purity potassium hydroxide offers unique selectivity to separate inorganic anions and organic acids in environmental samples (Mc Murray, 2000; Lu et al., 2002; Liu et al., 1999). The advantages of such IC methods have been exploited for the analysis of inorganic ions and organic acids in selected environmental samples (Alcazar et al. 2003; Tani et al. 2001; Morales et al. 1994), but are not fully utilized for a comprehensive analysis of airborne particulate matters (PM). It is therefore necessary to validate this commonly used analytical method by using a standard reference material (SRM) for direct determination of the accuracy of the measurement, or alternatively to compare this method against suitable analytical techniques measuring the same species of interest.

The methods used to obtain the total nitrogen concentration have themselves been the subject of quite considerable attention. Method used in the reported studies are Kjeldahl, UV photolysis, Wet chemical (persulfate) oxidation, High temperature, Catalytic oxidation and other or non-specified. Measuring TN involves releasing the nitrogen from organic molecules by chemical oxidation to NO_3; thermal/catalytic oxidation to NO; kjeldahl conversion; or by photolysis (Kjeldahl, 1883; Russell et al., 1998; Bronk et al., 2000; Cape et al., 2001). Sharp et al.'s (2002) inter-laboratory study of seawater DON found no systematic difference between the data generated by UV, persulfate and HTCO (as high-temperature catalytic oxidation) methods. Though new techniques such as HTCO have facilitated the determination of organic nitrogen, older techniques (kjeldahl method or persulfate oxidation) are still being used owing to their low specificity, sensitivity, ease of use and reproducibility (Cornell and Jickells, 1999; Cornell et al., 2003). However, the nitrogen present in forms other than amines, or amides is not sufficiently converted to ammonium. Furthermore, the method requires a tedious digestion procedure using concentrated sulfuric acid, followed by distillation of ammonia under alkaline medium. An alternative method for the determination of organic nitrogen is the alkaline persulfate digestion technique which promotes efficient hydrolysis and oxidation of most nitrogenous compounds resulting in nitrate ions. The final step requires the analysis of nitrate either by ion-chromatography, or a colorimetric technique.

Persulfate oxidation is carried out either in an autoclave or in a pressure cooker with the digestion time being generally in the range of 30–60 min (Bronk et al., 2000; Cornell et al., 2003; Sundarambal et al., 2007). On the other hand, microwave digestion is a well known technique for rapid sample preparation for inorganic and organic compounds in environmental samples. This advantage of digestion technique is that unlike conventional extraction methods that are subject to the boiling temperature of extraction solvents at atmospheric pressure, the microwave energy heats samples and solvents in a closed pressurized extraction vessel. As a result, the extraction of samples can be completed in minutes contrary to traditional methods where sample extraction requires hours together. For TN digestion, only very few researchers have explored the use of microwave-assisted digestion in wastewaters, sediments etc (He et al., 1990; Johnes and Heathwaite, 1992; Colombini et al., 1998; Colina and Gardiner, 1999; Maher et al., 2002; Lo et al., 2005). Furthermore, the microwave extraction can be effective even at low temperatures by using closed vessel system. The potential application of this sample preparation method has not been systematically evaluated for atmospheric wet and dry deposition samples yet (Karthikeyan et al., 2009a). A series of microwave-assisted sample preparation has been reported for the analysis of major ions (including NO_2, NO_3 and PO_4), organic acids, trace elements, PAHs, and total nitrogen (Karthikeyan and Balasubramanian, 2005a, b; Karthikeyan et al., 2006a, b; 2009a) in airborne particulate matter, and demonstrated their real-world applications with extensive field studies from different sources (See et al., 2006; See et al., 2007a, b). The quantity as well as the ratio of persulfate to sodium hydroxide used in the digestion is critically important in order to avoid the formation of chlorate (from chloride content) and high sulfate concentration (from persulfate) because of their potential interference in the IC analysis of nitrogen compounds for atmospheric wet and dry deposition samples (Karthikeyan et al., 2009a).

To date, most of the evaluations of atmospheric nitrogen deposition have focused exclusively on the inorganic (NO_3 and NH_4) fraction, while possible contribution of an organic component has either been ignored, or at best, is very uncertain. This is in large part due to the paucity of reliable dissolved organic nitrogen (DON) data. Cornell et al. (1995) have provided the first comprehensive evaluation of atmospheric DON flux to the world's oceans, based on measurements at various global locations. Aliphatic amines, free amino acids, total hydrolysable amino acids, urea and aromatic nitrogen are the various compounds reported to be present in wet and bulk deposition samples. Amorphous and largely uncharacterized macromolecules like humic materials also contribute significantly to DON (dissolved organic nitrogen). Although ON is ubiquitous, it is still a poorly characterized component of atmospheric deposition of nutrients (Neff et al., 2002). This lack of database is mainly because no single analytical technique can analyze the entire range of organic forms of nitrogen present. Nevertheless, the current practice is to only measure bulk DON through difference between the TN and IN ($IN = NO_3 + NO_2 + NH_4$), i.e. DON = TN - IN (Cornell et al., 2003).

A large number of studies have illustrated the dynamic nature of the nitrogen speciation and phosphorus fractionation balances in natural water, and the significance of the organic nitrogen and particulate phosphorus fractions in contributing to the total nutrient loading in a water body (Porter, 1975; Persson and Jansson, 1988). This eventually necessitates a rapid method for the simultaneous determination of TN and TP both for environmental studies on natural water, atmospheric deposition and routine control of sewage and wastewater. Persulfate digestion of water and sediment samples is the only digestion technique for simultaneous TN and TP determination (Valderrama, 1981; Koroleff, 1983; Ebina et al., 1983). This digestion procedure is accepted in the official methods of TP analysis (ASTM, 1988; APHA, 2005). The determination of nitrate and phosphate, formed in the oxidising procedure, is usually performed by colorimetry (ASTM, 1988; APHA, 2005) or ion chromatography (Ledo de Medina et al., 1994) but, to date, no simultaneous method of detection is available. Simultaneous determination by IC is prevented by the presence of a high amount of sulfate formed by the decomposition of the persulfate. The samples can be diluted for nitrate determination

(Ledo de Medina et al., 1994) but the detection limits of phosphate become too high for environmental application. The excess sulfate can be eliminated by using a barium loaded anion-exchange cartridge (Slingsby and Pohl, 1996), by liquid-liquid extraction (Mattusch and Wennrich, 1996) or by precipitation with lead perchlorate (Colina et al., 1996), however, these techniques are limited largely by total analysis time and costs. A column switching technique was applied to the determination of phosphate in high saline matrix in unsuppressed IC, but nitrate was not analyzed (Galceran and Diez, 1994). Colombini et al. (1998) used column switching for eliminating sulfate after microwave assisted persulfate digestion in order to get a fast simultaneous determination of TN and TP by suppressed IC without sample pretreatment.

2.2.6 Knowledge gaps in atmospheric deposition of nutrients in Southeast Asia

Although considerable progress has been made in reducing the amount of pollutants discharged from various sources in SEA, environmental contaminants generated by dispersed sources (such as runoff, or atmospheric depositions) remain poorly characterized. In particular, pollutants released in the atmosphere are spread much wider due to the initial transport and dispersion by prevailing winds, and may be deposited onto terrestrial or aquatic ecosystems as wet or dry fallouts. A number of field studies have been performed in recent years to characterize particulate pollutants and rainwater in Southeast Asian countries that were affected by the Indonesian forest fires (Chee et al., 1997; Orlic et al., 1997, 1999; Fang et al., 1999; Levine, 1999; Narukawa et al., 1999; Ikegami et al., 2001; Kunii et al., 2002; Okuda et al., 2002; Balasubramanian et al., 2003; See et al., 2006). However, these studies have not captured nutrients such as N and P species and no reliable experimental data on WAD and DAD nutrients in tropical environments exists. Recent studies have documented the importance of inorganic nitrogen deposited from the atmosphere to coastal water. Although organic nitrogen is ubiquitous, it is still a poorly characterized component of atmospheric deposition of nutrients in SEA. No detailed studies to date have yet been conducted on nutrient composition at aerosol particles and precipitation though they have significant effect on aquatic and terrestrial ecosystems. Although dry deposition is measured less often than wet deposition, it may contribute more nutrients than wet deposition. Therefore, studies of wet deposition alone may not provide an accurate characterization of total nutrient deposition.

The recurring haze episodes in SEA have attracted a lot of attention from both affected nations and international bodies because of their far-reaching and wide-ranging consequences. The air in Singapore and surrounding areas is frequently polluted by the transboundary smoke haze from the land and prolonged forest fires in Indonesia and neighboring countries. Due to recurring forest fires in SEA on a large scale and the abundant rainfall in this tropical region, DAD and WAD of nutrients to the ocean surface might be significant. Little is known about inputs and impacts of atmospheric N and P species to the Singapore coastal water than to coastal water of the USA and Europe, and also about the role of atmospheric inputs than those from runoff and outfall. It was therefore felt necessary to quantify the levels of macro-nutrients, N and P species, in aerosol and precipitation by developing sampling and laboratory methods to estimate annual N and P fluxes on aquatic ecosystem in the tropical region. These data will be useful for baseline studies of anthropogenic stresses on aquatic ecosystem, as well as to quantify contribution of N and P from atmospheric deposition into coastal eutrophication and primary productivity.

2.3 Eutrophication modelling

2.3.1 Eutrophication of seawater

Eutrophication is the enhanced inputs of nutrients and organic matter leading to changes in primary production, biological structure and turnover, resulting in a higher trophic state. The causative factors are elevated inputs of nutrients from land, atmosphere or adjacent seas, elevated dissolved inorganic nitrogen and dissolved inorganic phosphorus concentrations, and increased N/P ratios compared to the Redfield Ratio. Redfield ratio is the molecular ratio of carbon, nitrogen and phosphorus in phytoplankton (i.e. C:N:P = 106:16:1). Nixon (1995) defines marine eutrophication as "an increase in the supply of organic matter". The supply is not restricted to pelagic primary production, but also includes bacterial production, primary production of submerged aquatic vegetation, inputs of organic matter from land via rivers and point sources, distributed sources as well as the net advection from adjacent water. Gray (1992) focussed on the direct effects of nutrient enrichment on productivity and the secondary effects. Jørgensen and Richardson (1996) concentrated both on the process, the associated effects of nutrient enrichment and natural versus cultural (due to anthropogenic activities) caused eutrophication.

A balanced system in marine water (Figure 2.3) is supposedly characterised by: (1) a short pelagic food chain (phytoplankton-zooplankton-fish), (2) natural species compositions of planktonic and benthic organisms, and (3) a natural distribution of submerged aquatic vegetation. The changes in the structure and function of marine ecosystems are resulted by nutrient enrichment as indicated by bold lines in Figure 2.3. Dashed lines indicate release of hydrogen sulphide (H_2S) and phosphorus, which is positively linked to oxygen depletion. The manifestation of adverse effects of eutrophication in coastal marine environments is closely related to hydrodynamic processes, which mean physical processes such as advection, the development of stratification, establishment of fronts and mixing of water masses.

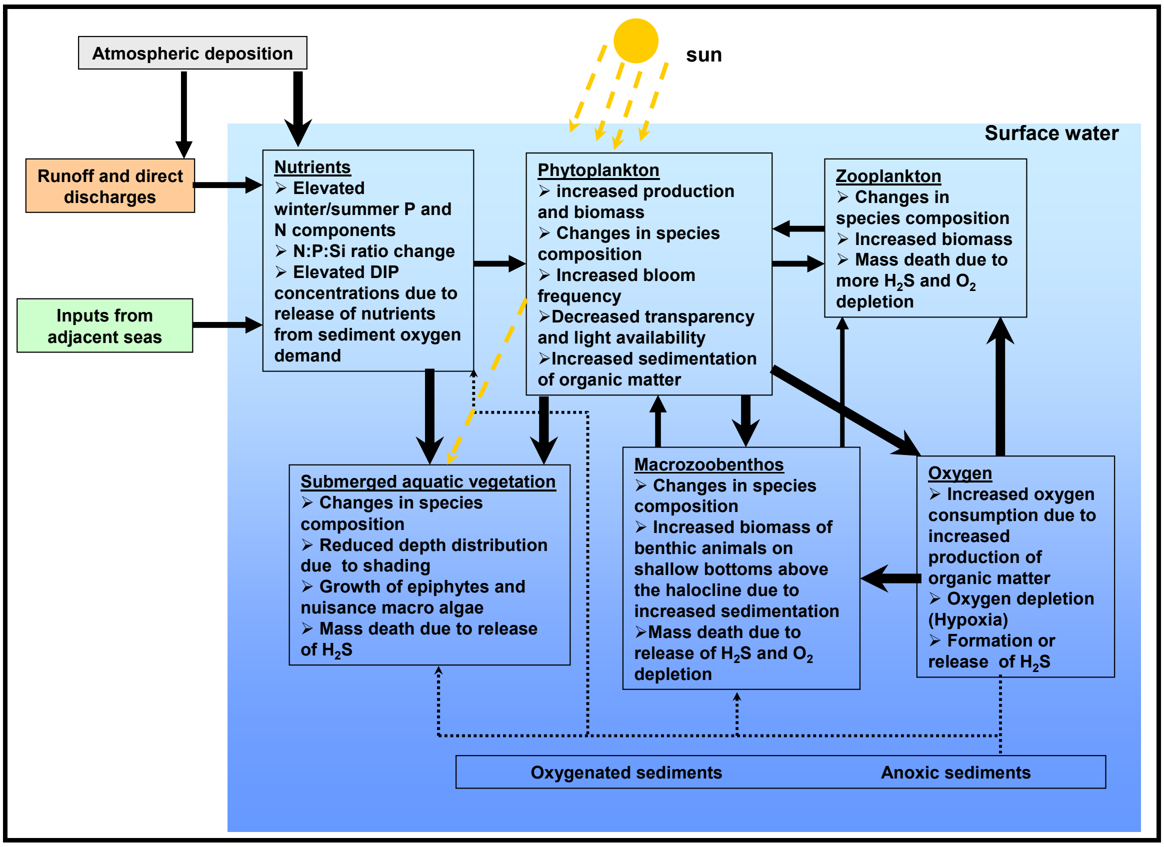

Figure 2.3 Conceptual model of marine eutrophication with lines indicating interactions between the different ecological compartments (adapted OSPAR, 2001).

The salinity and temperature stratification result in a spatial separation of photosynthetic and mineralization processes which may lead to oxygen depletion of the lower layers of the water column. The density of the seawater is of great importance for the transport processes in the sea. The vertical mixing is reduced when a vertical gradient (interface) is present and the horizontal movement of water is influenced by horizontal density gradient (fronts). The variation in salinity is very similar to the balance between evaporation and precipitation and, appears to be largely controlled by this balance in most areas. Overloading with nitrogen, phosphorus and organic matter may result in a series of undesirable effects. The major impacts of eutrophication include changes in the structure and functioning of marine ecosystems and reduction of biodiversity. The effects and consequences caused by eutrophication are changes in nutrient concentration and N:P:Si ratio, phytoplankton primary production and biomass, microbial loop and the pelagic system, light and sedimentation, oxygen concentrations, seasonal signals, sediments, submerged aquatic vegetation, benthic fauna and social consequences.

2.3.2 Necessity for modelling

Environmental models are essential for simulation of ecosystems that are either too large or too complex to isolate for experiments in the real world. Models allow scientists to estimate changes in an ecosystem due to changes in population, land use or pollution management. One set of input parameters describing the above properties constitutes the so-called scenario. Scenario modelling allow scientists to predict positive or negative changes within our ecosystem due to various management actions such as improved sewage treatment, controlling pollution loads and various developmental activities. Models use mathematical representations of the real world to estimate the effects of complex and varying environmental events and conditions. For instance, the eutrophication model NEUTRO (Tkalich and Sundarambal, 2003) estimates the delivery of nutrients to the Singapore water by simulating nutrient cycles, using inputs such as runoff, outfall discharge, and accidental spills. Models of water quality parameters, which including modelling of various trophic levels of the aquatic ecosystem, have evolved over the course of time in response to arising water quality issues. This evolution has included increased complexity in the number of aquatic processes/functions that have been incorporated (e.g., nitrogen and phosphorus cycling, interaction with primary and secondary trophic levels and their fate and transport processes in the surface water etc.). Thomann (1998) discussed the evolution of water quality models and their significance in prediction of surface water quality and ecosystem management and highlighted an evolution process of model credibility as schematically represented in Figure 2.4.

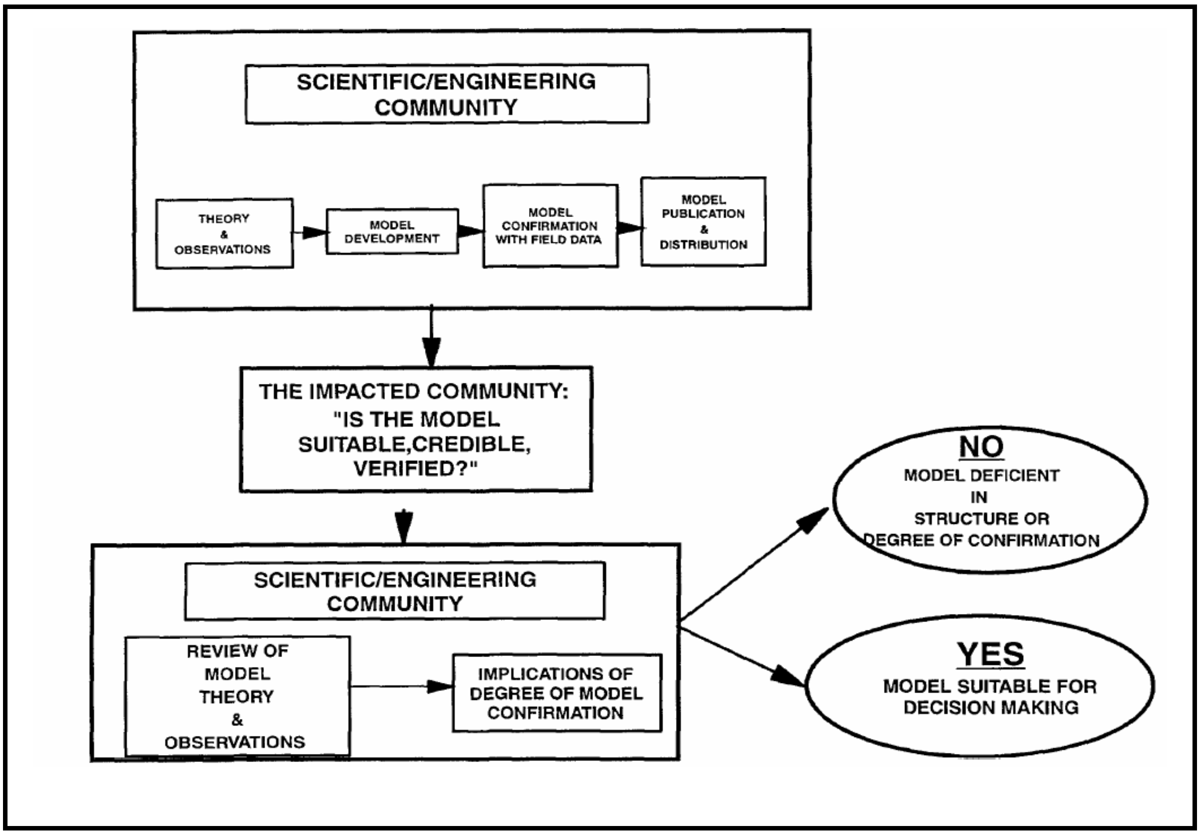

Figure 2.4 Schematic of processes for determining model credibility and utility by scientific and engineering community (Thomann, 1998).

Water quality models are implemented for the assessment of the impact of estuarine ecosystems change in response to variables inputs, as well as the interactions occurring within the system. The basic principle of model is the conservation of mass (both for water and pollutants) in space and time. The temporal variability and spatial distributions of nutrients in coastal water like Singapore are controlled by a complex physical–biological–chemical interaction process associated with external loading, tidal advection/dispersion, wind mixing etc. However, the use of numerical models promises to elucidate some of the important mechanisms and test hypotheses on the structure and function of ecosystems. In addition, models are used to predict and evaluate impacts on the coastal marine ecosystem from large-scale coastal development projects. While field measurements are necessary for characterizing baseline conditions, they are limited in that measurements are discrete, expensive and labour-intensive to obtain. Numerical modelling can help to avoid some of these problems and also allow the prediction of impacts and future scenarios, given perturbations to the system. Numerical models have been used as a key analytic tool to provide guidelines in setting goals of nutrient reduction to achieve water quality standards (Cerco and Cole, 1995; Cerco and Noel, 2004).

2.3.3 Review of modelling approches

Advanced eutrophication modelling of surface water started in response to practical necessities expressed by many researchers worldwide, most notably by Di Toro et al. (1971) and Thomann et al. (1975). As the water movement and mixing processes are closely related to biochemical kinetics in the water column, the ability to couple multidimensional hydrodynamic and mass transport simulations with algorithms to predict constituent kinetics may be critical to many water quality modelling studies. In recent decades, coupled physical-biological models have been widely applied to the marine environment to simulate both physical and biogeochemical processes and study the interactions between them, especially the effect of physical factors on biological communities. Besides the advection–diffusion contribution, a series of reaction kinetics for the biogeochemical interactions between non-conservative quantities is considered. Many models for the description of the trophic and biochemical evolution in lakes, reservoir and coastal environment have been developed in the past (Orlob, 1983) and continuously are being improved in the last few years (Angelini and Petrere, 2000). Arhonditsis and Brett (2004) compiled a comprehensive review of 153 aquatic biogeochemical models published between 1990 and 2002 and concluded that validation is increasingly complicated as biophysical models become more complex. The complexity of the physical models ranges from box (Li et al., 2000) and 1-D models (e.g., Marra and Ho, 1993; Doney et al., 1996; Hood et al., 2001) to fully 3-D water quality and hydrodynamic models (e.g., Skogen et al., 1995; Lima and Doney, 2004). The biological models range from simple NPZ (nutrient, phytoplankton, zooplankton) (e.g., McClain et al., 1996) or NPZD (nutrient, phytoplankton, zooplankton, detritus) models (e.g., Doney et al., 1996; Oschlies and Garcon, 1999; Hood et al., 2003) to multi-nutrient, multi-species and size-structured ecosystem models (e.g., Moore et al., 2002, 2004; Lima and Doney, 2004). When such models are applied to estuarine and coastal water, they may provide a means of assessing the potential impacts of local management strategies and hence provide useful information to decision-makers. In the aquatic ecosystems literature, there are numerous references to models that have been used for understanding oceanic ecosystems (e.g., bloom dynamics, the global carbon cycle) and predicting biotic responses to climate change (Fasham et al., 1993; Frost and Kishi, 1999; Boyd and Doney, 2002; Kawamiya, 2002), but this class of models has also been used as management tools for predicting eutrophication or integrating environmental with socioeconomic concerns (Ambrose et al., 1991; Cerco and Cole, 1995; Hamilton and Schladow, 1997; Turner, 2000; Arhonditsis et al., 2000, 2002).

With improved understanding of the eutrophication processes and hydrodynamics as well as more advanced computing capability, freshwater and marine hydrodynamics and water quality models have been developed and applied to study water quality problems (Thomann and Muller, 1987; Chapra, 1997; Gin et al, 2001, Tkalich et al, 2002). Some authors adopted a multi-elemental approach (organic carbon, nitrogen, phosphorus, silica and dissolved oxygen), which can particularly be useful for models that intend to make predictions and explore potential system dynamics outside the calibration domain (Reichert and Omlin, 1997; Reckhow and Chapra, 1999). To understand the complex, highly nonlinear algal dynamics varied in space and time, one can use process-based three-dimensional eutrophication model (often complex in nature and computationally demanding) or data driven models (Sundarambal et al., 2009b). A process-based model requires a lot of input data and model parameters (often unknown) such as initial boundary conditions of state variables, kinetic coefficients and hydrodynamic forcing. Models developed by data driven technique is very fast computationally and require much less input parameters as compared to process-based models. The neural network models are quite robust with respect to redundant inputs; co-predictors can play an important role in improving existing models, exploiting non-linear, even non-monotonic relationships between primary production and other variables that are not directly involved in photosynthetic processes (Sundarambal et al., 2008e, 2009b, c). In order to predict phytoplankton and nutrient concentrations, which depend on depth variation of light and vertical structure of the water column, it is necessary to use a three-dimensional eutrophication model, where coupled physical, chemical and biological processes are incorporated. CE-QUAL-ICM is a three dimensional (3D), time-variable, eutrophication model (Cerco and Cole, 1993, 1995) applied to Chesapeake Bay in the United States, which incorporates 22 state variables that include multiple forms of algae, carbon, nitrogen, phosphorus, and silica; and dissolved oxygen. The marine environment is N limited in the short term, in contrast to the freshwater P-limited system (Smetacek et al., 1991), an increase in N:P ratios can potentially have profound impacts on the phytoplankton community, not only in terms of increasing algal abundance but also by altering the relative abundance of species present (Jickells, 1998). If the ecosystem is under nutrient-limited conditions, nutrients fallout in the coastal waters might be a significant contributor toward regional eutrophication.

The field monitoring data are beneficial to understand the baseline marine environment of Singapore's coastal water, as well as the calibration and verification of the developed eutrophication model. Various studies on water quality and eutrophication in the Singapore Strait were carried out (Chiong, 1999; Xiaohua, 2000; Yi, 2001). The 3-D numerical eutrophication modelling study of tropical coastal water of Singapore is being carried out using NEUTRO (Tkalich and Sundarambal, 2003, Sundarambal and Tkalich, Submitted-a) which takes into account the nitrogen, phosphorus cycles, phytoplankton and zooplankton dynamics and dissolved oxygen balance with a total of 11 state variables.

2.3.4 Water quality assessment due to distributed sources

The marine coastal areas of islands are important in that they support ecosystems that are of direct importance to the island's economic resources. For water quality assessment, it is necessary to provide the coastal engineer with mathematical tools able to reproduce the present behaviour and to forecast the aquatic system behaviour at scenarios resulting from different design solutions of offshore or coastal structures (Cescon et al., 1998). Water quality models serve two critical functions: (a) to improve understanding of processes, particularly the complex interactions between abiotic and biotic components; and (b) provide continuous (through interpolatation) and forecast data for environmental management and assessment. Water quality impact assessment of pollution sources (point and distributed) onto the aquatic ecosystem can be obtained using numerical models. The most important distributed loads include the wet and dry deposition from the atmosphere, runoff and anthropogenic sources. The occurrence of frequent forest fire and high intensity precipitation may cause episodic water quality problems by delivery of particulate and soluble admixtures (e.g. nitrates and phosphorus) from atmosphere and runoff to water bodies (Owens et al., 1992; Michaels et al., 1993; Balasubramanian et al., 1999; Muraleedharan et al., 2000; Pinckney et al., 2001; Arhonditsis et al., 2002; Clark and Kremer, 2005). When a rainfall occurs after long dry period during hazy days, an episodic wet atmospheric deposition with high N concentration can occur. Pollution resulting from increased human activities is threatening aquatic ecosystems, its effects being characterised by eutrophication and the occurrence of unhealthy low dissolved oxygen levels. The fate and transport of atmospheric deposition of mercury, persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), herbicides and ozone to aquatic ecosystem were studied elsewhere.

There are very few well documented examples of causal relationships between environmental concentrations of chemical contaminants (N and P species) and adverse biological effects in Singapore and surrounding coastal water. Numerical modelling methodology can be adopted for impact assessment/understanding the effect due to distributed sources. This method provides a numerical evaluation of the influence of distributed sources (e.g atmospheric nutrient deposition) on the aquatic ecosystem.

2.3.5 Rationale for water quality modelling

The atmospheric input of macronutrients often has been claimed to be a missing element to explain anomalies in primary production. Atmospheric deposition in Singapore and surrounding countries appears to provide significant fluxes of nutrients of environmental concern and to play an important role in the coastal eutrophication. The haze events that have plagued SEA are likely to affect atmospheric fluxes of nutrients and other pollutants into aquatic systems. Most of local knowledge regarding contamination due to forest fires (biomas burning) originates from earlier studies conducted elsewhere, at various parts of the world (e.g., The United States, Australia, Brazil, Mexico, Africa). However, the results of these studies are of little use in assessing the environmental impacts of the resulting pollution since their main objective was to quantify the flux to the atmosphere of various trace gases like carbon dioxide, methane, nitrous oxide from biomass burning. We have to look at further fate of the airborne admixtures, including deposition on the water surface, because it could be a possible link between atmospheric deposition of nutrients and marine phytoplankton blooms. No studies have investigated the responses of SEA marine ecosystems to atmospheric deposition due to episodic haze events, such as forest fires. In order to examine the quantitative response of the pelagic food web to N and P events from atmospheric deposition, numerical modelling study is required. Accordingly, the present study is embarked on quantifying the distribution of nutrients from atmospheric deposition on coastal water and their contribution to the coastal eutrophication.

Nutrients are distributed throughout the seawater by advection and diffusion as a consequence of atmospheric deposition and direct introduction into aquatic ecosystems. The fate of nutrients in sea water depends on a number of mechanical (transport with moving flows), chemical (chemical decay, amalgamation with other chemicals, transfer to gaseous state, etc.), physical (transfer to another aggregative state, adsorption) and biological (pollutant accumulations and transport by biota) processes. These processes can only be fully taken into account with a three dimensional, hydrodynamic and water quality ocean model. Therefore, the objective of the present study is to develop such a water quality model and use it to investigate the cycling of nutrients in the Singapore costal water and the surrounding region. It should be remembered that such a study was not done earlier and it is emphasized that this is a first study of this kind.

Steps involved in numerical water quality assessment using the proposed model are

- obtain the required data for water quality and nutrient loadings from various sources by field monitoring;
- define model baseline and boundary conditions from available data;
- use water quality baseline as initial conditions and prescribe the boundary conditions;
- use fine-tuned coefficients for chemical kinetics;
- specify existing and projected (as the result of industrial development, natural and human activities) sources of nutrient flux;
- compute for different hydrodynamic and nutrient load scenarios until quasi-steady-state patterns are obtained;
- analyze and visualize the model output results to depict the temporal and spatial dynamics of each parameters.

Based on the literature review, the overall objectives of the study are (i) field monitoring to quantify nutrients from atmospheric deposition and (ii) modelling for the qualitative as well as quantitative understanding of the relative importance of atmospheric nutrient fluxes in the region and to estimate whether the quantified nutrients from atmospheric deposition is a significant contributor toward regional eutrophication. Therefore, this study endeavors to improve our understanding of atmospheric deposition of nutrients such as N and P species and to provide an assessment on their impacts on the aquatic ecosystems. These results would form the basis for a baseline study to access environmental effects of atmospheric deposition of nutrients onto the coastal aquatic ecosystem and to predict/forecast the coastal water quality due to atmospheric nutrient deposition for regional water quality management.

CHAPTER 3: MATERIALS AND METHODS

3.1 Experimental methods

3.1.1 Sampling instrumentation

The high volume air sampler (model 3800 AFC: HI-Q Environmental Products Company, USA) (Figure 3.1), provides a flexible sampling platform for the sampling of PM_{10}, $PM_{2.5}$ or Total Suspended Particulates (TSP), and was used to sample atmospheric particulates for dry deposition measurements. The high volume air sampler (HVAS) is a device for sampling large volumes of air containing particulate matter by filtration. HVAS is housed in a clear-anodized aluminium outdoor shelter. The units incorporate a maintenance-free, two or three stage centrifugal blower powered by a brushless, variable speed, maintenance-free motor. This air sampler has a motor that is controlled by an electronic mass flow sensor which detects changes in the operators pre-set flow rate caused by changes in temperature, barometric pressure, and pressure drop due to dust loading on filter media. Air flow is maintained at 40 SCFM (Standard Cubic Feet per Minute) by an automatic air flow control device. For dry deposition samples, a mini-volume air sampler can also be used and a detailed description of the dry deposition sampler can be found elsewhere (See et al., 2006; See et al., 2007a, b). TSP had been widely measured in the past and present for the characterization of its elemental composition and nutrients in aerosol for estimation of dry deposition fluxes (Caruso et al., 1981; Herut et al., 1999; Duarte et al., 2006; Chen et al., 2007; Ayars and Gao, 2007). The TSP samples were collected on 20.3 x 25.4 cm size Whatman QM-A high purity quartz (SiO_2) microfibre filter (CAT No. 1851-865, Whatman plc, Middlesex, U.K.) for water soluble ionic and nutrients analysis.

An automated wet-only rainwater sampler (Ecotech Model 200: Ecotech Pty Ltd, Australia) (Figure 3.1) was used for the collection of rainwater samples at the sampling locations. This collector consists of a High Density Polyethylene bucket with a diameter of 28.6 cm, which is equipped with a sensor (A tipping bucket precipitation gauge) that signals the lid to open and initiate rainwater sampling and closes just after the rain event. The automated wet collector thus prevents the contamination of rainwater by dust fall, taking place before and after a rain event.

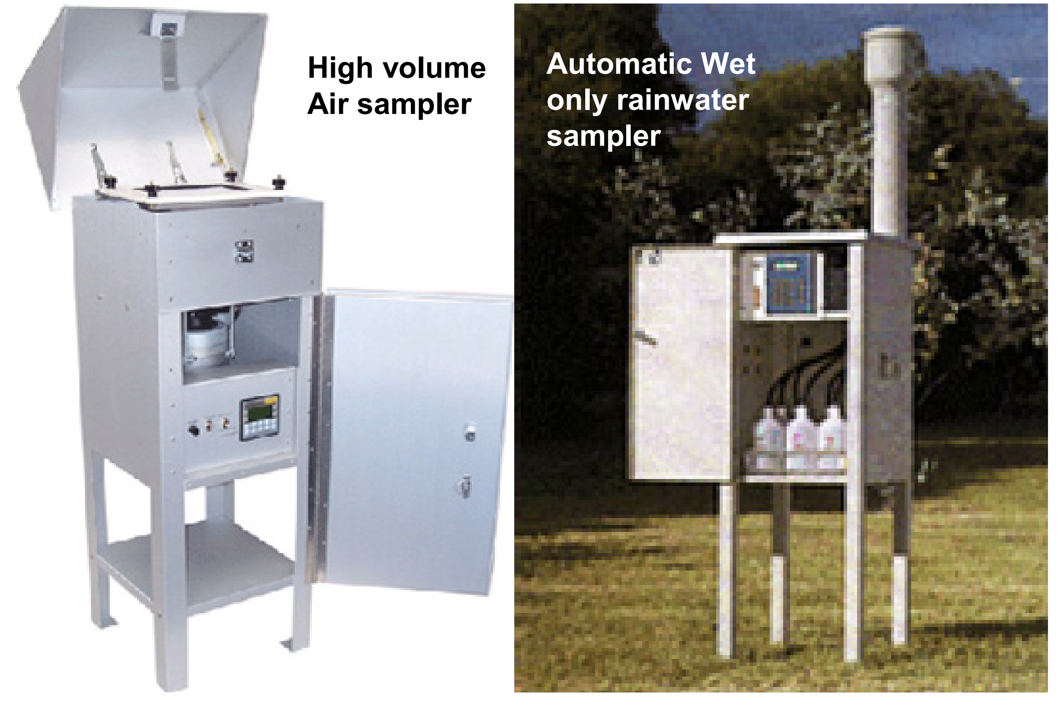

Figure 3.1 High volume air sampler and automatic wet-only rainwater sampler

3.1.2 Sampling locations

Singapore is a small island with total land area of 710 km^2 located at latitudes 1° 06' N and 1° 24' N and longitudes 103° 24' E and 104° 24' E, 137 km north of the equator (Figure 3.2). It is highly urbanized and industrialized with small water resources and limited ocean environment around the island. The boundaries of Singapore's territorial water coincide closely with the port limits. The Singapore Strait is a channel shaped, where three different water bodies (Java Sea to the South, the South China Sea to the East and Malacca Strait to the Northwest). Because of its geographical location, its climate is characterized by uniform temperature and pressure, high humidity and abundant rainfall. Singapore has two main seasons, the Northeast Monsoon (NEM) (November to March) and the Southwest Monsoon (SWM) season (June to September), separated by two relatively shorter inter-monsoon (IM) periods (April to May, and October respectively). The ambient air temperature ranges from 21.1 to 35.1 ºC, and the annual average rainfall is 2136 mm. The population of Singapore is 4.84 millions (Singapore Department of Statistics, 2008). In general, dry weather is the result of the lack of convection or stable atmosphere which prevents the development of rain-bearing clouds. Southwest (SW) and Northeast (NE) winds occurs in the coastal area periodically and the maximum wind speeds range from 5 m/s to 10 m/s.

For the present study, aerosol and rainwater samples were collected in two places, one located at the rooftop of building E2 (latitudes 1° 18’ N and longitudes 103° 46’ E, 67m above sea level), National University of Singapore (NUS) and another located at the Tropical Marine Science Institute in Saint John’s Island (SJI) (latitude 1° 13' 10" North of the Equator and longitude 103° 50' 54" East), Singapore (Figure 3.2). There are no industrial sources in close proximity to the sampling sites. The NUS site is approximately 1 km away from the open sea, free of any major emissions. The chemical industries are situated to the southwest of the station whereas heavy industries are found at the northwest direction. The sampling station in SJI is selected as it is close to the open coastal area in the southern part of Singapore and does not have local pollution sources. Except regional hazy days, the air is free from major air pollution. Climatological winds averaged over the years 1980–2006 are shown in Figure 3.3. During NEM period

(Figure 3.3a), the air mass masses are likely to bring air pollution from China, Myanmar, Cambodia, Vietnam, Laos and Thailand. During SWM period (Figure 3.3b), air masses pass by southern Sumatra, Borneo, Surabaya and Java Islands of Indonesia and potentially could transport air pollution from the region to Singapore area, Malacca Straits and Peninsular Malaysia.

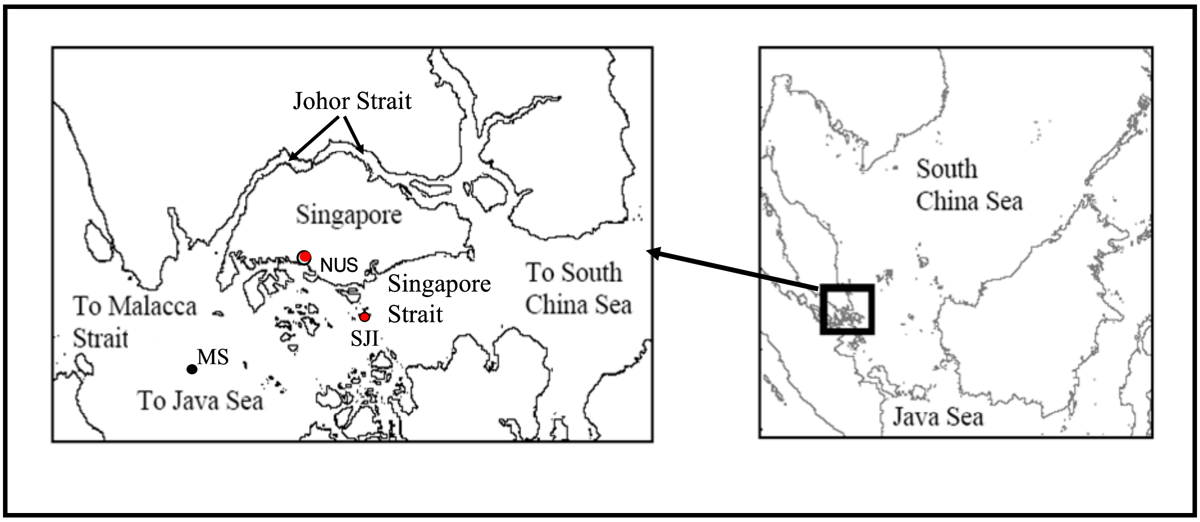

Figure 3.2 Sampling locations (NUS and SJI) in Singapore

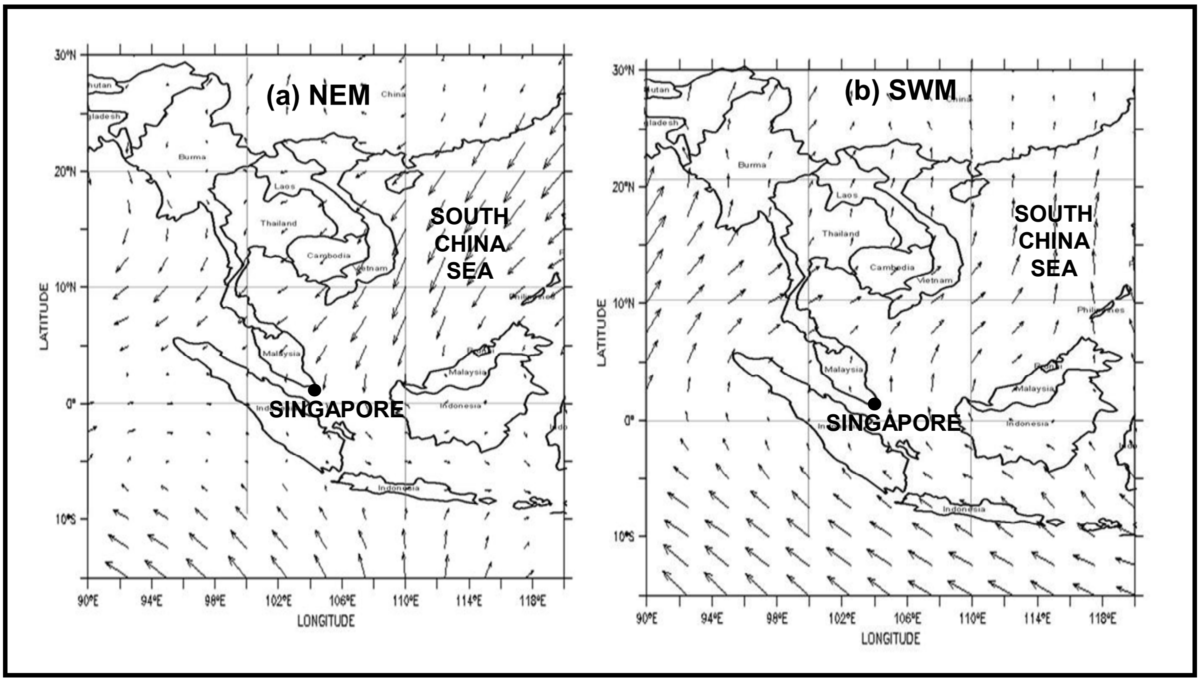

Figure 3.3 Climatological wind averaged over the years 1980–2006 (Sundarambal et al., 2009a)

3.1.3 Sample collection

The TSP samples were collected every 24 hrs three times a week at the sampling location mentioned before mainly during dry weather conditions. The filters were conditioned in a dry box at 30 % relative humidity and 25 °C temperature for 24 hrs prior to and after air sampling; pre- and post-sampling weights were used to obtain the TSP mass collected on the filters. Filters were then weighed using the MC5 microbalance (Sartorius AG, Goettingen, Germany) with 1 μg readability after passing the filters through a field of static eliminators for a few seconds. The balance was regularly checked with NIST-traceable standard calibrated weights. The particulate filters were stored in a refrigerator at 4 °C until extraction of analyte sample for subsequent analysis of nutrient compounds. All the filters were handled using stainless steel forceps with beveled, unserrated tips. The mass concentration of TSP ($\mu g/m^3$) was calculated from the collected mass of particulates (μg) divided by the volume of air passed through the filter (m^3) during sampling period.

Rainwater samples were collected whenever the rain event occured. Daily rainfall amounts and other meteorological parameters were obtained for October 2006 through January 2007 from an automated weather station (Department of Geography, NUS). Rainfall < 1 mm was not taken into account for laboratory analysis, firstly for analytical convenience, and secondly because even when the nutrient concentration was high, such events yield low or negligible nutrient loads. Rainwater samples were transferred from the sampler to pre-cleaned high-density polyethylene (HDPE) bottles after the rain event and immediately filtered using 0.45 nylon membrane filters and refrigerated at 4 °C for sample analysis.

Samples collected at NUS sampling site were daily rainfall amounts and other meteorological parameters for January 2006 through July 2006 from NUS weather station

(Department of Geography, NUS), the aerosol samples (n = 27) and rainwater samples (n = 24) for the period from January 2006 to July 2006. Samples collected at SJI sampling site were the aerosol samples (n = 55) and rainwater samples (n = 21, on event-to-event basis) from September 2006 to January 2007. About 14 seawater samples were also collected according to the standard sampling protocol (Parsons et al., 1984; APHA, 2005) during 2006 haze period from 8th October 2006 to 20 January 2007 from SJI ferry terminal situated approximately 6.5 km south of Singapore, off Singapore Strait.

3.1.4 Sample preparation

3.1.4.1 Reagents and apparatus

For preparation of reagents and standards, ultrapure water (MilliQ® Gradient A 10 System, Millipore, USA) was used. All reagents were of analytical grade. Anionic standards of chloride, nitrite, nitrate, and sulfate and that of ammonium were procured from AccuStandard, USA. Sodium hydroxide, potassium persulfate, EDTA, glycine, and urea were obtained from Merck, Germany.

SRM 1648 (Urban Particulate Matter), obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), was used for validation of the methods for both N and P species analysis. This standard consisted of natural atmospheric particulate matter collected at an urban location, and was certified for its major, minor and traces inorganic constituents.

Organic nitrogen standard

Nitrogen standards were prepared from ethylenediaminetetraacetic acid (ETDA, $(CH_2N(CH_2CO_2H)_2)_2$), urea ($(NH_2)_2CO$) and glycine (NH_2CH_2COOH) by dissolving appropriate amounts in ultra pure water so as to have a stock solution of 1000 mgN l-1. EDTA-based standard nitrogen solution was used for optimization of microwave-assisted persulfate oxidation (Karthikeyan et al., 2009a). The other two reagents, urea and glycine, were used to check the robustness of the optimized procedure.

Digestion reagent

Digestion reagent was prepared by dissolving 2.01 g low nitrogen (<0.001%N) potassium persulfate, $K_2S_2O_8$ and 0.3 g NaOH in water, and diluted to 100 ml just before use.

Borate buffer solution

Borate buffer solution was prepared by dissolving 6.18 g boric acid, H_3BO_3 and 0.8 g NaOH in water, and diluted to 100 ml.

Inorganic nitrogen standard

Potassium nitrate (KNO_3) was dried in an oven at 105 °C for 24 hrs. The stock standard nitrate solution was prepared by dissolving 0.7218 g in water and diluting to 100ml. 1ml of this standard stock solution contains 1000 ppm nitrate concentration.

Intermediate nitrate solution was prepared by diluting 100 ml stock standard nitrate solution to 1000 ml with water. 1 ml = 10 µg NO_3 N = 10 ppm.

Combined reagent

Ammonium molybdate solution was prepared by dissolving 4 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 100 ml of water. Ascorbic acid solution was in turn prepared by dissolving 1.76 g ascorbic acid in 100 ml water. This solution was stable for about 1 week at 4 °C. 5N H_2SO_4 solution was prepared by mixing 13.88 ml of concentrated H_2SO_4 with 100 ml of water.

All the above said reagents must be allowed to reach room temperature before a combined reagent is prepared (APHA, 2005). Individual reagents were mixed in the following proportions for preparing 100 ml of the combined reagent: 50 ml of 5N H_2SO_4, 15 ml of ammonium molybdate solution and 30 ml of ascorbic acid solution. The solution was mixed well after addition of each reagent in the above order. When the turbidity was noticed in the combined reagent, the reagent was shaken well and allowed to stand for a few minutes. The combined reagent was found to be stable for 4 hrs.

The analysis of the water-soluble inorganic ionic species and diluted digests were carried out by means of the integrated reagent-free ion chromatography (IC) (Model ICS-2000; Dionex Corporation, Sunnyvale, CA, U.S.A.) using a cation column and anion column according to our standard laboratory procedure (Karthikeyan et al., 2005a, b, 2007, 2009a). The cations, i.e. Li^+, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}, and anions, i.e. Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and PO_4^{3-} were usually analyzed by IC using cation and anion column respectively. It consisted of an eluent Generator (EG with CR-TC), isocratic pump, conductivity detector, anion self-regenerating suppressor (ASRS Ultra II- 4 mm), Rheodyne six-port injection valve with 25 μl injection loop, and AS-40 auto sampler. An AS-11-HC (4 mm) analytical column in conjunction with an AG-11-HC guard column was used for nitrate determination. The eluent is the carrier that moves the chemicals through the column. The peaks corresponding to different analytes in individual standards were identified according to their retention times. The whole IC operation including calibration and sample analysis was carried out using ChromeleonTM software. The ammonium ion content was also analyzed in order to account for dissolved inorganic nitrogen. For this determination, the cation ion-exchange column, CS-12 (4 mm), was used with 11.0 mM H_2SO_4 as the eluent. The IC operating conditions are shown in Table 3.1.

Table 3.1 IC operating conditions

Parameter	**Analysis of cations**	**Analysis of anions**
Analytical column	IonPac AS11-HC (4 x 250 mm)	IonPac CS11 (2 x 250 mm)
Guard column	IonPac AG11-HC (4 × 50 mm)	IonPac CG11 (2 x 50 mm)
Suppressor type	ASRS ULTRA II (4 mm) Anion Self-Generating Suppressor	CSRS ULTRA II (4 mm) Cation Self-Generating Suppressor
Suppressor current	200 mA	120 mA
Eluent	Hydroxide, 0–1 min: 1 mM 1–25 min: 1–25 mM, linear 25–29.9 min: 25–40 mM, linear 30 min: 1 mM	Sulfuric acid, 11 mM
Flow rate	1.50 ml/min	1.00 ml/min
Injection loop	25 µl	25 µl
Data collection rate	5.0 Hz	5.0 Hz
Cell temperature	35 °C	35 °C
Column temperature	30 °C	30 °C

The choice of analytical column is important since the nitrate is to be determined in the presence of large amount of sulfate. We have employed a high capacity anionic column, AS-11-HC, for this work. The eluent strength and its flow rate were varied and optimized in order to obtain better baseline resolution. The eluent strength of 20 mM at a flow rate of 0.8 ml/min was used for the determination of nitrate from digests. A four point calibration (0.2, 0.5, 1.0 and 2 mg/l NO_3) in the presence of equal amounts of sulfate and chloride was performed initially. Then a second set of calibration standards was prepared containing 200 mg/l of sulfate in all standards. The slope and the regression coefficient of both calibrations were 0.132 (R^2 = 0.95) and 0.129 (R^2 = 0.93), respectively, indicating the nitrate determination was satisfactory even in the presence of a significantly higher amount of sulfate concentration. The repeatability and reproducibility of the IC method were assessed by injecting 0.5 mg/l nitrate standard and they were estimated to be 3.2 % and 3.9 %, respectively.

The spectrophotometer measures quantitatively the fraction of light that passes through a given solution. In a spectrophotometer, light from the lamp is guided through a monochromator, which picks up light of one particular wavelength from a continuous spectrum. This light passes through the sample that is being measured. After the sample, the intensity of the remaining light was measured with a photodiode or other light sensor, and the transmittance for this wavelength was then calculated.

3.1.4.2 Extraction and analysis of inorganic ions

Aerosol particulate filter samples were taken as a fraction, for example, 1/4 or 1/8th part of total filter area and 20 or 50 ml Milli-Q water (Millipore) was added in a tapered bottle. It was sonicated for 30–60 min and then the extracts were filtered using a syringe filter. Rain water samples were taken after filtration for laboratory analysis. Samples were stored in the refrigerator prior to analysis, in the original polyethylene collection bottle; no other precaution was taken against biological activity in the stored sample, however samples were filtered through a 0.45 μm filter prior to analysis when required. The dominant ionic species were sulfate, nitrate, and ammonium of the total mass of the inorganic ions. The cations, i.e. NH_4^+ and anions, i.e. NO_2^-, NO_3^-, and PO_4^{3-} were analyzed by IC using cation and anion column, respectively. The aerosol and rainwater samples were first analyzed for dissolved and water-soluble inorganic nitrogen (NO_3 and NH_4). Another aliquot/filter extract was processed for total nitrogen (TN) and total phosphorous (TP) following the procedure described in Section 3.1.5.

3.1.5 Methods for nutrient analysis

The acquisition of relevant and reliable analytical data was a primary component in the research and monitoring programs associated with the assessment of nutrients in natural water and related environmental issues such as eutrophication. The identified types of nutrients coming from the atmosphere by atmospheric deposition are: N species such as ammonium (NH_4), nitrate (NO_3), nitrite (NO_2), total nitrogen (TN) and organic nitrogen (ON), and P species such as phosphate (PO_4), total phosphorous (TP) and organic phosphorous (OP). The sample analysis was done to characterize atmospheric wet and dry nutrient deposition. The aerosol particulate and rainwater samples were analyzed for the ionic species by IC using a cation column and anion column, for total nitrogen and total phosphorus according to our standard laboratory procedure developed for DAD and WAD samples in the tropical region (APHA, 2005; Karthikeyan et al., 2005a, b; Sundarambal et al., 2007, 2009a; Karthikeyan and Balasubramanian, 2006; Karthikeyan et al., 2007; 2009a, b). The quality of the methods for both N and P species was verified by a known NIST SRM 1648 (urban particulate matter) standard sampling procedure and a standard addition method (Sundarambal et al., 2007, 2009a; Karthikeyan and Balasubramanian, 2006; Karthikeyan et al., 2007; 2009a, b).

3.1.5.1 Nitrogen species

The collected aerosol and rainwater samples were analyzed for identified N species as follows.

Ammonium

The samples were analyzed for ammonium by IC cation column after initial calibration check and initial calibration blank demonstrated that the instrument performance was acceptable at the beginning of the sample analysis. In order to ensure continually acceptable performance, a continuing calibration check and continuing calibration blank were run every tenth sample. For every sample delivery group (SDG, 20 samples), a laboratory spike analysis and a laboratory duplicate analysis were performed.

Nitrate + Nitrite

There are two methods. In the first method, the samples were analyzed for NO_3+NO_2 by IC anion column. In the second method, the samples were analyzed for nitrate by a procedure whereby nitrate is reduced to nitrite by passing the sample through a copperized cadmium column (4500-NO_3^- E. Cadmium Reduction Method) and nitrite by 4500-NO_2^- B. Colorimetric Method. The nitrate reduced to nitrite plus any free nitrite present react under acidic conditions with sulfanilamide to form a di-azo compound which coupled with N-1-naphthylethylenediamine dihydrochloride to form a reddish–purple azo dye that is measured at 540 nm. The standard nitrite and nitrate was used for calibration. The calibration curve was then verified by a known nitrogen compound standards. This second source calibration check and initial calibration blank demonstrated that the instrument is capable of acceptable performance at the beginning of the sample analysis.

Total nitrogen

Measuring TN involves releasing the nitrogen from organic molecules by chemical oxidation to NO_3-N. To determine TN, the samples were placed in a bottle with an oxidizing reagent (potassium persulfate–sodium hydroxide) and borate buffer solution. Samples preserved with acid could not be analyzed by this method. In the bottle, 10 ml of sample or standard or a portion diluted to 10 ml, 5 ml digestion reagent and 1 ml borate buffer were added and mixed well. The bottles were placed in a pressure cooker at 100 to 110 °C for 30 min for sample digestion so that all N species could be converted into nitrate. After the samples were cooled to room temperature, the digested samples were filtered through a 0.45 μm filter. A boric acid–sodium hydroxide buffer was added to bring the pH of the sample within the range 7–8. If IC was used for TN determination, the digested sample pH would be adjusted to alkaline condition to avoid spoiling the IC columns. The sample was then ready for the determination of total oxidized nitrogen using IC as nitrate. EDTA standards were used for calibration. The quality of the methods for N species was verified by a known NIST SRM 1648 (urban particulate matter) standard sampling procedure and a standard addition method. For SRM, an accurately weighted amount (10 to 20 mg) of NIST SRM 1648 was transferred to the digestion vessel followed by addition of 10 ml of ultra pure water. Digestion and chemical analysis were carried out as described above.

Organic nitrogen

Organic nitrogen species are typically referred to as a subset of reactive nitrogen. These chemical species result from direct emissions of organic nitrogen compounds or from the interaction between nitrogen and biogenic or anthropogenic and natural sources. Organic nitrogen (ON) flux was quantified by subtracting the inorganic nitrogen (NH_4, NO_3 and NO_2) fluxes from TN flux. It should be noted that the organic nitrogen fractions of the total wet and dry depositions were not qualitatively specified by laboratory analysis.

3.1.5.2 Phosphorus species

The collected aerosol and rainwater samples were analyzed for identified P species as follows:

Phosphate (PO_4), total phosphorous (TP) and organic phosphorous (OP)

Measuring total phosphorus involves releasing the phosphorus from organic molecules by chemical oxidation to PO_4-P. The dissolved organic phosphorus is estimated by the difference between the total and inorganic P. The aerosol and rainwater samples were analyzed for PO_4 by the IC anion column and for TP by the Ascorbic Acid method (4500-P E., APHA, 2005). The principle involved in this analysis is that ammonium molybdate and potassium antimonyl tartrate reacts in acid medium with orthophosphate to form a heteropoly acid - phosphomolybdic acid - that is reduced to intensely colored molybdenum blue which is measured at 880 nm by ascorbic acid. The calibration curve was then verified by an external quality control sample from Environmental Resource Associates (ERA). This second source calibration check and initial calibration blank demonstrated that the instrument is capable of acceptable performance at the beginning of the sample analysis. The standard phosphate (potassium dihydrogen orthophosphate KH_2PO_4) was used for calibration. Digested sample (see Section 3.1.5.1) was used for TP determination as phosphate procedure. The phosphate analysis was carried out spectrophotometrically (by using longer path length cell) since it is usually present in very low concentration (2–30 µg/l). In ascorbic acid method, 10 ml of digested sample and 1.6 ml of combined reagent were added and mixed thoroughly. After about 10 min but no more than 30 min, the absorbance of each sample at 880 nm was measured using reagent blank as reference solution. The quality of the methods for P species was verified by a known NIST SRM 1648 (urban particulate matter) standard sampling procedure and a standard addition method. Organic phosphate (OP) was quantified by subtracting the PO_4 from TP.

3.1.6 Deposition flux calculations

3.1.6.1 Dry deposition

Dry atmospheric deposition (DAD) is a slow but continuous flux of airborne contaminants to an underlying surface. Dry deposition fluxes (F_{dry} in g/m^2/yr) were calculated from the product of dry deposition velocity (V_d in cm/s) and measured concentrations of nutrient species ($C_{aerosol}$ in µg/m^3) in aerosol, as shown in Equation (3.1) with unit conversion factor of 0.31536.

$$F_{dry} = 0.31536\ C_{aerosol}\ V_d \quad (3.1)$$

Deposition velocity, V_d, may be viewed as the velocity at which pollutant gases and aerosols existing at a given atmospheric concentration are deposited on the Earth's surface. Processes that control V_d include gravitational settling, impaction, and diffusion (Jickells and Spokes, 2001). All these processes occur simultaneously and are all affected by many variables including particle size, wind speed, relative humidity, and sea surface roughness. The term V_d is the result of many processes (for a full explanation see, e.g. Seinfeld and Pandis, 2006), and it is thus very difficult to determine. However, the calculation of F_{dry} is usually carried out using V_d found in the literature for many elements including nutrients (see e.g. Sehmel, 1980; Slinn and Slinn, 1980; William, 1982; Joffre, 1988; Dulac et al., 1989; Migon et al., 1991; 2001; Duce et al., 1991; Prospero et al. 1996; Nielsen et al., 1996; Zhuang et al., 1999; Spokes et al., 2000; Qi et al., 2005; Seinfeld and Pandis, 2006; Zhang et al., 2007). Dry deposition fluxes were calculated using dry depositional velocity V_d depending on the nutrient, since the nutrients are known to be associated with different particle fractions. The calculation of V_d (see Section below) is based on a simple parameterization of experimental meteorological measurements to determine atmospheric transport characteristics (Slinn, 1982; Zhang et al., 2001). The magnitude of V_d estimated were 1.2 and 0.6 cm/s for nitrate and ammonium respectively and 2 cm/s for phosphate, 1.2 cm/s for TN and ON and 2 cm/s for TP and OP, and similar results have been reported (Duce et al., 1991; Herut et al., 2002, Poor et al., 2006). These estimates result in an uncertainty of a factor of 2–3 in the calculated fluxes (Duce et al. 1991). Duce et al. (1991) proposed a mean V_d value of 0.1 cm/s for sub-micrometer particles, and 2.0 cm/s for aerosols greater than 1 μm in diameter depositing to ocean regions less than 1000 km from land. Dry deposition velocities for particles were found to range from 0.0062 cm/s, for particles with a diameter of 0.75 mm, to 5.4 cm/s for those with a diameter of 24 mm (Qi et al., 2005).

Deposition velocity (V_d) calculation

Aerosol dry deposition velocity (V_d) varies with particle size from gravitational settling of large particles to impaction and diffusion of small particles (sub-micrometer) and is dependent on climatological and physical conditions in the troposphere. While calculating V_d through empirical calculation, the most limiting parameters are standard deviation of wind speed (σ_θ), molecular diffusion, particle density and particle size. V_d at a particular vertical height was calculated as the inverse of the sum of a number of resistances (Seinfeld and Pandis, 2006) using the following equation.

$$V_d = \frac{1}{R_a + R_b + R_a R_b v_s} + v_s \qquad (3.2)$$

where v_s is the gravitational settling velocity (which is a function of particle size, density, and viscosity) (Seinfeld and Pandis, 2006), R_a is aerodynamic resistance refering to turbulent transport from the free atmosphere down to the receptor surface ($R_a = 9/[u\sigma_\theta^2]$, which is a function of wind speed, u and standard deviation of wind speed, σ_θ (Yamartino, 1984; Turner, 1986) and R_b is quasi laminar layer resistance. R_b is a function of particle size, Brownian diffusion, interception and impaction. R_b on water surface is given by van den Berg et al. (2000). Each of R_a and R_b is site specific and is determined to a large extent by atmospheric properties. The formula used for V_d calculation is given in Equation 3.2 and Table 3.2. Metrological parameters such as ambient temperature (K) of 300.8 ± 0.6 and 299.7 ± 0.7, wind speed (m/s) of 1.3 ± 0.49 and 1.0 ± 0.32, and standard deviation of wind direction σ_θ (rad) of 0.773 and 0.513 were observed in the sampling location during October 2006–November 2006 respectively. In SEA air, a majority of aerosols observed in the size range of 0.1–20 µm by the optical counter (Clarke et al., 2004) was in the fine mode (< 1 µm). Dominance of fine particles is typical for biomass burning plumes as observed, for example, in Brazil (Reid and Hobbs, 1998).

Both the mass and number concentrations are elevated across the entire size range on hazy days, and the increase in coarse and fine particles could be explained by increased emissions of fine particles during biomass burning through direct or indirect (gas-to-particle conversion) means and the agglomeration of these particles during the long-range transport (See et al., 2006). Based on the size distributed chemical composition data obtained in Singapore (See et al., 2006; unpublished data), the coarse ($PM_{2.5-18}$) particles for nitrate and phosphate case where as fine particles ($PM_{0-2.5}$) in the case of ammonium ions were considered in this study. This assumption is justified with reference to other reported results (Wall et al., 1988; Zhuang et al, 1999; Migon et al., 2001; Herut et al., 2002; Reid et al., 2005; Yang et al, 2005; Seinfeld and Pandis, 2006).

Table 3.2 Deposition velocity (V_d) calculation

Parameters	**Symbol**	**Formula**
Aerodynamic Resistance R_a	R_a	$R_a = \frac{9}{\left[u\sigma_\theta^2\right]}$
Quasi-laminar layer resistance	R_b	$R_b = \frac{1}{(1-\alpha_{bb})(\upsilon_B - \upsilon_i) + \alpha_{bb}(\upsilon_a + \upsilon_w)}$

Depending on particle sizes, the viscous (quasi-laminar) layer resistance is largely controlled by processes of Brownian diffusion, interception and impaction. The terms, υ_B (Brownian diffusion velocity), υ_i (impaction velocity), and υ_w (washout velocity) are calculated using following equations:

Friction velocity	u*	$u^* = \left(\frac{u}{R_a}\right)^{0.5}$
Area of bursting bubbles	α_{bb}	$\alpha_{bb} = 1.7 * 10^{-6} * u^{3.75}$
Brownian diffusion velocity	υ_B	$\upsilon_B = \frac{u^*}{\left[3(S_c R_e)^{0.5}\right]}$
Schmidt number	Sc	$S_c = \upsilon/D$
Kinematic viscosity of air (cm^2/s)	$\upsilon(T,1)$	$\upsilon(T,1) = \upsilon(273.15K,1) * (T/273.15K)^{1.81}$
Molecular diffusivity of specific molecule (cm^2/s)	$D(T,1)$	$D(T,1) = D(273.15K,1) * (T/273.15K)^{1.81}$
Hydraulic diameter in m	z_0	z_0 =5cm (assumed)
Reynolds number	R_e	$R_e = uz_0/\upsilon$
Stokes number	St	$S_t = \frac{v_{gi}(u^*)^2}{g\upsilon}$
Impaction velocity	υ_i	$\upsilon_i = u^* 10^{\left(-3/S_t\right)}$
Average particle deposition velocity in particle size interval i (v_{gi}) (m/s)	v_s	Obtain from gravitational settling velocity, v_s
υ_a	υ_a	$\upsilon_a = 1/R_a$
Washout velocity	υ_w	$\upsilon_w = 0.5(2\pi r_{sd}^2)(2z_d)F_{sd}$
Diameter of spray drop (m)	r_{sd}	$r_{sd} = 50\ \mu m$
The average height reached by the spray drops	z_{sd}	$z_{sd} = 50$ m
Flux of spray drops	F_{sd}	$F_{sd} = 5\times10^6\ (m^{-2}s^{-1})$

V_s (gravitational settling velocity) is calculated based on particle diameter, density, and viscosity:

Gravitational settling velocity (m/s)	v_s	$v_s = \frac{D_p^2 \rho_p g C_c}{18\mu}$
Particle diameter (m)	D_p	D_p
Particle density (kg/m^3)	ρ_p	$\rho_p = 1\ g/cm^3$
Cunninghan correction factor	C_c	$C_c = 1 + 2\lambda^*\left[1.257 + 0.4\exp\left(-1.1D_p/(2\lambda)\right)\right]/D_p$
Mean free path of gas molecules in air	λ	$\lambda = 0.065\times10^{-6}$ m
Absolute viscosity of air	μ	$\mu = \upsilon_{air}\rho_{air}$
Density of air (kg/m^3)	ρ_{air}	$\rho_{air} = Pressure_{air}/Temperature_{ambient} * 287.05J/(kg.K)$

3.1.6.2 Wet deposition

Wet atmospheric deposition (WAD) involves the removal of atmospheric substances within clouds and below the cloud base mainly by precipitation (Pryor and Barthelmie, 2000). Wet deposition fluxes (F_{wet} in g/m^2/yr) were calculated from the product of precipitation rate (P in m) and measured concentrations of nutrient species (C_{rain} in mg/l) by the following Equation (3.3).

$$F_{wet} = C_{rain}\,P \tag{3.3}$$

Precipitation Rate

Precipitation rate is the analogous term describing the velocity that pollutants present in precipitation and the pollutants that exist at a given liquid concentrations are deposited. Even during the period of low precipitation due to smoke haze episode in 2006, the samples were collected and analyzed. The cumulative total of rain events during the time interval may be expressed as the sum of all events. The cumulative total precipitation of 48 mm, 250.8 mm and 495.2 mm were observed during October, November and December 2006, respectively. In this study, the total precipitation by the above-mentioned three cumulative total precipitations was used for wet atmospheric flux calculation. Annual precipitation rate during the year 2006 was 2294.6 mm and the average precipitation rate was 203.1 ± 126.5 mm/month. The deposition fluxes may show short term variations, rendering the quantification of the annual atmospheric input of nutrients into the sea very difficult. Baeyens et al. (1990) described a method which allows estimation of the annual wet deposition flux of dissolved ions without measuring all rain events. When one rain event is recorded (sequential sampling), a nice, smooth dilution profile is obtained (Xianren and Baeyens, 1990) and the concentration decreases gradually with the volume of rainfall. Moy et al. (1994) found that slow air circulation coincided with a high concentration of pollutant gases in the atmosphere. High concentration of pollutants can be observed if high precipitation occurs during this time period. As indicated by Migon et al. (1991), the number of rain events has a greater influence on flux than the intensity of the rain. It was observed in our survey that after long dry periods (typically several days) nutrient concentrations in rainwater were systematically higher than monthly mean concentrations, regardless of the intensity of the rain event.

3.2 Eutrophication modelling

3.2.1 3-D Numerical eutrophication model (NEUTRO)

NEUTRO (3-D numerical eutrophication) model (Tkalich and Sundarambal, 2003) is capable to simulate eutrophication in coastal water as driven by physical, chemical and biological processes and other relevant forces. The conceptual framework for the eutrophication kinetics in water column is based on the WASP (Water quality analysis simulation program) model (US Environmental Protection Agency, Ambrose et. al. 2001). WASP is a generalized framework for modelling contaminant fate and transport in surface waters. The WASP system is a very simple 0-D link-node model, and 1-D or 2-D or 3-D set-ups are possible only for simple cases. Therefore in NEUTRO, the WASP eutrophication kinetics are transformed and programmed together with 3-D advection-diffusion contaminant transport to account more accurately for the spatial and temporal variability. The coupled physical-biochemical model simulates long-term physical circulation and nutrient dynamics in Singapore seawater and surrounding seas. This model provides information on nutrient concentrations, primary production and dissolved oxygen necessary to estimate large-scale ecological effects. Six interacting systems are selected, comprising the nitrogen, phosphorus and carbon cycles; phytoplankton and zooplankton dynamics; and dissolved oxygen balance (Figure 3.4). The modelled nutrients consist of ammonium nitrogen, nitrite + nitrate nitrogen (NO_2+NO_3), phosphate, organic nitrogen, organic phosphorus, total nitrogen and total phosphorous. The 11 state variables considered are: ammonia nitrogen (C_1), nitrite + nitrate nitrogen (C_2), phosphate (C_3), phytoplankton (C_4), carbonaceous biochemical oxygen demand (C_5), dissolved oxygen (C_6), organic nitrogen (C_7), organic phosphorus (C_8), zooplankton (C_9), bacteria (C_{10}) and total suspended solids (C_{11}). The model can simulate the fate of transport of nutrients from point source (outfalls, spills) (Sundarambal and Tkalich, 2005).

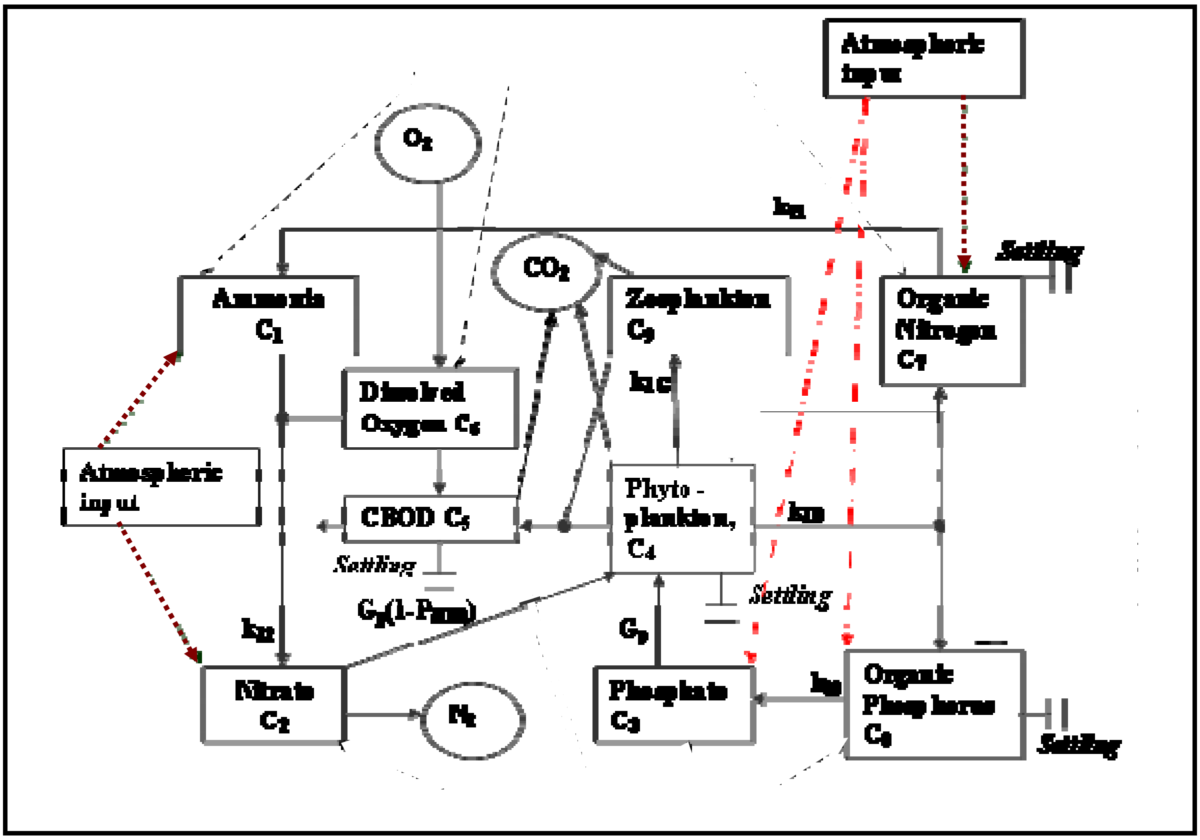

Figure 3.4 Flowchart of nutrients, plankton and the dissolved oxygen balance. Note: K12 - Nitrification rate; k71 - Organic nitrogen mineralization rate; k83 - Organic phosphorus mineralization rate; k1G - Grazing rate of zooplankton; k1D - Death rate for phytoplankton;Gp - phytoplankton growth rate; P_{NH3} - The ammonia preference factor.

Previous version of NEUTRO did not account for atmospheric nutrient inputs into the seawater. It is essential for current study to include these fluxes along with more detailed prescription of land based sources. This research is important in quantifying nutrient flux and its concentration from atmosphere into the coastal zone. However, the recent haze events (arising from forest fires and a strong El Niño influence) that have plagued South East Asia are likely to affect atmospheric inputs of nutrients and other pollutants into aquatic ecosystems. The effects of such events can be understood by further investigation. The experience and confidence gained in simulating water quality, which is validated by observed data, can be effectively used to study the biological processes. Simulation of the effects of potential changes in atmospheric deposition on seawater/coastal water quality was provided through the analysis of modelling results with implemented fluxes of atmospheric nutrients quantified using field measurements.

The transport equation for dissolved and suspended constituents in a body of water accounts for all materials entering and leaving through: direct and diffuse loading, as well as physical, chemical, and biological transformations. Consider the coordinate system with x- and y- coordinates in the horizontal plane and the z- coordinate in the vertical plane.

The 3-D transport equation is described as follows:

$$\begin{aligned}&\frac{\partial C_j}{\partial t}+\frac{\partial C_j U}{\partial x}+\frac{\partial C_j V}{\partial y}+\frac{\partial C_j\left(W-w_j\right)}{\partial z}-\frac{\partial}{\partial x}\left[E_x\frac{\partial C_j}{\partial x}\right]-\frac{\partial}{\partial y}\left[E_y\frac{\partial C_j}{\partial y}\right]-\frac{\partial}{\partial z}\left[E_z\frac{\partial C_j}{\partial z}\right]=\\&=\frac{Q\left(S_j-C_j\right)}{\Delta h\Delta x\Delta y}+R_j\end{aligned}\tag{3.4}$$

where C_j = concentration of j^{th} pollutant (mg/l); S_j = contamination of the liquid source with j^{th} pollutant (mg/l); Q = discharge of the source (m^3/sec); R_j = chemical reaction terms, corresponding to the interaction equations for j^{th} state variable (Tkalich and Sundarambal, 2003); E_x, E_y, E_z = turbulent diffusion coefficients; $\Delta x, \Delta y, \Delta z$ =

computational grid-cell sizes in x-, y-, and z- directions respectively; Δh = thickness of water layer affected by initial dilution; $C_j^0 = C_j(t_0)$ is the concentration of jth pollutant at initial time, C_j^B is the baseline concentration of jth state variable obtained from field measurements; w_j = settling velocity of jth pollutant; U, V, W = tidal current in x-, y-, and z- directions respectively. The values of U, V, and W, E_x, E_y and E_z were computed using the 3-D tropical marine hydrodynamic model (TMH, Pang and Tkalich, 2004) and were used as input to NEUTRO. Values of admixture (C_j) are computed at numerical nodes of a 3-D grid at different time instances using the transport/fate equation. The missing element of atmospheric input of macronutrients was included in NEUTRO to explain observed nutrient dynamics in the water column and the primary production. The enhanced NEUTRO model (Sundarambal et al, 2007, 2008a) was utilized to investigate the fate of atmospherically deposited (AD) nutrients in the water column, and its impact on water quality and aquatic ecosystems (Sundarambal et al, 2008b, d). The newly established atmospheric flux (F) in the model was quantified by source term F = QS_j in transport equation (3.4). The wet deposition flux (F) in the model was calculated as product of by *precipitation × surface area × concentration (S_j) of AD species* and the dry deposition flux (F) is defined as product of *settling velocity of AD species × surface area × concentration (S_j) of AD species*.

3.2.1.1 Nutrient dynamics

As eutrophication is caused by enrichment of the water by inorganic nutrients, dynamics of nutrient cycles (Figure 3.4) is important and described below in detail.

Ammonium nitrogen

Ammonia is naturally produced by the biodegradation of nitrogenous material, and is part of the nitrogen cycle. Industrial sources include cleaning operations, municipal wastewaters, manufacture and use of explosives, atmospheric deposition and distillation/combustion of coal. Other natural sources of ammonia include biological litter, animal waste and forest fires. Ammonia may enter the aquatic environment from groundwater, chemical and biochemical transformation of nitrogenous organic and inorganic matter, excretion of organisms, and nitrogen fixation processes. In aqueous solutions, the equilibrium equation is: $H_2O + NH_4^+ <=> NH_3 + H_2O^+$. Un-ionised NH_3 is toxic to fish, whereas NH_4^+ is only toxic at low pH levels when the proportion of ammonia as NH_4^+ becomes very high (Armstrong et al., 1978). Two key biological processes affect nitrogen cycling: nitrification (Equation (3.5) (by Nitrosococcus, Nitrosomonas) and denitrification (Equation 3.6) (by Nitrobacter, Nitrococcus). Nitrification is described by the following two-step biological oxidation process (Fenchel and Blackburn, 1979; Furnas, 1992). Nitrification rate is a function of the concentration of ammonium ion, nitrite and oxygen. Coral reefs and seagrass beds have been identified as areas of high nitrogen fixation rates in the marine environment (Furnas, 1992).

$$2NH_4^+ + 2OH^- + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 4H_2O \qquad (3.5)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (3.6)$$

Nitrate (nitrite + nitrate) Nitrogen

The model considers four nitrogen state variables: total nitrogen, nitrite + nitrate, ammonium and organic nitrogen. Both ammonium and nitrite + nitrate are incorporated by phytoplankton during growth. A fraction of the particulate organic nitrogen hydrolyzes to dissolved organic nitrogen and another fraction settles to the sediment. Dissolved organic nitrogen is mineralized to ammonium. In an oxygenated water column, ammonium is oxidized to nitrate through nitrification and its kinetics is modelled as a function of available ammonium, dissolved oxygen, temperature and light (Cerco and Cole, 1995; Tian et al., 2001). During anoxic conditions, nitrate is lost as nitrogen gas through denitrification. In tropical systems, denitrification is the most intense in the following areas: (a) where detritus accumulates, (b) in water bodies subject to enhanced nutrient loading from pollution and (c) in water bodies with long residence times stimulates coupled mineralization-nitrification-denitrification within organically rich sediments (Furnas, 1992).

Phosphorus

The model considers three P species such as total phosphate, phosphate and organic phosphate. Phytoplankton assimilates phosphate and redistributes the three forms of phosphorus through basal metabolism. Zooplankton basal metabolism and egestion of excess phosphorus during feeding release phosphate and dissolved and particulate organic phosphorus. Particulate organic phosphorus can be hydrolyzed to dissolved organic phosphorus, and another fraction settles to the sediment. Dissolved organic phosphorus is mineralized to phosphate through a first-order reaction. Particulate organic phosphorus in detritus is grazed by zooplankton. External phosphorus loads to the system and losses via the outflows are also considered.

3.2.1.2 DO balance

Nutrient enrichment/eutrophication may give rise to an increased rate of oxygen consumption, decreased oxygen concentrations and an increased frequency of oxygen depletion. The major sources and sinks of dissolved oxygen in the water column include phytoplankton photosynthesis and respiration, zooplankton and heterotrophic respiration, nitrification and atmospheric reaeration. Oxygen depletion only occurs in stratified water columns where stratification prevents oxygen-rich surface water to mix to the bottom. The oxygen concentration close to the sea bottom in stratified water depends on two processes each varying in time and space: the consumption rate, which is mainly dependent on the supply of organic matter and the temperature, and the oxygen supply rate, which is mainly dependent on wind conditions. Therefore, it is difficult to assess the reason for oxygen depletion. This may be due to increased consumption rate or decreased supply rate of oxygen.

3.2.1.3 Plankton dynamics

Phytoplankton and zooplankton

The governing equation for algal biomass considers phytoplankton production and losses due to basal metabolism, settling and herbivorous zooplankton grazing. Nutrient, light and temperature impacts on phytoplankton growth are included in the model. Phosphorus and nitrogen dynamics within the phytoplankton cells account for luxury uptake (Hamilton and Schladow, 1997; Asaeda and Bon, 1997; Arhonditsis et al., 2002), where phytoplankton nutrient uptake depends on both internal and external concentrations and is confined by upper and lower internal nutrient concentrations. Among the variety of mathematical formulations relating to photosynthesis and light intensities, i.e., light saturation curves (Jassby and Platt, 1976), Steele's equation with Beer's law is used to scale photosynthetically active radiation to depth. The extinction coefficient is determined as the sum of the background light attenuation and attenuation due to chlorophyll, while the optimal illumination considers physiological adaptations by phytoplankton based on light levels during the two preceding model days (Ferris and Christian, 1991; Cerco and Cole, 1995). Phytoplankton basal metabolism includes all internal processes that decrease algal biomass (respiration, excretion) as well as natural mortality. The zooplankton prey on phytoplankton as a food source, and its grazing rate varies from species to species (Di Toro et al., 1971), Grazing rates depend on temperature of water, and it varies from 0.1 to 1.5 l /mgC day (Ambrose et al, 2001). Zooplankton kinetics depends primarily on grazing of phytoplankton. When phytoplankton and zooplankton die, they form the organic carbon pool. A part of this carbon settles and the other part gets oxidized to oxygen.

3.2.1.4 Fluxes from the sediment

In marine sediments, organic matter is mainly degraded through bacterial processes, by which N and P bound in organic compounds production are released once again due to primary production. Up to half of the bacterial degradation takes place in the sediments proceeds through oxygen respiration. The remaining degradation takes place anaerobically through respiration of nitrate, iron, manganese or sulfate. Besides the release of CO_2, NH_4^+ and PO_4^{3-}, anaerobic degradation results in the formation of waste products (such as hydrogen sulphide from sulfate respiration) that are ultimately oxidised, thereby consuming the exact amount of oxygen that would have been used if the entire degradation process had been aerobic. The flux of nitrogen (and of phosphorus, for that matter) between the marine sediment and the bottom water is governed by the differences in concentrations between pore water (within the sediment) and water column.

3.2.2 Tropical marine hydrodynamic model (TMH)

A 3-D free surface primitive equation coastal ocean model TMH (Tropical Marine Hydrodynamic) developed at the Tropical Marine Science Institute, National University of Singapore, has been implemented to compute tidal-driven currents in the coastal water of Singapore (Tkalich et al., 2002; Pang et al., 2003; Pang and Tkalich, 2003, 2004). Relevant hydrodynamic and water quality processes in Singapore coastal zone were discussed previously in Pang and Tkalich (2003, 2004), Chan et al. (2006), Sundarambal et al. (2008c), and Sundarambal and Tkalich (Submitted-a).

3.2.2.1 Typical tidal currents of Singapore coastal water

Currents in Singapore Strait are mainly driven by tidal forces generated in the Pacific Ocean, South China Sea and Indian Ocean. Monsoon driven anomalies and tidal fluctuations are significant as well. Singapore Strait tides are predominantly of semi-diurnal nature with two high and two low tides per lunar day; the second high tide is usually lower than the first high tide due to the diurnal inequality. The measured tidal ranges are in the order of 2.5–3 m at the deep and narrow channel at southern water of Singapore during spring tides and 0.7–1.2 m during neap tides (Zhang, 2000; Pang and Tkalich, 2003). Tidal velocities vary spatially from 0.5–1 m/s in the open water of Singapore Strait to as much as 1.5–2 m/s in constricted channels between the islands but it is reduced to less than 0.5 m/s in Johor Strait. During the SWM, the observed mean water movement is from the Java Sea northward into Singapore Strait, after which the water split into two streams that move westward and eastward into Malacca Strait and South China Sea respectively. The mean sea surface currents around Singapore Strait during the monsoons are shown in Figure 3.5. Figure 3.6 clearly shows the net water movement from east to west with some contribution from the southern boundaries in NEM (Thickness of the arrows roughly indicates the mass of water).

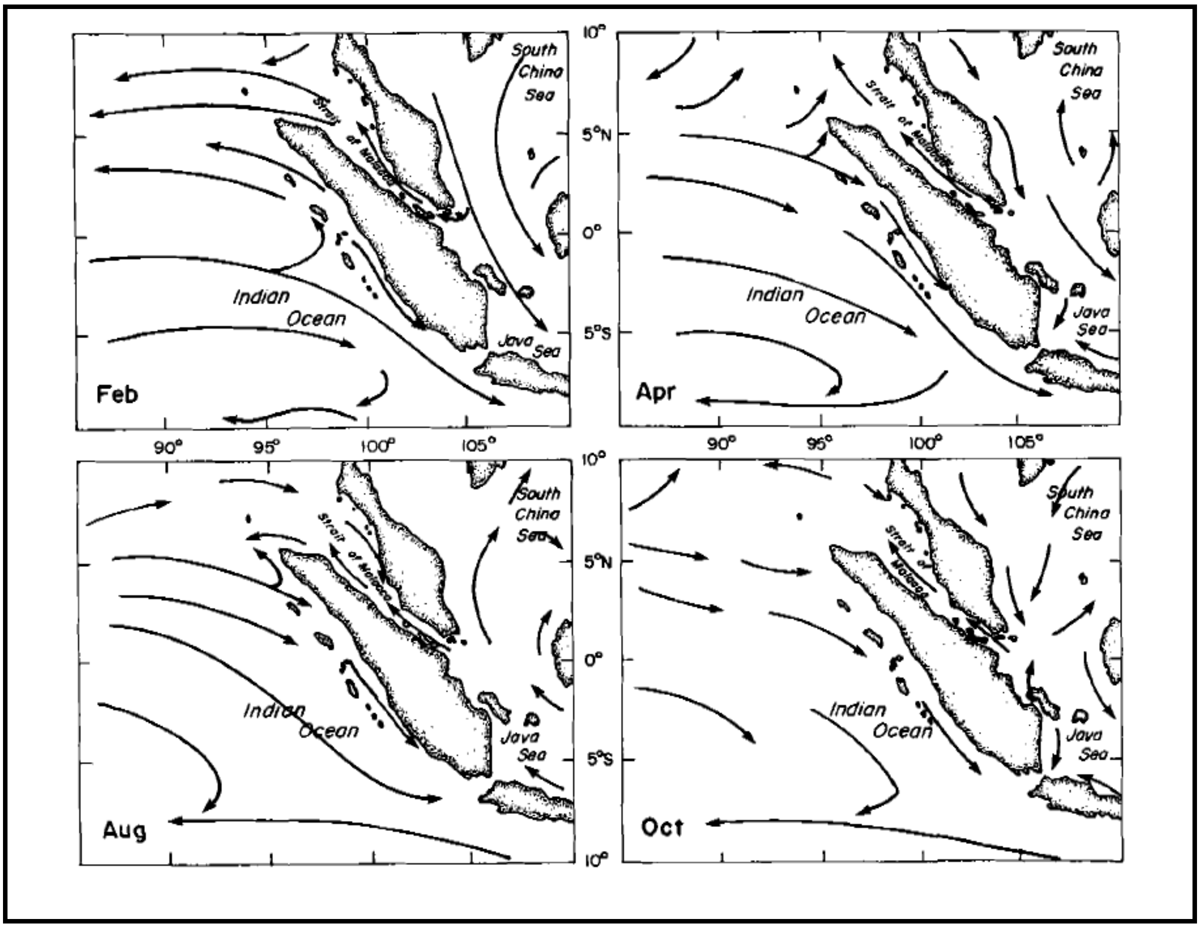

Figure 3.5 Ocean surface currents of the water around Singapore (Chia et al., 1988)

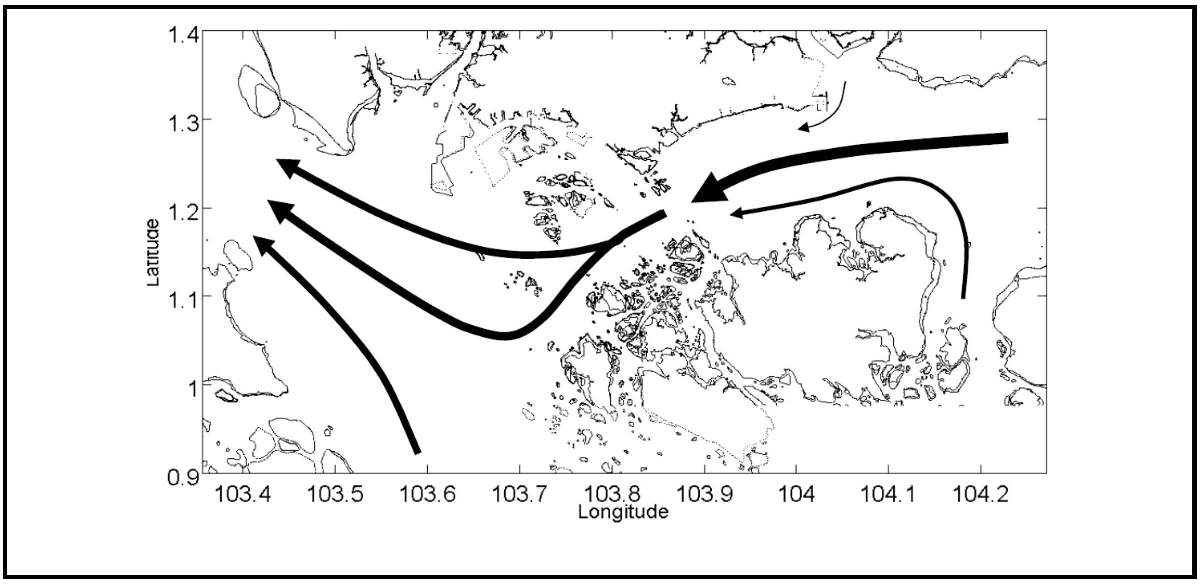

Figure 3.6 Schematic illustration of seasonal netwater movement during northeast monsoon (Pang and Tkalich, 2003)

In view of the large magnitude of tidal level variations and the associated currents in the coastal water of Singapore, the tidal hydrodynamic characteristics are important for the assessment of the baseline characteristics of Singapore marine environment. The three typical patterns of circulations are flooding, ebbing and slack tide. During flooding water flows in from South China Sea, the pattern is reversed during ebbing. Currents are weaker with no main direction during slack tide. In this study, a typical southwest monsoon covering a 5 days spring tide period from 30th June 2003 to 5th July 2003 was used for model simulation. Typical computed surface current patterns are shown in Figure 3.7. The maximum tidal current observed during three typical patterns of circulations of flooding, ebbing and slack tide were 1.48 m/s, 2.57 m/s and 0.98 m/s. respectively. Flood or "flooding" water is the incoming of seawater to create a high tide and Ebb or ebbing tide is the outgoing of seawater to create a low tide. The flooding or ebbing of a tide must stop before it proceeds in the opposite direction is called as "slack" water. In other words the tide has stopped moving and is slack with no movement up or down.

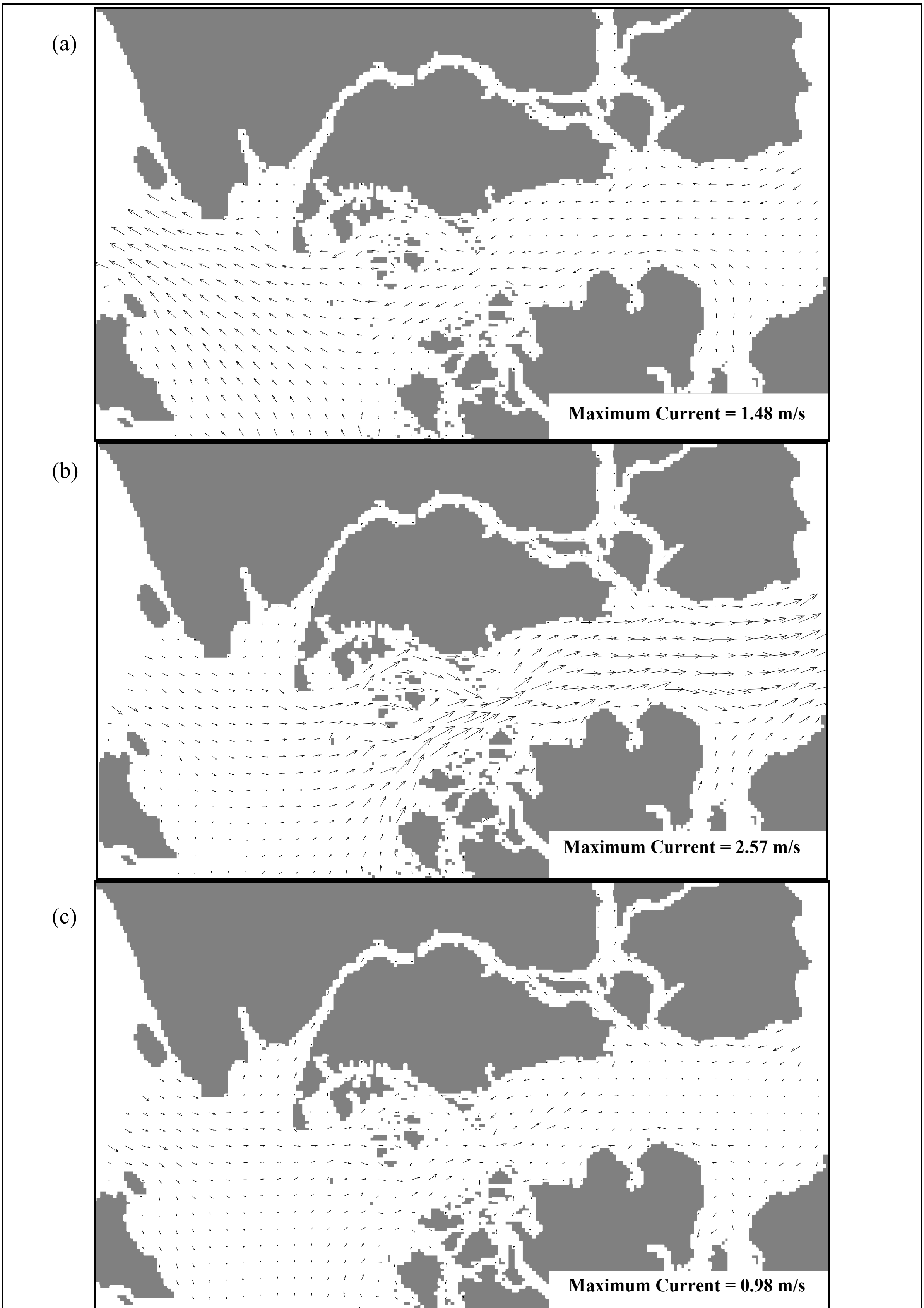

Figure 3.7 Surface current pattern during southwest monsoon; (a) Pattern during flooding, (b) Pattern during ebbing and (c) Pattern during slack tide.

3.2.3 Baseline water quality of Singapore coastal water

A summary of the environmental characteristics of the Singapore Strait and Johor Strait are shown in Table 3.3. In general, temperature and salinity variations in the tropical water of the Singapore Strait are small. For the Johor Strait, measurements of salinity are generally lower than the Singapore Strait, due to the freshwater inflow from the Johor River and other rivers draining into the Johor Strait. Vertical distribution of temperature and salinity was varied slightly along the Straits (Zhang and Chan, 1999) as shown in Figure 3.8.

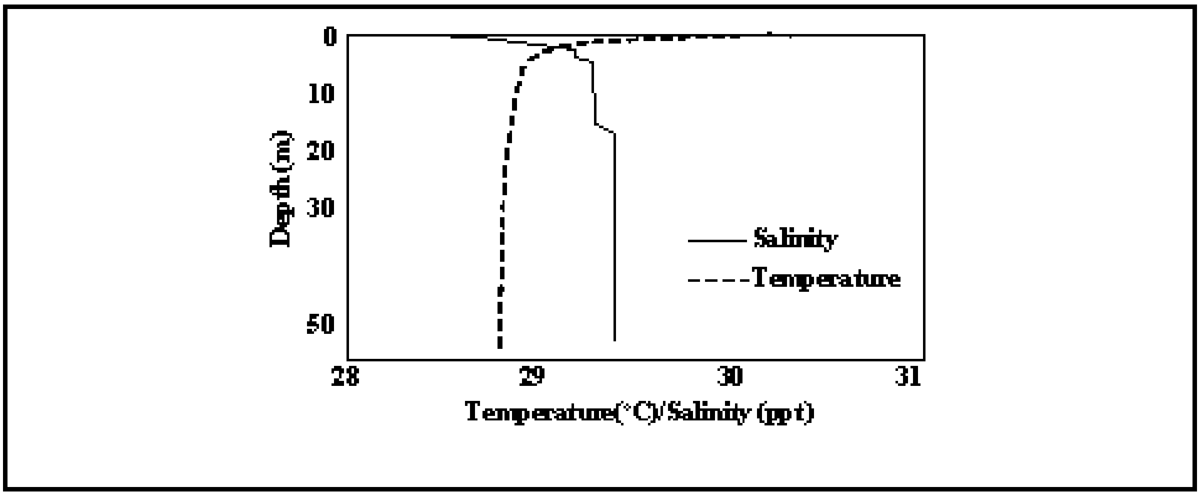

Figure 3.8 The vertical distribution of temperature and salinity in Singapore Strait.

Table 3.3 The concentration of water quality parameters measured in the Singapore Strait and Johor Strait (adapted from Gin et al., 2000)

Seawater	**T (°C)**	**Salinity**	**NO_2+ NO_3 (mg/l)**	**NH_4 (mg/l)**	**PO_4 (mg/l)**	**TN (mg/l)**	**TP (mg/l)**	**TSS (mg/l)**	**Chl-a (µg/l)**
Singapore Strait									
Average	29.7	30.6	0.036	0.015	0.009	0.55	0.016	15	1.7
Range	28.3–31.2	28.7–32.2	0.005–0.078	n.d–0.053	0.21–1.1	0.21–1.1	0.005–0.031	1.6–54	0.4–10.5
Johor Strait									
Average	29.8	28	0.146	0.098	0.04	1.6	0.075	22.4	21.5
Range	27.6–32.2	19–33	0.013–0.4	n.d–0.178	0.007–0.075	1.3–2.1	0.02–0.167	2.8–57.3	1–78.5

The water quality and plankton community in the Singapore water undergo significant short-term variations induced by tidal changes and seasonal variations induced by monsoon cycles. Dissolved oxygen (DO) levels in the water column range from 6 to 8 mg/1. DO levels are higher near the surface, due to re-aeration from the atmosphere and photosynthesis, and subsequently decrease with depth. Phosphate concentrations in the Singapore Strait comprise about 40–95 % of Total phosphorus (TP). Ammonium level is generally lower than nitrite + nitrate concentration. Usually, seasonal trends in phosphate and nitrite + nitrate concentrations are similar, with slightly elevated concentrations during the SWM but lower concentrations during the NEM. However, in the case of ammonia-N, no seasonal trend is observed. The vertical distribution of phosphorus is fairly uniform with depth, whereas nitrite + nitrate showed variation with depth (Gin et al., 2000). Overall, nutrients levels in the Johor Strait are higher than those of the Singapore Strait (Gin et al., 2000). Gin et al., 2006 reported that Singapore waters were generally nitrogen limited; however, for the Johor Strait, variable anthropogenic inputs and a N:P ratio close to the Redfield ratio implies that nutrient limitation can easily switch to phosphorus. As with nutrients, seasonal trends in chlorophyll are apparent, with higher chlorophyll observed during the SWM (average = 2.3 μg/1) compared with the wetter NEM (average = 1.4 μg/1). In terms of vertical distribution, phytoplankton biomass is generally concentrated in the upper 5–10 m layer, although in many shallow inshore water where the euphotic zone reaches the seabed, chlorophyll concentrations are uniform throughout the water column. Based on secchi depth readings, the euphotic zone is typically between 4 and 9 m.

Although the tropical water of Singapore is subject to relatively high temperature and light levels throughout the year, overall chlorophyll concentration in the Singapore Strait remains low. Presumably, nutrients are rapidly taken up by phytoplankton, which explains the generally low levels of nitrogen and phosphorus measured. There is also some seasonal variation in nutrients and chlorophyll due to different monsoons. In general, slightly higher values are recorded during the southwest monsoon compared with the northeast monsoon.

3.2.4 Model setup and model parameters

The selected model domain approximately covered surface area about 10000 km^2 regions from 1° 0’ N to 1° 33’ 10.43” N (latitude) and from 103° 20’ E to 104° 20’ E (longitude). The bathymetry of the Singapore seawater and the model domain is shown in Figure 3.9. Domain size, current velocities and free surface dynamics for NEUTRO were obtained using a semi-implicit sigma-coordinate hydrodynamic model TMH (Pang and Tkalich, 2004) having 500 m horizontal resolution and 10 vertical sigma layers. In water quality model, a horizontal grid of 500 m x 500 m covering 117.5 x 84.5 km^2 area (236 x 170 horizontal grid nodes) with 10 vertical layers at depths of 0, 2.5, 5, 7.5, 10, 20, 40, 60, 80 and 120 m was used. The mean concentrations of nutrients in Singapore seawater were taken as model baseline from our previous published paper Tkalich and Sundarambal (2003). Generally, the water column is well mixed in Singapore and Johor Straits due to strong high tidal currents. The initial condition of each state variable of the water quality model was assumed to be constant in the vertical planes of the computational boundaries with computed respective baseline concentration in the entire computational domain. Fluxes of nutrients from atmospheric deposition to surface water were obtained based on field monitoring and laboratory methods of nutrient analysis (as in Section 1.1; Sundarambal et al., 2009a). The open boundaries for the water quality modelling were the boundaries facing South-China Sea, Malacca Strait and Indonesia water. The water exchanged from above boundaries in and out of the Singapore domain carries nutrients and other contaminants with them (i.e. transboundary fluxes).

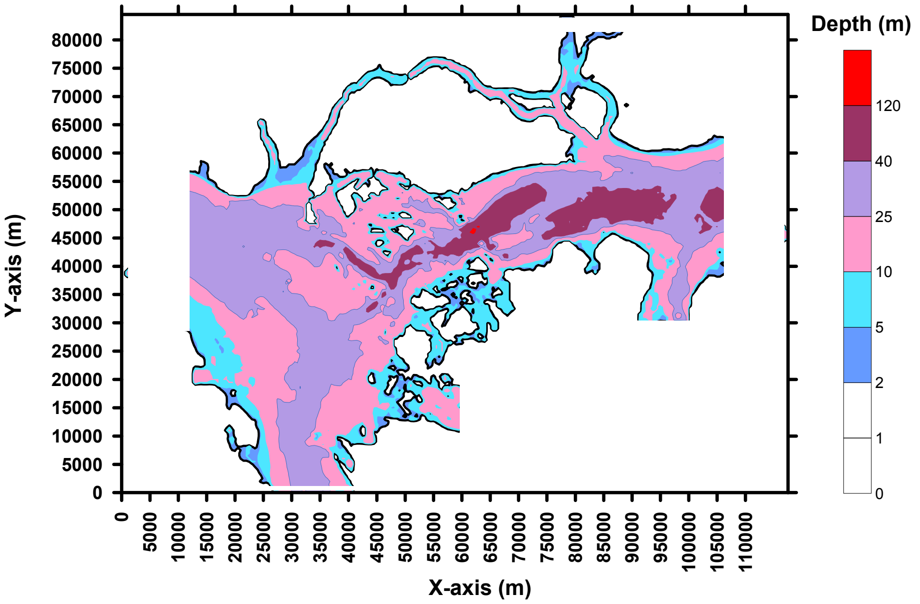

Figure 3.9 Bathymetry of Singapore seawater and NEUTRO model domain

Model parameters are mainly divided into the following generic groups.

1) Model identification parameters such as number of grids, domain size and state variables to be simulated.
2) Transport parameters such as description of modelling network of grids with corresponding advective and dispersive flux and volume of advective flow, diffusion coefficients (hydrodynamic data).
3) Boundary conditions such as boundary concentrations and waste load from rivers, land, sea and atmospheric deposition.
4) Transformation kinetic parameters such as specific to state variables being simulated (deoxygenating rate, nitrification rate, re-aeration rate, etc. and other chemical kinetics).

5) Initial conditions such as concentrations of all state variables being simulated at the beginning of simulation.
6) Simulation parameters such as initial time, final time, and integration time step, advection factor, initial concentrations and source concentrations of the state variables and all input file names.

3.2.5 Model calibration

Model calibration is the process of determining the structure of the model and its parameters on the basis of measurement and priori knowledge (Beck, 1987). For admixture transport simulation model, the concentration profiles obtained from field measurement can be used to calibrate a model at a given time by adjusting model parameter values, including kinetic coefficients, until acceptable accuracy is achieved (Ditmars, 1988). To further examine the validity of the calibrated model it needs to be tested with respect to additional set of field data preferably under different environmental conditions, such as river flow, atmospheric input, outfall discharge and runoff (Thoman and Muller, 1987). If the iterative model run are conducted to calibrate the water quality model parameters, the model is considered valid and can be used for validation. It is to be noted that model parameters are not adjusted based on field data during validation. The calibrated kinetic coefficients and constants for the water quality simulation should be consistent with literature values (Ambrose et al., 2001; Bowie et al., 1985; Cole and Buchak, 1995). Using the collected data on air and water, the models are validated for its reliable and effective usage for simulation of short-term scenarios, including acute spills, or long-term scenarios including chronic spills and seasonal (monsoon) variabilities. It is important that calibration and validation data covers the range of conditions over which predictions are desired.

The mean concentrations of nutrients in Singapore seawater were taken from Tkalich and Sundarambal (2003) as a NEUTRO model baseline. The model parameters were calibrated through the comparison of model predictions with field observations. Using baseline values of the state variables as initial conditions, chemical kinetic coefficients were fine-tuned by performing iterative model runs. The chosen values of the coefficients (Table 3.4) have to keep the state variables at quasi steady-state concentrations (baseline) under the fixed nutrient load conditions (Figure 3.10). The calibrated model was used to predict the water quality with an independent set of data as a part of validation exercise for model evaluation. Test runs show that NEUTRO reproduces the cycles of phytoplankton and nutrient concentrations with a good accuracy.

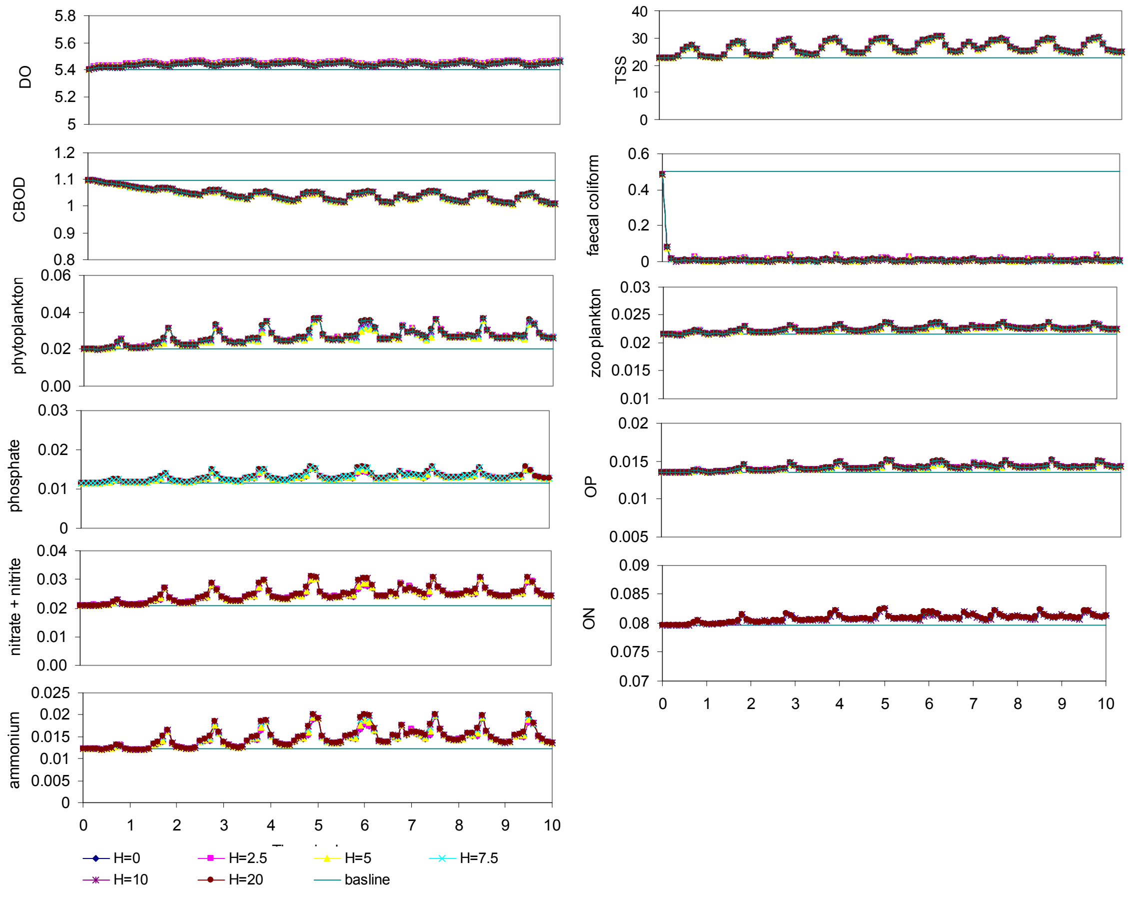

Figure 3.10 Model results for baseline concentration simulation at a monitoring station on the south coast of Singapore

Table 3.4 Verified kinetic coefficients and other parameters used in NEUTRO water quality model.

Variable description	**Symbol**	**Present study**	**Literature WASP + published**	**Units**
Temperature	Te	29.3		Celsius
Salinity	Sal	30.5		ppt
Nitrogen/carbon ratio	a_{nc}	0.25	0.25	mgN/mgC
Fraction of dead phytoplankton recycled to the organic nitrogen pool	f_{on}	0.5	0.5	dimensionless
Phosphorus/carbon ratio	a_{pc}	0.025	0.025	mgP/mgC
Fraction of dead phytoplankton recycled to the organic phosphorus pool	f_{op}	0.5	0.5	dimensionless
Organic nitrogen mineralization rate	k_{71}	0.187	0.075 0.01–0.15^{e}	1/day
Temperature coefficients	Θ_{71}	1.08	1.08	dimensionless
Nitrification rate	k_{12}	0.014	0.09–0.13	1/day
Temperature coefficients	Θ_{12}	1.08	1.08	dimensionless
Denitrification rate	k_{2d}	0.090	0.09	1/day
Temperature coefficients	Θ_{2d}	1.045	1.045	dimensionless
Organic phosphorus mineralization rate	k_{83}	0.0002	0.1–0.3	1/day
Temperature coefficients	Θ_{83}	1.08	1.08	dimensionless
Fraction of dissolved inorganic phosphorus in water column	f_{d3}	0.7	0.85,0.70	dimensionless
Fraction of dissolved CBOD in water column	f_{d5}	0.5	0.5	dimensionless
Fraction of dissolved organic nitrogen in water column	f_{d7}	0.8	1	dimensionless
Fraction of dissolved organic phosphorus in water column	f_{d8}	0.8		dimensionless
Endogenous respiration rate @ 20C	k_{1r}	0.006	0.125 0.05–0.2^{e}	1/day
Temperature coefficient	Θ_{1r}	1.045	1.045	dimensionless
Max specific growth rate @ 20C	k_{1c}	5	0.01–4	1/day
Temperature coefficients	Θ_{1c}	1.068	1.068	dimensionless
Half-saturation constant for nitrogen uptake	k_{mN}	25	25 10–20^{d}	µgN/l
Half-saturation constant for phosphorus uptake	k_{mP}	1	1–2	µgP/l
Carbon/chlorophyll-a ratio		30	20–50	dimensionless

Table 3.4 Verified kinetic coefficients and other parameters used in NEUTRO water quality model. (continued)

Variable description	**Symbol**	**Present study**	**Literature WASP + published**	**Units**
Death rate for phytoplankton	k_{1d}	0.01	0.02 0.015–0.2[e]	1/day
Non-algal extinction coefficient	DB	0.1	0.1–0.5	1/m
Fraction of day that is daytime	f	0.3	0.3–0.7	dimensionless
Solar radiation	sol	483.2	200–750	ly/day
Saturating light intensity	P_s	200	200–500	ly/day
Grazing rate of zooplankton	k_{1g}	0.1	0.1–1.5	l/mgC/s
Death rate of zooplankton	k_9	0.01	0.02	1/day
Temperature coefficients	Θ_9	1.047		dimensionless
Oxygen/carbon ratio	a_{oc}	2.667	32/12	mgO_2/mgC
Half-saturation constant for oxygen limitation denitrification	k_{NO3}	0.5	0.1	mgN/L
Oxidation	k_{BOD}	0.5	0.5	mgN/l
Half-saturation constant for phytoplankton limitation of phosphorus recycling	k_{mpc}	1	1	mgC/L
Half-saturation constant for oxygen limitation (nitrification)	k_{nit}	0.5	0.5	mgO_2/l
Temperature coefficients	Θ_a	1.028		dimensionless
Deoxygenation rate for CBOD	k_D	0.021	0.02–0.2	1/day
Temperature coefficients	Θ_D	1.08	1.047	dimensionless
Saturation concentration of dissolved oxygen	c_{sa}	5.4		mg/l
Settling velocity for ammonia nitrogen	$v_{setl}(1)$	0	0.1	m/day
Settling velocity for nitrite + nitrate nitrogen	$v_{setl}(2)$	0		m/day
Settling velocity for phosphate	$v_{setl}(3)$	0		m/day
Settling velocity for phytoplankton	$v_{setl}(4)$	0.10	0.05–0.5[e]	m/day
Settling velocity for CBOD	$v_{setl}(5)$	0.74	0.05–0.5[e]	m/day
Settling velocity for DO	$v_{setl}(6)$	0.00		m/day
Settling velocity for organic nitrogen	$v_{setl}(7)$	0.50	0.05–0.5[b]	m/day
Settling velocity for organic phosphorus	$v_{setl}(8)$	1.49	0.05–0.5[c]	m/day
Settling velocity for zooplankton	$v_{setl}(9)$	0.00		m/day
Settling velocity for bacteria	$v_{setl}(10)$	0.50		m/day
Settling velocity for total suspended solids	$v_{setl}(11)$	0.50		m/day
Bacteria decay rate	k_b	10		1/day
Suspended solids decay rate	T_{SS}	0		dimensionless
Temperature coefficients	Θ_{10}	1.07		dimensionless

Table 3.4 Verified kinetic coefficients and other parameters used in NEUTRO water quality model. (continued)

Variable description	**Symbol**	**Present study**	**Literature WASP + published**	**Units**
Depth of Benthic layer in m	DBL	0.2		m
Thickness of water column above benthic layer	DW	0.2		m
Diffusion of water layer above benthic (last layer)	DIFW	0.3		sq.m/sec
Diffusion of Benthic layer	DIFB	2.32E-07		sq.m/sec
Organic carbon and CBOD decomposition rate	TKds	7.776		1/day
Temperature coefficients	TETds	1.08		dimensionless
Initial benthic DO	CBinit	1		mg/l
Maximum benthic BOD	CBmax	2		mg/l
sediment oxygen demand maximum	SODmax	0.6		g/m^2/day
wind speed	wind	5		m/s

Source: [a]Ambrose et al. (2001); [b]Bowie et al. (1985); [c]Chapra (1997); [d]Thomann and Mueller (1987); [e]WDOE (1986).

3.2.6 Model validation

Validation of any numerical model is quite complicated. There are two standard ways to validate it: either by comparing model results with analytical solutions or by comparing model results with measurements. Comparison with measurements is preferable, because it can verify the governing equations of the model as well as the approximated numerical solution of the equations. The model simulation period was selected from 18th March 2002, 12.00 pm to 19th March 2002, 12.00 pm for 24-hrs hindcast to compare with field measurement data at a monitoring location in the East Johor Strait. NEUTRO's results were in close agreement with field measurements for 24 hrs hindcast (high resolution simulation) (Figure 3.11) and monsoon related variations (Sundarambal and Tkalich, Submitted-a and unpublished reports in Tropical Marine Science Institute, National University of Singapore). The average computed and observed values of state variables were in close agreement (Absolute Error diagram, Figure 3.11). The negative and positive error occurs when the predicted values of model are higher and lower than the observed values respectively.

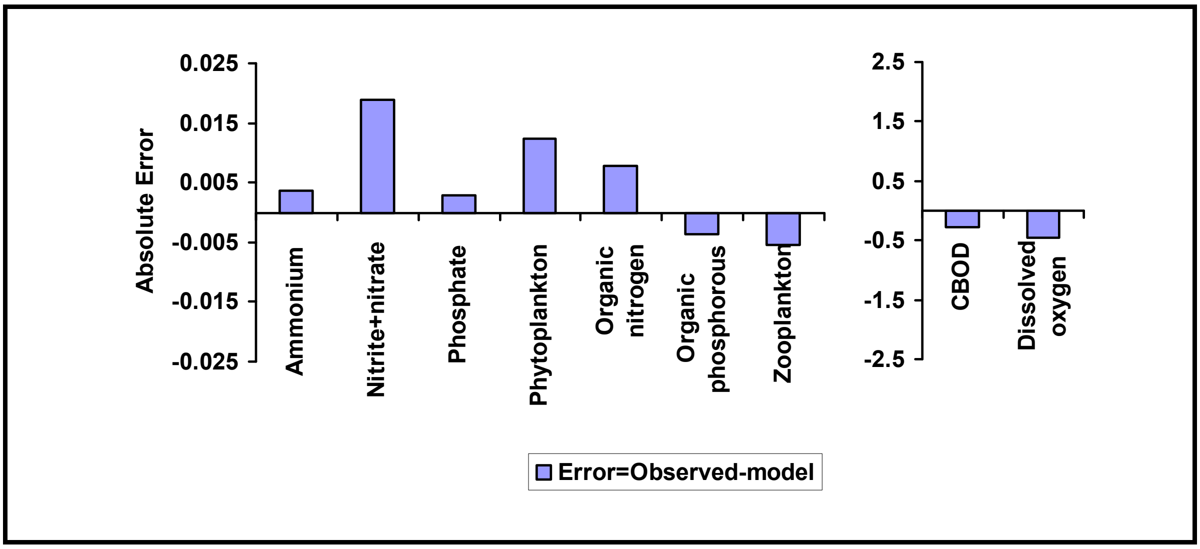

Figure 3.11 Absolute Error diagram of model results from field observation. Note: Parameters (Units): Ammonium (mg/l), nitrite + nitrate (mg/l), phosphate (mg/l), phytoplankton (mgC/l), organic nitrogen (mg/l), organic phosphorous (mg/l), zooplankton (mg/l), CBOD (mg/l) and DO (mg/l) (Sundarambal and Tkalich, Submitted-a).

3.2.7 Model limitations

While NEUTRO can be used to predict the fate and transport of pollutants and their subsequent impacts on primary production, there are some limitations to the model (Sundarambal and Taklich, Submitted-a; Sundarambal et al., 2010c). My present research work focus on eutrophication modeling to investigate impact of atmospheric nutrient deposition only on coastal water quality. Currently, only water column interactions are considered and there is benthic coupling only for DO. More advanced benthic layer modeling is currently being developed subject to data availability. Currently, there is a lack of exact quantitative information of all potential sources of nutrients on freshwater input fluxes into the coastal zone. NEURTO could predict the Singapore water quality accurately with additional data collection along with atmospheric nutrient deposition and by further fine-tuning of the kinetic rates.

3.2.8 Sensitivity analysis

Few studies on the effect of uncertainity in the model inputs and assumptions (including boundaries and model functional form) on the outputs have been reported (Morgan and Henrion, 1990; Saltellet et al., 2000). In this study, a sensitivity analysis was made to get an understanding of the likely model response to a small change of a model parameter or input, and to provide the relative importance of model parameters or variables. The sensitivity of the model output can be analyzed based on two sensitivity functions: absolute and relative sensitivity. The difference between the two sensitivity functions is not only the mathematical expression (see Equations 3.7 and 3.8) but also their dependency on the unit of the model variables and model parameters: the absolute sensitivity function depends on the unit of model parameters or variables, whereas the relative sensitivity function doesn't depend on either unit. For each sensitivity function, the sensitivity of the model output is calculated in two steps actor (De Pauw and Vanrolleghem, 2003). First, a reference simulation is run without changing the parameter value. Next, a new simulation is run (a perturbation simulation) in which the parameter value under consideration is perturbed by a certain factor (the perturbation factor, e.g. 0.01). By investigating the "relative sensitivity" of model parameters, the relative importance of nutrients loading in the model can be understood (Figure 3.12). Then, the absolute (S_A) and relative (S_R) sensitivity are calculated for each time step as follows:

$$S_A(t) = \frac{\Delta Y}{\Delta X} \tag{3.7}$$

$$S_R(t) = \frac{\Delta Y / Y(t)}{\Delta X / X} = \frac{\Delta Y}{\Delta X}\frac{X}{Y(t)} \tag{3.8}$$

where Y is the model output, X is the model parameter, $\Delta X/X$ is the perturbation factor. Both relative and absolute sensitivity can be used for the investigation of the model sensitivity to parameter changes.

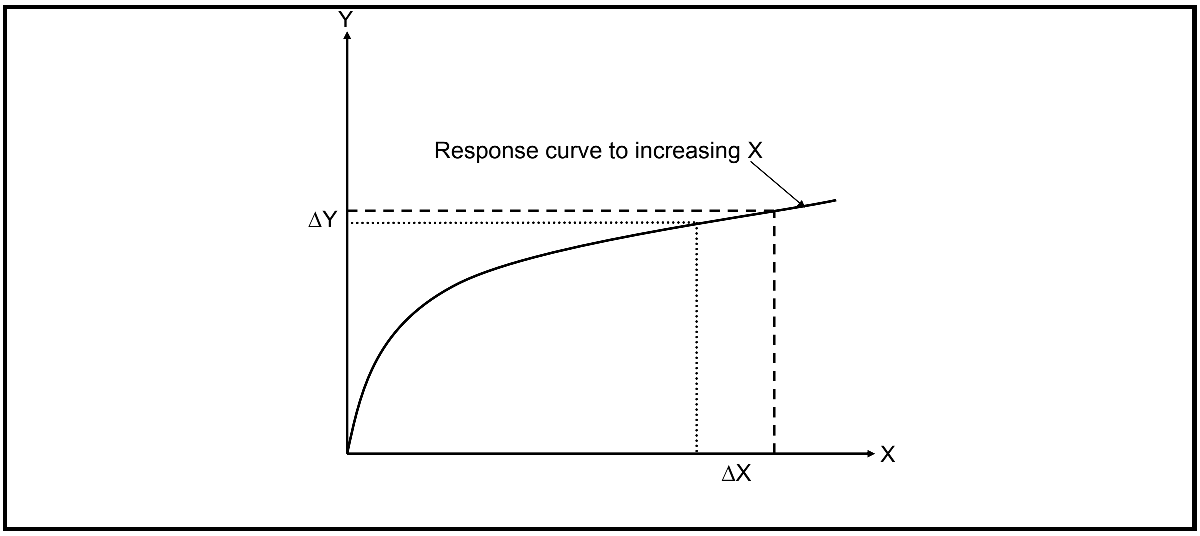

Figure 3.12 Model response (Y) to change in model input (X)

In this study, relative sensitivity (S_R) was used. The relative sensitivity measures the relative change of the model output in relation to a relative change of parameters. This choice is advantageous over absolute sensitivities because it does not depend on the units of model parameters nor the model output variables. The relative sensitivity (S_R) was calculated numerically, based on the change in predicted mass concentration (X) from its baseline (X) upon an increase of atmospheric nitrite + nitrate load input (Y) from its initial baseload (Y) at every simulation time step as follows:

$$\frac{Y+\Delta Y}{Y}.100\% = \frac{X+\Delta X}{X}.100\% \tag{3.9}$$

3.2.9 Modelling approach

Contaminant inputs into a coastal system are naturally subject to physical and biogeochemical processes that affect the concentration of the contaminant in the water column. A substance or property whose concentration depends solely on physical transport and dilution is said to be a ‘conservative’ substance. Conservative substances are solutes which are not significantly affected by biological metabolism. Conservative properties are those that are not gained or lost through ordinary reactions. Non-conservative solutes are changed in composition and concentration by aquatic biota. Most contaminants are non-conservative and therefore their distributions are subject to other processes in addition to physical transport including biological uptake and release, chemical transformations and interaction with the atmosphere. If the physical transport and mixing of a contaminant in a parcel of water can be estimated then the difference in concentration distribution of a non-conservative contaminant may be assumed to be due to additional processes**.** The mass balance of a non-conservative property of a two dimensional water mass can be estimated from the input and output of such a property along the two horizontal axes, physical advection and mixing terms and ambient concentration of the property. There is an exchange of water and nutrients between Singapore seawater and adjacent water bodies, such as the Malacca Strait, South China Sea and Java Sea. Simulation of the ambient concentration of a property under different contaminant loads may be undertaken assuming the same physical transport terms and transfer coefficients. The ambient concentrations obtained from the model can be compared with water quality standards for the property, such as those agreed by the Association of SouthEast Asian Nations (ASEAN, 1995).

A mass balance modelling approach was carried out to predict nutrient fate and transport in the coastal water that could result from the varying atmospherically deposited nutrient loading conditions. The atmospherically deposited nutrients were assumed to be deposited uniformly onto water surface and spatially distributed by the action of tidal currents. Once N or P was deposited onto water surface, they were transported to the water column followed by its spatial distribution by the action of tidal current. The water column nutrient dynamics within each computational cell was further controlled by the complex chemical, biological and physical processes. After specification of atmospheric wet and dry deposition loads and system boundary conditions, the changes in water column nutrients and planktons due to AD were computed.

In this study, two numerical experiments were carried out as follows. At the first set of numerical experiments, the model was run for verification of mass conservation of nitrite + nitrate nitrogen and to understand relative importance of atmospheric (vertical) fluxes in the region as compared with lateral (horizontal) fluxes via ocean boundaries. The enhanced NEUTRO model was run for three cases (Case I to III), considering (a) lateral (horizontal) flux of nutrients from ocean boundaries (B_j) only, (b) atmospheric fluxes only and (c) combination of fluxes from the ocean and atmosphere. The concentration of atmospheric wet deposition (WD) and initial concentration in water column is denoted as $\mathrm{Sj}_{\mathrm{WD}}$ and C_j^0 respectively. The model was run in a conservative mode (without kinetic exchange) for three cases as mentioned below.

Case I: $C_j^0 = 0$, $B_j \neq 0$, $\mathrm{S}_{\mathrm{jWD}} = 0$; equivalent to flux of nutrients from ocean boundaries only.

Case II: $C_j^0 = 0$, $B_j = 0$, $\mathrm{S}_{\mathrm{jWD}} \neq 0$; equivalent to atmospheric fluxes only.

Case III: $C_j^0 = 0$, $B_j \neq 0$, $\mathrm{S}_{\mathrm{jWD}} \neq 0$; equivalent to combination of fluxes from the ocean and atmosphere.

Computing mass of admixture in the Singapore Strait for each case, it is possible to quantify relative contribution of atmospheric and ocean fluxes into the domain. At the second set of numerical experiments, the model with complete eutrophication kinetics was run to investigate spatial and temporal distribution of nutrients and eutrophication rates in Singapore Strait. The typical hydrodynamic forcing from TMH (Pang and

Tkalich, 2004) was utilized to compute the changes in water column nutrients and planktons due to atmospheric wet deposition (uniform loads over the domain) along with system boundary conditions.

The results obtained from various methods explained in this chapter by using the materials there in and discussion in relation to the result will be dealt with in Chapter 4 for field monitoring and Chapter 5 for eutrophication modelling.

CHAPTER 4: RESULTS AND DISCUSSION – ATMOSPHERIC DEPOSITION OF NUTRIENTS : FIELD MEASUREMENTS

4.1 Quantification of typical atmospheric nutrients

Using the methods and materials described in Section 3.1, the aerosol and rainwater samples collected from January 2006 to July 2006 at NUS sampling station were analyzed for quantification of atmospheric nutrients. The results obtained from the analytical studies are discussed in the following sections.

4.1.1 Nutrients in aerosol

Though Total Suspended Particlulate matter (TSP) contains airborne particles of different sizes, a fraction of these particles may be inhalable. These are the particles with an aerodynamic diameter of 10 μm and less, generally referred to as PM_{10}. US EPA's Pollution Standards Index (PSI) is used in Singapore to report the ambient air quality i.e good (PSI : 0–50), moderate (PSI : 51–100), unhealthy (PSI : 101–200), very unhealthy (PSI : 201–300) or hazardous (PSI > 300). PSI is calculated by measuring the concentration levels of CO, SO2, NO2, O3 and PM_{10}. WHO guideline for TSP is 120 $\mu g/m^3$ (WHO, 1997). During the sampling period, the highest TSP was 93.2 $\mu g/m^3$ while PSI (Pollution Standard Index) was 51. Whenever there is a haze episode, high PM_{10} concentration contributes to PSI. It was also observed that measured nutrient concentrations were high when PSI was high. The maximum measured concentration levels of TN, ammonium, nitrate + nitrite, ON, TP, phosphate, OP concentrations ($\mu g/m^3$) in the aerosol were respectively 5.78, 0.997, 3.54, 2.13, 0.635, 0.355 and 0.339 at the highest TSP concentration of 93.2 μg/m^3. The average N species concentrations in the aerosol phase were 1.31 ± 0.91 μg/m^3 for nitrite + nitrate nitrogen, 0.374 ± 0.27 μg/m^3 for ammonium, 0.963 ± 0.661 μg/m^3 for ON and 2.67 ± 1.17 μg/m^3 for TN. The average P species concentrations in the aerosol phase were 0.156 ± 0.144 μg/m^3 for phosphate, 0.14 ± 0.122 μg/m^3 for OP and 0.296 ± 0.254 μg/m^3 for TP. Figure 4.1 shows average concentrations in the aerosol and the seawater baseline derived from Tkalich and Sundarambal (2003). Deposition was fairly evenly distributed between nitrate + nitrite, ammonium, and ON (50 %, 14 %, and 36 %, respectively). The percentage contribution of phosphate and OP on coastal water of SEA were 53 and 47 of TP, respectively.

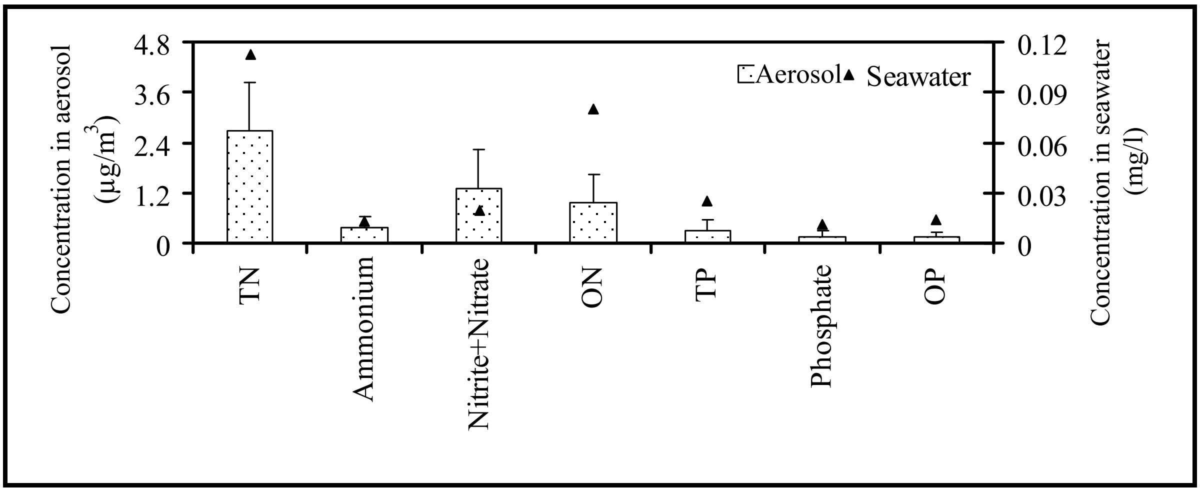

Figure 4.1 Average concentration of nutrients (N and P species) in aerosol and seawater in Singapore

The air mass back trajectories were plotted for each sampling period to identify the origin and history of air masses received at the sampling site in Singapore. The backward trajectories were plotted using NOAA HY-SPLIT model (Draxler and Rolph, 2003) at altitudes 1000, 500, and 60 m for the representative periods on 28th July 2006 (PSI = 51, SWM, Figure 4.2a) and 4th March 2006 (PSI = 40, NEM, Figure 4.2b). Archived data of the hot spots count in Sumatra (Singapore's National Environment Agency, NEA) showed that the area whereby most of the trajectories passed through in

South Sumatra (Regional haze map on 26th July 2006 by NEA) had more hot spots than the rest of Sumatra during hazy days. The transport of the smoke haze strongly depends on the prevalent wind direction (Figure 3.3). The smoke haze particles from fires in the northern ASEAN (Association of Southeast Asian Nations) region are carried over by mild winds, contributing to hazy conditions (NEA, Singapore). The maximum TN concentration of 5.78 $\mu g/m^3$ and 3.81 $\mu g/m^3$ was observed in DAD on 28th July 2006 and 4th March 2006 respectively. Both values were found to be higher than that of clear days. This observation is consistent with those made earlier during the previous smoke haze episodes at the same sampling site (Balasubramanian et al., 2003).

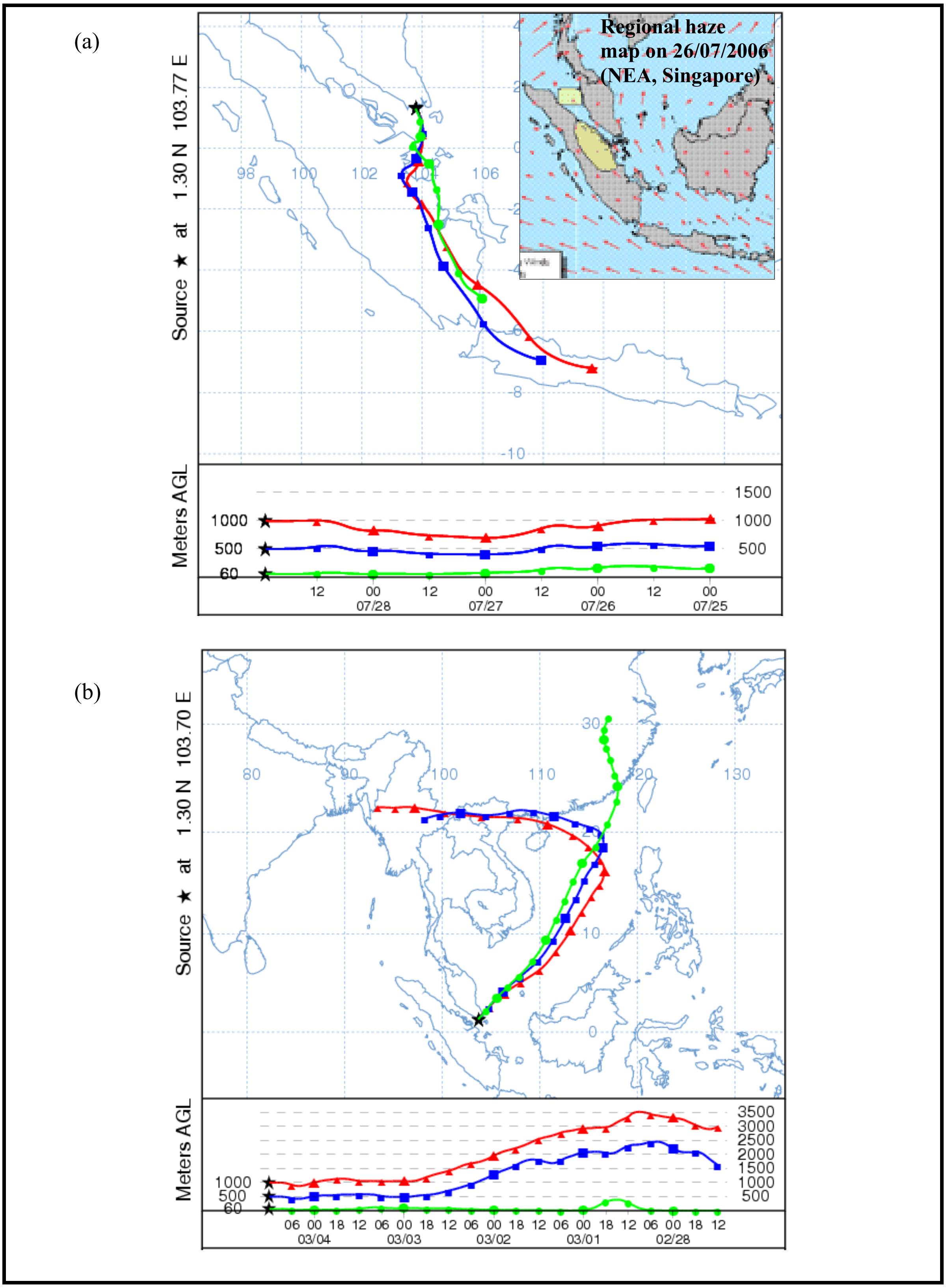

Figure 4.2 Representative 4 days air mass back trajectories for starting altitude of 1000 m, 500 m, and 60 m above ground level (AGL) calculated for the sampling site (a) on 28th July 2006 and (b) on 4th March 2006. The location of hotspots in Sumatra observed on 26th July 2006 is shown on the regional haze map.

4.1.2 Nutrients in precipitation

The concentrations of N species in precipitation were in the range of 0.725–5.783 mg/l for TN, 0.39–5.55 mg/l for nitrate + nitrite, 0.01–0.94 mg/l for ammonium and 0.12–2.66 mg/l for organic N. The results show that WAD is the predominant source of atmospheric nutrients over Singapore area. Figure 4.3 shows the average concentrations of nutrients in precipitation from January to July 2006 and the seawater baseline derived from Tkalich and Sundarambal (2003). N species concentrations in precipitation were the higher than P species. The dissolved phase in rainwater is regarded here as an approximation of its bioavailable fraction. The particulate fraction in rainwater that enters the marine surface layer partly dissolves, however. Though there exists no published DAD regional data, however, a few WAD data for ammonium and nitrate were published elsewhere (e.g. Ayer et al., 2000; Asiati et al., 2001; Ayers and Yeung, 1996). The importance of ON in TN from AD has recently been re-evaluated; it may represent half of the input of inorganic forms on a regional scale and be equal to them for global ocean (Cornell et al., 1995). Figure 4.4 shows the average concentration of nutrients (N species) in atmospheric wet deposition, dry deposition and seawater in Singapore during sampling period. The observed ON was 36 % of TN in the present study while that published was 41 % of TN (Cornell et al., 2003). Wet deposition was mainly contributed by nitrite + nitrate, followed by ON and then ammonium ion (55 %, 36 %, and 9 % respectively). The nitrite + nitrate, ammonium and ON contribution to TN in the Singapore Strait were 18 %, 12 % and 70 % respectively. Figure 4.5 shows the phosphate and OP contribution to TP in atmospheric wet deposition, atmospheric dry deposition and seawater baseline in Singapore. The percentage contribution of phosphate and OP to TP were 12 and 88, respectively for wet deposition and 46 and 54, respectively for seawater in the Singapore Strait.

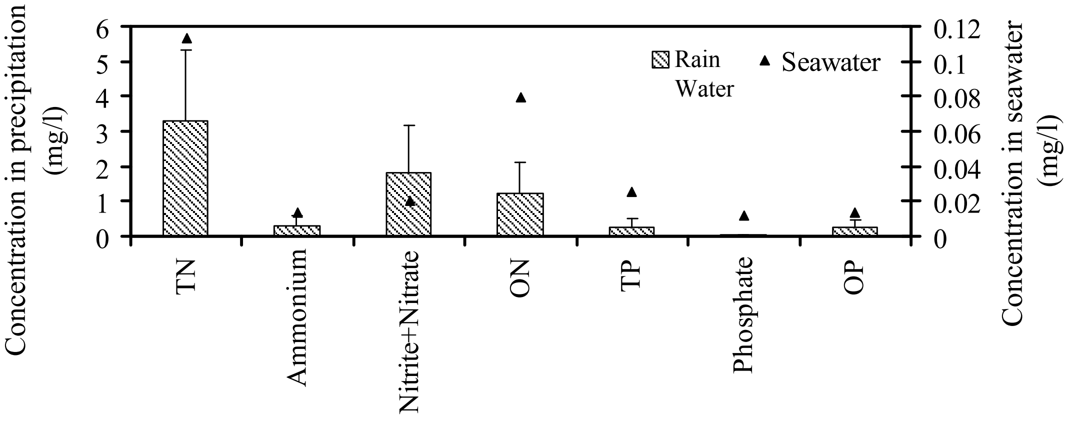

Figure 4.3 Average concentration of nutrients (N and P species) in precipitation and seawater in Singapore

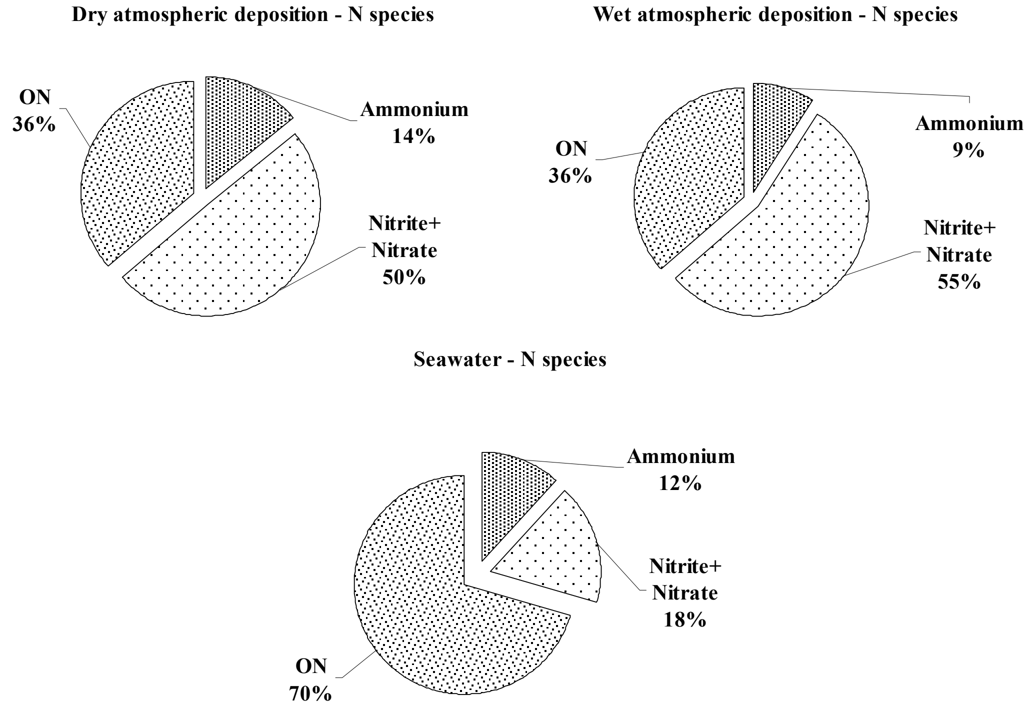

Figure 4.4 The nitrite + nitrate, ammonium and organic nitrogen contribution to total nitrogen in atmospheric wet deposition, atmospheric dry deposition and seawater baseline in Singapore.

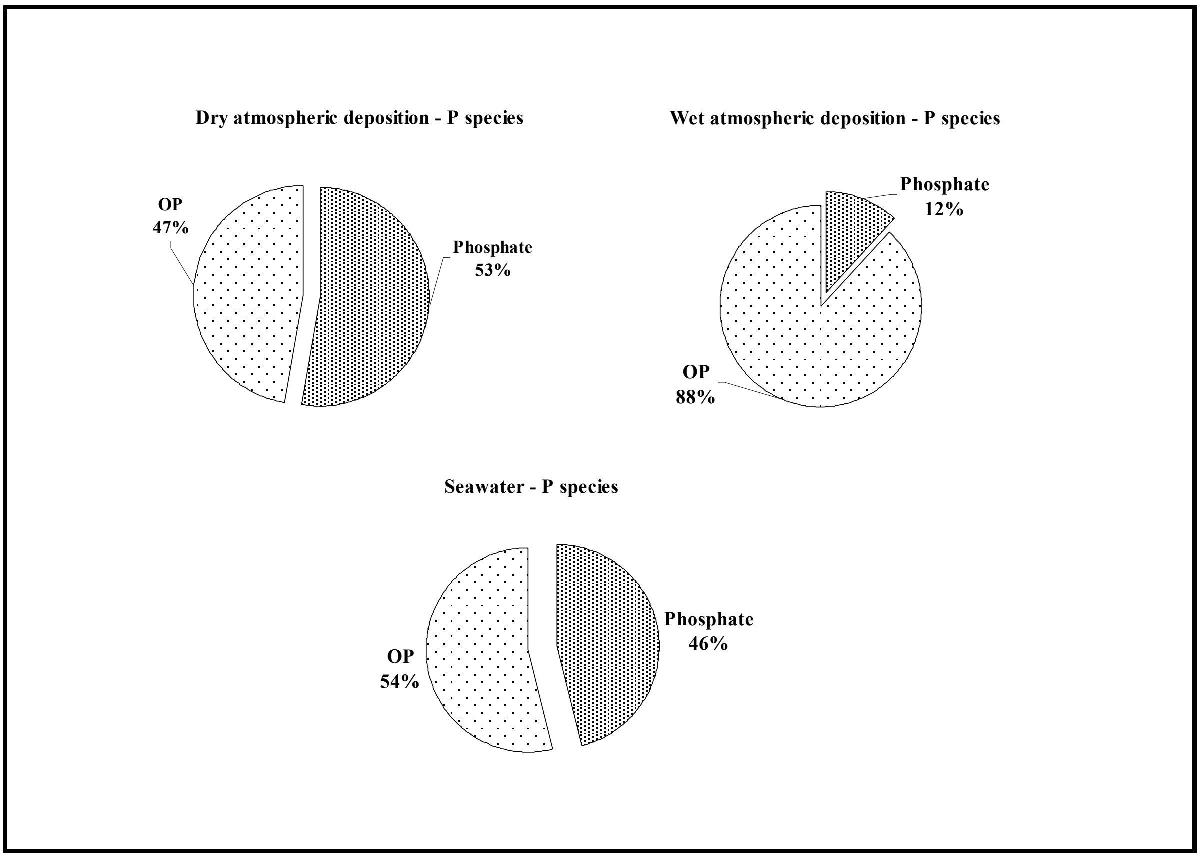

Figure 4.5 The phosphate and OP contribution to TP in atmospheric wet deposition, atmospheric dry deposition and seawater baseline in Singapore.

4.1.3 Estimation of atmospheric deposition fluxes

The mean DAD fluxes of organic and inorganic P species were estimated as 0.088 ± 0.077 and 0.098 ± 0.091 (g/m^2/yr), respectively. The mean WAD fluxes of organic and inorganic P species were estimated as 0.498 ± 0.525 and 0.068 ± 0.047 (g/m^2/yr), respectively. Table 4.1 shows the comparision of WAD flux of ammonium and nitrite + nitrate nitrogen in Singapore with those published elsewhere in SEA. The nutrient composition in DAD and WAD indicated a dominant anthropogenic source for N species and a continental, natural and anthropogenic source for P species (Herut et al., 1999). The WAD flux is higher than the DAD flux and the total budget shows that the biologically available N load to the surface water is significantly more than ~10 times the biologically available P load to the surface water (Figure 4.6). Based on model predictions, Duce et al. (2008) reported an increase in the ratio of deposition rates from 2030 to 2000 by a factor of 2 in SEA and an increase of TN deposition by 40 % of net external N supply.

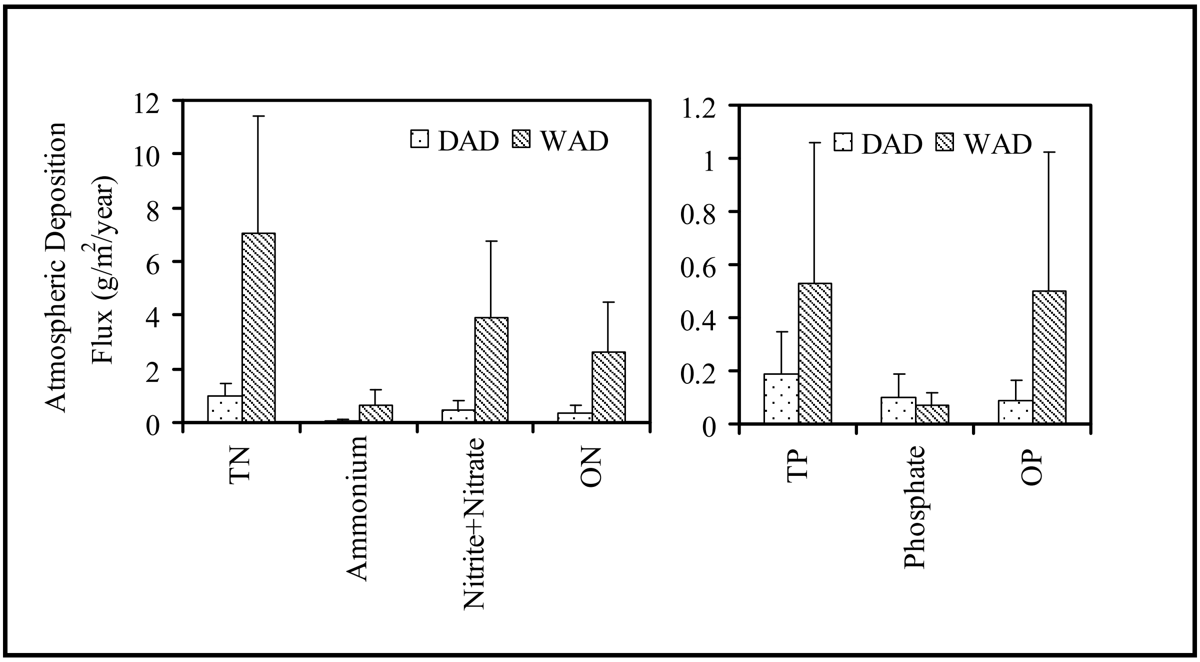

Figure 4.6 Atmospheric deposition flux of nutrients (N and P species) in atmospheric wet deposition and dry deposition during sampling period

Table 4.1 Comparison of WAD flux (g/m^2/yr) of ammonium and nitrate in some countries, SEA.

Country	Period	NH_4	NO_3	Reference
Malaysia	1993 – 1998	0.718	3.607	Ayers et al. (2000)
Indonesia	1992 and 1996	1.38	1.74	Asiati et al. (2001)
Hong Kong	1998 – 1991	0.439	2.32	Ayers and Yeung (1996)
Singapore	2006	0.631/0.071$^{\#}$	3.76/0.495$^{\#}$	Present study

Note: $^{\#}$ for DAD flux

4.1.3.1 Total atmospheric deposition fluxes of nutrients

The range and mean of total (WAD + DAD) fluxes of N and P species over the sampling period in Singapore based on the present study are given in Table 4.2. The maximum annual flux of atmospheric TP was 2.85 g/m^2/yr while that of TN was 21.9 g/m^2/yr. The proportion of DAD flux to total fluxes was in the range of 0.1 to 0.12 and

0.15 to 0.59 for N species and P species respectively. It was observed that the proportion of DAD to total fluxes for N compounds was smaller than that for P compounds. The transfer of atmospheric nutrients through precipitation is a more efficient deposition process for the particulate matter in the marine area as compared to DAD (Bergametti et al., 1992) which is consistent with the observations made in this study. Using the estimated nutrient fluxes from atmospheric deposition, water quality model (NEUTRO, Tkalich and Sundarambal, 2003; Sundarambal et al, 2007) was simulated to understand the effects of atmospheric nutrient input into Singapore and surrounding water and its detailed discussion is given in Chapter 5.

Table 4.2 Total atmospheric deposition fluxes of nutrient ($g/m^2/yr$) in Singapore.

Nutrients	**Mean**	**SD**	**Minimum**	**Maximum**
TN	8.09	5.96	1.33	21.9
Ammonium	0.70	0.673	0.016	2.20
Nitrite + nitrate	4.41	3.17	0.955	13.2
ON	2.98	2.12	0.363	6.49
TP	0.75	0.740	0.145	2.84
Phosphate	0.17	0.138	0.003	0.34
OP	0.59	0.602	0.142	2.50

4.2 Atmospheric deposition during 2006 haze episode

The results obtained for the aerosol and rainwater samples collected from September 2006 to January 2007 at SJI sampling station are presented and discussed in this section.

4.2.1 Smoke haze episode

A higher level of TSP was found in Singapore during the 2006 smoke haze event (maximum TSP ~ 140 $\mu g/m^3$) (this study) as compared to that measured during the 1997–1998 haze events (maximum TSP ~ 110 $\mu g/m^3$) (Balasubramanian et al., 1999) caused by prolonged forest fires in the nearby islands of Indonesia. The smoke haze originated from hundreds of brush, forest and peat fires across Sumatra and Borneo (National Environment Agency (NEA), Singapore). The prevailing southerly to southwesterly winds transported the smoke haze directly from southern Sumatra towards the Malacca Straits, peninsular Malaysia and Singapore; the smoke haze is also influenced by the prevailing southeasterly winds from Kalimantan to Singapore. The PSI (pollutant standards index) measured by NEA, Singapore and the API (air pollution index) by DOE (Department of Environment), Malaysia are shown in Figure 4.7a. These two indices are indicators of the prevailing air quality in Singapore and Malaysia, respectively. The air quality categories based on PSI or API and the general health effects associated with the different categories are summarized as follows: PSI or API up to 50 (Good); 51–100 (Moderate); 101–200 (Unhealthy); 201–300 (Very Unhealthy); > 300 (Hazardous). The air quality in Singapore during October 2006 was either moderate or unhealthy. Figure 4.7a also shows that day-to-day particle concentrations varied substantially in Singapore in response to spatial and temporal changes of meteorological factors such as wind conditions (example, arrows in Figure 4.9a) and intermediate rainfall (Figure 4.8), and of fire activity and intensity (hotspots in Figure 4.9 and Figure 4.10). The particle concentration exhibited a distinct rise and high fluctuation during October and after mid November it decreased and remained at background levels in the subsequent period. The highest 3-hr PSI (150) recorded during this haze episode occurred on 7 October 2006 (NEA, Singapore; Figure 4.7b).

The extreme smoke haze episodes that occurred on 6, 7, 15 and 19 October 2006 were selected for DAD estimation during hazy days and the 16 samples collected from 13 November 2006 to 4 January 2007 were selected for non-hazy days. The range of TSP was 99–138 $\mu g/m^3$ and 18–31 $\mu g/m^3$ respectively during hazy and non-hazy days; the range of PSI was 92–119 and 25–47 during hazy and non-hazy days, respectively. The arithmetic means of TSP and PSI during hazy days were 113 ± 17 µg/m^3 and 102 ± 12, respectively while those during non-hazy days were 24 ± 5 µg/m^3 and 35 ± 7, respectively. The air quality reached the unhealthy range (PSI > 100) in 3 days with the highest value being 128 (24 hrs average PSI) on 7 October 2006.

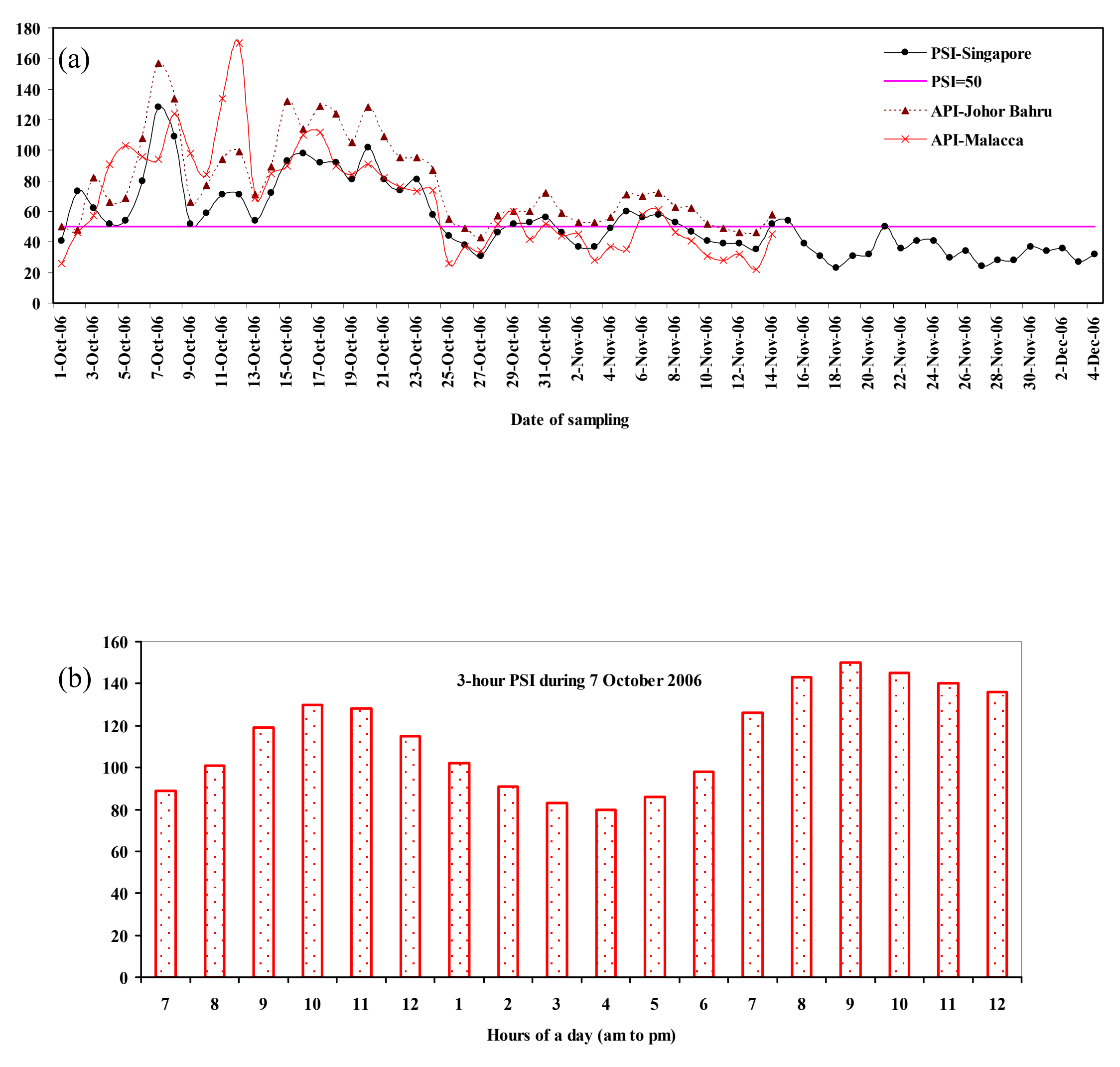

Figure 4.7 (a) Pollutant Standards Index (PSI) and Air pollution index (API) from October 2006 to December 2006 (Data from NEA, Singapore and DOE, Malaysia); (b) 3-hr PSI on 7 October 2006 (NEA, Singapore). Note: PSI or API < 50 (Good); 51–100 (Moderate); 101–200 (Unhealthy); 201–300 (Very Unhealthy); > 300 (Hazardous).

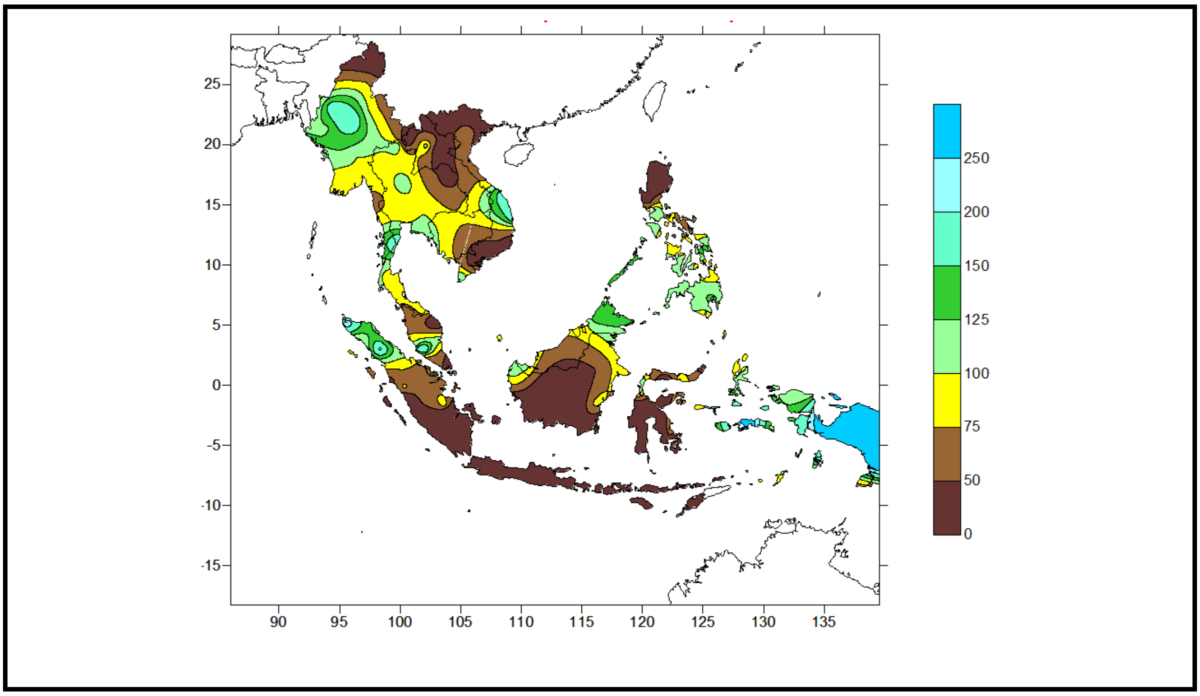

Figure 4.8 Percentage of normal rainfall distribution in SEA during September 2006 (NEA, Singapore).

To investigate the possible sources of particulate air pollution and assess the recent history and transport pathways of air masses before reaching the monitoring station in SJI, air mass back trajectories were constructed at 3 different heights 40, 100 and 500 m for a 5 days period using NOAA/ARL Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; Draxler and Rholph, 2003). The 2006 smoke haze event caused by continued uncontrolled burning from "slash and burn" cultivation in Indonesia affected several countries in the Southeast Asian region and beyond such as Malaysia, Singapore, southern Thailand (see Figure 4.9a), and as far as Saipan (Source: saipantribune.com on 05/10/2006). The fires originated mostly in Kalimantan, the Indonesian part of Borneo, and in Sumatra. The 5-day backward trajectories of air masses reaching the SJI sampling station on four representative days 7, 15, 17 and 20 October 2006 (SWM), and the extent of the haze at the same day in SEA are shown in Figure 4.9(a–b) and Figure 4.10(a–b), respectively. The PSI during these four sampling days was 128, 93, 92 and 102, respectively. During periods of active hotspots (forest fires) in

Sumatra and Borneo, spells of moderate to dense smoke haze could be expected in the vicinity of the larger fire/hotspot clusters in the affected areas (see Figure 4.9 and Figure 4.10). The HYSPLIT model calculation results showed that air mass was transported from different source areas to Singapore across the Indian Ocean at lower altitudes.

During the first haze event (Figure 4.9a) one air mass travelled from Australia land origin at higher altitude of 2000 m and others from Indian Ocean origin at low attitude through Sumatra, Java Sea and areas impacted by fires evidenced by the extent of smoke haze in SEA map by NEA, Singapore. The PM concentration is largely dependent on the direction of the prevailing winds (with southeasterly to southwesterly winds favouring the transport of haze towards Singapore), the fire activity (its location and intensity) and El Niño/Southern Oscillation (ENSO) (its effect on rainfall, atmospheric stability and convective activity). The monsoon transition (movement of airstream boundaries) shifted the wind pattern towards Peninsular Malaysia. It created convergence zones near Singapore and induced subsidence in the area as well (Koe et al., 2001). The local effects of land and sea breezes also contributed to the enhancement of PM concentration in Singapore, particularly during the transition period (Koe et al., 2001). During the other three haze events (Figure 4.10a–Figure 4.10b), the air mass mostly originated from the Kalimantan and surrounding areas. The air masses might contain mostly particulate matter and pollutants originating from biomass burning compared to that originated from other air pollution. Figure 4.11(a–f) shows scatter diagram of TSP with best fitted regression line and corresponding R-squared value against PSI and meteorological parameters in Singapore from October 2006 to mid December 2006. The measured TSP has a polynomial regression type fitting to relative humidity, incoming radiation, wind speed, rainfall as data fluctuates and exponential regression type fitting to air pressure as the values rise or fall at increasingly higher rates.

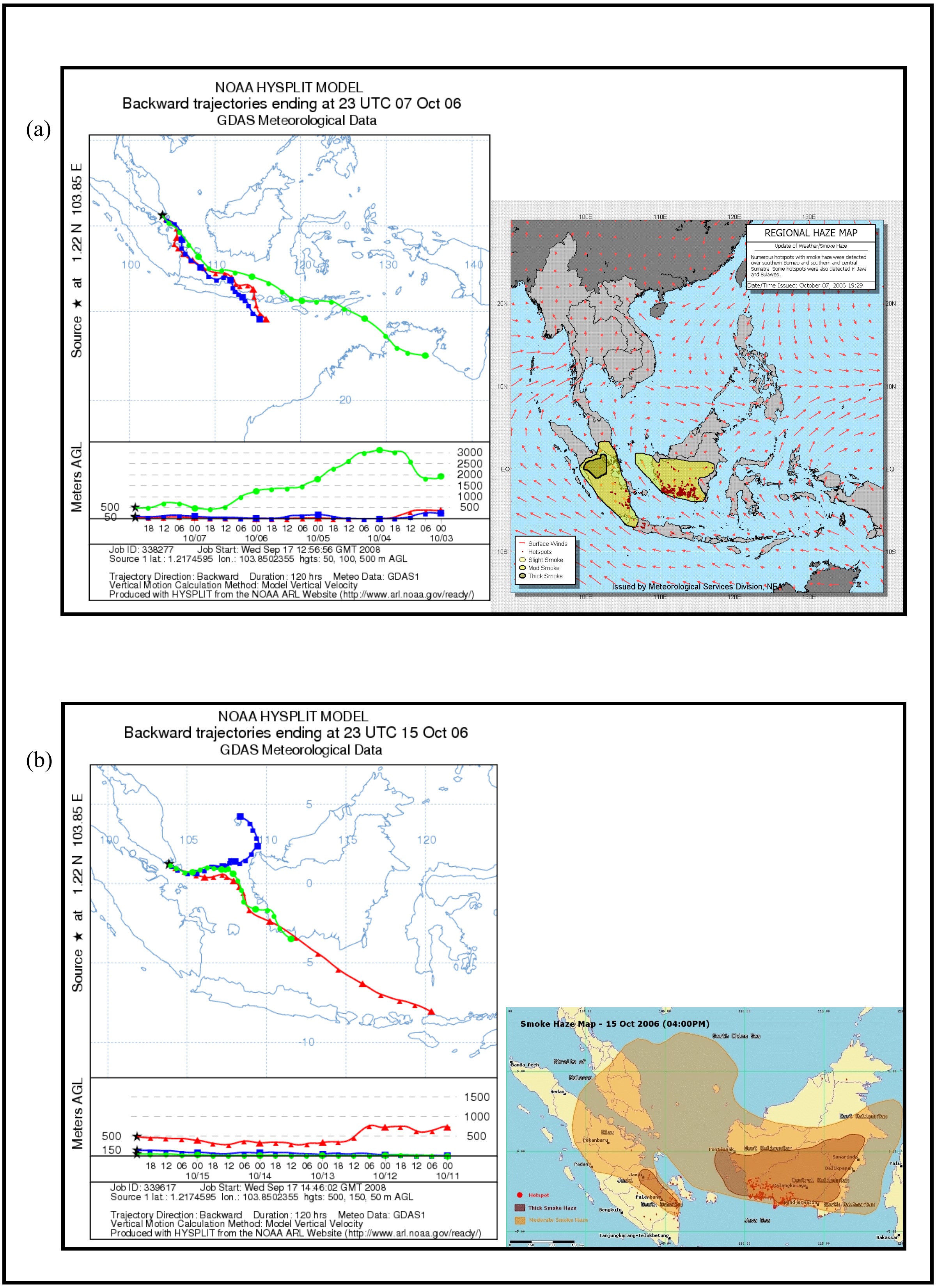

Figure 4.9 Back trajectories of air masses for starting altitude of 500 m, 100 m, and 40 m above ground level (AGL) calculated from NOAA HY-SPLIT model for the sampling site in SJI and the extent of the smoke haze in SEA due to forest fires in Indonesia (courtesy: NEA, Singapore) (a) 7 October 2006; (b) 15 October 2006.

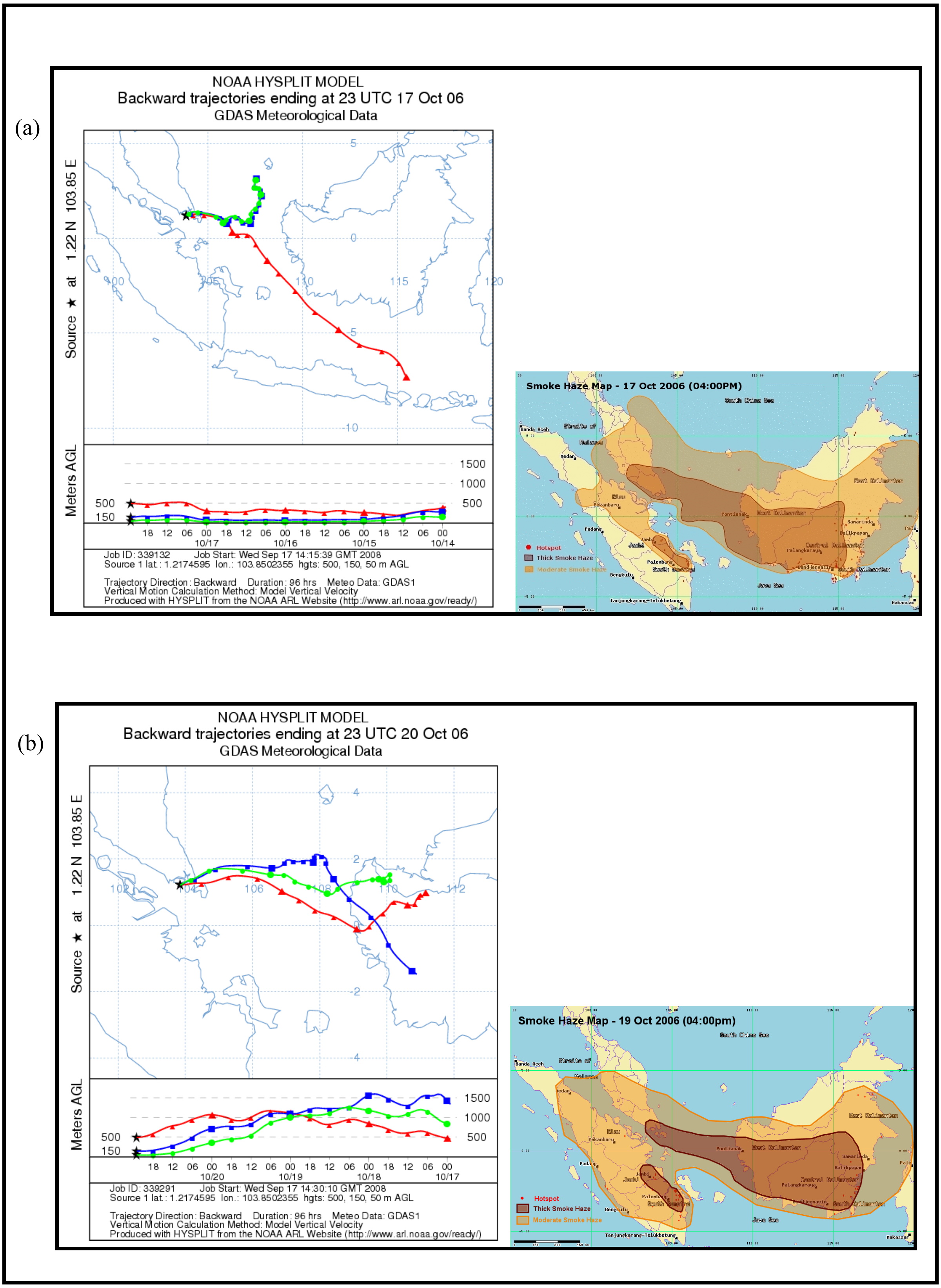

Figure 4.10 Back trajectories of air masses for starting altitude of 500 m, 100 m, and 40 m above ground level (AGL) calculated from NOAA HY-SPLIT model for the sampling site in SJI and the extent of the smoke haze in SEA due to forest fires in Indonesia (courtesy: NEA, Singapore) (a) 17 October 2006 and (b) 20 October 2006.

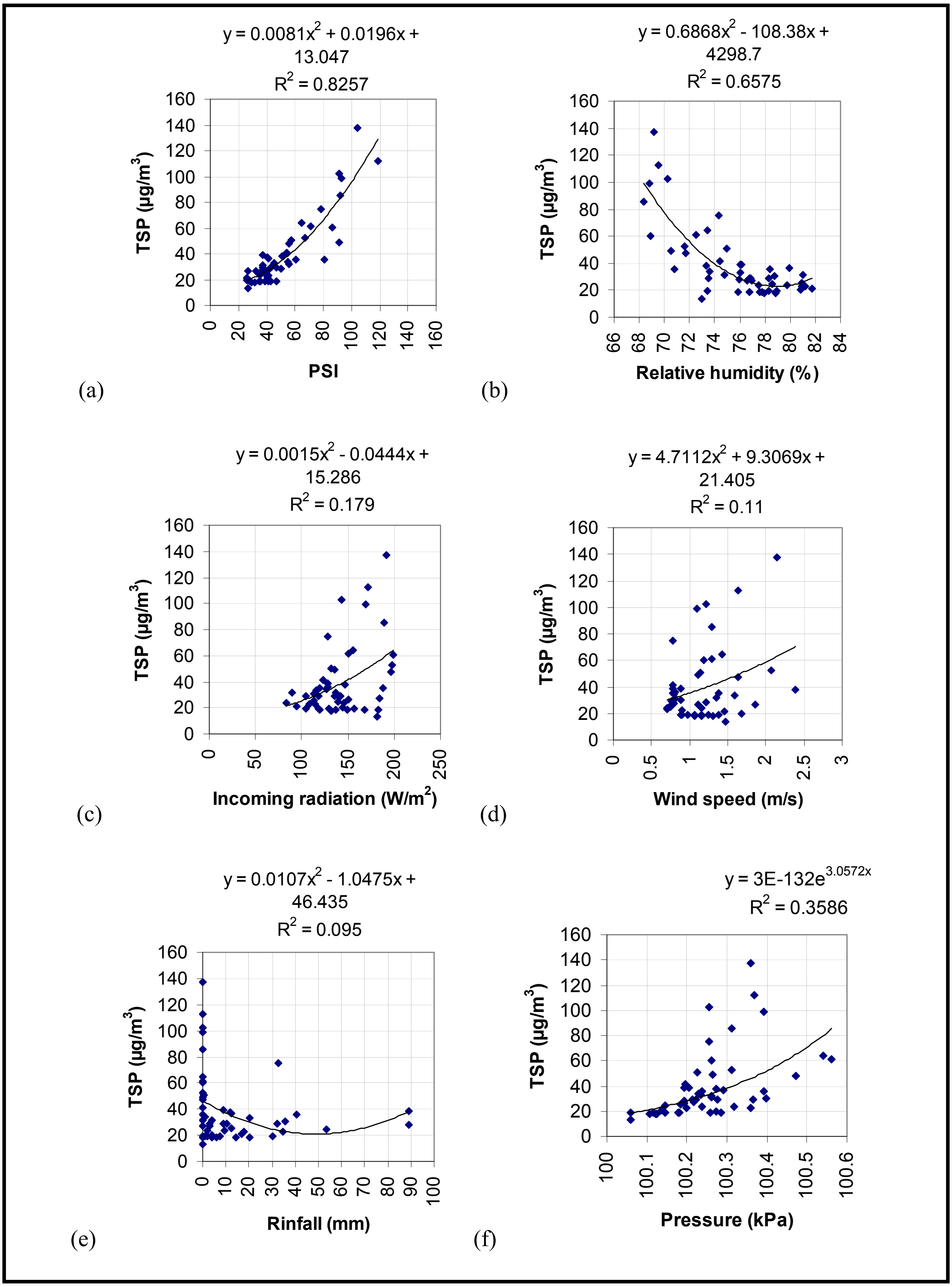

Figure 4.11 Scatter diagram of TSP against PSI and meteorological parameters, relative humidity, incoming radiation, wind speed, rainfall and air pressure, in Singapore from October 2006 to mid December 2006.

4.2.2 Dry deposition

The range, mean, median, geomean, range and standard deviation of the concentration of soluble inorganic and organic nutrients (N and P species) obtained from TSP samples during hazy and non-hazy days in Singapore are shown in Table 4.3. The baseline concentration of nutrients in Singapore seawater was referred from Tkalich and Sundarambal (2003). The range of concentrations of N species during hazy days was in the order of 10.1–14.9 μg/m^3 for TN, 5.15–8.16 μg/m^3 for ON, 2.28–6.36 μg/m^3 for NO_3 + NO_2, and 1.53–2.43 μg/m^3 for NH_4. The range of concentrations of N species during non-hazy days were in the order of 1.31–3.84 μg/m^3 for TN, 0.43–2.5 μg/m^3 for ON, 0.41–1.51 μg/m^3 for NO_3 + NO_2, and 0.01–1.6 μg/m^3 for NH_4. The high ratio of nutrients between hazy and non-hazy days (Figure 4.14) shows that smoke haze episodes provided a significant source of nutrients to the coastal water in Singapore and SEA. The order of occurrences of N and P species in terms of ratio between that observed during hazy and non-hazy days was NH_4>NO_3+NO_2>TN>ON and OP>TP>PO_4, respectively. The arithmetic mean of P species in aerosol were 0.48 ± 0.13 μg/m^3 for TP, 0.38 ± 0.16 μg/m^3 for OP and 0.09 ± 0.07 μg/m^3 for PO_4 in hazy days and 0.07 ± 0.02 μg/m^3 for TP, 0.05 ± 0.02 μg/m^3 for OP and 0.02 ± 0.01 μg/m^3 for PO_4 in non-hazy days.

DAD fluxes of N and P species were calculated from the field observations of DAD nutrients concentration (Table 4.3) using the equation (3.1) in Section 3.1.6. Figure 4.12 shows the DAD fluxes of N and P species during hazy and non-hazy days. The annual DAD fluxes of reactive (NO_2 + NO_3)-N estimated into the coastal water of Singapore were 1.61 ± 0.724 g/m^2/yr and 0.303 ± 0.102 g/m^2/yr during hazy days and non-hazy days respectively. The annual DAD fluxes of reactive PO_4-P estimated into the coastal water of Singapore were 0.059 ± 0.042 g/m^2/yr during hazy days and 0.014 ± 0.006 g/m^2/yr during non-hazy days. The mean (and range) DAD fluxes (g/m^2/yr) of TN, ammonium and ON were 4.78 (3.83–5.66), 0.362 (0.29–0.46) and 2.44 (1.95–3.09) respectively during hazy period. The mean (and range) DAD fluxes (g/m^2/yr) of TP and OP were 0.3 (0.222–0.413) and 0.242 (0.178–0.386), respectively during hazy period. The mean (and range) DAD fluxes (g/m^2/yr) of TN and TP species observed during non-hazy period were 0.91 (0.497–1.46) for TN and 0.046 (0.023–0.056) for TP, respectively. The contribution of nutrients through DAD nutrients follows the order: $TN>NO_2+NO_3>ON>NH_4$ for N species and $TP>OP>PO_4$ for P species with respect to their concentrations and fluxes.

Table 4.3 Concentration of nutrients (N and P species) (µg/m^3) in aerosol during hazy and non-hazy days and in seawater

Sample	Nutrients	Period	Mean	Median	GeoMean	SD	Min	Max
Aerosol	TN	Haze	12.6	12.7	12.5	2.05	10.1	14.9
Aerosol		Non-Haze	2.40	2.34	2.29	1.25	1.31	3.84
seawater		*	0.1129					
Aerosol	NH_4	Haze	1.92	1.85	1.89	0.38	1.53	2.43
Aerosol		Non-Haze	0.28	0.12	0.09	0.41	0.01	1.60
seawater		*	0.0133					
Aerosol	NO_3+NO_2	Haze	4.25	4.05	3.93	1.91	2.28	6.63
Aerosol		Non-Haze	0.80	0.77	0.76	0.27	0.41	1.51
seawater		*	0.02					
Aerosol	ON	Haze	6.44	6.23	6.35	1.29	5.14	8.16
Aerosol		Non-Haze	1.49	1.40	1.35	0.61	0.43	2.50
seawater		*	0.0796					
Aerosol	TP	Haze	0.48	0.45	0.46	0.13	0.35	0.65
Aerosol		Non-Haze	0.07	0.08	0.07	0.02	0.04	0.09
seawater		*	0.0251					
Aerosol	PO_4	Haze	0.09	0.07	0.08	0.07	0.04	0.19
Aerosol		Non-Haze	0.02	0.02	0.02	0.01	0.01	0.04
seawater		*	0.0116					
Aerosol	OP	Haze	0.38	0.32	0.36	0.16	0.28	0.61
Aerosol		Non-Haze	0.05	0.05	0.04	0.02	0.002	0.07
seawater		*	0.0135					
	TSP	Haze	113	107	112	17	99	138
		Non-Haze	24	25	24	5	18	31
	PSI	Haze	102	99	101	12	92	119
		Non-Haze	35	35	34	7	25	47

Note: * Seawater baseline (unit: mg/l) (Derived from Sundarambal and Tkalich, 2003); number of sample n = 4 for haze period; n = 16 for non-haze period.

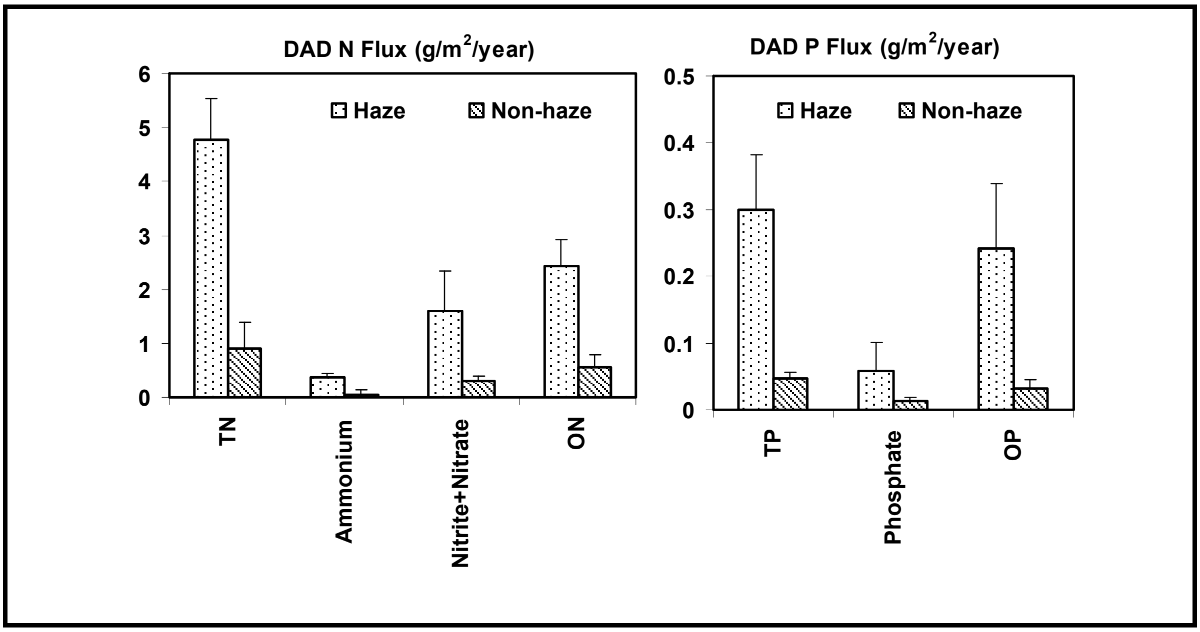

Figure 4.12 Fluxes of nutrients (N and P species) in DAD during hazy and non-hazy days

4.2.3 Wet deposition

The concentration of nutrients (N and P species) in rainwater was obtained from the laboratory analysis during hazy and non-hazy days. Rainwater samples (3 rain events) were selected based on PSI from 15 to 21 October 2006 for hazy days and rainwater samples (3 rain events) from 11 November 2006 to 23 December 2006 for non-hazy days. The concentration of nutrients (N and P species) (mg/l) in precipitation during hazy and non-hazy days and in seawater is shown in Table 4.4. The range of PSI during haze and non-hazy days were 81–93 and 35–39, respectively. The range of wet deposition concentrations of N species during hazy days was in the order of 11.8–20.4 mg/l for TN, 3.21–10.5 mg/l for ON, 7.78–9.48 mg/l for $NO_3 + NO_2$, and 0.77–1.19 mg/l for NH_4. The range of WAD concentrations of N species during non-hazy days was in the order of 2.38–4.79 mg/l for TN, 1.3–2.52 mg/l for ON, 1.03–2.24 mg/l for $NO_3 + NO_2$, and 0.03–0.39 mg/l for NH_4. On an event basis, the minimum and the maximum wet deposition fluxes of macro-nutrients were highly variable. The arithmetic mean of P species was 0.91 ± 0.09 mg/l for TP, 0.65 ± 0.29 mg/l for OP and 0.26 ± 0.2 mg/l for PO_4

for hazy days and 0.18 ± 0.08 mg/l for TP, 0.15 ± 0.09 mg/l for OP and 0.03 ± 0.01 mg/l for PO_4 for non-hazy days. The reported concentrations of NH_4 and NO_3 in rainwater were 0.312 mg/l and 1.04 mg/l during 1997 to 1998 in Singapore (Balasubramanian et al., 2001), and 0.247 mg/l and 1.23 mg/l respectively during 1996 to 1997 in Malaysia (Ayer et al., 2002). The concentration levels of nutrients such as ammonium, nitrate and phosphorous spikes from biomass burning have been already reported (Lobert et al., 1990; Crutzen and Andreae, 1990; Mayewski et al., 1993; 1997; Kondo et al., 2004; Mahowald et al., 2005, 2008). The contribution of nutrients through WAD nutrients follows the order: $TN>NO_2+NO_3>ON>NH_4$ for N species and $TP>OP>PO_4$ for P species with respect to their concentrations and fluxes. The order of occurrences of WAD N and P species in terms of ratio between that observed during hazy and non-hazy days is similar to DAD for N species and $PO_4>TP>OP$ respectively (Figure 4.14). The mean concentrations of atmospheric aerosol and rainwater were comparable to the fluxes from land-based sources such as wastewater treatment plants (TN = 2.13 mg/l and TP = 0.17 mg/l) and rivers (ammonium = 0.16 mg/l, nitrite + nitrate =0.34 mg/l and phosphate = 0.14 mg/l) (DHI, 2004) in Singapore coastal water.

The magnitude of wet deposition fluxes depends on precipitation rate. In this study, precipitation rate of 794 mm, cumulative rainfall amount of rain events during the study period of October 2006 to December 2006, was utilized for wet deposition flux estimation. A similar pattern of nutrient concentration was observed in rainwater and seawater (Figure 4.13a). Figure 4.13b shows the atmospheric fluxes of N and P species calculated based on the field measurements of wet deposition during hazy and non-hazy days from October 2006 to December 2006 in Singapore. The annual mean wet deposition fluxes of reactive $(NO_2 + NO_3)$-N and PO_4-P into the coastal water, Singapore were estimated to be 6.86 ± 0.672 $g/m^2/yr$ and 0.207 ± 0.161 $g/m^2/yr$ during hazy days, and to be 1.23 ± 0.496 g/m^2/yr and 0.027 ± 0.008 g/m^2/yr during non-hazy days, respectively. The annual mean wet deposition fluxes (g/m^2/yr) of ammonium observed was 0.746 ± 0.178 during hazy days and 0.122 ± 0.165 during non-hazy days. Nominal annual average wet deposition fluxes (g/m^2/yr) published elsewhere in SEA for NH_4 and NO_3 were 0.718 and 3.607 in Malaysia during 1993–1998 (Ayers et al., 2000; 2002); 1.383 and 1.74 in Indonesia during 1992 and 1996 (Gillett et al., 2000); 0.079 and 0.308 in Australia (Ayers and Yeung, 1996). The annual mean wet deposition fluxes of TN and TP in g/m^2/yr were 12.2 ± 3.53 and 0.726 ±0.074, and 2.71 ± 0.989 and 0.144 ±0.06 for hazy and non-hazy days, respectively. The observed organic N and P annual mean wet deposition fluxes in g/m^2/yr were 4.62 ± 3.23 and 0.52 ± 0.234 during hazy and 1.36 ± 0.554 and 0.117 ± 0.068 non-hazy days. The higher amount of WAD fluxes (about 3 times) were obtained when annual precipitation rate (2136 mm) was used instead of precipitation rate (794 mm) during the study period from October 2006 to December 2006. This ultimate WAD flux might be applied as a constant uniform load coming from the atmosphere over the coastal water in the study area for modelling study to understand their impact and effect. The ratio of haze and non-haze concentrations for aerosol and rainwater (Figure 4.14) clearly shows that AD contributes a larger proportion of nutrients into coastal water of SEA during haze events. Concentrations of most ions in rainwater were higher during periods of intense biomass fires and haze than during periods when there were no significant forest fires. The haze events that have plagued SEA are likely to affect the atmospheric fluxes of nutrients and other pollutants into aquatic systems. Atmospheric deposition in Singapore and surrounding countries appears to provide considerable fluxes of nutrients of environmental concern and it may play an important role in the coastal eutrophication. Field observations of atmospheric nutrient deposition during 2006 biomass burning in Southeast Asia will be published elsewhere (Sundarambal et al., 2010b).

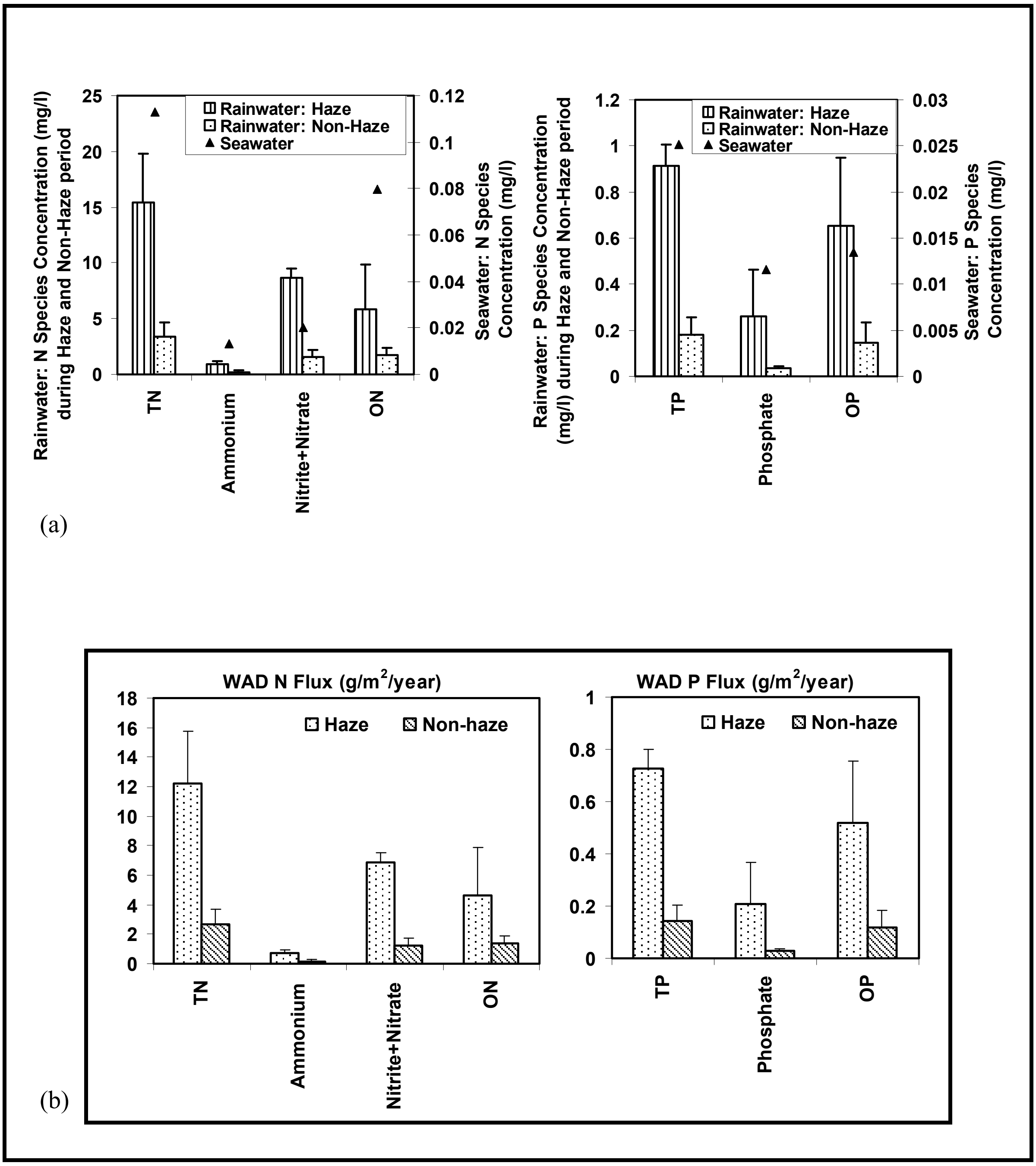

Figure 4.13 (a) Concentration of nutrients (N and P species) in rainwater during hazy and non-hazy days and seawater; (b) Fluxes of nutrients (N and P species) in WAD during hazy and non-hazy days.

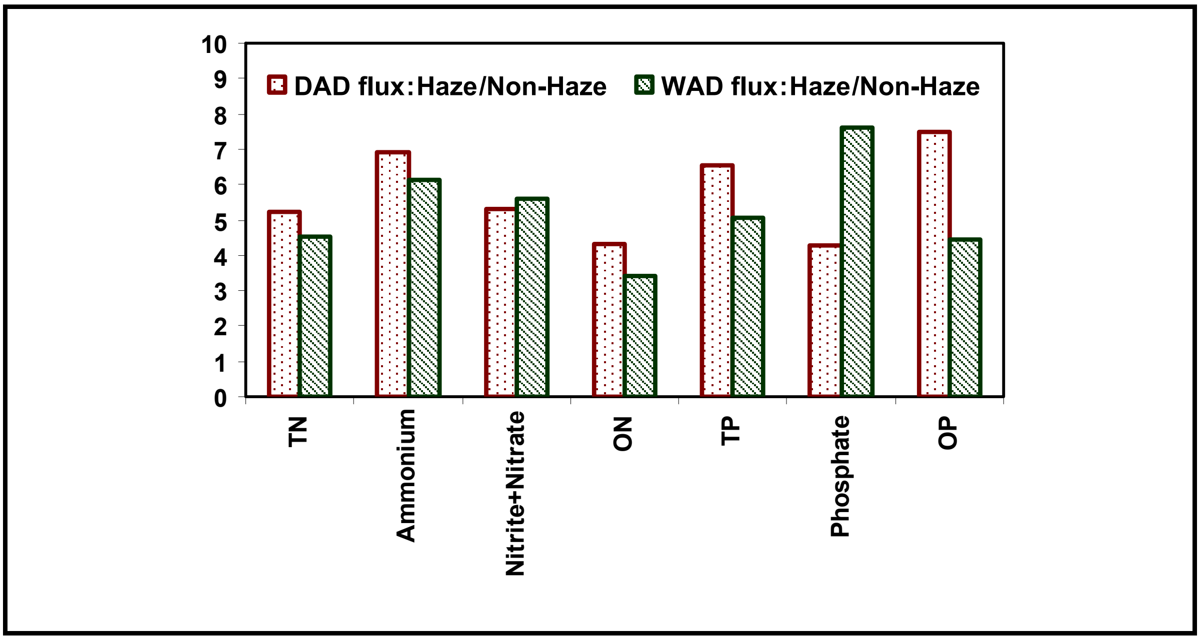

Figure 4.14 Ratio of fluxes of N species during hazy to non-hazy days in DAD and WAD during 2006 haze episodes, SEA

Table 4.4 Concentration of nutrients (N and P species) (mg/l) in precipitation during hazy and non-hazy days and in seawater

Sample	Nutrients	Period	Mean	Median	GeoMean	SD	Min	Max
Rainwater	TN	Haze	15.4	14.1	15.0	4.45	11.8	20.4
Rainwater		Non-Haze	3.41	3.05	3.27	1.25	2.38	4.79
seawater		*	0.1129					
Rainwater	NH_4	Haze	0.94	0.85	0.92	0.22	0.77	1.19
Rainwater		Non-Haze	0.15	0.04	0.08	0.21	0.03	0.39
seawater		*	0.0133					
Rainwater	NO_3+NO_2	Haze	8.64	8.66	8.61	0.85	7.78	9.48
Rainwater		Non-Haze	1.54	1.36	1.47	0.62	1.03	2.24
seawater		*	0.02					
Rainwater	ON	Haze	5.81	3.74	5.01	4.06	3.21	10.5
Rainwater		Non-Haze	1.71	1.32	1.63	0.70	1.30	2.52
seawater		*	0.0796					
Rainwater	TP	Haze	0.91	0.97	0.91	0.09	0.81	0.97
Rainwater		Non-Haze	0.18	0.2	0.17	0.08	0.10	0.24
seawater		*	0.0251					
Rainwater	PO_4	Haze	0.26	0.19	0.21	0.20	0.10	0.49
Rainwater		Non-Haze	0.03	0.03	0.03	0.01	0.02	0.05
seawater		*	0.0116					
Rainwater	OP	Haze	0.65	0.78	0.60	0.29	0.32	0.87
Rainwater		Non-Haze	0.15	0.18	0.12	0.09	0.05	0.21
seawater		*	0.0135					
	PSI	Haze	89	92	88	7	81	93
		Non-Haze	36	35	36	2	35	39

Note: * Seawater baseline (unit: mg/l) (Derived from Sundarambal and Tkalich, 2003); number of sample n = 3 both for haze period and non-haze period.

4.3 Seawater nutrients

About 14 seawater samples were also collected during 2006 hazy from 8th October 2006 to 20 January 2007 from SJI ferry terminal situated approximately 6.5km south of Singapore, off the Straits of Singapore. From the regression studies, it was observed that there exists correlaton between concentrations in the atmosphere with concentrations in seawater, indicating the significance of the atmospheric input of nutrients and pollutants in the Singapore and surrounding seawater. The measured concentration range of parameters (in terms of minimum–maximum) were given as phytoplankton (0.018–0.172 mgC/l), NH_4 (0.003–0.027 mg/l), NO_2 + NO_3 (0.006–0.027 mg/l), TN (0.037–0.199 mg/l), PO_4 (0.005–0.015 mg/l) and TP (0.028–0.035 mg/l) while during the sampling period PSI was in the range of 23–109. Chlorophyll-a significantly correlated with ammonium ($R^2 = 0.82$, $P = 0$), NO_3 ($R^2 = 0.605$, $P = 0.02$) and TN ($R^2 = 0.6$, $P = 0.02$) (Table 4.5). It is clear from Figure 4.15 that there is existence of relationship between atmospheric depositions and sea surface water quality. From the analysis of field measurements of AD and seawater during October 2006 haze event due to forest fires, a significant correlation between phytoplankton and atmospheric deposition (Pearson correlation coefficient > 0.6, P-value < 0.05) was found. A long term monitoring of both AD of nutrients and the corresponding changes in seawater is needed to establish the exact relationship between phytoplankton and atmospherically deposited nutrients in tropical coastal water. Average baseline concentrations of nutrients in Singapore seawater was taken from Tkalich and Sundarambal (2003) (see Table 4.3).

Table 4.5 Pearson correlation (P-value) for seawater nutrients

Prameters	**Phytoplankton**	**Ammonium**	**Phosphate**	**TP**	**Nitrite**	**Nitrate**
Ammonium	0.82 (0)					
Phosphate	-0.12 (0.68)	-0.14 (0.62)				
TP	-0.11 (0.71)	-0.38 (0.18)	0.03 (0.91)			
Nitrate	0.61 (0.02)	0.31 (0.28)	0.09 (0.75)	0.13 (0.67)	0.73 (0.03)	
TN	0.60 (0.02)	0.52 (0.06)	-0.13 (0.66)	-0.03 (0.91)	0.19 (0.51)	0.35 (0.23)

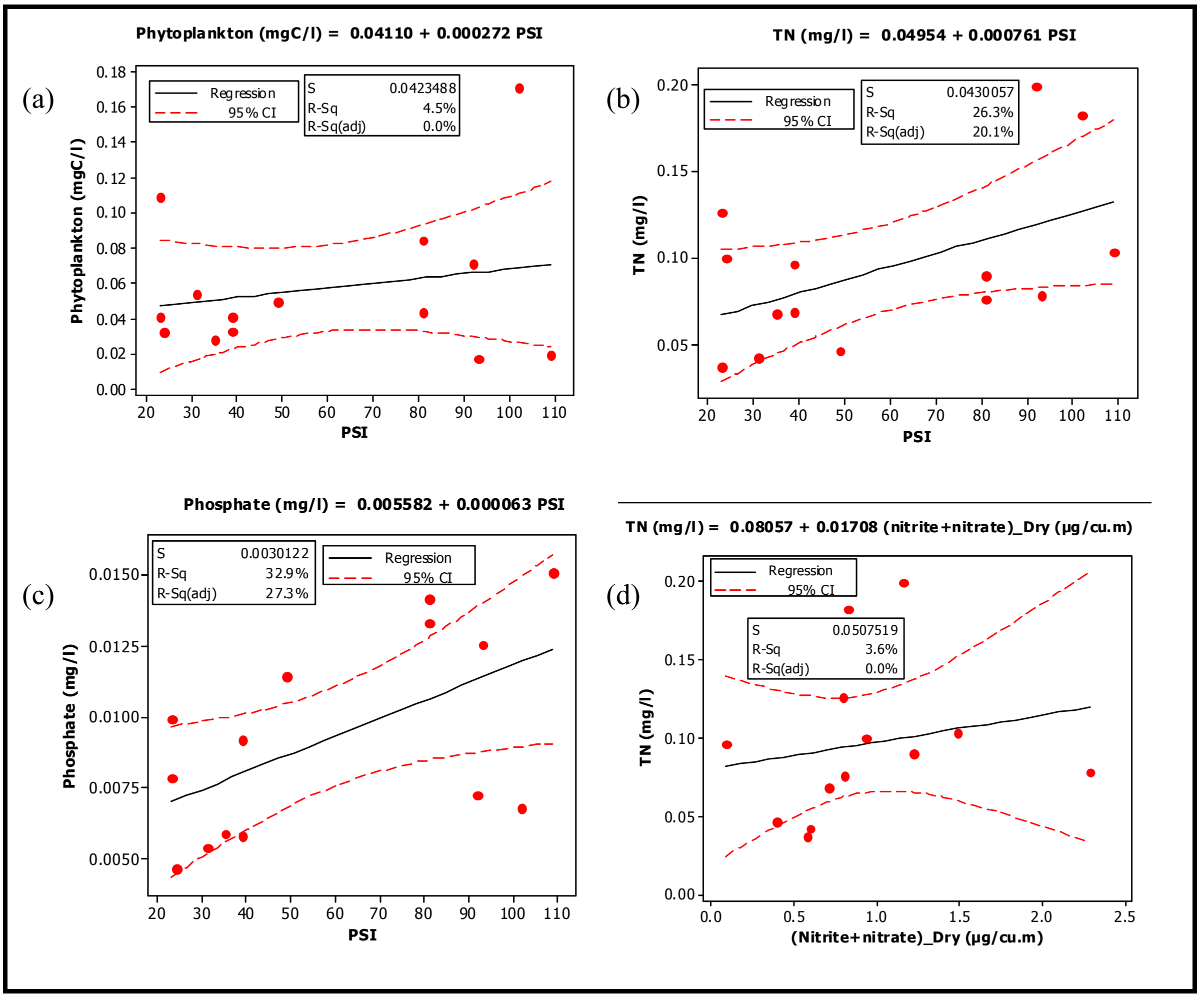

Figure 4.15 Relationship between Pollutant Standards Index (PSI) and seawater parameters (a) phytoplankton, (b) TN and (c) phosphate; (d) relationship between (NO_2+NO_3) from dry AD and TN of seawater.

4.4 Significance of atmospheric deposition

This study shows that significant quantities of both the inorganic and organic fractions of water soluble N and P species in dry atmospheric deposition and wet atmospheric deposition are released to a tropical marine environment of Singapore. The total (WAD + DAD) fluxes ($g/m^2/yr$) of inorganic and organic N species were in the range of 0.97–15.4 and 0.363–6.49, and those of P species were 0.003–0.344 and 0.142–2.51, respectively. The atmospheric depositions were mainly contributed by nitrite + nitrate nitrogen followed by ON and then ammonium ion (50 %, 36 %, and 14 %, respectively). In this study, it is found that biomass burning in and around SEA is a significant source of nutrients (both inorganic and organic N and P species) through atmospheric deposition to the regional surface water such as estuarine, coastal water and open ocean during haze episodes. The tropical and marine atmospheric deposition (AD) of nutrients (N and P species) in aerosol released by biomass burning during haze is in the order of factor of 3 to 8 when compared with non-hazy days into the coastal water of Singapore and SEA region. The increasing pollution load in air and rain may have consequences on receiving ecosystems and biogeochemical cycling. These quantitative and qualitative aspects of atmospheric nutrient sources may promote biotic changes now apparent in estuarine and coastal water with cascading impacts on water quality, and trophic and biogeochemical alterations (i.e., algal blooms, hypoxia, food web, and fisheries habitat disruption). Air mass back trajectories showed that large-scale forest fires in Sumatra and Kalimantan is a significant atmospheric nutrient source to aquatic environment in SEA region and Singapore’s coastal water quality degradation during haze episodes.

The information presented in this thesis enriches scientific knowledge in issues related to AD of pollutants, particularly nutrients, to coastal water of SEA. This investigation represents a baseline study for assessing the possible environmental effects of “new” AD of N and P compounds on the coastal aquatic ecosystem. It is essential to carry out further study as AD of nutrient fluxes could contribute a substantial fraction of dissolved inorganic N or P species to the euphotic zone, and to estimate the surface new primary production that could possibly be supported by new source. Hence, interdisciplinary studies will be carried out to test hypothesized effects of atmospheric inputs in these systems to expand our understanding of the interactions of physical, chemical, and biological processes controlling coastal water ecosystems. The estimated AD of nutrient fluxes is used in a water quality model (NEUTRO, Tkalich and Sundarambal, 2003; Sundarambal et al., 2007) to simulate the effects due to a “new” nutrient input into Singapore and SEA coastal water (Sundarambal et al., 2008a, b).

CHAPTER 5: RESULTS AND DISCUSSION - EUTROPHICATION MODELLING

The central hypothesis of this study is that the atmospheric input is an important external source of nutrients, supporting considerable fraction of excessive productivity in the region. During wet seasons, the removal of gaseous and particle-bounded compounds dominates other depositional processes. It is crucial to consider its spatial and temporal variability since the precipitation is intermittent and a local phenomenon. For the present study, NEUTRO is enhanced to incorporate the atmospheric input of macronutrients, and subsequently is utilized to investigate the fate of atmospherically deposited nutrients. This Chapter presents the results obtained using the 3-D eutrophication model NEUTRO that was used to assess the proportion of atmospheric nutrient fluxes and quantification of the relative contribution of atmospheric and ocean fluxes in the Singapore Strait. The model results obtained using NEUTRO agree with the observed data in both qualitatively and quantitatively. The analysis includes an assessment of the importance of typical atmospheric deposition fluxes of nitrogen for the coastal water quality. The significant correlation of atmospheric and seawater nitrogen over the modelled region (see Section 4.3) indicated that AD is an important factor contributing to the growth of phytoplankton during haze events. A particular case of the 2006 haze event was considered to explore association of the atmospheric fluxes with algal blooms observed in the regional coastal waters. The sensitivity analysis and the application of NEUTRO for atmospheric deposition fluxes of nitrogen are also discussed in the following sections.

5.1 Sensitivity analysis

The values of typical wet atmospheric nitrite + nitrate flux estimates fluctuate between 1.03–2.24 mg/l and 7.78–9.48 mg/l during non-haze and haze period respectively (Sundarambal et al., 2010b). Therefore, a sensitivity analysis on atmospheric deposition was conducted using nitrite + nitrate concentrations at different extremes. For sensitivity study, the calibrated model was analyzed for its response to an increase in nutrient fluxes due to wet atmospheric deposition. Two experiments were considered to investigate the increase in nitrite + nitrate nitrogen and phytoplankton at water surface in response to different atmospheric nitrogen fluxes. In the first experiment, the atmospheric nitrogen flux was assumed to increase by keeping constant precipitation rate (Q) of 2136 mm/yr and increasing nitrite + nitrate concentration (S) from atmosphere at 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l using four different model runs. In the second experiment, the precipitation rate (Q) was assumed to increase by 100 times that of Q (i.e. 100 X 2136 mm/yr) and the nitrite + nitrate concentration (S) from the atmosphere was assumed to be 1 mg/l and 100 mg/l. For both experiments, the total mass of nitrite + nitrate increase in the model domain (Figure 5.1) was computed.

The variation of atmospheric nitrite + nitrate fluxes into the model shows the increase in the total mass proportional to the magnitude of the increment (Figure 5.1). In each model run, the total mass increased gradually during the initial model simulation period until a steady state condition was reached. The percentage increase in mass due to various atmospheric nitrite + nitrate fluxes from its baseline was in the order of 0.01 %, 0.13 %, 0.63 % and 1.26 % for nitrite + nitrate concentration of 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l, respectively from atmospheric deposition (Figure 5.1a). In the second experiment, it was observed that the average percentage increase of 0.79 % and 82.9 % of resultant total mass when 1 mg/l and 100 mg/l of atmospheric nitrite + nitrate concentration get deposited respectively with very heavy rainfall (Figure 5.1b). It clearly shows that heavy precipitation with high nitrogen concentration significantly affects the water quality and aquatic ecosystem.

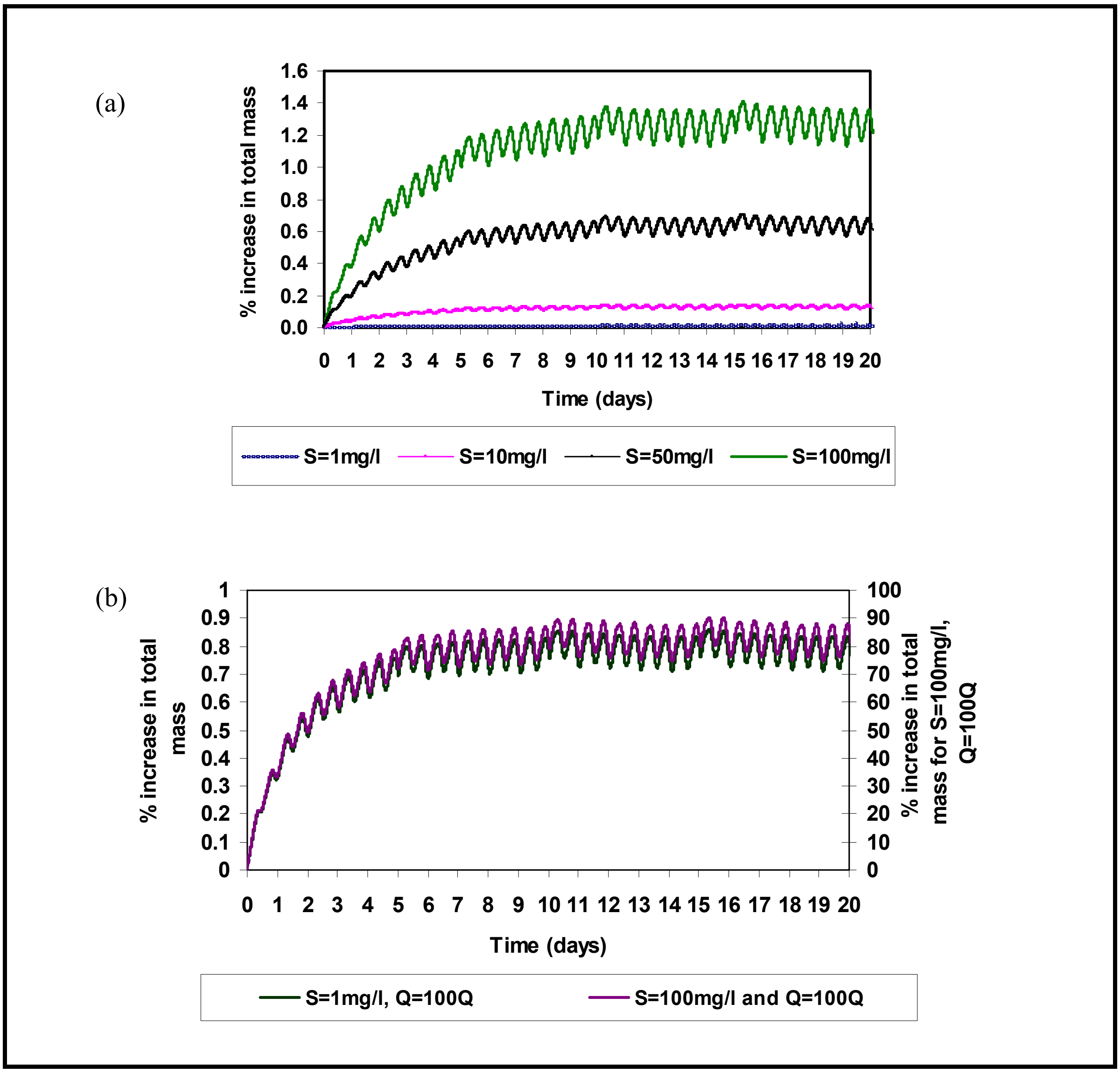

Figure 5.1 The percentage increase in total mass from its baseline due to various (a) atmospheric nitrite + nitrate fluxes and (b) precipitation rate in the Singapore Strait

Whenever the atmospheric nitrite + nitrate flux was increased, similar increases of the phytoplankton concentration and total mass in the Singapore Strait were observed accordingly (Figure 5.2). The computed spatial distribution of surface nitrite + nitrate nitrogen and phytoplankton concentration relative to their baseline in response to wet atmpospheric deposition of 1 mg/l and 100 mg/l nitrite + nitrate nitrogen concentration respectively are shown in Figure 5.3 and Figure 5.4.

Due to atmospheric deposition nitrite + nitrate species with a concentration of 100 mg/l, there was rise in the concentration levels of 1.5 mg/l and 0.05 mgC/l of nitrite + nitrate and phytoplankton respectively in the areas of Singapore and surrounding water (Figure 5.4). The effect of atmospheric deposition is most obvious in the coastal areas. An area is said to be sensitive to atmospheric nutrient fluxes and has a higher risk of becoming eutrophic, when the phytoplankton concentration is increased disproportionately. Increased atmospheric nutrient fluxes, even as much as 100 times above the typical atmospheric nitrogen flux, could cause eutrophication in nearshore waters of Singapore and sourrounding waters and also areas where tidal action is slow.

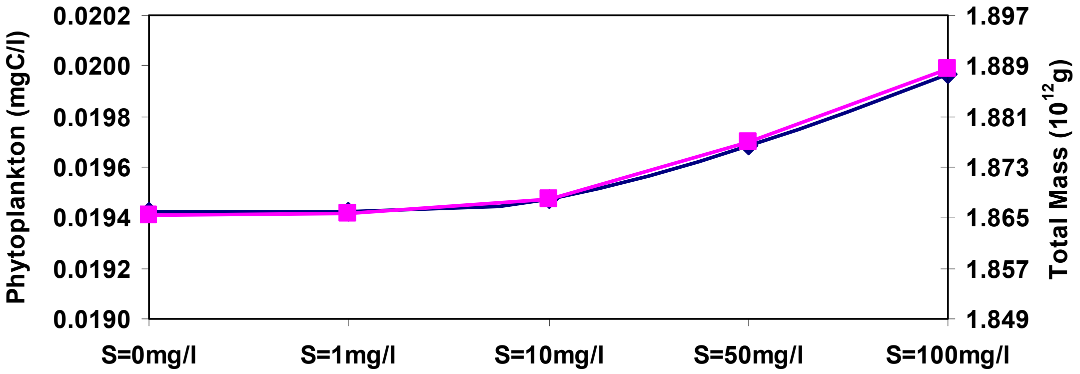

Figure 5.2 The phytoplankton concentration and total mass due to various atmospheric nitrite + nitrate fluxes in the Singapore Strait for the first experiment

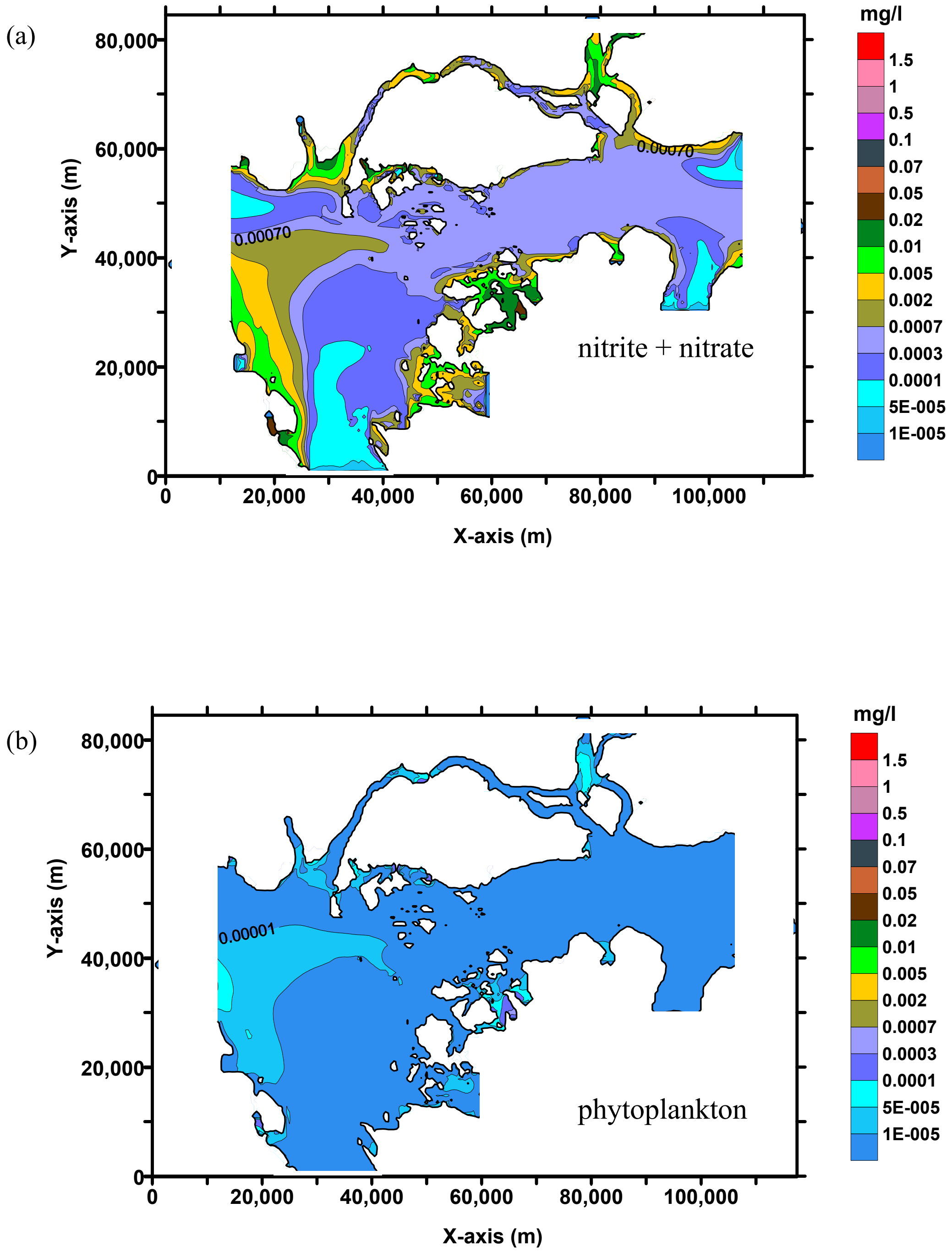

Figure 5.3 Sensitivity analysis of the responses of (a) nitrite + nitrate and (b) phytoplankton concentration at surface to wet atmpospheric deposition of 1 mg/l nitrite + nitrate nitrogen concentration .

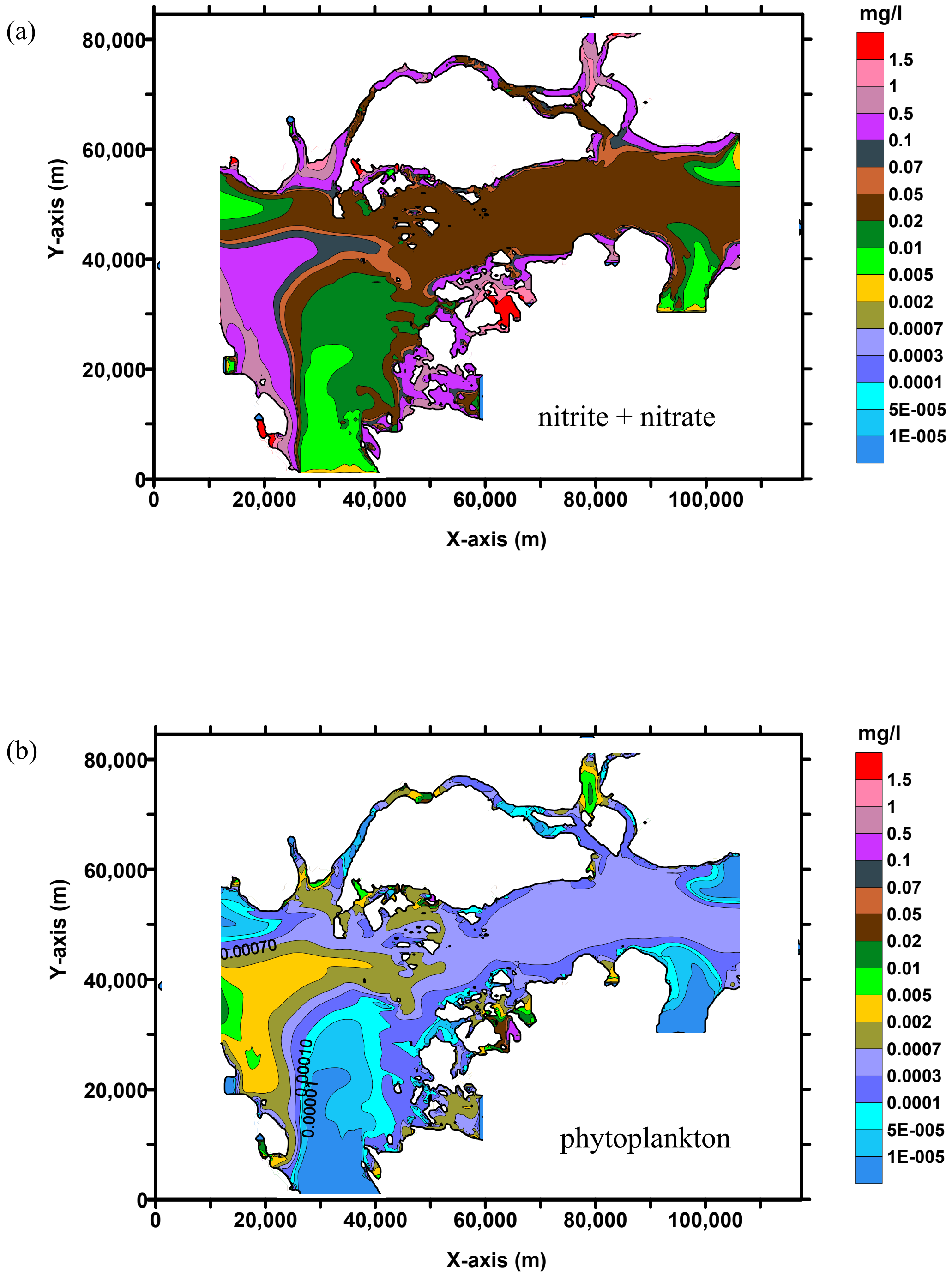

Figure 5.4 Sensitivity analysis of the responses of (a) nitrite + nitrate and (b) phytoplankton concentration at surface to wet atmpospheric deposition of 100 mg/l nitrite + nitrate nitrogen concentration

5.2 Modelling of fate of atmospheric deposition fluxes in the water column

This section evaluates the percentage increase of nitrite + nitrate nitrogen in the coastal water column due to fluxes of biologically available nitrogen in atmospheric wet depositions (WD) using methods described in Section 3.2.9. The tidal driven currents were computed for a typical southwest monsoon season using the 3-D hydrodynamic model TMH. To address and compare the impact of atmospheric wet deposition at different nitrogen fluxes in the Singapore Strait, three model cases (Case A, Case B and Case C) were considered. In the Case A, typical nitrogen flux from wet atmospheric deposition was assumed to be applied spatially uniform on the water surface in Singapore Strait. In the Case B, the nitrogen fluxes from wet atmospheric deposition during haze and non-haze period were considered. An assessment of the importance of high concentration episodic inputs of nitrate + nitrate nitrogen associated with transport of polluted air onto the surface water in the Singapore Strait is discussed in Case C. In each of the case, the model was run for both conservative and non-conservative modes to estimate the significance of atmospheric nitrogen fluxes and to investigate the spatial and temporal dynamics of nutrients in the Singapore Strait. Also, the contribution of atmospheric nitrogen fluxes into coastal water eutrophication was quantified.

The basic task of a conservative approach is to perform a continuous mass balance on the water and the conservative pollutant in the coastal system and to route both of these substances through the coastal system in such a way that closely approximates the actual field condition. In non-conservative approach, the contaminant inputs into a coastal system are subjected to physical and biochemical processes (eutrophication kinetics) that would affect the concentration of the contaminant in the water column. Thus, the impact of atmospheric nitrogen deposition onto aquatic ecosystem could be estimated by using non-conservative modelling approach. The typical precipitation rate and quantified concentrations of nitrite + nitrate concentration from atmospheric wet deposition (Section 0 for Case A and Section 4.2.3 for Case B) for atmospheric nitrogen fluxes were used as an input for the each case. The initial seawater concentration for ammonium, nitrite + nitrate, phosphate, ON, OP, phytoplankton, zooplankton, CBOD and DO were set to baseline concentrations of 0.0133 mg/l, 0.02 mg/l, 0.0116 mg/l, 0.0796 mg/l, 0.0135 mg/l, 0.02 mgC/l, 0.0279 g/m^3, 1.099 mg/l and 5.4 mg/l, respectively for eutrophication model run in non-conservative mode.

5.3 Case A: Typical wet atmospheric deposition of nitrogen

The estimated typical wet atmospheric flux of nitrite + nitrate nitrogen into coastal water of Singapore was 3.92 g/m^2/yr. The wet atmospheric deposition flux of nitrite + nitrate nitrogen and computational boundary conditions for ocean fluxes of model state variables were used in the model as in Table 5.1. The significance of atmospheric fluxes was investigated by conservative and non-conservative modelling using NEUTRO and is detailed in the following sections.

Table 5.1 Model inputs parameters and their values

Parameters (units)	**Symbol**	**Value**	**Remarks**
Nitrite + nitrate (mg/l)	S_{jWD}	1.835	For Case I to Case III scenarios in Section 5.3.1
	B_j	0.02	
	C_j^0	0	
Annual rainfall (mm)	P_r	2136	
Phytoplankton (mgC/l)	C_j^B	0.02	For full eutrophication model run in Section 5.3.2
Nitrite + nitrate (mg/l)		0.02	
Ammonium (mg/l)		0.0133	
Phosphate (mg/l)		0.0116	
ON (mg/l)		0.0796	
OP (mg/l)		0.0135	
Zooplankton (g/m^3)		0.0279	
CBOD (mg/l)		1.099	
DO (mg/l)		5.4	

5.3.1 Significance of atmospheric deposition: Conservative modelling

For verification of mass conservation of nitrate-nitrogen and to understand the relative importance of atmospheric (vertical) fluxes in the region as compared with lateral (horizontal) fluxes via ocean boundaries, NEUTRO was run initially in a conservative mode (without eutrophication kinetics) (see Section 3.2.9). For this study, the enhanced model for atmospheric nutrient loading was run for three exploratory scenarios (Case I to Case III) in the Singapore Strait considering: (Case I) flux of nutrients from lateral ocean boundaries only; (Case II) atmospheric fluxes only; and (Case III) combination of fluxes from the ocean and atmosphere (as explained in Section 3.2.9). This approach allows a qualitative as well as quantitative understanding of the relative importance of atmospheric nutrient fluxes in the region. The simulations were started with zero initial mass of nutrients in the study domain ($C_j^0 = 0$) and were continued for about 39 semi-diurnal tidal cycles (equivalent to 20 consecutive days). In the Case I, the ocean fluxes of nutrients were assumed to enter in the Singapore Strait only through ocean lateral boundaries and gradually accumulate in the domain until it reached a quasi equilibrium state (Figure 5.5). Due to the tidal-driven back-and-forth water movement, a wave-like behavior is clearly observed in the time series. One could derive a residence time of water in the Singapore Strait to be about 7 days. In the Case II, the mass of admixture was assumed to be entering the water column from atmospheric fluxes only; it was gradually accumulated until a quasi equilibrium state was reached due to lateral exchange through ocean boundaries. The case III combines the two above cases, where total nutrient mass was introduced by both, ocean boundary fluxes and atmospheric fluxes (CaseI and CaseII). Computations show that wet atmospheric fluxes of nitrite + nitrate nitrogen account for 10–15 % of total mass of nitrite + nitrate nitrogen in water column, which is a notable contribution into regional eutrophication.

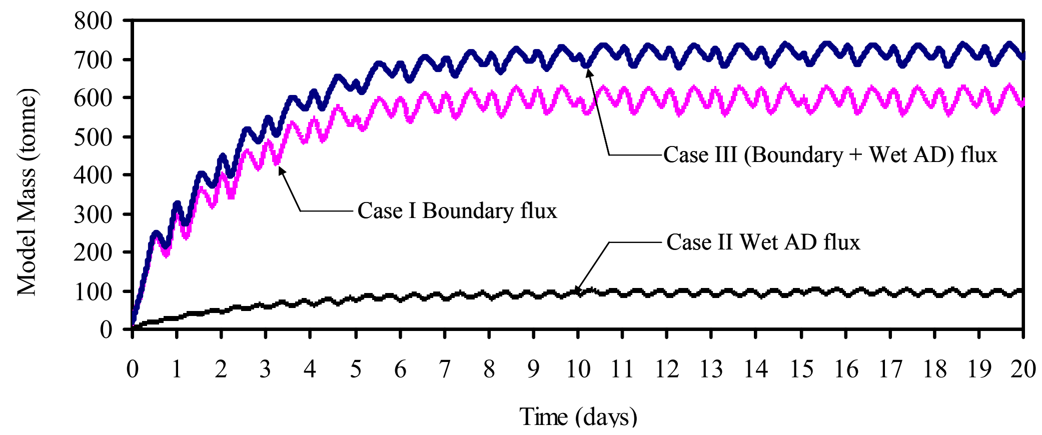

Figure 5.5 Increase of nutrient mass in the Singapore Strait due to atmospheric fluxes. Note: Mass due to the total flux (Case III) = Mass due to boundary fluxes from the ocean (Case I) + Mass due to atmospheric fluxes (Case II).

5.3.2 Significance of atmospheric deposition: Non-conservative modelling

In this section, a complete set of eutrophication kinetics, with realistic initial and boundary conditions is used to investigate spatial and temporal dynamics of nutrients in the Singapore Strait in this study. The atmospheric contribution to the nutrient load was specified as a constant concentration (g/m^3) uniformly distributed over the simulated area. The nutrient flux was computed using nutrient concentration and precipitation as discharge for wet atmospheric deposition. The model simulations were carried out for 20 consecutive days using the wet atmospheric flux and ocean boundary conditions as in Table 5.1. The time series of computed nitrite + nitrate nitrogen and phytoplankton at a location “MS” (Figure 3.2) in the Singapore Strait were analyzed in this study. The computed nitrite + nitrate nitrogen concentration in the water column shows an increase of 0.0033 mg/l (ranging from 0.0002 mg/l to 0.0019 mg/l) from seawater baseline (0.02 mg/l, Table 4.1) due to the atmospheric depositions. The simulations showed that atmospheric fluxes account for 1.1 % to 16 % (mean ~ 9.3 %) of nitrite + nitrate nitrogen concentration (Figure 5.6). The baseline surface water concentration of nitrite + nitrate nitrogen was 0.02 mg/l (Table 4.1 and Table 5.1).

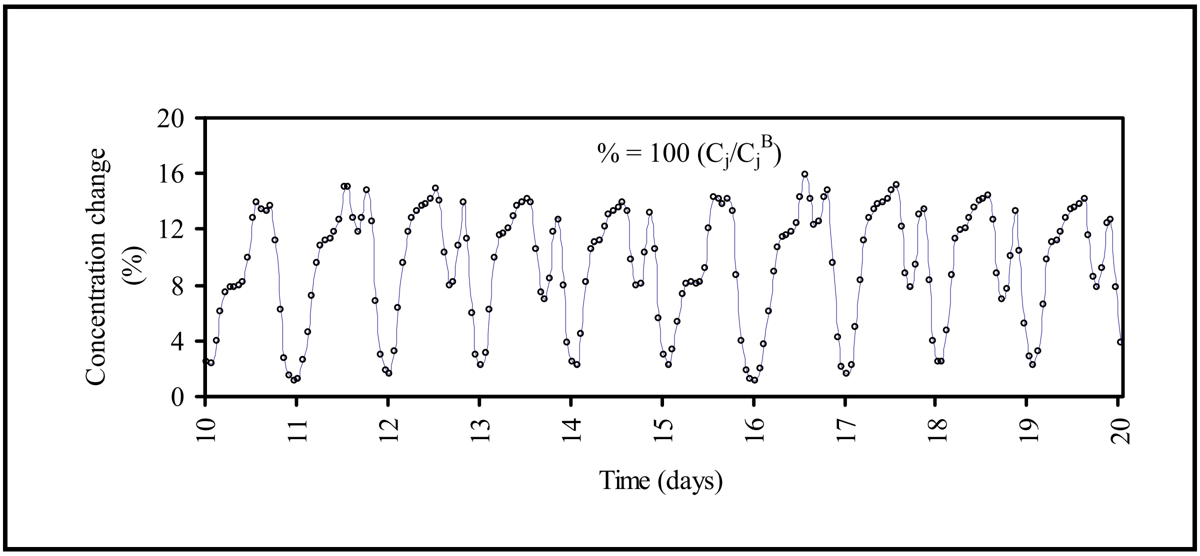

Figure 5.6 Percentage change of nitrite + nitrate nitrogen concentration at surface from seawater baseline (0.02mg/l) due to atmospheric deposition fluxes at a location “MS” in Singapore Strait.

The spatial distribution of surface water nitrite + nitrate nitrogen concentration in the Singapore Strait due to the atmospheric nitrite + nitrate nitrogen depositions is shown in Figure 5.7. The results indicate that the atmospheric fallout provides an additional nutrient flux to the water column, thus promoting the primary production. It was observed that the water surface at a shallow depth tends to have higher concentration of nitrite + nitrate nitrogen due to reduced vertical mixing with deeper layers of the water column. The computed concentration of nitrite + nitrate nitrogen in the main Singapore Strait having large depth is lower due to more efficient dispersion by tidal currents (Figure 5.7).

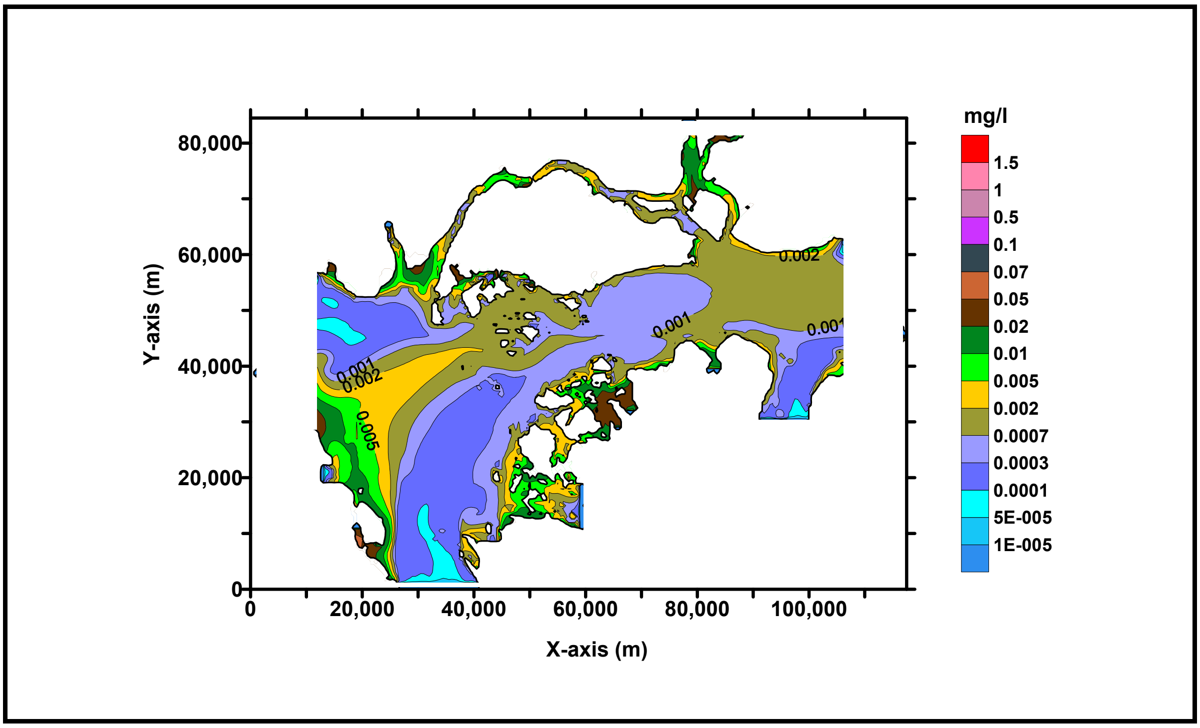

Figure 5.7 The absolute difference in spatial surface concentration distribution of nitrite + nitrate nitrogen from their baseline concentration (0.02 mg/l) due to atmospheric nitrite + nitrate nitrogen deposition.

Based on the modelling study, it was observed that atmospheric nutrient inputs into a coastal system are naturally subjected to physical and biogeochemical processes that affect the concentration of the nutrients in the water column. Atmospheric inputs contribute to the total nitrogen load in surface water and it may intensify eutrophication problems. The atmosphere provides a flux of nitrogen to the water column which is rapidly converted to organic nitrogen and joins the recycled nitrogen pool.

The spatial distribution of surface water phytoplankton concentration from their baseline due to atmospheric nitrite + nitrate nitrogen deposition is shown in Figure 5.7. The results indicate that nitrite + nitrate nitrogen from atmospheric fallouts provides an additional nutrient flux to the water column, thus promoting the primary production. The computed percentage increase of phytoplankton growth from its baseline concentration (0.02 mgC/l, see Table 4.1) was from 0.01 % to 0.22 % (mean ~ 0.12 %).

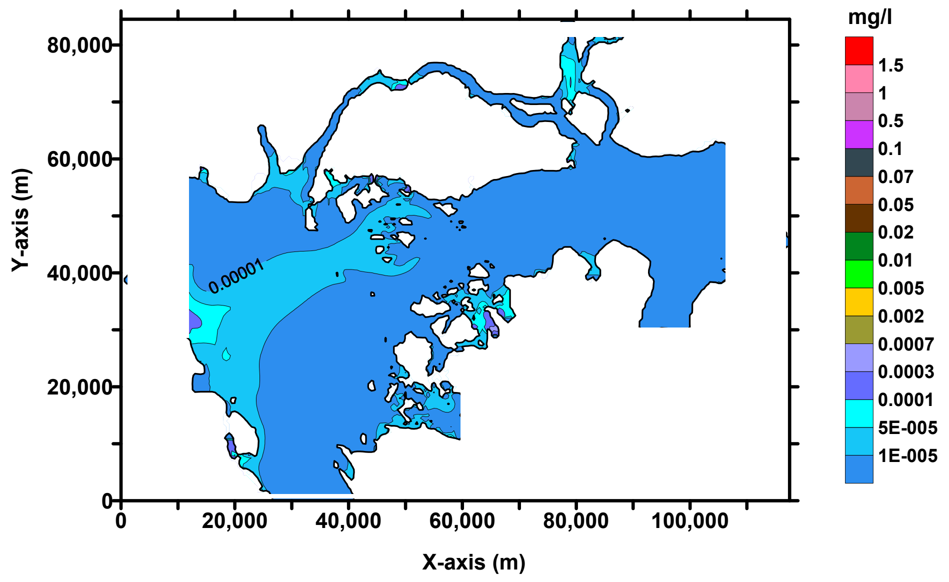

Figure 5.8 The absolute difference in spatial surface concentration distribution of phytoplankton from their baseline concentration (0.02 mgC/l) due to atmospheric nitrite + nitrate nitrogen deposition.

The absolute difference (increase) of surface water phosphate and organic phosphorous concentration from baseline due to the atmospheric wet deposition respectively is shown in Figure 5.9 and Figure 5.10. The computed concentration of P species was increased considerably from baseline value at the location “MS” (see Figure 3.2) in Singapore Strait. The percentage increase of phosphate at surface was ranging from 0.02 to 0.32 % (mean ± SD ~ 0.18 ± 0.08 %) of its baseline concentration of 0.0116 mg/l.

As can be seen from the modelling study, the effects of atmospheric deposition at various time- and spatial scales are to be studied. Firstly, there is a direct effect of atmospheric deposition where short-lived intensive fallouts appear to increase primary productivity. Secondly, atmospheric deposition enhance the overall nitrogen stock in the water column, potentially fuelling primary production on the longer term; thus contributing towards eutrophication problems in coastal regions.

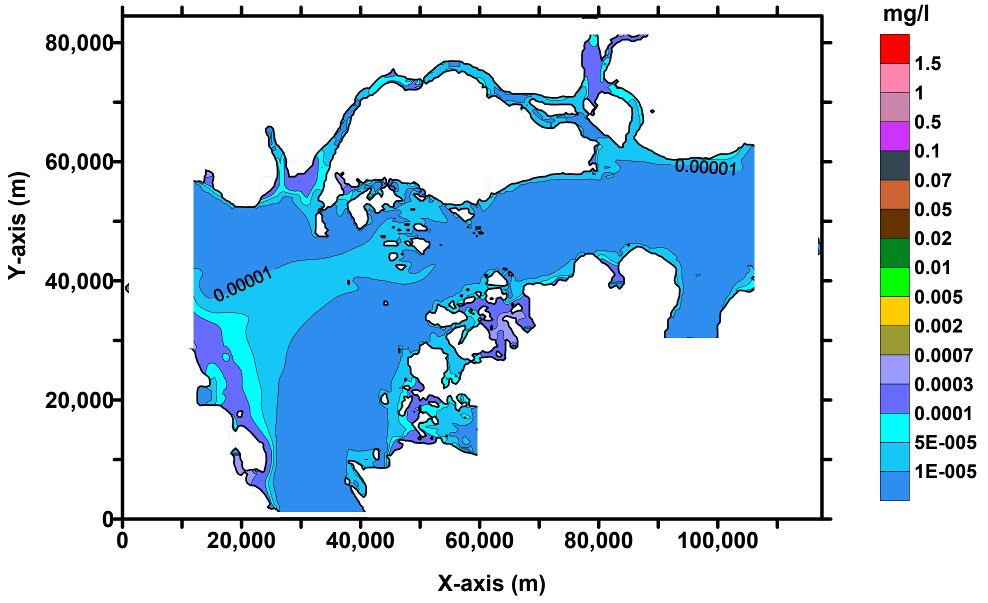

Figure 5.9 The absolute change of surface water phosphate and concentration from baseline due to the atmospheric wet deposition.

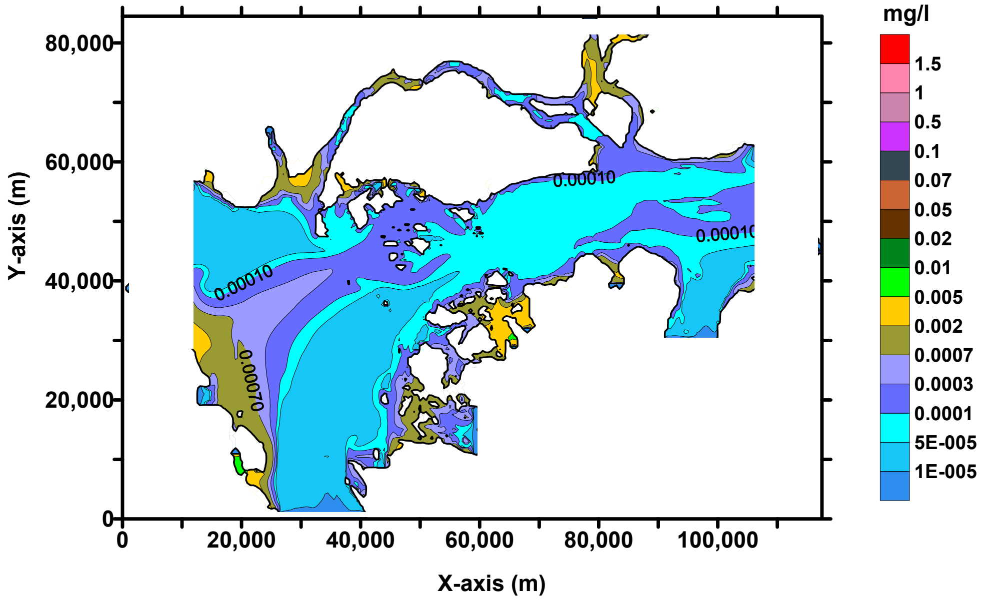

Figure 5.10 The absolute change of surface water organic phosphorous concentration from baseline (0.0135 mg/l) due to the atmospheric wet deposition.

5.4 Case B: Haze atmospheric deposition of nitrogen

5.4.1 Significance of atmospheric deposition: Conservative modelling

From the field measurement of nutrient concentrations from AD, it is evident that there is higher nutrient input into surface water during haze period as compared to clear non-haze period. The concentration of nitrite + nitrate nitrogen at ocean boundaries (B_j), atmospheric WD (S_{jWD}) for haze period and non-haze period, and the initial concentration in water column (C_j^0) were taken as 0.02 mg/l, 8.64 mg/l, 1.835 mg/l and 0 mg/l, respectively; and the annual average rainfall in the model region was taken as 2136 mm. The wet atmospheric flux (S_{jWD} X 2136) and ocean boundary conditions (C_j^B) used in the model as are given in Table 5.2. Here, the ocean boundary conditions for model state variables, including N and P species (Table 4.4), phytoplankton (0.02 mg/l), zooplankton (0.0279 mg/l) and dissolved oxygen (DO, 5.4 mg/l) were assigned using baseline concentrations.

Table 5.2 Model inputs parameters and their values

Parameters (units)	**Symbol**	**Value**	**Remarks**
Nitrite + nitrate (mg/l)	S_{jWD}	1.835	For non-haze period
		8.64	For haze period
	B_j	0.02	For Case I to Case III scenarios
	C_j^0	0	
Annual rainfall (mm)	P_r	2136	
Phytoplankton (mgC/l)	C_j^B	0.02	For full eutrophication model run
Nitrite + nitrate (mg/l)		0.02	
Ammonium (mg/l)		0.0133	
Phosphate (mg/l)		0.0116	
ON (mg/l)		0.0796	
OP (mg/l)		0.0135	
Zooplankton (g/m^3)		0.0279	
CBOD (mg/l)		1.099	
DO (mg/l)		5.4	

For verification of mass conservation of nitrate-nitrogen and to understand relative importance of atmospheric (vertical) fluxes during haze and non-haze period in the region as compared with lateral (horizontal) fluxes via ocean boundaries, NEUTRO was run initially in a conservative mode (without eutrophication kinetics) (see Section 3.2.9). For this study, the enhanced model for atmospheric nutrient loading during haze and non-haze period was run for three exploratory scenarios (Case I to Case III) in the Singapore Strait as explained in Section 3.2.9. The model mass (g) against simulation time (days) for Cases I - III for non-haze and haze period is shown in Figure 5.11. As there was an exchange of flux at open boundary, the model mass gradually accumulated into the computational domain until it reached the quasi-steady state condition. Total percentage of flux (%) from Case III is given by sum of boundary flux (%) from Case I and AD flux (%) from Case II. The percentage of mass increase due to AD N flux was calculated. For verification of mass conservation obtained through model during non-haze and haze period, the estimated wet atmospheric flux of nitrite + nitrate nitrogen of 3.92 g/m^2/yr and 18.5 g/m^2/yr into coastal waters are applied as AD N loading. The concentration of nitrite + nitrate nitrogen at open boundary (B_j), atmospheric wet deposition (S_{WD}) and initial concentration in water column (C_j^0) are shown in Table 5.2.

For verification of mass conservation and understanding of relative contribution of atmospheric fluxes, NEUTRO model was run in a conservative mode (without eutrophication kinetics). The simulations were carried out for 39 semi-diurnal tidal cycles (equivalent to 20 consecutive days). For Case I, if computations began with a zero initial mass of nutrients in the study domain, the ocean fluxes of nutrients were entering through “open” boundaries to gradually accumulate in the water column until a quasi equilibrium state was reached (Figure 5.11). In the Case II, the mass of admixture entering the water column from atmospheric fluxes gradually accumulated until a quasi equilibrium state was reached due to lateral exchange through ocean boundaries. Case III combines Cases I and II, with total admixture mass defined by the sum of ocean boundary fluxes and atmospheric fluxes.

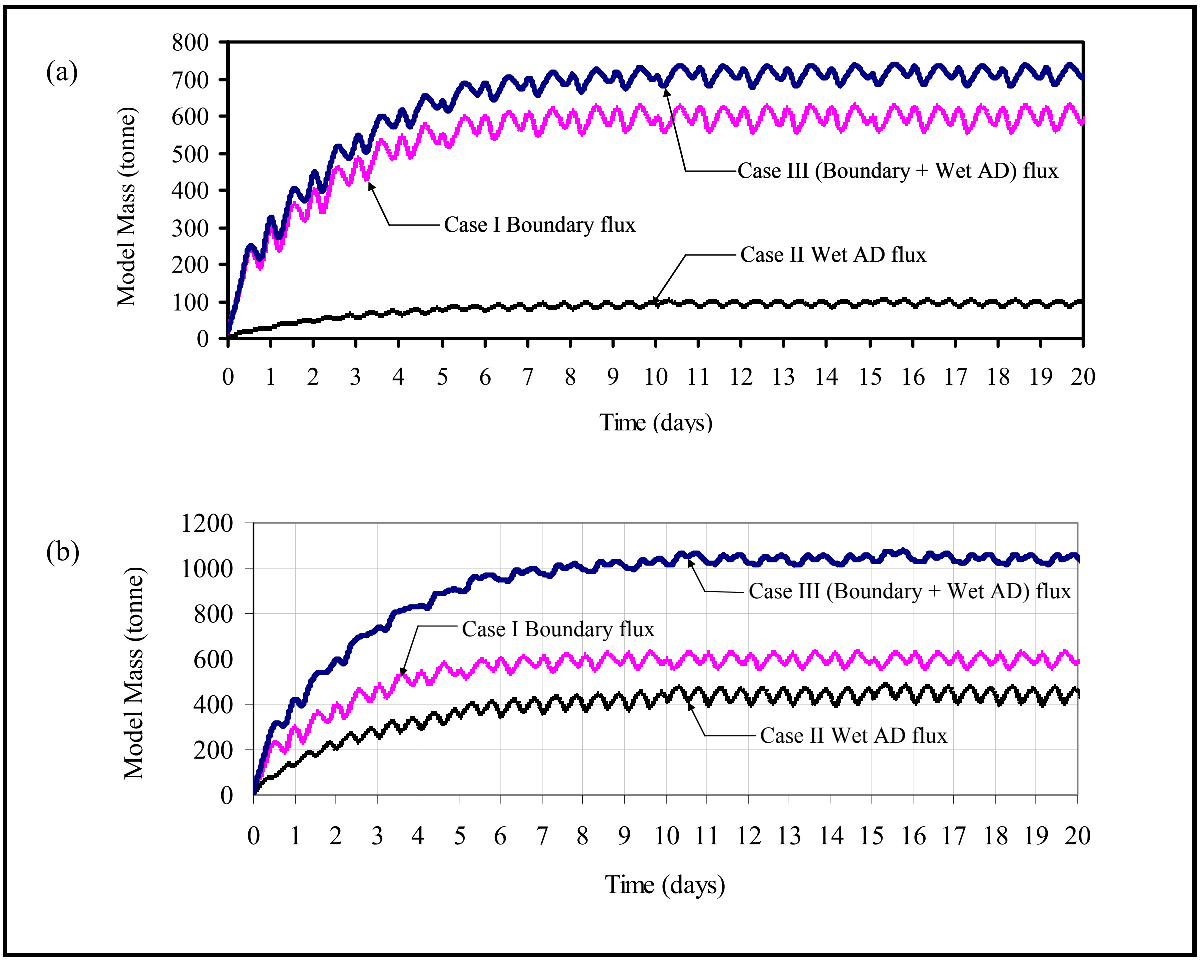

Figure 5.11 Increase of nutrient mass in the Singapore Strait due to atmospheric fluxes during (a) non-haze period and (b) haze period. Note: Mass due to the total flux (Case III) = Mass due to boundary fluxes from the ocean (Case I) + Mass due to atmospheric fluxes (Case II); The model mass (g) against simulation time (days).

The percentage of increase in mass due to AD N flux was calculated. Computations show that wet atmospheric fluxes of nitrite + nitrate nitrogen during non-haze period might account for 4 to 24 % (Figure 5.11a) of total mass of nitrite + nitrate nitrogen in water column. During haze period, it was observed that wet atmospheric fluxes of nitrite + nitrate nitrogen contributes about 17 to 88 % (mean ~ 72 %) of total nitrite + nitrate nitrogen mass into the water column (Figure 5.11b), which is a notable contribution into regional eutrophication. The percentage increase of nitrite + nitrate nitrogen concentration was 2 to 30 % (mean ~ 15 %) during non-haze period and 5 to 111 % (mean ~ 70 %) during haze period.

5.4.2 Significance of atmospheric deposition: Non-conservative modelling

The spatial and temporal dynamics of nutrients in the Singapore Strait was investigated. The results were obtained from model simulations using a complete set of eutrophication kinetics, with realistic initial and boundary conditions (as in Section 5.4.1). Computations showed that atmospheric fluxes might account for an increase of nitrite + nitrate nitrogen concentration in water column in the range of 1–16 % (mean ~ 9.3 %) and 5–76 % (mean ~ 45 %) during non-haze and haze periods respectively. The spatial distributions of surface water concentration of nitrite + nitrate, ammonium and organic nitrogen from their baseline due to atmospheric nitrite + nitrate nitrogen deposition during haze and non-haze period are shown in Figure 5.12 (a)–(b), Figure 5.13 (a)–(b) and Figure 5.14 (a)–(b), respectively. The baseline concentrations of nitrite + nitrate, ammonium and organic nitrogen were taken as 0.02 mg/l, 0.0113 mg/l and 0.0796 mg/l respectively. It was observed that the water surface at a shallow depth has a higher concentration of nitrite + nitrate nitrogen due to accumulation and reduced tidal mixing along the coastal areas in comparison to baseline data. It was also observed that the water surface at a deeper layer of water column, and far away from the coastal areas likely to have a lower concentration. This is due to dilution within the main stream by high tidal action in the Singapore Strait.

The absolute difference (increase) of surface water phosphate and organic phosphorous concentration from baseline due to the atmospheric wet deposition during haze and non-haze period respectively is shown in Figure 5.15 (a)–(b) and Figure 5.16 (a)–(b). With the estimated wet AD nitrite + nitrate nitrogen load, the computed concentrations of N and P species changed considerably from baseline value at a selected location in Singapore Strait (Table 5.3).

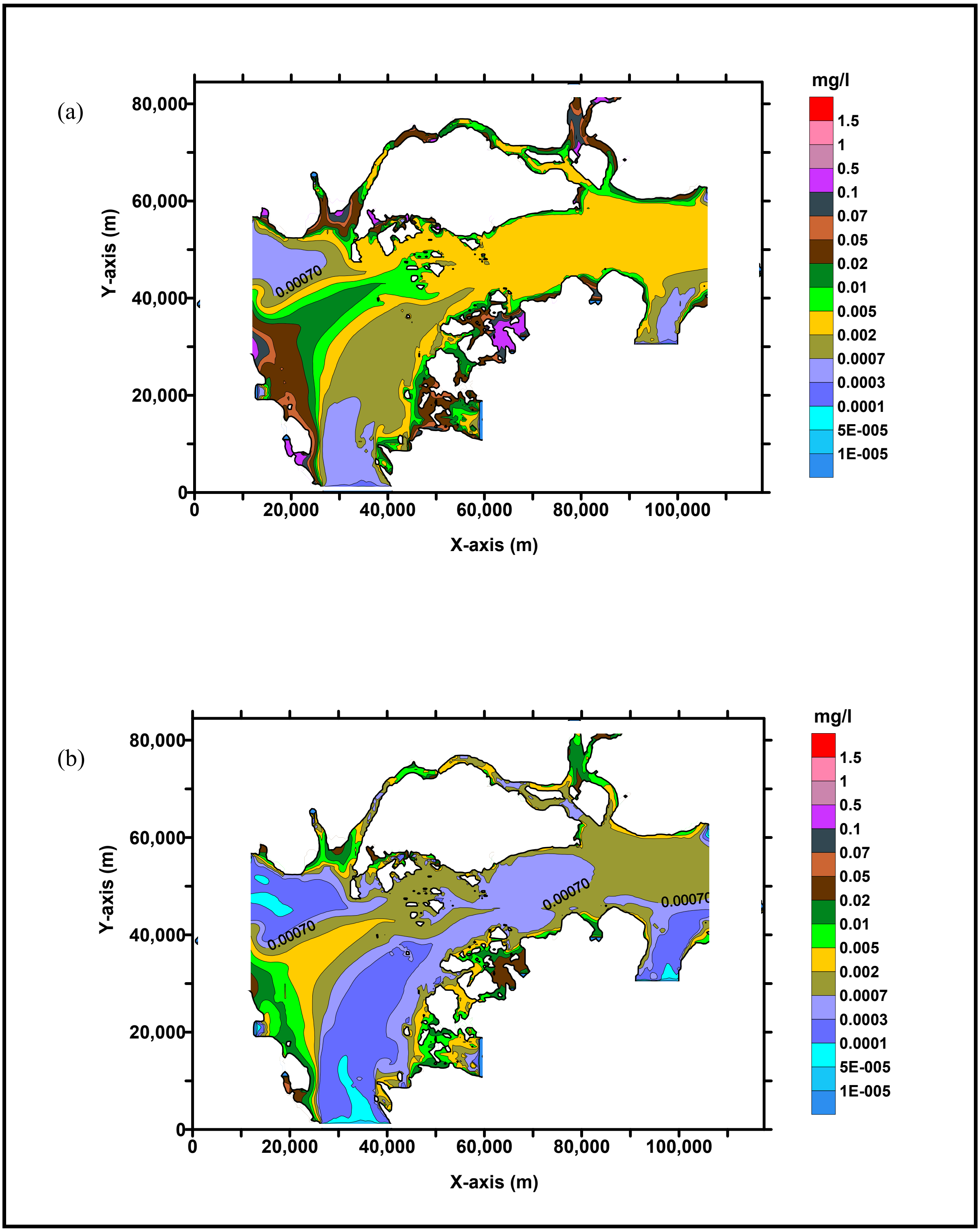

Figure 5.12 The absolute change of surface water nitrite + nitrate concentration from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

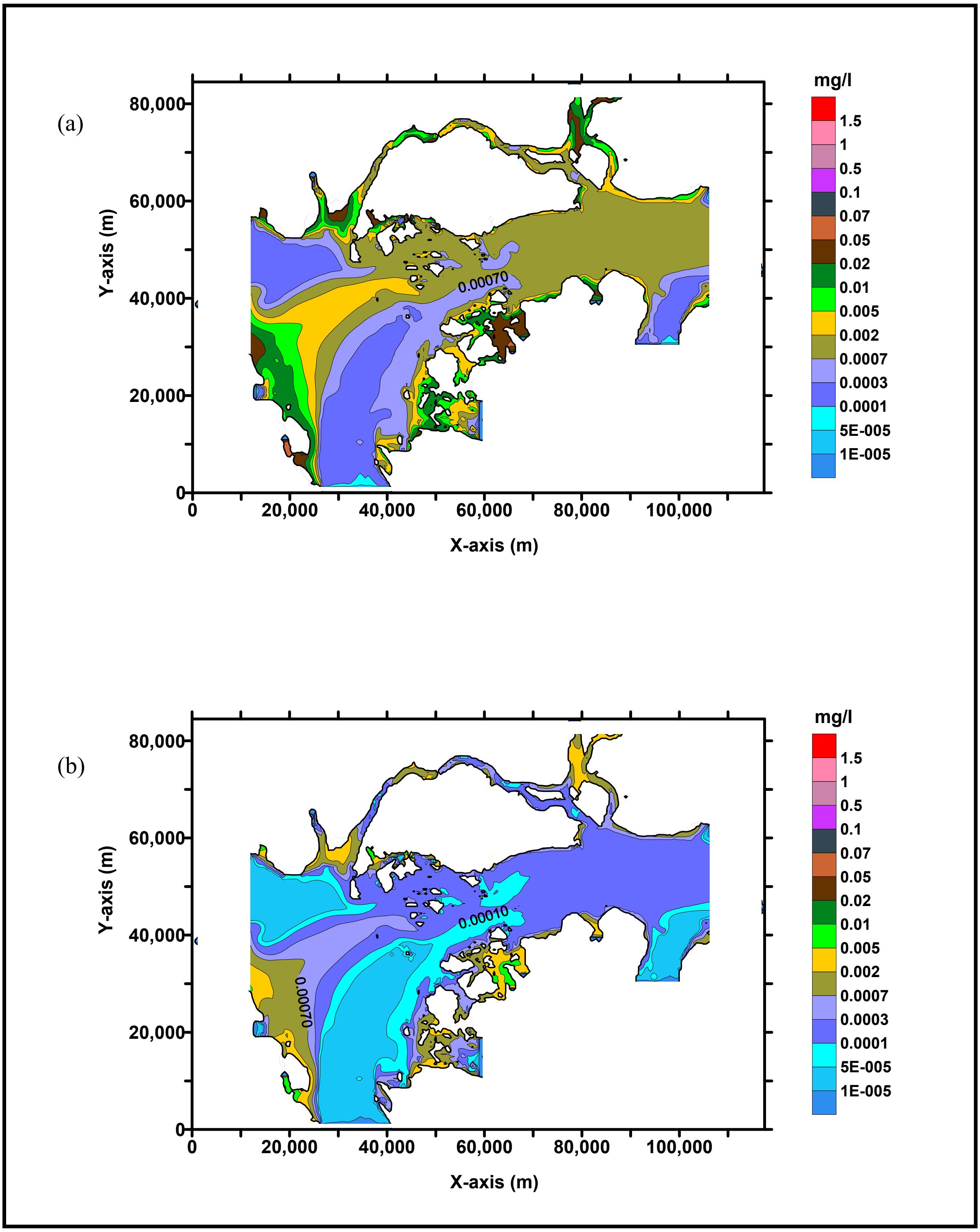

Figure 5.13 The absolute change of surface water ammonium concentration from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

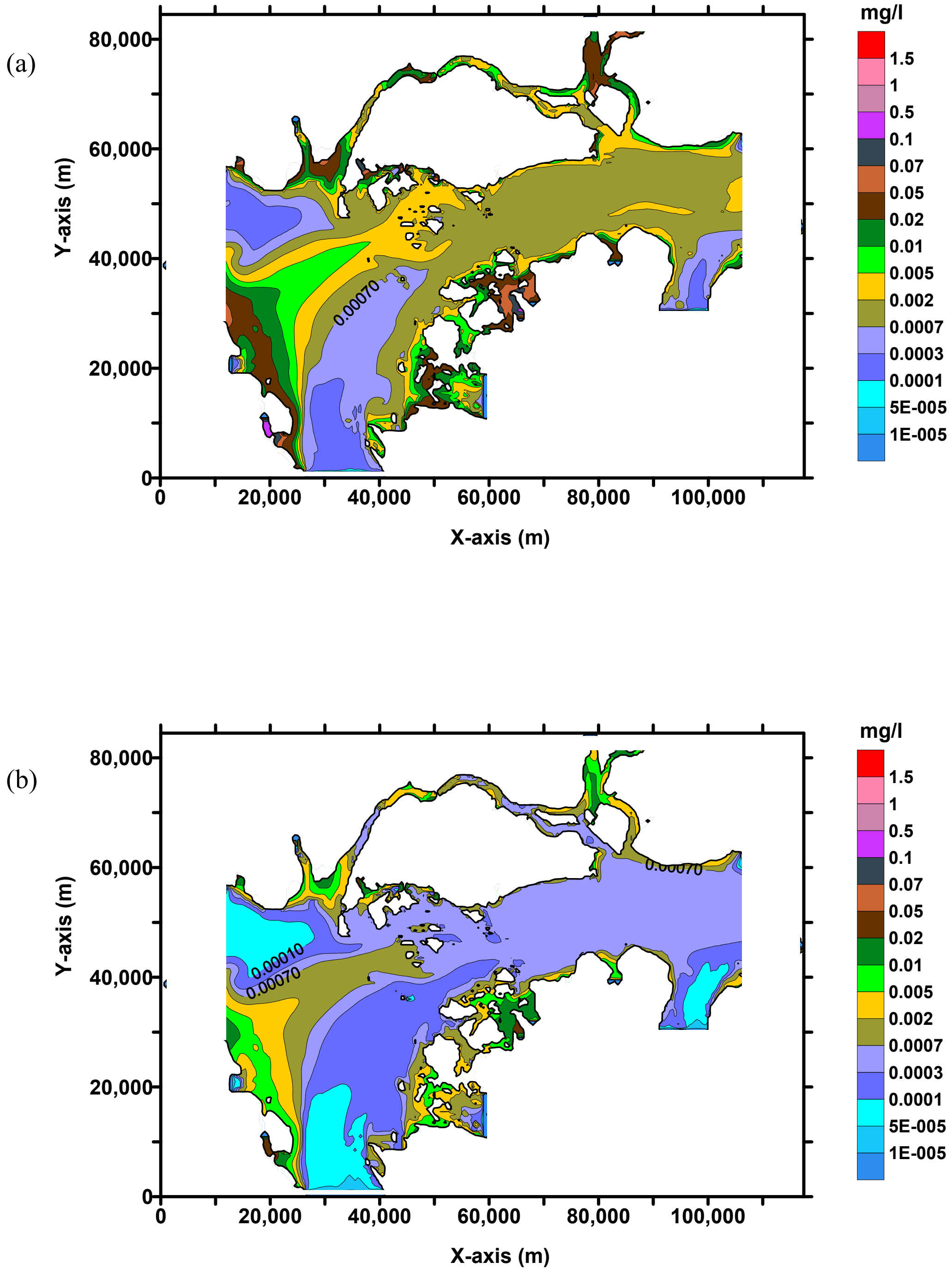

Figure 5.14 The absolute change of surface water organic nitrogen concentration from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

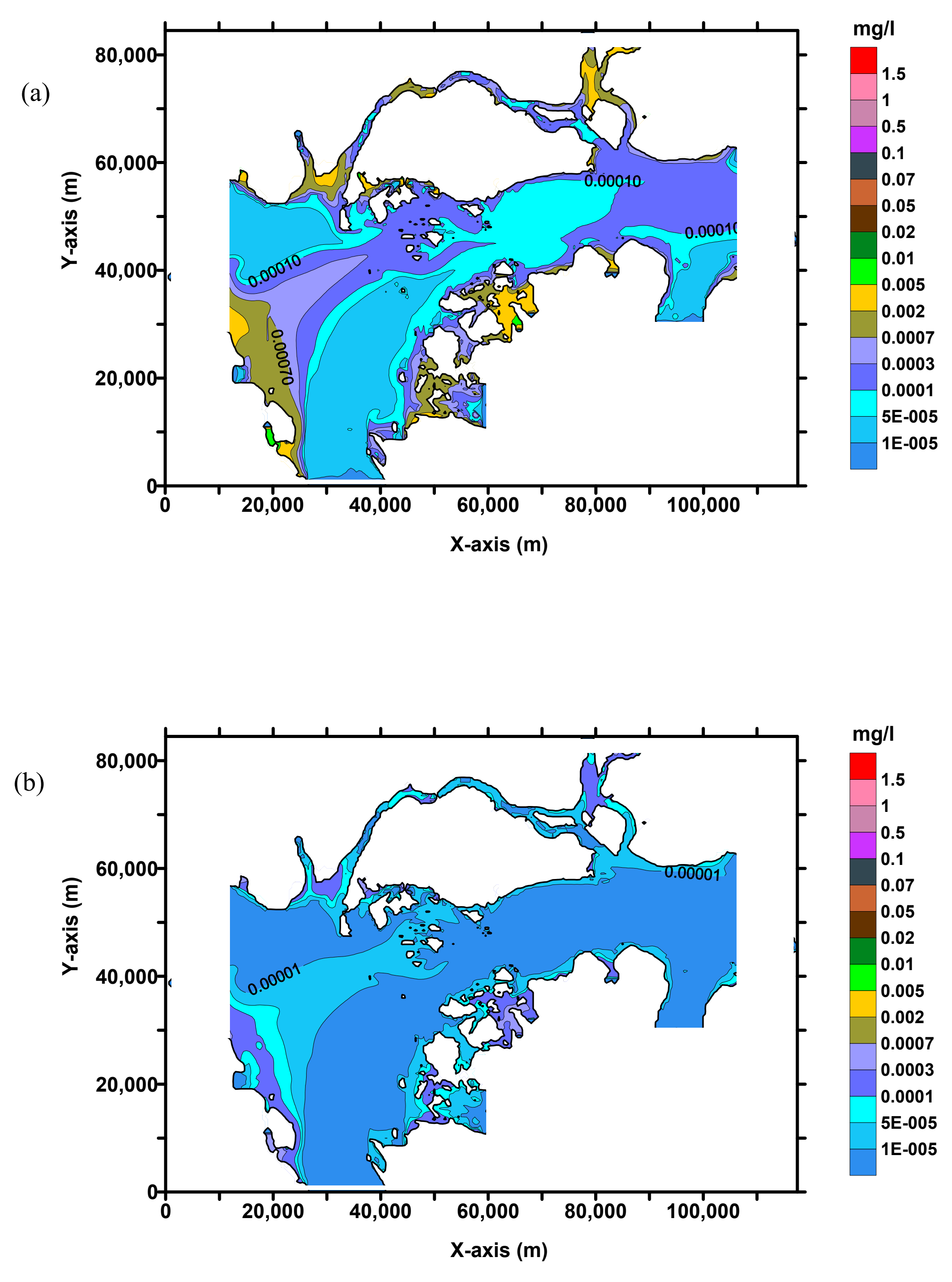

Figure 5.15 The absolute change of surface water phosphate and concentration from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

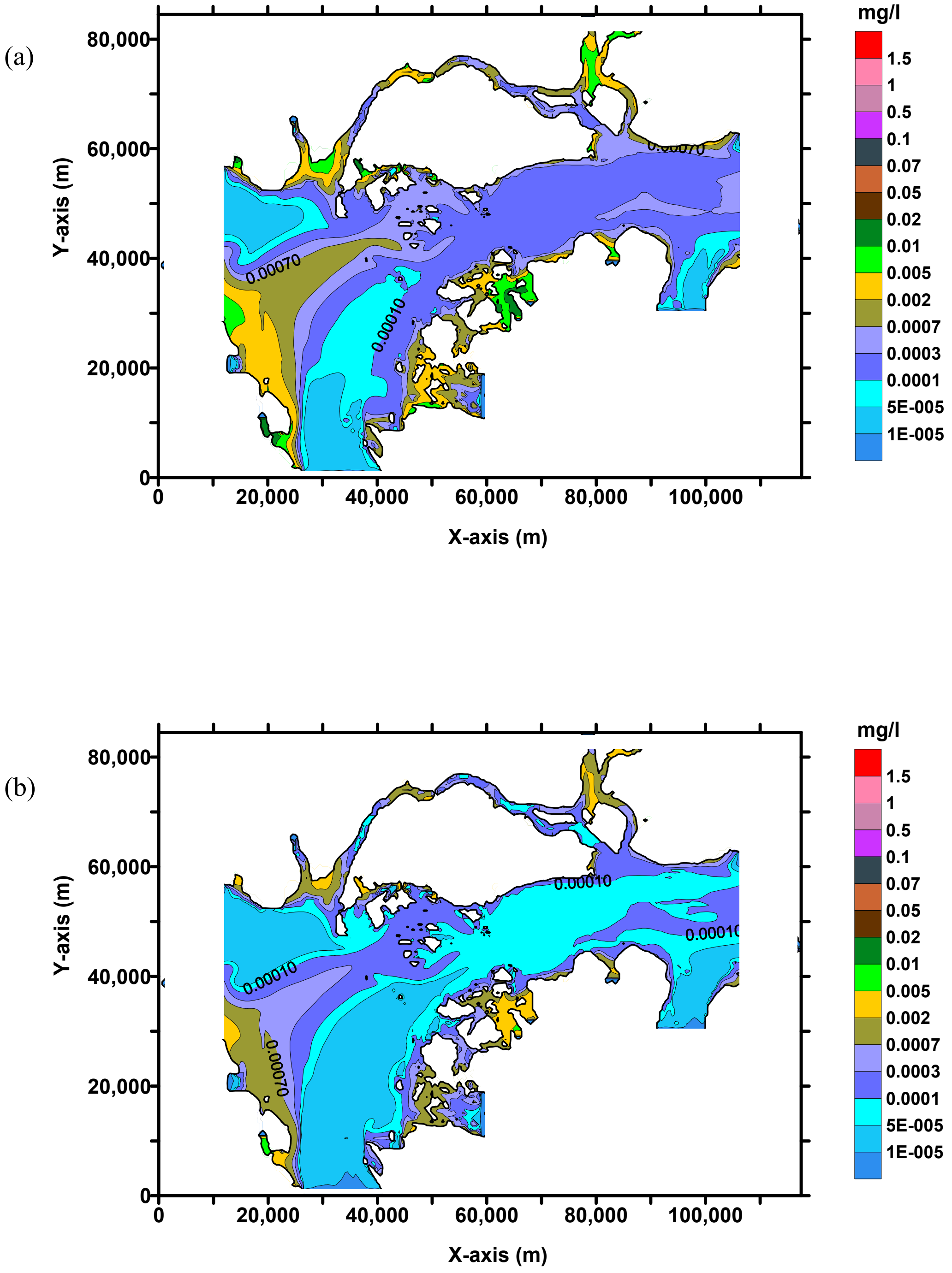

Figure 5.16 The absolute change of surface water organic phosphorous concentration from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

Table 5.3 The absolute difference of surface water concentration of N and P species from baseline due to atmospheric deposition fluxes during non-haze and haze period

Non-haze period

Parameters	**WQ change from model baseline due to mean wet AD**				**% Water Quality Change**			
Nutrients	**Mean**	**Min**	**Max**	**SD**	**Mean**	**Min**	**Max**	**SD**
NH_4	3.44E-04	3.73E-05	5.86E-04	1.55E-04	2.44	0.27	4.13	1.09
NO_3+NO_2	0.002	0.0002	0.0033	0.0009	9.37	1.09	15.9	4.17
ON	0.001	0.0001	0.0019	0.0005	1.43	0.17	2.43	0.64
PO_4	2.14E-05	2.44E-06	3.66E-05	9.71E-06	0.18	0.02	0.32	0.08
OP	0.0002	0.00003	0.0004	0.0001	1.80	0.21	3.06	0.81
Haze period								
NH_4	2.37E-03	2.73E-04	4.01E-03	1.05E-03	16.8	1.97	28.3	7.403
NO_3+NO_2	0.009	0.001	0.0155	0.004	44.7	5.17	75.9	19.9
ON	0.005	0.0005	0.0077	0.002	5.82	0.68	9.90	2.59
PO_4	2.65E-04	3.03E-05	4.52E-04	1.20E-04	2.28	0.26	3.90	1.033
OP	0.0007	0.00009	0.0012	0.00032	5.25	0.63	8.94	2.36

The model computed absolute difference in spatial surface concentration distribution of phytoplankton (Figure 5.17 and Table 5.4) indicated that the nitrite + nitrate species provide the necessary nutrient for low nutrient zone, but the biological response time is slow, as nitrogen is not a limiting nutrient for high nutrient zone. Only external (to the ocean) sources of N that reach the surface mixed layer can affect the steady-state balance of the biologically mediated flux of CO_2 across the air-sea interface. The open ocean sources of external N such as biological N_2 fixation and atmospheric deposition which together contribute a net oceanic input of N. These two sources support 'completely new production' and hence influence the global oceanic N, assuming an adequate supply of other nutrients (P, Fe) (Duce et al., 2008). It will impact the biogeochemistry of oceanic areas that are either perennially or seasonally depleted in surface nitrate, but will have little effect in high-nutrient, low-chlorophyll-a regions where the concentration of surface nitrate is always high.

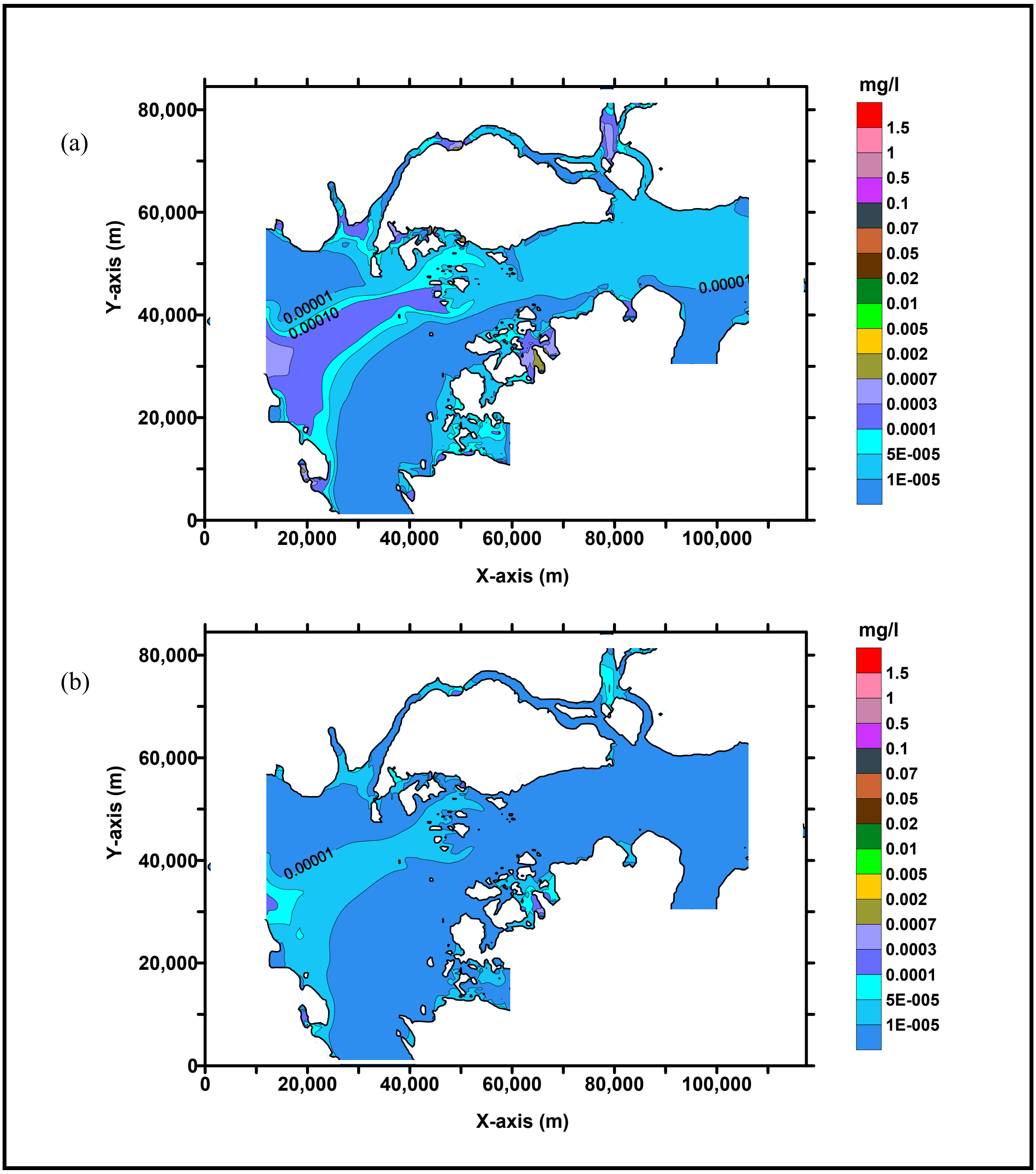

Figure 5.17 The absolute difference in spatial surface concentration distribution of phytoplankton from baseline due to the atmospheric wet deposition during (a) haze and (b) non-haze period.

Based on modelling study, we conclude that while individual AD events probably are not responsible for triggering algal blooms as hypothesized, but long-term nutrient additions are important and do contribute to eutrophication problems in coastal water. The study on impact of biomass burning during 2006 on surface water quality in

Southeast Asia through atmospheric deposition by eutrophication modelling will be published elsewhere (Sundarambal et al., 2010c).

Table 5.4 The percentage increase of surface water concentration of phytoplankton, zooplankton and dissolved oxygen (DO) from baseline due to atmospheric deposition fluxes during non-haze and haze period

Parameters	**Mean**	**Min**	**Max**	**SD**
Non-haze period				
Phytoplankton	0.12	0.01	0.22	0.06
Zooplankton	8.03E-04	3.68E-05	1.43E-03	4.16E-04
DO	-0.00012	-0.0004	0.00023	0.00012
Haze period				
Phytoplankton	0.63	0.03	1.11	0.31
Zooplankton	4.12E-03	1.47E-04	7.23E-03	2.13E-03
DO	-0.00118	-0.0038	0.00256	0.00115

5.5 Case C: Episodic nitrogen deposition event

Simulations were also carried out to explore the response of nitrite + nitrate nitrogen concentration relative to seawater baseline due to an episodic atmospheric deposition event (Sundarambal et al., 2010a). This atmospheric deposition remains confined to the upper layer of the water column, enabling intense surface phytoplankton blooms to occur (Michaels et al., 1993). AD loadings were applied to the model domain uniformly with in an upper layer of 1 m depth of water. The episodic wet deposition event with nitrite + nitrate nitrogen (S_{jWD}) concentration of 34.6 mg/l during October 2006 haze was used instead of the 1.835 mg/l as used in Case I and II. Figure 5.18 shows the absolute difference (increase) of surface water (a) nitrite + nitrate nitrogen and (b) phytoplankton concentration of surface water from baseline (0.02 mg/l) due to the episodic wet AD event. The percentage increase in computed phytoplankton concentration from its baseline was ranging from ~ 0.13 to 4.65 and its average percentage change was 2.62 ± 1.31 due to the episodic nitrite + nitrate nitrogen deposition event. This study confirmed the importance of high concentration episodic inputs of nitrite + nitrate nitrogen associated with transport of polluted air onto the surface water. In summary, it is concluded that the areas where deposition increase with haze event and future industrial development, episodic deposition events will have short-term impacts on the local nitrogen cycle.

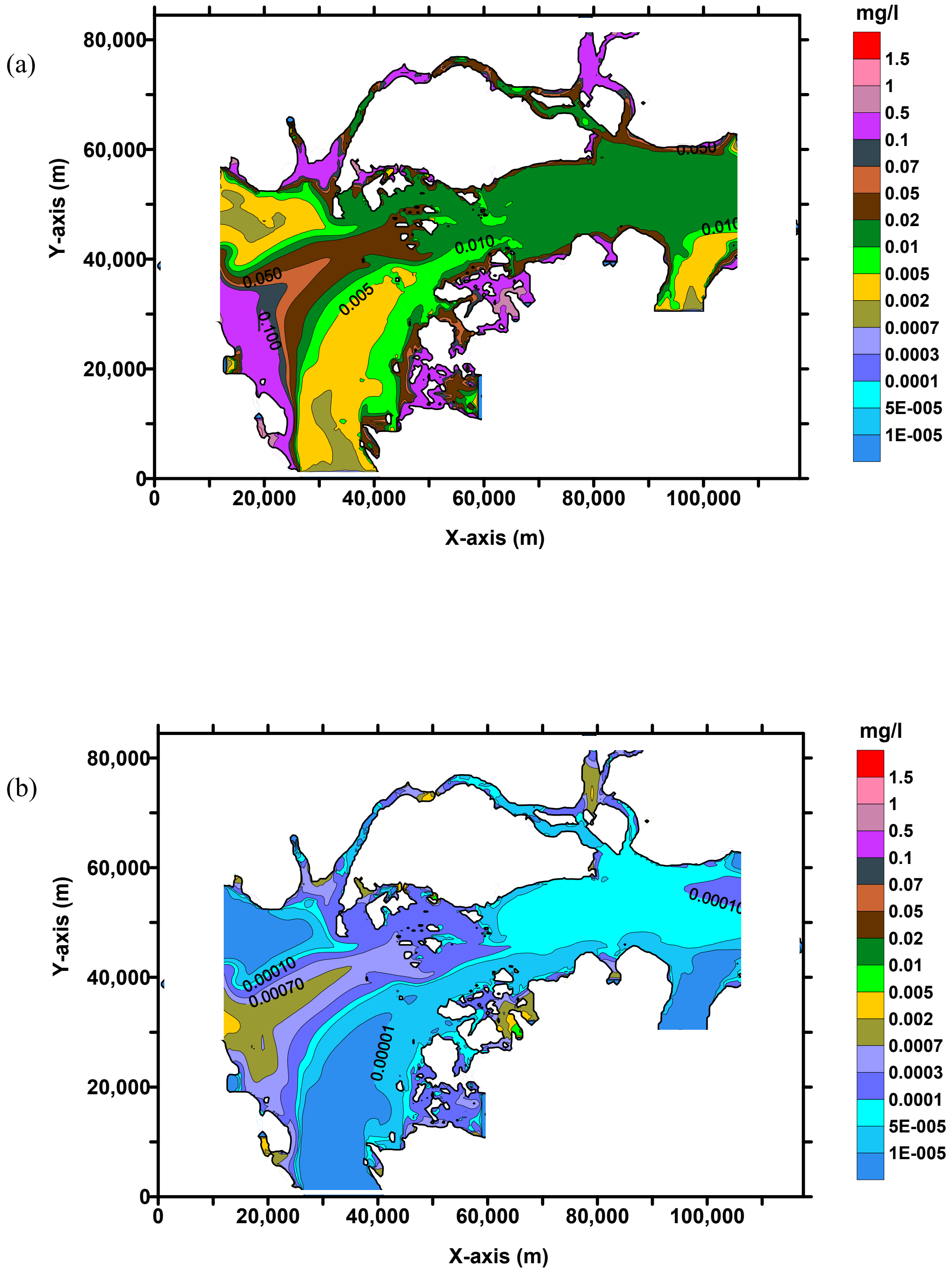

Figure 5.18 The absolute difference in spatial surface concentration distribution of (a) nitrite + nitrate nitrogen and (b) phytoplankton from their baseline concentration (0.02 mg/l and 0.02 mgC/l respectively) due to an episodic AD event.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and Conclusions

Atmospheric deposition (AD) is a significant source of N and P species to aquatic ecosystems in tropical regions. Atmospheric nutrients and other pollutants can be transported by prevailing winds and get deposited in other regions of the world, exposing aquatic ecosystems to chemicals not used in those regions. AD can accelerate eutrophication and its associated environmental consequences in freshwater, estuarine and coastal ecosystems. The effect of these atmospheric nutrients on marine productivity depends on the biological availability of both inorganic and organic fractions of water soluble N and P forms. Biomass burning is an important source of macro and micro nutrients, especially in Southeast Asia (SEA), where the smoke haze phenomenon is a major and recurring air pollution problem. In this research study, the effects of dry and wet atmospheric deposition and impacts of atmospheric nutrients during haze and non haze period were investigated using experimental and modeling studies in the coastal region of Singapore Strait.

As a part of experimental studies, the samples of aerosol particles for dry atmospheric deposition and rainwater for wet atmospheric deposition were collected periodically in Singapore to monitor and assess the effects of N and P species derived from atmospheric deposition onto the coastal system. Air and water samples were collected and analyzed during both clear and hazy days. In the course of the study, a long-term monitoring station has been established for AD studies to determine nutrients concentration and fluxes in both aerosols and precipitation. The identified nutrients in both airborne particulate matter and precipitation were nitrogen species including nitrite, nitrate, ammonium, total nitrogen, organic nitrogen and phosphorus species (phosphate, total phosphorus and organic phosphorus) in Singapore and surrounding areas. They were analyzed using reliable and validated analytical methods in the laboratory. These experimental studies represent one of the first studies that provide the analytical methods for quantifying nutrient composition in aerosol particles during dry and wet atmospheric deposition in the tropical region of Southeast Asia. The atmospheric deposition fluxes of inorganic and organic nitrogen (N) inorganic and organic phosphorous (P) resulting from dry deposition and wet deposition onto water surface in Singapore Strait were calculated.

The total (dry + wet) average concentrations of inorganic and organic N species were 2.13 mg/l and 1.22 mg/l, and those of P species were 0.03 mg/l and 0.23 mg/l respectively. Using these concentration values, DAD and WAD fluxes of N and P onto coastal water were estimated to be 1.01 and 7.05 ($g/m^2/yr$) of TN and 0.19 and 0.53 ($g/m^2/yr$) of TP, respectively. From the results obtained, it was observed that atmospheric deposition is fairly evenly distributed between nitrate + nitrite N, ammonium, and organic N (50 %, 14 % and 36 %, respectively) for dry deposition and (55 %, 9 % and 36 % respectively) for wet deposition in the Singapore Strait. It can therefore be concluded that deposition was mainly contributed by nitrite + nitrate, followed by ON and then ammonium ion. The percentage contributions of phosphate and OP to TP were 12 and 88 for wet deposition and 53 and 47, for dry deposition, respectively in the Singapore Strait. It was also observed that OP was found in wet deposition in higher concentration due to its dissolution in rainwater during haze period and the concentration of phosphate was higher in dry deposition compared to wet deposition during non-haze period. During hazy and non-hazy days, the order of occurrences of N and P species was NH_4>NO_3+NO_2>TN>ON and OP>TP>PO_4^{3-}, respectively. It was also noticed that the average concentration of nutrients increased approximately by a factor of 3 to 8 on hazy days when compared with non-hazy days. The high ratio of nutrients between hazy and non-hazy day shows that smoke haze episodes provided a significant source of nutrients to the coastal water in Singapore and SEA. The quantified nutrient fluxes from atmospheric deposition provide a baseline to study the possible ecosystem responses to atmospheric nutrient inputs into the water surface.

To test hypothesized effects of atmospheric inputs in these systems and to enhance our understanding of the interactions of physical, chemical, and biological processes controlling surface water ecosystems, modeling studies were carried out. The capability of NEUTRO was enhanced to incorporate the atmospheric input of macronutrients. An enhanced numerical 3D water quality model NEUTRO was applied to describe the dynamics of nutrients and plankton in coastal water in response to nutrients loads including atmospheric deposition from spatially distributed sources. Scenario runs with conservative mode (without eutrophication kinetics) and the sensitivity analysis were applied to understand the relative importance of atmospheric fluxes in the Singapore Strait in comparison with ocean fluxes via lateral boundaries. Model simulations showed that atmospheric deposition fluxes alone contributes nitrite + nitrate nitrogen mass up to 15 % onto the Singapore Strait. This estimated amount is one of the significant contributors toward regional eutrophication when the system is under nutrient-depleted conditions. Scenario runs with non-conservative mode (with complete set of eutrophication kinetics) were then used to observe the temporal and spatial distributions of nutrients and eutrophication rates in the Singapore Strait due to atmospheric wet deposition and ocean fluxes through lateral boundaries. Model calibrations for temporal and spatial variability of nutrients agreed with the obtained field data (both qualitatively and quantitatively). The spatial distribution of nutrients on surface water after deposition and their impacts on water quality in the water column were quantified. Also based on the observed values of surface inorganic nitrogen and phytoplankton concentrations relative to baseline (~ 10 % and ~ 1.5 %), it was perceived that "new" (nitrite + nitrate) N from atmospheric deposition has been added onto the surface water. This additional source of N accelerates the process of eutrophication in the coastal water.

The impacts of biomass burning on the surface water nutrients concentration in Singapore Strait were also estimated using NEUTRO in this research study. Model computations showed that atmospheric fluxes account for 17–88 % of total mass of nitrite + nitrate nitrogen in water column during haze period and 4 to 24 % during non-haze period. This increase in mass of nitrite + nitrate nitrogen might be a relatively significant contributor of regional eutrophication.

The model was also used to assess the importance of high concentration episodic inputs of nitrite + nitrate nitrogen associated with trans-boundary transport of polluted air onto the surface water. When the wet deposition of 34.6 mg/l of nitrite + nitrate nitrogen concentration occurred during October/November 2006 (episodic event) onto water surface, the model results showed that there was an increase in nitrite + nitrate concentration up to a maximum of 1 mg/l from its baseline concentration (0.02 mg/l). This event also resulted in an increase of computed phytoplankton concentration from its baseline ranging from ~ 0.13 to 4.65 % (mean ± SD = 2.62 ± 1.31 %). The occurrence of increased atmospheric deposition of nutrients during haze episodes was found to have negative consequences on receiving aquatic ecosystems with cascading impacts on water quality and trophic and biochemical alterations.

From this study, it was observed that atmospheric deposition is a potentially significant source of "new" nitrogen on yearly time scales in the coastal waters of Singapore and surrounding areas, but not a dominant and comparable to point source like sewage outflow and nutrient loading from rivers. The results of the present study depict that the impacts of nitrogen species through AD onto the coastal region are more significant than phosphorus species. Despite the uncertainty in quantifying atmospheric deposition and model computations, this study highlights the importance of addressing the issues of eutrophication in Singapore that the atmosphere is clearly the dominant source of "new' nutrients (N and P species) in the surface waters of Singapore and surrounding areas. Establishing field monitoring sites and conducting modelling study pertaining to Singapore coastal waters would be a good start to address the impacts of atmospheric deposition of nutrients onto surface water in Singapore and surrounding waters, and SEA.

6.2 Future work and recommendations

Based on the outcome of this study, future research directions together with appropriate recommendations for the management of coastal water eutrophication in Singapore and surrounding areas due to nutrient input from atmosphere, land and sea are provided below.

- Additional aquatic nutrient research is needed that encompasses a significant spatial range in atmospheric nutrient deposition. Apart from the atmospheric deposition which forms a standing stock of nutrients that are responsible for triggering phytoplankton growth as hypothesized (in the literature), the addition of long-term nutrients and the occurrence of episodic events are also important in the contribution of eutrophication in coastal waters.

- A regional field monitoring programme should be established to collect the representative temporal and spatial samples of dry atmospheric deposition and wet atmospheric deposition, as well as coastal water and offshore samples over the SEA region for measurement of nutrients and algal biomass. The atmospheric nutrient deposition database should be acquired for the regional environmental management.
- The eutrophication model domain for simulating the effect of atmospheric nutrient deposition onto the marine water should be expanded to a regional scale covering the entire SEA. Improved models can in turn lead to advanced design of monitoring programs and effective water quality management. Strengths and limitations of this model can guide future development of eutrophication models in this region.
- The contribution of this study as a part of worldwide understanding of biochemical processes and the scope of scientific debates should be widened by conducting atmospheric nutrient deposition field measurement and modelling in the whole SEA region.
- The frequent occurrences of widespread smoke and haze episodes due to forest and peat fires in SEA on a large scale and the abundant rainfall in this tropical region and atmospheric fallout of nutrients should be monitored continuously at a strategic network of sampling locations to understand possible impacts of biomass burning episodes on aquatic ecosystem in this region. A regional extensive continuous field monitoring programme is needed during episodic smoke haze events for managing both air quality and water quality to protect the sensitive ecosystems in SEA region.

- This work should be continued by investigating the role of other nutrients such as iron species and trace metals, and its related biochemical factors that may also be responsible for the eutrophication in this region. Also, tools like remote sensing and geostatistics can be applied to study the spread and distribution of atmospheric nutrient deposition.
- The field measurement of nutrient concentrations from various sources such as runoff, rivers, seaborne sources (ocean boundaries, shipping activities, fish farms, etc.) and sewage outfalls is needed for the estimation of contribution of these nutrient sources in the Singapore coastal waters.
- The speciation of phytoplankton is needed in the model for exactly simulating algal blooms. This is limited to lack of knowledge on blooms. This topic can be recommended for future research.

REFERENCES

Abram, N.J.; Gagan, M.K.; McCulloch, M.T.; Chappell, J.; Hantoro, W. Coral reef death during the 1997 Indian Ocean dipole linked to Indonesian wildfires. *Science* 2003, *301*, 952–955.

Alcazar, A.; Fernandez-Caceres, P.L.; Martin, M.J.; Pablos, F.; Gonzalez, A.G. Ion chromatographic determination of some organic acids, chloride, and phosphate in coffee and tea. *Talanta* 2003, *61*, 95–101.

Allen, S.E.; Carlisle, A.; White, E.J.; Evans, C.C. The plant nutrient content of rainwater. *Journal of Ecology* 1968, *56*, 497–504.

Ambio. Special issue: Marine eutrophication. *Ambio* 1990, *19*(3), 101–176.

Ambrose, R.B.; Martin, J.L.; Connolly, J.P.; Schanz, R.W. *WASP4, a hydrodynamic and water quality model. Model theory user's manual and programmer's guide*. Environmental Protection Agency, Athens, GA, 1991.

Ambrose, B.; Wool, T.A.; Martin, J.L. *The Water quality Analysis Simulation Program (WASP6) User Manual*, US EPA, Athens, GA, 2001.

Andreae, M.O.; Browell, E.V.; Garstang, M.; Gregory, G.L.; Harriss, R.C.; Hill, G.F; Jacob, D.J.; Pereira, M.C.; Sachse, G.W.; Setzer, A.W.; Dias, P.L.S.,; Talbot, R.W.; Torres, A.L.; Wofsy, S.C. Biomass-burning emissions and associated haze layers over Amazonia. *Journal of Geophysical Research* 1988, *93*, 1509–1527.

Andreae, M.O. Biomass burning: its history, use, and distribution and its impact on environmental quality and global climate. In *Global biomass burning.*

Atmospheric, climatic, and biospheric implications; Levine J.S. Ed; MIT Press: Cambridge, Massachusetts 1991; pp. 3–21.

Andreae, M.O.; Crutzen, P.J. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* 1997, *276* (5315), 1052–1058.

Angelini, R.; Petrere, M. A. model for the plankton system of the Broa Reservoir, São Carlos, Brazil. *Ecological Modelling* 2000, *126*, 131–137.

Antia, N.; Harrison, P.; Oliveira, L. The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. *Phycologia* 1991, *30*, 1–89.

APHA *Standard methods for the examination of water and wastewater*. 21st edn, American Public Health Association/American Water Works Association/Water Environment Federation: Washington, D.C., USA, 2005; p.1368.

Arhonditsis, G.; Tsirtsis, G.; Angelidis, M.; Karydis, M. Quantification of the effects of nonpoint nutrient sources to coastal marine eutrophication: applications to a semi-enclosed gulf in the Mediterranean Sea. *Ecological Modelling* 2000, *129*, 209–227.

Arhonditsis, G.; Karydis, M.; Tsirtsis, G. Integration of mathematical modeling and multicriteria methods in assessing environmental change in developing areas: a case study of a coastal system. *Journal of Coastal Research* 2002, *18*, 698–711.

Arhonditsis, G.B.; Brett, M.T. Evaluation of the current state of mechanistic aquatic biogeochemical modeling. *Marine Ecology Progress Series* 2004, *27*(1), 13–26.

Armstrong, D.A.; Chippendale, D.; Knight A.W.; Colt, J.E. Interaction of ionized and un-ionized ammonia on short-term survival and growth of prawn larvae, Macrobrachium rosenbergii. The Biological Bulletin 1978, *154*, 15–31.

Artaxo, P.; Hansson, H.C. Size distribution of biogenic aerosol particles from the Amazon Basin. *Atmospheric Environment* 1995, *29*, 393–402.

Asaeda, T.; Bon, T.V. Modelling the effects of macrophytes on algal blooming in eutrophic shallow lakes. *Ecological Modelling* 1997, *104*, 261–287.

ASEAN *Draft: ASEAN State of the Environment 1995*. Unpublished report. Association of South-East Asian Nations, 1995.

Asiati, S.; Budiwati, T.; Avia, L.Q. Acid deposition in Bandung, Indonesia. *Water, Air and Soil Pollution* 2001, *130*, 1571–1576.

Asman, W.A.H.; Sutton, M.A.; Schjorring, J.K. Ammonia: emission, atmospheric transport and deposition. *New Phytologist* 1998, *139*, 27–48.

ASTM *Method D-515-82, Annual Books of ASTM Standard*, ASTM, Philadelphia, PA, 1988; p. 474.

Ayers G.P. Atmospheric acidification in the Asian region. *Environmental Monitoring and Assessment* 1991, *19*, 225–250.

Ayers, G.P.; Peng, L.C.; Fook, L.S.; Kong, C.W.; Gillett, R.W.; Manins, P.C. Atmospheric concentrations and deposition of oxidised sulfur and nitrogen species at Petaling Jaya, Malaysia 1993–1998. *Tellus* 2000, *52B*(1), 60–73.

Ayers, G.P.; Yeung, K.K. Acid deposition in Hong Kong. *Atmospheric Environment* 1996, *30*(10/11), 1581–1587.

Ayers, G.P.; Peng, L.C.; Gillett, R.W.; Fook, L.S. Rainwater composition and acidity at five sites in Malaysia, in 1996. *Water Air and Soil Pollution* 2002, *133*, 15–30.

Ayars, J.; Gao, Y. Atmospheric nitrogen deposition to the Mullica River-Great Bay Estuary. *Marine Environmental Research* 2007, *64*, 590–600.

Baeyens, W.; Dehairs, F.; Dedeurwaerder, H. Wet and dry deposition fluxes above the North Sea. *Atmospheric Environment* 1990, *24A*(7), 1693–1703.

Baker, J.E.; Poster, D.L.; Clark, C.A.; Church, T.M.; Scudlark, J.R.; Ondov, J.M.; Dickhut, R.M.; Cutter, G. Loading of atmospheric trace elements and organic contaminants to the Chesapeake Bay. In *Atmospheric deposition of contaminants to the great lakes and coastal waters*; Baker, J.E. Ed.; SETAC, Pensacola, FL 1997; pp. 171–194.

Baker, A.R.; Kelly, S.D.; Biswas, K.F.; Witt, M.; Jickells, T.D. Atmospheric deposition of nutrients to the Atlantic Ocean. *Geophysical Research Letters* 2003, *30*(24), 2296–2299; doi:10.1029/2003GL018518.

Baker, A.R.; Jickells, T.D.; Biswas, K.F.; Weston, K.; French, M. Nutrients in atmospheric aerosol particles along the Atlantic Meridional Transect. *Deep-Sea Research II* 2006, *53*, 1706–1719.

Balasubramanian, R.; Victor, T.; Begum, R. Impact of biomass burning on rainwater acidity and composition. *Journal of Geophysics Research* 1999, *104*, 26881–26890.

Balasubramanian, R.; Victor, T.; Chun, N. Chemical and statistical analysis of precipitation in Singapore. *Water, Air, and Soil Pollution* 2001,*130*, 451–456.

Balasubramanian, R.; Qian, W.B.; Decesari, S.; Facchini, M.C.; Fuzzi, S. Comprehensive characterization of PM2.5 aerosols in Singapore. *Journal of Geophysics Research* 2003, *108*(D16), 4523.

Balasubramanian, R.; Qian, W.B. Characterization and source identification of airborne trace metals in Singapore. *Journal of Environmental Monitoring* 2004, *8*, 813–818.

Beck, M.B. *System analysis in water quality management.* Symposium-Proceedings, Oxford-Pergama press: London 1987; pp.3–63.

Beddig, S.; Brockmann, U.; Dannecker, W.; Korner, D.; Pohlman, T.; Puls, W.; Radach, G.; Rebers, A.; Rick, H.- J.; Schatzmann, M.; Schlüenzen, H.; Schultz,

M. Nitrogen fluxes in the German Bight. *Marine Pollution Bulletin* 1997, *34*(6), 382–394.

Bergametti, G.; Remoudaki, E.; Losno, R.; Steiner, E.; Chatenet, B. Source, transport and deposition of atmospheric phosphorus over the northwestern Mediterranean. *Journal of Atmospheric Chemistry* 1992, *14*, 501–513.

Boyd, P.W.; Doney, S.C. Modeling regional responses by marine pelagic ecosystems to global climate change. *Geophysical Research Letters* 2002, *29*, Art. No. 1806.

Boynton, W.R.; Garber, J.H.; Summers, R.; Kemp, W.M. Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* 1995, *18*(1B), 285–314.

Brauer, M.; Hisham Hashim, J. Indonesian Fires: Crisis and Reaction. *Environmental Science and Technology* 1998, *32*(17), 404A–407A.

Bronk, D.A.; Lomas, M.W.; Glibert, P.M.; Schukert, K.J.; Sanderson, M. Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods. *Marine Chemistry* 2000, *69*, 163–178.

Buat-Menard, P.; Duce, R.A. Precipitation scavenging of aerosol particles over remote marine regions. *Nature* 1986, *321*, 508–510.

Bourne, R.G. *Water quality effects of sewage effluent on a cypress dome system*. M.S. Thesis, University of Florida, Gainesville, Florida, 1976.

Bowden, R.D. Inputs, outputs and accumulations of nitrogen in an early successional moss (Polytrichum) ecosystem. *Ecological Monographs* 1991, *61*, 207–233.

Bowie, G.L.; Mills, W.B.; Porcella, D.B.; Campbell, C.L.; Pagenkopt, J.R.; Rupp, G.L.; Johnson, K.M.; Chan, P.W.H.; Gherini, S.A. *Rates, constants and kinetics formulation in surface water quality modeling*, 2nd ed. U.S. Environmental Protection Agency: Georgia, 1985.

Broberg O.; Persson G. External budgets for phosphorus, nitrogen and dissolved organic carbon for the acidified Lake Gardsjon. *Arch Hydrobiol* 1984, *99*, 160–175.

Butler, T.J.; Likens, G.E. A direct comparison of throughfall plus stemflow to estimates of dry and total deposition for sulfur and nitrogen. *Atmospheric Environment* 1995, *29*, 1253–1265.

Camargo, J.A.; Alonso, A.; Sagarin, R.D. Inorganic nitrogen pollution in aquatic ecosystems: causes and consequences. In *Environmental chemistry, Ecology and Marine ecology*; Cleveland, C.J. Ed.; Encyclopedia of Earth. Environmental Information Coalition, National Council for Science and the Environment: Washington, D.C 2007.

Cape, J.N.; Kirika, A.; Rowland, A.P.; Wilson, D.S.; Jickells, T.D.; Cornell, S. Organic nitrogen in precipitation: real problem or sampling artefact?. *The Scientific World* 2001, *1*(S2), 230–237.

Capone, D.G; Carpenter, E.J. Nitrogen fixation in the marine environment. *Science* 1982, *217*, 1140–1142.

Carlisle, A.; Brown, A.H.F.; White, E.J. The nutrient content of tree stem flow and ground flora litter and leachates in a sessile oak (Quercus petraea) woodland. *Journal of Ecology* 1966, *55*, 615–627.

Caruso, E.; Braga Marcazzan, G.M.; Redaelli, P. PIXE investigation of element concentration and particle size distribution in Milan atmospheric aerosol. *Nuclear Instruments and Methods* 1981, *181*, 425–429.

Cerco, C.F.; Cole, T. Three-dimensional, eutrophication model of Chesapeake, Bay. *Journal of Environmental Engineering* 1993, *119*, 1006–1025.

Cerco, C.F.; Cole, T.M. *CE-QUAL-ICM: a three-dimensional eutrophication model, version 1.0. User's Guide*, U.S. Army Corps of Engineers Waterways Experiments Station, Vicksburgh, M.S., 1995.

Cerco, C.; Noel, M. Process-based primary production modeling in Chesapeake Bay. *Marine Ecology Progress Series* 2004, *282*, 45–58.

Cescon, B.; Drago, M.; Gianfelici, F.; Lovenitti, L. Environmental impact study of projects affecting the quality of marine ecosystems. *Croatica Chemica Acta* 1998, *71*, 361–389.

Chan, E.S.; Tkalich, P.; Gin, K.Y.H.; Obbard, J.P. The physical oceanography of Singapore coastal waters and its implications for oil spills. In *The Environment in Asia Pacific Harbours*, Chapter 23; Wolanski, E., Ed.; Springer: Netherlands 2006; pp. 393–412.

Chapra, S.C. *Surface Water-Quality Modeling*; McGraw-Hill: New York, 1997.

Chee K.K.; Wong, M.K.; Lee, H.K. Microwave-assisted solvent extraction of air particulates for the determination of PAHs. *Environmental Monitoring and Assessment* 1997, *44*(1-3), 391–403.

Chen, L.; Arimoto, R.; Duce, R.A. The sources and forms of phosphorus in marine aerosol-particles and rain from Northern New Zealand. *Atmospheric Environment* 1985, *19*(5), 779–787.

Chen, Y.; Mills, S.; Street, J.; Golan, D.; Post, A.; Jacobson, M.; Paytan, A. Estimates of atmospheric dry deposition and associated input of nutrients to Gulf of Aqaba seawater. *Journal of Geophysical Research* 2007, *112*, D04309; doi:10.1029/2006JD007858.

Chia, L.S., Habibullah, K., Chou, L.M. *Coastal environmental profile of Singapore*; International Centre for living Aquatic Resources Management: Technical Publication series, 1988.

Chiong, C.K. Nitrification in Singapore's coastal waters. M.Engg. Thesis, Department of Civil Engineering, National University of Singapore, Singapore, 1999.

Clarke, A.D.; Shinozuka, Y.; Kapustin, V.N.; Howell, S.; Huebert, B.; Doherty, S.; Anderson, T.; Covert, D.; Anderson, J.; Hua, X.; Moore II, K.G.; McNaughton, C.; Carmichael, G.; Weber, R. Size-Distributions and Mixtures of Black Carbon and Dust Aerosol in Asian Outflow: Physio-chemistry, Optical Properties. *Journal of Geophysical Research* 2004, *109*, D15S09.

Clark, H.; Kremer, J.N. Estimating direct and episodic atmospheric nitrogen deposition to a coastal waterbody. *Marine Environmental Research* 2005, *59*(4), 349–366.

Cloern, J.E. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series* 2001, *210*, 223–253.

Cole, T.M., Buchak, E. *CE-QUAL-W2: A two-dimensional, laterally averaged, hydrodynamic and water quality model (version 2.0) Technical report*; U.S. Army Corps of Engineers Waterways Experiments Station: Vicksburgh, M.S., 1995.

Colina, M.; Ledo, H.; Gutierrez, E.; Villalobos E.; Matin, J. Determination of total phosphorus in sediments by means of high-pressure bombs and ion chromatography. *Journal of Chromatography A* 1996, *739*(1-2), 223–227.

Colina, M.; Gardiner, P.H.E. Simultaneous determination of total phosphorus, nitrogen and sulfate by means of microwave digestion and ion chromatography. *Journal of Chromatography A* 1999, *847*, 285–290.

Colombini, S.; Polessello, S.; Valsecchi, S. Use of column switching chromatography for the simultaneous determination of phosphorus and nitrogen after microwave assisted persulfate digestion. *Journal of Chromatography A* 1998, *822*, 162–166.

Conner, W.D.; Bennett, R.L.; Weathers, W.S.; Wilson, W.E. Particulate characteristics and visual effects of the atmosphere at Research Triangle Park. *Journal of Air and Waste Management Association* 1991, *41*, 153–160

Cornell, S.; Rendell, A.; Jickells, T. Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 1995, *37*6, 243–246.

Cornell, S.E.; Jickells, T.D.; Thornton, C.A. Urea in rainwater and atmospheric aerosol. *Atmospheric Environment* 1998, *32*, 1903–1910.

Cornell, S.E.; Jickells T.D. Water-soluble organic nitrogen in atmospheric aerosol: A comparison of UV and persulfate oxidation methods. *Atmospheric Environment* 1999, *33*(5), 833–840.

Cornell, S.; Mace, K.; Coeppicus, S.; Duce, R.; Huebert, B.; Jickells, T.; Zhuang, L.-Z. Organic nitrogen in Hawaiian rain and aerosol. *Journal of Geophysical Research* 2001, *106*, 7973–7983.

Cornell, S.C.; Jickells, T.D.; Cape, J.N.; Rowland, A.P.; Duce, R.A. Organic nitrogen deposition on land and coastal environments: a review of methods and data. *Atmospheric Environment* 2003, *37*, 2173–2191.

Correll, D.L.; Ford, D. Comparison of precipitation and land runoff as sources of estuarine nitrogen. *Estuarine, Coastal and Shelf Science* 1982, *15*, 45–56.

Crockford, R.H.; Richardson, D.P.; Sageman, R. Chemistry of rainfall, throughfall, and stemflow in a Eucalypt forest and a pine plantation in south-eastern Australia, 1, Rainfall. *Hydological Processes* 1996, *10*, 10–11.

Crutzen, P.J.; Heidt, L.E.; Krasnec, J.P.; Pollock, W.H.; Seiler, W. Biomass burning as a source of atmospheric gases CO, H2, N2O, NO, CH3Cl, COS. *Nature* 1979, *282*, 253–256.

Crutzen, P.J.; Delany, A.C.; Greenberg, J.; Haagenson, P.; Heidt, L.; Lueb, R.; Pollock, W.; Seiler, W.; Wartburg, A.; Zimmerman, P. Tropospheric chemical composition measurements in Brazil during the dry season. *Journal of Atmospheric Chemistry* 1985, *2*, 233–256.

Crutzen, P.J.; Andreae, M.O. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science* 1990, *250*, 1669–1678.

Crutzen, P.J.; Carmichael, G.J. Modeling the influence of fires on atmospheric chemistry. In *Fire in the environment: the ecological, atmospheric, and climatic importance of vegetation fires*; Crutzen, P.J., Goldammer, J.G., Eds.; Wiley: New York 1993; pp.89–105.

Daniel, T.C.; Sharpley, A.N.; Lemunyon, J.L. Agricultural phosphorus and eutrophication: A symposium overview. *Journal of Environmental Quality* 1998, *27*, 251–257.

De Leeuw, G.; Spokes, L.; Jickells, T.; Skjoth, C.A.; Hertel, O.; Vignati, E.; Tamm, S.; Schulz, M.; Sorensen, L.L.; Pedersen, B.; Klein, L.; Schlunzen, K.H. Atmospheric nitrogen inputs into the North Sea: effect on productivity. *Continental Shelf Research* 2003, *23*, 1743–1755.

Delaney, M.L. Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle. *Global Biogeochemical Cycles* 1998, *12*, 563–572.

De Pauw, D.J.W.; Vanrolleghem, P.A. Practical aspects of sensitivity analysis for dynamic models. In *Proceedings of the IMACS 4th MATHMOD Conference*; ARGESIM Verlag: 5-7 February 2003, Vienna, Austria, 2003.

DHI *Detailed studies on Tuas View extension and Pulau Tekong land reclamation-Final Report, Volume VIII Water quality impact assessment*; Danish Hydraulic Institute: Denmark 2004.

Dignon, J. NO_2 and SO_2 emissions from fossil fuels: a global distribution. *Atmospheric Environment* 1992, *26A*, 1157–1163.

Dillon, P.J.; Molot, L.A.; Scheider, W.A. Phosphorus and nitrogen export from forested stream catchments in central Ontario. *Journal of Environmental Quality* 1991, *20*, 857–864.

Ditmars, J.D. Performance evaluation of surface water transport and dispersion models. *Journal of Environmental Engineering* 1988, *113*(EE8), 961– 971.

Di Toro, D.M.; O'Connor, D.J.; Thomann, R.V. A dynamic model of the phytoplankton population in the Sacramento-San Joaguin Delta. *Advances in Chemistry Series* 1971, *106*, 131–180,

Doney, S.C.; Glover, D.M.; Najjar, R.B. A new coupled, one-dimensional biologicalephysical model for the upper ocean: applications to the JGOFS Bermuda Atlantic time-series study (BATS) site. *Deep-Sea Research II* 1996, *43*(2-3), 591–624.

Draxler, R.R., Rolph, G.D. *HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model*; Access via NOAA ARL READY Website: http://www.ready.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, MD, 2003.

Duarte, C. M.; Dachs, J.; Llabrés, M.; Alonso-Laita, P.; Gasol, J.M.; Tovar-Sánchez, A.; Sañudo-Wilhemy, S.; Agustí, S. Aerosol inputs enhance new production in the subtropical northeast Atlantic. *Journal of Geophysical Research* 2006, *111*, G04006; doi:10.1029/2005JG000140.

Duce, R. The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological productivity. In *The role of air-sea exchange in geochemical cycles*; Buat-Menard, P. Eds.; D. Reidael Publishing Company: Dordrecht, Netherlands 1986; pp. 497–529.

Duce, R.A.; Liss, P.S.; Merrill, J.T.; Atlas, E.L.; Buat-Menard, P.; Hicks, B.B.; Miller, J.M.; Prospero, J.M.; Arimoto, R.; Church, T.M.; Ellis, W.; Galloway, J.N.; Hansen, L.; Jickells, T.D.; Knap, A.H.; Reinhardt, K.H.; Schneider, B.; Soudine, A.; Tokos, J.J.; Tsunogai, S.; Wollast, R.; Zhou, M. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 1991, *5*, 193–259.

Duce, R.A.; LaRoche, J.; Altieri, K.; Arrigo, K.R.; Baker, A.R.; Capone, D.G.; Cornell, S.; Dentener, F.; Galloway, J.; Ganeshram, R.S.; Geider, R.J.; Jickells, T.; Kuypers, M.M.; Langlois, R.; Liss, P.S.; Liu, S.M.; Middelburg, J.J.; Moore, C.M.; Nickovic, S.; Oschlies, A.; Pedersen, T.; Prospero, J.; Schlitzer, R.; Seitzinger, S.; Sorensen, L.L.; Uematsu, M.; Ulloa, O.; Voss, M.; Ward, B.; Zamora, L. Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 2008, *320*(5878), 893– 897.

Dulac, F.; Buat-Ménard, P.; Ezat, U.; Bergametti, G. Atmospheric input of trace metals to the western Mediterranean Sea: uncertainties in modelling dry deposition from cascade impactor data. *Tellus* 1989, *41B*, 362–378.

Ebina, J.; Tsutsui, T.; Shirai, T. Simultaneous determination of total nitrogen and total phosphorus in water using peroxodisulfate oxidation. *Water Research* 1983, *17*(12), 1721–1726.

Eklund, T.J.; McDowell, W.H.; Pringle, C.M. Seasonal variation of tropical precipitation chemistry: La Selva, Costa Rica. *Atmospheric Environment* 1997, *31*, 3903–3910.

Eriksson, E. Composition of atmospheric precipitation, I. Nitrogen compounds. *Tellus* 1952, *4*, 216–232.

Erisman, J.W.; de Vries, W.; Kros, J.; O van der, L.; van Zeijts, E. H. An outlook for a national integrated nitrogen policy. *Environmental Science and Policy* 2001, *4*(2-3), 87–95.

Fang, M.; Zheng, M.; Wang, F.; To, K.L.; Jaafar, A.B.; Tong S.L. The solvent extractable organic compounds in the Indonesia biomass burning aerosols characterization studies. *Atmospheric Environment* 1999, *33*(5), 783–795.

Fang, G.C.; Wu, Y.S.; Chen, J.C.; Rau, J.Y.; Huang, S.H.; Lin, C.K. Concentrations of ambient air particulates (TSP, $PM_{2.5}$ and $PM_{2.5\text{-}10}$) and ionic species at offshore areas near Taiwan Strait. *Journal of Hazardous Materials* 2006, *132*, 269–276.

Fasham, M.J.R.; Sarmiento, J.L.; Slater, R.D.; Ducklow, H.W.; Williams, R. Ecosystem behavior at Bermuda station-S and ocean weather station India—a general circulation model and observational analysis. *Global Biogeochemical Cycles* 1993, *7*, 379–415.

Fenchel, T., Blackburn, T. H. *Bacteria and mineral cycling*; Academic Press: London, 1979.

Ferris, J.M.; Christian, R. Aquatic primary production in relation to microalgal responses to changing light-a review. *Aquatic Science* 1991, *53*, 187–217.

Frost, B.W.; Kishi, M.J. Ecosystem dynamics in the eastern and western gyres of the Subarctic Pacific—a review of lower trophic level modeling. *Progress in Oceanography* 1999, *43*, 317–333.

Fujiwara, M.; Kita, K.; Kawakami, S.; Ogawa, T.; Komala, N.; Saraspriya, S.; Suripto, A. Tropospheric ozone enhancements during the Indonesian forest fire events in 1994 and in 1997 as revealed by ground-based observations. *Geophysical Research Letters* 1999, *26*, 2417–2420.

Furnas, M.J. The behavior of nutrients in tropical aquatic ecosystems. In *Pollution in tropical aquatic systems*; Connell, D.W., Hawker, D.W. Eds.; CRC Press: London 1992; pp. 29–65

Galceran, M.T.; Diez, M. Column-switching techniques in the analysis of phosphate by ion chromatography. *Journal of Chromatography A* 1994, *675*(1-2), 141–147.

Galloway, J.N.; Levy II, H.; Kasibhatla, P.S. Year 2020: Consequences of population growth and development on deposition of oxidized nitrogen. *Ambio* 1994, *23*, 120–123.

Galloway, J.N.; Schlesinger, W.H.; Levy II, H.L.; Michaels, A.; Schnoor, J.L. Nitrogen fixation: Anthropogenic enhancement-environmental response. *Global Biogeochemical Cycles* 1995, *9*, 235–252.

Galloway, J.N.; Cowling, E.B. Reactive nitrogen and the world: 200 years of change. *Ambio* 2002, *31*, 64–71.

Galloway, J.N.; Dentener, F.J.; Capone, D.G.; Boyer, E.W.; Howarth, R.W.; Seitzinger, S.P.; Asner, G.P.; Cleveland, C.C.; Green, P.A.; Holland, E.A.; Karl, D.M.; Michaels, A.F.; Porter, J.H.; Townsend, A.R.; Vöosmarty, C.J. Nitrogen cycles: Past, present, and future. *Biogeochemistry* 2004, *70*, 153–226.

Galloway, J.N.; Townsend, A.R.; Erisman, J.W.; Bekunda, M.; Cai, Z.; Freney, J.R.; Martinelli, L.A.; Seitzinger, S.P.; Sutton, M.A.; Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* 2008, *320*, 889–892.

Garstang, M.; Tyson, P.D.; Cachier, H.; Radke, L. Atmospheric transport of particulate and gaseous products by fires. In *Sediment records of biomass burning and global change*; Clark, J.S, Cachier, H., Goldammer, J.G., Stocks, B. Eds.; Springer: New York 1997; pp.207–252.

Gao, Y.; Arimoto, R.; Duce, R.A.; Chen, L.Q.; Zhou, M.Y.; Gu, D.Y. Atmospheric non-sea-salt, sulfate, nitrate and methane sulfonate over the China Sea. *Journal of Geophysical Research* 1996, *101*, 12601–12611.

GEO *Global Environment Outlook 3: Past, present and future perspectives*; Division of Environmental Information, Assessment and Early Warning (DEIA and EW), UNEP: Nairobi, Kenya, 2003; http://grida.no/geo/geo3/english/index.htm.

GESAMP (The Group of Experts on Scientific Aspects of Marine Environmental Protection) *The atmospheric input of trace species to the world ocean*; Reports and Studies 38, GESAMP: New York, 1989; Reprinted 1990, UNEP Regional Seas Reports and Studies, No. 119.

GESAMP *The state of the marine environment*; UNEP Regional Sea Report and Studies 115, UNEP: Nairobi, Kenya, 1990.

Gillett, R.W.; Ayers, G.P.; Mhwe, T.; Selleck, P.W.; Harjanto, H. Concentrations of nitrogen and sulfur species in gas and rainwater from several sites in Indonesia. *Water, Air and Soil Pollution* 2000, *120*, 205–215.

Gin, K.Y.H.; Lin, X.; Zhang, S. Dynamics and size structure of phytoplankton in the coastal waters of Singapore. *Journal of Plankton Research* 2000, *22*(8), 1465–1484.

Gin, K.; Zhang, Q.; Chan, E.; Chou, L. Three-dimensional ecological-eutrophication model for Singapore. *Journal of Environmental Engineering* 2001, *127*(10), 928–937.

Gin, K.Y.H.; Holmes, M.J.; Zhang, S.; Lin, X. Phytoplankton structure in the tropical port waters of Singapore. In *The Environment in Asia Pacific Harbours*, Chapter 21; Wolanski, E., Ed.; Springer: Netherlands 2006; pp. 347–375.

Goldammer, J.G.; Seibert, B.; Schindele, W.; Fire in dipterocarp forests. In *Dipterocarp forest ecosystems: Towards sustainable management*; Schulte, A., Schöne, D. Eds.; World Scientific Publishers: Singapore 1996; pp. 155–185.

Gore, A.J.P. The supply of six elements by rain to an upland peat area. *Journal of Ecology* 1968, *56*, 483–495.

Grant, M.C.; Lewis, Jr. W.M. Chemical loading rates from precipitation in the Colorado Rockies. *Tellus* 1982, *34*, 74–88.

Gray, J.S. Eutrophication in the sea. In *Marine Eutrophication and Population Dynamics*; Colombo, G., Frerrari, I., Ceccherelli, V.U., Rossi, R. Eds.; Olsen and Olsen: Fredensborg, Denmark 1992; pp. 3–15.

Guildford, S.J.; Hecky, R.E. Total nitrogen, total phosphorus, and nutrient limitation in lakes and oceans: Is there a common relationship?. *Limnology and Oceanography* 2000, *45*, 1213–1223.

Hamilton, D.P.; Schladow, S.G. Prediction of water quality in lakes and reservoirs. 1. Model description. *Ecological Modelling* 1997, *96*, 91–110.

Hasager, C.B.; Carstensen, J.; Ellermann, T.; Gustafson, B.G.; Hertel, O.; Johnsson, M.; Markager, S.; Ambelas Skjøth, C. On extreme atmospheric and marine nitrogen fluxes and chlorophyll-a levels in the Kattegat Strait. *Atmospheric Chemistry and Physics* 2003, *3*, 797–812.

Haugarth, P.M.; Jarvis, S.C. Transfer of phosphorus from agricultural soil. *Advances in Agronomy* 1999, *66*, 195–249.

He, X.T.; Mulvaney, R.L.; Banwart, W.L. A rapid method for total nitrogen analysis using microwave digestion. *Soil Science Society of America Journal* 1990, *54*, 1625–1629.

Hendry, C.D.; Brezonik, P.L. Chemistry of precipitation at Gainesville, Florida. *Environmental Science and Technology* 1980, *14*, 843–849.

Herut, B.; Krom, M.D.; Pan, G.; Mortimer, R. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: sources, fluxes, and possible impact. *Limnology and Oceanography* 1999, *44*, 1683–1692.

Herut, B.; Collier, R.; Krom, M. The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean. *Limnology and Oceanography* 2002, *47*, 870–878.

Hood, R.R.; Bates, N.R.; Capone, D.G.; Olson, D.B. Modeling the effect of nitrogen fixation on carbon and nitrogen fluxes at BATS. *Deep-Sea Research II* 2001, *48*, 1609–1648.

Hood, R.R.; Kohler, K.E.; McCreary, J.P.; Smith, S.L. A four-dimensional validation of a coupled physical-biological model of the Arabian Sea. *Deep-Sea Research II* 2003, *50*(22-26), 2917–2945.

Howarth, R.W.; Swaney, D.P.; Butler, T.J.; Marino, R. Climatic control on eutrophication of the Hudson River Estuary. *Ecosystems* 2000, *3*, 210–215.

Holsen, T.M.; Zhu, X.; Khalili, N.R.; Lin, J.J.; Lestari, P.; Lu, C.-S.; Noll, K.E. Atmospheric particle size distributions and dry deposition measured around Lake Michigan. In *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*; Baker, J.E. Ed.; SETAC Press: Pensacola, FL 1997; pp. 35–50.

Hu, H.L.; Chen, H.M.; Nikolaidis, N.P.; Miller, D.R.; Yang, X. Estimation of nutrient atmospheric deposition to Long Island Sound. *Water, Air, and Soil Pollution* 1998, *105*, 521–538.

Hu, G.P.; Balasubramanian, R.; Wu, C.D. Chemical characterization of rainwater at Singapore. *Chemosphere* 2003, *51*, 747–755.

Ikegami, M.; Okada, K.; Zaizen, Y.; Makino, Y.; Jensen, J.B.; Gras, J.L.; Harjanto, H. Very high weight ratios of S/K in individual haze particles over Kalimantan during the 1997 Indonesian forest fires. *Atmospheric Environment* 2001, *35*, 4237–4243.

In, H.-J.; Byun, D.W.; Park, R.J.; Moon, N.-K.; Kim, S.; Zhong, S. Impact of transboundary transport of carbonaceous aerosols on the regional air quality in the United States: A case study of the South American wildland fire of May 1998. *Journal of Geophysical Research* 2007, *112*, D07201; doi:10.1029/2006JD007544.

Jänike, R. Tropospheric aerosols. In *Aerosol-cloud-climate interactions*; Hobbs, P.V. Ed.; International Geophysics Series 54. Academic Press: San Diego 1993; p.235.

Janet, P. Is coastal eutrophication out of control?. *Environmental Science and Technology* 1998, *1*, 462A–466A.

Jassby, A.D.; Platt, T. Mathematical formulation of relationship between photosunthesis and light for phytoplankton. *Limnology and Oceanography* 1976, *21*, 540–547.

Jassby, A.D.; Reuter, J.E.; Axler, R.P.; Goldman, C.R.; Hackley, S.H. Atmospheric deposition of nitrogen and phosphorus in the annual nutrient load of Lake Tahoe (California-Nevada). *Water Resources Research* 1994, *30*, 2207–2216.

Joffre, S.M. Modelling the dry deposition velocity of highly soluble gases to the sea surface. *Atmospheric Environment* 1988, *22*(6), 1137–1146.

Jickells, T. Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Marine Chemistry* 1995, *48*, 199–214.

Jickells, T.D. Nutrient biogeochemistry of the coastal zone. *Science* 1998, *281*, 217–222.

Jickells, T.D.; Spokes, L.J. Atmospheric iron inputs to the oceans. In *The biogeochemistry of iron in seawater*; Turner, D.R., Hunter, K.A. Eds.; Wiley: New York 2001; pp. 85–121.

Joffre, S.M. Modelling the dry deposition velocity of highly soluble gases to the sea surface. *Atmospheric Environment* 1988, *22*(6), 1137–1146.

Johnes, P.J.; Heathwaite, A.L. Procedure for simultaneous determination of total phosphorus and nitrogen in fresh waters using microwave digestion. *Water Research* 1992, *26*, 1281–1287.

Jørgensen, B.B., Richardson, K. Eds. Eutrophication in coastal marine ecosystems. In *Coastal and estuarine studies*; American Geophysical Union: Washington, D.C. 1996; *52*, pp. 1-19.

Kato, N.; Akimote, H. Anthropogenic emissions of SO_2 and NO_x in Asia: emission inventories. *Atmospheric Environment* 1992, *26*A, 2997–3017.

Karthikeyan, S.; Balasubramanian, R. Evaluation of microwave assisted extraction for determination of water soluble inorganic species in airborne particulate matter. *Analytical and Bioanalytical Chemistry* 2005a, *381*, 1604–1608.

Karthikeyan, S.; Balasubramanian, R. Rapid extraction for water soluble organic compounds in airborne particulate matter. *Analytical Sciences* 2005b, *21*, 1505–1508.

Karthikeyan, S.; Balasubramanian, R. Determination of water-soluble inorganic and organic species in atmospheric fine particulate matter. *Microchemical Journal* 2006, *82*, 49–55.

Karthikeyan, S.; Balasubramanian, R.; See, S.W. Optimization and validation of low temperature microwave assisted extraction method for the analysis of PAH in airborne particulate matter. *Talanta* 2006a, *69*, 79–86.

Karthikeyan, S.; Joshi, U.M.; Balasubramanian, R. Microwave assisted sample preparation of water soluble fraction of trace elements in urban airborne particulate matter: Evaluation of bioavailability. *Analytica Chimica Acta* 2006b, *576*, 23–30.

Karthikeyan, S.; See, S.; Balasubramanian, R. Simultaneous determination of inorganic anions and selected organic acids in airborne particulate patter by Ion Chromatography. *Analytical Letters* 2007, *40*, 1–12.

Karthikeyan, S.; He, J.; Sundarambal, P.; Balasubramanian, R.; Burger, D. Determination of total nitrogen in atmospheric wet and dry deposition samples. *Talanta* 2009a, *77*(3), 979–984.

Karthikeyan, S.; Balasubramanian, R.; He, J. Inter-laboratory study to improve the quality of the analysis of nutrients in rainwater chemistry. *Atmospheric Environment* 2009b, in press; doi: 10.1016/j.atmosenv.2009.03.025.

Kawamiya, M. Numerical model approaches to address recent problems on pelagic ecosystems. *Journal of Oceanography* 2002, *58*, 365–378.

Kjeldahl, J.G.C. A new method for the determination of nitrogen in organic matter. *Fresenius' Journal of Analytical Chemistry* 1883, *22*, 366–372.

Koe, L.C.C.; Arellano, A.F.; McGregor, J.L. Investigating the haze transport from 1997 biomass burning in Southeast Asia: its impact upon Singapore. *Atmospheric Environment* 2001, *35*, 2723–2734.

Koroleff, F. Determination of phosphorus. In *Methods of seawater analysis*; Grasshoff, K., Ehrhardt, M., Kremling, K. Eds. Verlag Chemie: Weinheim 1983; pp.125–131.

Kondo, Y.; Morino, Y.; Takegawa, N.; Koike, M.; Kita, K.; Miyazaki, Y.; Sachse, G. W.; Vay, S.A.; Avery, M.A.; Flocke, F.; Weinheimer, A.J.; Eisele, F.L.; Zondlo, M.A.; Weber, R.J.; Singh, H.B.; Chen, G.; Crawford, J.; Blake, D.R.; Fuelberg, H.E.; Clarke, A.D.; Talbot, R.W.; Sandholm, S.T.; Browell, E.V.; Streets, D.G.; Liley, B. Impacts of biomass burning in Southeast Asia on ozone and reactive nitrogen over the western Pacific in spring. *Journal of Geophysical Research* 2004, *109*, D15S12; doi:10.1029/2003JD004203.

Kopacek, J.; Prochazkova, L.; Hejzlar, J.; Trends and seasonal patterns of bulk deposition of nutrients in the Czech Republic. *Atmospheric Environment* 1997, *31*, 797–808.

Knap, A.; Jickells, T.; Pszenny, A.; Galloway, J. Significance of atmospheric-derived fixed nitrogen on the productivity of the Sargasso Sea. *Nature* 1986, *320*, 158–160.

Kunii, O.; Kanagawa, S.; Yajima, I.; Hisamatsu, Y.; Yamamura, S.; Amagai, T.; Ismail, I.T.S. The 1997 haze disaster in Indonesia: its air quality and health effects. *Arch Environ Health* 2002, *57*, 16–22.

Ledo de Medina, H.; Colina de Vargas, M.; Marin, J.; Pirela, D. Determination of total nitrogen in water samples by means of high-pressure bombs and ion chromatography. *Journal of Chromatography A* 1994, *671*(1-2), 287–293.

Levine, J.S. The 1997 fires in Kalimantan and Sumatra, Indonesia, Gaseous and particulate emissions. *Geophysical Research Letters* 1999, *26*, 815–818.

Lewis, W.M.Jr. Precipitation chemistry and nutrient loading by precipitation in a tropical watershed. *Water Resources Research* 1981, *17*, 169–181.

Li, M.; Gargett, A.; Denman, K. What determines seasonal and interannual variability of phytoplankton and zooplankton in strongly estuarine systems? Application to the semi-enclosed estuary of Strait of Georgia and Juan De Fuca Strait. *Estuarine, Coastal and Shelf Science* 2000, *50*(4), 467–488.

Lima, I.D.; Doney, S.C. A three-dimensional, multinutrient, and size structured ecosystem model for the North Atlantic. *Global Biogeochemical Cycles* 2004, *18*(3), Art. No. GB3019.

Liu, Y.; Kaiser, E.; Avdalovic, N. Determination of trace-level anions in high-purity water samples by ion chromatography with online eluent generator system. *Microchemical Journal* 1999, *62*, 164–173.

Lo, K.V.; Wong, W.T.; Liao, P.H. Rapid determination of total kjeldahl nitrogen using microwave digestion. *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances and Environmental Engineering* 2005, *40*, 609–615.

Lobert, J.M.; Scharffe, D.H.; Hao, W.M.; Crutzen, P.J. Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature* 1990, *346*, 552 – 554.

Lobert, J.M.; Warnatz, J. Emissions from the combustion process in vegetation. In *Fire in the environment: The ecological, atmospheric and climatic importance of vegetation fires*; Crutzen,P.J., Goldammer, J.G. Eds.; Dahlem Workshop

Report, Chemical importance of vegetation fires, John Wiley and Sons: Chichester, England 1993; pp. 15–37.

Lu, Z.Q.; Liu, Y.; Barreto, V.; Pohl, C.; Avdalovic, N.; Joyce, R.; Newton, B. Determination of anions at trace levels in power plant water samples by ion chromatography with electrolytic eluent generation and suppression. *Journal of Chromatography A* 2002, *956*, 129–138

Lyddy-Meaney, A.J.; Ellis, P.S.; Worsfold, P.J.; Butler, E.C.V.; McKelvie, I.D. A compact flow injection analysis system for surface mapping of phosphate in marine waters. *Talanta* 2002, *58*, 1043–1053.

Mackenzie, F.T.; Ver, L.M.; Sabine, C.; Lane, M.; Lerman, A. C, N, P, S biogeochemical cycles and global change. In *Interactions of C, N, P, and S Biogeochemical Cycles and Global Change*; Wollast, R., Mackenzie, F. T., Chou, L. Eds.; Springer: Verlag, Berlin 1993; pp. 1–61.

Mahowald, N.M.; Artaxo, P.; Baker, A.R; Jickells, T.D.; Okin, G.S.; Randerson, J.T.; Townsend, A.R. Impacts of biomass burning emissions and land use change on Amazonian atmospheric phosphorus cycling and deposition. *Global Biogeochemical Cycles* 2005, *19*, GB4030; doi:10.1029/2005GB002541.

Mahowald, N.; Jickells, T.D.; Baker, A.R.; Artaxo, P.; Benitez-Nelson, C.R.; Bergametti, G.; Bond, T.C.; Chen, Y.; Cohen, D.D.; Herut, B.; Kubilay, N.; Losno, R.; Maenhaut, C.L.W.; McGee, K.A.; Okin, G.S.; Siefert, R.L.; Tsukuda, S. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. *Global Biogeochemical Cycles* 2008, *22*, GB4026; doi:10.1029/2008GB003240.

Maher, W.; Krikowa, F.; Wruck, D.; Louie, H.; Nguyen, T.; Huang, W.Y.; Determination of total phosphorus and nitrogen by oxidation with alkaline potassium peroxidisulfate and low temperature microwave digestion, autoclave heating or the use of closed vessel in hot water bath: Comparison with kjeldahl digestion. *Analytica Chimica Acta* 2002, *463*, 283–293.

Markaki, Z.; Oikonomou, K.; Kocak, M.; Kouvarakis, G.; Chaniotaki, A.; Kubilay, N.; Mihalopoulos, N. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: spatial and temporal variability and its role in seawater productivity. *Limnology and Oceanography* 2003, *48*, 1557–1568.

Marra, J.; Ho, C. Initiation of the spring bloom in the northeast Atlantic (47°N, 20° W): a numerical simulation. *Deep-Sea Research II* 1993, *40*(1-2), 55–73.

Martin, J.H.; Coale, K.H.; Johnson, K.S.; Fitzwater, S.E.; Gordon, R.M.; Tanner, S.J.; Hunter, C.N.; Elrod, V.A.; Nowicki, J.L.; Coley, T.L.; Barber, R.T.; Lindley, S.; Watson, A.J.; Van Scoy, K.; Law, C.S.; Liddicoat, M.I.; Ling, R.; Stanton, T.; Stockel, J.; Collins, C.; Anderson, A.; Bidigare, R.; Ondrusek, M.; Latasa, M.; Millero, F.J.; Lee, K.; Yao, W.; Zhang, J.Z.; Friederich, G.; Sakamoto, C.; Chavez, F.; Buck, K.; Kolber, Z.; Greene, R.; Falkowski, P.; Chisholm, S.W.; Hoge, F.; Swift, R.; Yungel, J.; Turner, S.; Nightingale, P.; Hatton, A.; Liss, P.; Tindale, N.W. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 1994, *371*, 123–129.

Martin, J.M.; Elbaz-Poulichet, F.; Guieu, C.; Loye-Pilot, M.D.; Han, G. River versus atmospheric input of material to the Mediterranean Sea: an overview. *Marine Chemistry* 1989, *28*, 159–182.

Mattusch, J.; Wennrich, R. Elimination of sulfate interferences in the Chromatographic determination of o-phosphate using liquid-liquid extraction. *Fresenius' Journal of Analytical Chemistry* 1996, *356*(5), 335–338.

Mayewski, P.; Meeker, L.D.; Morrison, M.C.; Twickler, M.S.; Whitlow, S.I.; Ferland, K.K.; Meese, D.A.; Legrand, M.R.; Steffensen, J.P. Greenland ice core "signal" characteristics: An expanded view of climate change. *Journal of Geophysical Research* 1993, *98*, 12,839–12,847.

Mayewski, P.A.; Meeker, L.D.; Twickler, M.S.; Whitlow, S.I.; Yang, Q.; Lyons,W.B.; Prentice, M. Major features and forcing of high latitude northern hemisphere atmospheric circulation over the last 110,000 years. *Journal of Geophysical Research* 1997, *102*(C12), 26,345–26,366.

McClain, C.R.; Arrigo, K.; Tai, K.S.; Turk, D. Observations and simulations of physical and biological processes at ocean weather station P, 1951-1980. *Journal of Geophysical Research* 1996, *101*(C2), 3697–3713.

McDowell, R.W.; Sharpley, A.N.; Condrom, L.M.; Haygarth, P.M.; Brookes, P.C. *Nutrient Cycling in Agroecosystems* 2001, *59*, 269–284.

McMurry, P.H. A review of atmospheric measurements. *Atmospheric Environment* 2000, *34*,1959–1999.

Michaels, A.F.; Siegel, D.A.; Johnson, R.J.; Knap, A.H.; Galloway, J.N.; Episodic inputs of atmospheric nitrogen to the Sargasso Sea: contributions to new production and phytoplankton blooms. *Global Biogeochemical Cycles* 1993, *7*, 339–351.

Migon, C.; Morelli, J.; Nicolas, E.; Copin-Montégut, G. Evaluation of total atmospheric deposition of Pb, Cd, Cu and Zn to the Ligurian Sea. *The Science of the Total Environment* 1991, *105*, 135–148.

Migon, C.; Sandroni, V. Phosphorus in rainwater: partitioning inputs and impact on the surface coastal ocean. *Limnology and Oceanography* 1999, *44*(4), 1160–1165.

Migon, C.; Sandroni, V.; Béthoux, J.P. Atmospheric input of anthropogenic phosphorus to the northwest mediterranean under oligotrophic conditions. *Marine Environmental Research* 2001, *52*(5), 413–426.

Moore, R.M.; Milley, J.E.; Chatt, A. The potential for biological mobilization of trace elements from aeolian dust in the ocean and its importance in the case of iron. *Oceanologica Acta* 1984, *7*, 221–228.

Moore, J.K.; Doney, S.C.; Kleypas, J.A.; Glover, D.M.; Fung, I.Y. An intermediate complexity marine ecosystem model for the global domain. *Deep-Sea Research II* 2002, *49*(1-3), 403–462.

Moore, J.K.; Doney, S.C.; Lindsay, K. Upper ocean ecosystem dynamics and iron cycling in a global three-dimensional model. *Global Biogeochemical Cycles* 2004, *18*(4), Art. No. GB4028.

Morales, J.A.; Demedina, H.L.; Denava, M.G.; Velasquez, H.; Santana, M. Determination of organic acids in rain water in the state of Zulia, Venezuelia. *Journal of Chromatography A* 1994, *671*, 193–196.

Muraleedharan, T.R.; Rajojevic, M.; Waugh, A.; Caruana, A. Chemical characteristics of haze in Brunei Darussalam during the 1998 episode. *Atmospheric Environment* 2000, *34*, 2725–2731.

Morgan, M. G.; Henrion, M. The Nature and Sources of Uncertainty. In *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*;. Cambridge University Press: New York 1990; pp. 47–72.

Moy, L.A.; Dickerson, R.R.; Ryan W.F. Relationship between back trajectories and tropospheric trace gas concentrations in rural Virginia. *Atmospheric Environment* 1994, *28*, 2789–2800.

Narukawa, M.; Kawamura, K.; Takeuchi, N.; Nakajima, T. Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires. *Geophysical Research Letters* 1999, *26*, 3101–3104.

NEA *National Environment Agency*, Ministry of the Environment and Water Resources, Singapore; URL: http://app.nea.gov.sg/psi/.

Neff, J.C.; Holland, E.A.; Dentener, F.J.; McDowell, W.H.; Russell, K.M. The origin, composition and rates of organic nitrogen deposition: a missing piece of the nitrogen cycle?. *Biogeochemistry* 2002, *57/58*, 99–136

Nichol, J. Bioclimatic impacts of the 1994 haze event in Southeast Asia. *Atmospheric Environment* 1997, *31*, 1209–1219.

Nichol, J. Smoke haze in Southeast Asia: a predictable recurrence. *Atmospheric Environment* 1998, *32*, 2715–2716.

Nicholls, K.H; Cox, C.M. Atmospheric nitrogen and phosphorus loading to Harp Lake, Ontario, Canada. *Water Resources Research* 1978, *14*, 589–592.

Nielsen, T.; Pilegaard, K.; Egelarv, A.H.; Granby, K.; Hummelshøj, P.; Jensen, N.O.; Skov, H. Atmospheric nitrogen compounds: occurrence, composition and deposition. *The Science of the Total Environment* 1996, *189/190*, 459–465.

Nixon, S.W. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* 1995, *41*, 199–219.

NRC (National Research Council) *Clean coastal waters. Understanding and reducing the effects of nutrient pollution*; National Academy Press: Washington, D.C, 2000.

Okuda, T.; Kumata, H.; Zakaria, M.P.; Naraoka, H.; Ishiwatari, R.; Takada, H. Source identification of Malaysian atmospheric polycylcic aromatic hydrocarbons nearby forest fires using molecular and isotopoic compositions. *Atmospheric Environment* 2002, *36*, 611-618.

Orlic, I.; Welan, B.; Watt, F.; Tang, S.M. Air pollution in Singapore: Its multielemental aspect as measured by nuclear analytical techniques. *Environmental Monitoring and Assessment* 1997, *44*, 455–470.

Orlic, I.; Wen, X.; Ng, T.H.; Tang, S.M. Two years of aerosol pollution monitoring in Singapore: A review. *Nuclear Instruments and Methods B* 1999, *150*, 457–464.

Orlob, G.T. *Mathematical modelling of water quality: Streams, lakes and reservoirs*; Wiley: Chichester, UK, 1983; p. 518.

Oschlies, A.; Garcon, V. An eddy-permitting coupled physical- biological model of the North Atlantice-1. Sensitivity to advection numerics and mixed layer physics. *Global Biogeochemical Cycles* 1999, *13*(1), 135–160.

OSPAR *Current status of elaborated ecological quality objectives for the Greater North Sea with regard to nutrients and eutrophication effects (EcoQOs–eutro)*; OSPAR EUC/01/5/3-Rev.1. Meeting of the Eutrophication Commitee (EUC): Berlin, 26-30 Nov 2001, 2001.

Owens, N.J.P.; Galloway, J.N.; Duce, R.A. Episodic atmospheric nitrogen deposition to the oligotrophic oceans. *Nature* 1992, *357*, 397–399.

Paerl, H.W. Coastal eutrophication in relation to atmospheric nitrogen deposition: Current perspectives. *Ophelia* 1995, *41*, 237–259.

Paerl, H.W. Coastal eutrophication and harmful algal blooms importance of atmospheric deposition and groundwater as new nitrogen and other nutrient sources. *Limnology Oceanography* 1997, *42*(5/2), 1154–1165.

Paerl, H.W.; Fogel, M.L. Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters. *Marine Biology* 1994, *119*, 635–645.

Paerl, H.W.; Boynton, W.R.; Dennis, R.L.; Driscoll, C.T.; Greening, H.S.; Kremer, J.N.; Rabalais, N.N.; Seitzinger, S.P. Atmospheric deposition of nitrogen in coastal waters: biogeochemical and ecological implications. In *Nitrogen loading in coastal water bodies, coastal and estuarine studies No. 57*; Valigura, R.A., Alexander, R.B., Castro, M.S., Meyers TP, Paerl HW, Stacey PE, Turner RE, Eds.; American Geophysical Union Press: Washington, D.C. 2000; pp. 11–52.

Pang, W.C.; Tkalich, P. Modeling tidal and monsoon driven currents in the Singapore Strait. *Singapore Maritime and Port Journal* 2003, 151–162.

Pang, W.C.; Tkalich, P.; Chan, E.S. Hydrodynamic forecast model for the Singapore Straits. In *Proceedings of the XXX IAHR Congress*; August 2003, Thessaloniki, Greece, 2003.

Pang, W.C.; Tkalich, P. Semi-implicit sigma-coordinate hydrodynamic model. In *Proceedings: 14th IAHR-APD Congress*; 15-18 Dec. 2004, Hong Kong, pp.489–494, 2004.

Parsons, T.R.; Maita, Y.; Lalli, C.M. *A manual of chemical and biological methods for seawater analysis*; Pergamon Press: New York, 1984; p.173.

Peierls, B.L.; Paerl, H.W. The bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton. *Limnology Oceanography* 1997, *42*, 1819–1880.

Persson, G., Jansson, M. Eds. *Phosphorus in freshwater ecosystems*; Kluwer Academic Publishers: Dordrecht, 1988; Reprinted from Hydrobiologia 170.

Pillai, A.G.; Naik, M.S.; Momin, G.A.; Rao, P.S.P.; Safai, P.D.; Ali, K.; Rodhe, H.; Granat, L. Studies of wet deposition and dustfall at Pune, India. *Water, Air and Soil Pollution* 2001, *130*, 475–480.

Pinckney, J.L.; Cifuentes, L.A.; Gill, G. *Assessing the importance of atmospheric deposition of pollutants to nearshore waters of the Gulf of Mexico*; Texas AandM University, 2001. http://www-ocean.tamu.edu/~pinckney/deposition.htm

Poor, N.; Pollman, C.; Tate, P.; Begum, M.; Evans, M.; Campbell, S. Nature and magnitude of atmospheric fluxes of total inorganic nitrogen and other inorganic species to the Tampa Bay watershed, FL, USA. *Water, Air and Soil Pollution* 2006, *170*, 267–283.

Porter, K.S. *Nitrogen and phosphorus: Food production, waste and the environment*; Ann Arbor Science Publishers: Ann Arbor, Michigan, U.S.A., 1975.

Prospero J.M.; Savoie D.L. Effect of continental sources on nitrate concentrations over the Pacific Ocean. *Nature* 1989, *339*, 687–689.

Prospero, J.M.; Barrett, K.; Church, T.; Dentener, F.; Duce, R.A.; Galloway, J.N; Levy II, H.; Moody, J.; Quinn, P. Atmospheric deposition of nutrients to the North Atlantic Basin. *Biogeochemistry* 1996, *35*(1), 27–73.

Pryor, S.C.; Barthelmie, R.J. Particle dry deposition to water surfaces: processes and consequences. *Marine Pollution Bulletin* 2000, *41*, 220–231.

Qadri, S. T. *Fire, smoke, and haze: The ASEAN response strategy*; A joint publication of Asian Development bank (ADB) and the Association of Southeast Asian Nations (ASEAN): Metro Manila, Philippines, 2001; 246p; http://www.adb.org/Documents/Reports/Fire_Smoke_Haze/.

Qi, J.; Li, P.; Li, X.; Feng, L.; Zhang, M. Estimation of dry deposition fluxes of particulate species to the water surface in the Qingdao area, using a model and surrogate surfaces. *Atmospheric Environment* 2005, *39*, 2081–2088.

Rabalais, N. Nitrogen in aquatic ecosystems. *Ambio* 2002, *31*, 102–112.

Radojevic, M. The haze in Southeast Asia. *Environmental Scientist* 1997, *6*(6), 1–3.

Radojevic, M. Burning issues. *Chemistry in Britain* 1998, *34*(12), 38–42.

Radojevic, M.; Hassan, H. Air quality in Brunei Darussalam during the 1998 haze episode. *Atmospheric Environment* 1999, *33*, 3651–3658.

Radojevic, M.; Tan, K.S. Impacts of biomass burning and regional haze on the pH of rainwater in Brunei Darussalam. *Atmospheric Environment* 2000, *34*, 2739–2744.

Radojevic, M. Haze research in Brunei Darussalam during the 1998 Episode. *Pure and applied geophysics* 2003, *160*, 251–264

Reckhow, K.H.; Chapra, S.C. Modeling excessive nutrient loading in the environment. *Environmental Pollution* 1999, *100*, 197–207.

Redfield, A.C. The biological control of chemical factors in the environment. *American Scientist* 1958, *46*, 205–221.

Redfield, A.C.; Ketchum, B.H.; Richard, F.A. The influence of organisms on the composition of seawater. In *The Sea*; Hill, M.N. Ed.; Interscience: New York 1966; pp 26–77.

Reichert, P.; Omlin, M. On the usefulness of over parameterized ecological models. *Ecological Modelling* 1997, *95*, 289–299.

Reid, J.S.; Hobbs, P.V. Physical and optical properties of young smoke from individual biomass fires in Brazil. *Journal of Geophysical Research* 1998, *103*, 32013–32030.

Reid, J.S.; Koppmann, R.; Eck, T.F.; Eleuterio, D.P. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmospheric Chemistry and Physics* 2005, *5*, 799–825.

Rejesus, R.M.; Hornbaker, R.H. Economic and environmental evaluation of alternative pollution-reducing nitrogen management practices in Central Illinois. *Agriculture, Ecosystems and Environment* 1999, *75*, 41–53.

Rendell, A.R.; Ottley, C.J.; Jickells, T.D.; Harrison, R.M. The atmospheric input of nitrogen species to the North Sea. *Tellus* 1993, *45B*, 53–63.

Ridame, C.; Guieu, C. Saharan input of phosphorus to the oligotrophic water of the open western Mediterranean. *Limnology and Oceanography* 2002, *47*, 856–869.

Roberts, G.; Hudson, J.A.; Blackie, J.R. Nutrient inputs and outputs in a forested and grassland catchment at Plynlimon, mid-Wales, Agric. *Water Management* 1984, *9*, 177–191.

Rodhe, H.; Soderlund, R.; Ekstedt, J. Deposition of airborne pollutants on the Baltic. *Ambio* 1980, *9*, 168–173

Rosenberg, R.; Elmgren, R.; Fleischer, S.; Jonsson, P.; Persson, G.; Dahlin, H. Marine eutrophication case studies in Sweden. *Ambio* 1990, *19*, 102–108.

Russell, K.M.; Galloway, J.N.; Macko, S.A.; Moody, J.L.; Scudlark, J.R. Sources of nitrogen in wet deposition to the Chesapeake Bay region. *Atmospheric Environment* 1998, *32*, 2453–2465.

Saltelli, A.; Tarantola, S.; Campolongo, F. Sensitivity analysis as an ingredient of modeling. *Statistical Science* 2000, *15*, 377–395.

Schlesinger, W.H.; Hartley, A.E. A global budget for atmospheric NH_3. *Biogeochemistry* 1992, *15*(3), 191–211.

Scudlark, J.R.; Russell, K.M.; Galloway, J.N.; Church, T.M.; Keene, W.C. Organic nitrogen in precipitation at the mid-Atlantic US coast - Methods evaluation and preliminary measurements. *Atmospheric Environment* 1998, *32*, 1719–1728.

Seaton, A.; MacNee, W.; Donaldson, D.; Goddon, G. Particulate air-pollution and acute health-effects. *Lacent* 1995, *345*(8943), 176–178.

See, S.W.; Balasubramanian, R.; Wang, W. A study of the physical, chemical and optical properties of ambient aerosol particles in Southeast Asia during hazy and non hazy days. *Journal of Geophysical Research* 2006, *111*, D10S08; doi:10.1029/2005JD006180.

See, S.W.; Balasubramanian, R.; Elizabeth, R.; Karthikeyan, S.; Streets, D.G. Characterization and source apportionment of airborne particulate matter ≤2.5 μm in Sumatra, Indonesia during recent Peat fire episode. *Environmental Science and Technology* 2007a, *41*, 3488–3494.

See, S.W.; Wang, Y.H.; Balasubramanian, R. Contrasting reactive oxygen species and transition metal concentration in combustion aerosols. *Environmental Research* 2007b, *103*, 317–324.

Seinfeld, J.H.; Pandis S.N. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*; 2nd ed.; John Wiley: New York, 2006; 1203 pp.

Seitzinger, S.P.; Sanders, R.W. Atmospheric inputs of dissolved organic nitrogen stimulates estuarine bacteria and phytoplankton. *Limnology and Oceanography* 1999, *44*, 721–730.

Seitzinger, S.P.; Harrison, J.A.; Dumont, E.; Beusen, A.H.W.; Bouwman, A.F. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: an overview of Global NEWS models. *Global Biogeochemical Cycles* 2005, *19*, GB4S05; doi:10.1029/2005GB002453.

Selman, M.; Greenhalgh, S.; Diaz, R.; Sugg, Z. *Eutrophication and hypoxia in coastal areas: A global assessment of the state of knowledge*; WRI Policy Note, Water Quality: Eutrophication and Hypoxia No.1, Washington, D.C., 2008; http://pdf.wri.org/eutrophication_and_hypoxia_in_coastal_areas.pdf.

Sharp, J. H. The distribution of dissolved inorganic and organic nitrogen in the sea. In *Nitrogen in the marine environment*; Carpenter, E.J., Capone, D.G., Eds.; Academic Press: New York 1983; pp.1–35.

Sharp, J.H.; Rinker, K.R.; Savidge, K.B.; Abell, J.; Benaim, J.Y.; Bronk, D.; Burdige, D.J.; Cauwet, G.; Chen, W.; Doval, M.D.; Hansell, D.; Hopkinson, C.; Kattner, G.; Kaumeyer, N.; McGlathery, K.J.; Merriam, J.; Morley, N.; Nagel, K.; Ogawa, H.; Pollard, C.; Pujo-Pay, M.; Raimbault, P.; Sambrotto, R.; Seitzinger, S.; Spyres, G.; Tirendi, F.; Walsh, T.W.; Wong, C.S.; A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater. *Marine Chemistry* 2002, *78*, 171– 184.

Shaw, R.W. Air pollution by particles. *Science of the Total Environment* 1987, *255*, 96–103.

Shaw, R.D.; Trimbee, A.M.; Minty, A.; Fricker, H.; Prepas, E.E. Atmospheric deposition of phosphorus and nitrogen in central Alberta with on Narrow Lake. *Water Air Soil Pollution* 1989, *42*, 119–143.

Sehmel, G.A. Particle and gas dry deposition: a review. *Atmospheric Enuironment* 1980, *14*, 983–1011.

Shon, Z.-H. Atmospheric input of nitrogen to the coastal region of southeastern Texas. M.S. thesis, Texas AandM University, College Station, 1994.

Skjøth, C. A., Hertel, O., Ellermann, T., 2002. Use of a trajectory model in the Danish nation-wide background programme. *Physics and Chemistry of Earth* 27 (35), 1469–1477.

Skogen, M.D.; Svendsen, E.; Berntsen, J.; Aksnes, D.; Ulvestad, K.B. Modeling the primary production in the North-Sea using a coupled 3-dimensional physicalechemicalebiological ocean model. *Estuarine, Coastal and Shelf Science* 1995, *41*(5), 545–565.

Slingsby, R.W.; Pohl, C.A. Approaches to sample preparation for IC: sulfate precipitation on barium-form ion exchangers. *Journal of Chromatography A* 1996, *739*, 49–55.

Slinn, S.A.; Slinn, W.G.N. Predictions for particle deposition on natural waters. *Atmospheric Environment* 1980, *14*, 1013–1016.

Slinn, W.G.N. Predictions for particle deposition to vegetative canopies. *Atmospheric Environment* 1982, *16*, 1785–1794.

Smetacek, V.; Bathmann, U.; Nothig, E.M.; Scharek, R. Coastal eutrophication: Causes and consequences. In *Ocean margin processes in global change*; Mantoura, R.C.F., Martin, J.M., Wollast, R., Eds.; John Wiley and Sons: Chichester 1991; pp 251–279.

Smith, V. Eutrophication of freshwater and coastal marine ecosystems: a global problem. *Environmental Science and Pollution Research* 2003, *10*(2), 126–139.

Smil, V. Nitrogen in crop production: an account of global flows. *Global Biogeochemical Cycles* 1999, *13*, 647–662

Spokes, L.; Jickells, T.; Rendell, A.; Schulz, M.; Rebers, A.; Dannecker, W.; Kruger, O.; Leermakers, M.; Baeyens, W. High atmospheric nitrogen deposition events over the Sea, North Sea. *Marine Pollution Bulletin* 1993, *26*, 698–703.

Spokes, L.J.; Yeatman, S.G.; Cornell, S.E.; Jickells, T.D. Nitrogen deposition to the eastern Atlantic Ocean: The importance of south-easterly flow. *Tellus* 2000, *52B*, 37–49.

Stocks, B.J.; Kauffman, J.B. Biomass consumption and behavior of wildland fires in boreal, temperate, and tropical ecosystems: Parameters necessary to interpret historic fire regimes and future fire scenarios. In *Sediment records of biomass burning and global change*; Clark, J.S., Cachier, H., Goldammer, J.G., Stocks, B.J., Eds.; Springer-Verlag: Berlin, Germany 1997: pp 169–188.

Sundarambal, P.; Tkalich, P. Assessment of accidental nutrient spills from ships into the Singapore marine environment. In *Proceedings Asia Oceania Geosciences Society (AOGS) 2005*; Singapore 2005.

Sundarambal, P.; Balasubramanian, R.; Karthikeyan, S.; Tkalich, P. Atmospheric deposition of nutrients and its role on coastal eutrophication in Southeast Asia. In *Advances in Geosciences, Vol. 9: Solid Earth, Ocean Science and Atmospheric Science*, Chen, Y.-T. Ed.; World Scientific Publishing Company: Singapore 2007; pp. 149–166.

Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Enhancement and Development of Water Quality Model (NEUTRO) for Atmospheric Deposition Loads. In *Proceedings Asia Oceania Geosciences Society (AOGS) 2008*; Korea 2008a.

Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Numerical assessment of atmospherically promoted seawater phytoplankton production: Significance of wet deposition events of nitrogen compounds. *Geophysical Research Abstracts* 2008b, *10*, EGU2008-A-05134.

Sundarambal, P.; Dao, M. H.; Tkalich, P. Modeling of hydrodynamic and water quality processes in coastal zones. In *Proceedings International Conference on Marine*

Problems and Specific Solutions (COMPASS) 2008; 15-18 Jun 2008, Maldives 2008c.

Sundarambal, P.; Balasubramanian, R.; Tkalich, P. Impacts of atmospheric nutrients deposition on aquatic ecosystems. In *Proceedings International Conference on Marine Problems and Specific Solutions (COMPASS) 2008*; 15-18 Jun 2008, Maldives 2008d.

Sundarambal, P.; Liong, S. Y.; Tkalich, P. ANN application for water quality forecasting. *Marine Pollution Bulletin* 2008e, *56*(9), 1586–1597.

Sundarambal, P.; Balasubramanian, R.; Tkalich, P. Atmospheric fluxes of nutrients onto Singapore Strait. *Water Science and Technology* 2009a, 59(11), pp. 2287-2295.

Sundarambal, P.; Liong, S. Y.; Tkalich, P. Eutrophication modeling of Singapore seawater using Artificial Neural Networks. In *Advances in Geosciences - Vol. 12: Ocean Science*: Jianping Gan et al., Eds., World Scientific Publishing Company: Singapore 2009b; pp.55–70.

Sundarambal, P.; Liong, S. Y.; Tkalich, P.; Jegathambal, P. Development of a neural network model for dissolved oxygen in seawater. *Indian Journal of Marine Sciences* 2009c, *38*(2).

Sundarambal, P.; Tkalich, P. Numerical 3-D water quality model (NEUTRO) for eutrophication and pollutant transport. *Marine Environmental Research* 2009, Submitted-a.

Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Modeling the effect of atmospheric nitrogen deposition on marine phytoplankton at the Singapore Strait. *Water Science and Technology* 2010a, 61(4), pp.859-867.

Sundarambal, P.; Balasubramanian, R.; Tkalich, P.; He, J. Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Field observations. *Atmospheric Chemistry Physics Discussion* 2010b, 10, pp.7745–7778, in Special issue: Measurement and modeling of aerosol emissions from biomass burning.

Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Eutrophication modeling. *Atmospheric Chemistry Physics Discussi*on 2010c, 10, pp.7779–7818.

Swackhamer, D.L.; Paerl, H.W.; Eisenreich, S.J.; Hurley, J.; Hornbuckle, K.C.; McLachlan, M.; Mount, J.; Muir, D.; Schindler, D. Impacts of atmospheric pollutants on aquatic systems. *Issues in Ecology* 2004, *12*, 2–23.

Swap, R.; Garstang, M.; Greco, S.; Talbot, R.; Kallberg, P. Saharan dust in the Amazon Basin. *Tellus* 1992, *44B*(2), 133–149.

Tanner, P.A.; Fai, T.W. Concentrations of bulk deposition from Hong Kong. *Water, Air, and Soil Pollution* 2000, *122*, 433–448.

Tani, M.; Shida, K.S.; Tsutsuki, K.; Kondo, R. Determination of low molecular weight organic acid in soils by ion chromatography. *Soil Science and Plant Nutrition* 2001, *47*, 387–397.

Tarrant, R.F.; Lu, K.C.; Chen, C.S.; Bollen, W.B. Nitrogen content of precipitation in a coastal Oregon forest opening. *Tellus* 1968, *20*, 554–556.

Thomann, R.V.; Di Toro, D.M.; Winfield, R.P.; O'Connor, D.J. *Mathematical modeling of phytoplankton in Lake Ontario, 1: model development and verification*; USEPA National Environmental Research Center: Office of Research and Development, Corvallis, OR, 1975; EPA-600/-75-005.

Thomann, R.V. The future “golden age” of predictive models for surface water quality and ecosystem management. *Journal of Environmental Engineering* 1998, *124*(2), 95–103.

Thomann, R.V.; Muller, J.A. *Principles of surface water quality modelling and control*; Harper and Row Publishers: Newyork, 1987.

Tian, R.C.; Vezina, A.F.; Starr, M.; Saucier, F. Seasonal dynamics of coastal ecosystems and export production at high latitudes: a modeling study. *Limnology and Oceanography* 2001, *46*, 1845–1859.

Timperley, M.H.; Vigor-Brown, R.J.; Kawashima, M.; Ishigami, M. Organic nitrogen compounds in atmospheric precipitation: their chemistry and availability to phytoplankton. *Canadian Journal of Fisheries and Aquatic Science* 1985, *42*, 1171–1177.

Tkalich, P.; Pang, W.C.; Sundarambal, P. Hydrodynamics and eutrophication modelling for Singapore Straits. In *Proceedings of The seventh workshop on ocean models for the APEC Region (WOM-7)*; Singapore 2002; pp. 5–1-5–9.

Tkalich, P.; Sundarambal, P. Eutrophication modelling for the Singapore waters. *Singapore Maritime and Port Journal* 2003, 122–136.

Turnbull, A.B.; Harrison, R.M. Major component contributions to PM_{10} composition in the UK atmosphere. *Atmospheric Environment* 2000, *34*, 3129–3137.

Turner, D.B. Comparison of three methods for calculating the standard deviation of the wind direction. *Journal of Climate and Applied Meteorology* l986, *25*, 703–707.

Turner, R.K. Integrating natural and socio-economic science in coastal management. *Journal of Marine Systems* 2000, *25*, 447–460.

UNESCAP and ADB *State of the Environment in Asia and Pacific 2000*; Economic and Social Commission for Asia and the Pacific and Asian Development Bank, New York, United Nations, 2000; ST/ESCAP/2098; http://www.unescap.org/esd/environment/soe/2000/

UNEP *Wildland fires and the environment: A global synthesis*; Levine, J.S., Bobbe, T., Ray, N., Singh, A., Witt, R.G., Eds.; United Nations Environment Programme (UNEP): Nairobi, Kenya, 1999; UNEP/DEIAEW/TR.99-1.

UNEP and WHRC *Reactive nitrogen in the environment: Too much or too little of a good thing*; United Nations Environment Programme: Paris, 2007; 51p.

Urban, N.R.; Eisenreich, S.J. Nitrogen cycling in a forested Minnesota bog. *Canadian Journal of Botany* 1988, *66*, 435–449.

USEPA (U.S. Environmental Protection Agency) *Particulate matter (PM) speciation guidance, Final Draft, Edition 1*; U.S. Environmental Protection Agency: Monitoring and Quality Assurance Group. Emissions, Monitoring and Analysis Division. Office of Air Quality Planning and Standards. Research Triangle Park, NC, 1999.

Valderrama, J.C. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry* 1981, *10*(2), 109–122.

Valiela, I.; Teal, J.M.; Volkmann, S.; Shafer, D.; Carpenter, E.J. Nutrient and particulate fluxes in a salt marsh ecosystem: Tidal exchanges and inputs by precipitation and groundwater. *Limnology and Oceanography* 1978, *23*, 798–812.

Valiela, I.; Teal, J.M. The nitrogen budget of a salt marsh ecosystem. *Nature* 1979, *280*, 652–656.

Valigura, R.A.; Luke, W.T.; Artz, R.S.; Hicks, B.B. *Atmospheric nutrient input to coastal areas: Reducing the uncertainties*; Decision Analysis Series no. 9; Coastal ocean program, National Oceanic and Atmospheric Administration: Silver Spring, MD, 1996.

Valigura, R.A., Alexander, R.B., Castro, M.S., Meyers, T.P., Paerl, H.W., Stacey, P.E., Turner, R.E., Eds. *Nitrogen loading in coastal water bodies: An atmospheric perspective*; American Geophysical Union: Washington, D.C., USA, 2000; pp. 11–52.

van den Berg, A.; Dentener, F.; Lelieveld, J. Modelling the chemistry of the marine boundary layer: Sulfate formation and the role of sea-salt aerosol particles. *Journal of Geophysical Research* 2000, *105*, 11671–11698.

Van Dolah, F.M.; Roelke, D.; Greene, R.M. Health and ecological impacts of harmful algal blooms: risk assessment needs. *Human and Ecological Risk Assessment* 2001, *7*(5), 1329–1345.

Verry, E.S.; Timmons, D.R. Waterborne nutrient flow through an upland-peatland watershed in Minnesota. *Ecology* 1982, *63*, 1456–1467.

Vitousek, P.M.; Aber, J.D.; Howarth, R.W.; Likens, G.E.; Matson, P.A.; Schindler, D.W.; Schlesinger, W.H.; Tilman, D.G. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 1997, *7*, 737–750

Wall, S.M.; John, W.; Ondo, J.L. Measurement of aerosol size distribution for nitrate and major ionic species. *Atmospheric Environment* 1988, *22*, 1649–1656.

Watson, R.T.; Meira Filho, L.G.; Sanhueza, E.; Janetos, A. Greenhouse gases: sources and sinks. In *Climate change 1992: the supplementary report to the IPCC scientific assessment*; Houghton, J.T., Callander, B.A., Varney, S.K., Eds.; Cambridge University Press: Cambridge 1992; pp. 23-46.

Watson, A.J. *Surface Ocean-Lower Atmosphere Study (SOLAS)*; Global Change Newsletter: IGBP, 31, September, 1997; pp. 9–12.

WDOE (State of Wasington Department of Environment), 1986. *Comprehensive circulation and water quality study at Budd inlet, Southern Puget Sound water quality assessment study*; Prepared by URS Corporation for the Washington State Department of Ecology, 27.

Williams, P.M. Sea surface chemistry: Organic carbon and organic and inorganic nitrogen and phosphorus in surface films and subsurface waters. *Deep-Sea Research* 1967, *14*, 791–800.

William, R.M. A model for the dry deposition of particles to natural water surfaces. *Atmospheric Environment* 1982, *16*(8), 1933–1938.

Wilson, A.T. Organic nitrogen in New Zealand snows. *Nature* 1959, *183*, 318–319.

WHO (World Health Organization) *WHO guidelines for air quality*; Fact Sheet No.187, World Health Organization: Switzerland, Geneva, 1997; http://www.who.int/inf-fs/en/fact187.html.

WHO *Biregional workshop on health impacts of haze-related air pollution (Kuala Lumpur, Malaysia, 1-4 June 1998)*; World Health Organization: Kuala Lampur, Malaysia, 1998.

World Bank *World development indicators*; The World Bank: Washington, D.C., United States, 1997.

Xianren, Q.; Baeyens, W. The chemical composition of precipitation and atmospheric aerosols in relation to rain water acidity. In *Global and Regional Atmospheric Chemistry*; Proceedings of the International Conference on Global and Regional Atmospheric Chemistry: Bejing, China, 1990; pp. 622–625.

Xiaohua Eutrophication studies of Singapore's coastal waters. M.Engg. Thesis, Department of Civil Engineering, National University of Singapore, Singapore, 2000.

Yamartino, R.J. A comparison of several "single-pass" estimators of the standard deviation of wind direction. *Journal of Climate and Applied Meteorology* 1984, *23*, 1362–1366.

Yang, X.S.; Miller, D.R.; Xu, X.; Yang, L.H.; Chen, H.-M.; Nikolaidis, N.P. Spatial and temporal variations of atmospheric deposition in interior and coastal Connecticut. *Atmospheric Environment* 1996, *30*(22), 3801–3810.

Yang, H.H.; Hsieh, L.T.; Cheng, S.K. Determination of atmospheric nitrate particulate size distribution and dry deposition velocity for three distinct areas. *Chemosphere* 2005, *60*, 1447–1453.

Yi, T.C. Water quality studies of Singapore coastal waters: measurement of micro-zooplankton grazing rates. M.Engg. Thesis, Department of Civil Engineering, National University of Singapore, Singapore, 2001.

Yokelson, R.J.; Susott, R.; Ward, D.F.; Reardon, J.; Griffith, D.W.T. Emissions from smouldering combustion from biomass measured by open-path fourier transform infrared spectroscopy. *Journal of Geophysical Research* 1997, *102*, 18865–18877.

Yokelson R.J.; Susott, R.A.; Babbitt, R.E.; Hao, W.M.; Ward, D.E. Trace gas emissions from specific biomass fire types. In *Proceeding of SARCS/IGAC/LUCC Synthesis workshop on greenhouse gas emission, aerosols and land use and cover change in Southeast Asia*; Moya, T.B., Ed.; China-Taipei, 15-18 Nov 1997, Republic of China 1999; pp. 60–68.

Yong, K.C. Air quality monitoring in Singapore. In *Proceeding of The regional workshop on Better Air Quality in Asia and Pacific Rim Cities*; 16– 18 Dec 2002, Hong Kong Convention and Exhibition Centre (HKCEC), Hong Kong 2002; http://www.cleanairnet.org/caiasia/1412/article-35730.html

Zhang, H.; Chan, E.S. The physical characteristics of the water column in Singapore Straits. In *Proceeding of the Oceanology International 99 Pacific Rim*, 26-29 April 1999, Singapore 1999.

Zhang, Q.Y. A three-dimensional eutrophication model for Singapore costal waters. PhD Dissertation, National University of Singapore, Singapore, Singapore, 2000.

Zhang, L.; Gong, S.; Padro, J.; Barrie, L. A Size-Segregated Particle Dry Deposition Scheme for an Atmospheric Aerosol Module. *Atmospheric Environment* 2001, *35*, 549–560.

Zhang, J.Z.; Chi, J. Automated analysis of nanomolar concentrations of phosphate in natural waters with liquid wave guide. *Environmental Science and Technology* 2002, *36*, 1048–1053.

Zhang, G.; Zhang, J.; Liu, S. Characterization of nutrients in the atmospheric wet and dry deposition observed at the two monitoring sites over Yellow Sea and East China Sea. *Journal of Atmospheric Chemistry* 2007, *57*, 41–57.

Zhuang, H.; Chan, C.K.; Fang, M.; Wexler, A.S. Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong. *Atmospheric Environment* 1999, *33*, 843–853.

APPENDIX A: LIST OF PUBLICATIONS FROM THIS WORK

A.1 Journal Articles

1. Sundarambal, P.; Balasubramanian, R.; Tkalich, P. Atmospheric fluxes of nutrients onto Singapore Strait. *Water Science and Technology* 2009, 59(11), pp. 2287-2295.
2. Karthikeyan, S.; He, J.; Sundarambal, P.; Balasubramanian, R.; Burger, D. Determination of total nitrogen in atmospheric wet and dry deposition samples. *Talanta* 2009, *77*(3), 979-984; doi:10.1016/j.talanta.2008.07.053.
3. Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Modeling the effect of atmospheric nitrogen deposition on marine phytoplankton at the Singapore Strait. *Water Science and Technology* 2010, 61(4), pp.859-867.
4. Sundarambal, P.; Balasubramanian, R.; Tkalich, P.; He, J. Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Field observations. *Atmospheric Chemistry Physics Discussion* 2010, 10, pp.7745–7778; In Special issue: Measurement and modeling of aerosol emissions from biomass burning, H. Moosmuller, A. Chen, and T. Kirchstetter. Eds.
5. Sundarambal, P.; Tkalich, P.; Balasubramanian, R. Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Eutrophication modeling. *Atmospheric Chemistry Physics Discussion* 2010, 10, pp.7779–7818.

6. Sundarambal, P; Tkalich, P; Balasubramanian, R.; Jegathambal, P. ANN application for prediction of atmospheric nitrogen deposition onto aquatic ecosystem. *Atmospheric Environment* 2010; Under Review.
7. Sundarambal, P.; Tkalich, P. Numerical 3-D water quality model (NEUTRO) for eutrophication and pollutant transport. *Marine environmental Research* 2009; Under Review.

A.2 Book Chapters

1. Sundarambal, P.; Balasubramanian, R.; Karthikeyan, S.; Tkalich, P. Atmospheric deposition of nutrients and its role on coastal eutrophication in Southeast Asia. In *Advances in Geosciences, Vol. 9: Solid Earth, Ocean Science and Atmospheric Science*, Chen, Y.-T. Ed.; World Scientific Publishing Company: Singapore 2006; pp. 149–166. This paper is abstracted in NASA's Astrophysics Data System http://adsabs.harvard.edu/abs/2006aogs....9..149P.

A.3 Meetings and Conferences

1. Sundarambal, P; Tkalich, P; Balasubramanian, R.; Jegathambal, P. Prediction of atmospheric nitrogen deposition onto aquatic ecosystem using artificial neural network. In *Proceedings of IAHR-APD 2010*: Auckland, New Zealand 2010.
2. Sundarambal, P; Balasubramanian, R.; Tkalich, P. Quantification of the effects of atmospheric nutrient deposition to coastal marine eutrophication, In *Proceedings of ChemBiotech '09-10 conference*: Chemical and Biomolecular Engineering, National University of Singapore, Singapore 2010.
3. Sundarambal, P; Tkalich, P; Balasubramanian, R.; Jegathambal, P. Prediction of atmospheric nitrogen deposition onto aquatic ecosystem using artificial neural network. In *Proceedings of IAHR-APD 2010*: Auckland, New Zealand 2010.

4. Sundarambal, P; Balasubramanian, R.; Tkalich, P. Nonpoint pollution of surface waters with nutrients: biomass burning in Southeast Asia. In *Proceedings of EWRI's 3rd developing nation's conference India 2010 - An International Perspective on Current and Future State of Water Resources and the Environment*: IIT Madras, Chennai, India 2010.
5. Sundarambal, P; Balasubramanian, R.; Tkalich, P.; Sing L. C.; Teo S. Prediction of atmospheric dry deposition of total phosphorous using neural network. In *Proceedings of EWRI's 3rd developing nation's conference India 2010 - An International Perspective on Current and Future State of Water Resources and the Environment*: IIT Madras, Chennai, India 2010.
6. Sundarambal, P.; Balasubramanian, R.; Tkalich, P.; He, J. Biomass burning in Southeast Asia and its impact on aquatic ecosystems. In *Proceedings of AAAR 2009*: Minneapolis, USA, 2009 and also in *Workshop on N deposition, Critical loads and Biodiversity*: Scotland, UK, 2009.
7. Sundarambal, P; Balasubramanian, R.; Tkalich, P. Modeling the impact of atmospheric nutrient deposition onto tropical surface water quality during hazy and non-hazy days. In *Proceedings of Asia Oceania Geosciences Society (AOGS 2009)*: Singapore 2009.
8. Sundarambal, P; Tkalich, P; Balasubramanian, R. Marine nutrient pollution and environmental issues of Southeast Asia. In *Proceedings of the Third International Conference in Ocean Engineering (ICOE 2009)*: IIT Madras, India 2009.
9. Sundarambal, P; Tkalich, P; Balasubramanian, R. Numerical assessment of atmospherically promoted seawater phytoplankton production: Significance of

wet deposition events of nitrogen compounds. In *Proceedings of EGU General Assembly 2008*: Vienna, Austria 2008.

10. Sundarambal, P; Tkalich, P.; Balasubramanian, R. Enhancement and development of water quality model (NEUTRO) for atmospheric deposition loads. In *Proceedings of Asia Oceania Geosciences Society (AOGS) 2008*: Korea 2008.

11. Sundarambal, P.; Dao, M. H.; Tkalich, P. Modeling of hydrodynamic and water quality processes in coastal zones, In *Proceedings of COMPASS 2008*: Maldives 2008.

12. Sundarambal, P.; Balasubramanian, R.; Tkalich, P. Impacts of atmospheric nutrients deposition on aquatic ecosystems –A review. In *Proceedings of COMPASS 2008*: Maldives 2008.

13. Sundarambal, P; Tkalich, P; Balasubramanian, R. Modeling studies of the effect of atmospheric nitrogen deposition on marine phytoplankton in seawater, South-East Asia. In *Proceedings of 12th International Conference on Integrated Diffuse Pollution Management (IWA DIPCON 2008)*: Thailand 2008.

14. Sundarambal, P.; Balasubramanian, R.; Tkalich, P. Estimating nutrients loading from atmospheric deposition on coastal waters, South-East Asia. In *Proceedings of IWA DIPCON 2008*: Thailand 2008.

15. Sundarambal, P.; Balasubramanian, R.; Karthikeyan, S.; Tkalich, P. Estimating direct atmospheric nitrogen deposition onto a coastal waterbody in Southeast Asia and its bioavailability to coastal phytoplankton. In *Proceedings AOGS 2007*: Bangkok 2007.

16. Sundarambal, P.; Balasubramanian, R.; Karthikeyan, S.; Tkalich, P. Coastal eutrophication in Southeast Asia: Importance of atmospheric deposition of nutrients. In *Proceedings of AOGS 2006*: Singapore 2006.
17. Sundarambal, P.; Tkalich, P. Assessment of accidental nutrient spills from ships into the Singapore marine environment. In *Proceedings of AOGS 2005*: Singapore 2005.
18. Tkalich, P.; Sundarambal, P. Nutrient dynamics in Singapore coastal water. In *Proceedings of AOGS 2004*: Singapore 2004.