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# A 3-D MODEL ON THE POSSIBLE ROLE OF ATMOSPHERIC DEPOSITION IN TROPICAL COASTAL EUTROPHICATION

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***ABSTRACT.*** — Human activities often lead to increased inputs of nutrients from point and distributed sources into the coastal environment, causing algal blooms and eutrophication. The pollution load from point sources can be quantified and controlled directly since they are discrete and identifiable locations; however, airborne admixtures cannot be easily be quantified since they are dispersed and highly variable in time and space. Recent research has suggested that atmospheric deposition can be a major source of nutrients to aquatic ecosystems. It is important to identify and quantify nutrients deposited onto the water surface and subsequent biogeochemical cycles for understanding the eutrophication potential and primary productivity in the ocean. In a view of recurring forest and peat fires in Southeast Asia (SEA) and abundant rainfall in tropical Southeast Asia, the role of atmospheric deposition of nutrients contributing towards coastal zone pollution in Singapore may be significant. The nutrients (nitrogen (N) and phosphorus (P) species) from atmospheric fallout of airborne particles through dry atmospheric deposition (DAD) and wet atmospheric deposition (WAD) to the ocean surface were investigated in this study. The atmospheric deposition of nutrients was determined through periodical field monitoring of airborne particles and rainwater, as well as laboratory measurements of nutrients. It was observed that the average concentration of nutrients in WAD was higher than DAD and increased significantly on hazy days to those with non-hazy days. An estimation of atmospheric deposition of nutrient fluxes and their possible impacts on aquatic ecosystems using a three-dimensional (3-D) numerical eutrophication model "NEUTRO" are discussed. NEUTRO model computations showed that smoke haze episodes were a significant source of nutrients to the coastal waters around Singapore and appear to play an important role in the coastal eutrophication.

***KEY WORDS.*** — Atmosphere, wet and dry deposition, nutrients fluxes, tropical environment, coastal waters, eutrophication, Singapore Strait, water quality model

## INTRODUCTION

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. 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. Eutrophication of coastal waters is recognized as a major environmental problem and a threat to the health of marine ecosystems all around the world (Seitzinger et al., 2005). In recent years, the occurrence of Harmful Algal Blooms (HABs) has increased dramatically in Southeast Asia (SEA) and have been reported in Indonesia, Thailand, Brunei Darussalam, Singapore, Vietnam, Philippines (Bajarias and Relox, 1996; Azanza and Taylor, 2001; Sim, 2010), and Hong Kong (Kedong, 2004). Various factors can influence the rate of eutrophication, including climate change, land utilization pattern and coastal geomorphology. Increases in nutrient concentration, changes in N:P ratio, accelerated phytoplankton primary production and biomass, malfunctioning of marine

ecosystems and reduction of biodiversity, increases in sedimentation and light reduction, depletion of oxygen concentration as well as downstream effects on economy and human health implications are some of the consequences of eutrophication (OSPAR, 2001). A need exists to identify key nutrient sources (and changes therein) supporting eutrophication and its socio-economic consequences. In recent decades, nutrient loads and concentrations in coastal waters and the open sea have increased 10–20 fold (Jickells, 1998). The external supply of nutrients to aquatic ecosystems can originate from point sources (ex. Sewage and industrial outfalls) that are localized and thus more easily monitored and controlled, or from nonpoint/distributed sources (ex. runoff, atmospheric wet and dry depositions), which are diffuse and much more difficult to monitor and regulate. Atmospheric deposition (AD) has recently gained attention as a significant additional source of nutrient loading to the coastal and open seas, either as "wet atmospheric deposition (WAD)" or as "dry atmospheric deposition (DAD)" (Figure 1). These nutrients may be delivered constantly during the year, in a pulse due to an accidental release, or periodically driven by human activities and environmental fluctuations. The excessive supply of biologically active nutrients such as nitrogen (N) and phosphorus (P), silica, iron and various trace metals could cause coastal/ocean eutrophication and alter biogeochemical cycles (Duce et al., 1991; Duce et al. 2008). The global projected ratio of the estimated deposition of oxidized nitrogen in 2020 to that for 1980 is between 1.5 and 3 and in some limited areas up to 4 (Watson, 1997). Airborne P typically accounts for 10 to 20 percent of total phosphorus loading to water bodies from all sources (Swackhamer et al., 2004).

Recurring forest and peat fires on a large scale in SEA, especially in Indonesia, combined with abundant rainfall in this region together may contribute significantly to the atmospheric fallout of particles (dry deposition) and wet deposition of nutrients into aquatic systems (Balasubramanian et al., 1999; Sundarambal, 2009). It is necessary to bring together field-based investigations to quantify atmospheric nutrient deposition and eutrophication modeling to investigate the impact of atmospheric nutrient deposition on coastal water quality. Hence, both field-based investigations and modeling work are addressed here. This study quantifies critically important individual nutrient species, fills the knowledge gap on the significance of AD of nutrients pertaining to coastal water eutophication, and provides a scientific basis for a more in-depth future study in this region. The water-soluble nutrients (N and P species only) resulting from DAD (aerosol particulates) and WAD (rainwater) to the coastal waters in Singapore are quantified. The atmospheric nutrients analyzed were: 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 ($PO^{3-}_4$), total phosphorous (TP) and organic phosphorous (OP). The three dimensional (3-D) numerical eutrophication model "NEUTRO" was used to simulate various biochemical processes in the coastal water and explore various possible scenarios concerning the atmospheric deposition of nutrients.

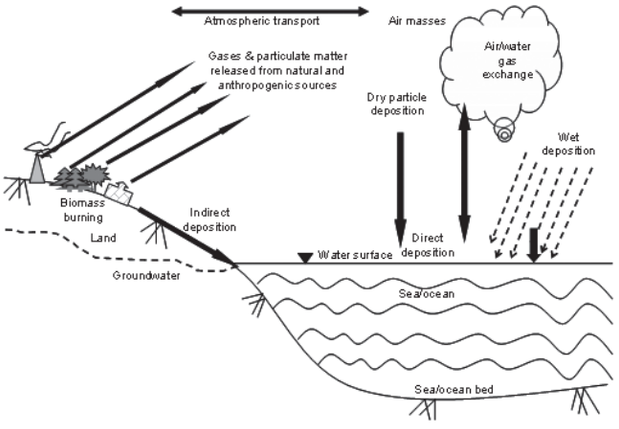


Fig. 1. Schematic illustration of atmospheric deposition processes.

## MATERIAL AND METHODS

***Study area.*** — Singapore is a small island nation with total land area of 710 km$^2$ located approximately 137 km north of the Equator, between latitudes 1°09'N and 1°29'N, and longitudes 103°36'E and 104°25'E. The Johor Strait in the North and the Singapore Strait in the South comprise the coastal waters of Singapore. The Singapore Strait is a shallow and narrow water body connected to the South China Sea and Pacific Ocean to the east and the Indian Ocean via the Strait of Malacca to the west. The seabed topography of the Singapore Strait is complicated, ranging from 30m to the maximum depth of 120 m (Chan et al., 2006). Singapore is highly urbanized and industrialized with limited freshwater resources and confined ocean environment surrounding the island. Because of its geographical location, Singapore's climate is characterized by uniform temperature and pressure, high humidity and abundant rainfall throughout the year. Singapore has two main seasons, the Northeast Monsoon (NEM) (November to March) and the Southwest Monsoon (SWM) season (June to September). Southwest (SW) and Northeast (NE) winds occur in the coastal area periodically. Smoke haze has been observed frequently due to forest and peat fires in neighbouring countries.

***Sampling location, sample collection and analysis.*** — Both aerosol and rainwater samples were collected at the Tropical Marine Science Institute (TMSI) on St. John's Island (SJI; 1°13'10"N, 103°50'54"E), Singapore. SJI was selected due to its proximity to the open coastal environment in the southern part of Singapore and free from major air pollution except on regional hazy days. Dry deposition (from aerosol samples; n=55) and wet deposition (rainwater samples; n=21) samples were collected at SJI during the 2006 SEA haze episode from September 2006 to January 2007 (days including hazy (October 2006) and non-hazy (November 2006 –January 2007) conditions). Pollution Standard Index (PSI), an indicator of ambient air quality, was obtained from the National Environment Agency (NEA) of Singapore for the entire sampling period. The PSI in Singapore is usually below 50 (i.e., the air quality is good) in the absence of regional

smoke haze episodes and goes beyond 50 (i.e., moderate to unhealthy range for air quality) when smoke haze of biomass burning origin is advected across Singapore. The hazy and non-hazy days were differentiated based on the PSI values. In addition, the satellite images and constructed backward air trajectories were used to confirm the presence of smoke haze and the origin of air masses received in Singapore, respectively. Aerosol samples (total suspended particulates (TSP)) were collected using a High Volume Air Sampler (HVAS, model 3800 AFC: HI-Q Environmental Products Company, USA). Rainwater samples were collected on an event-to-event basis by using an automated wet only rainwater sampler (Ecotech Model 200: Ecotech Pty Ltd, Australia), which is specially designed to collect only rainwater with no interference from dust fall and gases i.e. dry deposition. The rainwater collector remains completely sealed in the absence of rainfall and opens automatically upon commencement of rainfall. Seawater samples were also collected from 8 October 2006 to 20 January 2007 off the pontoon at SJI ferry terminal situated approximately 6.5 km south of Singapore in the Singapore Strait. The types of nutrients, N & P species from atmospheric wet and dry nutrient depositions were quantified by analyzing the collected aerosol and rainwater samples at SJI during hazy and non-hazy days using validated laboratory techniques (APHA, 2005; Sundarambal, 2009; Sundarambal et al., 2010a). The magnitude of wet deposition fluxes depends on precipitation rate (He & Balasubramanian, 2008; Karthikeyan et al., 2009a). The analytical quality of the data obtained was determined using suitable parameters such as limits of detection, recovery, linearity, and by eliminating sampling artifacts (Karthikeyan et al., 2009a, b). Daily rainfall and other meteorological parameters during the sampling period were obtained from an automated weather station by Department of Geography, NUS.

### *The 3-D Model and Parameters Used*

***Smoke haze episode during biomass burning.*** — Biomass burning is an important source of air pollution comprising trace gases and aerosol particles (Crutzen & Andreae, 1990; Balasubramanian et al., 1999), reactive nitrogen (Kondo et al., 2004) and phosphorus (Mahowald et al., 2005) which all affect global biogeochemical cycles. Elevated levels of airborne particulate matter occur in air impacted by biomass burning (Koe et al., 2001). Uncontrolled forest and peat fires are becoming more frequent in a number of SEA countries (Figure 2(a)). Hotspots in the northern and the southern parts of the SEA region respectively during NEM and the SWM period of El-Niño years resulted in transboundary haze pollution (Figure 2(b); Wang et al., 2004). During October 2006, Singapore air quality categories were either moderate

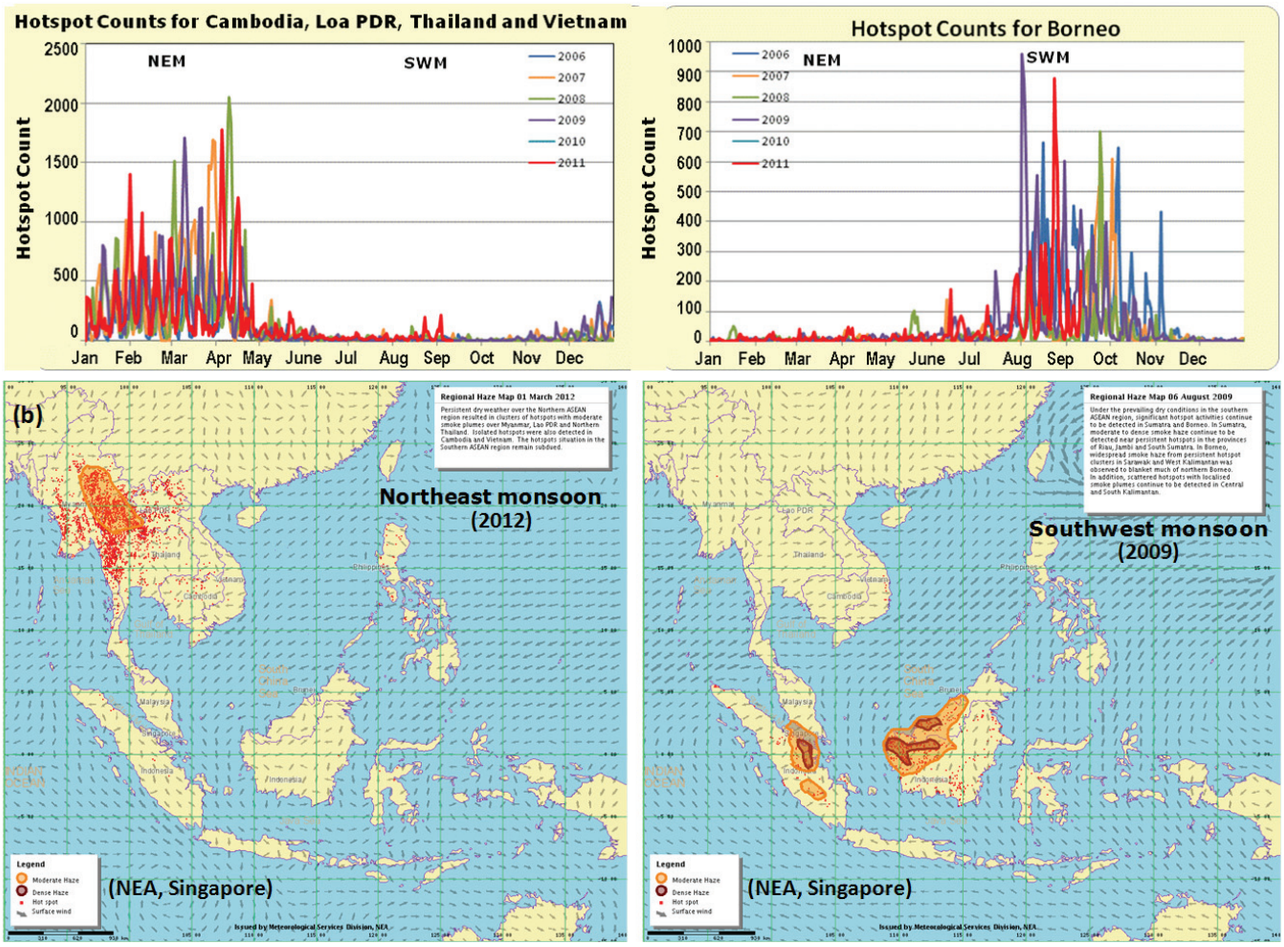


Fig. 2. (a) Hotspot counts at various countries from 2006 to 2011 and (b) smoke haze occurrences in Southeast Asia in 2012 (Northeast monsoon) and 2009 (Southwest monsoon) (NEA, Singapore).

or unhealthy based on PSI (NEA, Singapore). A high level of TSP (TSP~140 µg/m$^3$) was recorded in Singapore (this study) than during the 1997–98 haze event (TSP~110 µg/m$^3$; Balasubramanian et al., 1999). Although the impact of biomass burning on human health and the environment is well recognized, our understanding of atmospheric nutrient deposition resulting from biomass burning and their impact on regional air and water quality is very limited due to paucity of systematic field studies.

***Deposition flux calculations.*** — Dry deposition fluxes ($F_{dry}$ in g/m$^2$/year) are calculated from the product of dry deposition velocity ($V_d$ in cm/s) and measured concentrations of nutrient species ($C_{aerosol}$ in µg/m$^3$), as shown in Equation (1) with unit conversion factor of 0.31536 [=1/1000000 (g//m$^3$)*1/100 (m)*(365*24*60*60)(1/year)]. Owing to the absence of measured deposition rates, the reported $V_d$ values for phosphate, nitrate and ammonium are respectively 2.0, 1.2 and 0.6 cm/s and those assumed for both TN & ON, and TP & OP are 1.2 cm/s and 2 cm/s, respectively (Sundarambal et al., 2010a). Wet deposition fluxes ($F_{wet}$ in g/m$^2$/year) were calculated from the product of precipitation rate (P in m) and measured concentrations of nutrient species ($C_{rain}$ in mg/l) by Equation (2).

$$F_{dry} = 0.31536\ C_{aerosol}\ V_d \quad (1)$$

$$F_{wet} = C_{rain}\ P \quad (2)$$

***Hydrodynamics.*** — Seasonal variation of coastal hydrodynamics in Singapore is controlled by the Asian monsoon cycle. In the Singapore Strait, the influences of monsoon currents and tidal fluctuation are both significant. During the NEM, water is forced along the east coast of the Malay Peninsula and turns into the Singapore Strait, which diverts to the west and south with the main drift being from east to west. During the SWM, the main stream of water comes from the Java Sea in the south, going through Selat Durian and filtering through the Riau Islands, then flowing toward the eastern (SW) and western (NE) directions (Figure 3, Chan et al., 2006). Singapore tides are predominantly of a semi-diurnal nature with two high and two low tides per lunar day. The mean tidal elevation is about 2.2 m and the maximum range is up to 3 m during spring tides. In general, maximum tidal currents are typically less than 2 m/s in most parts of the Singapore Strait except in the narrow channel at the Singapore Deeps. In view of the large magnitude of tidal level variations and the associated currents in the coastal waters of Singapore, tidal hydrodynamic conditions are important for the assessment of baseline characteristics of Singapore marine environment. The tidal-driven currents in the Singapore coastal waters were computed using a 3-D hydrodynamic model (TMH), developed at TMSI, NUS (Pang & Tkalich, 2003). TMH was calibrated and validated using available high-quality data from the Singapore Strait and Johor Strait. TMH has been applied in several research coastal studies in the Singapore and Johor Straits.

***Water Quality.*** — In general, temperature and salinity variations in the tropical waters of the Singapore Strait are small. However, due to freshwater inflow from the Johor River and other rivers, the salinity in the Johor Strait is generally lower than the Singapore Strait. The water quality and plankton community in the Singapore water undergo significant short-term variations induced by tidal changes and seasonal variations imposed by monsoon cycles. Dissolved oxygen (DO) is higher near the surface, due to re-aeration from the atmosphere and photosynthesis, but subsequently decreases with depth. Nutrient levels in the Johor Strait are higher than the Singapore Strait. 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 imply that nutrient limitation can easily be switched with phosphorus. The measured concentration ranges of parameters at SJI ferry terminal (Figure 3) during the sampling period were: 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), $PO^{3-}_4$ (0.005– 0.015 mg/l), TP (0.028–0.035 mg/l) and PSI (23–109).

***3-D Eutrophication model (NEUTRO).*** — Pollutant inputs into a coastal system are naturally subject to complex chemical, biological, and physical processes that affect the concentration of the pollutants in the water column. 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 and forecasting data for impact assessment and environmental management. The 3-D eutrophication model (NEUTRO, Tkalich & Sundarambal, 2003) is being utilised in several research projects to predict the environmental impacts of coastal development and

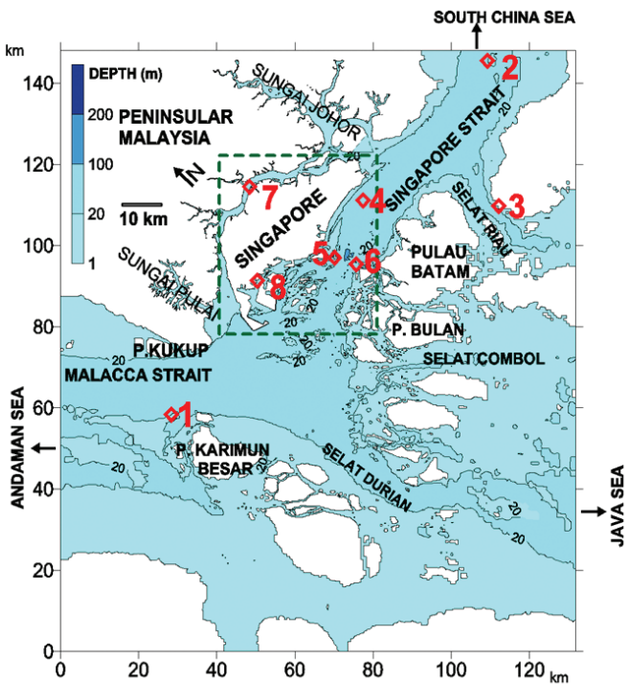


Fig. 3. Bathymetry of Singapore Strait and surrounding seas. Marked locations: 1: Pulau Iyu Kechil, 2: Horsburgh Lighthouse, 3: Tanjung Uban, 4: control point, 5: St. John's Island (SJI), 6: Pulau Lengkana,7: Sembawang, 8: Jurong, 9: Pulau Sebarok and10: Pulau Semakau (Derived from Chan et al., 2006).

discharges from point and distributed sources to assist in the management of Singapore's marine resources. NEUTRO consists of 3-D transport, WASP (US EPA model) kinetics (N, P, DO and plankton dynamics) and silica cycles. It takes into consideration tidal forcing, advection, diffusion and settling of the admixture and suspended particles, as well as chemical and physical kinetic reactions of the diluted and suspended substances. It is capable of assessing the possible system response to increases in nutrient and pollutant loading under typical hydrodynamic scenarios. NEUTRO was enhanced to incorporate atmospheric nutrients loading, and subsequently was utilized to investigate the relative influence of atmospherically deposited nutrients on coastal water eutrophication (Sundarambal et al., 2007). A typical SWM tidal current was computed using TMH having 500 m horizontal resolution and 10 vertical sigma layers. The computed concentrations were then compared with the ASEAN marine water quality criteria (ASEAN, 1995). Model concepts used, key parameters, calibration, validation, sensitivity analysis and modeling approach were outlined by Sundarambal (2009). Figure 4 shows an overview of field monitoring and modeling adopted in this study. In this field-based study, we quantified AD fluxes of nutrients from both dry and wet depositions, which were then fed into a 3-D water quality model (eutrophication modeling) using inputs from sources, ocean boundary and hydrodynamic forces. This modeling provides a qualitative as well as quantitative understanding of the relative importance of atmospheric nutrient fluxes in the region so as to provide an estimate of the contribution of atmospheric nutrients deposition toward regional eutrophication (Sundarambal et al., 2010b, c).

A scenario-based analysis was also carried out to evaluate the percentage nitrate-nitrogen flux in the water column due to biologically available nitrogen from atmospheric wet deposition (WD), and to simulate their impact for supporting significant fraction of excessive productivity in the Singapore coastal waters. During the wet monsoon season, the removal of gaseous and particle-bounded compounds dominates other depositional processes. It is crucial to consider its spatial and temporal variability since precipitation is an intermittent and local phenomenon. In this study, biologically available nutrients from WD were assumed to have been deposited uniformly onto the water surface, and then transported through the water column followed by its spatial distribution by the action of tidal current.

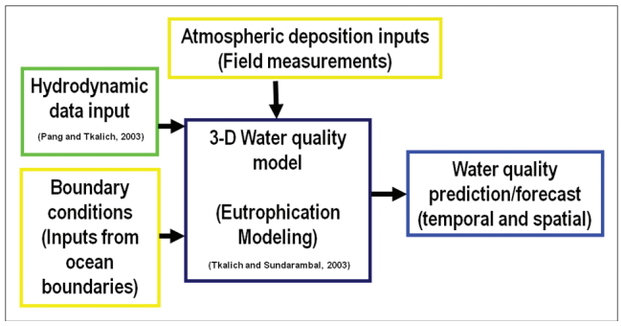


Fig. 4. Overview of field monitoring and modeling adopted in this study.

## RESULTS AND DISCUSSION

***Dry and Wet deposition.*** — Most chemical species (including inorganic ions) of atmospheric nutrients were higher on hazy days as compared to clear days (Sundarambal et al., 2010a). Day-to-day particle concentrations varied substantially in Singapore (Figure 5a) in response to spatial and temporal changes of meteorological factors such as wind conditions (red color arrows in Figure 5b), rainfall, and fire (hotspots in Figures 2 & 5b). Below-average rainfall was received in most areas of the ASEAN region during November 2006 and less than 50% of the normal rainfall in Singapore during September/November 2006. In general, dry weather is the result of either a lack of convection or a stable atmosphere that prevents the development of rain-bearing clouds. Air mass back trajectories were constructed for each sampling period to investigate the possible sources of particulate air pollution. We also assessed the origin, recent history and transport pathways of air masses received at the sampling site SJI in Singapore. The United States National Atmospheric and Oceanic Administration (NOAA) HYSPLIT-4 (HYbrid Single-Particle Lagrangian Integrated Trajectory; Draxler and Rholph, 2003) online transport and dispersion model using Meteorological data from NCEP's Global Data Assimilation System (GDAS, global, 2005-present) was used. Figure 5b shows the backward air trajectories, tracing the origin of air masses to Australia and Indian Ocean during the 2006 haze event, at different altitudes (NEA, Singapore). The prevailing southerly to southwesterly winds transported the smoke haze directly from southern Sumatra towards the Malacca Straits, peninsular Malaysia and Singapore. At the same time, the smoke haze was also influenced by the prevailing southeasterly winds from Kalimantan to Singapore. The air masses might contain mostly particulate matter and pollutants originating from biomass burning compared to those from other sources of air pollution. The PM concentration at SJI was largely dependent on the direction of the prevailing winds (with southeasterly to southwesterly winds favoring the transport of haze towards Singapore), fire activity (its location and intensity) and El Niño/Southern Oscillation (ENSO) (its effect on rainfall, atmospheric stability and convective activity).

Concentrations of most ions in rainwater were higher during periods of haze than during non-haze periods (Balasubramanian et al., 1999). Thus, the air pollution episodes affected the local air quality in Singapore, and contributed to the increase in TN content in precipitation samples (Sundarambal, 2009). The total budget showed that the biologically available N load to the surface water was more than ten times the biologically available P load to the surface water (Sundarambal et al., 2010a). 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 waters. The proportion of N & P species in DAD, WAD and Singapore seawater is shown in Figure 6.

***Deposition fluxes.*** — 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 magnitude of wet deposition fluxes depends on precipitation rate. The annual mean WAD fluxes of reactive ($NO_2$ + $NO_3$)-N and $PO_4$-P into the coastal waters of 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. 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 for hazy days. This observation is comparable to those made earlier for dry and wet atmospheric nitrogen fluxes during non-hazy days in Singapore (Karthikeyan et al., 2009a). The WAD flux is higher than the DAD flux. The high proportion of OP observed in this study (Figure 6) is consistent with those reported elsewhere (about 30–80% of TP; Mahowald et al., 2008). The deposition fluxes of P species in DAD are greater than WAD as both DIP and OP originate from soil and may be more associated with fine-mode aerosols (Anderson & Downing, 2006), which are less likely to be washed out by wet deposition (He & Balasubramanian, 2008). The high ratio of nutrients (N and P species) in aerosol and rainwater between hazy and non-hazy days in the order of factor of 3 to 8 (Sundarambal et al., 2010a) shows that smoke haze episodes provided a significant source of nutrients to the coastal waters in Singapore and SEA region.

***Significance of atmospheric deposition.*** — In this study, it was found that biomass burning in and around SEA is a significant source of nutrients (both the inorganic and organic fractions of water soluble inorganic and organic N and P species) through atmospheric deposition to the regional

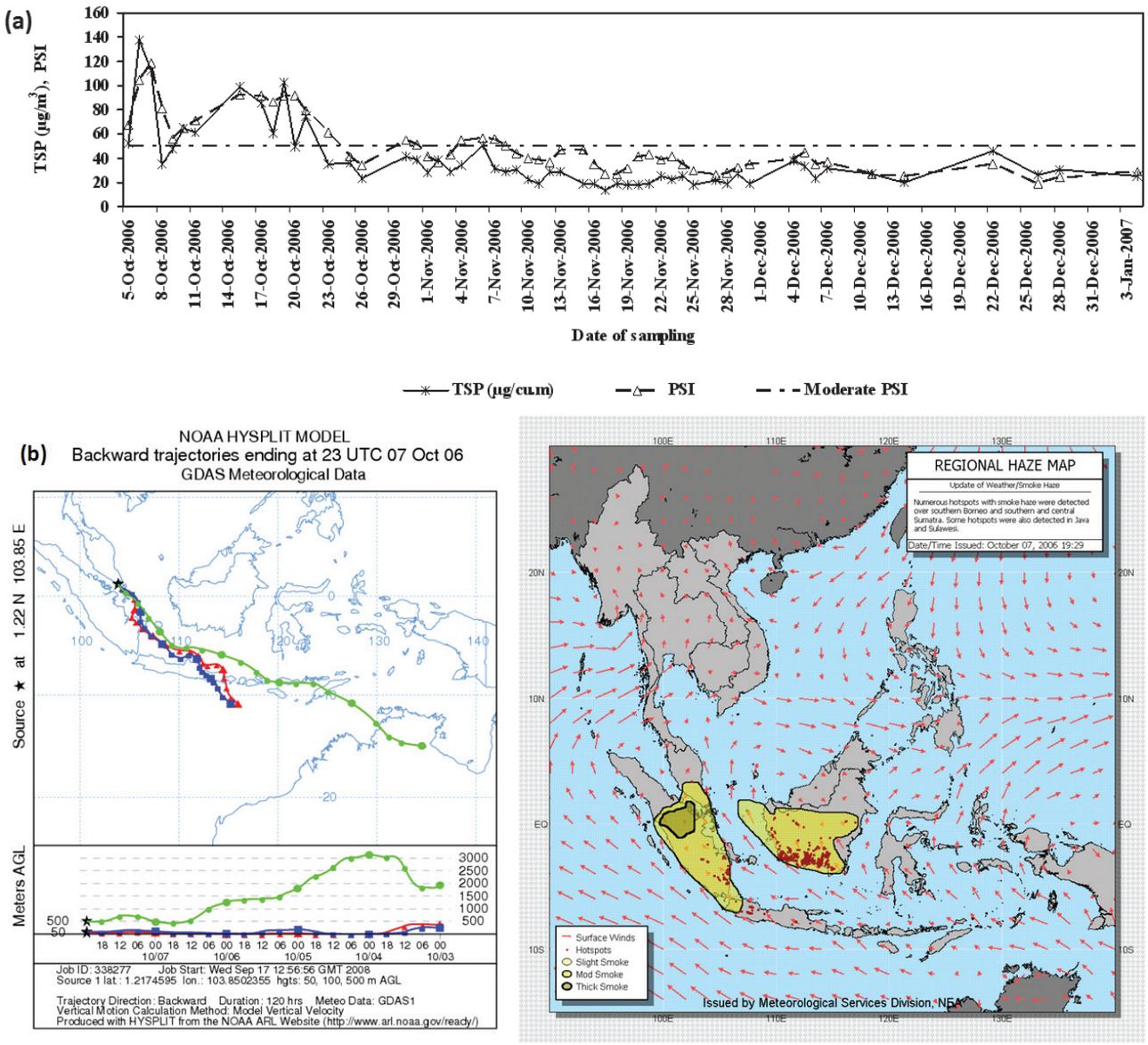


Fig. 5. Smoke haze events in SEA region and it effect on Singapore air quality: (a) Temporal changes in Total Suspended Particulate matter (TSP) concentrations and Pollutants Standard Index (PSI) from October 2006 to December 2006 in Singapore (NEA, Singapore), and (b) Air mass back trajectories (left) and the extent of the 2006 SEA smoke haze due to biomass burning in Indonesia (right) (NEA, Singapore).

surface water such as estuarine coastal waters and the open ocean during haze episodes. Dry and wet deposition fluxes trends are influenced by different meteorological conditions (He et al., 2011). Depending on the intensity of smoke haze events, nutrient fluxes of different magnitudes are delivered to Singapore coastal waters during dry episodes (Sundarambal et al., 2010a). 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 waters 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

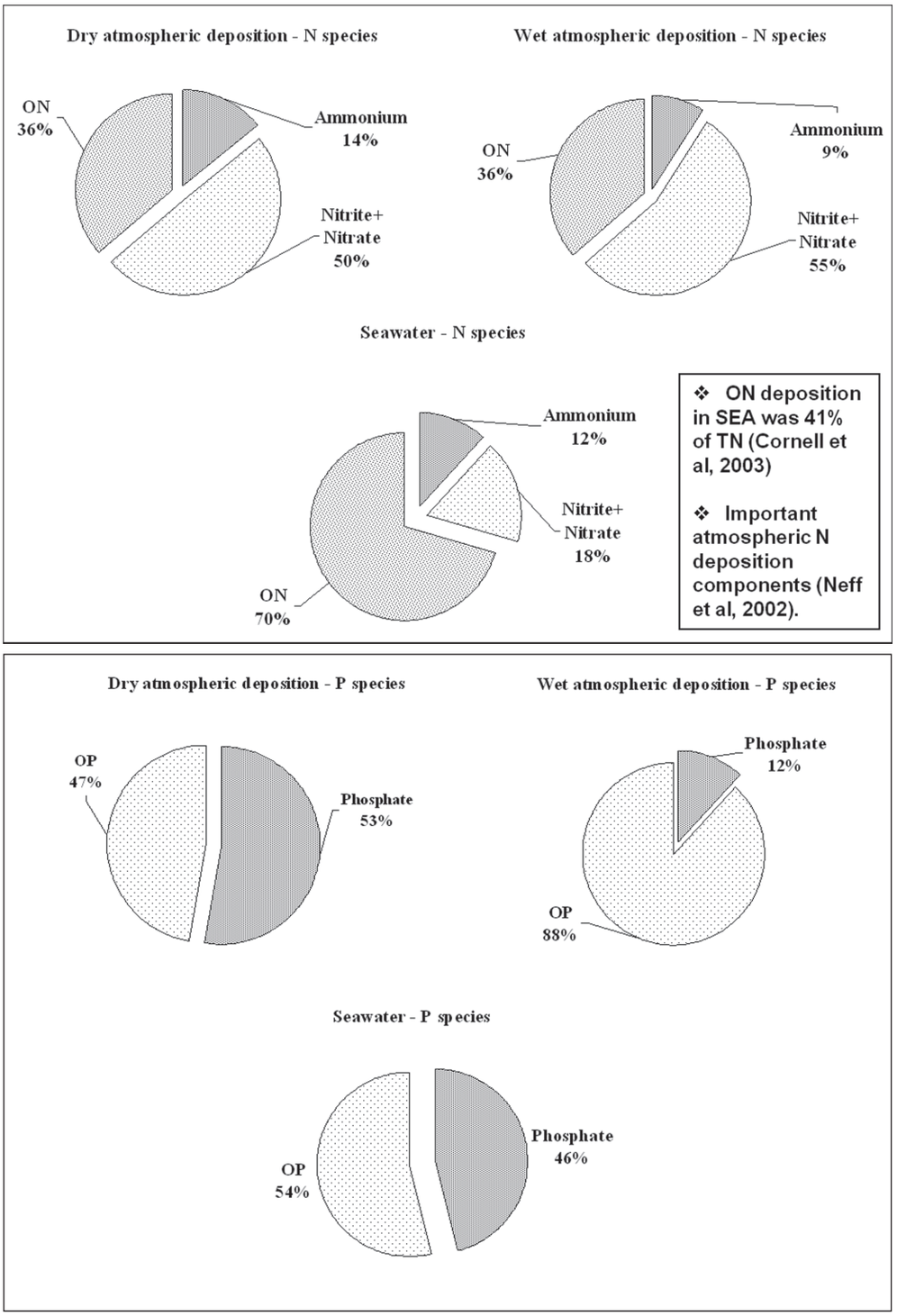


Fig. 6. The proportion of nitrogen and phosphorous species in dry atmospheric deposition, wet atmospheric deposition and Singapore seawater.

episodes. The impact of "new" atmospheric nutrient input into the Singapore coastal water was simulated using NEUTRO (Figure 7; see also Sundarambal et al., 2010b, c). The spatial and temporal dynamics of nutrients and plankton in the Singapore Strait was investigated from model simulations using a complete set of eutrophication kinetics, with realistic initial and boundary conditions (Sundarambal, 2009). This investigation provides a baseline for assessing the possible environmental effects of "new" AD of N and P compounds on coastal aquatic ecosystems. The spatial distribution of surface water phytoplankton concentration from their baseline (Figure 7b) indicates that nitrite + nitrate nitrogen from atmospheric fallouts provides an additional nutrient flux to the water column, thus promoting primary production. 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 (Figure 7a). 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 and vertical mixing in the Singapore Strait. From field measurements of AD nutrient concentrations, it is evident that there is higher nutrient input into water surface during periods of haze (Sundarambal et al., 2010a). The percentage increase in mass of nitrite+nitrate nitrogen in water surface due to AD N flux was typically limited to 4–24% during non-hazy days and 17–88% during hazy days (Sundarambal et al., 2010b). The increase in computed phytoplankton concentration from its baseline ranged between ~ 0.13 and 4.65% and its average percentage change was 2.62 ± 1.31% due to the episodic nitrite + nitrate nitrogen deposition event.

***Contribution to Eutrophication.*** — Eutrophication due to nutrient pollution from non-point sources is a global issue, and has greater impacts in the developing regions of the world like SEA. Atmospheric transport is a significant and increasing source of nutrient supply from the continents to the oceans and surface waters. Once the atmospheric nutrients enter surface seawater, the chemical form of the dissolved iron is altered, thus changing its solubility, retention and bioavailability in the euphotic zone. The impact of nutrient-enriched atmospheric inputs is enhanced under oligotrophic conditions (Chen et al., 2010). AD nutrients remain confined to the upper layer of the water column, enabling intense surface phytoplankton blooms (Harmful Algal Blooms) to occur (Michaels et al., 1993). Excessive N loading to surface waters is the key cause of accelerating eutrophication with associated environmental consequences (Nixon, 1995; Jickells, 1998). Ecological effects include enhanced productivity, but may also result in changes in species diversity, excessive algal growth, reduction in dissolved oxygen and associated fish kills, as well as the increased prevalence or frequency of toxic algal blooms. Regionally, atmospheric N inputs can have significant impacts on marine biogeochemistry, which potentially support >25% of export production (Krishnamurthy et al., 2010). Atmospherically derived dissolved ON may stimulate bacterial and algal growth (Peierls & Paerl, 1997) and selective growth of dinoflagellates and cyanobacteria (Antia et al., 1991).

The occurrences of increased AD nitrogen in SEA during smoke haze episodes have undesirable consequences on receiving aquatic ecosystems. Sundarambal (2009) recently reported the biogeochemical importance of the atmospheric N and P flux to the marine environment in Singapore and surrounding region. The N:P ratio has been widely used to determine whether the growth of phytoplankton in surface waters is N-limited or P-limited, based on the Redfield ratio of 106C:16N:1P (Ren et al., 2009). The N:P ratio in annual total (dry particulate + wet) atmospheric deposition flux in this study was 9.84, which was comparable to that (10.5) calculated from the data reported by He et al. (2011) but lower than the Redfield ratio. Gin et al. (2006) reported that Singapore waters were generally N limited; however, the variable anthropogenic inputs and a N:P ratio being close to the Redfield ratio imply that nutrient limitation can easily switch to phosphorus in the Johor Strait (see Sundarambal, 2009 and Sundarambal et al., 2010b, c). 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. It is concluded that while individual AD events are not probably responsible

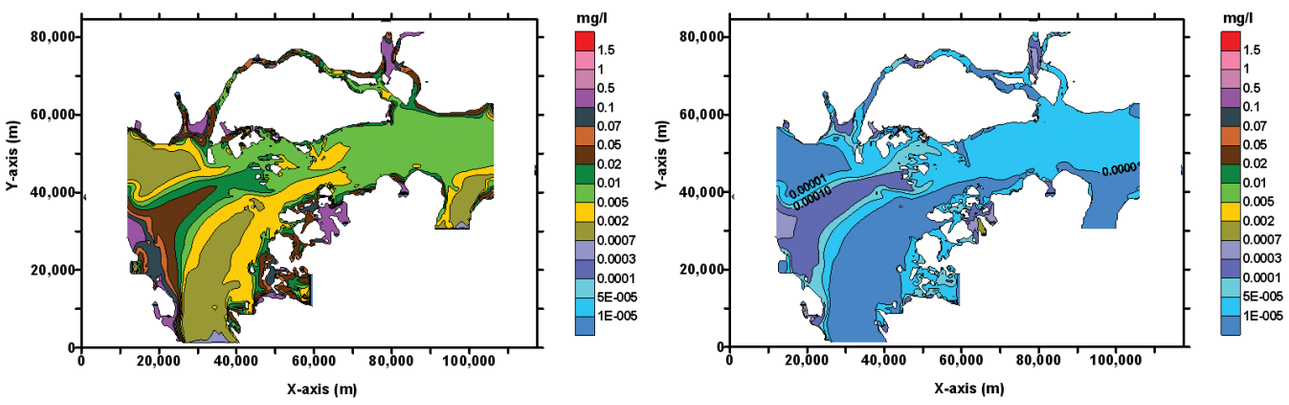


Fig 7. The absolute change of surface water (a) total nitrogen and (b) phytoplankton concentration from Singapore coastal water baseline due to the atmospheric wet deposition during October 2006 smoke haze event (Sundarambal et al., 2010b). The baseline concentrations of total nitrogen and phytoplankton were taken as 0.1109 mg/l and 0.02 mgC/l, respectively.

for triggering algal blooms as hypothesized, but long-term nutrient additions are important and do contribute to regional eutrophication problems under lower concentrations of nutrients or nutrient-depleted conditions in coastal waters. Atmospheric deposition needs to be considered at various time spatial scales, including short-term high deposition events and longer-term low deposition events.

***Recommendations and future directions.*** — Based on this study, future research directions and recommendations for the management of coastal water eutrophication in Singapore and surrounding areas due to nutrient input from atmosphere are listed below:

- Atmospheric fallout of nutrients should be monitored continuously based on a strategic network of sampling locations in Singapore and Southeast Asia. A long term regional field monitoring to collect representative temporal and spatial samples of both atmospheric deposition of nutrients and the corresponding changes in seawater is needed to establish the relationship between phytoplankton and atmospherically deposited nutrients in tropical coastal water.
- Database on atmospheric deposition and water quality should be acquired for regional environmental management. Tools like remote sensing and geostatistics can be applied to study the spread and distribution of atmospheric nutrient deposition.
- Conduct eutrophication modelling to simulate the effect of atmospheric nutrient deposition onto the marine water in the entire SEA region. 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.
- Estimate the contribution of atmospheric deposition to overall pollutant loadings in the Singapore and surrounding waters; 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 recommended.
- Investigate 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.
- Fill knowledge gaps on blooms and speciation of phytoplankton responsible for Harmful Algal Blooms; a good understanding of phytoplankton and model development are both needed for simulating harmful algal blooms accurately.
- Model emission, transport and fate of pollutants (especially nutrients), and calculate the "airshed" of distant as well as local sources, to estimate and characterize risk of atmospheric loadings on Singapore and surrounding waters.
- Examine and quantify the ecological effects of atmospheric deposition, to better quantify water quality benefits of air pollution controls.
- Quantify the transboundary contributions of pollutants of concern and to share technology, information, and expertise with other countries on reducing releases to the environment and on cost-effective alternatives to their use.

## CONCLUSIONS

Atmospheric deposition (AD) is a significant source of nutrients (both inorganic and organic N and P species) to aquatic ecosystems in tropical regions, especially during biomass burning in SEA where the smoke haze phenomenon is a major and recurring air pollution problem. 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. The present study was conducted to quantify both the inorganic and organic fractions of water-soluble N and P species in dry and wet atmospheric depositions to a tropical marine environment of Singapore. A systematic study on the methodologies of DAD and WAD measurements and the quantification of nutrients (N & P species) were carried out for the first time in Singapore during clear days and the SEA 2006 haze episode. It is found that the biologically available AD N load to the surface water is significantly more than 10 times the biologically available AD P load to the surface water. The WAD flux is higher than the DAD flux. The high ratio of the average concentration of nutrients (factor of 3 to 8) in aerosol and rainwater between hazy and clear days shows that smoke haze episodes provided a significant source of nutrients to the coastal waters in Singapore and SEA region. The quantified atmospheric deposition fluxes of nutrients provide a baseline to study the possible ecosystem responses to atmospheric nutrient inputs into the water surface. The biogeochemical importance of the atmospheric N and P flux to the Singapore coastal water was explored using eutrophication modeling. NEUTRO 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. In conclusion, we found that biomass burning in SEA is a highly significant source of nutrients through atmospheric deposition to the regional surface water such as estuarine, coastal waters and the open ocean during haze episodes.

Despite the uncertainty in quantifying atmospheric deposition and model computations, this study highlights the importance of addressing the issues of eutrophication in Singapore. The atmosphere is clearly a dominant source of "new' nutrients (N and P species) in the surface waters of Singapore and surrounding areas. Establishing field-monitoring sites and conducting modeling 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. 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.

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