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Impact of biomass burning on ocean water quality in Southeast Asia through atmospheric deposition: eutrophication modeling

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Abstract. Atmospheric deposition of nutrients (N and P species) can intensify anthropogenic eutrophication of coastal waters. It was found that the atmospheric wet and dry depositions of nutrients was remarkable in the Southeast Asian region during the course of smoke haze events, as discussed in a companion paper on field observations (Sundarambal et al., 2010b). The importance of atmospheric deposition of nutrients in terms of their biological responses in the coastal waters of the Singapore region was investigated during hazy days in relation to non-hazy days. The influence of atmospherically-derived, bio-available nutrients (both inorganic and organic nitrogen and phosphorus species) on the coastal water quality between hazy and non-hazy days was studied. A numerical modeling approach was employed to provide qualitative and quantitative understanding of the relative importance of atmospheric and ocean nutrient fluxes in this region. A 3-D eutrophication model, NEUTRO, was used with enhanced features to simulate the spatial distribution and temporal variations of nutrients, plankton and dissolved oxygen due to atmospheric nutrient loadings. The percentage increase of the concentration of coastal water nutrients relative to the baseline due to atmospheric deposition was estimated between hazy and non-hazy days. Model computations showed that atmospheric deposition fluxes of nutrients might account for up to 17 to 88% and 4 to 24% of total mass of nitrite + nitrate-nitrogen in the water column, during hazy days and non-hazy days, respectively. The results obtained from the modeling study could be used for a better understanding of the energy flow in the coastal zone system, 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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1 Introduction

Increasing population, industrialization and agricultural activities lead to an excessive supply of a wide variety of inorganic and organic nitrogen (N) and phosphorous (P) species to both the pelagic and coastal oceans through atmospheric deposition (AD) (Duce et al., 1991; Spokes et al., 1993; Cornell et al., 1995; Prospero et al., 1996; Herut et al., 1999, 2002; Paerl et al., 2000; De Leeuw et al., 2003; Mahowald et al., 2005, 2008). Sources of "new" nutrients in the open ocean are deep waters transported up into the euphotic zone by diffusive and advective processes, atmospheric inputs, and in the case of nitrogen, in situ fixation by marine organisms. AD being an important source of limiting nutrients could cause substantial increases in eutrophication of coastal regions, and modest productivity increases and food web alteration in oligotrophic pelagic regions (Jickells, 1995; Paerl, 1995, 1997; Markaki et al., 2003). Biomass burning being an important source of atmospherically-derived nutrients can lead to excess nutrient enrichment problems (eutrophication) (as discussed in the companion paper, Sundarambal et al., 2010). The regional smoke haze resulting from the forest and peat fires in Southeast Asia (SEA), especially in Indonesia, has received considerable concern because of its impact on regional biogeochemistry (Brauer and Hisham-Hashim, 1998; Balasubramanian et al., 1999; Muraleedharan et al., 2000; Balasubramanian et al., 2001). The regional smoke haze events in SEA are amplified during the Southwest Monsoon (SWM) period of *El-Niño* years, because of increased fires, and prevailing wind conditions and dryer weather (Andrea, 1990; Wong et al., 2004). The burning activities usually begin in July/August and cease by October/November when the gradually interspersing northern monsoon brings abundant rainfall.

Most of the local knowledge regarding tranboundary air pollution in SEA, caused by forest fires (biomass burning) and land (peat) fires, originated from earlier studies conducted elsewhere, at various parts of the world (e.g., The United States, Australia, Brazil, Mexico, Africa) (Crutzen et al., 1979, 1985; Andreae et al., 1988; Crutzen and Andreae, 1990; Lobert et al., 1990; Qadri, 2001; Mahowald et al., 2005; In et al., 2007). These studies quantified the flux of various trace gases such as CO_2, CH_4, NO_x, NH_3 and aerosols from biomass burning to the atmosphere. Biomass burning has been reported to be a major source of reactive nitrogen and phosphorous (Kuhlbusch et al., 1991; Vitousek et al., 1997; Kondo et al., 2004; Mahowald et al., 2005; Baker et al., 2006; UNEP and WHRC, 2007; Sundarambal et al., 2010b). Crutzen and Andreae (1990) reported that biomass burning emission can contribute 6 to 20% N when compared to terrestrial N fixation rate. Mahowald et al. (2008) and Vitousek et al. (1997) reported the different forms of P and N species emitted from various atmospheric sources, respectively. A significant fraction of the N and P species entering coastal and estuarine ecosystems along the Singapore and surrounding countries arises from atmospheric deposition; however, the exact role of atmospherically derived nutrients during episodic regional smoke haze events in the decline of the health of coastal, estuarine, ocean, and inland waters in SEA is still uncertain (Sundarambal et al., 2006, 2009, 2010b; Sundarambal, 2009). The increased levels of particulates and nutrients in atmospheric samples during biomass burning in SEA were demonstrated by the use of backward air trajectories coupled with satellite images of point biomass burning sources (Koe et al., 2001; Sundarambal et al., 2010b), the chemical characteristics (such as non-sea salt, non-soil K^+) of aerosols (See et al., 2006), and FLAMBE and NAAPS models (Hyer et al., 2010). The results of these studies are important in assessing the environmental impacts of the resulting AD nutrient pollution.

SEA coastal waters receive a large nutrient supply of which a substantial portion is of anthropogenic origin (Chou, 1994; UNEP, 2000). Occurrence of algal blooms, harmful types in particular, are steadily increasing in coastal waters of SEA (Pearl, 1988; Azanza, 1998; Smetacek et al., 1991; Watson et al., 1998; Azanza and Taylor, 2001; Selman, 2008). Accelerated eutrophication and its subsequent effects such as nuisance algal blooms and reduced oxygen levels pose significant problems for coastal waters and aquatic ecosystems in SEA (Nixon, 1995; Azanza and Taylor, 2001; Selman, 2008). The nutrients, dissolved oxygen and phytoplankton concentrations in coastal waters of Singapore were found to vary in space and time, and fluctuations of nutrients concentration were observed depending on the monsoons and various sources of pollution in the region (Gin et al., 2000, 2006). In general, waters in the Johor Strait are more eutrophic than the Singapore Strait consistent with the higher nutrient concentrations measured in the Johor Strait. This eutrophication problem could be due to variable anthropogenic inputs, coupled with suitable tidal conditions (e.g. neap low tides generally resulted in higher levels of chlorophyll) (Gin et al., 2000, 2006). No studies have investigated the responses of marine ecosystems to atmospheric deposition of nutrients due to episodic smoke haze events in SEA. It is critically important to assess the fate of the airborne admixtures deposited onto the water surface in order to understand the possible link between atmospheric nutrients deposition and marine phytoplankton blooms. The concentrations of nutrients in atmospheric samples during hazy and non-hazy days are elaborated in the companion paper of field observations (Sundarambal et al., 2010b).

Water quality impact assessment of pollution sources (point and distributed) onto the aquatic ecosystem can be obtained using numerical models. The model provides a convenient tool for testing hypotheses about the processes, otherwise not fully understood from direct measurements. In order to examine the quantitative response of the pelagic plankton to atmospheric N and P deposition events and possible links between them, a numerical modeling study can be used (Sundarambal et al., 2006, 2009, 2010a). The motivation for applying this numerical modeling approach is to explore and quantify water quality variability due to the transfer of atmospherically-derived nutrients onto coastal water and to predict the resultant nutrient and phytoplankton dynamics in this region. 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. Besides the advection–diffusion transport, a series of terms for the biochemical interactions between non-conservative quantities should be considered. The impacts of atmospheric N and P species deposition fluxes on the Singapore coastal water quality were studied comprehensively for the first time using a 3-D numerical eutrophication model "NEUTRO" (Tkalich and Sundarambal, 2003). NEUTRO is a dynamic biochemical model that takes into consideration time-variable chemical transport and fate of nutrients, and plankton, carbonaceous biochemical oxygen demand (CBOD) and dissolved oxygen (DO) in the water column due to nutrient loadings from point and distributed sources. The original NEUTRO model, used in our earlier studies (Tkalich and Sundarambal, 2003; Sundarambal and Tkalich, 2005), did not have a module to address the nutrients loading from atmospheric deposition. In this study, the capability of the NEUTRO model is enhanced with features to predict the fate of nutrients deposited from atmospheric deposition by assessing the resulting water quality changes during hazy and non-hazy days in Singapore waters. In this study, wet-only atmospheric deposition (rainfall) of nutrients was modeled, as it was clearly observed that the wet atmospheric deposition is more dominant than the dry atmospheric deposition (Sundarambal et al., 2009, 2010b (the companion paper)). The details of model simulations pertaining to dry deposition alone and the total atmospheric (dry + wet) deposition and their influence on water quality will be presented elsewhere with a more extensive database.

The present study aims at estimating the relative contribution of atmospheric nutrient deposition to coastal water eutrophication using a combination of the atmospherically deposited nutrients concentration data from field observations (Sundarambal et al., 2010b) and the 3-D modeling program, NEUTRO. There are two steps involved in the application of the model, (i) conservative admixture assumption and (ii) non-conservative admixture assumption. In the first step, data on atmospheric nutrient fluxes (Sundarambal et al., 2010b) and baseline concentration of diluted nutrients in the water column of the Singapore Strait waters are employed 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 full-scale model is used to study spatial and temporal variability of eutrophication rates in the Singapore waters due to changes in nutrient fluxes from atmospheric deposition in the model domain.

2 Materials and methods

2.1 Study area

Singapore is a very environment conscious city state in SEA with a total land area of 710 km^2 (Fig. 1). The country is immediately north of the Equator and positioned off the southern edge of the Malay Peninsula between Malaysia and Indonesia (Fig. 1a). Singapore's strategic location at the entrance to the Malacca Strait, through which roughly one-third of global sea commerce passes each year, has helped it become one of the most important shipping centers in Asia. During the Northeast Monsoon (NEM), northeast winds prevail, whereas southeast/southwest winds prevail during the SWM season. Smoke haze has been frequently observed in this region from August to October almost every year due to bush and peat fires in neighboring countries, especially Indonesia. In general, dry weather is the result of lack of convection or stable atmosphere which prevents the development of rain-bearing clouds. Depending on the intensity of smoke haze events, nutrient fluxes of different magnitudes are delivered during dry seasons to the Singapore coastal waters (Sundarambal et al., 2010b). The coastal waters of Singapore are bound by the Johor Strait in the North and the Singapore Strait in the South. 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 and it is one of the world's busiest sea lanes, connecting trade routes from Asia to Africa and to Europe. The sea bed topography of the Singapore Strait is complicated, ranging from 30 m to the maximum depth of 120 m (Chan et al., 2006).

The hydrodynamic and water quality processes in Singapore coastal zone are discussed in detail by Chan et al. (2006), Gin et al. (2006), Sundarambal et al. (2008), Sundarambal (2009) and Sundarambal and Tkalich (2010). General features of Singapore seawaters covering NEUTRO model domain are shown in Fig. 1b. The model domain covers the Johor Strait in North and some part of Java Sea in South. Seasonal variation of coastal hydrodynamics is dominated by the Asian monsoon. Observations show that during the NEM, water is forced along the east coast of the Malay Peninsula and turns into the 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 and western exits. Inter-monsoon (IM) periods are believed to be intermediates of the two major monsoons. In the Singapore Strait, the monsoon currents and tidal fluctuation are significant. Singapore tides are predominantly of semi-diurnal nature and travel mainly in the eastern (SWM) and western (NEM) directions, 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. Currents, in general, are typically less than 2 m/s in most parts of the Singapore Strait except in the narrow channel at The Singapore Deeps. The mean tidal range is about 2.2 m and the maximum range is up to 3 m during spring tides. The river discharges do not greatly affect hydrodynamics in the Johor Strait because the tidal flux in the Johor Strait is much higher than that results from river discharges (Chan et al., 2006). The sampling location (latitude 1°13′10″ N and longitude 103°50′54″ E, Fig. 1a) at the Tropical Marine Science Institute (TMSI) in St. Johns Island (SJI) in Singapore was selected for sampling of aerosol and rainwater to estimate the nutrient fluxes from atmospheric (dry and wet) deposition onto the coastal waters and ocean of SEA during the recent 2006 SEA smoke haze episodes and non-hazy days.

2.2 Data

The dry deposition (55 number of aerosol samples) and wet deposition (21 number of rainwater samples) samples were collected by the field monitoring during September 2006 to January 2007 study of atmospheric (dry and wet) deposition. The above sampling period included both hazy days during 2006 SEA haze episode and non-hazy days, and their

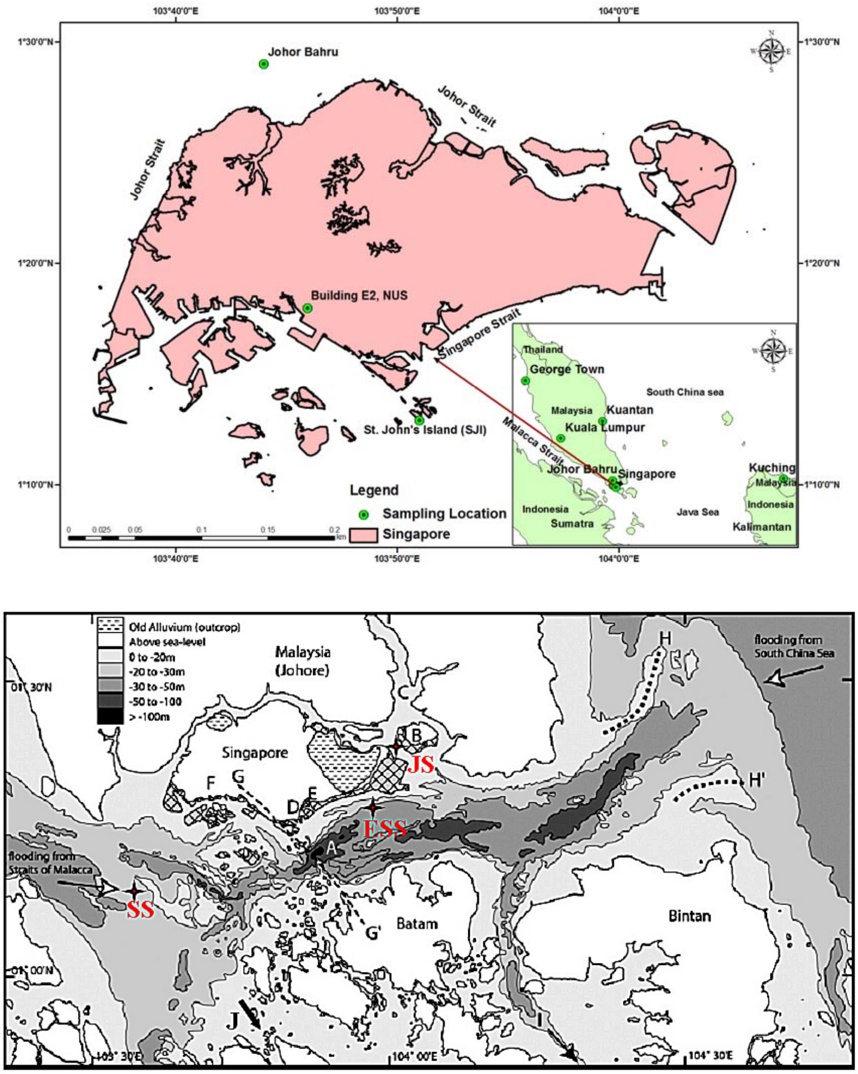

Fig. 1. (a) Map showing sampling locations (NUS and SJI) in Singapore and surrounding regions; **(b)** general features and high-resolution bathymetry of Singapore seawaters (Admiralty Chart 2403 "Singapore Strait and Eastern Approaches") covering NEUTRO model domain (Courtesy from Chan et al., 2006). Note: cross-hatching:Reclaimed areas in Singapore, A: The Singapore Deeps, B: Pulau Tekong, C: Johor River, D: Singapore Central Business District, E: Bedok, F: Jurong; G-G': Fault, H-H': splays of sediment, I: Riau Strait, J: Selat Durian and SS, ESS and JS: observation points.

complete details are given in the companion paper on field observations (Sundarambal et al., 2010b). The types of nutrients identified from atmospheric wet and dry nutrient depositions 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^{3-}), total phosphorous (TP) and organic phosphorous (OP). The various chemical forms of nutrients (N and P species) from atmospheric deposition were quantified by analyzing the collected atmospheric (both dry and wet) deposition samples using validated laboratory techniques (APHA, 2005; Sundarambal et al., 2006, 2009; Karthikeyan et al., 2009; Sundarambal et al., 2010b).

The hazy and non-hazy days were defined for dry and wet atmospheric deposition studies based on Pollutant Standards Index (PSI) measured by National Environment Agency (NEA, 2006 and http://app2.nea.gov.sg/psi_faq.aspx), Singapore (Sundarambal et al., 2010b). The water soluble concentration of nutrients (N and P species) in dry atmospheric deposition and wet atmospheric deposition during hazy and non-hazy days is respectively shown in Tables 1 and 2 and their detailed atmospheric deposition flux calculations can be found in the companion paper on field observations (Sundarambal et al., 2010b). The concentrations of nutrients in Table 2 were selected for wet atmospheric deposition study based on PSI (ranging 81–93 during hazy and 35–

Table 1. Concentration of nutrients (N and P species) in atmospheric dry deposition during hazy and non-hazy days in Singapore.

Parameters	Dry deposition (µg/m^3): Hazy[a]				Dry deposition (µg/m^3): Non-Hazy[a]			
Nutrients	Mean	Min	Max	SD	Mean	Min	Max	SD
TN	12.61	10.13	14.94	2.05	2.40	1.31	3.84	1.25
NH_4^+	1.92	1.53	2.43	0.38	0.28	0.01	1.60	0.41
$NO_3^-+NO_2^-$	4.25	2.28	6.63	1.91	0.80	0.41	1.51	0.27
ON	6.44	5.14	8.16	1.29	1.49	0.43	2.50	0.61
TP	0.48	0.35	0.65	0.13	0.07	0.04	0.09	0.02
PO_4^{3-}	0.09	0.04	0.19	0.07	0.02	0.01	0.04	0.01
OP	0.38	0.28	0.61	0.16	0.05	0.002	0.07	0.02

[a] Dry deposition: Hazy days (4 numbers) samples during 6, 7, 15 and 19 October 2006 (unit: µg/m^3); [b] dry deposition:Non-Hazy days (16 numbers) samples from 13 November 2006 to 4 January 2007 (unit: µg/m^3); $NO_3^-+NO_2^-$ = nitrate + nitrite (or) nitrate-nitrogen.

Table 2. Concentration of nutrients (N and P species) in seawater and atmospheric wet deposition during hazy and non-hazy days in Singapore.

Parameters	Seawater baseline[a]	Wet deposition (mg/l):Hazy[b]				Wet deposition (mg/l):Non-Hazy[c]			
Nutrients		Mean	Min	Max	SD	Mean	Min	Max	SD
TN	0.1129	15.39	11.76	20.36	4.45	3.41	2.38	4.79	1.25
NH_4^+	0.0133	0.94	0.77	1.19	0.22	0.15	0.03	0.39	0.21
$NO_3^-+NO_2^-$	0.02	8.64	7.78	9.48	0.85	1.54	1.03	2.24	0.62
ON	0.0796	5.81	3.21	10.50	4.06	1.71	1.30	2.52	0.70
TP	0.0251	0.91	0.81	0.97	0.09	0.18	0.10	0.24	0.08
PO_4^{3-}	0.0116	0.26	0.10	0.49	0.20	0.03	0.03	0.05	0.01
OP	0.0135	0.65	0.32	0.87	0.29	0.15	0.05	0.21	0.09

[a] Seawater baseline (unit: mg/l) (Tkalich and Sundarambal, 2003); [b] wet deposition: Hazy days (3 rain events) samples from 15 to 21 October 2006 (unit: mg/l); [c] wet deposition: Non-Hazy days (3 rain events) samples from 11 November 2006 to 23 December 2006 (unit: mg/l); $NO_3^-+NO_2^-$ = nitrate + nitrite (or) nitrate-nitrogen.

39 during non-hazy days). From the field measurement of nutrient concentrations from AD, it was evident that there was higher nutrient input into ocean water during the hazy days as compared to clear or non-hazy days (Sundarambal et al., 2010b). The quantified wet atmospheric deposition flux of inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$) was 0.083 and 0.015 g/m^2/day into coastal waters during hazy and non-hazy days, respectively. On an event basis, the minimum and the maximum wet deposition fluxes of macro-nutrients were highly variable. The day-to-day particle concentrations varied substantially in response to spatial and temporal changes of meteorological factors (Sundarambal et al., 2010b).

About 14 seawater samples were also collected during the 2006 haze from 8 October 2006 to 20 January 2007 from SJI ferry terminal situated approximately 6.5 km south of Singapore, off the Strait of Singapore (Fig. 1a) using established methods (Gin et al., 2000; APHA, 2005) as frequently as possible. The analytical precision/accuracy associated with the analysis of atmospheric samples was described elsewhere by Sundarambal (2009) and for seawater by Gin et al. (2000). It was found (Gin et al., 2000; Tkalich and Sundarambal, 2003) that the sampling point represented the baseline characteristics of the Singapore Strait reasonably well. Therefore, the field monitoring data could be considered to be representative of the large domain. The details of the water quality monitoring program, seawater sample collection, and spatial and temporal distributions of chlorophyll-a and nutrients in Singapore's coastal waters were reported by Gin et al. (2000, 2006). Data were collected on a monthly basis at fixed sampling sites over different depths in the Singapore waters during alternate spring and neap tidal cycles to capture the scenarios of high and low tidal flushing characteristics. The analyzed data provided information on the baseline as well as spatial and temporal variations of water quality parameters bracketing the major geographical area of interest. The surface nutrients concentration varied uniformly over time and space in the Singapore Strait except the Johor Strait where more fluctuations were observed depending on the monsoons and local sources of pollution (river discharges, runoff, ship spills, fish farms etc.) (Gin et al., 2006; Sundarambal and Tkalich, 2010).

Table 3. Model inputs parameters and their values.

Parameters (units)	Symbol	Value	Remarks
For conservative admixture assumption			For Case I to Case III scenarios
Nitrate-nitrogen (mg/l)	$S_{j\mathrm{WD}}$	1.54	For non-hazy days
		8.64	For hazy days
Nitrate-nitrogen (mg/l)	B_j	0.02	
Nitrate-nitrogen (mg/l)	C_j^0	0	
Annual rainfall (mm)	Pr	2136	
For non – conservative admixture assumption			For full eutrophication model run
Nitrate-nitrogen (mg/l)	$S_{j\mathrm{WD}}$	1.54	For non-hazy days
		8.64	For hazy days
Ammonium (mg/l)	$S_{j\mathrm{WD}}$	0.15	For non-hazy days
		0.94	For hazy days
ON (mg/l)	$S_{j\mathrm{WD}}$	1.71	For non-hazy days
		5.81	For hazy days
Phosphate (mg/l)	$S_{j\mathrm{WD}}$	0.03	For non-hazy days
		0.26	For hazy days
OP (mg/l)	$S_{j\mathrm{WD}}$	0.15	For non-hazy days
		0.65	For hazy days
Phytoplankton (mgC/l)	C_j^B	0.02	
Nitrate-nitrogen (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	
DO (mg/l)		5.4	
CBOD (mg/l)		1.099	

Note: $S_{j\mathrm{WD}}$ – concentration of nutrients from wet atmospheric deposition; B_j – concentration of $^{\mathrm{th}}_{j}$ pollutant or state variable in seawater at the boundary; C_j^0 – seawater concentration of j^{th} pollutant or state variable in seawater at initial time; Pr – precipitation rate; C_j^B – baseline concentration of j^{th} pollutant or state variable in seawater obtained from field measurements (Tkalich and Sundarambal, 2003).

The average concentration values (used as model baseline values, derived from Tkalich and Sundarambal (2003), to estimate model kinetics coefficients in this study) of nutrients (Table 2), plankton, DO and CBOD (Table 3) were obtained following the statistical analysis of the concentration data measured in the Singapore seawaters (as part of the routine water quality monitoring program by the TMSI, National University of Singapore (NUS), Singapore). The various steps involved in the exploratory data analysis to obtain baseline concentrations are: (i) initial data collection from field measurements; (ii) qualitative analysis of data obtained; (iii) construction of baseline values for NEUTRO; and (iv) statistical analysis of data. The statistical analysis was used to examine different types of data, collected in different ways, in order to to determine whether or not the data have a statistically significant difference. Observational data sets were collected on a monthly basis at all monitoring stations. Most of the data were collected from a population of samples that showed "normal distributions". The stations that showed minimum variations (i.e. stations free from local sources of pollution) were considered and the data were analyzed statistically to find the mean baseline values by ANOM (Analysis of Mean) at confidence limits of 95%, a graphical analog to ANOVA (Analysis Of Variance), using a statistical software MINITAB Release 13.2 (2000). Box plots tend to be most useful when there are many observations in the data set.

2.3 The concept of the model

Contaminant inputs into a coastal system are subjected to physical and biogeochemical processes that affect their concentration in the water column. A chemical species whose concentration depends solely on physical transport and dilution is considered to be a "conservative" species. Most contaminants are non-conservative; therefore, their distributions are subjected 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, the difference in concentration distributions of a non-conservative contaminant may then 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 the Singapore Strait waters and adjacent water bodies, such as the Malacca Strait, South China Sea and Java Sea. Simulation of the ambient concentration of admixtures 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).

2.3.1 Three dimensional numerical eutrophication model (NEUTRO)

NEUTRO (3-D numerical eutrophication) model (Tkalich and Sundarambal, 2003) is capable of simulating 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 (EPA), Ambrose et al., 2001). WASP is a generalized framework for modeling 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 were transformed and programmed together with 3-D advection-diffusion contaminant transport to account accurately for the spatial and temporal variability. The coupled physical-biochemical model simulated long-term nutrient dynamics in Singapore seawater and surrounding seas. This model provided information on nutrient concentrations, primary production and dissolved oxygen necessary to estimate large-scale ecological effects.

The modeled nutrients consist of ammonium nitrogen, nitrite + nitrate ($NO_2^- + NO_3^-$) nitrogen (hereafter denoted as nitrate-nitrogen), PO_4^{3-}, ON, OP, TN and TP. Detailed NEUTRO model description, schematic of interactions between nutrients, plankton (phytoplankton and zooplankton) and the dissolved oxygen balance, and eutrophication kinetics can be found elsewhere (Tkalich and Sundarambal, 2003; Sundarambal, 2009). For the present study, NEUTRO was enhanced in its capability to address the atmospheric input of macronutrients as a distributed source. The enhanced model (Sundarambal et al., 2006) was subsequently utilized to investigate the fate of atmospherically deposited nutrients in the water column, and its impact on water quality and aquatic ecosystems in Singapore and surrounding regions (Sundarambal et al., 2010a). The present model can simulate the fate of transport of nutrients from point sources (outfalls, spills) (Sundarambal and Tkalich, 2005) and non-point sources (runoff, AD) (Sundarambal et al., 2006). 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; advective-diffusive transport; and physical, chemical, and biological transformation. Considering 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 can be described as follows:

$$\frac{\partial C_j}{\partial t} + \frac{\partial C_j U}{\partial x} + \frac{\partial C_j V}{\partial y} + \frac{\partial C_j \left(W - w_j\right)}{\partial z} - \frac{\partial}{\partial x}\left[E_x \frac{\partial C_j}{\partial x}\right] - \frac{\partial}{\partial y}\left[E_y \frac{\partial C_j}{\partial y}\right] - \frac{\partial}{\partial z}\left[E_z \frac{\partial C_j}{\partial z}\right] = \frac{Q\left(S_j - C_j\right)}{\Delta h \Delta x \Delta y} + R_j \quad (1)$$

where C_j = concentration of j^{th} pollutant or state variable (mg/l); S_j = contamination of the source with j^{th} pollutant (mg/l); Q = discharge of the source (m^3/s); R_j = chemical reaction terms, corresponding to the interaction equations for j^{th} state variable (eutrophication kinetic equations of model state variables are given in Tkalich and Sundarambal, 2003); E_x, E_y, E_z = turbulent diffusion coefficients; Δx, Δy, Δz = computational grid-cell sizes in x-, y-, and z-directions, respectively; Δh = thickness of water layer affected with initial dilution; $C_j^0 = C_j(t_0)$ is the concentration of j^{th} pollutant or state variable at initial time, C_j^B is the baseline concentration of j^{th} pollutant or state variable obtained from field measurements; w_j = settling velocity of j^{th} 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 hydrodynamic model (TMH, Pang and Tkalich, 2004) and were used as inputs to NEUTRO. Values of concentration (C_j) were computed at the nodes of a 3-D grid at different instances of time using transport equation (Eq. 1). The missing element of atmospheric input of macronutrients was included in NEUTRO to explain anomalies in primary production. The new atmospheric flux (F) in the model was quantified by the source term$F = QS_j$ in transport equation (Eq. 1). The wet deposition flux (F) in the model was calculated by precipitation rate x concentration (S_j) of AD species and the dry deposition flux (F) by settling velocity of AD species x concentration (S_j) of AD species.

2.3.2 Hydrodynamic Model (TMH)

A 3-D semi-implicit sigma-coordinate free surface primitive equation hydrodynamic model (TMH), developed at the TMSI, NUS, was implemented to compute tidal-driven currents in the coastal waters of Singapore (Tkalich et al., 2002; Pang et al., 2003; Pang and Tkalich, 2003, 2004). TMH is extensively used for modeling hydrodynamics in Singapore Strait and has been applied in several commercial and research coastal studies in Singapore and Johor Strait (http://www.porl.nus.edu.sg/main/research/hydro-model). In this study, TMH model with 500 m horizontal resolution and 10 vertical sigma layers was used. Calibrated and tested TMH against available field data showed general accuracy within 10% (Pang and Tkalich, 2004; Chan et al., 2006). Figure 2a shows the comparison of predicted and measured currents at the transition from spring tide to neap tide at the control point (ESS in Fig. 1b) off the east coast of Singapore in the Singapore Strait. 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.

2.4 NEUTRO model setup, forcing data, initial conditions and limitations

The selected model domain approximately covered surface area about 10 000 km^2 regions from 1°0′ N to 1°33′10.43″ N (latitude) and from 103°20′ E to 104°20′ E (longitude) (Fig. 1a). The general features, bathymetry of the Singapore Strait and the model domain are shown in Fig. 1b. In the water quality model, a horizontal grid of 500 m × 500 m covering 117.5 × 84.5 km^2 area (236 × 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. Current velocities and free surface dynamics for NEUTRO were obtained using the TMH model. For this study, extreme tidal conditions were chosen to represent the "worst case" scenario of a typical SWM covering a 5 days spring tide period from 30 June 2003 to 5 July 2003 for model simulation. The tidal current speeds during the selected typical SWM was ranging between −1.26 m/s and 1.09 m/s for U component, −0.27 m/s and 0.18 m/s for V component and −0.0002 m/s and 0.0001 m/s for W component (Fig. 2b). 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 (Sundarambal, 2009). The mean concentrations of nutrients in Singapore seawater were taken from Tkalich and Sundarambal (2003) as model baseline concentrations. Generally, the water column is well mixed in Singapore and Johor Strait due to intensive tidal currents. The initial condition of each state variable 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 AD of nutrients to the coastal waters were obtained based on field monitoring (Sundarambal et al., 2010b) and laboratory methods of nutrient analysis (as in Sundarambal et al., 2009, 2010b). The open boundaries for the water quality modeling were the boundaries facing South-China Sea, Malacca Strait, and Indonesia waters. The water exchanged from the above boundaries in and out of the Singapore domain carried nutrients and other contaminants with them (i.e. transboundary fluxes).

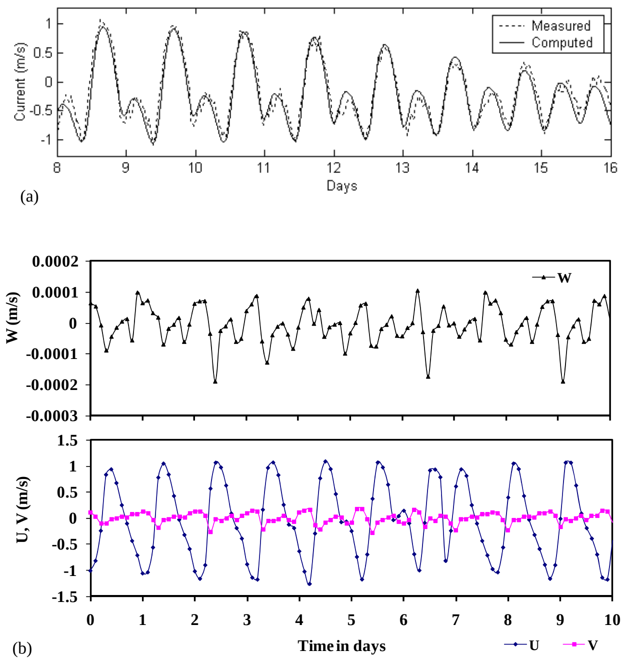

Fig. 2. (a) Comparison of TMH model computed and measured currents at the control point "ESS" in the east of the Singapore Strait (Chan et al., 2006); **(b)** current velocity components U, V and W from TMH model at "SS" station during typical SWM in the west of the Singapore Strait.

The modeling assumptions and limitations in the present study are as follows:

i. In order to delineate atmospheric and ocean fluxes, the model was tuned to a quasi-equilibrium state by assuming constant boundary fluxes in the vertical planes of the computational boundaries.

ii. The model was run again with atmospheric fluxes to allow for a new quasi-equilibrium state to be established; and the two solutions were then compared.

iii. Another assumption in this study was that the water-soluble nutrients of atmospheric origin were assumed to be deposited directly and uniformly onto the water surface. They were then transported spatially through the water column by the action of tidal currents, while the nutrients underwent a complex physical (tidal forcing, advection, diffusion, temperature and sunlight), chemical (chemical interaction between nitrogen, phosphorous and dissolved oxygen cycles) and biological processes (plankton (phytoplankton and zooplankton) dynamics) and transformations in the water column.

iv. The model was run for 20 days to achieve steady-state/equilibrium conditions which reflected the long-term water quality changes due to a constant pollution loading from sources. The equilibrium conditions without atmospheric fluxes corresponded to long-term monitoring observations. As per the established modeling practice, if a load of nutrients corresponds to the usual annual load into the water body, the established quasi-equilibrium level must be close to observed baseline concentrations. The smoke haze phenomenon addressed in this study is a regional air pollution event and occurs on a larger scale in terms of both time and space, as compare to the tidal currents. The short-term non-equilibrium responses were not addressed, because the atmospheric sources considered are of a regional lateral scale and a few days of temporal resolution.

2.5 NEUTRO Model calibration and validation

Model calibration is the process of determining the model parameters and/or structure based on measurement and a prior knowledge (Beck, 1987). For admixture transport model, the concentration profiles obtained from field measurements can be used to calibrate a model at a given time by adjusting model parameter, including kinetic coefficients, until acceptable accuracy is achieved (Ditmars, 1988). Average baseline concentrations of nutrients in Singapore seawater (derived from Tkalich and Sundarambal, 2003) were used to estimate kinetic coefficients by means of iterative model runs through the comparison of model predictions with baseline concentrations. The optimal values of the coefficients (Sundarambal, 2009) are capable of keeping state variables at quasi steady-state (baseline) concentrations under the fixed nutrient load conditions. The calibrated model was used to simulate the water quality with an independent set of data as a part of validation exercise for model evaluation. Test runs showed that NEUTRO reproduced the cycles of phytoplankton and nutrient concentrations with a good accuracy (Sundarambal et al., 2008; Sundarambal and Tkalich, 2010).

2.6 NEUTRO model validation

Validation of any numerical model is a quite complicated process. There are several standard steps to validate it by comparing model results with analytical solutions, sensitivity tests, or by comparing model results with measurements. Comparison with measurements is important because it can verify the governing equations of the model as well as the approximated numerical solution of the equations. For 24-h hindcast exercise, the model simulation period was selected from 18 March 2002, 12:00 p.m. to 19 March 2002, 12:00 p.m. Simulations were compared with the long-term monitoring data to examine how well the model can represent the baseline. The computed time- series (Fig. 3a) and box-plot diagram (Fig. 3b) compared well with the measured baseline values represented as box-plots in Fig. 3c. The simulations were also compared with the 24-h observational data at a monitoring location “JS” in the East Johor Strait (Fig. 1b). NEUTRO’s computed state variables were in close agreement with field measurements for 24-h hindcast, as shown by absolute error bars in Fig. 3d. The absolute error between predicted and observed DO was −0.5 mg/l. The negative and positive errors occurred when the predicted values of model were higher and lower than the observed values, respectively. The model performed well according to established worldwide modeling practices and criteria. Further model validations were focused on monsoon related variations (Sundarambal and Tkalich, 2010; unpublished reports in TMSI, NUS).

2.7 Sensitivity analysis

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

$$\frac{Y+\Delta Y}{Y}\cdot 100\% = \frac{X+\Delta X}{X}\cdot 100\% \tag{2}$$

For sensitivity study, the calibrated model was experimented for its response to an increase in nitrogen fluxes due to wet atmospheric deposition using Eq. (2). Here this sensitivity study describes increment of total mass of nitrate-nitrogen in seawater due to atmospheric deposition of nitrate-nitrogen concentrations at different extremes (minimum to maximum) for modeling worse case scenarios. From Table 2, the observed higher maximum concentration of nitrogen species at hazy days during biomass burning shows that occurrence of these higher concentrations may cause episodic extreme deposition events on the coastal water in the region. A modeling experiment was considered to investigate the increase in nitrate-nitrogen and phytoplankton at water surface in response to different atmospheric nitrogen fluxes. In the experiment, the atmospheric nitrogen flux was assumed to increase by keeping constant precipitation rate (Pr) of 2136 mm/yr and increasing nitrate-nitrogen concentration (S) from the atmosphere at 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l using four different model runs.

2.8 Modeling approach

In this study, two numerical experiments, a conservative approach and a non-conservative approach, were carried out as follows. The basic task of a conservative approach was to perform a continuous mass budget of non-reactive pollutant

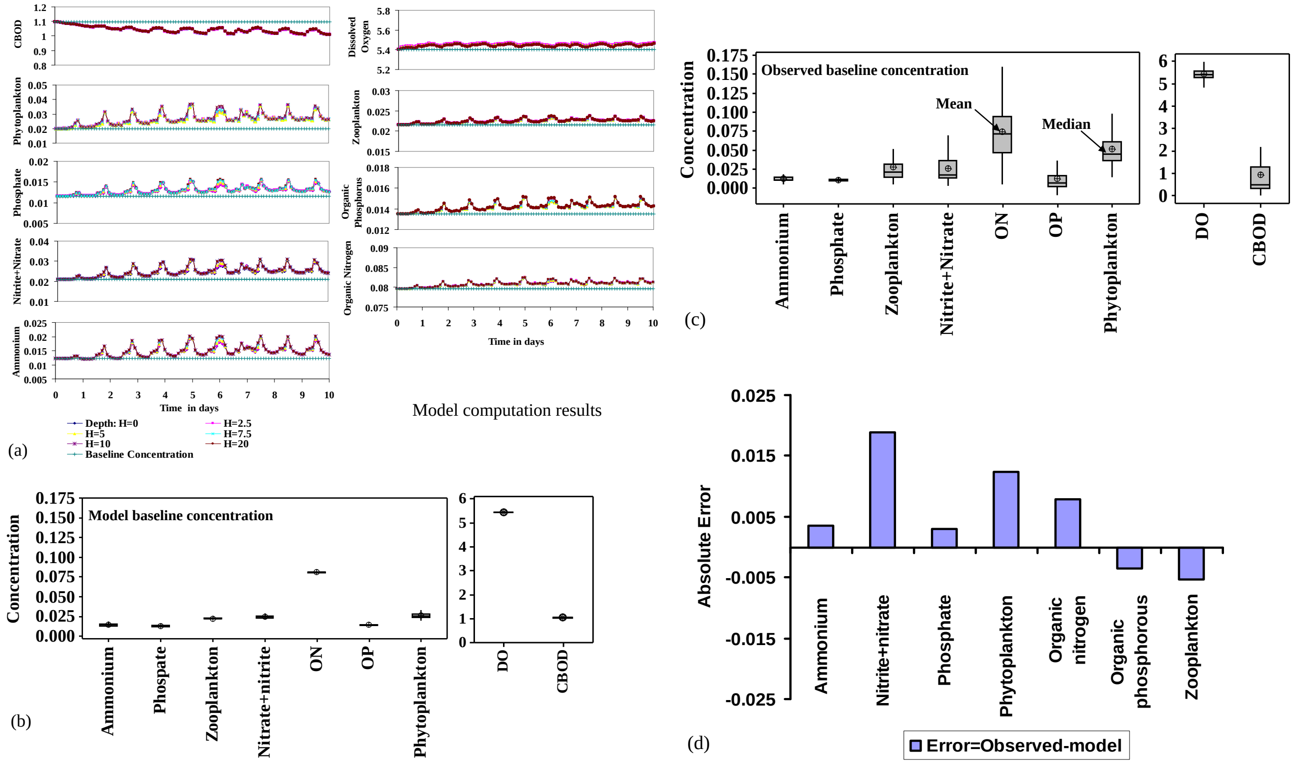

Fig. 3. Comparison of computed and measured baseline concentrations. **(a)** Computed time-series of baseline concentrations at a monitoring station "SS" on the South Coast of Singapore; **(b)** box-plots of computed baseline concentrations; **(c)** observed baseline concentration in the domain (Tkalich and Sundarambal, 2003; Sundarambal, 2009); **(d)** absolute error diagram of model state variables between computed model results and field observations for 24-h hindcast at a monitoring station "JS". Note: Parameters (Units): Ammonium (mg/l), nitrate-nitrogen (mg/l), phosphate (mg/l), phytoplankton (mgC/l), organic nitrogen (mg/l), organic phosphorous (mg/l) and zooplankton (mg/l).

in the coastal system. In a non-conservative approach, the contaminant inputs into a coastal system were subjected to physical and biochemical processes (eutrophication kinetics) that would affect the concentration of the contaminants in the water column. Similarly, the impact of atmospheric nitrogen deposition onto aquatic ecosystem could be estimated by using a non-conservative modeling approach. The modeling approaches mentioned above were carried out to simulate nutrient fate and transport in the coastal water that could result from the varying atmospherically deposited nutrient loading conditions. In this modeling study, N and P species from AD were considered. Once N or P is deposited onto water surface, it is transported to the water column followed by its spatial distribution by the action of tidal currents. 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 plankton due to AD were computed. At any given location and time, the concentration of organic particulate matter is not only controlled by biological/ecosystem production and the vertical removal of particles, but also depends on horizontal transport to and from adjacent water masses. The physical transport terms, including advection rates and diffusion processes, can be estimated using hydrodynamic principles but, in an open water system where the horizontal gradients of contaminant and particulate concentrations are usually small, mixing does not cause large net horizontal transport and the advection term is significant. The typical hydrodynamic forcing from TMH (Pang and Tkalich, 2004) was utilized to compute the dynamics in water column nutrients and plankton due to atmospheric wet deposition (uniform loads over the domain) along with ocean boundary fluxes.

At the first set of numerical experiments, the model was run for verification of mass conservation of 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, considering: (I) flux of nutrients from lateral boundaries only; (II) atmospheric fluxes only; and (III) combination of fluxes from the ocean and atmosphere. The concentration of atmospheric wet deposition (WD) and initial concentration in water column is denoted as $S_{j\mathrm{WD}}$ and C_j^0, respectively. The model was run in a conservative mode (without kinetic exchange) for the three cases as below:

Case I: $C_j^0 = 0$, $B_j \neq 0$, $S_{j\text{WD}} = 0$; equivalent to flux of nutrients from ocean boundaries only.

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

Case III: $C_j^0 = 0$, $B_j \neq 0$, $S_{j\text{WD}} \neq 0$; equivalent to combination of fluxes from the ocean and atmosphere.

By computing the mass of admixture in the Singapore Strait for each of the case, it is possible to quantify relative contribution of atmospheric and ocean fluxes into the domain. The concentration of nitrate-nitrogen was taken as 0.02 mg/l in water column (C_j^0), 0 mg/l at ocean boundaries (B_j) and atmospheric WD ($S_{j\text{WD}}$) of 8.64 mg/l for hazy days and 1.54 mg/l for non-hazy days (Table 2, Table 3 and comparable to Sundarambal et al., 2009), respectively. The annual average rainfall (P_r) in the model region was 2136 mm (Singapore Department of Statistics, 2005). The maximum WAD flux was applied as a constant uniform load deposited from the atmosphere over the coastal water in this region for an eutrophication modeling study to understand their impact on water quality as a worst case scenario.

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 the Singapore Strait. The wet atmospheric flux ($S_{j\text{WD}} \times P_\text{r}$), ocean boundary conditions (C_j^B) for model state variables including N and P species, phytoplankton, zooplankton, CBOD and DO used in the model are shown in Table 3.

3 Results and discussion

In this study, an attempt was made to evaluate the percentage change of inorganic nitrogen in the coastal water column due to biologically available nitrogen from atmospheric wet deposition. The central hypothesis of this study was that the atmospheric input is an important external source of nutrients, supporting significant fraction of excessive productivity in the region. From the regression studies (Fig. 4), the positive correlation between the PSI (indicator of air pollution) and concentrations of surface nutrients in seawater indicate that deposition may affect surface nutrient concentrations in the coastal waters of Singapore. The percentage increase of phytoplankton, PO_4^{3-} and TN in seawater during hazy days was approximately 50%, 86% and 100%, respectively. The present model study was carried out to test whether this hypothesis is supported by model computation results. The measured concentration ranges of parameters (in terms of minimum-maximum) 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_4^{3-} (0.005–0.015 mg/l) and TP (0.028–0.035 mg/l) while PSI was in the range of 23–109 during the sampling period (more information about the PSI can be found in the companion paper). Chlorophyll-a showed significant correlation with ammonium ($R^2 = 0.82$, $P = 0$), NO_3^- ($R^2 = 0.605$, $P = 0.02$) and TN ($R^2 = 0.6$, $P = 0.02$). Figure 4 shows the correlation between atmospheric depositions and seawater quality at the surface, and also the correlation between phytoplankton and TN in seawater. The correlation between the PSI and dry or wet deposition concentration of nutrients is also shown. It is observed that the PSI has a positive correlation ($R^2 > 0.4$) with NH_4^+, NO_2^-+ NO_3^-, TN and PO_4^{3-} from dry and wet deposition. Although the statistical correlation coefficient is not high due to a limited number of atmospheric samples collected in the study, the smoke haze appears to have a significant role in affecting the ocean water quality as there was a 100% increase of nutrients in the water column.

3.1 Sensitivity analysis

Simulation of the effects of potential changes in the atmospheric deposition on seawater/coastal water quality (sensitivity study) was performed through the analysis of modeling results with fluxes of atmospheric nutrients quantified using field measurements. The values of typically observed wet atmospheric nitrate-nitrogen concentration varied between 1.03–2.24 mg/l and 7.78–9.48 mg/l during non-hazy and hazy days, respectively. Therefore, a numerical sensitivity study is conducted to describe the increment of total mass of nitrate-nitrogen in seawater (Fig. 5) due to atmospheric deposition of nitrate-nitrogen concentrations at different extremes. The variation of atmospheric nitrate-nitrogen fluxes into the model showed the increase in the total mass of nitrate-nitrogen in seawater proportional to the magnitude of the increment of atmospheric nitrate-nitrogen fluxes (concentration multiplied by the annual average rainfall of 2136 mm in the model region) into the model domain (Fig. 5a). Whenever the atmospheric nitrate-nitrogen flux increased, similar increases in the phytoplankton concentration and total mass of nitrate-nitrogen in seawater in the Singapore Strait were also computed (Fig. 5b). 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 total mass of nitrate-nitrogen in seawater due to various atmospheric nitrate-nitrogen fluxes over the seawater baseline value of 0.02 mg/l was in the order of 0.01%, 0.13%, 0.63% and 1.26% for nitrate-nitrogen concentration of 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l from atmospheric deposition, respectively (Fig. 5a). An area that is sensitive to atmospheric nutrient fluxes has a higher risk of becoming eutrophic, when the phytoplankton concentration is increased disproportionately.

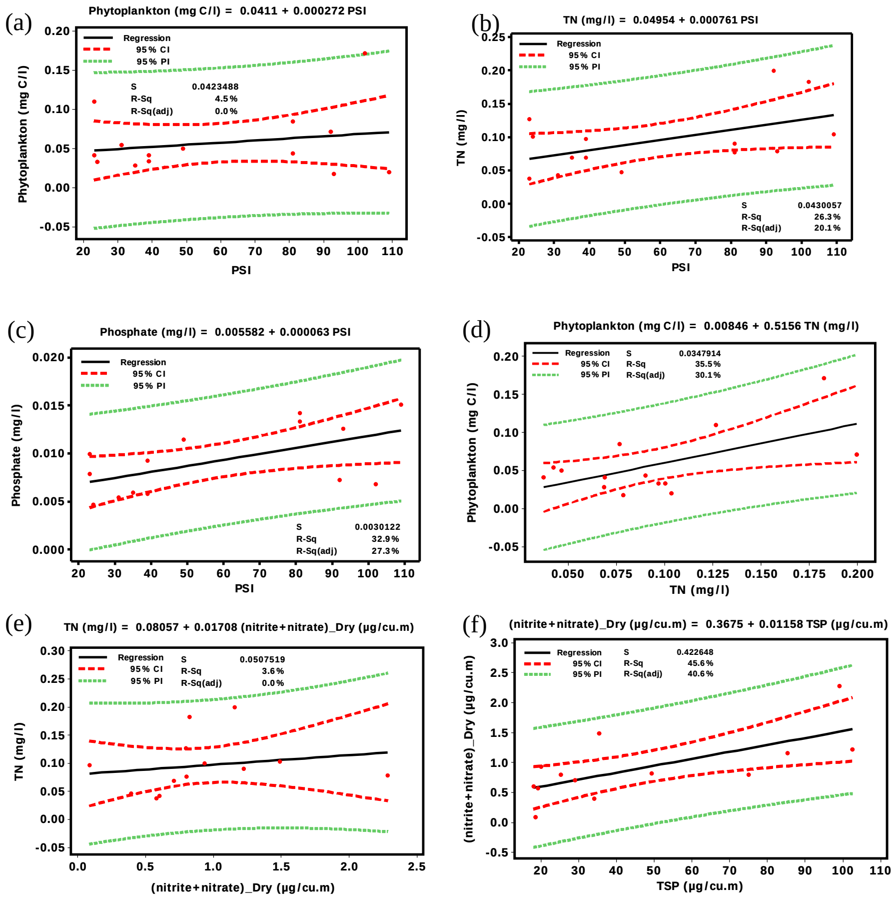

Fig. 4. Relationship between **(a)** Pollutant Standards Index (PSI) and phytoplankton in seawater, **(b)** PSI and TN in seawater and **(c)** PSI and phosphate in seawater; **(d)** phytoplankton and TN in seawater; **(e)** nitrate-nitrogen from dry atmospheric deposition and TN in seawater, and **(f)** TSP and nitrate-nitrogen from dry atmospheric deposition. Note: Dry – Dry atmospheric deposition.

3.2 Significance of atmospheric deposition during smoke haze events: conservative admixture assumption

For verification of mass conservation of nitrate-nitrogen and to understand relative importance of atmospheric fluxes during hazy and non-hazy days in the region as compared with lateral fluxes via ocean boundaries, NEUTRO was run initially in a conservative mode (without eutrophication kinetics) (see Sect. 2.8). In this study, the concentration of nitrate-nitrogen at ocean boundaries (B_j), atmospheric WD ($S_{j\mathrm{WD}}$) for hazy days and non-hazy days, and the initial concentration in water column (C_j^0) were taken as 0.02 mg/l, 8.64 mg/l, 1.54 mg/l and 0 mg/l, respectively; and the annual average rainfall in the model region were taken as 2136 mm (Table 3). For this study, the enhanced model for atmospheric nutrient loading during hazy and non-hazy days was run for three exploratory scenarios (Case I to Case III) in the Singapore Strait as explained in Sect. 2.8. The model simulations were carried out for 39 semi-diurnal tidal cycles (equivalent to 20 consecutive days). The model mass increment (tonne) against simulation time (days) for Cases I–III for non-hazy and hazy days is shown in Fig. 6. As there is an exchange of flux at open boundaries, 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 of N flux was calculated. For Case I, if computations began with a zero initial mass of nutrients in the study domain, the ocean fluxes of nutrients entered through "open" boundaries to gradually accumulate in the water column until a quasi equilibrium state is reached (Fig. 6). Due to tidal-driven back-and-forth water movement, a wave-like behavior was clearly observed in all the time series. One could obtain a residence time of water in the Singapore Strait to be about 7 days. In 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 II was run

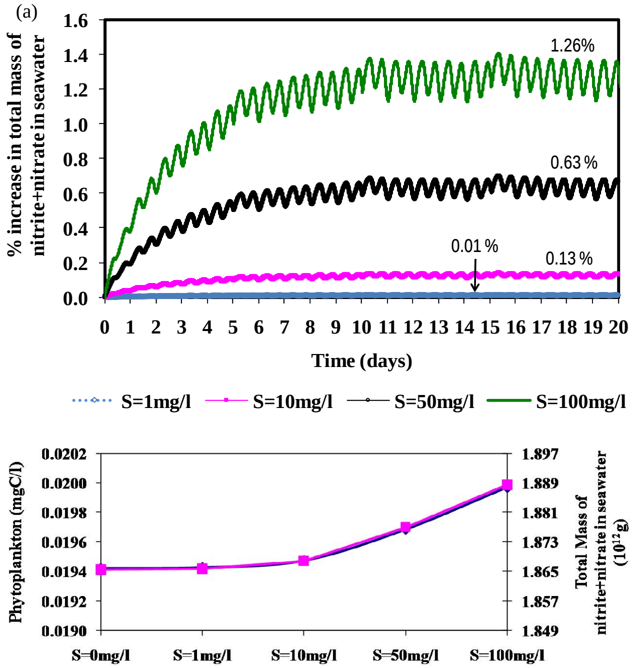

Fig. 5. (a) The percentage increase in total mass of nitrite + nitrate nitrogen in seawater from its baseline and **(b)** phytoplankton biomass concentration increase due to various atmospheric nitrate-nitrogen loading in the Singapore Strait. Note: S-Concentration of nitrate-nitrogen from atmosphere and deposition flux = Concentration S multiplied by the annual average rainfall of 2136 mm in the model region.

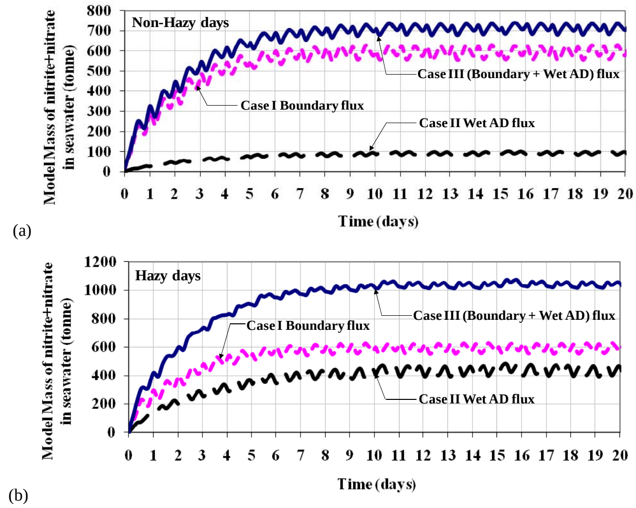

Fig. 6. Increase of nitrite+nitrate mass in the Singapore Strait due to atmospheric fluxes during **(a)** non-hazy days and **(b)** hazy days. Note: mass due to the total flux (Case III) = Mass due to boundary fluxes from the ocean (Case I) + Mass due to atmospheric nitrite+nitrate deposition (AD) fluxes (Case II).

to delineate relative contribution of atmospheric deposition flux only when compared to that of regional ocean flux. Case III combined Cases I and II, with total admixture mass defined by the sum of ocean boundary fluxes and atmospheric fluxes.

The percentage increase in mass due to AD N flux was calculated. Model computations showed that wet atmospheric fluxes of nitrate-nitrogen during non-hazy days might account for 4 to 24% (Fig. 6a) of total mass of nitrate-nitrogen in water column. During the hazy days, it was computed that wet atmospheric fluxes of nitrate-nitrogen contributed about 17 to 88% (mean ∼ 72%) of total nitrate-nitrogen mass into the water column (Fig. 6b), which is a notable contribution into regional eutrophication. The percentage increment of nitrate-nitrogen concentration in seawater (Fig. 6) was 2 to 30% (mean ∼ 15%) during the non-hazy days and 5 to 111% (mean ∼ 70%) during hazy days based on conservative admixture assumption. The percentage change of simulated nutrients and phytoplankton from seawater baseline during non-biomass burning and biomass burning (Tables 4 and 5) clearly showed the impacts on water quality following a haze event. Also, the sensitivity study showed the model water quality changes with respect to high N loading conditions and also corresponding phytoplankton growth (Fig. 5). In this study, only limited seawater samples were collected and analyzed (as in Sect. 2.2) at the surface level to establish seawater nutrients correlation with atmospherically deposited nutrients during hazy days. There was a moderate correlation, but significant, with contribution of atmospheric fluxes typically limited to 4–24% (Fig. 6a) during non-hazy days and 17–88% during hazy days (Fig. 6b). The model supports the hypothesis that atmospheric nutrient deposition may notably affect surface seawater nutrient concentrations as observed from the field study (Fig. 4). The rest of the nutrients were supplied to the water bodies via ocean and land-based fluxes.

3.3 Significance of atmospheric deposition during smoke haze events: non-conservative admixture assumption

The spatial and temporal dynamics of nutrients in the Singapore Strait was investigated by means of model simulations using a complete set of eutrophication kinetics and typical SWM tidal currents, with realistic initial and boundary conditions (Table 3). The atmospheric contribution to the nutrient load was specified as a constant concentration (g/m^3) uniformly distributed over the model domain area at all time steps. The similar patterns of changes in air quality observed from the different sites showed that the atmospheric nutrients deposition loading to the coastal water is uniform in this region (Sundarambal et al., 2010b). The model calculated the nutrient flux by using concentration and precipitation (wet deposition). The nutrients are transported to the water column, as well as spatially distributed by the action of tidal

Table 4. Model computed concentration of N and P species at water surface due to atmospheric deposition fluxes during non-hazy and hazy days.

Parameters (units)	Water quality change from model baseline due to mean wet AD deposition				% Water quality change			
Nutrients	Mean	Min	Max	SD	Mean	Min	Max	SD
Non-hazy days								
NH_4^+ (mg/l)	3.44E-04	3.73E-05	5.86E-04	1.55E-04	2.44	0.27	4.13	1.09
NO_3^-+NO_2^- (mg/l)	0.002	0.0002	0.0033	0.0009	9.37	1.09	15.9	4.17
ON (mg/l)	0.001	0.0001	0.0019	0.0005	1.43	0.17	2.43	0.64
PO_4^{3-} (mg/l)	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
Hazy days								
NH_4^+ (mg/l)	2.37E-03	2.73E-04	4.01E-03	1.05E-03	16.8	1.97	28.3	7.403
NO_3^-+NO_2^- (mg/l)	0.009	0.0010	0.0155	0.004	44.7	5.17	75.9	19.9
ON (mg/l)	0.005	0.0005	0.0077	0.002	5.82	0.68	9.90	2.59
PO_4^{3-} (mg/l)	2.65E-04	3.03E-05	4.52E-04	1.20E-04	2.28	0.26	3.90	1.033
OP (mg/l)	0.0007	0.00009	0.0012	0.00032	5.25	0.63	8.94	2.36

currents following the atmospheric deposition onto the water surface.

Computations obtained with the non-conservative admixture assumption (with full eutrophication kinetics) showed that atmospheric fluxes might account for an increase of nitrate-nitrogen concentration in the water column in the range of 1–16% (mean ∼ 9.3%) and 5–76% (mean ∼ 45%) during non-hazy and hazy days, respectively. The spatial distributions of surface water concentration of nitrate-nitrogen, NH_4^+ and ON from their baseline (0.02 mg/l, 0.0133 mg/l and 0.0796 mg/l, respectively) due to atmospheric nitrate-nitrogen deposition during hazy and non-hazy days are shown in Figs. 7(a1–a2), 7(b1–b2) and 7(c1–c2), respectively. It was observed that the water surface at a shallow depth had a higher concentration of 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 the one far away from the coastal areas are likely to have a lower concentration. This is due to dilution within the main stream by high tidal action in the Singapore Strait. When a rainfall event occurs after long dry period during hazy days, an episodic AD wet deposition with high N concentration can also occur. Occurrences of large episodic events of atmospheric nitrogen inputs can strongly impact the surface ocean biogeochemistry (Paerl, 1985). Episodic wet deposition event with nitrate-nitrogen concentration of 34.6 mg/l occurred during October/November 2006 onto water surface and the absolute change of surface water nitrate-nitrogen concentration of maximum 1 mg/l from baseline (0.02 mg/l) was computed due to the assumed episodic wet deposition event (Sundarambal et al., 2010a). The absolute difference (increase) of surface water PO_4^{3-} and OP concentrations from baseline due to the atmospheric wet deposition during hazy and non-hazy days is shown in Fig. 8a1 and b1, and Fig. 8a2 and b2, respectively. Model computations showed that atmospheric fluxes might account for an increase of PO_4^{3-} concentration in surface water in the range of 0.02–0.32% (mean ∼ 0.18%) and 0.26–3.9% (mean ∼ 2.3%) during non-hazy and hazy days, respectively. The increase of OP concentration in surface water observed from the model computation was in the range of 0.21–3.1% (mean ∼ 1.8%) and 0.63–8.9% (mean ∼ 5.3%) during non-haze and haze periods respectively. The soluble aerosol fraction of P species is likely to be the most biogeochemically reactive, especially in aquatic systems (Mahowald et al., 2008). It was observed that the atmospheric N species deposition was higher by a factor of 10 than that of P species (Tables 1–2 and Sundarambal et al., 2010b) and model simulation results (Fig. 7 and Fig. 8) similarly showed the changes in the concentration of N and P species in seawater. The observation of P enrichment due to atmospheric deposition in the present study is in contrast to other studies (Krishnamurthy et al., 2007, 2009, 2010; Zamora et al., 2010). In present modeling study, the impact of both organic N (Fig. 7c) and P (Fig. 8b) deposition from atmosphere was investigated. Our results demonstrate the sensitivity of marine biogeochemical cycling in Singapore and surrounding regions to variations in atmospheric N and P deposition during hazy and non-hazy days. With the estimated nutrient load from wet AD, the computed concentrations of N and P species changed considerably from the baseline value as shown in Table 4 at a selected location "SS" in Singapore Strait.

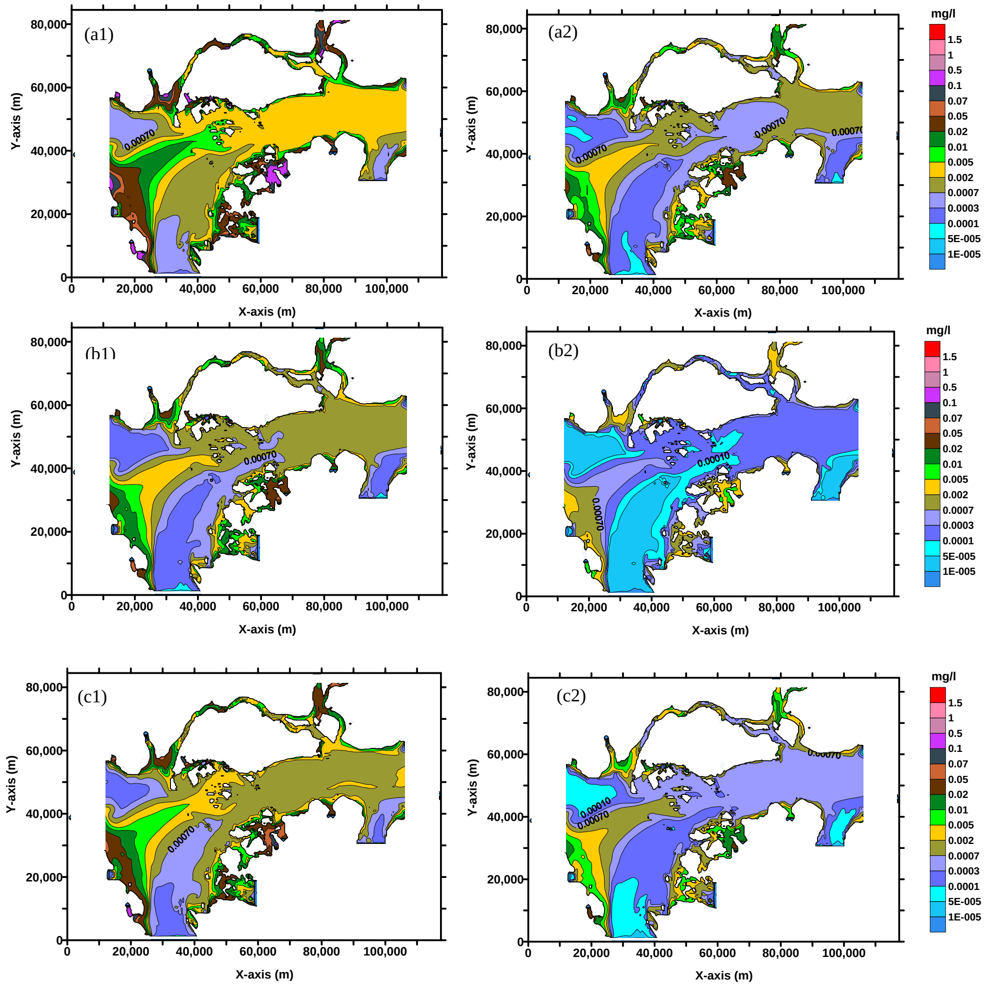

Fig. 7. The absolute change of **(a)** nitrate-nitrogen, **(b)** ammonium and **(c)** organic nitrogen concentration at surface water from baseline due to the atmospheric wet deposition during (1) hazy and (2) non-hazy days.

3.4 Contribution to eutrophication

The algal growth in the marine environment is N-limited usually (Smetacek et al., 1991), although PO_4^{3-} or even trace metals may also play a role in regulating phytoplankton growth (Galloway, et al., 1994; Herut et al., 1999; Gin et al., 2006). 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). Besides N and P, other factors such as physical properties of water (temperature, salinity), light, tidal currents, trace elements and micro-nutrients may limit the algal growth depending on the environmental conditions in the location and time. The atmospheric nutrients deposited to the surface ocean must be in a bioavailable form in order to be utilized by marine phytoplankton. The model computed absolute difference in spatial surface concentration distribution of phytoplankton (Fig. 9 and Table 5) indicated that the nitrate-nitrogen species provided the necessary nutrient for low nutrient zone, but the biological response time was slow, as nitrogen is not a limiting nutrient for high nutrient zone. The computed maximum absolute change of surface water phytoplankton concentration (mgC/l) from baseline (0.02) was 0.0007 and 0.0003 during hazy and non-hazy days, respectively. The computed maximum absolute change of surface water zooplankton concentration (g/m^3) from baseline (0.0279) was <0.001 and <0.0001 during hazy and non-hazy days, respectively. The variation of DO concentration was also observed following the changes in nutrients concentration in the Singapore Strait. 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 nutrients across the air-sea interface. The open ocean sources of external N such as biological N_2 fixation and atmospheric deposition together contribute a net oceanic input of N. These two sources support "completely new production" and hence influence global oceanic N, assuming an adequate supply of other nutrients (P, Fe)

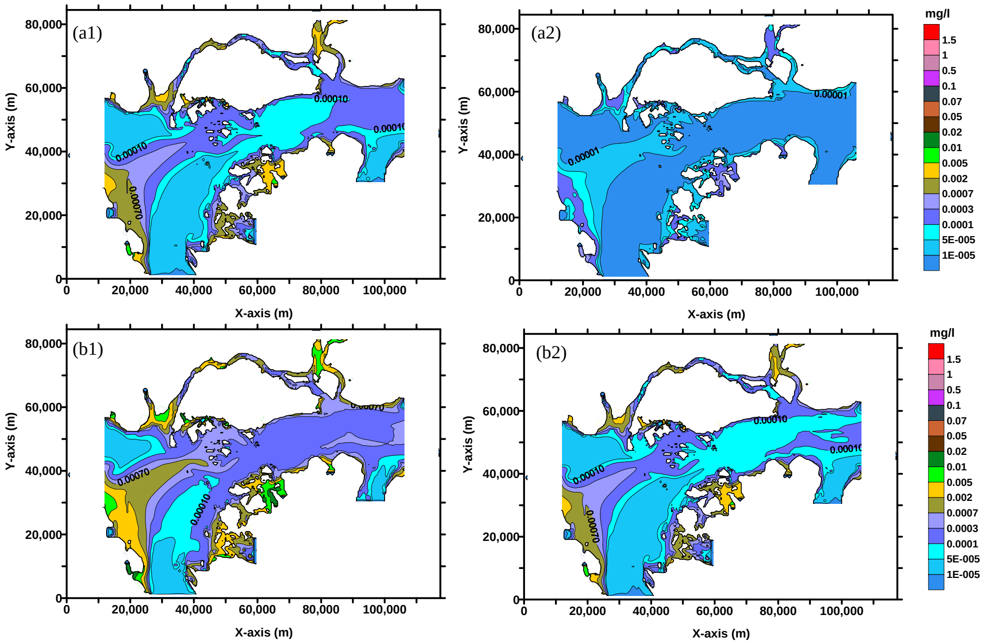

Fig. 8. The absolute change of **(a)** phosphate and **(b)** organic phosphorous concentration at surface water from baseline due to the atmospheric wet deposition during (1) hazy and (2) non-hazy days.

Table 5. The percentage increase of model computed concentration of phytoplankton, zooplankton and dissolved oxygen (DO) at surface water from baseline during non-hazy and hazy days.

Parameters (units)	Mean	Min	Max	SD
Non-hazy days				
Phytoplankton (mgC/l)	0.12	0.01	0.22	0.06
Zooplankton (mg/l)	8.03E-04	3.68E-05	1.43E-03	4.16E-04
DO (mg/l)	−0.00012	−0.00040	0.00023	0.00012
Hazy days				
Phytoplankton (mgC/l)	0.63	0.03	1.11	0.31
Zooplankton (mg/l)	4.12E-03	1.47E-04	7.23E-03	2.13E-03
DO (mg/l)	−0.00118	−0.00380	0.00256	0.00115

(Duce et al., 2008). These sources 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. Based on the modeling study, we conclude that while individual AD events are not probably responsible for triggering algal blooms as hypothesized, but long-term nutrient additions are important and do contribute to regional eutrophication problems under nutrient-depleted conditions in coastal waters.

3.5 Environmental impacts

Concerns on rising nutrient loads and their adverse effects on large scale freshwater, estuarine and marine environment have led to a strong need for extensive research and management of nutrients. Atmospheric deposition has been shown to contribute an increasing fraction of the overall nitrogen and phosphorus load. Furthermore, the atmospheric inorganic input is 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 the time, particularly high depositions can occur (Spokes et al., 1993, 2000).

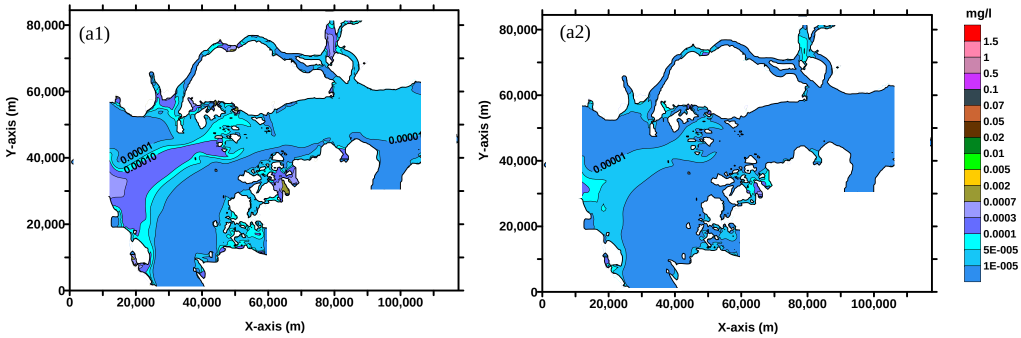

Fig. 9. The absolute change of phytoplankton concentration at surface water from baseline due to the atmospheric wet deposition during **(a1)** hazy and **(a2)** non-hazy days.

Once the atmospheric nutrients enter surface seawater, the chemical form of the dissolved nutrinets may be altered, thus changing their solubility, retention in the euphotic zone, and bioavailability. The impact of nutrient-enriched atmospheric inputs is enhanced under oligotrophic conditions. The resulting 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). The causative factors of algal blooms are elevated inputs of nutrients from land, atmosphere or adjacent seas, elevated DIN and dissolved inorganic phosphorous (DIP) concentrations, and increased N/P-ratios compared to the Redfield Ratio. Since atmospheric inputs do occur all year round, the flux of N from the air may not only trigger summer blooms, but also contribute to the water column N standing stock.

Atmospheric deposition of nitrogen compounds can contribute significantly to eutrophication in coastal waters, where plant productivity is usually limited by nitrogen availability. Duce et al. (2008) studied both organic and inorganic nitrogen deposition over global oceans and estimated that $\sim$3% of the annual new production could be accounted for by atmospheric deposition of anthropogenic nitrogen. The coastal and oceanic primary production due to atmospherically transported N and other nutrient sources may be promoting the major biological changes that are now apparent in coastal and oceanic waters, including the proliferation of harmful algal blooms (HAB) and decline in water quality and fish stock (Jickells, 1998). The modeling study of Krishnamurthy et al. (2007, 2009, 2010) and Zamora et al. (2010) investigated the effects of nutrient deposition on surface biogeochemistry. Regionally atmospheric N inputs can have significant impacts on marine biogeochemistry, potentially supporting $>$25% of the export production, an impact that is increasing due to human activities (Krishnamurthy et al., 2010). Zamora et al. (2010) indicated that atmospheric deposition may contribute 13–19% of the annual excess N input to the ocean main thermocline in the subtropical North Atlantic. 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). Excessive N loading to surface waters is the key cause of accelerating eutrophication and the associated environmental consequences (Nixon, 1995). Ecological effects caused by eutrophication are enhanced productivity, but these can also result in changes in species diversity, excessive algal growth, DO reductions and associated fish kills, and the increased prevalence or frequency of toxic algal blooms. The main toxic action of nitrate on aquatic animals like fish and crayfish seems to be the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen. High nutrient conditions favoring coastal HAB have also been associated with some cholera outbreaks. 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). 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. A regional extensive field monitoring programme is strongly needed for managing both air quality and water quality to protect the sensitive ecosystems in the SEA region. It is necessary to extend the modeling study covering the SEA region to estimate the possible impacts on aquatic ecosystems. This research work motivates the investigation of the role of other nutrients such as iron species and their related biogeochemical factors for the eutrophication in this region.

4 Conclusions

The importance of regional smoke episodic events, hazy days in relation to non-hazy days, to atmospheric nutrient deposition in terms of biological responses in the coastal water of the Singapore region was investigated. The water quality variability due to the transfer of atmospherically-derived nutrients into coastal water was quantified and the resultant nutrient and phytoplankton dynamics in this region was predicted by the present numerical modeling approach. The 3-D numerical eutrophication model NEUTRO was enhanced in its capability to address the atmospheric input of macronutrients. The enhanced model was subsequently utilized to investigate the fate of atmospherically deposited nutrients. In this study, both organic and inorganic nitrogen and phosphorous dynamics were quantified and modeled by incorporating phytoplankton and DO dynamics. Model results showed that higher nutrient loading onto the coastal and estuarine ecosystems of the Singapore and surrounding regions from the atmospheric wet deposition during hazy days has remarkable impacts on their water quality, with the contribution of nutrients during hazy days being doubled compared to that of non-hazy days. Model computations showed that atmospheric fluxes might account for a considerable percentage of total nitrate-nitrogen mass found in the water column of the Singapore Strait. It was observed that the water surface at a shallow depth had a higher concentration of 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 is likely to have a lower concentration due to dilution within the main stream by high tidal action in the Singapore Strait. The results of the present study revealed that the impacts of nitrogen species through AD onto the coastal region are significant and that of phosphorus species are also notable. The percentage increase in computed phytoplankton concentration from its baseline ranged from $\sim$0.03 to 1.11 during hazy days and $\sim$0.01 to 0.22 during non-hazy days. Our results demonstrated the sensitivity of marine biogeochemical cycling to variations in atmospheric nutrients deposition during hazy and non-hazy days.

It was found that the atmosphere is a potentially significant source of "new" nitrogen on yearly time scales in the coastal waters of Singapore and surrounding areas. The information presented in this paper advances scientific knowledge in issues related to AD of pollutants, particularly nutrients, to coastal and ocean waters of SEA and in modeling approach to predict/forecast the coastal water quality due to atmospheric nutrient deposition for regional water quality management. Despite the uncertainty in quantifying atmospheric deposition and model computations, this study highlighted the importance of addressing the issues of eutrophication in Singapore. This research showed the importance of quantification of atmospheric nutrient flux into the coastal zone and investigation of possible effects on aquatic ecosystem by water quality changes and eutrophication. Based on the findings from the present research work, a local and regional long-term field monitoring program 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 Singapore waters and the SEA region for measurement of nutrients and assessment of their impact on water quality.

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References

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

Andreae, M. O.: Biomass Burning in the Tropics: Impact on Environmental Quality and Global Climate, Popul. Dev. Rev., 16(Supp), 268–291, 1990.

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., and Wofsy, S. C.: Biomass-burning emissions and associated haze layers over Amazonia, J. Geophys. Res., 93, 1509–1527, 1988.

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

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

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

Azanza, R. V.: Harmful Algal Bloom Management Programs in Southeast Asia, in: Proceedings of IOC/WESTPAC International Scientific Symposium – Role of Ocean Sciences for Sustainable Development, Okinawa, Japan, 2–7 February, 1998, Intergovernmental Oceanic Commission Workshop Report, 148, UNESCO, 1998.

Azanza, R. V. and Taylor, F. J.: Are Pyrodinium blooms in the Southeast Asian region recurring and spreading? A view at the end of the millennium, Ambio, 30(6), 356–364, 2001.

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

Balasubramanian, R., Victor, T., and Begum, R.: Impact of biomass burning on rainwater acidity and composition in Singapore, J. Geophys.Res., 104, 26881–26890, 1999.

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

Beck, M. B. (Ed.): System analysis in water quality management, in: Proceedings of a Symposium sponsored by the IAWPRC Specialist Group, Oxford-Pergama press, London, UK, 30 June–2 July 1987, 13–63, 1987.

Brauer, M. and Hisham-Hashim, J.: Fires In Indonesia: Crisis And Reaction, Environ. Sci. Technol., 32(17), 404A–407A, 1998.

Cornell, S., Rendell, A., and Jickells, T.: Atmospheric inputs of dissolved organic nitrogen to the oceans, Nature, 376, 243–246, 1995.

Chou, L. M.: Marine environmental issues of Southeast Asia: state and development, Hydrobiologia, 285, 139–150, 1994.

Chan, E. S., Tkalich, P., Gin, K. Y. H., and 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, edited by: Wolanski, E., Springer, The Netherlands, 393–412, 2006.

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

Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollock, W. H., and Seiler, W.: Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl, COS, Nature, 282, 253–256, 1979.

De Leeuw, G., Spokes, L., Jickells, T. D., Skjoth, A. C., Hertel, O., Vignatic, E., Tamme, S., Schulze, M., Sorensen, L. L., Pedersen, B., Klein, L., and Schlunzen, K. H.: Atmospheric nitrogen inputs into the North Sea: effect on productivity, Cont. Shelf Res., 23, 1743–1755, 2003.

Ditmars, J. D.: Performance Evaluation of Surface Water Transport and Dispersion Models, J. Environ.l Eng.-ASCE, 113(EE8), 961–971, 1988.

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., and Zhou, M.: The atmospheric input of trace species to the world ocean, Global Biogeochem. Cy., 5, 193–259, 1991.

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., and Zamora, L.: Impacts of atmospheric anthropogenic nitrogen on the open ocean, Science, 320(5878), 893–897, 2008.

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

Gin, K. Y. H., Lin, X., and Zhang, S.: Dynamics and size structure of phytoplankton in the coastal waters of Singapore, J. Plankton Res., 22, 1465–1484, 2000.

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

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

Herut, B., Collier, R., and Krom, M.: The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean, Limnol. Oceanogr., 47, 870–878, 2002.

Hyer, E. J. and Chew, B. N.: Aerosol transport model evaluation of an extreme smoke episode in Southeast Asia, Atmos. Environ., 44(11), 1422–1427, 2010.

In, H.-J., Byun, D. W., Park, R. J., Moon, N.-K., Kim, S., and 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, J. Geophys. Res., 112, D07201, doi:10.1029/2006JD007544, 2007.

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

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

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

Krishnamurthy, A., Moore, J. K., Zender, C. S., and Luo, C.: Effects of atmospheric inorganic nitrogen deposition on ocean biogeochemistry, J. Geophys. Res., 112, G02019, doi:10.1029/2006JG000334, 2007.

Krishnamurthy, A., Moore, J. K., Mahowald, N., Luo, C., Doney, S. C., Lindsay, K., and Zender, C. S.: Impacts of increasing anthropogenic soluble iron and nitrogen deposition on ocean biogeochemistry, Global Biogeochem. Cy., 23, GB3016, doi:10.1029/2008GB003440, 2009.

Krishnamurthy, A., Moore, J., Mahowald, N., Luo, C., and Zender, C.: Impacts of atmospheric nutrient inputs on marine biogeochemistry, J. Geophys. Res., 115(G1), 1–13, 2010.

Koe, L. C. C., Arellano Jr., A. F., and McGregor, J. L.: Investigating the haze transport from 1997 biomass burning in Southeast Asia: its impact upon Singapore, Atmos. Environ., 35, 2723–2734, 2001.

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., and Liley, B.: Impacts of biomass burning in Southeast Asia on ozone and reactive nitrogen over the western Pacific in spring, J. Geophys. Res., 109, D15S12, doi:10.1029/2003JD004203, 2004.

Kuhlbusch, T. A., Lobert, J. M., Crutzen, P. J., and Warneck, P.: Molecular nitrogen emissions from denitrification during biomass burning, Nature, 351, 6322, 135–137, 1991.

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

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

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., and Tsukuda, S.: Global distribution of atmospheric phosphorus sources, concentrations and deposition rates and anthropogenic impacts, Global Biogeochem. Cy., 22, GB4026, doi:10.1029/2008GB003240, 2008.

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

Muraleedharan, T. R., Rajojevic, M., Waugh, A., and Caruana, A.: Chemical characteristics of haze in Brunei Darussalam during the 1998 episode, Atmos. Environ., 34, 2725–2731, 2000.

NEA: National Environment Agency, Ministry of the Environment and Water Resources, Singapore, available at: http://app2.nea.gov.sg/images/Regional_PSI_for_2006.pdf, 2010.

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

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

Paerl, H. W.: Enhancement of marine primary productivity by nitrogen enriched acid rain, Nature, 315, 747–749, 1985.

Paerl, H. W.: Nuisance phytoplankton blooms in coastal, estuarine and inland waters, Limnol. Oceanogr., 33, 823–847, 1988.

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

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

Paerl, H. W., Boynton, W. R., Dennis, R. L., Driscoll, C. T., Greening, H. S., Kremer, J. N., Rabalais, N. N., and Seitzinger, S. P.: Atmospheric deposition of nitrogen in coastal waters: biogeochemical and ecological implications, in: Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective, Coastal and Estuarine Studies 57, edited by: Valigura, R. A., Alexander, R. B., Castro, M. S., Meyers, T. P., Paerl, H. W., Stacey, P. E., and Turner, R. E., AGU Press, Washington, DC, 11–52, 2000.

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

Pang, W. C. and Tkalich, P.: Semi-Implicit Sigma-Coordinate Hydrodynamic Model, in: Proceedings of 14th IAHR-APD Congress, Hong Kong, 15–18 December 2004.

Pang, W. C., Tkalich, P., and Chan, E. S.: Hydrodynamic forecast model for the Singapore Straits, in: Proceedings of the XXX IAHR Congress, Thessaloniki, Greece, 24–29 August 2003, 9–16, 2003.

Peierls, B. L. and Paerl, H. W.: The bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton, Limnol. Oceanogr., 42, 1819–1880, 1997.

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

Qadri, S. T.: Fire, smoke, and haze: The ASEAN response strategy, The Association of Southeast Asian Nations (ASEAN)-Asian Development bank (ADB) joint publication, Metro Manila, Philippines, 246 pp., 2001.

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

Selman, M., Greenhalgh, S., Diaz, R., and 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, DC 20002, 2008.

Smetacek, V., Bathmann, U., Nothig, E. M., and Scharek, R.: Coastal eutrophication: Causes and consequences, in: Ocean Margin processes in Global Change, edited by: Mantoura, R. C. F., Martin, J. M., and Wollast, R., John Wiley & Sons, Chichester, 251–279, 1991.

Spokes, L., Jickells, T., Rendell, A., Schulz, M., Rebers, A., Dannecker, W., Krueger, O., Leermakers, M., and Baeyens, W.: High Atmospheric Nitrogen Deposition Events Over the North Sea, Mar. Pollut. Bull., 26, 698–703, 1993.

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

Sundarambal, P.: Estimation of the contribution of atmospheric deposition to coastal water eutrophication, Ph.D. Thesis, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 2009.

Sundarambal, P. and Tkalich, P.: Assessment of accidental nutrient spills from ships into the Singapore marine environment, in: Proceedings of Asia Oceania Geosciences Society 2nd Meeting, Singapore, 20–24 June 2005, 2005.

Sundarambal, P. and Tkalich, P.: Numerical 3-D water quality model (NEUTRO) for eutrophication and pollutant transport, Mar. Environ. Res., in review, 2010.

Sundarambal, P., Balasubramanian, R., Karthikeyan S., and 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 & Atmospheric Science, edited by: Chen, Y.-T., World Scientific Publishing Company, Singapore, 149–166, 2006.

Sundarambal, P., Dao, M. H., and Tkalich, P.: Modeling of hydrodynamic and water quality processes in coastal zones, in: Proceedings of International Conference on Marine Problems and Specific Solutions (COMPASS) 2008, 15–18 June 2008, Maldives, 2008.

Sundarambal, P., Balasubramanian, R., and Tkalich, P.: Atmospheric fluxes of nutrients onto Singapore Strait, Water Sci. Technol., 59(11), 2287–2295, 2009.

Sundarambal, P., Tkalich, P., and Balasubramanian, R.: Modeling the effect of atmospheric nitrogen deposition on marine phytoplankton at the Singapore Strait, Water Sci. Technol., 61(4), 859–867, 2010a.

Sundarambal, P., Balasubramanian, R., Tkalich, P., and He, J.: Impact of biomass burning on ocean water quality in Southeast Asia through atmospheric deposition: field observations, Atmos. Chem. Phys., 10, 11323–11336, doi:10.5194/acp-10-11323-2010, 2010b.

Tkalich, P. and Sudarambal, P.: Eutrophication modelling for the Singapore waters, Singapore Maritime and Port Journal, 122–136, 2003.

Tkalich, P., Pang, W. C., and Sundarambal, P.: Hydrodynamics and eutrophication modelling for Singapore Straits, in: Proceedings of 7th Workshop on Ocean Models for the APEC Region (WOM-7), Singapore, 5-1–5-9, 2002.

UNEP: Chia, L. S. and Kirkman H.: Overview of Land-Based Sources and Activities Affecting the Marine Environment in the East Asian Seas, UNEP/GPA Coordination Office & EAS/RCU, Regional Seas Report and Studies Series, 74 pp., 2000.

UNEP (United Nations Environment Programme) and WHRC (The Woods Hole Research Center): Reactive Nitrogen in the Environment: Too Much or Too Little of a Good Thing, UNEP, Paris, 51 pp., 2007.

Van Dolah, F. M., Roelke, D., and Greene, R. M.: Health and ecological impacts of harmful algal blooms: Risk assessment needs, Hum. Ecol. Risk Assess., 7, 1329–1345, 2001.

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

Wang, Y., Field, R. D., and Roswintiarti, O.: Trends in atmospheric haze induced by peat fires in Sumatra Island, Indonesia and El Niño phenomenon from 1973 to 2003, Geophys. Res. Lett., 31, L04103, doi:10.1029/2003GL018853, 2004.

Watson, R. T., Moss, R. H., and Zinyowera, M. C. (Eds.): The Regional Impacts of Climate Change: An Assessment of Vulnerability. Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, 1998.

Zamora, L. M., Landolfi, A., Oschlies, A., Hansell, D. A., Dietze, H., and Dentener, F.: Atmospheric deposition of nutrients and excess N formation in the North Atlantic, Biogeosciences, 7, 777–793, doi:10.5194/bg-7-777-2010, 2010.